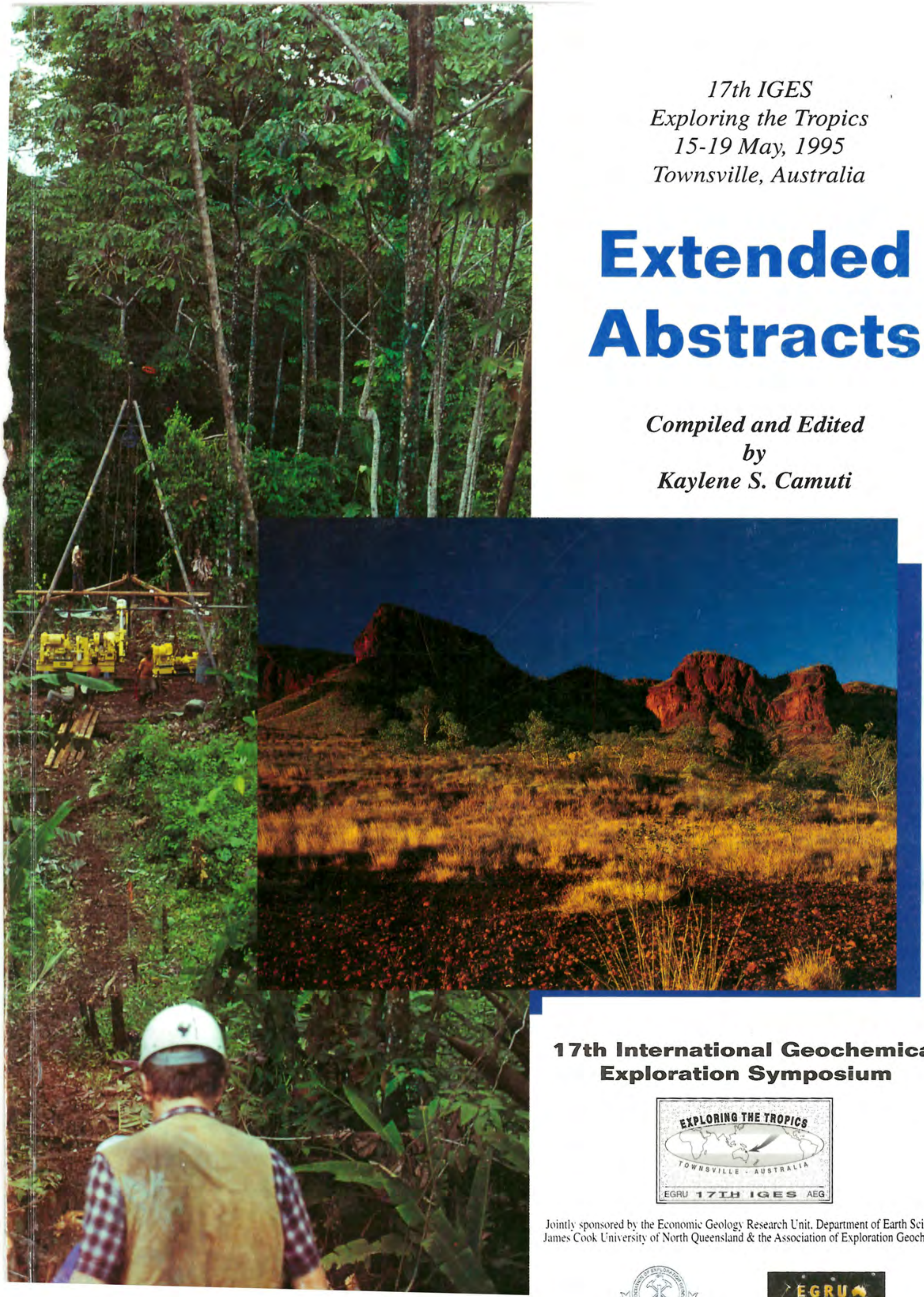

17th IGES
Exploring the Tropics
15-19 May, 1995
Townsville, Australia

Extended Abstracts

Compiled and Edited
by
Kaylene S. Camuti

17th International Geochemical Exploration Symposium

EXPLORING THE TROPICS
TOWNSVILLE · AUSTRALIA
EGRU 17TH IGES AEG

Jointly sponsored by the Economic Geology Research Unit, Department of Earth Sciences, James Cook University of North Queensland & the Association of Exploration Geochemists

EGRU

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EGRU CONTRIBUTION 54

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Sponsored by:
the Economic Geology Research Unit
James Cook University, Townsville, Australia
and
the Association of Exploration Geochemists.

James Cook University of North Queensland.

Camuti, K. (Kaylene), 1958-.
Exploring the Tropics - Extended Abstracts

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ISBN 0 86443 537 1

1. Geochemical prospecting - Tropics - Congresses. I. Camuti, K. (Kaylene), 1958-. II. James Cook University of North Queensland. Economic Geology Research Unit. III. Association of Exploration Geochemists. IV. Title. (Series : Contributions of the Economic Geology Research Unit ; 54).

622.13

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Preface

This volume of extended abstracts was prepared for the 17th International Geochemical Exploration Symposium (IGES), held in Townsville from the 15-19 May, 1995. The 17th IGES, with the theme "*Exploring the Tropics*", resulted from the collaborative efforts of the Association of Exploration Geochemists (AEG), and James Cook University's Economic Geology Research Unit (EGRU). It also marked the 25th anniversary of the AEG, a world-wide organisation which, through its publication the *Journal of Geochemical Exploration*, and regional and international meetings, promotes the advancement of techniques and applications in exploration geochemistry. Co-sponsor of the IGES, EGRU, an industry funded organisation founded in 1982, organises workshops, short courses and symposiums, provides facilities for training in economic geology, and produces publications covering topics relevant to economic geology.

Order of Abstracts

Within this volume abstracts of keynote addresses are presented first, in alphabetical order of first author. Abstracts of oral and poster presentations follow, divided into the major themes of the symposium, and listed in alphabetical order of first author within each theme. Many abstracts could fit equally well into two or more themes, so a subject index has been provided and follows the author index at the back of the volume. The subject index is based on keywords listed by authors.

Responsibility for Abstracts

Authors are responsible for the contents of their abstracts. Abstracts were requested in camera-ready format and the majority have been reproduced directly from authors' original contributions. In some cases, however, contributions were not of a standard suitable for printing. Where this occurred abstracts were re-typed and formatted and, sometimes, lightly edited; edited abstracts were sent to authors for checking. Where abstracts have been re-typed, a great deal of care was taken to check for errors and we apologise to authors for any that we missed.

Many authors had difficulty finalising travel to Townsville for the Symposium. Abstracts included in this volume represent papers that were intended to be presented at the time of going to press.

Acknowledgements

The 17th IGES Committee would like to thank all authors, and the following individuals and organisations, for their help in compiling this volume:

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May 1995

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Keynote Presentations

Genesis and classification of ferruginous regolith materials in the Yilgarn Craton: Implications for mineral exploration

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Key words: Yilgarn Craton, ferruginous materials, regolith, classification, origin, geochemical exploration, lateritic residuum

Introduction

Ferruginous regolith materials are abundant and widespread in the landscapes of the Yilgarn Craton. Many of these materials preserve geochemical dispersion patterns from concealed mineral deposits (Smith *et al.*, 1992; Anand, 1993; Anand *et al.*, 1993). There is a wide variety of ferruginous materials and their geochemical response to mineralisation and bedrock differs according to their mode of origin. They occur as crusts, as lag, as a gravel component in soil, colluvium and alluvium, and as segregations and infusions in saprolite. Furthermore, several types may occur in a single weathering profile and have developed in different parent materials or substrates. Understanding these materials is important for selection of suitable sampling media and subsequent interpretation of geochemical data in mineral exploration. In addition, close study of the relationship of ferruginous materials to the landscape contributes to the general understanding of landscape evolution in the Yilgarn Craton.

Classification and environments of formation

The topographic relationships, position within the weathering profile, mineralogical, chemical and mesoscopic characteristics of ferruginous materials suggest four main environments for their formation.

1. *Lateritic residuum.* Lateritic residuum is a collective term for lateritic duricrust and loose lateritic nodules and pisoliths. These are thought to have formed, during lateritic weathering, within the zone of water table fluctuation. Ferrous iron, released by breakdown of the primary minerals under relatively reducing conditions has been redistributed and precipitated as pisoliths and nodules under oxidising conditions of this zone. As a result, a ferruginous horizon typically develops in upper parts of the deeply weathered profile. Nodules and pisoliths commonly have thin (1 mm) goethite- and kaolinite-rich cutans, that have developed by deposition of Fe and Al around a core. Pisoliths with multiple cutans are rare being found mainly at the base of palaeo-channel infill.

Major minerals are hematite, goethite, maghemite, kaolinite and gibbsite with some quartz and other resistant minerals. Maghemite is formed by heating of goethite during bush fires. Lateritic pisoliths and nodules contain highly Al-substituted goethites, indicating ample availability of aluminium during their formation. The major and trace element composition of these materials is largely lithodependent at a landscape scale; Fe and Al are largely derived from the underlying rocks. However, lateral accumulation of Fe and Al also occurs.

Several types of lateritic duricrusts (massive, vermiform, fragmental, nodular and pisolitic) have been identified in Yilgarn Craton. Some are related to pisolitic-nodular lateritic residuum; others to ferruginous saprolite.

2. *Ferruginous saprolite and mottled zone.* Ferruginous saprolite is commonly developed over mafic and ultramafic rocks by infusion of kaolinite- rich saprolite with goethite and is hard, massive to mottled. It occurs below the ferruginous zone and is younger than overlying pisoliths and nodules. Fragmentation and collapse of ferruginous saprolite may lead to the generation of nodules. Mottled zone is characterised by hematite-rich mottles in a kaolinite-rich matrix. Mottles may evolve into nodules and pisoliths.

3. *Iron segregations.* These include stratabound and discordant to sub-horizontal Fe-rich bodies and lenses occurring dominantly in saprolite. They are dense, dark brown to black and rich in Fe, Mn, Zn, Cu and Co. They are non-magnetic and are dominated by low Al -substituted goethite (< 5 mole %), with variable amounts of hematite and quartz; maghemite and kaolinite are absent.

Iron segregations are the result of extreme ferruginisation, the Fe being derived from a variety of sources, including weathering of Fe-rich and/or sulphidic rocks, and by lateral enrichment by groundwater. Very low Al substitution in the goethites of iron segregations indicates that they must have developed in an environment that was very poor in Al.

4. *Ferruginous materials characteristic of sub-aqueous environments* consist of Fe-oxides which have impregnated and indurated sediments of various ages and may overlie either complete or truncated profiles. The Fe is contributed by broad scale lateral movements so that there is no genetic relationship between these ferruginous materials and the underlying geology. Typical examples include bog iron ore, and mega-mottles in palaeo-channel sediments. These commonly mark former lakes, valley floors, swamps, rivers, streams and channels. Some now occupy low hills, due to relief inversion.

Modification and distribution

These ferruginous materials were formed within the regolith but their present distribution in the landscape has been affected by later *erosional and depositional processes* . The distribution can thus best be described by establishing a framework and regolith-landform regimes (Anand and Smith, 1992; Anand, 1993).

Lateritic duricrusts, lateritic gravels and lag of lateritic nodules and pisoliths outcrop in *relict regimes*, whereas outcrop and lag of hardened mottles and ferruginous saprolite occur in transitional to *erosional regimes*. Lateritic duricrusts, ferruginous saprolites and mottled zones are commonly present beneath colluvium and alluvium in depositional regimes that have not suffered post-lateritic erosion.

Erosion of the upper saprolite has lead to exposure of bodies of iron segregations at the surface, where they disintegrated and contribute to a coarse lag in the erosional regimes.

Where erosion has removed most of the pre-existing lateritic regolith, more recent weathering has led to the formation of indurated, goethite- and hematite-rich bedrock. This later weathering has not been intense and weatherable primary minerals are retained as important components. Disintegration has formed a coarse lag of ferruginous, lithic fragments.

Horizons of lateritic pisoliths and nodules are generally developed above, or laterally associated with, indurated, lateritic duricrust. This gravelly horizon commonly arises from *in situ* breakdown of pisolitic-nodular duricrust, followed by limited colluvial transport. However, if the lateritic residuum in upland areas is entirely dismantled, the resultant gravels may be deposited in flanking low lying areas. These gravels progressively lose their cutans on transport and are incorporated, with other clasts of diverse origin, within colluvial-alluvial units or occur as gravelly lenses. These may be recemented by Fe-oxides and resemble the residual duricrusts from which they were derived.

There are also *regional trends* in the distribution of ferruginous materials in the Yilgarn Craton. For example, in the Leonora-Wiluna region, lateritic residuum and ferruginous saprolite form commonly extensive buried blankets whereas, in the Kalgoorlie region, they are much less widespread. Similarly, iron segregations are abundant in erosional regimes of the Leonora-Wiluna region but rare to absent in the Southern Yilgarn Craton, around Kalgoorlie. These differences may reflect contrasts in the tectonic history, geomorphology and /or weathering conditions between the two regions. Thus, it may be that neither lateritic residuum nor Fe segregations were ever extensively developed in the Kalgoorlie region or that subsequent weathering has caused their modification or destruction.

Relief inversion

There is no evidence of large scale *relief inversion* within the Yilgarn Craton despite reports to the contrary (Ollier *et al.*, 1988). This is shown by a lack of any dendritic pattern in exposed or buried duricrust, and that the palaeo-drainage systems dominantly occupying lower parts of the present landscape. However, very localised relief inversion is indicated by small hills formed by detrital duricrusts and mega-mottled zones along edges of some lakes.

Geochronology

The ferruginous materials are of varying ages but none has been dated precisely. However, stratigraphic relationships suggest that some pisoliths and nodules may date from at least the late Mesozoic. Transported maghemite-rich, pisolitic and nodular gravels occur in basal sediments of palaeo-channels that elsewhere contain late- Eocene lignites. The transported pisoliths were presumably derived by erosion of the earlier lateritic regoliths that predates incision of the palaeo-drainage. Eocene sediments themselves have been further weathered to form mega-mottles, probably during Oligocene and Miocene.

Sampling strategies, regolith mapping and identification of ferruginous materials

Understanding the nature and distribution of ferruginous materials helps to develop geochemical sampling strategies for weathered terrain. This can be achieved by regolith-landform mapping and establishing regolith stratigraphy. When regolith-landform regimes are mapped in an area, it generally becomes clear which geochemical sampling media are the most appropriate (Anand, 1993).

Where preserved, lateritic residuum forms an ideal sampling medium to detect the widespread dispersion haloes from Au and base metal deposits. Lateritic nodules and pisoliths may be collected from the surface or near-surface in relict regimes or by drilling in depositional regimes (Smith *et al.*, 1992; Anand *et al.*, 1993). Mechanical dispersion of loose nodules and pisoliths (5-50 m) is very common and thus results in wider anomaly than in underlying duricrust. There appears to be no special advantage in sampling magnetic nodules and pisoliths despite the greater homogeneity of the sample. On the contrary, some non-magnetic materials are more useful because both target and pathfinder elements are associated with goethite and hematite that can comprise either the core or cutans of nodules and pisoliths (Anand and Smith, 1992).

In drilling to sample buried laterite, it is important to be able to recognise and distinguish transported lateritic debris from residual laterite. Nodules and pisoliths with yellowish-brown to olive green cutans are believed to be confined to residual laterite or those with minimal transport. Layers of well- sorted lateritic gravels and a large proportions of nodules and pisoliths with chipped cutans may indicate transported laterite. Similarly, layers of maghemite -rich gravels within clay-rich units are indicative of transported laterite.

Where the profile has been truncated, ferruginous saprolite, mottles and iron segregations are suitable sampling media, although much closer sample intervals are necessary. Drilling is necessary in depositional regimes. Different thresholds must be applied for each sample type.

Pisolitic and nodular lateritic residuum can be distinguished from ferruginous saprolite by loss of the primary fabric and by having abundant hematite and less kaolinite. Maghemite is typically absent in mottles and ferruginous saprolite. Ferruginous saprolite differs from iron segregations in that it has generally yellow-brown colour, less Fe and may have diffuse mottling and incipient nodular structures.

Ferruginous materials formed in sub-aqueous environments may not be suitable sampling media because they are not genetically related to the underlying lithologies. Low Al-substituted goethite is the dominant Fe-oxide mineral in bog iron ore whereas hematite dominates mega-mottles of palaeo-channels. Hematite present in mega-mottles may reflect age differences; older materials are generally higher in hematite content than younger ones, and may reflect an ageing or warmer conditions during formation. Ferruginised wood fragments commonly occur in bog iron ore.

In some situations, mottling has developed in younger transported horizons overlying older lateritic residuum, mottled zone or saprolite. Small manganese nodules may also occur at the base of such units. Transport is indicated by unconformable contacts. Where no obvious unconformity is present, mineralogical data may demonstrate different origins of units in which separate parts of weathering profiles have developed.

Outlook

Future research activities should include:

1. Development of uniform and consistent terminology across Australia.
2. Assesing Satellite and air craft scanner imagery for regolith mapping.
3. Geochronology of ferruginous materials.
4. Application of geophysical methods to delineate the distribution of buried lateritic residuum in the alluvial sump areas.
5. Testing effectiveness (geochemical sampling media) of ferruginous materials developed in transported overburden.
6. Establishing the geochemical expression in lateritic residuum of a Au or base metal deposits completely immersed within the hypersaline groundwater environment.

Acknowledgements

Most of the work reported in this paper was carried out in CSIRO/AMIRA projects. The sponsors of the projects are thanked for their support.

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Research trends on supergene ore deposits: Turning points, current dilemma and emerging opportunities.

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Keywords: supergene oxidation, ore deposits, climate, microbeam, environmental geochemistry

Methods and trends

In order to attempt to summarize a meaningful portion of the current state of knowledge of supergene deposits and to use this as background to encompass fruitful new directions, long-term publication trends were constructed here using computer-based bibliographic search of the GeoRef data base (Fig. 1). As summarized by Sato (1992), systematic investigations in this field date as far back as Whitney's 1855 work on the Ducktown, Tennessee deposit, but it was not until the turn of the century that a continuous stream of seminal publications emerged (De Launay, 1893; Weed, 1901; Emmons, 1901; Van Hise, 1901; and Ransome, 1910 and 1912). Initial development of large new ore deposits like Butte, Montana (Penrose, 1894) and Broken Hill, N.S.W. (Jaquet, 1894) propelled these rapid advances. From field and microscopic studies, these authors recognized the fundamental paragenesis of ore deposits enriched by weathering, particularly the derivation of secondarily-enriched metals by oxidative leaching in the vadose zone, their downward aqueous transport and reprecipitation at or near the mine ground water table with the effects of enrichment diminishing with depth within "unaltered" primary ore.

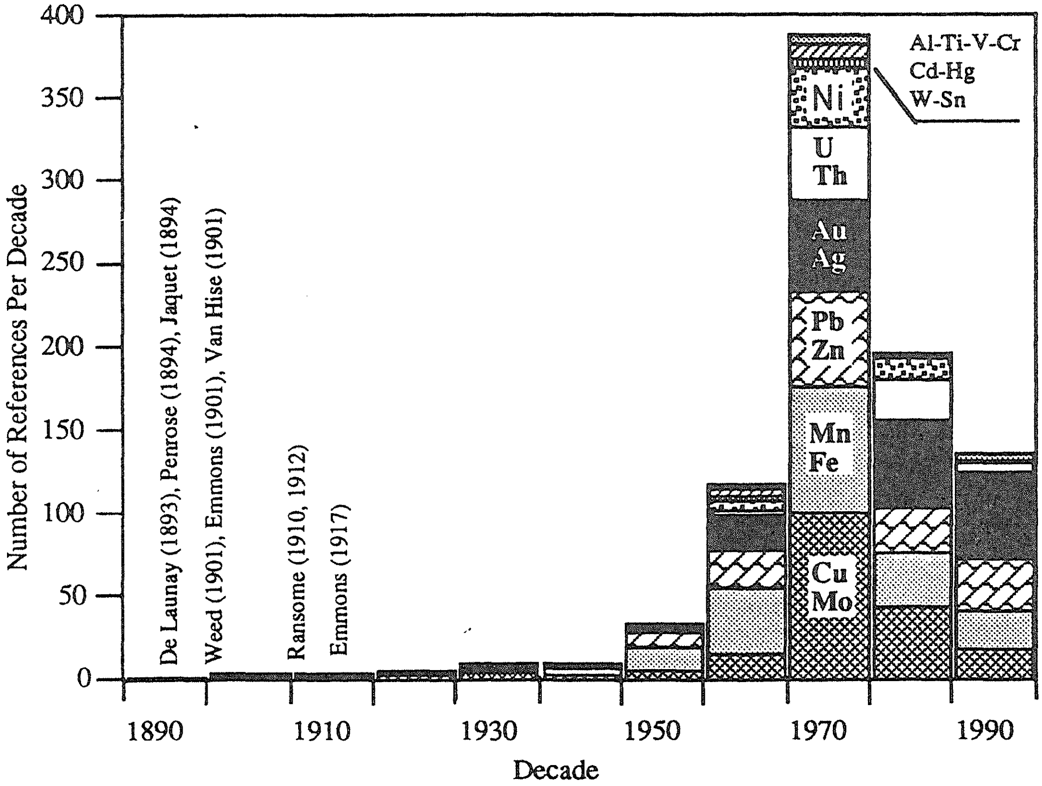

Fig. 1 Number of published references in the GeoRef data base per decade for the groups of metals shown subdivided into major associations. The 1990 decade, incomplete in 1994, is corrected by projecting publications an additional 5 years past the number of references contained in the present data base from 1990 through 1994.

Beginning with these papers published before the turn of the century which defined a productive new realm of research with immediate practical benefits in exploration, the total number of papers on supergene enriched ore deposits grew only slowly at first, but accelerated rapidly into the 1970's as knowledge of supergene effects became an essential part of successful exploration strategies globally in arid as well as in tropical regions. As exploration geochemistry thrived, this same decade saw increasing diversification of the metal suites of interest which included U and Ni in addition to Cu-Mo-Au, Mn-Fe, Pb-Zn, Au-Ag, W-Sn, Cd-Hg and Al-Ti-V-Cr.

Turning points

That dramatic changes are afoot today is evident in the profile of publication over the past 20 years compared with its peak activity in the 1970's which was clearly a turning point in this research field. The significance of this precipitous downturn, the probability of recovery and its likely time-scale can only be appreciated in light of current trends affecting industry, academia and research agencies. Clearly evident in Fig. 1 are two trends reflecting major changes in research activity on supergene ore deposits. First, since the peak activity in the 1970's, there is a rapidly-declining rate of publication to less than one half of the previous level. Second, gold emerged as the sole surviving metal of intense interest. This shift away from base metals was driven simply by the need to maintain industrial economic viability. Consequently, over the past 25 years, research on gold deposits has eclipsed, at least in number of papers, efforts focused on base metal and silver behavior from which had emerged many of the earlier advances in basic conceptual understanding. These earlier break-throughs included supergene differentiation itself, broad understanding of multi-element lithogeochemistry (eg. Le Long, et al, 1976), leached outcrop interpretation (Blanchard, 1968) and the importance of geomorphic understanding (Finkl, 1982). Although the diversity of metal investigations has therefore declined markedly, the recent focus on enriched gold deposits has nevertheless provided critical economic stability and has in fact contributed its own break-throughs in understanding. These advances include better appreciation of the complexities of exploration in lateritized terrains (Smith, 1983) in the cratonal regions of Australia, Africa and South America and clarifying supergene gold mobility (Mann, 1984; Webster and Mann, 1984) ultimately culminating in the discovery lateritic gold deposits (Davy and El-Ansary, 1986; Olson, et al, 1992).

Objectives

While these changes in focus and overall activity reflect some successes, they are dominated by the economic austerity of the past two decades especially the impact of industrial down-sizing and a shift in academia towards professional careers in environmental areas rather than in the previously-attractive fields of economic geology, geochemistry and petrology. Acknowledging the sobering implications and causes of the present research trends, the aim of this talk is threefold; (1) to review briefly the current state of knowledge of supergene enrichment in selected areas, (2) provide insight towards resolving an existing scientific controversy particularly lateritic bauxite genesis (Grubb, 1971; Brimhall et al, 1988, 1991, 1992 and 1994), and (3) highlight exciting opportunities which are unique to surficial aspects of geochemistry which could help offset the present state of declining activity in this field.

High-lighted advances

Selected advances highlighted here will include: interpretation of leached outcrops and use of relict sulfides (Hunt, 1985); electro-chemistry and persistency-field Eh-pH diagrams of Sato (1992); ferrolysis (Mann, 1984); mass balance and dynamics of supergene enrichment (Brimhall et al., 1985; Alpers and Brimhall, 1988, 1989; Colin et al., 1992); gold enrichment mechanisms in laterites, level of exposure and paleoclimatic controls (Freyssinet et al, 1990ab; Gray et al, 1992; Zeegers and Butt, 1992); theoretical numerical modeling (Ague and Brimhall, 1989); geochronology of weathering systems and correlation's with global climates (Vasconcelos et al., 1992); and micro-scale supergene enrichment mechanisms (Danti and Brimhall, in progress).

Conclusions and emerging opportunities

If researchers and practitioners in this field appreciate the current dilemma, we could reverse the state of decline in this field of research. The impact of downsizing is not necessarily all negative. Obviously the intense and diversified activity of the 1970's could not be sustained under the pressures of shifting metal prices. Translating such inevitable effects into educational realities, I perceive a need to better match the orientation and output of new young scientists to the demands of the professional market place so that they will be hirable, and sufficiently flexible to adapt to future changes and can remain competitive throughout their careers. The scientific mission and range of opportunities is distinct: to reverse the declining trend and to seek a sustainable level of activity by developing a range of new and unprecedented opportunities. My interpretation of the immediate needs in this field is to oppose the trend towards over-specialization and instead, to significantly broaden the scope of geochemical studies. Make them more interdisciplinary by developing linkages to the rapidly emerging fields of paleoclimatology, low temperature isotope geochemistry, high-resolution microbeam geochronology, geomorphology, global change and soil genesis. The unique record of supergene activity can be best developed in this broad context and will become more widely-appreciated as an integral part of surficial process studies. Immediate applications emerge in environmental geochemistry, sulfide oxidation and acid mine water remediation (Alpers and Blowes, 1994).

In the opposite direction of enormous global scales of interest, the advent of new microbeam instrumentation appropriate to studies on the scale of microns is ripe for development. The SHRIMP ion microprobe developed at the ANU by Compston and Williams offers exciting new ways to attack problems in surficial systems including establishing the identity of parent material and provenance of detrital minerals (Brimhall et al, 1994). Laser Ar/Ar dating provides the first direct means of establishing a quantitative framework for understanding chemical weathering and supergene processes (Vasconcelos, et al, 1992) in a much broader geological and paleoclimatic framework.

By better integrating mineralized supergene systems into the global record of surficial processes, including sea level fluctuations and paleoclimates, the current practical necessity of proceeding from prospecting in exposed areas where surface indicator methods of exploration have been effective to confronting the intrinsically more difficult challenges of working in concealed ground (Woodall, 1993) may be eased. Better understanding of the age and origin of overlying regolith, its transport history and sites of redeposition can only help. The significance of unconformities and the origin of sedimentary sequences including lake bed deposits should be useful in evaluating aqueous complexing agents like chlorides. In order to more widely integrate ore deposits research with advances in other fields of earth sciences, a resurgence of interest in a wide array of base metals besides gold, especially those in types of ore deposits proven to be of large size and high grade such as porphyry Cu and Au, stratabound Pb-Zn and Cu-U is necessary.

The broader issue is how can conceptual and technical break-throughs continue to be made and better utilized in three in different areas undergoing revolutionary change: (1) exploration (Adams, 1993), (2) basic earth science and (3) environmental geochemistry. Current revolution is not unique to earth sciences, but is being experienced in other physical sciences where restructuring is already underway (Langenberg, 1994).

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Evolution of regoliths and landscapes in deeply weathered terrain: implications for geochemical exploration

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Keywords: regolith, weathering history, exploration models, dispersion, supergene deposits

An understanding of the evolution of regoliths and landscapes is a fundamental requirement for long-term exploration success, particularly in deeply weathered terrains. By this is meant an interpretation of the weathering history as it affects the physical and chemical geology of the upper few hundred metres of the Earth's crust, as a basis for planning geochemical and geophysical exploration programmes. That such an approach is either desirable or necessary has only become fully recognized in the last two decades, and it is only within the last five years that exploration procedures based on these precepts have been applied regularly, and then only in restricted areas. The purpose of this presentation is to demonstrate why this approach is both appropriate and necessary for cost- and technically-efficient, successful exploration.

Initial mineral discoveries in regolith-dominated terrains, whether glaciated or deeply weathered, have generally been made in areas of outcrop, commonly where there is moderate relief, or where the commodity is either a weathering resistate or product (*e.g.* gold) that is readily identifiable. Development has then extended into adjacent concealed areas, although not necessarily to the extent of investigating features that would assist "green fields" exploration. It is when easily explored areas have been exhausted that is becomes necessary to develop a *geological* understanding of the terrain itself, including both the regolith and the landscape in which it occurs. Such an understanding requires a wide appreciation of the Phanerozoic history of a region, encompassing aspects of its tectonism, volcanism and sedimentology and their influence on, and interactions with, climate, weathering and erosion. The last three topics are ones that are not adequately covered in conventional geology or earth science courses, so that most exploration professionals are ill-equipped to adopt this approach. This neglect is understandable when the focus of attention is in regions of strong relief or in the high latitudes, but even in the latter, too little attention has been paid to glacial geology in conventional courses. In consequence, study of the earth surface is not regarded as truly part of geology, to the detriment of the exploration industry. Geologists are taught to recognise and map fresh rocks, even though, in practice, they will mostly only encounter weathered ones. Subjects such as geomorphology, weathering and regolith development have been studied largely by physical geographers, soil scientists and agriculturalists, with the priorities that those disciplines impose. For geological and, particularly, exploration geochemical purposes, the most important features are:

1. the distribution and provenance of all regolith components;
2. the physical and chemical processes involved in regolith formation and development;
3. the conditions under which these processes operated, and their relative timing and significance.

Knowledge of the evolution of the regolith and the landscape in which it occurs enables these features to be determined and provides the context within which the findings of other disciplines can be more readily applied to exploration. Thus, information about the climatic and tectonic history of a region may assist in determining the overall weathering and dispersion characteristics, including the potential for supergene mineral deposits. More locally, the geomorphology and soil distribution can provide information as to the potential usefulness of various regolith materials as sample media, and contribute to the interpretation of their geochemical and other characteristics.

The stable, Precambrian cratons of the major continental landmasses have been dominantly emergent for most of the last 1 billion years and, in places, for much longer. They have therefore been subjected to sub-aerial conditions during this period, except where local downwarping has resulted in regions of mostly shallow sedimentation. In consequence, their land surfaces potentially retain evidence of successive cycles of weathering and erosion, with the products of these processes contributing to the sediments on the cratons or adjacent basins. Although it is arguable that geomorphological evidence of ancient landscapes may persist on most continents, ancient regoliths are best preserved on the continents of the present tropics and sub-tropics that escaped scouring during the last glaciation. Even here, regolith materials older than the Permian are rare and, in any case, dating of the preserved remnants remains problematical. The cratons and adjacent basins of South America, Africa, India and Australasia are characterized by regionally extensive, deeply weathered, residual and sedimentary regoliths. These regoliths have a number of organizational, geochemical and mineralogical properties that point to a similar origin, namely that they are the product of seasonally humid, warm to tropical climates, broadly similar to those of the present wetter savannas. Such conditions are generally considered to have been more widespread from the Cretaceous to the mid-Tertiary, later contracting to the present near-equatorial distribution. Palaeomagnetic data support the suggestion that much of South America, Africa and India were largely within the lower, warmer latitudes during this period. However, Australia was mostly at high latitudes where, although climates were more humid and warmer than at present, they may not have been tropical. Nevertheless, Australia shares the heritage of a deep, intensely weathered, leached and commonly lateritic regolith, and a landscape of generally low relief. Many geochemical, mineralogical and geomorphological characteristics are similar, indicating that the chemical and physical processes involved in their formation are also very similar. This seems to be more important, from an exploration viewpoint, than precise details of the climates, and particularly the temperatures, under which they occurred. The inherent properties of this regolith have a profound influence on the surface geochemical expression of mineralization, so much so that these remain dominant despite later modification influenced by more recent climatic and tectonic changes. Accordingly, recognition of the early phase(s) of deep weathering is paramount and is fundamental to geochemical dispersion and exploration models (Butt, 1987). A similar concept applies in areas of higher relief and greater tectonic activity, if chemical modification of the regolith is more rapid than destruction by erosion.

Table 1: Modifications to lateritic regoliths due to changes in tectonic and climatic conditions (after Butt and Zeegers, 1992)

A. Tectonic Activity

Uplift:

- increased erosion;
- lowering of the water-table;
- irreversible dehydration and hardening of ferruginous and siliceous horizons;
- increased leaching of upper horizons under more oxidizing conditions.

Downwarping:

- decreased erosion, increased sedimentation in valleys;
- waterlogging of lower parts of the landscape and imposition of reducing conditions.

B. Climatic Change

To a more humid climate:

- decreased erosion (due to thicker vegetation);
- increased leaching and deeper soil development.

To a less humid climate:

- increased erosion (due to less vegetation);
- lowering of the water-table;
- irreversible dehydration and hardening of ferruginous and siliceous horizons;
- decreased leaching.

To a semi-arid or arid climate:

- increased erosion from uplands, with sedimentation on plains and in valleys;
- lowering of the water-table;
- irreversible dehydration and hardening of ferruginous and siliceous horizons;
- decreased leaching;
- salinization of groundwater;
- retention and precipitation of silica, alkaline earths and alkalis.

The effects on the regolith induced by change from a seasonally humid climate (whether tropical or temperate) and by tectonic uplift or downwarping are summarized in Table 1. These effects may lead to both physical and chemical modifications to the regolith; some of these are similar and the precise cause may be difficult to identify, particularly when the events are essentially contemporaneous.

Physical modifications have a profound influence on the surface expression of mineralization, since they control whether the pre-existing, deeply weathered regolith is preserved, partly or wholly eroded, or buried.

Chemical modifications alter the nature of the geochemical signature of mineralization in the regolith. They are induced by changes in drainage status due to tectonic events, or in water flux and quality due to climate change, and affect the composition of particular horizons or materials, and distributions of elements within the regolith as a whole.

Efficient and successful exploration of an area is contingent on establishing the influence of these modifications. The degree of preservation of the regolith, and the distributions of critical horizons and units, is best achieved by regolith mapping, supplemented by drilling to test regolith 'stratigraphy'. Geochemical modifications can be established by careful orientation studies, interpreted in the context of the climatic history of the region. The benefits and scope of the landscape-regolith evolution approach to exploration can be demonstrated for many supergene ore deposits (e.g. bauxite, lateritic Ni-Co, gold) and for primary deposits concealed beneath thick regolith. These are discussed with particular reference to conditions in Australia, where modifications are due largely to the imposition of arid conditions.

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Data processing and manipulation: Turning geochemical data into information and knowledge

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Keywords: Computers, database management, exploration geochemistry, geographic information systems, image processing, interactive graphical analysis, integration, statistical methods.

Extended Abstract

The use of computers to archive geochemical data and its easy accessibility via corporate information systems neccessitates the use of data processing and manipulation techniques that can efficiently summarize and organize the analytical results into a form that the geochemist can digest - the process of turning geochemical data into information. Commonly, such data are multi-element in nature owing to the success of recent developments in multi-channel analysis. Exploration geochemists, especially, amass large amounts of geochemical data which have a spatial component such as that generated from a large regional geochemical survey.

An important part of a geochemists work is to think of ways to represent these data so that they and others can understand what is going on. Reduction of multi-element data can be carried out utilising statistical and graphical techniques. Experience has shown that visual images greatly assist the geochemist to develop and share their insights and theories with colleagues, by providing an effective way to pass along their mental images that are the basis of their thoughts. Computer graphics are a very effective way to perform this task and when the relatively new capability of animation is applied to graphical representations, more insight into the data can be obtained. The presentation of existing data sets using interactive graphical analysis systems allows the geologist to assess new geochemical data quickly and in an intuitive way. Other techniques utilised in CRAE include automated classification systems that have been developed to assist geologists in assessing the results of gossan and ironstone sampling (Eggo, 1983). These knowledge-based systems rely on the identification of multi-element geochemical "fingerprints" in samples using a base of geochemical data representing the surface expression of a large number of known ore deposits.

Geotechnical computing in CRAE has matured to a stage where a significant proportion of data processing tasks are now being performed using personal computers and scientific workstations, both in the field and the district offices. Historical geotechnical data, cartographic information (e.g. land ownership, tenement, infrastructure, etc.) and catalogue-type information such as reports, publications, plans, remote sensing scene purchases, geochemical sampling programme boundaries, etc., are made freely available to all CRAE staff who require it using CD-ROM technology. Accordingly, integration of geochemical data with other critical information gained from geological mapping, geophysical and topographical surveying and remote sensing is carried out increasingly by geologists using "desktop mapping" and "geographic information systems" (GIS). Recent developments in digital image analysis are now being applied to the display and interpretation of geochemical data which has a spatial component. Continuous tone images allow for the recognition of spatial features inherent in geochemical data as the eye and brain can resolve pattern differences more easily than that provided by raw data or conventional methods of interpretation based on symbol plots (Björklund & Gustavsson, 1987; Eggo, 1989). Methods which can be used to correct geochemical data for geological and secondary environmental processes further add value to the unprocessed geochemical data (Eggo, *et. al.*, 1995).

The "added value" products can be merged and combined with second and third generation magnetic, gravity, topographic, and remote sensing imagery (Harding & Forrest, 1989; Wilford, *et. al.*, 1995). Considerable new insight into geochemical processes can be provided by the application of these tools allowing the geologist to identify the critical blend of geological features characterising areas prospective for potential mineralisation.

Future discovery of new ore deposits and extensions to existing ones will rely increasingly on the detection of mineralisation in areas that have already undergone intensive exploration (e.g. Century) or are concealed by thin surficial deposits which increase the noise component in geochemical data. Subtle geochemical signatures will need to be detected more reliably probably

using techniques which rely on the recognition of multi-element geochemical "signatures" and aberrant patterns rather than detection of simply high geochemical concentrations. Integration of the geochemical data with other critical information contained in magnetic and topographic data using GIS will also increase the confidence in the interpretation.

Acknowledgements

The author thanks CRA Exploration Pty. Limited for allowing permission to publish this paper.

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Exploration geochemistry in Southeast Asia: soils, sediments and potential for anthropogenic effects

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Keywords: Tropical rain forest, soils, sediments, heavy minerals, anthropogenic effects

Regional setting

The region extends from Thailand and Indo-China, down the Malaysian Peninsula through the Indonesian archipelago to Papua New Guinea and the Solomon Islands. The equatorial core of the region is largely perhumid tropical rain forest having an annual rainfall in excess of 2000 mm and a mean temperature above 18°C in the coolest month. (Whitmore, 1984). Drier, more seasonal climates are found in much of Thailand and Indo-China, and in a fragmented north-south zone through the centre of the Indonesian archipelago. Topographic relief varies from near flat planation surfaces and coastal lowlands, through hills of low to moderate relief, to the steep topography of the mountains, the highest peaks of which exceed 4000 m above sea level. As a result of active tectonism and volcanism, steep slopes, human activity and heavy rainfall, the rivers of the region deliver some of the highest yields of suspended sediment (from 500 to more than 1000 $t.km^{-2}.yr^{-1}$) in the world to the surrounding seas (Milliman and Meade, 1983). (Although not strictly within the region, the island of Taiwan delivers roughly the same sediment load to the ocean as the entire conterminous United States!). Part of this suspended sediment is trapped in the fringing mangrove swamps.

Soils

The chemical and physical characteristics of soils of the humid tropics and the significance of their origin and properties to exploration geochemical surveys, will be considered in greater detail by other speakers. Nevertheless, it is important to note that generalized landscape models can be developed in which the soils (and the closely related forest formations) are related to altitude and parent material (Butt and Zeegers, 1992). Distinctive soils in such models include the gley soils of the mangrove swamps and floods plains; peat soils of the lowland freshwater swamps; heath soils developed on sandy coastal plains and montane sandstones; colluvial regosols on steep slopes; and montane peat soils (Burnham, 1984). However, the principal soils of the lowland and lower montane rain forests are red and yellow latosols (also know as ferrasols or oxisols) that grade into podzols (spodosols) at higher elevations. These soils, particularly at lower elevations, are developed on deeply weathered saprolites. Because of the very complete weathering the soils are usually rich in kaolinitic clays, and oxides and hydroxides of iron and aluminium.

As described by Lecompte and Zeegers (1992) and Butt and Zeegers (1992) the residual or near-residual latosolic regolith, even where deeply weathered, usually retains some of the geochemical signature of the local bedrock and therefore does not present major problems to exploration geochemistry (though there may be logistical problems of access, steep slopes and forest cover) provided downslope movement, differential mobility of elements, and presence of locally transported material are taken into account. An example from moderate to steep slopes in the lower montane forest of Malaysia exemplifies these characteristics (Fletcher et al, 1984). At an elevation of 960m and with a rainfall that exceeds 3600 mm per year, a podzolic soil has developed on a pallid granitic saprolite up to 2m thick. Primary mineralization (cassiterite, arsenopyrite, chalcopyrite, galena, sphalerite) in the granite is clearly reflected by soil geochemical anomalies. The Sn anomaly is enhanced in the surface horizons by preferential loss of fines whereas As and base metals are depleted by leaching and loss of fines. The anomalies can be traced back to, but are displaced downslope from the bedrock source. For Sn the degree of downslope movement increases with decreasing grain size - probably a consequence of greater movement of fine cassiterite by sheetwash.

Sediments

Although heavy tropical rains can occur at any time of the year in the perhumid zone, they are most frequent in the two annual monsoon seasons when heavy rains often fall several times a week. For example, in West Malaysia during the November-January monsoon period there are, on average, three rainstorms per week of sufficient intensity to increase the discharge of the Sungai Petal and initiate bedload transport of sediment (Fletcher and Low, in prep.). Movement of sediment is thus much more frequent than in drier climates and fine sand, silt and clay are flushed from the stream bed to be carried downstream and deposited in and alongside low-lying alluvial channels, trapped in coastal mangrove swamps, or swept out to sea. Thus, in their natural state, streams in areas of even gentle to moderate relief have clean, sandy or gravel beds that typically contain less than 1% silt and clay. The texture of the clay-rich latosols and the sediments of the streams that drain them is thus very different.

These relations have interesting consequences for the exploration geochemistry of elements associated with heavy minerals. If the heavy minerals are present as fine to sand-sized heavy mineral grains (e.g., cassiterite) there is commonly an inverse relation between the concentration of the associated element and the size distribution of the soil or sediment. Thus in soils the best geochemical contrast is obtained in the coarser fraction, whereas in sediments the elimination of clay, silt and fine sand leads to the finer fractions becoming enriched in heavies that "lag" behind during sediment transport. This lag effect counteracts downstream anomaly dilution and results in the finer fractions of the sediments having long anomalous dispersion trains that, even several kilometres from their source, can have anomalous values comparable to those in soils in proximity to the mineralization (Fletcher et al, 1987; Fletcher and Low, in prep.). It is therefore generally expected that use of the finer fractions (-63 μm) of the sediments will benefit geochemical drainage surveys for gold and other heavy minerals in the wet tropics. This contention is empirically supported by case histories throughout the region (e.g., Watters et al, 1989; Carlile et al 1990; Nuchanong et al, 1991; van Leeuwen, 1994). Also in this context, the gold content of fine sediment from coastal mangrove swamp sediments has been successfully used as a guide to adjacent areas of gold mineralization in the Yap and Palau islands (Rytuba and Miller, 1990).

For the base metals and other elements that tend to be leached and/or become associated with the finer fractions of the soils during weathering, both dilution and elimination of fines from the sediments suggests that stream sediment anomalies are likely to be weaker than in the soils and the anomalous dispersion trains relatively short compared to those of the heavy minerals. This appears to be the case in the S. Petal. In this situation use of the finer fractions of the sediment (to minimize effects of dilution by barren sand) or coarser, multi-mineralic (+180 μm) fractions (to minimize the effects of weathering) should be evaluated.

Anthropogenic effects

Recent surveys estimate that the rate of removal of tropical rain forest in the region has averaged about 1% annually between 1981 and 1990 (FAO, 1993). Primary forests have been substantially removed from some areas (e.g., Thailand) but are still very extensive in others (e.g., Papua New Guinea). Logging activity assists mineral exploration by facilitating access to otherwise remote regions. However, removal of the vegetation decreases infiltration of rain and increases overland flow and rates of erosion. For example, logging activity in lowland tropical rain forest in Malaysian Borneo was found to increase the sediment yield nearly twenty fold (Douglas et al, 1992). Part of this increased yield is deposited in and alongside stream channels and takes at least several years to be flushed from the channel after logging has ceased. During this period it seems likely that heavy mineral anomalies in the fine fractions of the sediment will be diluted compared to nearby undisturbed catchments.

In areas where the forest cover is completely removed and the land converted to agriculture, rates of erosion are likely to be more extreme and longer term. This is particularly the case if, as in northeast Thailand, the land is plowed prior to planting maize at the onset of the monsoon season (Paopongsawan and Fletcher, 1993). In this situation the catchment may have a much larger yield of clay-rich sediment than the stream is able to transport. This changes the texture of the sediments from a clean sandy-gravel to a sandy-gravel with large amounts of silt and clay. An important consequence is that gold anomalies in the sediments can be diluted below the detection limit (5 ppb) of conventional fire assay-atomic absorption methods (Paopongsawan and Fletcher, 1993; Fletcher et al, in press). However, investigations by Sirinawin et al (1986) of a Sn anomaly in a mature rubber plantation in West Malaysia suggests that if a permanent cover of surface vegetation is reestablished, rates of soil erosion decline to the extent that Sn anomalies in drainage sediments are again enhanced in much the same manner as they are in undisturbed catchments.

Conclusions

In summary, the principle problems associated with geochemical surveys in the tropical rain forests of southeast Asia are likely to be logistical rather than geochemical: in general, the presence of bedrock mineralization should be detected in related soils and stream sediments. For elements transported in drainage sediments as the principal constituents of heavy minerals, both the contrast and length of anomalous dispersion trains are likely to be enhanced in the fine sand and silt fractions as a result of elimination of fines from the stream bed. This beneficial effect can, however, be offset by logging and land clearance that increases rates of soil erosion and the supply of fine sediment to the streams.

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Should Exploration Geochemists be Involved in the Environment?

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Keywords: geochemistry, environment, Pb isotope fingerprinting, human health, mining.

With the cyclical nature of the mining industry and the concern for the future of mining in the U.S., Canada and Australia arising from litigation and native title claims, should exploration geochemists and geologists be involved in environmental issues?

There has been some parry and thrust on this position in Explore and the SEG Newsletters with some correspondents taking the negative stance whereas the overall opinion seems to be on the positive side. Even though there has been discussion, neither Economic Geology nor Journal of Geochemical Exploration seem to have been inundated with environmental papers.

For too long tertiary education courses directed to the environment have been the domain of the biologist, chemist or engineer. But the majority of environmental issues involve earth sciences in some form or other and this applies especially to those concerned with mining.

Unfortunately, in many instances the geologists and geochemists address only part of the environmental spectrum usually related to their own specialised area. However, it is critical that they address the full range of issues. This applies especially to implementation of abatement and remediation measures and impact on human and animal health - not just the impact on, for example, the lithosphere, hydrosphere and atmosphere.

One of the fundamental stumbling blocks in environmental issues related to mining activities is the suspicion and lack of co-operation between the company or companies, the community and any self-interested parties. One community where this has been overcome is in Trail, British Columbia, but such co-operation appears rare.

How do we rectify this problem? To begin with, we have to decide whether as geologists and geochemists we wish to be involved in environmental issues, especially those related to mining activities. Given the state of play in North America centred on Superfund legislation, the potential for such litigation to proliferate elsewhere, and concerns expressed by leaders of mining companies in Australia about environmental (and Aboriginal) "constraints", it would seem imperative that geologists and geochemists become more involved. Furthermore, given the sensitivity of environmental issues, earth scientists need to play a major role in environmental impact studies, i.e. before mining starts.

Examples

It is becoming increasingly recognised within the earth sciences community that much of the data collected for geological/exploration outcomes provides a magnificent data base for regulatory purposes, for water/soil/dust guidelines, for standards of clean-up criteria all focused on the assessment and remediation of contaminated areas. A very recent example is the excellent compilation of Painter, Cameron, Allan and Rose in JGE, volume 51 (1994). Also much of the work of the U.S. Geological Survey Branch of Geochemistry and the Geological Survey of Canada is directed towards the above objectives.

Three examples of the application of geochemistry to solving environmental problems will be briefly described, two dealing with mining problems and the other a social problem.

Example 1: Sources of lead in Humans from the Broken Hill Mining Community

Even though mining (and earlier on, smelting) has been carried out for more than 100 years in this city of 25,000 inhabitants, lead as a public health issue was only recognised in 1991. The issue arose from publicity over high lead (Pb) dust levels in ceilings of houses (up to 3.6% Pb), three children born with delayed visual maturation, and later, a NSW Health Department survey of 899 children aged 1-4 years which identified about 59% of them having a Pb blood level of >15 mg/dL, the Centres for Disease Control level of intervention. As the city is built around mining dumps, they have been identified as the probable source of Pb in the children.

To assist in recommendations for the most suitable lead abatement policies in Broken Hill, knowledge of the sources and pathways of the lead into humans is critical. We have approached these problems using the lead isotope fingerprinting method, combined with mineral speciation and "bioavailability" tests, approaches which have in the past been largely applied to mineral exploration.

High precision lead isotope ratio measurements and lead contents were determined by thermal ionisation mass spectrometry on biological samples (blood, urine) and environmental samples from 27 families, encompassing 60 children, 41 female adults and 17 male adults. Environmental samples analysed (not from every household) included soils, gutter sweepings, ceiling dust, vacuum cleaner dust, long-term dust, surface dust wipes, external and internal air, food, water, and gasoline.

Sources of lead have been identified in the blood of children, using lead isotopes, with dominant contributions from the Broken Hill orebody, but with individual cases having a dominant source of lead from gasoline or paint (Fig. 1). Nevertheless, of 28 children with blood lead (PbB) >15 µg/dL, ~30% have more than 50% of their PbB from sources other than the orebody. Female adults generally have low PbB, <10 µg/dL, and the source of their lead is attributed to air (gasoline, orebody), food and water. The source of lead in male adults can be usually correlated with their

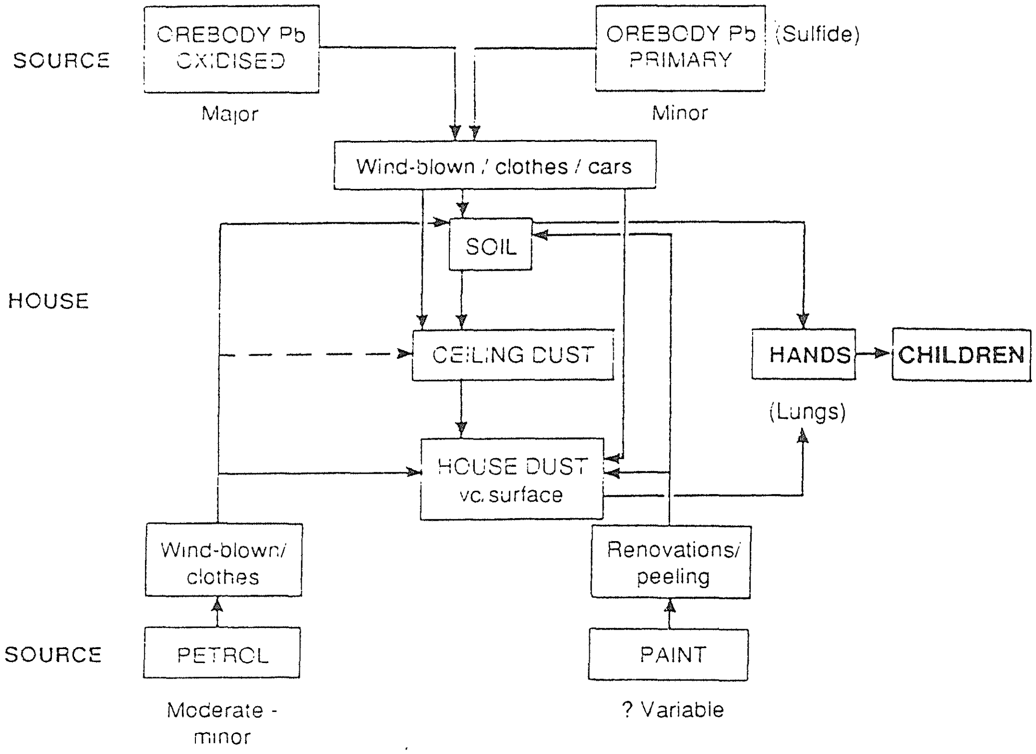

Figure 1 Sources and pathways of lead in Broken Hill

occupation, depending on whether it is related to high-risk activities such as mining (dominantly orebody lead) or service stations (gasoline lead) or "non-exposed". Knowledge of the occupation and lead isotope composition in the father's blood is an important indicator of lead pathways. Other potential sources of lead such as food and water have lead contents too low to be significant contributors to PbB in most children.

Scanning Electron Microscopy (EDX analyses) identified the most common lead species in soils and dusts in houses close to the central mining activity to be composed of as a complex Pb Fe Mn Ca Al Si O material with rare galena. These lead complexes are quite different from other mining communities, such as found in the U.S., where the lead may be in less soluble forms such as pyromorphite, or encapsulated in less soluble anglesite, pyrite or quartz. Approximations of "bioavailability" (more correctly, solubility) were made by leaching, with 0.1M HCl for 2 hours at 37°C, bulk both unsized and a 'critical' size fraction of -53+38 µM. The 0.1M HCl extracts 33 - 61% (mean 47;10%, N=7) of the total leachable lead from gutter sweepings, from 41 - 84% (mean 60;10%, N=10) from soils, and 17 - >100% (mean 47;38%, N=5) from vacuum cleaner dusts. Thus a Broken Hill child ingesting soil ('dirt') and dust at the currently suggested amounts of ~100 mg/day, can readily account for the elevated PbB's compared with many other mining communities. Based on these investigations it is possible to construct a flow sheet of sources and pathways for the lead into humans at Broken Hill on which to base correct remedial actions (Figure 1)

Example 2. Monitoring leakage around a uranium tailings dam

Ranger uranium mine in the Northern Territory of Australia has been operating for 11 years. Waste from the milling of the ore is stored in a dam covering about 110 hectares. Any potential leakage from the dam could contaminate the groundwaters and the environmentally sensitive Kakadu National Park and is therefore very carefully monitored.

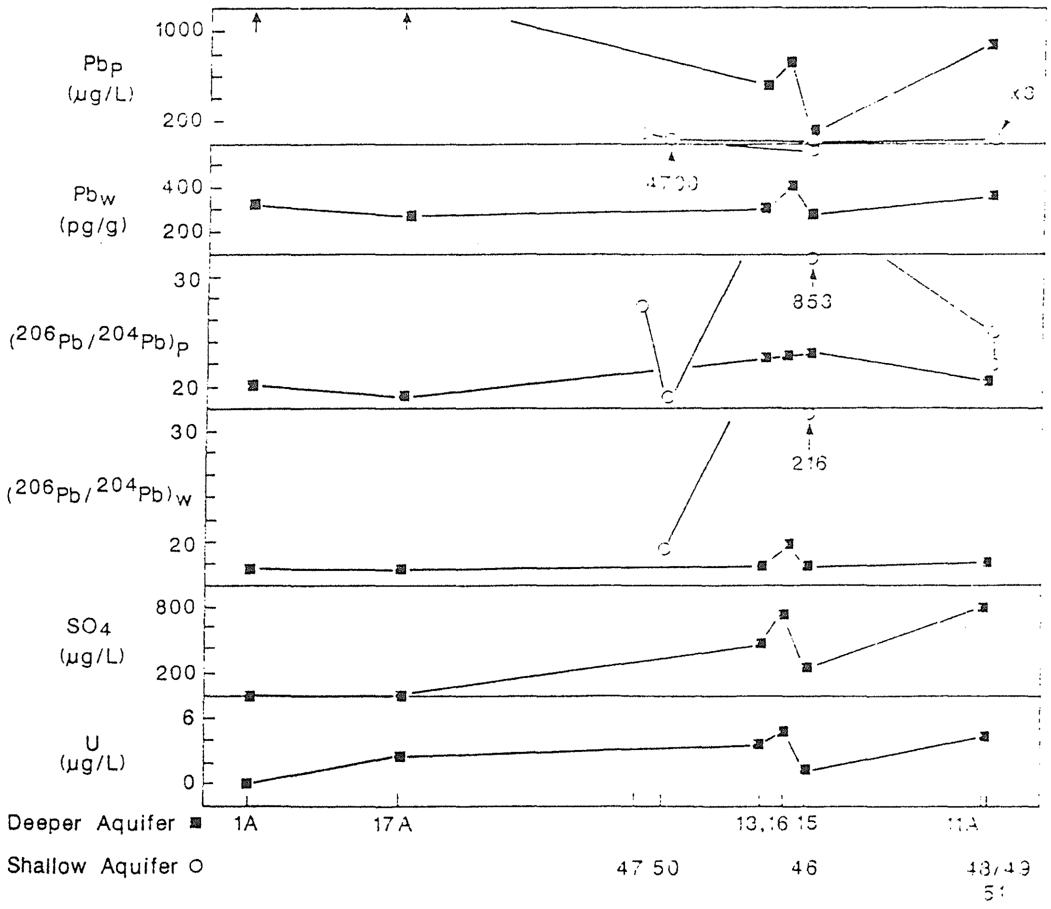

Figure 2 - Results of monitored bores around the Ranger Tailings Dam

Lead isotopes in uranium ores have a characteristic fingerprint with 206Pb/204Pb values often >10,000 and low amounts of the thorium-derived 208Pb. For this study, Pb isotopes and Pb contents were compared in water and particulates filtered from the water from the tailings dam and from monitoring bores around the dam (Fig. 2.).

The 206Pb/204Pb value in the tailings water is >10,000 whereas that in the 'background' bores is generally from 17 to 20. Particulates (0.45 mm+) generally give an enhanced 'signal' compared with the waters of any leakage from the tailings dam as shown in Figure 2. It is possible, using Pb isotopes in the particulates, to observe isotopic differences in different aquifer systems and therefore ascertain whether there is leakage from the tailings dam or other sources.

Example 3. Journey through a bottle of wine

Food authorities in many countries have moved to reduce the dietary intake of lead. In this context, wine with a lead content of 0.1 mg/kg is a significant dietary source of lead for a person who consumes moderate amounts of wine daily; e.g. consumption of 250 ml daily, would constitute about 6% of the provisional tolerable weekly intake for an adult as recommended by FAO/WHO.

From recent studies it appears that the 'natural' lead content of wine falls in the range 0.05-0.100 mg/kg. However, for many years a proportion of wines has been found to contain lead significantly in excess of this range. The data suggest that these wines are contaminated with the soluble corrosion products of the tin-lead capsule, either by migration of the corrosion products through or past the cork into the wine or during the pouring process. The corrosion products, which have been shown to consist of lead carbonate hydroxide and its hydrated form are considered to form from the reaction of the acidic wine with the capsule.

The source of the lead was determined using Pb isotopes based on the expectations that:

1) the Pb capsules were manufactured from Pb from different mines and would have a variable Pb isotope signature different from that of the wine, and
2) because of the low Pb concentration in the wine (usually <50 ppb), any Pb drawn back through the cork would be obviously identified by both the Pb content and isotopic value of the cork.

Wines, cork, capsules and corrosion products were analysed from >50 bottles of Australian and some German wines, including bottles with and without capsules, the former with varying states of corrosion. The Pb isotopic composition of the wine was the same for bottles with and without lead capsules even though the wine leaked out through the cork and reacted with the capsules. Furthermore, no Pb concentrations or Pb isotopic gradients were discernible from analyses of different segments of corks - except for the top 1-2 mm. However, for bottles with corroding Pb capsules, Pb can be introduced into the wine either by pouring, during which the wine dissolves the soluble Pb compounds on the neck of the bottle, or by entrainment of Pb through the cork if the bottom of the cork is pierced during its removal.

In conclusion

There needs to be a concerted effort on the part of educators, societies such as the AEG, and individuals to take a leading role in environmental issues, especially dealing with mining activities. We also need to convince the community that we can give objective advice even if we work for a mining company or in an organisation where the focus is on exploration and mining.

Progress in hydrogeochemical surveys, from the great white north

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The Analytical Method Development Section at the Geological Survey of Canada has been active in both designing and applying methodologies to determine, precisely and accurately, trace elements in surface waters at their 'natural' ppb and ppt (ng l^{-1}) levels. Both lake and stream waters and their corresponding sediments are collected routinely under the National Geochemical Reconnaissance Program of Canada; the data and maps thus produced are then used for both exploration and environmentally oriented objectives. While the sediments are analysed commercially for a large suite of elements (>50), the high cost of of determining a wide range of elements to *adequate* detection limits in waters has precluded such broad analysis. The progress of ICP mass spectrometry (ICP-MS) from the research/pioneering stage to routine use has altered that situation. The analytical methods now designed are divided into 'packages' of compatible elements, all based on the technique of ICP-MS but grouped according to different pretreatments and sample introduction mechanisms. The packages discussed in this paper comprise:

(1) pneumatic nebulisation ICP-MS;

(2) ultra-sonic nebulisation ICP-MS;

(3) fully automated chelation ICP-MS for the rare-earth and transition elements; and

(4) hydride generation ICP-MS for Se, Sb, Te, and Bi.

The complementary role of ICP-MS in water analysis with other techniques such as ICP emission spectrometry and ion chromatography is also discussed in this paper. Other concerns such as sample preservation for species analysis, the introduction of filtration artifacts and cross contamination will be addressed.

Application of these methods in hydrogeochemical surveys conducted in different geological terrains in Newfoundland and Nova Scotia will be presented. Specific objectives of these surveys were to:

(1) establish a database of elemental concentrations in stream and lake waters largely unaffected by anthropogenic input, particularly for parameters (e.g., REEs) hitherto unmeasured due to analytical limitations;

(2) ascertain the factors (e.g., underlying geology, till cover, bulk water composition, sediment character) controlling the distribution of these elements in solute form; and

(3) evaluate hydrogeochemistry as an exploration methodology.

Terbium (and other REEs), for example, in the lakes of the Baie d'Espoir region delineates the bedrock geology clearly, even at the low and narrow range of 1-20 ppt. Subtle though definite anomalies in such gold pathfinder elements as Te and Bi are seen in streams collected in areas of high gold potential in Baie Verte. Daily variations in trace element composition of the surveys' 'control' streams have been found to be minimal, except during heavy rain events; the consequence of this 'disturbance' will be examined within the context of the entire survey.

Overview of the lithogeochemical architecture of volcanic-hosted massive sulphide deposits

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Keywords: VHMS, alteration, lithogeochemistry, base metals

Previous researchers in submarine volcanic terrains in Australia, Canada and Japan have documented the presence of various styles of mineralogical and geochemical alteration, some of which are related spatially and genetically to VHMS deposits. A summary diagram showing our current thinking on the spatial relationships of massive sulphides and alteration styles is given in figure 1. The major alteration facies outlined in this figure are discussed below.

1. Footwall alteration pipes: are developed below most major mound style VHMS deposits and result from focussed upward flow of hydrothermal fluids to the seafloor. Previous studies (e.g. Riverin and Hodgson, 1980; Shirozu, 1974; Gemmell and Large, 1992) have resulted in a clear understanding of the mineralogy, geochemistry and zoning in the pipes. The pipes themselves are a direct vector to mineralisation. However, most Australia deposits do not have well defined alteration pipes.

2. Stratabound footwall alteration: extensive zones of footwall alteration, up to 200 m thick below the ore position, extend for several square kilometres around some deposits (e.g. Rosebery, Mt Chalmers, Que River). These may reflect zones of low-temperature regional fluid discharge onto the seafloor as documented by Rona (1988) for off-axis zones along the present mid-oceanic ridges. Little research has been conducted into the detailed characterisation of these stratabound zones in terms of mineralogy, geochemistry and vectors to ore.

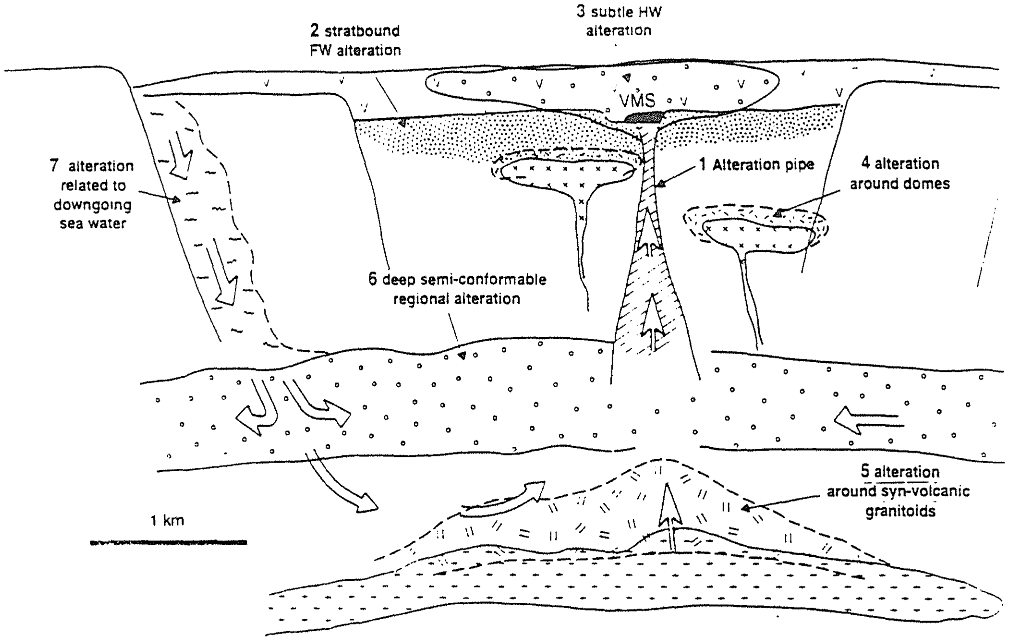

Figure 1 — Current understanding of alteration architecture in VHMS systems.

3. Hangingwall alteration: subtle alteration extending tens to hundreds of metres into post-ore volcanics has only been documented in a few Australian cases (e.g. Hellyer — Jack, 1989; Scuddles — Ashley et al., 1988; Mt Chalmers — Large, 1992). There is scope for further research on the mineralogy and geochemistry of hangingwall alteration associated with VHMS deposits in order to develop a more complete database and determine vectors to ore.

4. Alteration around porphyritic subvolcanic domes: alteration with associated low grade base metal mineralisation has been recorded around the margins of felsic porphyritic domes, for example at Elliott Bay in the Mt Read Volcanics, Tasmania (MRV) (Large et al., 1987) and in the vicinity of Thalanga in the Mt Windsor Volcanics, Queensland (MWV). Such alteration zones may be unrelated to VHMS deposits and yet their characterisation is important in order to prevent excessive exploration expenditure on "false" targets.

5. Alteration associated with syn-volcanic granitoids: Syn-volcanic granitoids occurring as sill-like bodies at depth in the volcanic pile may have acted as heat engines and/or metal sources for VHMS mineralisation. Polya et al. (1987) considered the Murchison granite in the MRV to be the heat engine for circulating seawater which ultimately produced the Rosebery ore deposit. The Flavrian pluton and Beidleman Bay pluton are also considered to be heat engines for VHMS mineralisation in the Noranda and Sturgeon Lake camps (e.g. Cathles, 1993; Galley et al., 1993). Our recent research in the MRV indicates that a semi-continuous sill of granite intruded deep into the footwall volcanic pile extends over 40 km from the Murchison Gorge to Mt Darwin. Complex alteration patterns of K-feldspar, chlorite and sericite associated with magnetite-pyrite-copper mineralisation are related to the granite sill (Eastoe et al., 1987; Hunns, 1990; Doyle, 1991; Payne, 1992; Jones, 1993). Our current research indicates a relationship between the granitoid sill, K-feldspar chlorite-magnetite±apatite alteration and the Mt Lyell Cu-Au deposits (Raymond, 1992; Large et al., 1994).

6. Deep semi-conformable regional alteration: Extensive zones of stratabound alteration have been mapped in some of the Archean VHMS districts in Canada (Galley et al., 1993). These zones which include epidote, albite, amphibole and silica alteration occur at depths of greater than 1 km below the seafloor massive sulphides. They are considered to represent zones of high temperature lateral fluid flow which are an integral part of the sub-volcanic fluid convection system. Similar alteration zones have not been recorded in Australian VHMS belts; however, this may be due to lack of recognition rather than absence of the zones.

7. Alteration related to downgoing seawater: the seawater convection model for VHMS genesis requires seawater flow downwards along structurally controlled zones. These downgoing (or input) zones should be characterised by relatively low temperature alteration assemblages, possibly involving Ca and Mg metasomatism.

In addition to these seven facies of alteration there are two other processes that cause mineralogical change in submarine volcanic rocks, and may be confused with hydrothermal alteration processes.

- diagenetic alteration (e.g. devitrification of volcanic glass) related to cooling and ageing of volcanic rocks
- metamorphic re-equilibration that generates new mineral assemblages related to deformation and/or later igneous intrusive events.

Use of alteration geochemistyry to determine vectors to ore

Alteration zones in volcanic piles are commonly several orders of magnitude larger that the related ore deposit (e.g. fig. 1). Consequently the recognition of mineralogical, chemical or isotopic zonation within areas of alteration may provide a basis for developing vectors to the ore deposit. Some alteration zones have no related ore deposit, and therefore the recognition of discriminators between fertile and barren alteration zones is also very important for exploration. Research in VHMS districts world-wide has led to definition of the following alteration vectors to ore:

1. Sodium depletion: it has long been recognised that Na_2O decreases with intensity of hydrothermal alteration in proximity to VHMS deposits, due to replacement of plagioclase by sericite and chlorite. Although this factor is successfully used to define the boundary of strong alteration zones, it is of little use as a direct vector to ore.

2. Alteration index: $$AI = \left[\frac{MgO + K_2O}{MgO+K_2O+Na_2O+CaO}\right] \times 100$$ increases from about 10 to 100 with increasing intensity of alteration. This index was developed by Ishikawa et al. (1976) for Kuroko Deposits and remains the best available geochemical vector to ore for VHMS systems. It has been used most successfully in studies on the intensity of footwall alteration, but also has application to defining hangingwall alteration (e.g. Large, 1992). However, barren alteration systems also show positive AI anomalies that are unrelated to ore, and we therefore need to develop other criteria that can be used to discriminate barren from fertile AI trends.

3. Whole-rock oxygen isotopes: research on whole-rock oxygen isotope fractionation in VHMS districts (e.g. Green, et al., 1983; Green & Taheri, 1992; Cathles, 1993) demonstrates that prospective alteration zones can be defined by the use of detailed isotope mapping. This work has shown that zones of ^{18}O depletion correspond to regions of footwall alteration associated with the major massive sulphide deposits. Cathles (1993) has also demonstrated that ^{18}O depletion marks the margins of plutons that have driven sufficient hydrothermal circulation to produce economic massive sulphide deposits up section. In this project there is scope for regional studies of oxygen isotope fraction patterns related to sub-volcanic intrusions and mineralisation both in the MRV and MWV.

4. Sulphur isotope patterns: Previous studies in the MRV (e.g. Solomon et al., 1988) have shown that the VHMS deposits have a characteristic sulphur isotope signature that relates to the mixing of contributions from reduced seawater and primary volcanic rock sulphur. Gemmell and Large (1992) and Jack (1989) have recorded variations in $\delta^{34}S$ values away from the centre of the hydrothermal system both in the footwall and hangingwall alteration zones at Hellyer that provide a basis for developing S-isotope vectors to mineralisation.

The challenge for the next decade is to develop a series of integrated mineralogical, geochemical and isotopic vectors that relate to hydrothermal fluid flow and massive sulphide mineralisation within the context of both the volcanic facies architecture and the seven facies of regional and local alteration depicted in figure 1.

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Redox controls on the formation of supergene gold deposits

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Keywords: gold, supergene, redox, ore genesis

Introduction

Fluid/rock geochemistry and structural traps are familiar essential components of primary metallogenic ore genesis. Similarly, supergene gold ore genesis requires physio-chemical transport, concentration and deposition. But, under most supergene conditions of temperature, pressure and geochemistry, metallic gold is essentially inert. However, with the exception of gold locked in resistant primary oxides, supergene gold is commonly displaced, typically into thin sub-horizontal enrichment/dispersion zones within the regolith, and shows ubiquitous evidence of chemical reworking, such as unique morphologies and modified chemical composition, from its primary derivative (Lawrance, 1988; 1991; Lawrance and Griffin, 1994). Clearly the processes of supergene gold ore genesis are highly specialised and efficient.

Gold Geochemistry

On oxidation, gold forms Au^+ and Au^{3+} species. As unassociated ions, these gold cations are strongly redox affected and have negligible solubility, but in the presence of particular ligand species and suitable Eh and pH conditions, they form soluble low charged anionic organic and inorganic complexes (Table 1). These complexes have limited stability in the weathered environment being highly soluble only under very specific conditions of Eh, pH and fluid composition. The supergene gold product precipitated shows distinctive composition and morphology indicative of the dissolution mechanism.

Regolith Geochemistry

Iron is also strongly redox affected and is an important indicator of geochemical environments in the regolith. Under reducing conditions, iron is mobile as an unassociated ferrous ion (Fe^{2+}). With access of sufficient oxygen, Fe^{2+} is unstable and is oxidised to ferric ion (Fe^{3+}). The Fe^{3+} is insoluble, except at very low pH, and is hydrolysed and precipitated as visually distinct yellow-brown-red iron oxyhydroxides. Typically, Eh and pH increase towards the surface and the oxyhydroxides are precipitated at a sub-horizontal front in the regolith referred to as the *redox front.* This precipitation of iron oxyhydroxides releases hydrogen ions, which result in acid conditions as low as pH 2, just above the redox front. These acid conditions promote weathering which causes an increase in pH in the upper profile away from the reaction front. The dominant iron oxide produced under acid conditions is goethite (Schwertmann, 1988).

$$\underset{\text{mobile ferrous ion}}{2\,Fe^{2+}} + 1/2\,O_2 + 3\,H_2O \Rightarrow \underset{\text{goethite}}{2\,FeOOH} + 4\,H^+$$

This redox reaction is rapid and of limited reversibility, except by specific organic processes. Therefore, iron oxides are largely stable to further weathering and are immobile unless transported as a colloidal sol. As such, they are an indication of past and present weathering intensities and of Eh-pH conditions within the profile. A *redox zone* commonly develops just above a stable redox front over time due to an extraneous accumulation of iron oxides by Fe^{2+} diffusion to the redox front from below and an influx of colloidal iron oxides in groundwater from above.

Aqueous conditions of the regolith, and therefore the depth of the redox front, are constantly changing with changes in climate and topography. Laterite and analogous ferruginous accumulations in the near-surface form above high watertables under wet climates (rainfall > 1m/yr), and are generally the first formed redox zones. The associated underlying mottled zone is a redox transition zone resulting from variable access of water and oxygen particularly with seasonal fluctuations in the watertable. The strongest acid zone occurs at the base of the laterite and upper mottled zone. It is unlikely under these wet conditions, that the acid produced at the redox front has a strong affect on groundwater pH. However, its local production results in enhanced weathering in the laterite where there is a distinct change from partial isovolumetric weathering in the mottled zone to strong leaching and profile subsidence in the laterite.

Table 1 Summary of chemical environments suitable for gold mobilisation by ligand species commonly found in the regolith (modified from Lawrance, 1988).

Ligand	Chemical environment for gold dissolution	Dissolution reactions	Gold product on precipitation
Organic humic acid amino acid	Oxidising neutral-acid biological activity	Au (electrum) + Organic Acid + $O_2 + H^+$ $\Rightarrow$ Au(Organic)$^{n+}$ + H_2O	Fine-grained high fineness
Cyanide CN^-	Oxidising moderately acid-neutral-alkaline presence of cyanide from biological activity	2Au (electrum) + $4CN^- + 1/2O_2 + 2H^+$ $\Rightarrow 2Au(CN)_2^- + H_2O$	Fine-grained low fineness
Halide Cl^- Br^- I^-	Strongly oxidising acid pH < 4 high salinity [halide] > 1M	2Au (electrum) + $8Cl^- + 3/2O_2 + 6H^+$ $\Rightarrow 2AuCl_4^- + 3H_2O$	Coarse-grained very high fineness
Thiosulphate $S_2O_3^{2-}$	Reducing-neutral mildly acid-neutral-mildly alkaline weathering of sulphides low-moderate carbonate	Au (electrum) + $2S_2O_3^{2-} \Rightarrow Au(S_2O_3)_2^{3-}$	Fine-grained medium fineness
Bisulphide HS^-	Strongly reducing alkaline-neutral	Au (electrum) + $2HS^- \Rightarrow Au(HS)_2^-$	Fine-grained medium-high fineness

With the onset of dryer climates, weathering generally becomes less intense as the volume and activity of water is reduced and the salinity increased. However, the progressive movement of the acid redox front down through the mottled zone and saprolite with the watertable, causes local enhanced weathering and the overprinting of the upper saprolite with iron oxides. The iron oxides, predominantly goethite, are precipitated in voids throughout the upper saprolite above the descending redox front without the destruction of primary fabric. Some destruction of primary fabric may occur with standstills in the redox front and the formation of distinct saprolitic redox zones. Most regolith profiles have from one to three distinct redox zones, where the lower most zone separates the upper and lower saprolite. Under extended arid conditions, dehydration and soluble salt accumulation leads to alkaline conditions in the upper profile resulting in the predominance of haematite, which characterises palaeo-redox zones.

Supergene Gold Ore Genesis

With the exception of placer deposits, supergene gold enrichment zones in most climatic zones and regolith situations, are generally flat-lying bodies associated with palaeo- and/or present iron redox zones within laterite, saprolite and/or transported horizons. These bodies are commonly thin (0.5-5.0 m thick) and laterally extensive, in plan section up to 20 fold the sub-crop area of the primary mineralised body. As the position of the redox front in the regolith changes with variations in climate, so does the site of vertical accumulation and lateral dispersion of gold above the redox front.

Wet profiles

In seasonally humid tropical terrain, lateritic gold is concentrated at the base of the laterite and upper mottled zones above the redox front. The gold precipitate is commonly fine-grained and high fineness, consistent with dissolution and mobilisation by organic processes (Bowell, 1993). During this lateritisation process, acid conditions at the redox front may enhanced biological activity, and hence the dissolution and lateral migration of gold in the laterite. Dispersion, controlled by topography, groundwater movement and the style of primary mineralisation, up to 200 metres from the primary source is not uncommon. The limited stability of organic gold complexes prevent the gold from being completely leached from the profile. The formation of inorganic gold complexes in groundwater of low ionic strength (rainfall > 1m/yr) is likely to be limited to local environments, such as in coastal profiles where sea salt spray contributes chloride to the groundwater.

Secondary gold within the partially water-saturated, semi-reducing environments of the regolith beneath the redox front is fine-grained and low fineness and generally confined to the host unit. The percentage of secondary gold increases towards the redox front at the expense of primary gold. Dissolution near the base of the profile, under these reducing conditions, probably only occurs in the presence of weathering sulphides, locally by bisulphide complexes and, under slightly more oxidising conditions higher in the profile, by meta-stable thiosulphate complexes. Migration of gold here with limited groundwater through flow is a local semi-diffusion process.

Dry profiles

Saprolitic gold enrichment horizons, separated by depletion zones, are a common feature of arid auriferous profiles. The enriched gold is generally coarse-grained and very high fineness (contains no detectable silver). This gold probably accumulated due to the progressive dissolution of gold from the mottled zone and upper saprolite beneath the lateritic enrichment zone with overprinting of the profile by saline, acid oxidising groundwaters associated with the descending redox front. Gold electrum exposed to these solutions is soluble as a gold chloride complex and is laterally mobile just above the redox front. The dispersion distance from the primary source is commonly between 50 and 500 metres depending on topography, groundwater and style of primary mineralisation. However, when the chloride complex encounters the alkaline conditions higher in the profile it is destabilised and gold is precipitated as high fineness crystals. The superior mobility of silver complexes separates gold and silver above the redox front and gold of increased purity is precipitated. The high porosity of the upper saprolite allows the uninhibited growth of gold crystals form a large volume of pore fluid. The strong affinity of gold for its own metal results in the growth of large crystals, particularly in hydrous profiles such as lake environments. This precipitation occurs independently of the accumulation of iron oxides. Although Fe is a strong reducing agent, there is no conclusive evidence of its exclusive participation in the deposition of gold as (a) microscopically gold is not necessarily associated with iron oxides (b) gold deposition universally corresponds to a strong change in pH within the profile regardless of iron concentration and (c) large hexagonal plates and dodecahedrons characteristic of natural gold crystals can be produced synthetically from solutions without iron species. Apart from local mobilisation down along fractures, gold is not reprecipitated below the redox front. The secondary and primary gold distribution in the lower profile, beneath the redox front, is largely confined to the host unit and shows similar chemistry to that produced under wet climates beneath the redox front, where the percentage of secondary gold increases towards the redox front at the expense of primary gold.

Under extended arid conditions, the upper regolith dries out and is exposed to erosion. With erosion, lateritic gold is physically reworked and dispersed into the transported overburden. Weathering processes *overprint* the modified profile and gold is continuously reworked in the upper profile. Depending on the development of the redox front, with topography and available groundwater, the gold distribution may be modified. In topographically high regolith situations, previously developed saprolitic dispersion zones are largely maintained as limited groundwater in the profile restricts gold mobility to local dissolution in pore fluids, with reprecipitation commonly being on the source grain. Repeated dissolution and reprecipitation results in increased grain size and rounding of the crystals into irregular masses of gold often with the incorporation of matrix materials, predominantly clay, iron oxides and quartz. The accumulation of regional groundwater in topographically low lake environments may reactivate redox processes. Where gold is exposed to these redox conditions, it is vertically concentrated and laterally dispersed above the redox front.

Implications for Exploration

The enrichment and lateral dispersion of gold in the laterite above a near-surface redox front under wet climates, coupled with the ability of iron oxides, particularly goethite, to trap trace elements, makes laterite the premier sampling medium for exploration. In the absence of laterite, the dissolution, mobilisation and reprecipitation of gold from the upper saprolite into sub-horizontal saprolitic enrichment zones, in plan section up to twenty fold the area of primary subcrop, significantly increases the exploration target for buried mineralisation. These saprolitic dispersion zones are generally accessible by relatively shallow drilling of the regolith to less than 40 metres depth. Visual recognition of palaeo- and present redox zones in the profile as sites of potential gold enrichment allows the explorationist to interpret the regolith situation and make valued judgements on the extent of gold enrichment and dispersion in relation to climatic history, topography and primary mineralisation style and, importantly, to plan cost effect exploration strategies (e.g. sampling techniques, drill spacing and depth) to target these zones.

Recent research suggests that redox processes not only affect gold mobility and deposition but also other ore elements which produce broader exploration targets. In addition, the structure and chemistry of goethite is ideal for element adsorption and, away from the active redox front, trace element anomalies are associated with the upper part of the redox zone. The subsequent conversion of goethite to haematite in the drier upper part of the profile, causes some element depletion as haematite is less capable of retaining trace elements.

Conclusions

Iron redox processes associated with weathering, and controlled by the access of water and oxygen into the regolith, control supergene gold ore genesis. Lateritic and saprolitic ores are produced primarily as a function of changes in the depth of, and solution chemistry associated with the redox front with changing climates. Under wet climates, redox processes result in the concurrent formation of the laterite and promotion of gold dissolution and dispersion by organic species which result in the deposition of fine-grained, high fineness gold within the laterite and upper mottled zones. The most efficient process of gold enrichment occurs under dry climates, with the mobilisation of gold from the upper oxidised profile from beneath the laterite, above a descending redox front, and the formation of one or more saprolitic enrichment zones with standstills in the redox front. Under these conditions, gold is dissolved and transported in saline, oxidising solutions, made acid above the redox front, as a by-product of the iron redox reaction, and precipitated as coarse-grained, high fineness gold. Beneath the redox front, reducing conditions limit gold dissolution to sulphide and thiosulphate species in the presence of weathering sulphides under alkaline conditions, and gold is generally confined to the host unit with minimal vertical displacement. In addition to the obvious exploration advantages of understanding the formation of supergene gold enrichment and dispersion in the regolith, the near-surface natural refining and enrichment of supergene gold by redox processes make supergene deposits economically attractive resources.

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Partial extractions and mobile metal ions

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Introduction

Partial extractions have a long history in geochemistry. Their use probably reached an hiatus in the 1970s when the transition to full sample digestion with rapid turn-around through large laboratories became the standard method for exploration analysis. At that time, detection limits stood at the low ppm level for most elements. Since then, the lower detection limits for most elements, particularly those of economic interest, have decreased by three orders of magnitude, to the ppb level. This almost imperceptible 'revolution by stealth', whilst readily welcomed by most explorationists, has not been fully exploited. In addition to being able to carry out 'routine' geochemistry at lower levels, the new instrumentation has opened up new avenues in the methods of selecting sample material for analysis which will maximize the opportunity for detection of ore-bodies. Partial extraction is one technique which has benefited and will continue to benefit from that revolution.

The aim of a partial digestion is to release some of the metal contained in a soil to solution. Mobile metal ions, are those which are released to solution from the use of very weak extractants – extractants which deliberately do not attack the substrate or matrix. A large percentage of mobile metal ions appears to be derived from metal-containing ore-bodies, and careful use of weak extractants and very low level chemical pre-concentration and analysis techniques can be used to obtain significant and reliable element signals to enable the anomaly patterns to be enhanced, resolved, and interpreted for the detection of blind ore-bodies. Whilst the exact mechanisms for release, transport, and 'fixation' of the metals are, in our case, the subject of sponsored research and confidential, the technique is of considerable importance to the exploration industry, because of its apparent ability to operate in deeply-weathered terrain, and in some cases through considerable thicknesses of overburden. Some 7000 samples, involving over 50,000 individual analyses have now been subjected to the Mobile Metal Ion Process.

The Mobile Metal Ion (MMI) Process®

The following are the major steps in the process:
- evaluation of background information, including existing geochemical data;
- field inspection, programme design, and sampling;
- digestion and extraction of metals;
- analysis and QC (Cu, Pb, Zn, Ni, Cd, Au, Ag, Pt, and Pd); and
- interpretation, recommendations, and report.

A number of separate digestions is required, because no one digestant is capable of providing optimum extraction of all nine metals. Digestants, details of which must remain proprietary, have been screened and selected for their ability to extract only the very weakly-attached (mobile) metals. Extractants used are multi-component mixtures of water soluble organic and inorganic chemicals. Following digestion and analysis, 'background' for each element is calculated to provide a 'Response Ratio' at each sample point for each element. All subsequent interpretation of data is based upon application of the appropriate thresholds to the Response Ratios.

Case history results

Over 70 case history and working studies have been carried out using the MMI Process in four continents. The following table gives an indication of the range of situations covered, and the relative success achieved – Table 1.

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Table 1. Summary of case histories investigated by the Mobile Metal Ion Process.

Style	Cases	Range of Settings	MMI Geochemistry
Base Metals Pb,Zn,Cu (+/- Ag,Pd)	24	VMS, Miss. Valley, massive and disseminated. Very high to low rainfall. Some deeply buried.	Very sharp ore element anomalies directly above and/or up-dip. 3 'Failures'
Ni (+/- Cu,Pt,Pd)	9	Massive to disseminated komatiitic Ni in ultramafics. All arid zone, some in partly transported material.	Two levels, one distinguishes U/m units, the other Ni within U/m units. 2 'Failures' on disseminated Ni.
Au (+/- Ag)	37	Mainly Archaean qz vein style, some porphry. Most in arid zones, but several in high rainfall areas. Most on deeply weathered profiles, some with extensive sheetwash or dune cover.	Many with > 30 times background anomalies, sharper than conventional geochemistry - sharp enough to provide direct drilling targets (50% holes with >1g/t Au at this level). 5 'Failures' on transported overburden.
Sub-economic	4	Various settings & depths	No 'Failures', i.e. no false anomalies.

Two of these examples will be examined in some detail. Figure 1 shows the MMI Anomaly on a transect across strike of buried base metals mineralization.

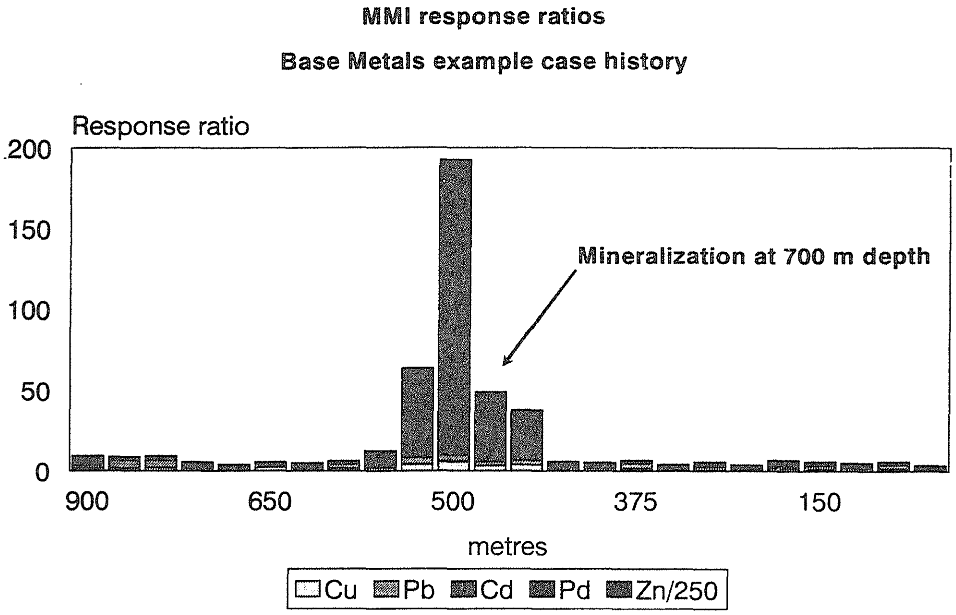

Figure 1. MMI Response Ratios over a base metals deposit, at 700 m depth.

In the above example, note that the zone of mineralization at a depth of 700 m, projects to surface at very closely the position of the very sharp, multi-element MMI anomaly (the Response Ratio for Zn has been divided by 250 to appear on the same scale).

The second example, is from the Nepean nickel deposit near Coolgardie, Western Australia. The ore zone contains massive nickel sulphide, with sulphides of copper, lead, cobalt and minor gold, platinum, and palladium mineralization. Several factors are of interest in this particular study. Firstly, the nodular ferruginous material to the west of the mineralized zone, which shows high nickel responses by conventional analytical procedures, does not have a high MMI response. This is shown in Table 2.

Table 2. Ni responses over mineralized and 'ferruginized' barren ultramafic.

Sample	Soil	Over	MMI Response	Total Ni
NP11 (975E 5100N)	Pale Red/brown sandy clay	8.6m @ 2.75% Ni	38600 ppb 75 times B/G	720 ppm 6 times B/G
NP15 (875E 5100N)	Strongly ferrug. red/brown soil with ironstone	Barren Ultramafic	3000 ppb 6 times B/G	800 ppm 7 times B/G

This table highlights that two different MMI thresholds are appropriate in the case of nickel, one which distinguishes ultramafic rocks from rocks with lower nickel contents (e.g. mafics), and the second to distinguish potentially-mineralized areas within ultramafic sequences, from "barren" ultramafic. The MMI response over Ni mineralization is, in this case, 75 times background, whilst the MMI response over barren ultramafic is 6 times background. The data in Table 2 also show that in this case conventional geochemistry fails to provide a distinction between the Ni content of the ferruginized soil over barren ultramafic, and the Ni content in soil over mineralization, whereas the MMI partial extraction clearly does.

At Nepean, the MMI response for Ni is at a maximum over the ore zones, and delineates several ore zone(s) with remarkable accuracy. As noted in the case of other base metals, there is the coincidence of several anomalies from individual elements contained in the mineralization, principally Pd and Cu. In many cases, there is an associated, but laterally-displaced, weak Au-Ag anomaly over the basal contact of the ultramafic unit with mafic units in the sequence. Several other previously-undetected, prospective zones are indicated by MMI Ni Response Ratios to the east of the mined ore zone, and to the east of a postulated fold axis (Kirkpatrick,1985). They may represent anomalies which are associated with a possible structural repeat of mineralization.

Discussion

1) *Summary of essential features of MMI anomalies*

Our case history studies to date, lead us to the following conclusions:

- MMI anomalies exist, and can be used to detect buried mineralization;
- MMI anomalies are clearly different to conventional geochemical anomalies in their appearance, intensity, and potential application to exploration;
- The mechanism of formation of MMI anomalies is almost certainly very different from that responsible for the formation of normal multi-element geochemical anomalies;
- Not all elements behave in exactly the same manner; and
- MMI anomalies are sometimes 'swamped' in areas of recent, rapid transport.

Some of the individual and relevant observations which lead us to these conclusions are:

- MMI anomalies comprise only elements present in the mineralization in significant amounts.
- The anomalies are sharp, and in most cases directly overlay and define the extent of the surface projection of buried primary mineralized zones;
- When primary mineralization is of high grade, MMI anomalies are capable of penetrating significant thicknesses of overburden; and
- The incidence of false anomalies is very low, compared to normal geochemical methods.

2) *Relationship of MMI to other partial extraction geochemical methods*

One of the first reports of the 'geogas' phenomenon was by Malmqvist and Kristiansson (1984). In this report the primary gases detected were nitrogen, argon, oxygen, and methane over a massive sulphide deposit in Central Sweden. Subsequent variations of the technique utilize plastic collection strips and very sophisticated instrumentation to detect ultra-trace levels of metal ions on the collectors. Compared to other techniques, sample collection is not as robust, and the technique is very expensive, when applied on the scale required for exploration.

The CHIM, MPF, and TMGM methods developed in the USSR (Antropove *et al.*, 1992) during the nineteen eighties recently came under increasing scrutiny. The United States Geological Survey recently published their findings on this technique (Smith *et al.*, 1993). The CHIM method is clearly very similar to the MMI technique, even to the use of carbon electrodes for pre-concentration, and polarographic techniques for the low level analysis. The enzyme leach method (Clark, 1993), and the

Gas Vapour Phase method (Magellan,1993) are other methods of accessing metal ions from soils, which differ from traditional partial extraction techniques. The traditional methods, have in many cases used special extractants to perform selective extraction – release of metals from specific substrates. These methods need to ensure that the extractant does not dissolve an excessive amount of the substrate, and release metal which contributes to 'background noise'.

3) *Possible mechanisms of formation of MMI anomalies*

The Geochemical Research Centre (GRC) at Technology Park Bentley, Western Australia, operates a research programme with the aim of providing participants with information on the mechanism of formation of mobile metal ion anomalies. The Centre is currently considering mechanisms involving vapour (aerosol) transport and chemical release of metals during weathering. The elucidation of the mechanism is not just concerned with the mode of transport, but also with the form of fixation of the metals in the soil regime. For this, The Centre is utilizing the study areas provided by participating companies to examine the effects of different regolith, mineralogical, climatic, and geomorphological situations on the presence, strength, and persistence of anomalies.

Conclusions

Due to the increasing need for exploration techniques to operate effectively in areas of deeply-weathered or transported overburden, this new geochemical technique has the potential to complement geophysical methods for the detection of 'blind' mineralization. Because of the very sharp, and coincident nature of the anomaly peak, it has the potential to significantly reduce drilling costs. As such, it is the total exploration budget which will be affected by the introduction of the technique into the exploration programme, and in some cases by reductions of up to 30%-50%. It is for this reason, and due to the fact that any partial digestion process is dependent on the correct, systematic and careful execution of a number of steps, that these methods cannot be easily translated to a rapid/routine analysis technique. As such, partial extractions of quality, will remain relatively expensive, compared to routine analysis, and they must be implemented into exploration programs with due diligence and care. Another word of caution is also required. There is often a tendency, after the initial scepticism has abated, to regard any new geochemical technique as a universal panacea, and in some cases to misapply it. The Mobile Metal Ion technique will be no different; there is a practical limit to its usefulness, which we hasten to add is dependent upon future developments in analytical techniques and extractants. However, if carefully applied in an integrated and systematic manner it seems certain to make a large contribution to the detection of buried mineralization.

Acknowledgments

The work described in this paper precludes any carried out under the auspices of the GRC. Acknowledgments are due to those companies who have kindly permitted us to release the broad outlines of the case history surveys, and to those companies and MERIWA who have committed to the long term research .

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The application of soil geochemistry to gold exploration in the Black Flag area, Yilgarn Block, Western Australia

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Keywords: gold, soil, Yilgarn Block

Soil geochemistry has been used to good effect throughout the 1980s and into the 1990s in exploration for gold in the Black Flag area, situated some 50 km north-west of Kalgoorlie in Western Australia. Since 1991, Mining Corporation of Australia Ltd (MCA) has conducted a systematic programme of soil geochemistry within a tenement area of some 400 square kilometres, much of which had been previously explored by many different operators using a variety of geochemical techniques. A GIS database incorporating over 30,000 samples, partly from MCA work, but also using data from previous exploration where appropriate, has been assembled. This compilation provides a good basis for evaluating the effectiveness of soil geochemistry under the range of conditions encountered, and allows a direct comparison between various sampling and analytical techniques.

The MCA programme is based on the sampling of near-surface soils at depths of 10-20cm, and analysis of the <2mm fraction (after pulverizing) for Au and As. Sampling grids vary from 400 to 100 metres in reconnaissance work, to 40 by 40 metres for detailed delineation of anomalies prior to drilling. Each sample is described in terms of its mechanical (grain size) composition, distinguishing characteristics and likely origin during collection. These data are used in conjunction with a broad classification of geomorphological setting in the interpretation of results.

The simple low cost sampling procedures adopted by MCA have proved robust and effective in delineating mineralization, even under extreme conditions of concealment. Mineralization located by recent work ranges from palaeochannel deposits covered by 30 metres of transported overburden to deeply weathered primary lodes under thin residual soil. Surface sampling has also been used in playa lake environments, where the most effective samples often consist of saprolitised bedrock.

Many previous explorers collected "soil" samples at depths of 50-100cm using hand-held augers. In the Black Flag area, this technique was successful in locating the major Racetrack deposit, for which production and reserves total more than 4 million tonnes. However, geochemical data using this technique are noticeably more noisy than near-surface soils, due to the more localized influence of bedrock response. In areas where the lateritic weathering profile is preserved, response in auger samples can be amplified in both concentration and lateral extent. Under such conditions an appropriate sample density is required to ensure delineation of the bedrock source.

Deeper bedrock sampling using rotary-air-blast drilling (RAB), which was popular in the 1980s, frequently sampled the most intensely leached saprolite horizon, and was thus ineffective. The Zsa Zsa mineralization, located during follow-up of a strong and extensive gold anomaly in near-surface soils, had been previously missed by such a RAB drilling programme.

Several areas previously tested by the bulk cyanide leach (BCL or BLEG) method, showed essentially similar dispersion patterns to those using the simpler and much lower cost MCA techniques. There is no evidence that the BCL method provides any advantage, either in terms of enhanced anomaly contrast or reproducibility of anomalies. The homogeneous character of dispersion patterns based on the small (200g) MCA samples can be taken as evidence that most of the gold particles present in the soils are exceedingly fine (probably less than 10 microns), resulting from reconstitution during lateritic weathering.

It will take several years to evaluate fully the significance of all the geochemical anomalies located in the Black Flag area. However, the evidence to date suggests that basic soil geochemistry based on near-surface sampling is an effective tool for locating gold mineralization, even in areas of transported cover.

Pseudomorphic replacement versus physical displacement in laterites : petrographic evidence mechanisms, and consequences for modelling

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Keywords : Laterites, isovolumetric replacement, kinetic-rheological feedback.

Introduction

Chemical weathering is particularly intense in present-day tropical humid areas covering one third of emerged lands in the world. Under such climates weathering mantles called laterites are well developed and reach thicknesses of > 100 metres, especially on continental areas that have been tectonically stable over the last million years. Enormous volumes of igneous, metamorphic and sedimentary rocks forming the epidermic portion of exposed lands are weathered.

This involves enormous solute transfers crucial for both chemical weathering and sediment formation. Therefore, understanding of mass transfers in weathering systems and their bulk chemical change are of a paramount importance. To evaluate the degree of mass transfer of elements from and within a saprolitic profile (lower four-fiths of lateritic weathering profiles), whole-rock analyses were referred to a constant-volume frame (Millot and Bonifas 1955). But in recent work, Brimhall and Dietrich (1987) have instead referred analyses to an element which is assumed to be immobile and thus showing the occurence of strong volumetric deformation of saprolites.

Nevertheless, there is a lot of empirical support for the isovolumetric preservation in saprolite.

In part, the controversy arises from a failure in properly observing and understanding macro and microfabrics of saprolite. The aim of this work is (i) to identify field and petrographic evidence in extensive and stringent support of constant volume transformations in saprolite and (ii) to discuss genetic mechanisms for constant-volume mineral reactions.

Petrographic evidence

In open lateritic weathering systems, removal of mobile elements leads to residual saprolites the bulk dry density of which can reach as low values as < 1g/cm3, consistent with high porosities of 30 to 60%. Saprolite formation requires gross subtraction and addition of material. The crucial question is whether saprolite-forming minerals show strain or deformation. The same question has been raised for metasomatism by Carmichael (1986).

Observation of many textures and structures of the parent rock can be used as "inert-marker reference frame" to assess whether the original rock volume is conserved in saprolites. Most parent rocks are Fe and/or Al bearing, and under lateritic weathering undergo preferential release of other elements. Fe and Al oxides and oxyhydroxides along with kaolinite make up a network of precipitated secondary minerals which replace parent minerals. This replacement is pseudomorphic : it preserves original grain outlines and/or cleavages.

Whatever the orientation of thin sections, parent mineral grains are seen carved up by weathering pseudomorphic products into several fragments all of which remain in optical continuity : that means under cross nicols, the positions of extinction for each piece of a given original euhedral or anhedral parent grain, are identical. In addition for plagioclases and pyroxenes, twins and cleavages are uninflected across weathering front boundaries which separate each fragment of a given mineral. Boxworks and septa consist of rigid networks that ensure that the saprolite preserves the texture of the parent rock. Such and other evidence lead to the unavoidable, clear conclusion that in lateritic saprolite the pseudomorphic replacement by secondary products does not displace the reactant mineral remnants, and that deformation is absent. Toward the base of the saprolite the reactant-mineral remnants are therefore stationary relative to each other (Nahon 1991), and constitute an excellent reference frame for calculation of mass transfer.

We have described above evidence for constant-volume replacement during weathering regardless of why the bulk volume remains constant. The reasons for this constancy are explained by Merino et al. (1993, 1994) and below.

Replacement mechanism

Imagine the plight of a growing grain, B, in a rigid rock. Space is scarce, and the growing grain soon abutts and presses against its neighbor grains, A, raising their free energy, solubility, and dissolution rate. The A grains dissolve as B pushes against them. But the stress also acts on B itself, making it grow less fast. The volumetric rate of A-dissolution increases while that of B-growth decreases, quickly becoming equal to each other. This is why replacement characteristically preserves volume. Since the growth of B and the dissolution of A take place in tiny, alternative (practically simultaneous) increments, the process can preserve internal details of the A grains, which accounts for the second crucial characteristic of pseudomorphic replacement.

Implications of replacement for modeling

The stress-mediated genesis of replacement just described has two consequences for modeling of mass transfer and reactions in rocks (Merino et al., 1993 ; Wang et al., 1995) :

1. Replacement reactions need to be balanced on volume, which is what the eye sees. The resulting stoichiometry controls the coefficients on transport terms in the continuity equation.

2. Rate laws for mineral reactions to be used in reaction-transport calculations in rocks should include a strong stress dependence ; see a tentative choice in Merino et al. (1993). (Rate laws currently in use -- see Steefel and Lasaga's 1994 review -- do not contain this dependence because they have been obtained in water-based experiments, where grains cannot press against each other). Not even the stress dependence of mineral solubilities is well known (but see Elias and Hajash, 1992, a welcome exception), let alone that of rates.

Replacement vs displacement : New kinetic-rheological feedback

Two conditions for replacement are, as mentioned, limited space and a rigid rock. But the viscosity of a material is in general a nonlinear function of the rate at which the material is being strained (e.g., Verhoogen et al., 1970, p. 508).

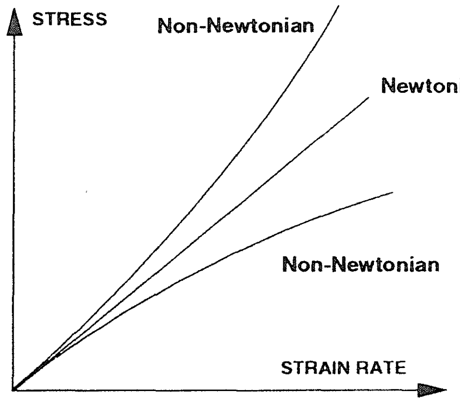

Fig. 1 - Newtonian and non-Newtonian behavior. The viscosity is the slope of the curves.

This is precisely what characterizes so-called non-Newtonian materials, of which there are two kinds (Fig. 1) -- those whose viscosity increases with increasing strain rate, and those whose viscosity decreases with increasing strain rate. In the stress-mediated feedback described above between A-dissolution and B-growth that, we think, leads to replacement, we assumed that, within the time scale of the replacement, the rock stays rigid or very viscous, which is tantamount to assuming that the rock's viscosity probably increases with strain rate. We now realize that the stress-mediated feedback is itself subsumed within another feedback, a kinetic-rheological feedback.

The kinetic-rheological feedback we propose here (see Fig. 2) involves the two possible types of non-Newtonian materials. As soon as the growing B grain abutts against an adjacent A grain, it starts to strain it and its neighbors. As the strain rate increases, the viscosity may grow or decrease (Fig. 1). If it grows, then the rock will find it more difficult than before to flow viscously as B grows, the stress between A and B soars, A dissolves faster and B grows more slowly, and pseudomorphic replacement results. But if the local rock viscosity decreases, then it may be possible for A to flow viscously out of B's way, producing physical displacement.

We need therefore to find out more about the viscoelastic behavior of rocks under appropriate conditions, and how their viscosity varies with strain rate.

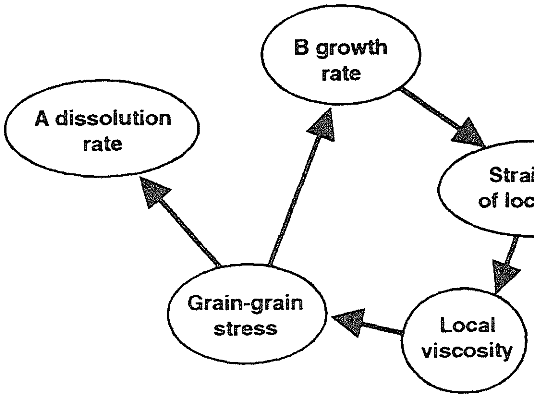

Fig. 2. proposed kinetic-rheological feedback. Grain B is growing in a rock at some rate. As it strains its neighbors, A, the evolution of local rock viscosity dictates whether the stress between A and B grows or decreases, which makes replacement or displacement more likely, respectively, and which modifies B's growth rate and A's dissolution rate.

Conclusions

Pseudomorphic replacement is extensive in the saprolitic portion of laterites. The evidence is petrographic. It implies that replacement reactions should be balanced on volume. If replacement results from a stress-mediated feedback between A- dissolution and B-growth, then replacement also implies that modelling of reaction-transport should include the stress-dependence of mineral rates.

The stress-mediated feedback that produces replacement is subsumed within a new kinetic-rheological feedback that may account for two alternative behaviors of growing crystals in rocks -- pseudomorphic replacement, in which the growing crystals take the place of a preexisting grain by pressure dissolving it, and physical displacement, in which the growing crystals physically push their neighbors out of the way. Replacement is widespread in rocks of all kinds, but physical displacement appears to be less common. The feedback hinges on whether the non-Newtonian rock hardens or softens upon being subjected to crystal-growth-generated strain. If it softens, then it may flow plastically out of the way. If it hardens, then it becomes impossible for it to flow within the time scale of the growth, stress builds up at grain/grain contacts, and replacement follows via the stress-mediated feedback.

Quantification of the kinetic-rheological feedback proposed and of its inclusion in models of reaction-transport is difficult. Experiments and theory are needed on both the effect of stress on mineral reaction rates and on the visco-elastic properties of rocks.

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Regolith research in Australia

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Keywords: Regolith evolution, geochemical exploration, landscape geochemistry

Ancient Landscapes

Parts of the Australian continent have been emergent for some 2 Ga, and many of the landscapes have their origins 300 Ma ago when break up of Gondwana began (Veevers, 1994). During this long history, the rock sequences that comprise the Australian landscape have been subjected to a wide range of climates, including glacial, humid temperate, tropical, and arid, and to tectonic events including uplift, continental breakup, tilting and warping of land surfaces.

Major changes in the near-surface chemical environments, their hydrology and water quality, have intensively altered the exposed bedrock sequences to produce a thick weathered mantle. Accompanying these changes commonly are accumulations of sediments in local lowlands, particularly where the weathered mantle has undergone partial or extensive dismantling due to erosion. The resulting regoliths (soils, deeply weathered mantle and accumulated sediments) are complex in their stratigraphy and associated chemical and mineralogical properties.

The purpose of this presentation is to review current regolith research, present the main issues that the exploration industry is facing, and to forecast important future trends in research in relation to exploration and, particularly, exploration geochemistry.

Needs of the Australian Mineral Industry

In order to replace ore deposits being mined, the mineral industry in Australia is vitally concerned with locating new mineral resources. Regolith-dominated terrains have become the main focus because generally they are little explored, many being essentially unexplored (Meiklejohn, 1995). In such terrain, the surface expressions of ore deposits are commonly altered beyond visual recognition, concealed beneath duricrusts, or buried beneath cover sequences. The strategic need for new discoveries is the driving force behind much of the regolith research in Australia. The next most important force is the need for knowledge and survey documentation as a framework for environmental studies.

There are at least three approaches used for mineral exploration in regolith-dominated terrain and in the corresponding research. The approaches are: (i) understand ore systems and sequence stratigraphy and be able to work with isolated observations and data points provided by drilling; (ii) develop geophysical (Atkinson, 1994) or geochemical methods that see through the regolith cover; and (iii) understand the regolith environments and weathering processes and use these to advantage in exploration (Butt and Zeegers, 1992; Smith, 1989). Commonly, these approaches are used in combination.

Some key issues facing the mineral exploration industry in Australia, listed below, are particularly focused on the search for gold, base metals, iron or diamond deposits.

1. In exploring terrain having substantial transported overburden, do buried ore deposits have a surface or near-surface geological, geophysical or geochemical expression?

2. What methods can be used in exploration through Phanerozoic basin cover? Where the cover ranges from very thin, to about 100m this issue merges with that of exploring through transported overburden. In cases where weathering has permeated the basin cover, the possibilities of using regolith geochemistry arise. Extensive research on this topic is underway. An experimental method with considerable promise is the use of isotope geochemistry on ground and formation waters, to provide vectoring methods for location of concealed ore deposits.

3. Can large ore systems be recognised and distinguished from minor occurrences at the prospect stage? This is a general exploration issue yet it is particularly pertinent to exploration in regolith-dominated terrain because of the difficulty of obtaining sufficient data.

4. What procedures can be employed to explore across heterogeneous terrain (mixtures of outcrops, transported cover, salt lakes, etc) unimpeded by terrain variation and terrain boundaries?

These key issues will be discussed in terms of regolith research being carried out by the main research groups in Australia, as well as by some of the more specialised groups and individuals.

Regolith Research

The dominant development over the last decade in regolith research to do with mineral exploration in Australia is the emergence of well-focused interdisciplinary studies (AMIRA, 1994). Studies have included substantial industry funding, mostly for pre-competitive research. Project groups and task forces have involved skills spanning geology, geomorphology, soil science, geochemistry and geophysics. This breadth is seen to be particularly wide when the subdisciplines are considered: petrology, mineralogy, remote sensing, sedimentology, isotope geochemistry including dating, palaeoclimatology, electrical geophysics (both ground and airborne), and hydrogeochemistry.

Projects involving two or more organisations working in collaboration with industry are becoming the norm with scientists pooling resources and skills. By focusing activities on selected regions and well-defined problems, significant advances have been made with practical applications arising from the research leading to ore deposit discoveries. Examples in gold exploration are the use of laterite and ferruginous saprolite geochemistry, gold in carbonates, and the comprehensive use of regolith control for exploration geochemistry.

In terms of regolith research some of the most prominent current issues are: providing a reliable time frame (age of weathering, exposure, burial, correlations across the continent); establishing the climatic history for key areas (original formation, variation and subsequent changes); methods of presenting regolith mapping at broad scales (eg 1:250,000 to 1:500,000); standardising regolith terminology (Anand, 1995); understanding calcretes and carbonates in the landscapes, including calcrete duricrusts (Arakel, 1994); reconciling the marine record with weathering history of the continent; and reconciling the record from sedimentary basins with the corresponding uplands.

Exploration Geochemistry

From the perspective of exploration geochemistry, fundamental questions to be answered in regolith research are: how do major and trace elements become dispersed in this slowly evolving environment; what are the speciation, transport and diffusion mechanisms; what are the kinetics of the reactions involved, how does the landscape as a whole respond and, how can such knowledge be used to predict three-dimensional haloes of dispersion of critical elements around as yet undetected ore bodies? A common practical issue in exploration is the difficulty of being able to tell, from drill spoil, a buried weathered profile from the transported cover sequence. This is crucial to know when conducting downhole geochemistry.

Findings related to those questions can be summarised into appropriate models. Research along these lines has been done in specific regions, the most extensive being in the Yilgarn Craton in Western Australia. A further question that then arises is: to what extent is it possible to transfer knowledge, such as dispersion models, from one regolith district or region to another?

Extending from research, there is growth in regolith mapping by government authorities, especially the Australian Geological Survey Organisation (AGSO), now being coupled with initiatives in geochemical mapping in Queensland (Cruikshank and Butrovski, 1994; Pain *et al.*, 1994) and Western Australia (Kojan and Faulkner, 1994).

Outlook

The most substantial new initiative in regolith research in Australia is the newly funded Cooperative Research Centre for Landscape Evolution and Mineral Exploration, CRC LEME. The Centre brings together the main research groups in regolith geology, geomorphology and exploration geochemistry, as well as involving industry and state geological surveys. The Centre thus brings research, development, applications, education and training together in a substantial way to provide a national focus. Core participants in the CRC are the regolith groups from Australian National University, University of Canberra, AGSO and the CSIRO Division of Exploration and Mining.

In outlook two perspectives are presented: one for the next three to five years, the other for the next five to ten years. In terms of Australian regolith research, some topics that should be worked on but are not, will be discussed. For example, much needs to be done to translate ore systems, their isotopic characteristics and alteration haloes to specific regolith settings.

Conclusion

In Australia, regolith-landscape research is seen to be very much interdisciplinary in its characteristics. It is undergoing considerable growth, particularly in response to the needs of the mineral exploration industry and facilitated by recent successful applications. Growth is also in response to major environmental issues, such as rising salinity of irrigation and crop lands, and the rehabilitation of areas disturbed by mining. The regolith realm is now widely recognised as a major frontier, both nationally and internationally, one which is providing exciting careers and challenging scientific opportunities for new graduates and post-graduates.

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K-Ar and ^{40}Ar/^{39}Ar Geochronology of Weathering Reactions

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Keywords: weathering, geochronology, K-Ar, ^{40}Ar/^{39}Ar, landscape

The exploration for ore deposits in deeply weathered terrains requires sound understanding of the weathering and geomorphological history of target areas for proper interpretation of geochemical surveys. Cratonic areas in the Southern Hemisphere, currently intensely explored for concealed ore deposits, are covered by thick weathering blankets. Their surficial history during the Mesozoic and Cenozoic suggests a polycyclic evolution, with alternating weathering-prone and erosion-prone conditions. Interpretation of exploration geochemical surveys in these regions requires information on the relative roles of mechanical and chemical processes, and their relative and absolute chronology, in the genesis of the geochemical characteristics of the regolith.

Until recently, chronology in weathering and landscape evolution was primarily established from field observations, and weathering surfaces were recognised based on their elevation, soils, stratigraphic and topographic relations, surface morphology, and the nature of their duricrust or weathering profiles. This stratigraphic approach to landscape evolution was very useful when other means of measuring absolute and relative ages of soils, weathering profiles, and landforms were not available. However, stratigraphic geochronological studies have become insufficient to address current problems in geomorphology, exploration, and environmental geochemistry. Direct dating of minerals precipitated during weathering reactions may yield more accurate information about periods in the geologic past conducive to deep weathering, providing quantitative constraints to landscape evolution models. Unfortunately, the complexity of the mineralogy in weathering profiles, the close association between minerals precipitated during weathering reactions and unweathered primary minerals, the poorly crystalline character of many minerals found in weathering profiles, and uncertainties related to the stability and preservation of weathering minerals through time have prevented gathering of widespread information on geochronology of weathering processes.

Weathering profiles are inherently open systems, resulting from interactions between the lithosphere, hydrosphere, atmosphere, and biosphere. The constant state of mass and energy flux through the profile may suggest that the system is in a permanent state of alteration, changing and reequilibrating with newly imposed geochemical conditions, which would imply that no information about ancient processes could be derived from weathered assemblages. Under these continuously reequilibrating conditions, the profiles would only record the most recent events, and any ancient geochemical record would be erased or significantly altered by more recent processes. Despite the "infinite" reservoir of reactants provided by the atmosphere, hydrosphere, and biosphere, field observation and thermodynamic and kinetic models predict that metastable equilibrium may be attained locally in weathering systems. The persistence of a state of metastable equilibrium is necessary if absolute dating of weathering reactions is to provide information about past surficial geological/geochemical conditions.

K-Ar dating of supergene alunite, jarosite, and hollandite-group minerals has been used to delimit ages of Cenozoic weathering processes. K-Ar analysis of various samples distributed at different depth-horizons within a single profile has also been used to date the advance of weathering fronts, indicating that minerals do persist metastably in weathering profiles and may reflect weathering conditions prevailing in a remote past. Moreover, the application of highly sensitive and fully automated laser-heating and resistance furnace ^{40}Ar/^{39}Ar systems has facilitated the analysis a large number of very small samples, contributing to the successful dating of the advance of weathering fronts.

Advantages of the application of the $^{40}Ar/^{39}Ar$ method in weathering studies are: 1) the large time-span datable by this method, which can be used to determine the age of supergene minerals as young as ~ 250,000 years and as old as the solar system; 2) the fine-scale resolution of the method, which allows the age determination of very fine-grained phases (50-100 μm grains can be dated); 3) the multiple-step analysis of single grains, which enables the determination of the Ar retention history of minerals, the presence of excess/inherited Ar, and the possibility of K and/or Ar loss; 4) the ease of automated analysis, which allows multiple age determinations for each profile, resulting in improved statistics and providing a comprehensive weathering history database.

Expanding application of K-Ar and $^{40}Ar/^{39}Ar$ absolute dating of weathering minerals is increasing our ability to test geochemical and climatological models for the evolution of deep weathering profiles. In particular, absolute dating of weathering reactions by the methods above allows testing of the following hypothesis:

- That weathering reactions lead to the precipitation of metastable minerals, such as K-bearing manganese oxides and sulfates, which remain impervious to recrystallisation/exchange reactions after precipitation, thus recording weathering ages.
- That deep weathering profiles and laterites common in Southern Hemisphere landscapes have resulted from a protracted and episodic history of weathering which might have initiated in the Mesozoic.
- That the surficial Mesozoic and Cenozoic histories of Australia, Africa, and South America have been shaped by the alternation between weathering and erosion prone conditions, leading to the development of the distinct weathering surfaces that characterise the stepped landscape patterns in these regions.
- That ore forming elements often assumed to be chemically inert in the surficial environment (precious metals, titanium, zirconium) may be relatively mobile when exposed to changing climatic conditions during a protracted weathering history.
- That the migration and consequent dispersion or concentration of ore-forming elements depends on the paleoclimatic and paleohydrologic regimes prevailing in the past, and that these conditions might be drastically different from those existing today.

Application of these absolute dating techniques to weathering profiles in Australia, Africa, and South America suggests that the Late Cretaceous/Early Paleocene, the Early Eocene, and the Miocene were periods conducive to strong weathering in the Southern Hemisphere. The strong weathering pulse in the Miocene, present in all three continents and also detected in North America, indicates that weathering conditions in the Miocene may have played a major role in the formation of supergene enrichment blankets in ore deposits. Identifying and locating areas exposed to pervasive weathering conditions in the past may be instrumental in locating attractive target areas for geochemical exploration.

Applying Geochemical Methods in the Wet Tropics: more Facts than Figures

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Keywords: weathering, exploration, gold, base metals, mapping.

Introduction

The intense chemical weathering processes that occur in wet tropical environments, such as are found in a large part of Africa and South America, result in drastic changes to the mineralogical and chemical compositions of the bedrock above the weathering front. The geochemical signals obtained from these altered sampling media can therefore be considered as coded and it is up to the exploration geochemist, aiming to trace primary mineralization and bedrock characteristics, to decode them correctly. The decoding, or interpreting, of geochemical data from wet tropical environments cannot rely on a purely quantitative statistical approach; the analytical results have to be weighted by parameters describing the sample itself and its position relative to both the landscape and the weathering profile. In other words, certain facts need to be observed if one is to obtain a good understanding of the analytical figures.

As wet tropical environments cover a large variety of landscapes and correspond to distinct degrees of weathering intensity, and as the present situation at any locality is the result of a complex evolution under the influence of successive paleoclimates and tectonics, geochemical dispersion halos around mineralized bodies vary in shape and intensity from place to place. Moreover, the geochemical signatures obtained from a given country rock can show significant variations according to the intensity and local conditions of the weathering profile.

Applying geochemical methods to mineral exploration, geological mapping and environmental studies in such extreme environments can be very effective as long as their present limitations are clearly recognized. Improvement in this field still represents a major challenge for earth scientists.

Mineral Exploration

The use of geochemical methods for precious- and base-metal exploration in the wet tropics brings distinct problems at each exploration stage. The major problem is always to find the best fit between the geochemical dispersion model and the sampling pattern with respect to the sampling and analytical procedures. Economic considerations also play a very important role, for although exploration costs should always be kept to a minimum, the cost of non-discovery must also be taken into consideration.

As a general rule it can be said that regional geochemical exploration in the wet tropics will reveal few characteristics of the target mineralization, and the corresponding signature(s) will generally be of very low intensity and contrast. The dispersion model will depend on the balance between chemical and mechanical processes for a given element, i.e. on the morphoclimatic conditions. When selecting the methodology for a regional geochemical survey, particularly the sampling density and type of analysis, account must also be taken of the high cost involved in following up poorly defined regional anomalies (planning and costing of an exploration program should be considered as a whole and not separately according to the different stages). In the more detailed phases of the geochemical exploration program (semi-regional, follow up), the geochemical signature of the derived sampling media (stream-sediments, soils) will give a much better reflection of the target mineralization and gangue. The target can now be described by several quantitative and qualitative attributes, making it possible to assess its potential economic interest, and to proportion the effort required for further assessment. Nevertheless, even at the detailed phase, the procedure can be seriously hampered by the severe conditions prevailing in the weathering profile and their consequences on the geochemical behavior of target or pathfinder elements.

For gold it has been shown that present climatic conditions in the tropics can result in a distinct behavior in the upper part of the weathering profile, with significant enrichment under rainforest conditions and a strong leaching under dryer savanna conditions (Zeegers and Freyssinet, 1993). Organic matter present in the topsoil of wet tropical areas is shown to play an important role on the mobility of gold (Freyssinet, 1995). Neglecting such information could result in overestimating the interest of prospects showing strong Au anomalies in soil samples (or underestimating others where Au at the surface is strongly leached and no longer reflects the Au grades at depth).

For base metals, the weathering profile in the wet tropics represents nothing more than a full-scale chromatograph, where each element is transported over a certain distance before it (partly) reprecipitates or combines with amorphous minerals or organic matter. This is fairly well illustrated by an example from French Guiana (Butt and Zeegers, 1992) where Zn, which is dominant in the primary ore, is totally leached in the soil overlying the mineralization and can only be traced in the organic phase of stream-sediment samples downstream of the source. Pb however, which is a minor component of the primary ore, shows up as the main metal present in the overlying soil geochemical anomaly.

Geological Mapping

The scarcity and poor quality of outcrops in the wet tropics make reliable geological mapping difficult and expensive. Obviously stream-sediment multi-element geochemistry, combined with other techniques such as satellite imagery, side-looking radar and airborne geophysics, may considerably enhance the field geologist's work. Surprisingly, in deeply weathered environments such as are found in Gabon or French Guiana, active mechanical erosion along the minor drainage axes gives a mineral assemblage (and therefore a geochemical signature) in the stream sediments that is not so different from that of underlying bedrock, except for a few poorly resistant minerals; this is because, along the drainage axes only, quite strong erosion results in truncating most of the weathering profile, so that almost fresh bedrock material is mechanically dispersed in the streams. The geochemical data from such samples should no longer be considered as analytical figures, but as depicting minerals and, possibly, rocks. Obviously, an improved knowledge of regional geology through multielement geochemistry will enable regional exploration programs to be more reliable and selective, and also cheaper when one considers that fewer poorly defined targets will need to be followed up.

Environmental Studies

In temperate climates, the geochemical techniques developed for mineral exploration already play an important role in environmental studies. In the wet tropics the weathering profile represents a possible Non Saturated Zone having a thickness of between 20 and 100 m (compared with 1-10 m in temperate regions) and having a specific surface ranging from 20 to 120 g/m^2 (compared with 10-40 g/m^2 in temperate zones). The weathering profile therefore represents an active interface between surface and groundwater, and tracing metallic contaminations and their possible confinement by natural processes is another challenge for geochemists.

Challenges for the future

Optimizing regional geochemical exploration techniques is still a priority for the future, this being one of the most effective ways for generating new targets in the wet tropics where bedrock is generally covered by a thick weathering profile. But 100 per cent exhaustiveness remains in the realm of wishful thinking rather than scientific reality. The surprisingly good geochemical response to lithology observed in stream sediments along drainage axes of strongly erosional zones in the wet tropics, although adequate for geological mapping purposes, is too restrictive from the exploration standpoint where the whole of the exploration area must be investigated; i.e. including the interfluves where most of the weathering profile is preserved and where mechanical erosion is far less active than chemical weathering. Even where mechanical erosion does occur in these interfluve areas, the upper horizons of the profile that are concerned are severely leached and carry little information about fresh bedrock characteristics. Moreover, considering that the target metals can be easily solubilized and transported in solution, the question is to be able to decode the corresponding contribution to the total chemical composition as obtained by conventional geochemical analysis. It is of note that few major base-metal discoveries in the wet tropics are recorded in the literature as resulting from geochemical surveys; the exceptions correspond to large porphyry-type deposits.

I would like to suggest that the problem of exploring for massive sulfide mineralization in the wet tropics be reconsidered in view of the considerable experience gained, over the last 10-15 years, in geochemical exploration techniques and in our fundamental knowledge of weathering processes in these climatic zones. Modeling geochemical dispersion and designing innovative sampling and analytical procedures should improve the efficiency and reliability of geochemical techniques for base-metal exploration.

We also face a major challenge in optimizing the Very Low Density geochemical approach for precious-metal exploration in the wet tropics. Can we reliably locate gold mineralization which is only a fraction of a km^2 in size, sometimes hardly outcropping, by collecting samples in large catchment areas (>10 km^2)? And what is the most appropriate sampling and analytical procedure? What we lack at present are comparative studies over large areas, where the performances of different techniques (e.g. BLEG, heavy concentrates, partial dissolution) should be tested. Of course, modeling precious-metal dispersion over large distances should be a prerequisite.

Conclusions

Notwithstanding the major changes in the chemical composition of rocks and ores brought about by weathering conditions in the wet tropics, geochemical techniques have proved to be efficient in this environment when used for mineral exploration or geological mapping purposes. Their effective use for environmental purposes will certainly increase in the near future. Nevertheless, qualitative and quantitative data interpretation can only be achieved if careful account is taken of the regional and local parameters describing the morphology and weathering profile. Otherwise, misleading results may lead to wrong decisions in the mineral exploration process, with project overcost and/or failure as a consequence.

At least two major problem areas relating to mineral exploration in the wet tropics need to be addressed by research during the coming years. The first is to improve the efficiency of regional geochemical techniques for base-metal exploration, and the second is to develop a reliable Very Low Density geochemical methodology for precious-metal exploration.

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Oral & Poster Presentations

Applied Geochemistry and Case Studies

Some problems with and bonuses from the use of humic substances in geochemical exploration.

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Keywords: Humic substances, Au, Cu, Pb, Zn, Tasmania

Introduction

The humic substances are complex, essentially aromatic heteropolycondensates of high molecular weight that are produced by bacterial degradation and synthesis within the decaying plant and animal matter of soils. They contain an abundance of reactive groups such as – COOH, – OH, and – NH_2 which are capable of complexing numerous metals. Since these metal complexes are concentrated in the "A" horizon of the soil they provide an excellent source of geochemical information for exploration purposes. In climates where the soil is not subjected to cyclic drying events the metal humates enter the drainage system and can be used to improve the reliability of hydrogeochemical exploration.

The application of humic substances to soil based geochemical exploration

The humic sustances are alkali soluble and numerous alkaline extractants may be used to recover them from soils. The degree of recovery varies with the proportion of differing types of humic substance present in the soil and the type of extractant, but for soils in the one climatic regime reasonably constant recoveries can be achieved. In the TDR Laboratories the extractant used is 0.5 M NH_4OH which is ideally suited to subsequent A.A.S flame determination of the metal content.

As the depth of sampling of the soils rarely exceeds 200 mm the operation results in insignifiant environmental disturbance. The soil samples are freed as far as possible from residual root material and stored in sealed plastic bags to reduce drying. Processing of the humic sustances extracts is rendered difficult by their high "molecular weight" which can exceed 100,000 and which results in an unfilterable product. To enable a sample preparation rate that is adequate for geochemical exploration it is advisable to design equipment capable of handling large numbers of samples and incorporating automatic volume measurement and dilution. The procedure in use at the TDR Laboratories extracts the humic substances from 25 g of soil with 50 ml of 0.5 M NH_4OH and recovers the liquid by centrifuging. The volume recovered is measured to allow correction for the loss of extractant to absorbents in the soil.

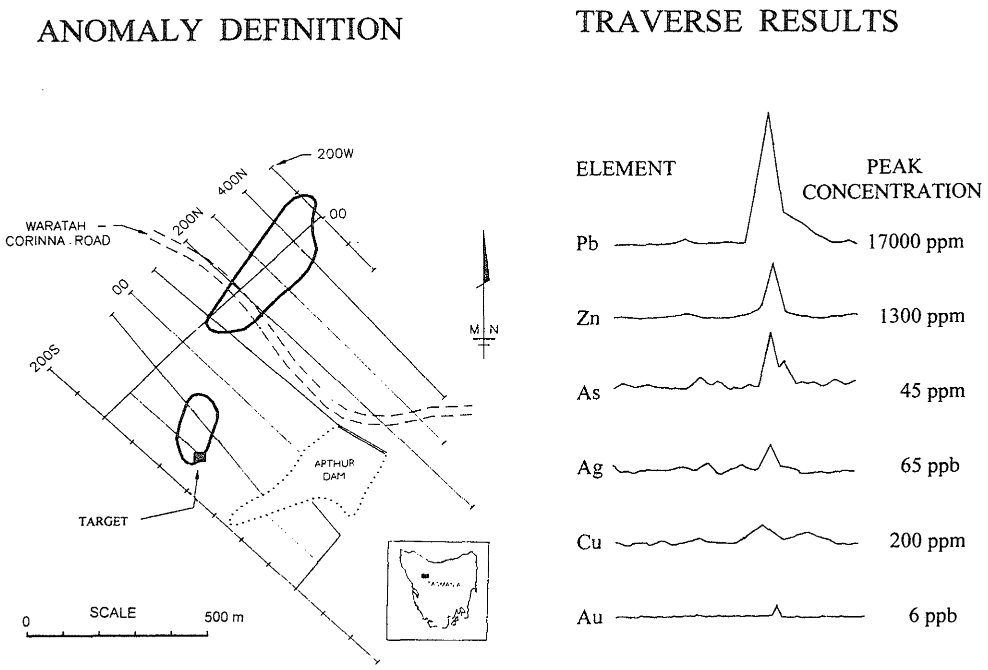
The extracts are made up to a volume of 50 ml which can be directly presented to an atomic absorbtion spectophotometer for the determination of Cu, Pb and Zn by flame AAS. Aliquots of 10 ml each are taken for further processing to concentrate Au and As by solvent extraction followed by graphite furnace AAS determination of these elements. A dissolved organic carbon analyser is used to give a measure of the humic sustances content of the extract.

The ratio of metal to carbon is the significant value from the analytical determinations and is generally expressed as µg metal to g organic carbon (or ppm metal in the extractable humic substances of the soil). An example of a lead anomaly detected by this procedure is given in Figure 1 and a traverse showing anomalous gold is shown in Figure 2.

Diamond drilling below the anomaly shown in Figure 1 located a 25 m zone of vein style sub-economic mineralisation at 90 m below surface. The veins varied in width from 0.2 - 1.0 m and assayed up to 23% Zn, 19% Pb, 0.8% Cu, 460 g/t Ag and 5 g/t Au.

The application of humic substances to hydrogeochemical exploration

As noted above the humic substances formed in soil will, under suitable climatic conditions, migrate through the drainage system and be ultimately discharged to the sea. Within this climatic regime a large proportion of the the metals migrating do so as humic complexes. These complexes are ideal substances for use as a sample medium in hydrogeochemical exploration. Within any region of a size likely to be considered for mineral exploration the formation of humic substances is slow and relatively constant. In their dispersion through the drainage system the variable factor is the amount of rainfall which when high


ANOMALY DEFINITION

TRAVERSE RESULTS

Figure 1. Anomaly definition (Pb), Traverse 100 S profiles and target location from the application of metal : carbon ratios in "A" horizon soil samples near Waratah, north-west Tasmania.

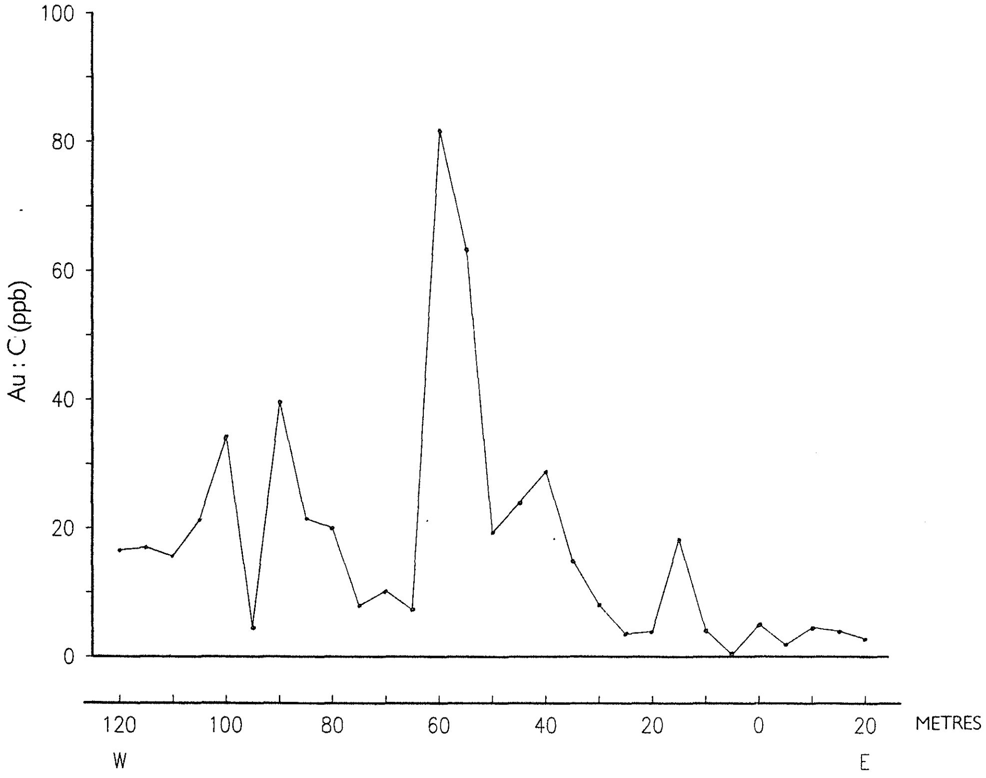


Figure 2. Distribution of Au as indicated by Au : C ratios across the Henty Fault zone, western Tasmania.

will dilute the concentration by direct runoff that leaches little from the soil. This situation applies also to the metals migrating through the drainage system. Since the effect applies to both humic substances and metals during their migration it can be allowed for by using the ratio between them in a manner similar to that used for soils. Looked at from another direction the approach offers a solution to the water volume problem which arises where conventional methods need to compare results from creeks and major rivers.

The analytical procedures for drainage waters are to some extent more simple than those for soils. The determination of As, Cu and Pb can be carried out by direct application of graphite furnace AAS techniques whilst Zn can be determined by flame AAS. The analysis for Au requires solvent extraction of this metal from a large volume of water prior to determination by graphite furnace AAS. In this procedure one of the less desirable traits of humic substances causes problems. When subjected to solvent extraction these substances invariably form a crud layer at the solvent-water interface which ,in addition to interfering with the recovery of solvent , absorbs most of the Au extracted. The only solution to this problem found to date in the TDR Laboratories is to oxidise the humic substances prior to extraction.

The results of applying this procedure to river and creek waters along part of the south-west Tasmania coast are shown in Figure 3 and results for Au in part of the Wanderer River in Figure 4.

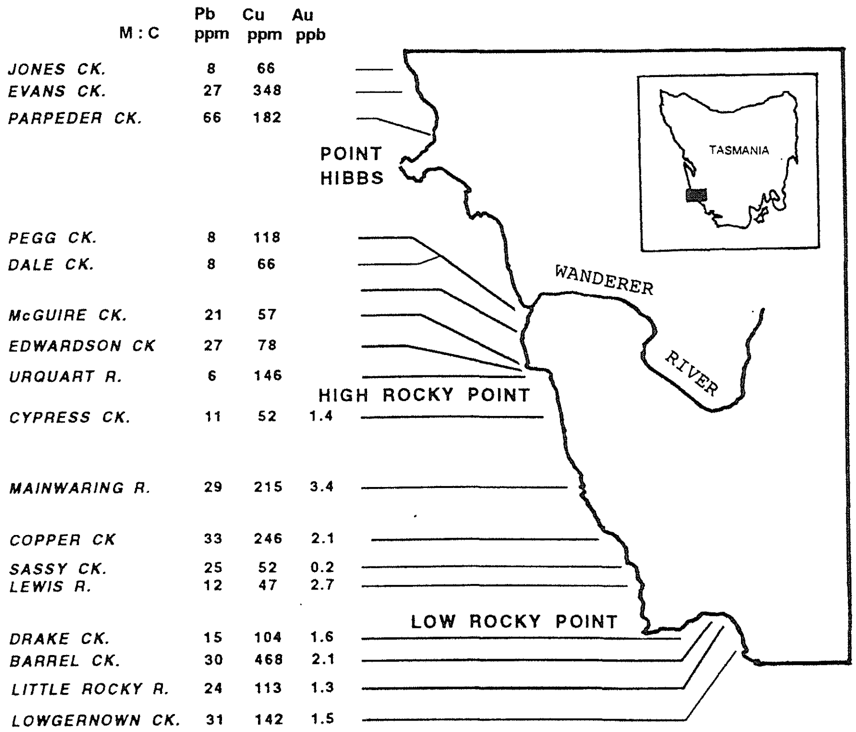


Figure 3. Metal : carbon ratios for Pb, Cu and Au in rivers and creeks in south-west Tasmania.

In Figure 3 it can be seen that a high Au value occurs at the Mainwaring River and this river has produced alluvial gold. Further south Cu and Au appear in waters that are known to drain areas of Cambrian mineralisation.

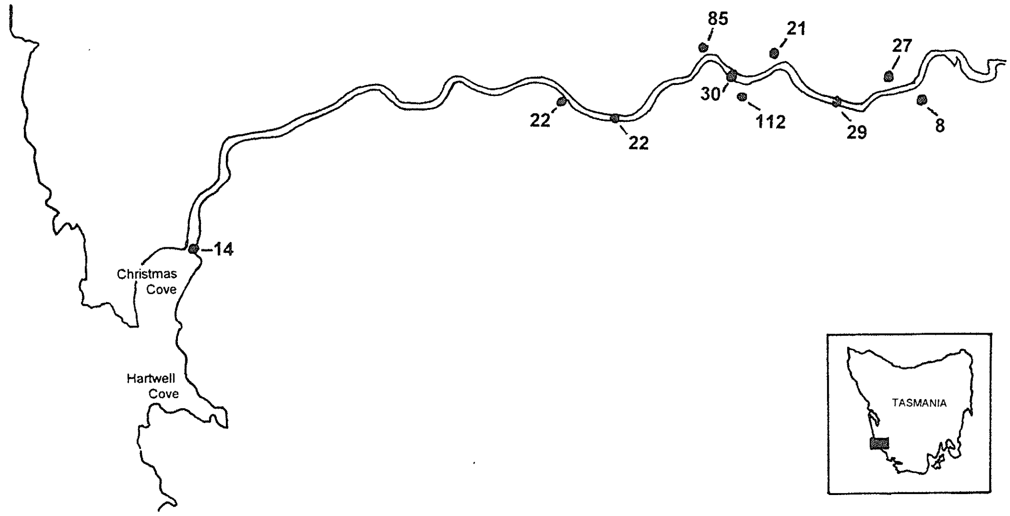


Figure 4. Au : C ratios for the Wanderer River and tributary creeks in south-west Tasmania.

For the Wanderer River (Figure 4) two creeks entering from opposite sides carry anomalous Au which may be indicative of the presence of a mineralised zone in this area.

Concluding Remarks

The information given above demonstates that the humic substances provide a very useful medium on which to base geochemical exploration. Although TDR experience with the methods so far developed has been limited to a temperate climate it is likely they would be applicable in any region that supports sufficient vegetation to allow generation of humic sustances in the soil. Use of the methods descibed, allow very cost effective sampling in terraines where heavy vegetative cover or adverse topography cause problems with transport of equipment required for a conventional "C" horizon survey. The sampling procedures are environmentally friendly and with a little care the area under investigation can be left with less damage than the resident population of nocturnal marsupials cause during their overnight forays !

Geochemical orientation for stream sediment and soil sampling at the Yandan gold deposit, Drummond Basin, North Queensland.

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Keywords: stream sediment, soil, gold, arsenic, dispersion, size fraction

Extended Abstract

The Yandan gold deposit is situated close to the junction of Yandan Creek with the Suttor River about 230 kilometres west of Mackay. The discovery of this deposit was the culmination of a systematic exploration program which commenced in 1985 and which was designed to locate epithermal gold mineralisation in this portion of the Drummond Basin (Sharpe, in prep.). A 34 ppb Au response in a -200μ stream sediment sample collected during 1986 led to field checking and further sampling in the anomalous catchment. This work resulted in the immediate discovery of outcropping gold mineralisation in both silicified sediments and altered volcanics.

Yandan has a mineable ore reserve of 4.72 million tonnes of gold ore grading 2 g/t and an additional 3.44 million tonnes of heap leach gold ore grading 0.46 g/t (Maxey and Ryan, 1993). The gold mineralisation is low-sulphidation epithermal in character (adularia-sericite) and is disseminated within tuffaceous sediments of the St Anns Formation of Devono-Carboniferous age (Johnston, 1994). This formation is the basal unit of the Drummond Basin sequence on the west side of the Anakie Inlier (Hutton et al., 1991). Further details about the geological setting of the deposit are given by Goulevitch (1992). The Au in the Yandan deposit is generally very fine-grained, 50% being less than 4.5μ in size and 90% less than 30μ (Sharpe, in prep.). The general maximum size for the Au is 50μ. This probably explains why the deposit was not found by prospectors, even though it outcrops well. The Au has a fineness of about 900.

Although the gold mineralisation outcrops on a low hill and rock samples containing as much as 26 g/t Au can be collected at the surface, its expression in the stream sediment sample that led to its discovery is quite subtle. As a result geochemical orientation was undertaken in order to improve the sampling methodologies for both stream sediment and soil sampling in the Drummond Basin. Previous work (Chenoweth, 1989) has shown that the best pathfinder elements in stream sediments at Yandan are Au and As.

A total of 19 stream sediment samples was collected around the Yandan deposit for the orientation survey. At each site 5 kilograms of -2 mm active sediment were collected for determining bulk leach extractable gold (BLEG). At the same locations 3 kilograms of -6 mm active sediment also were collected for size fractionation and more conventional analysis. Possible trap sites in the streams were avoided as much as possible. The samples were sent to the laboratory where they were dried and sieved into the following nominal fractions: -6 +2mm, -2mm +400μ, -400 +200μ, -200 +125μ, -125 +75μ, and -75μ. Each fraction was weighed, pulverised if coarser than 75μ, and then analysed for As and Au. For the Au analyses 30 grams of material were digested in aqua regia and, after solvent extraction, Au was determined by A.A.S. using a carbon furnace. The detection limit for Au is 1 ppb. For the As analyses 0.2 grams of material were digested in concentrated nitric/perchloric acid and, after leaching, As was determined by A.A.S. using hydride evolution. The detection limit for As is 1 ppm. The BLEG analyses were undertaken by CLASSIC COMLABS using their method "BLEG2" which requires 24 hours of leaching for each sample in dilute sodium cyanide solution. The quoted detection limit for BLEG is 0.05 ppb.

It is found that the dominant fraction in the stream sediments is the -2mm +400 μ fraction and it comprises about 48% of the average sample by weight. The -75μ fraction only comprises about 0.3% of the average sample by weight. Because of the scarcity of the latter fraction some of the analytical data are incomplete. The method of Booth et al. (1988) has been used to calculate the enrichment/dilution (Fi) of each element in each size fraction relative to its content in the bulk sample. However, instead of calculating it on a sample by sample basis, I have calculated it for the average sample. I have found that this gives a good indication of which size fractions are best to use for routine exploration. The plots of Fi show quite conclusively that Au and As are most enriched in the -6 +2mm fraction.

Dispersion trains have been plotted for the stream draining from the centre of the gold deposit at Yandan. For gold the contrast is highest for the -6 +2 mm fraction and the dispersion train extends as far as 1650 metres downstream. However, there is a marked drop in values at about 900 metres downstream. The dispersion train for BLEG is about 1100 metres long before background levels of Au are reached. For arsenic the contrast is highest for the -6 +2 mm fraction and the dispersion train only goes about 900 metres downstream before values drop to background levels.

From this work it was decided that the -6 +2 mm fraction gives both an excellent contrast and the longest dispersion trains for the two main pathfinder elements, namely As and Au. It is also well represented in the average sample by weight. It offers ease of collection and small sample weights (about 1 kg is required) when compared with BLEG sampling. Analysis of this fraction also is significantly cheaper than analysis for BLEG. Although the statistics of taking such a coarse size fraction may seem doubtful, it is found that the analytical reproducibilty is quite good. This is due to the very fine-grained nature of the gold in the lithic and silica-rich fragments which dominate this size fraction. The gold in the fragments is protected from weathering by both silica and lithic encapsulation. On weathering and erosion the lithic and silica fragments become smaller, exposing some of the tiny gold grains. These tend to dissolve in water (when it is present) and are carried away. Rarely do they remain to be incorporated into the finer stream sediments as micro-nuggets of free gold. Thus there should be a progressive decrease in gold content from the coarse to fine fractions. However, the graph of Fi for Au shows an apparent enrichment in the very fine fractions, but this effect is caused by swamping of the lithic and silica fragments in the intermediate size fractions by barren quartz of sand size.

Plots for the distribution of Au and As in the -6 +2mm fraction of the orientation stream sediments show that the Yandan deposit is delineated very well. The responses in the east relate to the mineralisation at East Hill (see Goulevitch, 1992 for more details about this mineralisation).

There are two major soil types in the vicinity of the Yandan deposit. In areas of outcrop and sub-crop lithosols are present. These are characteristically quite thin and are very stony. The lithosols are generally light grey to buff in colour. In areas away from outcrop there is extensive development of sandy to silty loams. These soils lack stony fragments and characteristically are deep red to deep brown in colour. These loams are very immature since new alluvium is deposited on them every time the Yandan Creek and/or Suttor River flood.

In order to delimit the extent of the deposit soil sampling was undertaken using the -200μ fraction of the soils. Samples were collected on a 100 x 10 metre pattern. There is relatively good match between Au >250 ppb in soil and the ore zone. Interestingly, As in soil forms a halo around the deposit.

Orientation soil sampling was undertaken at 10 metre intervals along two lines across the deposit, namely 14300 and 14500 mE. A total of 120 samples was collected. These were sieved into the same size fractions as the stream sediments, weighed, and analysed in the same manner. No samples for BLEG analysis, however, were collected.

It is found that the dominant fraction in the soil samples is the -2mm +400μ fraction and it comprises about 35% of the average soil sample by weight. All other size fractions are well-represented, except the -75μ fraction which comprises just 2% of the average sample by weight. Again the method of Booth et al. (1988) has been used to calculate the enrichment/dilution (Fi) of each element in each size fraction relative to its content in the bulk sample. The plot for Au shows that it is most enriched in the -75μ fraction. It is also enriched in the -6 +2mm fraction. Unlike the stream sediments it is apparent that the fine-grained Au is accumulating as micro-nuggets in the soil as it is liberated from the lithic and silica-rich fragments in the soil. This is probably due to the short times of contact between gold and water in the soils. The plot for As shows that As is best determined in the -6 +2mm fraction. It shows a progressive decrease in content from coarse to fine fractions. Again there is swamping of the middle size fractions by barren quartz which probably accumulates in the soil profile.

From this work it was decided that the -6 +2mm fraction of the soil offers excellent contrasts for both Au and As. The size fraction is well-represented and sampling is easy. Even though this is a coarse fraction, the analytical reproducibility is good and profiles for the -6 +2mm fraction are essentially identical in shape to those for the finer size fractions. The profiles for the -6 +2mm fractions of the soils along lines 14300 mE and 14500 mE show very strong and broad Au responses that closely relate to the ore zone. Peak values exceed 5000 ppb Au. On line 14300 mE, towards the west end of the main geochemical response, As and Au tend to correlate. On line 14500 mE, which is close to the centre of the main geochemical response, there is a clear zoning pattern with As responses fringing the most intense Au response. The sharp cut-off along the south side of the main response is due to the transition from lithosols to alluvially-derived loams where soil sampling is ineffective for mineral exploration.

Acknowledgments

I would like to thank both Ross Mining N.L. and Western Mining Corporation for their permission to publish the material included in this paper. Acknowledgement is also made to the staff of both companies for their contributions to the geology of the deposit.

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Gold Mines in the Quartz Mountain Area - Systematic Geochemical Prospecting, Misima Island, Papua New Guinea

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Keywords: gold, stream sediment, soil, trenching, intrusives, Misima

Introduction

Misima Island is located in the Louisiade Archipelago some 670 km ESE of Port Moresby (Fig. 1). Gold was first discovered at Misima in 1888. Almost all the early production coming from alluvial workings, with some 6,200 kg of gold produced up to 1911. Lode gold was discovered in 1904 and exploited until 1951 at various prospects including Gold Mines in Papua, Umuna and Kulumalia (Fig. 2). Total recorded production from underground mining was 6,804 kg Au and 20,412 Ag.

Early work on the regional geology of Misima Island was carried out by E.R. Stanley who produced a comprehensive report on gold mineralisation and compiled a geological map (Stanley, 1915). More recent work by the BMR - Davies (1958), De Keyser (1961) refined interpretations on regional geology and mineralisation. Misima Island has been mapped in detail more recently by the Geological Survey of Papua New Guinea (Williamson and Rogerson, 1983).

Placer Exploration carried out extensive investigations on the main centre of historic mining, the Umuna Fault Zone (Fig. 2), and defined a mineable reserve of 55.9 Mt grading 1.38 g/t Au and 21.0 g/t Ag at a cutoff grade of 0.7 g/t Au equivalent. The Umuna deposit is a epithermal Au-Ag deposit located in a steep SW dipping fault zone with a strike length of 3 km and up to 300 metres in width. Mineralisation is commonly associated with galena and sphalerite with trace chalcopyrite. Construction began in 1988 and the mine has been in operation since June of 1989, with over 1.5 million ounces of gold produced to date. Since 1989 exploration efforts have been divided into extensive exploration and drilling in the pit area, to fully identify the in-pit reserves, and more recently a greater emphasis on prospects away from the main Umuna Fault Zone.

This paper outlines the geochemical exploration completed in the Quartz Mountain area located to the south west of the main Umuna deposit (Fig. 2). Replacement style mineralisation has been mined historically and recently by Misima Mines at the Quartz Mountain and Kobel pits located to the south east of Quartz Mountain. Mineralisation is located at the eastern margins of a large 2x5 km porphyry intrusive complex (Fig. 2) within a silicified marble unit called the Halibu Calc-silicate.

Methodology

Regional exploration in Misima has involved the use of stream sediment sampling and regional mapping. This work is aimed at defining drainages with anomalous Au ± Pb - Zn for more detailed examination by mapping, ridge and spur soil sampling, rock chip sampling and trenching.

Drainages on Misima are juvenile and steep with most major head waters within 5 km of the coastline. Programs involving BLEG (bulk leach extractable gold), -150 mesh and -80 mesh stream sediment sampling were used in the area to south and west of Quartz Mountain.

The first work conducted in the Quartz Mountain area by Placer Exploration was late in 1987 when detailed mapping and preliminary a -150 mesh stream sediment sampling program was completed in the drainages to the south and west of Quartz Mountain. Samples were collected from above creek junctions, dried, sieved and assayed for Au, Ag, Cu, Pb and Zn.

As part of a regional assessment a program involving Bulk Leach (BLEG) stream sediment sampling was carried out on the eastern half of Misima Island during early 1989. Wet 2-3 kg -20 mesh samples were collected near the mouths of main drainages and assayed for Au, Cu and Ag. A review of the earlier -150 mesh sampling indicated that the sample size required to obtain the required amount of sieved sediment was too large to be transported easily in the rugged terrain. A program involving -80 mesh stream sediment sampling was carried out and found to be suitable for detailed stream sampling in Misima. Samples consisted of approximately 2-3 kg of coarse sieved (-4mm) sediment which was dried, sieved to -80 mesh and assayed for Au, Ag, Cu, Pb and Zn. All over size material was kept for panning.

The soil profile at Misima is generally thin (20-25cm) and residual with very poorly developed A and B horizons on ridge tops. Soil sampling is used extensively as an exploration tool. The rugged terrain was also a factor in selecting ridge and spur soil sampling in preference to soil sampling on a regular grid when evaluating anomalous drainage basins. The ridge and spur soil sampling involved digging small pits, to 20-25 cm deep, at 5m spacing for collection of 25m composite samples, which were dried and sieved to -80# and assayed for Au, Ag, Cu, Pb and Zn.

Mapping, rock chip sampling and trenching were the next steps in the follow-up of soil anomalies. Due to the remoteness of the area trenching was all completed by hand and was aimed at relating soil geochemistry to the bedrock. Trenches ranged to 2 metres in depth and up to 170 metres in length. These trenches were mapped in detail and channel sampled at 2 metre intervals.

Results

The -150 mesh stream sampling program recorded a large area of coincident Au-Pb-Zn anomalies and covering an area of 2 km^2 . Gold ranged up to 8.45 g/t with Ewatinona Creek, in the north west of the sampled area, recording 1.49 g/t Au, 175 ppm Pb and 395 ppm Zn, occurring at the edge of the defined anomaly. Mapping showed that the area of the anomaly is dominated by porphyry of the Boiou Microgranodiorite with minor greenschist and schist.

Results of the regional assessment programme confirmed anomalous streams were identified by all sampling methods. The Bulk Leach (BLEG) stream sediment sampling carried out during early 1989 showed that the Habalona drainage basin , which has an area of 3-4 km^2, has an anomalous BLEG gold value of 25.5 ppb in -20 mesh sediment. Maika Creek which drains the historic Quartz Mountain workings (which were subsequently mined in the Quartz Mountain and Kobel pits) contained a significant BLEG value of 85ppb.

A detailed -80 mesh stream sediment sampling program was completed. This program located several anomalies including a broad anomaly with values of up to 3.7 g/t Au, with 1345 ppm Pb and 375 ppm Zn, in Ewatinona Creek in the head waters of Habalona Creek .

An extensive regional ridge and spur soil sampling program, involving the collection of 507 samples over 12.6 line km, was carried in the Quartz Mountain area in 1991. This program located a number of significant anomalies, with large areas of +0.2 g/t Au recorded. The best of the soil anomalies were selected for trenching with the aim of exposing bedrock and try and relate soil anomalies to a bedrock source. A total of 17 trenches for 1139 metres were completed in the Quartz Mountain area. These trenches revealed that mineralisation could generally be related to stockwork veined and brecciated porphyry which in most cases appeared to be of only limited extent. This was shown to be the case when reconnaissance drilling was completed in the last half of 1992.

The last trench in the program was dug on what is now referred to as the Ewatinona Discovery Ridge , to test a significant soil anomaly of 75 metres at 1.05 g/t Au, 649 ppm Pb and 420 ppm Zn. This trench exposed a mixed porphyry and greenschist sequence including a gossanous vein up to 2 metres in width. Channel sampling of this trench returned assays of 8.44 g/t Au, 18.2 g/t Ag, 1.94% Zn over a 30 metre interval, including 6 metres at 52.5 g/t Au, 168 g/t Ag and 14.8% Pb over the cerussite gossan. In response to these results a more detailed soil sampling program was completed over the Ewatinona area. This program outlined a coincident Au-Pb-Zn (and weaker Cu) anomaly over an area of approximately 200x300 metres.

Rock chip sampling of creek exposures also located broad zones of mineralisation including 120 m @ 1.00 g/t Au and 60 m @ 1.56 g/t Au. Access was established with all new tracks mapped and channel sampled. Several very encouraging zones of mineralisation were encountered in channel sampling near Discovery Ridge including 75 m @ 1.21 g/t Au, 60 m @ 3.20 g/t Au and 145 m @ 1.27 g/t Au. All mineralisation was found to be associated with anomalous lead and zinc, with copper recording a more subdued anomaly.

The first phase of drilling, completed between late 1992 and early 1993, was successful in intersecting significant mineralisation, including the discovery hole - QRC385 which recorded 60 m at 2.25 g/t Au and 3.6 g/t Ag. A more extensive drill program was completed during 1993 and early 1994 and involved establishment of access tracks, mapping and channel sampling of all new access tracks, mapping and sampling of creek exposures. The extensive drill program completed early in 1994 has delineated a measured and indicated resource of 3.16 Mt at 1.49 g/t Au and 4.22 g/t Ag and an inferred resource of 0.96 Mt at 1.4 g/t Au. Mineralisation occurs as vein and cavity fill within brecciated porphyry on the western margins of a major 2x5 km pluton of Boiou Microgranodiorite. The Ewatinona breccia is irregular to roughly ovate in plan and in section forms an irregular cap over the granodiorite. The breccia is intensely phyllic (sericite-pyrite-leucoxene) altered and appears to be related to intrusion of the granodiorite stock. The hydrothermal system responsible for the intrusion prepared the ground for a later mineralising event which involved Au-Pb-Zn rich epithermal fluids localised along fault zones.

Conclusions

A systematic approach to geochemical sampling has been successful in the discovery of Ewatinona which represents a new ore body in an area which has been extensively prospected over the last 106 years. Stream sediment sampling, ridge and spur soil sampling, rock chip sampling and trenching have all been used to focus in on areas of anomalous geochemistry.

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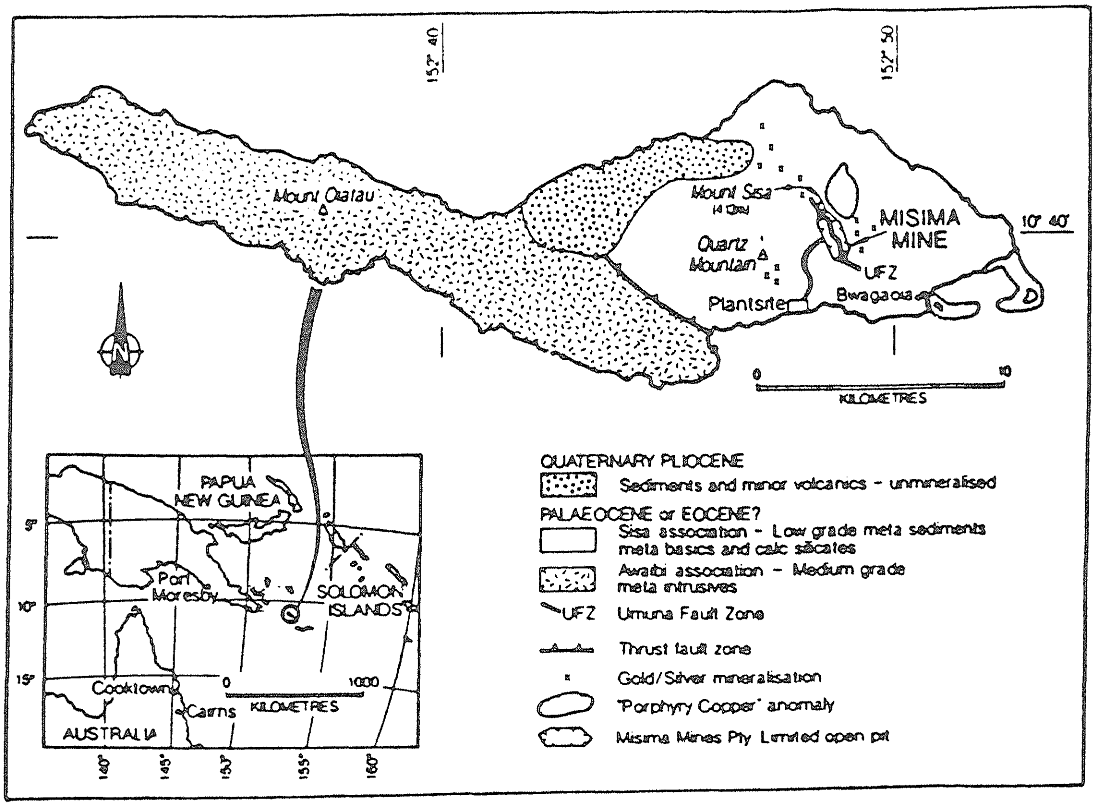

figure 1. Location of Misima Island, with simplified geology

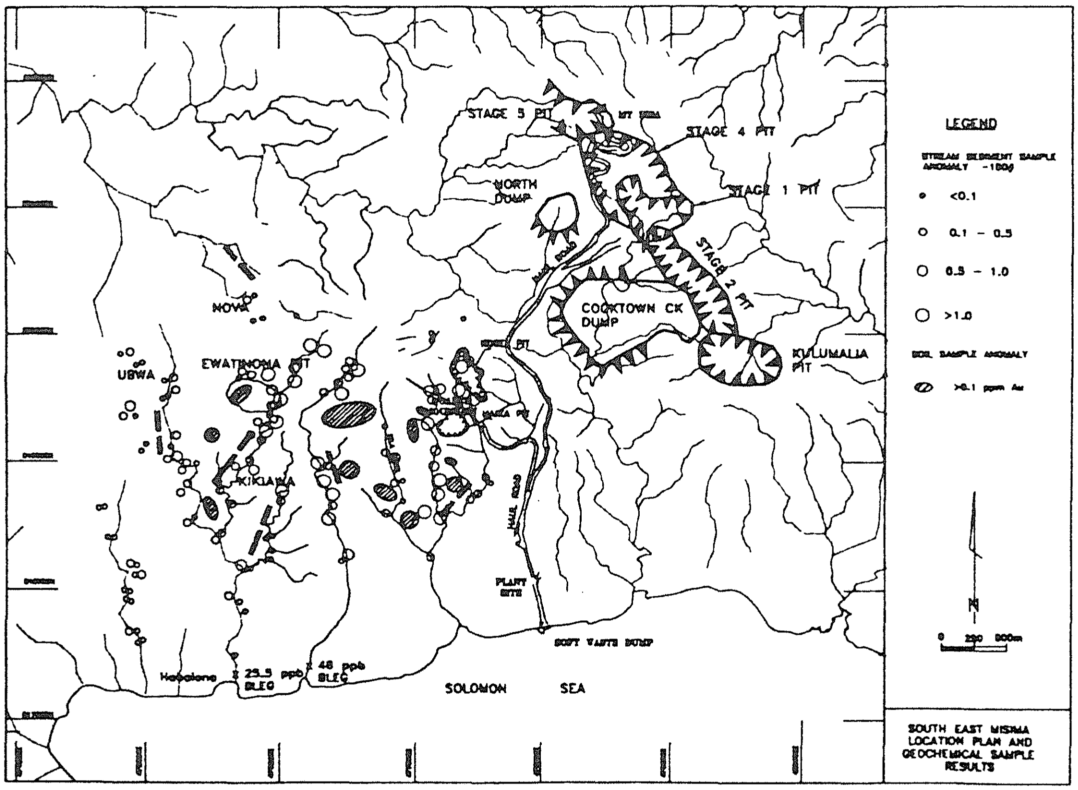

figure 2. Location of pits and geochemical sample results.

Geochemistry for gold exploration in Proterozoic Birrimian areas of Guinea

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Surface weathering is a major handicap to exploration, as the weathering literally digests the upper part of the lithosphere. Geochemical exploration in the Birrimian greenstone soils of Guinea often results in false anomalies due to severe leaching. These false anomalies, called "allochthon anomalies", result from secondary enrichment unrelated to the underlying rocks. It is therefore necessary to dig control trenches before planning a drill program.

Interpretation of the structural setting is also difficult, as supergene weathering masks not only the lithologies, but also the structures.

In 1986-87 a program of geochemical sampling of lateritic cuirasse led to the discovery, at Lero, of highly anomalous gold mineralisation with a strike length of 300m. In the following year, a trench dug on the anomaly cut 29m of highly anomalous mineralisation in saprolite, with an average grade of 10.4 g/t Au. As a result, in 1992-93, 40 core holes were drilled and confirmed the gold potential of the Lero prospect.

The main mineralisation is located within the oxidised zone, and contains gold only. Gold is fine-grained and not visible with the naked eye ($<60\mu m$). High gold values (up to 175 g/t Au) occur near the surface. The mineralised material consists largely of clay, kaolin, silica, hematite and limonite. Gold is accompanied by trace amounts of Ag, Pb, As, Cu, and Zn.

The form and limits of three units associated with the mineralisation have been defined; these consist of:

- a few metres of horizontal lateritic cover (maroon surface);
- a main mineralised oxidised body, trending east-west, and dipping 40 to 70° to the south (red surface). This body grades into sulphide mineralisation (green surface) below the level of oxidation which is located at a depth of about 80m;
- an aureole within the weakly anomalous saprolite which broadens towards the surface in a funnel shape (yellow surface).

The overall shape of the Lero gold mineralisation corresponds to a mushroom, the base of which is made up of the main mineralised body, the cap by lateritic cover, the ring laminae by the weakly anomalous saprolite.

A mining development project was carried out between 1985 and 1988, in the Mandiana sector of eastern Guinea. Soil geochemistry was used to only a minor extent due to the degree of leaching, and exploration focussed on structural interpretation, and rock geochemistry at structural intersections. Soil and rock geochemistry resulted in the discovery of three locally mineralised targets in the Mandiana area (N'Zima, Tamana and Daoulen).

At Daoulen, soil geochemical sampling over anomalous areas (200 x 100m) on 25m x 25m grids, and rock geochemistry were used. All stockworks were systematically sampled. On the N'Zima lode, systematic sampling of 20-25kg of rock was carried out on a 5m grid. The results of this sampling were combined with geophysical interpretation before trenching. In the Tamana target area, further drilling has been recommended in areas of coincident VLF and IP anomalies.

Some regional structural targets have been identified. Geophysics has been recommended, in particular resistivity, to help with structural interpretation.

Exploration for gold mineralisation in the Birrimian areas of Guinea requires the complementary use of geochemistry and geophysics.

Regional drainage geochemical sampling in the mountainous regions of northern Pakistan

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Keywords: gold, base metals, stream geochemistry, Kohistan Arc, Eurasian Plate, Pakistan

Introduction

Regional drainage geochemical sampling over an area of 80,000km^2 in the rugged mountainous areas of northern Pakistan commenced in January 1991, under the guidance of the authors, as a major component of a collaborative effort between the Australian International Development Assistant Bureau (AIDAB) and the Government of Pakistan - the Gold Exploration and Mineral Analysis Project (GEMAP).

The principal objectives of GEMAP comprise:-

- initiation of exploration programs for gold and related minerals leading to the discovery of economic mineral deposits and ultimately to the development of profitable mining operations
- provision of technical assistance and training to enable the recipient organisations to continue and further develop systematic, cost-effective mineral exploration appropriate for local conditions on a basis sustainable beyond the completion of GEMAP
- generation of sufficient relevant data to demonstrate the mineral potential of northern Pakistan and to facilitate private sector investment in the mineral exploration and mining industry in Pakistan.

The relevant recipient agencies are (1) Sarhad Development Authority (SDA); North West Frontier Province (NWFP), and (2) Pakistan Mineral Development Corporation (PMDC); executing agency for Northern Areas, a federally administered region.

Geology and Mineral Potential of Northern Pakistan

Northern Pakistan can be sub-divided into three geotectonic units separated by major suture zones:-

- Eurasian Plate: comprising dominantly Palaeozoic continental shelf-type sediments, with minor volcanics, and intruded by Mesozoic-Tertiary calc-alkaline Andean-type batholiths.
- Kohistan Arc: comprising late Jurassic to Cretaceous Island Arc and back-arc volcanics, sediments and batholithic intrusives together with deeper crustal-level mafic-ultramafic layered complexes and amphibolites. Following closure of the Northern Suture in Late Cretaceous times the arc became the site for Andean igneous activity.
- Indian Plate: comprising late Precambrian to early Palaeozoic crystalline rocks that have been thrust southward over younger sediments.

The mineral potential of these geological environments for a wide variety of gold, base metal and PGE deposit types by the presence of many mineral occurrences scattered throughout northern Pakistan and the early results of GEMAP exploration.

Current Status of Mineral Exploration

There has been little systematic mineral exploration or metalliferous mining in Pakistan (except for minor chromite, stibnite and alluvial gold production). Exploration carried out under the GEMAP project therefore represents the first, systematic, regional exploration undertaken in northern Pakistan using modern concepts and methodology.

Topography and Climate

Situated at the junction of the Hindu Kush, Karakoram and Himalayan Ranges, northern Pakistan encompasses some of the highest mountains, longest glaciers and largest snow-fields in the world. Because it is located beyond the reach of the monsoon, much of the region can be classed as a high altitude desert environment with steep slopes and little natural vegetation in many parts; local agriculture in the valley floors is dependent on artificial irrigation.

Relief in northern Pakistan ranges from extreme in the Karakoram Range to moderate in the Dir area. K2 (8611m), the second highest mountain on earth, is located in the northeast of the region.

The region experiences a wide range of climatic extremes; in the hottest months, June and July, temperatures reach into the 40's (celsius) in some valleys, and in winter temperatures are commonly less than 10°C falling to minus 20°C in the northern mountains.

GEMAP Exploration

Following an initial compilation and evaluation of available data, GEMAP exploration, primarily based on drainage sampling, commenced in 1991 with an annual cycle comprising:-

- Drainage sampling with assistance from the authors in the early part of the field season
- Continuation of sampling by the recipient agencies for the remainder of the field season
- Data compilation and evaluation with assistance from the authors

The program was designed as a cost-effective approach for first-pass exploration for outcropping mineral deposits in northern Pakistan, under prevailing local conditions (geology, geomorphology, access, climate, and technical and financial resources), and to be sustainable beyond the involvement of the authors.

In addition to stream sediment geochemistry, other components of the drainage sampling include detailed examination of drainage float (transported rock fragments), site geology and panned concentrate mineralogy, in particular for gold particles.

To date, almost 2,000 sites have been sampled under GEMAP, representing about 40% effective coverage of the 80,000km^2 project area at the initial sampling density.

Methodology for Drainage Geochemical Sampling

Samples are collected and geological observations made at pre-planned locations representing clearly defined drainage catchment areas (cells) of 10 to 50km^2 with supplementary samples taken at intervals along lower order streams to cover areas not represented in individual cells. At each location, a thorough examination of stream float is made and the local geology noted.

Panned concentrate heavy minerals (pancon) and minus 80 mesh (-80#) stream sediment samples are collected at each sample site, including duplicate samples for future reference.

Relatively large pancon samples of 20 litres of minus 7mm material are collected from at least three heavy minerals traps in the active drainage channel and hand-panned down to produce a heavy mineral concentrate of no less than about 50gms. The concentrates are examined closely with a pocket microscope for visible gold as well as other ore, indicator and accessory minerals, and then bagged for more detailed petrological examination and geochemical analysis. Large sample size and precise sampling techniques are used to enhance repeatability of panned concentrate samples and reduce the chance of operator error resulting in anomalous metal content going undetected.

Composite -80# samples are collected from a combination of heavy minerals traps and fine sediment deposits in the active stream to provide additional geochemical data for base metals and fine gold which may not necessarily report in pancon samples.

Pancon and -80# samples are analysed for Au, Ag, Cu, Pb, Zn, Bi, Co & Ni. The list of analysed elements is governed largely be the capability of the responsible laboratory, SDA's Mineral Testing Laboratory in Peshawar.

Results

Initial evaluation of the geochemical and visible gold data is based on simple frequency distributions prepared for each element, for each sample type. Pancon geochemical data are "standardised" to a nominal 100gms concentrate weight prior to evaluation.

Anomalous levels of gold and other metals have been identified in many drainage systems, including some areas not previously considered prospective for gold. In other areas where the presence of gold was previously recognised, GEMAP exploration has identified specific source drainages which can now be prioritised for detailed follow-up investigations to locate primary sources of mineralisation.

Most of the anomalous geochemical values report from the pancon samples, reflecting that mechanical weathering is the dominant process of rock and mineral breakdown in this region of high erosion rates and generally cool climate at higher altitudes.

Many of the anomalous gold drainages identified have been classified as "high-order" anomalies having visible and/or analytical gold contents equivalent to 50 or more colours (colour is a field description for a particle of gold <0.3mm in size - 15 or more colours equivalent is regarded as anomalous).

These high-order gold anomalies can be characterised on the basis of one or more of the following parameters:

- Gold particle character in the panned concentrate
- Associated anomalous metal values
- Association with major structures

Other significant results with potential mineral exploration significance include the identification of previously unknown, regional zones, geochemically anomalous in base metals; the identification of correlations between known geotectonic units and drainage geochemistry; and as noted above, the association between a number of high-order gold drainage geochemical anomalies and major regional structures.

Conclusions

Northern Pakistan has a complex history of crustal evolution and a rich diversity of geological and metallogenic environments which compare favourably with geologically similar mineral producing belts elsewhere in the world.

Under the GEMAP project, the first stage of systematic exploration for gold and other metals based on "first-pass" integrated regional drainage sampling is in progress over an area of more than 80,000km^2 of northern Pakistan.

Work to date has identified a substantial number of specific areas which contain anomalous levels of gold and other metals potentially indicating mineralisation. These areas can now be prioritised as targets for the next stages of more detailed exploration aimed at locating primary sources of mineralisation and the discovery of economic mineral deposits.

Confidence in the sensitivity and reliability of the drainage sampling methods has been reinforced by the results to date - all of the known mineral occurrences covered by the drainage sampling have been readily detected, duplicate pancon sample data generally correlates well, and check sampling shows good repeatability.

The systematic, regional, drainage geochemistry database generated by GEMAP should form the basis for more detailed GEMAP-type drainage sampling surveys, and for mineral exploration in northern Pakistan for many years to come.

Acknowledgments

The authors wish to acknowledge AIDAB for permission to present the data at this symposium. Further acknowledgment is due to SDA and PMDC for their participation and assistance in the GEMAP project in Pakistan. It should be noted that most of the base data for this paper were generated by these two groups.

The Geochemical Discovery of a Porphyry Copper/Gold Deposit in the Owen Stanley Ranges, Papua New Guinea

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Keywords: porphyry, epithermal, panned concentrate

Follow up of a regional stream sediment sampling program led to the discovery of the Mt Bini porphyry copper-gold deposit in January 1993. The deposit lies 50kms east of Port Moresby.

The Mt Bini porphyry is a dioritic to monzonitic stock 650m x 350m in area. It intrudes phyllites of the Mesozoic Owen Stanley Metamorphics. An alteration halo of 2km^2 encloses the porphyry. Early potassic (biotite+ orthoclase) alteration is pervasive within the intrusive. Phyllic, intermediate argillic and propylitic alteration overprint the early potassic and extends into the basement phyllites. Dominant hypogene mineralisation consists of pyrite, magnetite, chalcopyrite, molybdenite, gold and bornite. Galena and sphalerite veining occurs proximal to the porphyry. Structurally controlled low sulphidation epithermal quartz veins are peripheral to and overprint porphyry mineralisation. Secondary mineralisation is minor. Oxidation is deepest under ridges where it may reach 70m and shallowest under water courses. Minor malachite occurs within this zone. Supergene chalcocite and covellite is evident within creek outcrops.

Sampling Methodology

Sample points were selected from published 1:100,000 scale topographic maps to achieve a sampling density of 1 sample per 10km^2 or 1 sample per 5km of stream length. Sampling density during follow-up was increased to 2 samples per 1km^2. This density compares to that of Watters et al., 1992. Four sampling teams with helicopter support were used during the first pass survey. A total of 483 sites were sampled during a 4 week period over an area of 4000km^2. Two to three sites were sampled on average per 1 hour of helicopter time. Rugged terrain restricted helicopter (MD500) access and follow up was completed by 3-5 day foot traverses.

A heavy mineral panned concentrate (PC) and bulk cyanide leach (BCL) sample were collected at each site, together with rock float samples where appropriate. Geological observations for rock float and outcrop were recorded. PCs were collected from gravel traps and BCL samples from active sediment. PC trapsites were usually on the sides of drainages and best where sediment was poorly sorted with a high fraction of compacted clay in gravel. Grass clumps were also suitable trap sites. BCL samples comprised silty /sandy sediment from run-of-stream. One standard pan load (5kg) of -2mm material was used for each of the PC and BCL samples. Each sample was wet sieved on site and stored in plastic bags.

Within anomalous drainage basins soil samples were collected along ridges and spurs at either 25m or 50m intervals. Five hundred grams of unsieved "B" horizon material was sampled from between 100mm and 300mm below the surface.

All samples were analysed by commercial laboratory methods. PCs were fire assayed in entirety for gold only. BCL samples were oven dried and 100gms of -2mm material split off. This material was prepared and analysed for Cu, Pb, Zn Ag and Mo by AAS following an acid digest. The remaining bulk sample was analysed without further preparation for Au, Cu and Ag by AAS following a tumbled cyanide leach for 24 hours.

Soil samples were oven dried and without fine sieving were analysed for Au by fire assay and Cu, Pb, Zn, Ag, Mo and As by AAS following an acid digest.

Discussion of Results

All analytical data from each sample type were plotted on log-probability plots and histograms to estimate regional thresholds between anomalous samples and background populations. PC results were first normalised to a standard 50gram sample weight.

Regional stream sediment results defined an anomalous area of approximately 100km^2 within which the previously undiscovered Mt Bini porphyry and several smaller mineralised centres occur. PC gold (Figure 1) showed the best clustering of high order anomalies (+30 ppm) with 157ppm Au in the sample immediately downstream (2km) from mineralisation. BCL Cu (+400ppb), Cu (+60ppm), Zn (+200ppm) and Pb (+80ppm) clearly defined mineralisation from the regional program results with Pb showing a spectacular dispersion train 9km downstream (Figure 2). BCL Au did not clearly define mineralisation associated with the Mt Bini porphyry but outlined mineralisation in nearby drainages.

Sampling of rock float of pyritic and silicified boulders during the regional program yielded highest values of 20.7 ppm Au, 463 ppm Ag, 0.14% Cu and 0.6% Pb 2 km downstream from mineralisation. These results were critical in focussing further follow up and is analogous with the discovery of mineralisation at the Wafi River Gold Deposit (Funnell, 1990).

Results of follow-up sampling indicated a clear cut-off between highly anomalous panned concentrate Au results downstream of a significant waterfall with 150m relief and highly anomalous BCL Au upstream of the waterfall. The panned concentrate Au results reflect coarse gold associated with pyrite in bonanza-style epithermal quartz veins which are exposed below the level of the top of the waterfall. This style of mineralisation is absent above the waterfall reflecting a topographically higher level in the epithermal system. The porphyry copper/gold mineralisation is reflected by the relatively elevated BCL gold levels above the waterfall.

The 0.2ppm gold soil contour defines a discontinuous zone of dimensions 2000m x 200m (Figure 3). This is similar to the definition of mineralisation at the Wafi River Gold deposit (Erceg et al., 1991). Copper (+150ppm) and molybdenum (+18ppm) are broadly coincident defining a zone of 650m x 350m. A central area defined by the +700ppm copper contour is coincident with a cluster of 0.2-0.5ppm gold values over an area of 500m x 150m. This zonation reflects the outcrop pattern of the potassic altered and mineralised Mt Bini Porphyry. Both Pb (+200ppm) and Zn (+150ppm) are anomalous peripheral to the central Cu/Au/Mo mineralisation and define a large geochemical halo of dimension 1500m x 2200m.

Conclusion

Regional helicopter supported stream geochemical sampling is the most effective and rapid method for assessing large areas of rugged, wet, tropical terrain.

The discovery of the Mt Bini deposit is an exploration success using stream sediment and soil geochemistry techniques. Panned concentrate gold and BCL gold results clearly define significant anomalous drainage basins at the regional scale. Base metal analyses of 100grams of material split from the BCL sample and in particular, Pb is a highly effective and inexpensive tool to characterise and rank gold anomalies. This is in contrast with fine mesh size stream sediment samples which require greater sampling time and with lesser economical use of helicopter and personnel time.

Associated epithermal bonanza-style veins greatly enhance the regional geochemical signature. High sampling density during follow up delineated mineralisation where panned concentrate gold and BCL gold differentiate between epithermal style veins and porphyry-style mineralisation respectively. Identification and sampling of altered/mineralised rock float in streams was critical to the ranking of the regional stream geochemical results.

Ridge and spur soil sampling effectively established metal zonation of Pb/Zn peripheral to Cu/Au/Mo.

Acknowledgments

The authors would like to thank BHP Minerals for permission to publish this paper and in particular to Leigh Bettenay for his valuable contribution.

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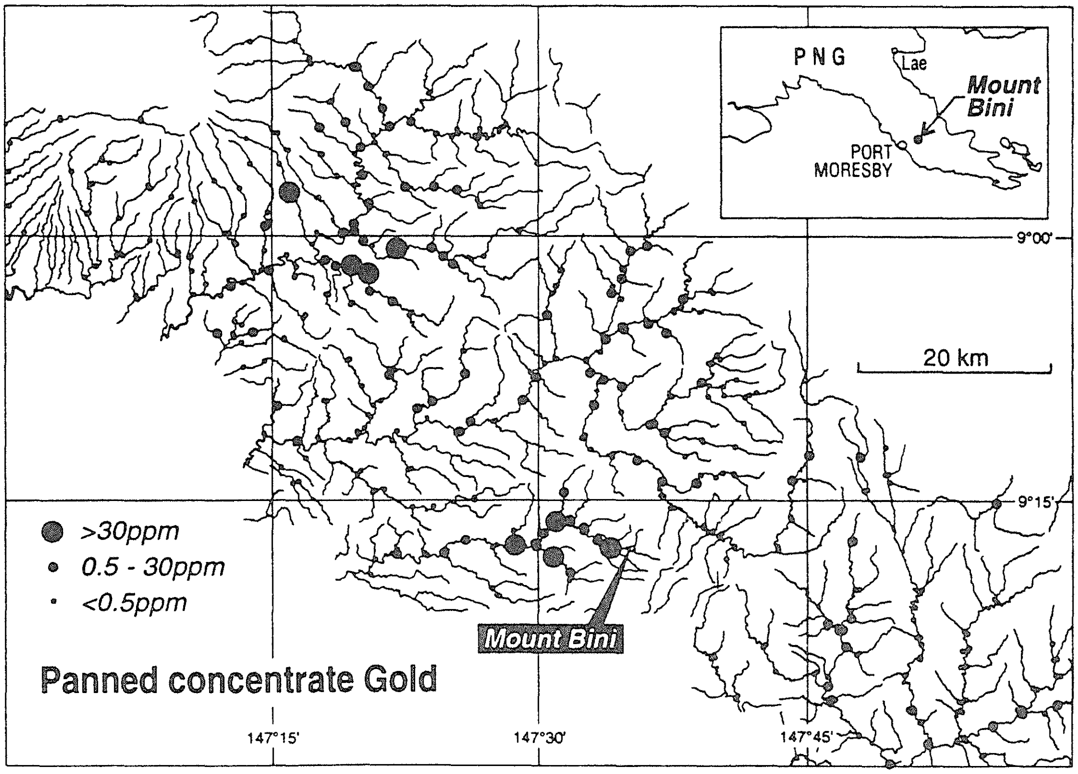

Figure 1 Gold in panned concentrate stream sediment samples

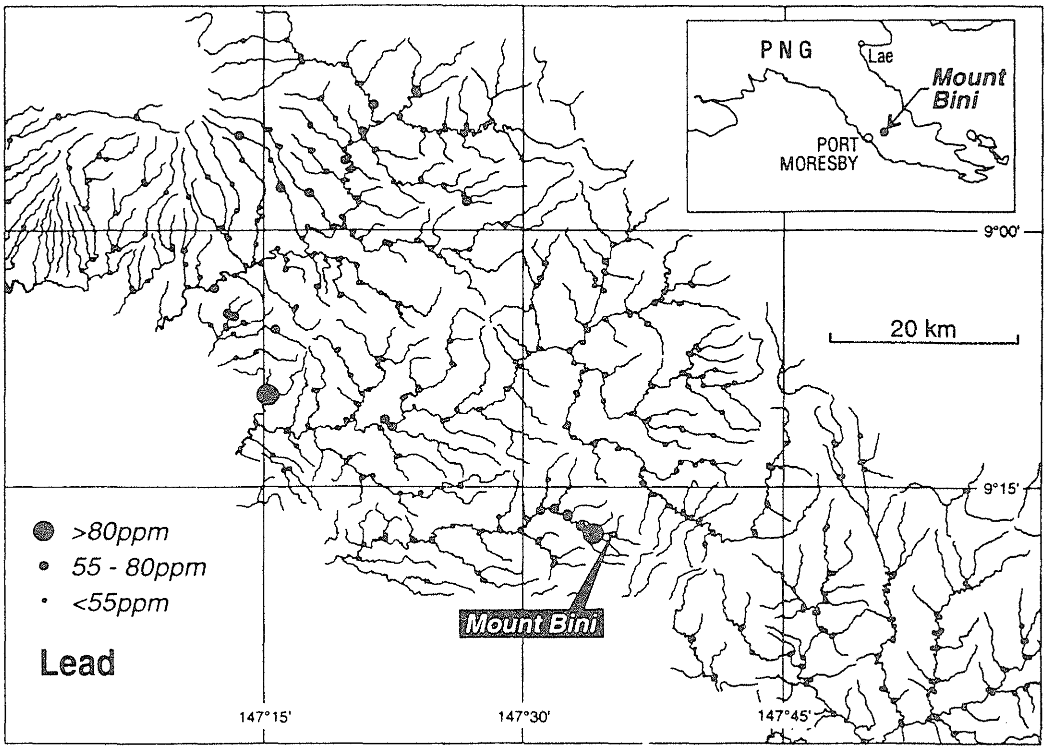

Figure 2 Lead in BCL stream sediment samples

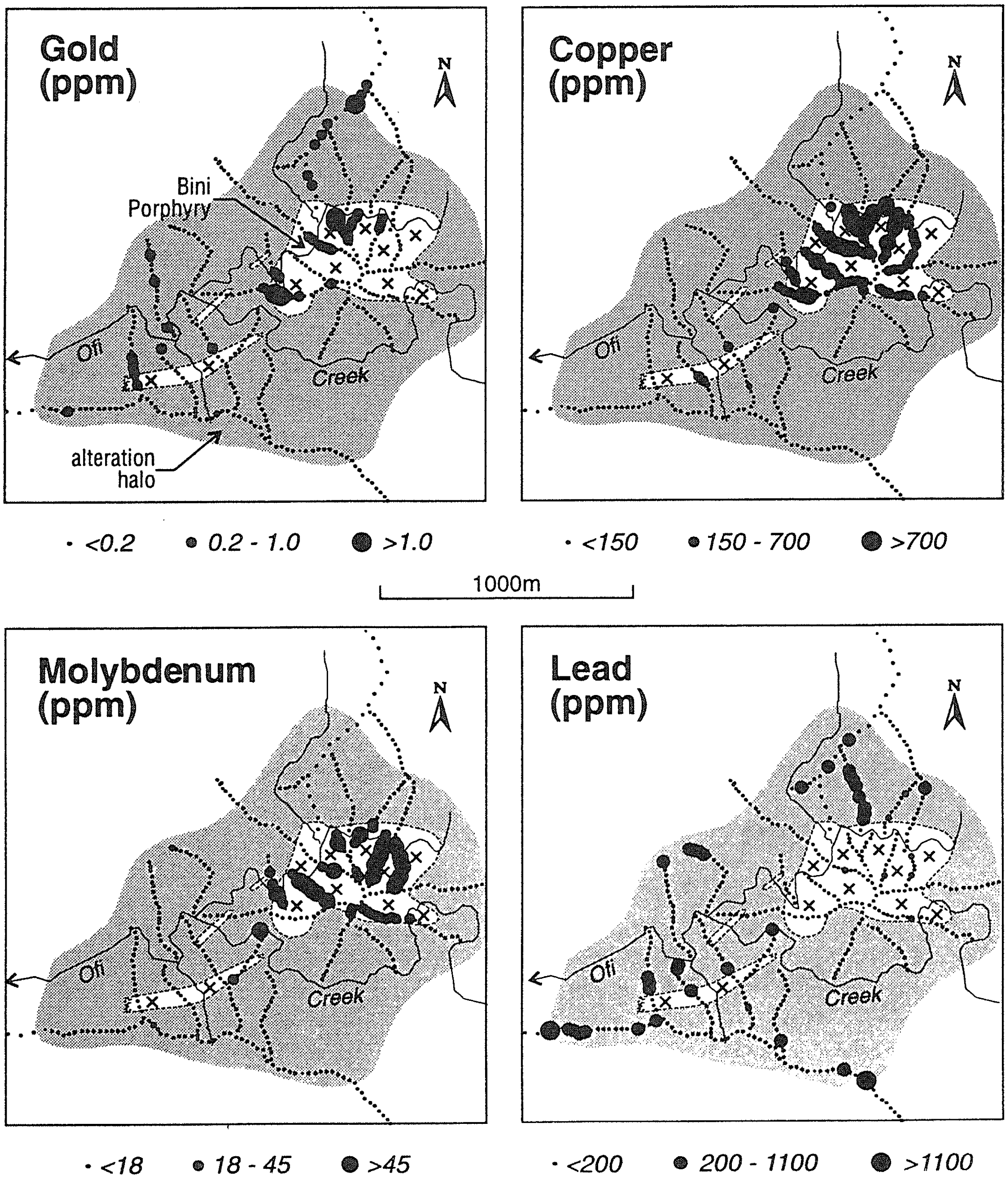

Figure 3 Soil geochemistry

Transport of cassiterite in a Malaysian stream: virtual velocities and real anomalies

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Keywords: tin, cassiterite, heavy minerals, sediments, bedload, anomalies

The preferential accumulation of heavy minerals, such as gold and cassiterite, on stream beds is a well known phenomenon that can be both an advantage and disadvantage in exploration geochemical and heavy mineral surveys (Fletcher and Day, 1989). It is generally supposed that such accumulations develop because heavy minerals, by virtue of their greater density, are transported at different rates to the sediment as a whole (Day and Fletcher, 1989, 1991). However, insofar as relative transport rates of heavy minerals and sediments have not been measured in natural streams, details of the underlying sedimentological processes remain poorly understood. To address this problem and to provide improved criteria for the design and interpretation of exploration geochemical surveys, we have measured transport rates of cassiterite and sediments in the Sungei Petal, a cassiterite-rich stream in Perak, Malaysia.

Our methodology, which follows that of Fletcher et al (1992), involved installation of a pit-type trap, 30 cm in diameter, in the bed of the S. Petal. Stream discharge was then monitored and the trap repeatedly emptied as it filled with the sediments transported by a series of flood events during the monsoon season in October-November, 1993. Sediments from the trap were dried and sieved into sixteen size fractions between <63 μm and 32 mm. All size fractions were weighed and the Sn content of seven size fractions, from <63 μm to 500 μm, determined by atomic absorption spectrometry.

Under base level flow conditions (0.5 m^3 per sec) no bedload sediment is transported. However, after heavy rain storms the stream rises rapidly to discharges that exceed 3.5 m^3 per sec. Bedload transport starts at a discharge of approximately 1.0 m^3 per sec and thereafter increases exponentially for all size fractions up to discharge of 2.2 m^3 per sec when the rate of sediment accumulation in the trap exceeds 5 kg per minute. At discharges >2.2 m^3 per sec rates of sediment accumulation in the trap decrease slightly for all except the two coarser fractions. This decrease is presumably a consequence of suspension transport becoming more important than bedload transport.

Transport rates for Sn also show an exponential increase, up to roughly 1000 mg per hour, as discharge rises to 2.2 m^3 per sec. However, concentrations of Sn in sediments caught in the trap also increases as discharge and sediment transport rates increase. This increase in relative concentrations of Sn results from the preferential retention of cassiterite in the bedload as more of the less dense sediments are transported in suspension with increasing discharge. Because fine sediment is swept away in suspension at the onset of bed movement, the smallest differences between Sn concentrations at low and high flows are found in the fine sand and silt fractions. In contrast, because coarser-sized particles of sediment and cassiterite are initially transported as bedload, these fractions only become enriched in Sn under high flow conditions. This has important consequences for geochemical surveys insofar as it shows that enrichment of high density heavy minerals, such as cassiterite, can occur in the silt and fine sand fractions under even relatively low flow conditions. Conversely, heavy minerals will only become enriched in the medium and coarse sand fractions under higher flow conditions: the heavy mineral content of these fractions can thus be expected to exhibit greater local spatial variability on the bed of the stream.

In interpreting exploration data for elements transported as the principal constituents of heavy minerals it would be useful to be able to minimize variability related to hydraulic effects. Conceptually this can be achieved by ratioing the concentration of the heavy mineral (or associated element) to the abundance of the sediment fraction having the same net transport rate (virtual velocity). Knowledge of the transport rates of different sizes of cassiterite and sediment in the S. Petal allows this possibility to be tested. Estimates of grain sizes of cassiterite and sediment having the same net transport rates indicate that, on a coarse sand or gravel stream bed, cassiterite grains up to 180 μm in diameter (i.e., 80-mesh ASTM) are transport at approximately the same rate as quartz grains three times larger. We have therefore tested, using data from a previous geochemical survey (Fletcher et al, 1987), the effect of recalculating the Sn content of the 53 to 75 μm fraction relative to the abundance of the 150 to 212 μm sediment fraction. Results clearly distinguish "real" Sn anomalies, close to their bedrock source, from hydraulic Sn anomalies developed several kilometres downstream from the source.

It is concluded that Sn anomalies in stream sediments become further enhanced as a result of differences in transport rates of cassiterite and sediment. This effect, which counteracts downstream dilution and can thus extend the length of the Sn anomaly, is expected to be most consistent for the silt and fine sand fractions. During interpretation of exploration geochemical survey data, enhanced concentrations of Sn resulting from accumulation of cassiterite on the stream bed can be recognized and corrected for by calculating Sn concentrations relative to the abundance of the transport equivalent size of sediment. The same procedures should be applicable to interpretation of geochemical anomalies for other elements, for example gold, that are transported in drainage sediments as the principal constituents of heavy minerals.

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Mechanical dispersion around calcrete-covered base-metal deposits: case histories from the north western Cape Province, South Africa

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Keywords: calcrete, base-metals, South Africa

Introduction

Calcretes form a chemical and physical barrier to the movement of many anions and cations in the regolith. This results in subdued surface geochemical expression above mineral deposits. Anomalies are generally restricted and are localised above the mineralisation, with little detectable down slope dispersion. At the calcrete-covered Putsberg (Cu) and Kantienpan (Zn) deposits, in the north-western Cape Province of South Africa, sampling of the top of the calcrete gives better anomaly definition than in the overlying soils. However, although the anomalies are better defined they tend to have a more restricted lateral extent and therefore still require a high sample density to detect them (Garnett et al, 1982; Garnett, 1983).

Any reduction in sample density without compromising the effectiveness of the survey is attractive. Consequently sheetwash/stream sediment samples from the above prospects were examined as an alternative sample medium to soils and calcretes in the hope that they might yield enhanced anomaly definition. The results of this study are presented here.

Regional setting of the deposits

The Putsberg and Kantienpan prospects are located within the high-grade metamorphic terrain of the Namaqualand Metamorphic Complex. Both occur on, or close to, the African erosion surface which is a mature peneplain dating back to Cretaceous times (Fig. 1). Pedogenic calcrete is a common feature of its weathering profile, often overlain by a thin stone line which, in turn, is overlain by variable amounts of reworked windblown sand. The calcrete is similar to that described from other arid and semi-arid regions (Wright and Tucker, 1991) in that it has a well-defined boulder or laminar top, grading down through honeycomb and/or nodular calcrete to powder calcrete at the base It is 0.5 to 3 metres thick, with incipient calcretisation of bedrock recognisable down to about 7 metres.

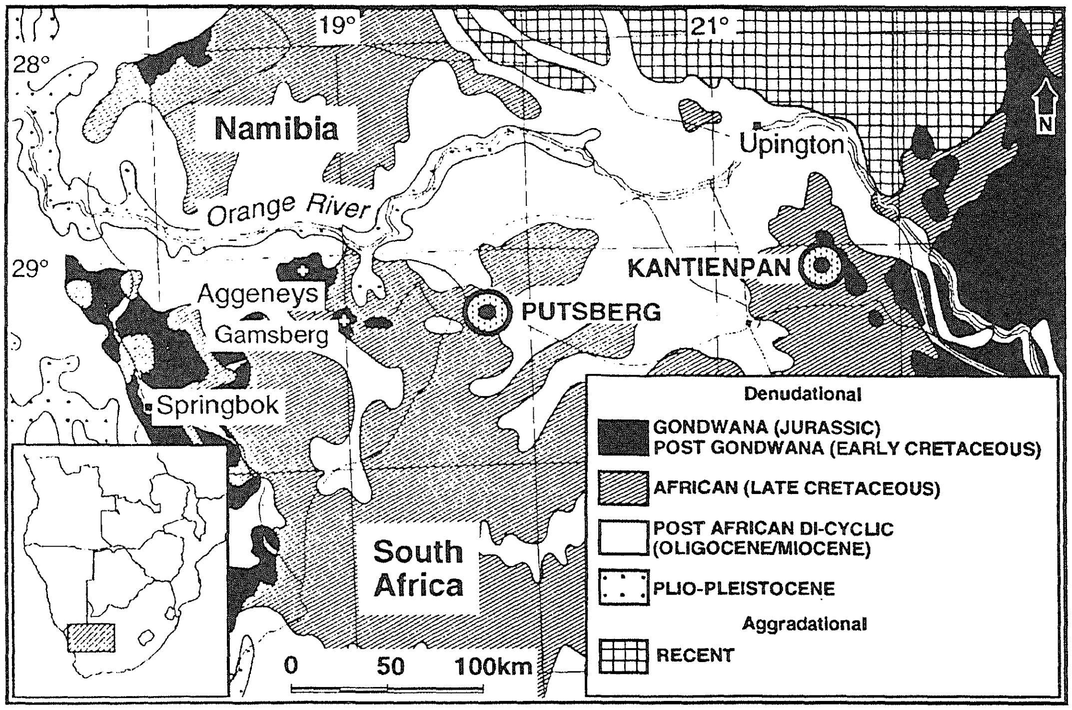

Fig. 1. Land surfaces of the north-western Cape Province, South Africa (adapted from Partridge, 1975), showing the location of the Putsberg and Kantienpan prospects.

The NW Cape is covered by open grassland. Thicker concentrations of vegetation, including small shrubs and trees, are developed along the sand-choked drainage courses, which rarely contain any water. It is probable that a very large proportion of the sand fraction is of wind-blown origin. This poses a serious problem in that it has the potential to dilute any anomalous material that might be liberated at the surface by mineralisation below the calcrete. Rainfall, generally in the form of thundershowers between December and May, rarely exceeds 100mm per annum. This alternation of wet and dry seasons may be important in driving calcrete formation (Wang et al, 1994). The region is subjected to wide fluctuations in temperature, from below freezing in winter to over 40°C in summer, with mean temperatures ranging between 32°C in January and 17°C in July.

Base metal anomalies of up to 15km were detected around the well exposed Aggeneys (Cu,Pb,Zn) and Gamsberg (Zn,Pb) deposits (Beeson et al, 1974, 1978), but these represent restricted remnants of an older Gondwana surface and dispersion patterns in soils are limited to 100 - 200 metres on the more extensive African surface with its blanket of calcrete and windblown sand e.g. at the Prieska copper deposit, south of Kantienpan (Beeson et al, 1974).

Sheetwash/stream-sediment sampling

The Putsberg deposit is drained by three broad, sand-choked channels while Kantienpan has no well defined drainage ways and drainage is entirely by sheetwash. At both prospects 2 - 3 kg of drainage sediment were collected at intervals of 10 to 100 metres both upslope of the mineralisation and for about one kilometre down slope. Samples were sieved to yield the following fractions: >2mm, 1-2mm, 0.5-1mm, 0.18-0.5mm, 0.075-0.18mm and <0.075mm. In addition, heavy minerals were isolated from the 1-2mm fraction. An attempt was also made to hand-pick dark brown, desert varnished ironstone chips from the >2mm fraction, in the hope that at least some of these would prove to be genuine gossan chips. Most of these chips weighed less than a gram. At Kantienpan individual chips were analysed in order to assess potential variability at each sample point. Fractions coarser than 0.18mm were pulverised before analysis. Most of the heavy mineral concentrates and ironstone chips were pulverised by hand because of the limited amount of material that was available. All samples were analysed for Cu,Pb,Zn,Ni,Mn,Ba,Co,Cd and Ag using atomic absorption spectrometry following a perchloric/nitric/hydrofluoric acid digest.

Results

The most reliable guides to the position of the mineralisation are the ore metals themselves - copper at Putsberg and zinc at Kantienpan. Copper and zinc are both preferentially concentrated in the finer fractions of conventional stream sediments. The best contrast is in the <0.075mm fraction, but even here anomalous values are subdued - about 80 ppm Cu over a background of 40 ppm at Putsberg; and about 120 ppm Zn over a background of 80 ppm at Kantienpan - and are restricted to a distance of 100 to 200 metres down slope from the mineralisation.

By far the strongest anomalies are developed in the 1-2mm heavy mineral and >2mm ironstone chip fractions (Fig 2). The 1-2mm heavy minerals gave the most consistent results and were particularly successful at Putsberg where values of about 1000 ppm Cu could still be detected at a distance of one kilometre from the deposit. Microscopic examination of the concentrates showed that they were dominated by dark brown, jasperoidal grains which were almost certainly derived from the mineralisation. In contrast, at Kantienpan the 1-2mm heavy minerals yielded elevated values over a distance of less than 300 metres. The decay of the anomalous values was clearly due to dilution by large amounts of heavy minerals derived from the surrounding country rocks. Ironstone chip sampling gave more variable results, to the extent that they would be an unreliable sample medium at Putsberg. This was partly due to an inability to identify chips with confidence because of clay coatings and desert varnish. This was also a problem at Kantienpan e.g the sample collected directly over the mineralisation gave background values. However, individual chips at each sample site were analysed at Kantienpan and many of these yielded encouraging results, even at a distance of 1km from the mineralisation.

Grain size analysis of the bulk samples showed that they closely resemble wind-blown sand with 90% of the material falling in the 0.18-1.0mm range. Only small amounts of the 1-2mm fraction were obtained from the initial samples, and of these only about 0.2% consisted of heavy minerals. In practical terms this meant that a bulk sample of 2 - 3 kg yielded only about 0.2g of 1-2 mm heavy minerals. Ironstone chips were more common at Kantienpan than at Putsberg, but even at Kantienpan they averaged less than four chips per sample point. Two thirds of the chips collected weighed less than 1g, while only 5% weighed over 10g. Clearly this poses particular problems for sample preparation since the majority need to be pulverised by hand.

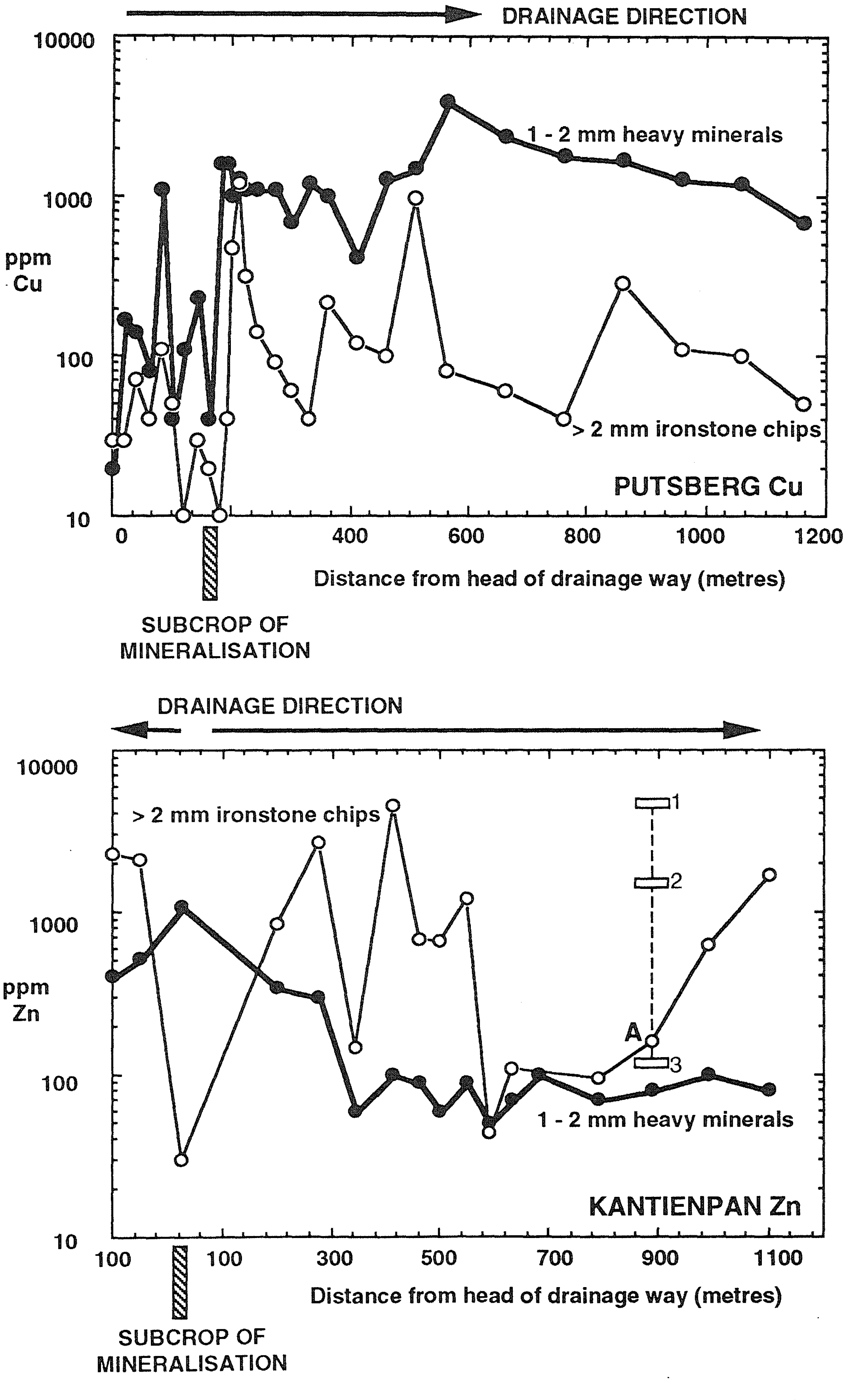

Fig. 2. Mechanical dispersion patterns around the calcrete-covered Putsberg (Cu) and Kantienpan (Zn) deposits. Values for the >2mm ironstone chips at Kantienpan are weighted means of analyses of individual chips. These proved to be highly variable e.g. position A shows the range of values encountered in the three chips collected at that point. Weights of the chips and Zn content were: 1 - 0.2g (4800ppm Zn); 2 - 0.15g (1600ppm Zn); 3 - 23.9g (110ppm Zn).

Discussion and conclusions

These results show that considerably enhanced anomaly definition can be achieved by isolating the few mechanically dispersed gossan chips which are liberated at the surface above calcrete-covered base metal deposits. At Putsberg values of about 1000ppm Cu in the 1-2mm heavy mineral concentrates provide unequivocal evidence of the presence of mineralisation even at a distance of one kilometre from the deposit. At Kantienpan values of over 1000 ppm Zn can be detected at a similar distance in the hand-picked >2mm ironstone chips. There is clearly potential to achieve a significant reduction in sample density by using these fractions, but a number of factors must be addressed before such a sampling scheme can be adopted with confidence. These are:

- Only very small amounts of material may be available for analysis. For example at Putsberg 2 - 3 kg of bulk sample yielded only about 0.2g of 1-2mm heavy minerals.
- Gossan chips may not always dominate the heavy mineral fraction. At Putsberg gossan chips remained as a significant component even at a distance of one kilometre, whereas at Kantienpan there was rapid dilution of this fraction by large amounts of heavy minerals derived from the surrounding country rocks.
- True gossan chips are not easy to recognise when attempting to hand pick >2mm samples, hence the variable results achieved at both prospects. Desert varnish is common and leads to the inclusion of barren material in the sample. Conversely, gossan chips at Putsberg were difficult to identify because of presence of pale clay coatings.

Care should be taken when extrapolating these results to other parts of the world. In the NW Cape there is no evidence of a past history of deep weathering under a humid tropical climate - calcrete grades downwards directly into fresh rock and there is no sign of any past deep lateritic (sensu lato) regolith described by Butt (1992) as being typical of most of the present arid zone. It is also possible that the rate of calcrete disintegration at the surface may be faster than in other calcrete-covered areas due to frost action in winter. This may accelerate the release of gossan chips to a point where they are more readily detected. Activities of large burrowing mammals such as porcupines may also speed this process.

Acknowledgement

This work was completed while I was with Johannesburg Consolidated Investments, South Africa. My thanks are due to them, and in particular to my colleagues both in the Geological Research Unit and in the Exploration Division, without whom it would not have been possible.

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Ok Tedi: One million years old, ten million millimeters of rain and four kilometers of weathering.

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The Ok Tedi mine is a porphyry copper-gold deposit adjacent to the western border of Papua New Guinea and Irian Jaya (Fig. 1). The remaining reserve after ten years of production (as at end of November 1994) is 450 million tonnes grading 0.70% Cu and 0.70 g/t Au. Ok Tedi mine produces 600, 000 tonnes of copper concentrate annually, containing 200, 000 tonnes of copper, 350, 000 oz of gold and 800, 000 oz of silver.

The Ok Tedi area, located within 5 degrees south of the equator is covered by dense tropical rain forests. Topography is characterised by deeply incised mountains with steep slopes. There are no climatic seasons with the temperature normally ranging between 25 and 30 °C. Extremely high rainfall (10 meters/yr), rapid plate movement (122 mm/yr) and uplift has resulted in high erosional rates (0.3 cm/yr) and development of a supergene enrichment blanket. An estimated four kilometers (Danti, 1991) have been eroded during the last 1.2 million years since the ore deposit was initially formed.

The deposit is located on the margin of the Indo-Australian plate within the Papuan Fold Belt. The region is oblique to the convergence direction with respect to the Pacific Plate which is currently moving at a velocity of 122 mm/yr in WSW direction. This has resulted in folding, thrusting and rapid uplift of the area. The folds and thrusts in the Papuan Fold Belt trend approximately WNW-ESE. In the mine area, the angle between the structural trend and convergence direction is 45°. Contemporaneous with these structural developments are Miocene to Pleistocene calc-alkaline intrusives and volcanoes (Davies & Norvick, 1977). The major structures within the mine area are the Ok Tedi anticline, Taranaki and Parrots Beak thrusts. These structures appear to be contemporaneous with the emplacement of the intrusive complex and controlled some of the major skarn bodies.

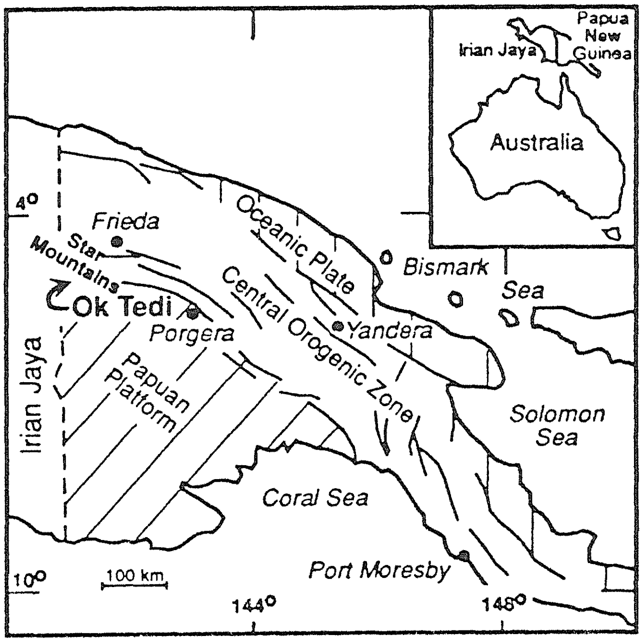

Fig. 1 Locality map of Ok Tedi Mine and structural setting of mainland Papua New Guinea

The geology of the mine area consists of a Pleistocene calc-alkaline intrusive (locally known as "Fubilan Latite Porphyry")[1] that intruded a slightly older intrusive (Sydney Monzodiorite) and three sedimentary units (Fig 2). The average total thickness of the overlying sedimentary pile ranges between 2500m and 3200m. Early to late Cretaceous Ieru Formation (1350 - 1500 m thick) is the oldest sedimentary unit in the mine area and comprises siltstones and mudstones. This is overlain unconformably by late Eocene to mid Miocene Darai Limestone (200 - 1000m thick). Overlying the Darai Limestone is mid Miocene Pnyang Formation (1200 m thick) consisting of mudstones with sandy horizons (Davies & Norvick, 1977; Mason, 1994).

The Sydney Monzodiorite has been radiometrically dated to be 2.6 million years old (Page et al, 1975 & Losada, 1994). The hydrothermal alteration event, that was contemporaneous with the crystallisation of the Fubilan Latite Porphyry has been dated to be 1.2 ma. Field relationships and Ar-Ar dating confirm that Southern Monzonite Porphyry is the youngest (0.5 ma) intrusive within the mine area and its emplacement was structurally controlled. Late stage hornblende porphyry dykes commonly cross-cut the various intrusives.

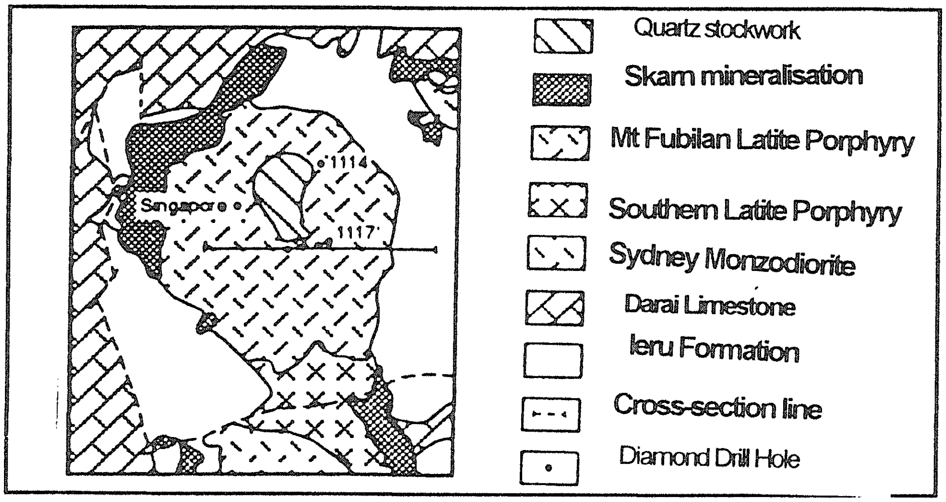

Fig 2 . Local Geology of Ok Tedi Mine area after Danti (1991)

The hypogene hydrothermal alteration zonation within the Fubilan Latite Porphyry is characterized by a central late stage silica flooding and quartz stockwork veining that postdates the earlier potassic alteration event which grades into a poorly developed argillic zone at the periphery. The potassic alteration is typified by secondary biotite and potassium feldspar (orthoclase). The potassic feldspar commonly occur as overgrowths, veinlets and fine grained alteration in the groundmass. Secondary biotite commonly pseudomorph clinopyroxenes, amphiboles and primary biotite that are then commonly replaced by chalcopyrite, pyrite and bornite. Although, propylitic alteration is poorly developed within the latite porphyry, it is well developed within the Sydney Monzodiorite. Propylitic alteration is characterised by chlorite, actinolite and epidote. The absence of mesothermal-epithermal regimes; and the direct contact between propylitic and potassic alteration zones suggest that the current exposure is at a deeper level of the magmatic-hydrothermal system. Supergene alteration is characterised by intense goethitic clay-sericite which decreases systematically with depth (Garry, 1993).

The major proportion of the hypogene copper mineralisation is associated with the potassic alteration event. This is shown by the presence of chalcopyrite and pyrite replacing secondary biotite. Minor amounts of primary copper minerals are also associated with quartz veining. The major hypogene sulphide minerals in decreasing abundance are: pyrite, chalcopyrite, bornite, molybdenite, marcasite, galena and sphalerite. Subsequent chemical weathering processes gave rise to a copper-leached cap, oxide zone, and chalcocite supergene enrichment zone, all of which overlies an unaffected primary zone. In the secondary enriched zone, copper has increased in grade by

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[1] "Monzonite Porphyry" has been used in the past literatures (Bamford, 1972) but technically it is a "Latite Porphyry" because of the fine grained nature of the groundmass (Mason, 1993 and Doucette, 1993)

diffussional processes. Danti (1991) estimated from mass balance analyses that the rate for secondary copper enrichment by solute transport is 1x10^{-7} g/cm^{3} /yr, (4x10^{-2} ppm Cu/ yr).

Geochemical analyses has established that higher gold grades within the Fubilan Latite Porphyry surrounds the upper portion of the silica flooded zone and decreases laterally and vertically. Preliminary fluid inclusion studies (Garry, 1993) revealed hypersaline (45-60 wt. % NaCl + KCl), gas-rich, and lower homogenisation temperature (300^{0}C - 400^{0}C) within the silica flooded and stockwork zones than elsewhere in the deposit. This suggest that gold was probably transported as chloro-complexes and precipitated due to boiling during the silicification event.

Supergene enrichment of gold unlike copper at Ok Tedi was not clearly understood until recently. Utilising petrography, mineralogy, hydrogeochemistry and mass balance analyses, Danti (1991) estimated that gold was enriched 50 times compared to protore during supergene processes prinicipally by regolith reduction and less commonly by solute transport at a rate of 2.9 x10^{-11} g Au/cm^{3} /yr, (11x10^{-6} ppm Au/yr). In the protore ore, gold occur predominantly as "invisible[2] gold" within pyrite, marcasite, bornite, idaite and chalcopyrite. Invisible gold decreases systematically upwards with 80% as invisible auriferous sulphides at depth (protore), 50% visible gold in the copper-enriched and 80% visible gold in the copper-leached cap. Danti (1991) also concluded that the source of the enriched gold is not present in the current weathering profile unlike the copper profile (Fig 3).

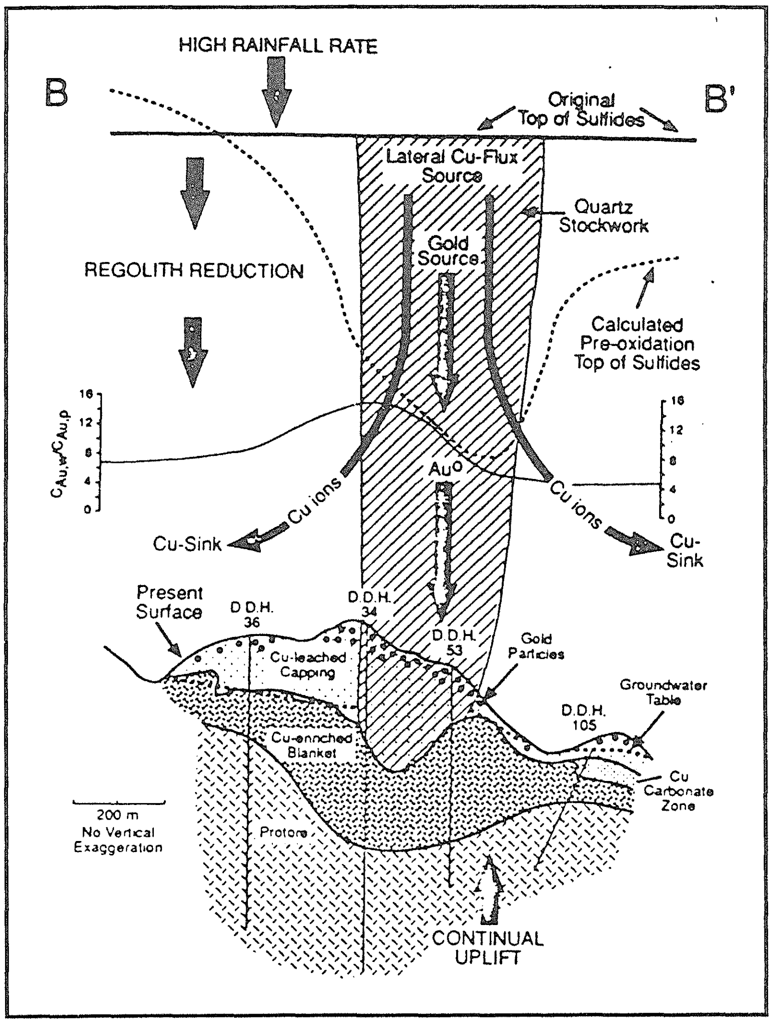

Fig.. 3 A generalised model at Ok Tedi showing gold and copper enrichment by regolith reduction and solute transport due to rapid uplift and high rainfall, after Danti (1991)

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[2] Invisible gold is used here after Cook's et al (1990) to define gold contained in the structures of common sulphide minerals and present as discrete inclusions smaller than 1000 ^{0}A , not detctable by optical and scanning microscope.

The Ok Tedi operation continues to face challenges in mining and processing the high grade oxidised skarn bodies and the lower grade oxidised porphyry. The geometry of an ore deposit affected by supergene chemical and mechanical weathering processes has necessitated the use of two extraction methods. The carbon-in-pulp extraction method was employed for gold ore in the copper-leached cap from 1984 to 1988 and flotation for copper-gold ore in the oxide, supergene enriched primary ore zones from 1986 to present.

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Geochemical Exploration for Gold Mineralisation in Malaysia

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Keywords: gold, mineralisation, Malaysia, geochemistry, exploration

Introduction

The investigations described in this paper were carried out under a collaborative programme between the British Geological Survey (BGS) and the Geological Survey of Malaysia (GSM) to study primary gold deposits in Malaysia. The British contribution was funded by the Overseas Development Administration of the Foreign and Commonwealth Office. The results of the programme have been summarised in a recent technical report (Gunn, 1994).

Geological Setting of Gold Deposits in Malaysia

Primary gold deposits of several different types are distributed widely throughout Malaysia. The bulk of output is a by-product from the Mamut porphyry copper mine in Sabah, East Malaysia. Significant production is also derived from epithermal siliceous replacement deposits in the Bau district of Sarawak, East Malaysia. In West (Peninsular) Malaysia current gold production is modest with the majority of output coming from small alluvial workings. However, primary mesothermal lode gold deposits which have locally supported significant operations are widely distributed, especially in Kelantan and Pahang (Figure 1). At Raub in north Pahang in excess of one million ounces of gold was produced between 1889 and its closure in the 1960s. Other significant deposits are found in the Kuala Lipis area of north Pahang and close to the Selangor - Negri Sembilan border, although production at these sites has generally been erratic and short-lived. Similar mineralisation has also recently been discovered at widely spaced localities in the east coast belt of Carboniferous metasediments of Peninsular Malaysia, notably at Lubuk Mandi in Terengganu and at Mersing in Johor.

The Malay Peninsular is divided into three belts, Western, Central and Eastern, based originally on the nature of the metallic mineralisation found in each. The majority of primary gold occurrences lie within the Central Belt which is characterised by a predominance of gold and base-metal mineralisation in contrast to the tin-bearing Western and Eastern Belts. The Central Belt is underlain by predominantly Permian and Triassic shallow marine and continental margin sediments, together with extensive developments of volcanic rocks of acid and intermediate composition. The western margin of the Central Belt is a complex structural zone, termed the Raub-Bentong suture, which is thought to indicate the position of a Benioff zone along which westerly-directed subduction commenced in Late Carboniferous times (Yeap, 1993). Continental collision during the Permo-Triassic triggered off the major regional episode of granite genesis now evident in the Main and East Coast Ranges of Peninsular Malaysia. The structure of the Central Belt is dominated by major north– and north-north-west–trending strike-slip faults and associated shear zones related to the collision event.

Several examples of mesothermal lode–style gold mineralisation were studied in the GSM-BGS programme in order to gain a better understanding of the controls on their distribution in West Malaysia and to determine the optimum exploration methodology for application in new target areas elsewhere in the country. The mineralisation is found in a variety of host rocks, mainly low grade pelitic metasediments, but also locally including limestones, volcaniclastic sediments and minor intrusions. Favoured sites are areas of high strain within fault- and shear-zones subsidiary to major regional strike-slip faults oriented north or north-north-west. The form of the mineralisation is determined by the deformation style and intensity but comprises principally late veins post-dating regional deformation and metamorphism. The mineralised structures have considerable vertical and horizontal extent, but are generally narrow, seldom exceeding 5 m in width. For example, at Raub in north Pahang the north–south oriented ore zone has been mined over a strike length of 6 km to a maximum depth of 335 m. Discontinuous high grade ore shoots occur sporadically in zones of repeated late brittle deformation where multiple episodes of

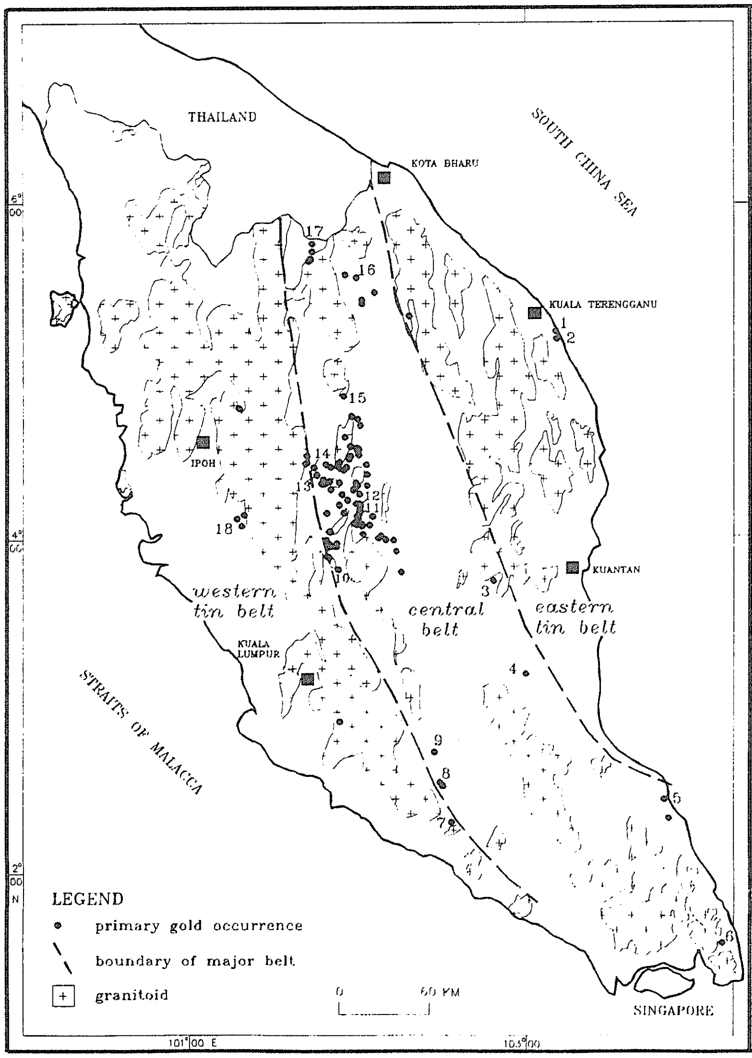

Figure 1:

The distribution of primary gold occurrences in West Malaysia

1	Panji
2	Lubuk Mandi
3	Mengapur
4	Tasek Cini
5	Mersing
6	Pengerang
7	Gunung Ledang
8	Chindras
9	Batu Bersewah
10	Raub
11	Penjom
12	Kechau
13	Buffalo Reef
14	Selinsing
15	Katok Batu
16	Ulu Sokor
17	Batu Melintang
18	Bidor

veining and recrystallisation have taken place. Low grade disseminated ore may form a near continuous envelope around the rich ore shoots.

The gold mineralisation is accompanied by low concentrations of metallic sulphides which rarely exceed 1 % by volume. Pyrite and arsenopyrite are most abundant and occur as ubiquitous early-formed phases. In contrast gold is typically deposited at a late stage in the ore mineral paragenesis as free grains of widely varying size. A large proportion occurs as coarse grains exceeding 100 μm in size and commonly visible in hand specimen. At the Lubuk Mandi deposit in Terengganu gold was introduced into the vein system contemporaneously with galena and sphalerite. In contrast, at Penjom in north Pahang a complex ore mineral paragenesis has been established with gold associated or intergrown with galena, molybdenite, chalcopyrite and a range of Bi, Pb, Ag and Au telluride minerals. Lithogeochemical studies of drillcore indicate that elevated Au concentrations in these deposits are often accompanied by enrichment in As, Ag, Pb, W, Bi and Mo. Less commonly, enhanced levels of Sb, Cu, Zn and Te may also be present. Hydrothermal alteration around the gold-bearing veins is generally of low intensity and of limited areal extent. Minor chloritisation is common in pelitic host rocks, but, where volcaniclastic sediments and microgranite intrusives are present, intense sericitisation, carbonatisation and silicification may be developed.

Exploration Methodology

Regional geochemical drainage data has been acquired by the GSM over a considerable part of the Central Belt during the past 20 years. In north Pahang, which contains the largest number of known deposits, the sample density is approximately 1 per km^2. Geochemical data are available for a wide range of elements, including gold which is routinely determined by the lead fire-assay method providing a minimum detection limit of 3 ppb in a 30 g sample. Sediment is collected from several low-energy points in the active stream channel at each site and is dry-screened through a 125 μm mesh. Orientation surveys carried out in the present study in the Kuala Lipis area of north Pahang have shown that this method provides results closely comparable with those obtained from -150 μm samples collected by wet screening in the field. Both sample types were effective in indicating the disposition of known lode gold deposits.

Wherever possible heavy mineral concentrates are also collected during the regional geochemical surveys. They are prepared in the field by panning a standard volume of sediment, derived from high-energy trap sites, down to a point at which the ratio of light to heavy minerals is about 2:1. The concentrate samples are analysed in their entirety to avoid sub-sampling errors introduced by splitting. The analytical results are recalculated to gold tenor and reported as mg Au per m^3 of original sediment This procedure not only provides a guide to the potential for alluvial gold mineralisation but also reduces the effects of in-situ upgrading in the stream and of different panning techniques. The concentrate data for gold in the Kuala Lipis test area were also effective in locating known mineralisation, but yielded more sporadic enrichments probably due to the coarse particle size of the gold. Nevertheless concentrates provide a valuable complement to stream sediments in this environment and collection of both sample types is recommended.

The GSM regional stream sediment data effectively delineate areas of past and present gold mining in north Pahang and indicate many new target areas (Lee et al., 1986). This is clearly demonstrated by images of the geochemical data showing the distribution of various elements over the Kuala Lipis map sheet. The Au data not only pinpoint sites of mining and known gold occurrences but also highlight the preferential Au enrichment associated with major faults oriented north and north-north-west. Pb and As show similar distribution patterns to Au in this district and together they provide a reliable indication of potentially mineralised structures. Bi and W are sporadically enriched over known mineralised zones in the same map sheet. In the Raub district, about 50 km to the south, Au is most closely associated with As and W, while local enrichments in Sb, Ag, U and Fe are found with elevated Au levels at some localities.

Follow-up geochemical surveys utilising high density soil sampling have been widely used to delineate mineralisation in this environment. At Raub, high tenor gold enrichment in B horizon soil samples provides excellent resolution of the known mineralised structures. A close correlation is noted between the distribution of Au, As and W in soils over the Raub deposit. At Bukit Panji in Terengganu the anomalous geochemical distributions for a suite of elements clearly focuses attention on the zone of known gold mineralisation. Sporadic gold enrichment, up to a maximum of 700 ppb, is accompanied by locally elevated contents of Ag, As, Pb, W and Mo.

At Penjom commercial soil surveys, in conjunction with geological mapping and remote-sensing studies, had previously delineated a high amplitude soil anomaly, 50 - 100 m wide, continuous for several kilometres and controlled by the geological structure. The present study has confirmed the high tenor of the soil anomaly with maxima of several ppm Au in the -125 μm fraction of B horizon soils. Over the mineralised structure As is enriched up to 400 ppm compared with background levels of 20 ppm. The distributions of Pb and W also reflect the disposition of the gold mineralisation, but the anomaly contrasts are more subdued than for As.

At Penjom and Bukit Panji shallow pits were excavated to bedrock at selected sites in order to examine the distribution of gold within the overburden profile. Bulk channel samples, collected from each horizon, were screened to provide five size fractions for analysis. The distribution of gold within a pit profile over mineralisation at Penjom is shown in Figure 2. The data show that the Au levels are markedly increased in the A and B horizons relative to the saprolite. The gold is not consistently enriched in a single size fraction, although the highest concentrations are commonly found in fractions coarser than 63 μm. Generally similar results were obtained from the overburden profiles examined at Bukit Panji. Analysis of panned concentrates from the same pits provided similar erratic distribution patterns, but also allowed effective discrimination between mineralised and background sites. Concentrates offer improved sample representativity over a single size fraction of soil, but the high costs involved in their collection and processing reduce their attraction for routine use.

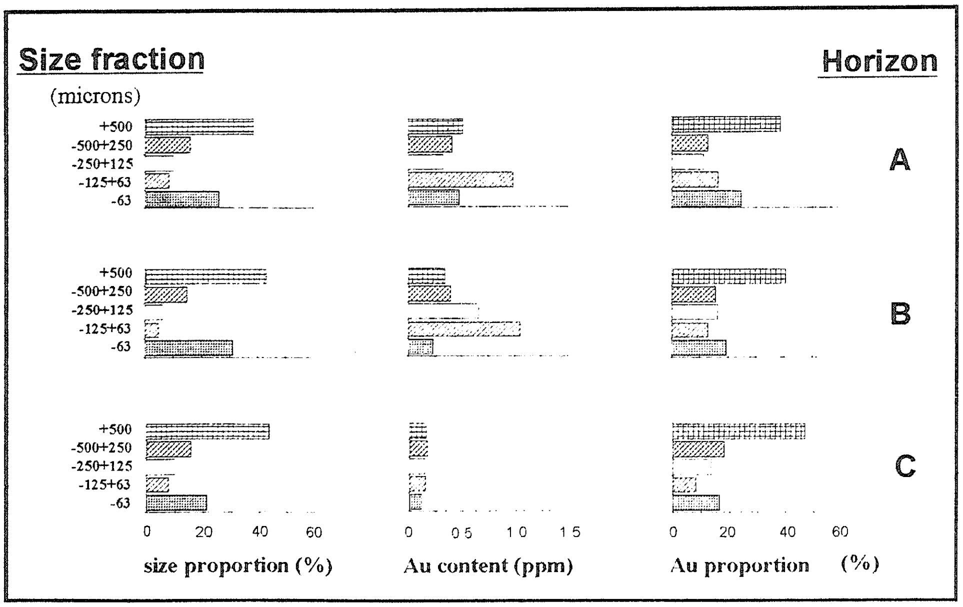

Figure 2: The distribution of gold in an overburden profile at Penjom, Pahang

Discussion and Conclusions

Mesothermal lode gold deposits in Malaysia present a major challenge for the explorationist on account not only of their narrow steeply-inclined form, but also because of the paucity of attendant hydrothermal alteration and their association with limited enrichment in other metals. Nevertheless, geochemical methods can be utilised effectively in this terrain to detect potentially mineralised regional structures and to pinpoint targets for detailed sub-surface investigation. Various pathfinder elements, especially As and Pb, are potentially useful although they should not be employed without caution. Wherever possible catchment geology should be taken into account during data evaluation due to the varying background concentrations of these elements in different lithologies. In addition the dispersion mechanisms of these elements in the secondary environment will generally differ from that of gold.

The data obtained in this study highlight the severity of the nugget effect associated with lode gold mineralisation and the consequent difficulty of obtaining a reliable estimate of the gold contents of geochemical samples. Analysis of a range of elements, in addition to gold, is preferred in order to increase the probability of recognising potentially mineralised structures.

Considerable potential exists for the discovery of mesothermal lode gold deposits in areas of West Malaysia which are poorly known geologically and in which little systematic exploration has been undertaken. In addition to the geochemical techniques outlined above, geological and geophysical methods also have an significant role to play on account of the importance of structure in localising these deposits.

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Geology and mineralization of the Big Gossan Cu-Au Skarn Deposit, Ertsberg District, Irian Jaya, Indonesia

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Keywords: copper, gold, skarn, Big Gossan, Ertsberg, Irian Jaya

The Big Gossan Cu-Au skarn deposit is located beneath extremely rugged terrain (elevation 3200-3700m), one kilometer southwest of the Ertsberg in the Big Gossan bedding-plane fault (-80°), at the boundary of the Tertiary Waripi (Tw) and Cretaceous Kembelangan (Kkl) Formations.

The surface expression is base-metal sulfide occurrences and altered monzonite porphyry and quartz-bearing diorite dikes in Tw carbonate breccias in and along the Big Gossan Fault. Epidote-diopside hornfelsing with sphalerite and galena veinlets occurs in Kkl south of the fault.

The alteration assemblage in the monzonite porphyry dikes is quartz, pyrite, K-feldspar, and sericite and amorphous silicate clays. Alteration in quartz-bearing diorite dikes is epidote, chlorite, calcite, and pyrite.

Surface geochemical sampling in 1975-76, and again in 1990, revealed elevated values of As, Hg, Sb, as well as Au, Ag, Pb, Zn, and Cu. Copper values increase vertically downward. Helicopter-supported surface drilling commenced in 1991 to explore down dip for possible skarn-related Cu mineralization based on a thermal model.

To date, 187 surface and underground diamond drill holes (63,000m) have delineated a minable reserve of 31.7 million tonnes (t) grading 2.5% Cu (chalcopyrite), 0.73g/t Au, and 13g/t Ag in the steeply dipping tabular skarn body 1100m+ long, 4-60m wide, and up to 700m+ vertically. This reserve extends from the 3000m elevation to below the 2300m elevation. Mineralized skarn continues below the 1965m elevation. Diamond drilling is ongoing.

Copper-Au-Ag mineralization is hosted by prograde diopsidic ($Di_{97}Hd_3$ to $Di_{59}Hd_{38}Jo_3$), andradite to grandite ($Ad_{99}Sp_1$ to $Ad_{49}Gr_{47}Sp_4$), magnetite skarn in Tw, with gangue anhydrite, pyrite, calcite, and quartz. Retrograde tremolite, actinolite, and chlorite occur locally with lesser phlogopite, talc, gypsum, and serpentine. Massive pyrrhotite occurs as a "cap" on the skarn. Inclusions in clinopyroxene indicate temperatures of vapour homogenization from 440-460°C, and a total salinity over 60wt%, and in quartz and sphalerite of 250-390°C, and a salinity of 2.5-20wt%.

Subsurface zoning toward skarn consists of unaltered carbonates grading to marble containing serpentine, epidote, and pockets and veins of pyrite, sphalerite, galena, and rare chalcopyrite. The marble-skarn contact zone is 1-5mm. Within skarn, garnet-pyroxene ratios decrease, iron (Fe) content in garnet decreases, and Fe content in pyroxene increases distally from a center believed to be near the source of hydrothermal activity. This source and the source of mineralization are not yet determined.

The relationship between false gold anomalies, sedimentological processes and landslides in Harris Creek, British Columbia, Canada

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Keywords: gold, landslides, stream sediments, anomalies

Traditional models of the dilution of geochemical anomalies downstream from their source make many simplifying assumptions that do not consider the possible influence of point sources of sediment from, for example, landslides. Such effects might complicate interpretations of exploration data. We have therefore investigated the influence of active landslides on a gold anomaly in Harris Creek, British Columbia.

Harris Creek is a gravel-cobble bed stream that drains the Okanagan Plateau in southern British Columbia. Preliminary studies (Ryder and Fletcher, 1991) identified fourteen landslides that have historically been sources of sediment to Harris Creek: four of these slides are currently active. For this study the active toes of the four active landslides were sampled and their erosion rates monitored. Sediment samples were collected from high (bar head) and low (bar tail) energy environments along a study reach roughly 12 km in length and in more detail for 2.5 km downstream from one active landslide. Gold content of various size and density fractions of landslide and sediment samples was determined. In addition, to allow geochemical fingerprinting of sediment sources and dispersion processes, the -53 μm size fractions of the landslide and stream sediments were analyzed by a multi-element method.

The distribution of gold along Harris Creek shows that abnormally high gold values occur in sediments from high and low energy environments a short distance downstream from two of the active landslides. Accumulation of gold at both these locations coincides with a decrease in stream gradient and an increase in bed roughness. Also in both cases, the general form of the gold anomalies gives them the appearance of anomaly cut-off points that could be interpreted to suggest that the landslides are the source of the gold.

Detailed study of one of the landslides shows that it contributes roughly 1.5 m^3 of mostly fine grained sediment to Harris Creek each year. Compared to sediments from Harris Creek this material has higher concentrations of Al and Mg and lower concentrations of Ba, Na, P, Sr and Ti. Because of its cohesive nature, material eroded from the toe of the landslide forms soft, clay-rich balls in the cobble-gravels downstream from the landslide. These balls gradually disappear from the stream bed over a distance of 1 km. Geochemical patterns downstream from the landslide are of two distinct types that depend on whether elemental concentrations in the eroded material are lower or higher than in sediments of Harris Creek. For the former (e.g, Sr), concentrations first decrease at high energy sites downstream from the landslide, but then increase again further downstream while concentrations in the associated low energy sites show a concomitant decrease. Conversely, elements with relatively high concentrations in the landslide material (e.g., Al) show the exact opposite trends. The physical and geochemical evidence clearly points to a transfer of fine sediment from high to low energy environments as the clay-rich balls breakdown with increasing distance from their source. The behaviour of gold, with low concentrations developing in the low energy environment beyond 500 to 1000 m downstream of the landslide, falls into that of the group of elements with concentrations that are diluted by the input of landslide material into Harris Creek.

Field observations (Day and Fletcher, 1989; Paopongsawan and Fletcher, 1993) and theory (Day and Fletcher, 1991) show that concentrations of gold and other heavy minerals can increase down streams in response to changes in gradient and sedimentological conditions. Here we conclude that the similarity of the gold anomalies to anomaly cut-off points and their apparent association with the landslides results from the interaction of two processes: (i) gold concentrations increasing down Harris Creek in response to decreasing gradient and changes in bed roughness, and (ii) point-source dilution of the gold dispersion train by landslide material. Because fine sediment eroded from the toe of the landslide is only fully incorporated into the fine fractions of the sediment some distance downstream from the landslide, maximum gold values occur a short distance downstream from the landslide but before dilution of the gold anomaly caused by the landslide material takes effect. Insofar as the landslide and sedimentological process involved are apt to be of a very general nature, the appearance of apparent anomaly cut-off points downstream of landslides should be interpreted with caution for elements, such as gold, that are transported in streams as the principal constituents of heavy minerals.

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The geochemistry of six gold-bearing quartz-carbonate-tourmaline vein systems, Estado Bolivar, Venezuela

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Keywords: gold, Venezuela, Precambrian, greenstone, veins

This study was undertaken as part of a 5 year cooperative project between the U.S. Geological Survey (USGS) and Técnica Minera, C.A. (TECMIN), a part of the Corporación Venezolana de Guayana (CVG) to assess the mineral resources of the Venezuelan Guayana Shield (U.S. Geological Survey-Corporación Venezolana de Guayana, Técnica Minera, C.A., 1993). The Guayana Shield is an Archean-Middle Proterozoic craton and underlies much of eastern and southeastern Venezuela.

Rock samples from six vein systems and panned concentrate samples from stream sediment were collected from the northeastern Guyana Shield, Bolivar State, Venezuela and analyzed as part of a geochemical study of gold-bearing quartz-carbonate-tourmaline veins exposed at the surface, near the surface in trenches, and at depth in an underground mine. All samples were analyzed by one or more of the following methods; atomic absorption, atomic emission spectroscopy, and ion-specific electrode. The vein systems in this study are in meta-volcanic host rocks, mostly mafic to intermediate metalava and metatuff containing greenstones, felsic metatuff and flows, and mica schist and phyllite. The associated (and probably slightly younger) gold-bearing quartz-carbonate-tourmaline veins generally occur in the greenstones. The veins are discontinuous and occupy ductile, high angle shear zones generally parallel to strike or cutting foliation at very oblique angles. Field observations and analysis of samples suggest the deposits are gold bearing metamorphic veins (Colvine and others, 1984) termed "low-sulfide gold-quartz veins (Berger, 1986). Gold values are variable in the quartz-carbonate-tourmaline veins and range from 0.004 to over 10.0 ppm. The apparent inconsistent values are probably due to the nugget effect, to variations in the weathering of the quartz-carbonate-tourmaline and host rocks, or to small sample number bias. It is clear that the gold is related to the veins and that the schist host rock has lower gold values (0.002-0.3 ppm).

Surface environment--Of the six vein systems studied, only Zone 4 of the Marwani area had surface exposures. Zone 4 is on the southwest side of a large northwest-trending structural zone that separates rocks of Early Proterozoic age on the northeast from younger rocks of Early Proterozoic age to the southwest. The rocks in zone 4 consist of metavolcanic and metasedimentary rocks intercalated with metalavas of intermediate composition. These rocks have been intruded by a large diabase-gabbro sill and many small diabase dikes. In the central part of zone 4 is a layered, upper greenschist facies, schist-phyllite unit. Quartz-carbonate-tourmaline veins cut the foliation of the host rocks at an oblique angle and are offset by at least one northwest-trending fault. During this study 33 rock samples and a total of 87 panned-concentrate samples from streams draining the area, were taken. Of the 33 rock samples collected 23 were taken from quartz-carbonate-tourmaline veins and gold was detected in all of them. The gold values ranged from less than 0.002 to 0.25 ppm. These results indicate that even at the surface of this deeply weathered terrain, detectable gold remains in the quartz-carbonate-tourmaline veins. The panned concentrate samples were taken from small streams draining the quartz-carbonate-tourmaline veins. Of the 87 panned concentrate samples taken a total of 59 (68 percent) contained visible gold in amounts from 1 to 43 observed grains. In general, the gold grain size was less than 1 mm.

Near Surface Environment--Two trenches, a road cut, and an open pit were sampled in detail to observe the geochemical variations of the quartz-carbonate-tourmaline veins in the near surface environment. Three locations in the Bochinche area were sampled, trench T1, trench 2A, and a quartz vein that crops out in a road cut along the main road between Esperanza and Bochinchita.

Trench T1

This north-south trench is about 70 m long and at its deepest point is about 6 m below the natural grade. It exposes a major quartz-carbonate-tourmaline vein (2.5 m wide) and smaller zones of quartz veining on either side. The major vein strikes N 65° E and dips 75° N. Many smaller quartz-carbonate-tourmaline veins are adjacent to the large vein and generally strike N 70° E and dip steeply 70°-80° N. The veins contain abundant tourmaline, and the quartz in the veins contains small inclusions of tourmaline and pyrite. The presence of other sulfide minerals is likely but could not be determined in the field. The smaller veins commonly have manganese oxide minerals developed on their margins. Many small silicified zones are present and pinch and swell along small fractures. These silicified zones start with manganese oxide staining along a fracture, swell into small zones of silicification, and then pinch out entirely. The altered schistose wall-rock is silicified, sericititzed, and very weathered, in places almost to clay, but the schistose texture is mostly preserved. Manganese-oxide and iron-oxide staining is evident on surfaces and margins of the veins.

Trench 2A

Trench 2A trends north-south,is 120 m long, and as much as 15m deep. Exposed material in the trench is red, thinly-bedded, micaceous, metavolcanic schistose rock containing abundant black layers and lenses. Schistosity strikes N 75°-80° E and dips 72° N. throughout the trench. Quartz-carbonate-tourmaline veins obliquely cut the host schist and generally strike N 60°-70° W and dip 65°-70° S in the southern part of the trench. Northward along the trench these veins are more northeast trending, N 45°-55° E, and the dip remains steep to the south. Zones near the quartz-tourmaline veins are silicified, and the host rock is bleached in places.

A very low frequency electromagnetic (VLF-EM) survey was performed along trench 2A. This technique uses low frequency radio signals (18-24 kHz) transmitted from several locations around the world. The instrument allows a calculation of resistivity in the field. Major quartz veins give resistive highs. Background resistivity for the schist is about 500 ohm-m. The low-sulfide quartz-carbonate-tourmaline gold-bearing veins have a resistivity of about 2,000- 3,000 ohm-m. It should be noted that only the larger veins or silicified zones can be identified using this technique and this technique will not distinguish between gold-bearing and barren quartz veins. Many of the veins are only 2-3 mm in width; not wide enough to be resolved by this type of geophysical survey.

The resistivity contrast of approximately 5:1 between the host rocks and the gold-bearing veins should lend themselves well to an airborne electromagnetic survey. A survey over areas suspected to contain large quartz-carbonate-tourmaline veins designed to use multiple frequencies like 22,000, 7,200, and 900 Hertz should easily map the extent and the trend of the veins and provide estimates of the depth to veins where the veins are covered by several meters of soil.

Bochinche Road Cut

A large vertical quartz-carbonate-tourmaline vein that strikes N 20° E and crops out in a road cut between Bochinchita and Esperanza was also sampled. The road cut is about 5 km southwest of Esperanza on the main road from Tumeremo to Bochinche. The vein (about 10 m wide) obliquely cuts host rocks of schist and fine grained greenstone with foliation striking N 50° E and dipping 55° S. The quartz-carbonate-tourmaline vein is barren of gold and only boron is elevated, due to the presence of tourmaline. The surrounding schist and greenstone host rocks contain little boron but are enriched in Cu, Cr, Fe, Mg, Ni, Ti, Zn, and Cd as compared to the vein. Gold values for the vein are low, .002 to .030 ppm, generally lower than the gold values of the host metavolcanic rocks. The lack of gold in this normally favorable environment of a quartz-carbonate-tourmaline vein perhaps can be explained by weathering or by the localized distribution of gold in this environment.

Lo Increíble district

The Lo Increíble district, 5-10 km northwest of El Callao, contains a series of small placers, open pits, and underground mines on and in a northeast-trending, southeast-dipping shear zone. The shear zone contains many discontinuous quartz-carbonate-tourmaline veins and separates rocks of the Yurauri Formation from rocks of the El Callao Formation. The Yurauri Formation at Lo Increíble is composed of amphibolite-grade, medium-grained, quartz-biotite-muscovite schist whose protolith ranges from felsic volcaniclastic tuff and tuff breccia to mafic volcanic rock. The El Callao Formation consists of magnesium-rich tholeiitic metabasalt deposited as subaqueous flows, that are locally strongly deformed and metamorphosed to chlorite-amphibolite schist near the shear zone. These metaflows are locally crossed by northwest-trending fractures (U.S. Geological Survey-Corporación Venezolana de Guayana, Técnica Minera, C.A., 1993).

Gold in the Lo Increíble district occurs as native gold in discontinuous quartz-carbonate-tourmaline veins that pinch and swell along strike within the shear zone. The shear zone is mined along strike for a distance of several kilometers.

Mining operations in the Lo Increíble district use both underground (Mina Lapa) and open-pit methods (Mina-A and Mina San Pedro). Many of the open pit mines, which commonly occupy sites of former underground mines use bulldozers to break up surface exposures of the quartz veins. Gold is commonly visible on freshly broken surfaces of quartz boulders that sometimes exceed 1 meter in diameter. The deposit at Mina-A is extremely rich; at the time of sampling the mine had been in operation for about three months and had produced almost 45 kg of gold. Approximately two-thirds of the gold production at Mina A is from outcrop and one-third from reworking tailings from previous mining. The mine currently produces about 350 metric tons of vein quartz per month at an average grade of 80 g/metric ton (28 kg gold/month). About 12 kg of gold per month are recovered from the tailings of the old underground mine.

Mina San Pedro is an east trending open pit along the shear zone. A north-south trench, roughly 15 m below the natural grade at its deepest, crosses the trend of the vein-shear zone system. The sampled trench is roughly perpendicular to the trend of a large quartz-carbonate-tourmaline vein and two smaller veins, which strike east-west and dip 80° S. The rocks in this area are brecciated, silicified, and altered to clays, sericite, and iron oxide minerals and even the quartz-carbonate-tourmaline veins are brecciated and silicified. Nine samples were collected from the trench wall to characterize the altered bedrock lithologies, quartz-carbonate-tourmaline veining, and silicified breccia zones. The veins contain pockets and holes where a carbonate mineral has apparently weathered out.

At Mina San Pedro, only boron and gold are enriched in the veins relative to the host rocks. Iron is unchanged between host and vein rocks and other elements are lower in the veins relative to the host rock. The lack of elemental enrichment may reflect weathering in the near surface environment.

The irregular distribution of gold values in relation to the spatial distribution of the quartz veins and the secondary brecciation of the quartz veins suggests at least two episodes of silicification. The large quartz vein has low gold content whereas the two relatively small quartz veins have elevated gold contents.

Underground Environment--Mina Colombia, an active underground gold mine operated by Compañia General de Minería de Venezuela, C.A., (Minerven) is approximately 5 km south-southeast of the town of El Callao. Mina Colombia produces ore from a zone of quartz-carbonate-tourmaline veins that strike N 60°-70° E and dip 35°-45° S. Production is about 700 metric tons of ore per day with grades as much as 30 g/metric ton and averaging about 9.9 g/metric ton The gold is present in pyrite as free gold. The gold-bearing quartz-carbonate-tourmaline veins are in greenstone (metavolcanic and metavolcaniclastic rocks) that has been faulted and fractured. At Mina Colombia two main veins, the America and the Colombia are currently being mined on three levels. These veins are 2 to 5 m wide including adjacent fracture and breccia zones. Host rocks adjacent to the veins contain abundant pyrite (cubes as much as .5 cm) and tourmaline. The vein systems occupy fault structures and tension fractures in the greenstone; associated breccia zones and silicified areas are in both the veins and the host rocks. A zone of smaller secondary gold-bearing quartz veins normal to the primary veins extends approximately 10 m from the foot- and hanging-walls into the host rock. These secondary veins occupy fractures interpreted to be the result of tension and dilation of the primary America and Colombia veins.

Vein samples collected from Mina Colombia are enriched in the elements Y, Ba, As and Au as compared to the host rocks while lead contents are the same for veins and host rock samples. The measured levels of arsenic are low (about 5-87 ppm) probably related to arsenopyrite, a common mineral in the low-sulfide, gold-quartz, vein model (Bliss, 1986) although no arsenopyrite was identified. There is little difference in iron content between the veins and the host rock although the gold content is much higher in the veins. This probably indicates that most of the gold in this deposit is free gold and not chemically associated with the pyrite found in the mine.

Conclusions--Reconnaissance geochemical sampling of the gold bearing quartz-carbonate-tourmaline veins in Estado Bolivar, Venezuela, in surface, near surface, and subsurface environments indicates that the chemistry of the veins does not vary significantly between these three environments with the gold being irregularly distributed in individual samples. Field observations, chemical analyses, and statistical analysis indicate that although some pyrite was observed the veins are primarily low-sulfide and gold-bearing. Because of their similarities, all of the vein samples were considered as a single population and all of the host rock samples were considered as a single population for statistical analysis. A total of 68 vein samples and 76 host rock samples were used in statistical analyses. Elements with more than 75% qualified data (not detected or less than) were eliminated and R-Rmode factor analysis was performed on the resulting data set. For the host rock samples, a seven factor analysis was selected that resolved 71% of the variance. In this analysis loadings gold, lead, and minor vanadium are isolated in factor 7 indicating that the gold is present mainly as elemental gold and not related to iron, manganese, or boron. The same procedure was used for samples of the quartz-carbonate-tourmaline veins. For any number of factors from 5 to 8, gold was always included in a carbonate factor including calcium, magnesium, and sodium indicating that the gold is associated with carbonate.

Two samples of quartz-carbonate-tourmaline veins from trench 2A contained tellurium, indicating a possibility of gold tellurides. Copper, lead, and zinc are present in the veins at very low levels and probably represent remobilization of these elements from the host metavolcanic rocks. The solutions forming the veins apparently did not carry base metals and were probably not chloride brines. The veins are depleted in most elements except for gold and, on occasion, manganese and boron. The solutions forming the veins were probably carbonate bearing (calcium, magnesium, and sodium) and contained the gold, boron, and manganese. The manganese content of the veins is relatively constant except in the surface environment where it has been removed by weathering.

Exploration--As part of this study, several exploration techniques were used and four were found to be particularly useful. Before going into the dense jungle in the Marwani Concession, zone 4, aeromagentic maps and side looking airborne radar (SLAR) imagery were examined. From the SLAR imagery linear topographic features were identified that might indicate resistant quartz-vein systems. Field checking of several of these features showed that this was a valid exploration approach, especially in the initial stages of exploration. Interpretation of aeromagnetic maps of the area prior to field work identified faults and offsetting linear features. These faults were confirmed during field examination of the Marwani Concession, zone 4 area, and their location made mapping of the discontinuous and offset quartz veins much easier. Once in the field, the gold pan was the most effective tool for determining the extent of the gold bearing quartz-carbonate-tourmaline veins. In the tropical weathering environment carbonate in the veins weathers, freeing particulate gold, which then accumulates at the clay-sediment interface in the streams draining the area. because the areas examined are of generally low relief (50-100 m) the distribution of the gold in sediments is proximal to the quartz-carbonate-tourmaline veins. The very low frequency electromagnetic (VLF-EM) survey done along trench 2A near Bochinche indicates that this technique may also be used as an exploration tool. The quartz-carbonate-tourmaline veins were recorded as resistive highs as compared to background. An effective exploration procedure would be to select potential areas from interpretation of SLAR imagery and aeromagnetic maps, field check using VLF-EM and the gold pan, and then trench the most promising sites collecting rock samples for geochemistry. Very little of the greenstone terrain in the jungle covered Guayana Shield has been explored, especially with modern techniques, and there is a high potential for the occurrence of more of these gold bearing quartz-carbonate-tourmaline vein systems.

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Magnetic concentrates — a proven sampling medium for oxidized arid landscapes

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Keywords: paleodispersion, immobilized elements, maghemite, gold

Introduction

The problem of mechanical dilution of anomalies by barren detritus such as clays, rock fragments and quartz from alluvial and aeolian components has long been recognised as limiting geochemical response in terms of anomaly contrast and hence dispersion. This applies equally to stream sediments and soils, where high sampling density may be necessary for effective exploration. In alkaline environments such as mafic/ultramafic terranes, and arid areas where calcareous soils are prevalent, cation mobility is restricted.

Sampling desert lag containing remnant lateritic pisolites from the degradation of ferricrete and mottled zone laterite profiles has proved cost effective over peneplained land surfaces for a wide spectrum of heavy metals. This has advantages as a regional preliminary to closer spaced bedrock sampling by drilling (Mazzucchelli and James, 1966; Smith and Perdrix, 1983; and others). Changes in response due to variable iron content of lag can be normalised by regression on the iron content (Carver et al, 1987; Dunlop et al, 1983). There are instances however where the geochemically active, secondary iron oxide component is too sparsely preserved for this refinement to succeed.

In dissected terrains where dry, sandy streams are routinely sampled, problems with effective anomaly contrast and dispersion persist. Despite the use of various size fractions, from -80# to coarse to ultra fine, or trials with selective leaches, or BLEG sampling with its high cost and poor reproducibility, there have been few practical advances.

Consideration of some basic principles prompted the collection of coarse maghemite rich magnetic concentrates from dry, sandy soils and streams using a composite magnet with a large surface area. This simple field procedure has been orientation tested and successfully used by this author in large routine surveys throughout Australia for gold, base metals, tin (as stannite), uranium and associated pathfinder elements since 1979. Comparative multi-media case histories from various landscapes and mineralized provinces are illustrated.

Paleodispersion and anomaly speciation

Gossan formation is a particular case of intense local ferruginization via oxidation of sulfide rich assemblages, aided by electrochemical activity in the surficial environment. Stable iron oxide assemblages with coprecipitated and adsorbed metal complexes may form in situ, with preservation of sulfide boxworks, or metals may be transported either as cations or anionic complexes, (depending on Eh and pH) and dispersed chemically. When transported, these can be coprecipitated with iron along channel ways, or adsorbed on to ferric hydroxide to form transported gossans.

Where distal from a mineralizing source, or where the source has a low sulfide content, gossanous development may manifest only as thin limonitic veinlets, or in the limiting case, as pervasive ferruginization. This can be geochemically anomalous but visually blends in with arid ferruginized terrain and ferricretes, making it difficult to recognise for outcrop or float sampling.

A more general approach than direct gossan sampling is therefore desirable to detect blind mineralization, or to define secondary dispersion trains in a regional sampling program.

Metal speciation studies show that the bulk of heavy metals in anomalous stream sediments occurs in combination with hydrated iron oxides (Bogle and Nichol, 1981; Chao and Theobald, 1976). Nickel (1979) considered the saturation limit of goethite for minor elements, and showed that goethite can contain up to 6% Cu, 2.5% Zn, 4% Pb and 1.5% As. Experimental work by Beevers (1966) demonstrated that Pb, Cu and uranyl ions can be strongly adsorbed on to ferric hydroxide from dilute solutions to the extent of 7.2%, 1.2% and 6.5% by weight respectively.

Details of the mechanisms of sulfide oxidation and gossan formation are reviewed in a recent summary by Thornber and Taylor (1992), and details of chemical mobility, precipitation-coprecipitation and adsorption are summarized by Thornber (1992). Jenne (1968) proposed that the hydrous oxides of Fe and Mn exert chemical activity far out of proportion to their total concentrations.

These oxides, which are nearly ubiquitous in soils and stream sediments, act as a "sink" for heavy metals. Relative adsorption or desorption (which is rarely completely reversible) is dependent on a number of factors including Eh and pH. Cation exchange on clays is of only minor significance, except where the clay fraction carries colloidal Fe oxides.

Butt and Smith (1980) introduced the concept of immobilized elements as being those which are bound in primary or secondary minerals during weathering. Once immobilized in iron oxides, formerly mobile elements such as Cu, Zn and As, hydromorphically dispersed during earlier paleo weathering, are then generally limited to mechanical dispersion.

At the onset of aridity, ferric hydroxide, $Fe(OH)_3$ dehydrates to aFeO.OH, goethite and dimorphous gFeO.OH, lepidocrocite. Further dehydration develops hematite, aFe_2O_3 and maghemite, gFe_2O_3. Maghemite is a spinel with a cation deficiency, and is magnetic, while hematite is weakly magnetic (Deer et al, 1978).

Mechanical dispersion along with barren clastic diluents then becomes the predominant mechanism during arid zone erosion.

Magnetic iron oxides are selectively enriched in heavy metals, with consequently enhanced backgrounds and anomaly thresholds. "Scavenging" is relative to the source, however, such that "gossanous" responses are superimposed on background fluctuations which can reflect lithology — eg) higher Pb-Zn-As from carbonaceous shales, or higher Ni from more mafic lithologies. Because the sample approaches a monomineralic composition with more constant iron content, relative background variations within a constant lithology are reduced. This leads to an improved "signal: noise" ratio allowing more confidence in the recognition of weaker anomalies.

The analysis of maghemite (not magnetite) rich stream and surface soil concentrates has proved to be very effective, not only in present day arid to savanna zone tropical areas of moderate to low relief, but also at higher latitudes such as in the Yilgarn of Western Australia, parts of eastern Australia, and in Nevada, USA. Such areas are those where weathered regolith with stable resistates and secondary minerals, including iron oxides formed under previous morphoclimatic environments are preserved. Subsequent factors such as tectonic uplift, with lowering of the water table and change to a more arid climate cause increased erosion, irreversible dehydration to Fe oxides, and hardening of ferruginous and siliceous horizons with retention of alkalis. In areas of high relief, the rate of physical erosion may exceed chemical weathering, precluding formation or preservation of thick regoliths (Butt and Zeegers, 1992).

In the absence of dehydration and induration, the lateritic soil profile remains as a latosol, rather than laterite, and colloidal iron hydroxides, goethite and lepidocrocite remain. For this reason, coarse maghemite particles tend not to occur in humid equatorial landscapes such as in PNG. Magnetic concentrates, where available, tend to consist of fine primary magnetite from background lithologies, unrelated to chemical dispersion from oxidizing mineralization.

Field and Laboratory Procedures

In field sampling practice, about 50g of +1mm magnetic lag or magnetic stream sediment concentrate is collected from the dry soil surface or stream bed. Depending on the local landscape, the sample consists of a mixture of one or more of earthy secondary Fe oxide grains, ferruginized rock fragments, lateritic fragments, micropisolites and composites. Primary magnetite is undesirable and where present as a minor constituent can usually be selectively discarded by sieving to +1mm.

Analysis for Au to 1 ppb detection is carried out by aqua regia digest followed by solvent extraction and atomic absorption spectrometry using graphite furnace atomization. An aliquot of the sample digest is then used for multi-element analyses by ICP.

Magnetic lag sampling on soil flats gives similar but usually enhanced responses compared to sampling of larger hand picked pisolites, due to higher Fe (as opposed to alumina) content. Compared to surface sweeping and sieving of fine lag heavily diluted by quartz and barren rock detritus, the magnetic lag approach gives superior responses for gold, base metals and pathfinder elements, as illustrated by case histories.

In practice, where lag development is sparse, it may be necessary in regional programs for a two man crew to spend up to ten minutes collecting sufficient composite sample over an area of up to 50m radius. This sampling medium tends not to be developed on outcrop areas, stony rises or desert armour surfaces. It is best developed on bare, sandy areas which have been subjected to some denudation by wind winnowing of clays.

Some areas of transported overburden (up to 6-7m thick), as alluvial sheet wash and/or aeolian cover, have been effectively sampled as a targeting tool for closer spaced RAB drilling. This has been made possible due to the effects of profile homogenisation and biturbation by ant and termite activity (Butt and Zeegers, 1992).

Case histories are presented of mineralization discovery using magnetic concentrates from dry, sandy, higher order streams which can be of the order of 10m wide or more, using practical sampling intervals of the order of 500 - 1000 m. Comparisons with conventional stream sediment surveys, which work best for hydromorphic dispersion rather than mechanical dispersion of immobilized elements, show that in some instances these fail to give a satisfactory response even where mineralized gossan float is present near by in the stream bed. Open file reports reveal many instances where systematic stream sediment surveys using -80# have failed to reveal known outcropping mineralization, yet similar surveys have been repeated in the search for blind mineralization

Gold

The problem of reproducible sampling of stream sediments for gold is well known and centers around a consideration of nugget effect and meaningful analytical sample size. BLEG techniques do not appear to solve this problem of reproducibility, and can give rise to anomalies which disappear on repeat sampling.

Despite the relatively small size of magnetic concentrate samples, and their coarse grained (usually 1-5 mm) nature, repeat sampling of anomalous gold sites gives adequately consistent results.

This is attributed to the dispersion model of gold dissolution as thiosulfate, organic or chloride complexes, and its subsequent redeposition as ultra fine, chemically coprecipitated and/or adsorbed gold in iron oxides present in gossanous material and laterite (Gray et al, 1992; Mann, 1984). This results in a more homogeneous sample, akin to the situation for formerly mobile base metals. Although some particles of coarse gold can also occur within Fe oxide segregations, their occurrence in samples of the order of 50g is statistically remote, and this sampling medium is not as prone to the vagaries of gravity concentration as is free gold in normal stream sediments.

Conclusions

Gold, pathfinder elements and base metals hydromorphically dispersed in a former tropical weathering regime are immobilized in gossans and lateritic iron oxides. During subsequent arid cycle erosion, anomalous concentrations are mechanically dispersed along with a larger mass of barren detrital diluents, including transported overburden. The resultant low contrast is often a problem in conventional soil and stream sediment surveys. When these iron oxides commonly include a maghemite component, they can be readily collected in the field from dry surface soils and streams using a magnet.

Such samples, unlike BLEG samples for gold, have the advantage of low sample weight, fairly constant composition, and relatively minor fluctuations in background compared to reproducible, high anomaly response. Both background and anomaly levels are enhanced, but contrast is often superior to conventional sampling. Anomalies near source have typical gossan signatures which for base metals and arsenic can be in the hundreds to thousands of ppm range, with hundreds of ppb up to several ppm for gold.

Numerous case histories from routine surveys have demonstrated that kilometer scale regional sampling can be effective.

In Nevada, USA, samples "found" known epithermal gold deposits several kilometers downstream. It is suggested that this technique can be applied to many of the world's arid, oxidized landscapes.

Acknowledgements
Permission by the directors of Cloncurry Mining NL, Roebuck Resources NL and Queensland Metals Corporation Limited to use recent orientation and routine survey data is gratefully acknowledged. I am indebted to their respective technical managers Steve Milner, Peter Allchurch and Dave Horton for their encouragement and support.

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Grasberg porphyry Cu-Au deposit

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The Grasberg porphyry copper-gold deposit, owned and operated by P.T. Freeport Indonesia Co., is located on the island of New Guinea, in the eastern-most province of Irian Jaya, Republic of Indonesia. The deposit is approximately 3 kilometers northwest of the Ertsberg Skarn Deposit.

The published mineable reserve is 976,000 million tonnes (t) containing 1.25% Cu, 1.55g/t Au, and 3.45g/t Ag. The deposit was discovered in 1988 and production started in late 1989. Ore production has increased steadily since 1989 through a series of mine and mill expansions. Present ore production is in the 80,000 t/day range, and is expected to be in the plus 100,000 t/day range in early 1995.

Disseminated mineralization occurs in the Grasberg intrusive complex, a multiphase intrusion of dioritic to monzonitic composition which intruded tightly folded Tertiary carbonate rocks. The Grasberg intrusive complex is a succession of coincident intrusive and mineralizing events about three million years old, which formed three principal concentric nested lithologies. A volcanoclastic-pyroclastic cap was formed which has since been partly eroded. Overprinting and telescoping of the silicate alteration zones is common throughout the deposit. Principal copper minerals are chalcopyrite and bornite with very minor amounts of covellite and digenite.

Multielement geochemical exploration in deeply weathered terrain : the McKinnons gold deposit near Cobar, NSW, Australia - a case study.

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Keywords: epithermal, gold, McKinnons, multielement, maghemite, Cobar

Introduction

A broad hydrothermal alteration system associated with epithermal/mesothermal style gold - silver mineralisation at the McKinnons deposit, 37 km southwest of Cobar, NSW coincides with multielement geochemical haloes in the primary zone that are retained within the regolith. The regolith extends to an average depth of 60m and comprises a weak lateritic profile containing maghemite pisoliths overlying saprolite (3 to 35 m) and ferruginous - goethitic saprolite (35 to 60 m) units. The saprolitic profile has generally preserved primary lithic fabrics and exhibits a thin transition zone (1 to 2 m) with the underlying bedrock. The McKinnons deposit occurs on a slight rise where outcropping siliceous sedimentary country rocks and locally brecciated chalcedonic pods have resisted erosion and provide evidence for a hydrothermal origin for the mineralisation (Tate, 1994). Outcrop is generally poor and the area is typified by the presence of a medium to thick soil cover with transported sheetwash alluvium occurring to the north of the deposit.

Maghemite pisoliths are ubiquitous in the Cobar area and provide a consistent sampling medium (Scott, et al., 1991, Alipour, et al., 1994). Alternatively, sampling of the Ao humic soil horizon is supported by the thick vegetation cover in the area including acacias, eucalypt and Cypress Pine that facilitate biogenic transportation of trace elements to the surface. Both sampling mediums have been subject to various digestion methods during the present study and have successfully defined broad anomalous haloes associated with the mineralisation at McKinnons.

Geology and Structure

The McKinnons deposit is hosted by weakly metamorphosed arenites and argillites of the Amphitheatre Group (Glen, 1987) and occurs on the western margin of the Cobar Basin. The Amphitheatre Group forms part of the early Devonian Cobar Super Group that hosts base - metal and gold - copper deposits (Elura (Pb - Zn), CSA (Cu - Pb - Zn) and Peak (Au - Cu) Mines) on the eastern margin of the deformed and inverted basin (Glen et al., 1994). The McKinnons deposit is structurally controlled and appears to follow the axial trace of the northwesterly trending F1 Nullawarra Anticline that has been affected by a series of subtle northeasterly and possibly, northerly trending structures. Gold mineralisation is associated with quartz breccias typically comprising subhedral to euhedral buck quartz veins ± sulphides overprinted by fine comb-textured quartz veins and healed by chalcedony near the surface. Quartz stockwork veining, interpreted to occur in the core of the system, is enveloped by disseminated auriferous pyrite in the quartz - sericite altered host metasediments. Mineralisation appears to have accompanied superposed deformation phases confirmed by the presence of an anastomosing schistosity, the weak deformation of quartz veins and the development of fibrous quartz pressure shadows adjacent to pyrite euhedra. Gold has been released from finely dispersed pyrite (2 - 5%) within the regolith and has been locally enriched at the redox boundary. The healed quartz breccia veins have largely avoided strong weathering.

Primary Geochemistry

Primary lithogeochemical trends, apparent in drill holes penetrating below the base of weathering (~60m), mirror vertical and lateral alteration/mineralisation zones within the deposit. Vein sulphides (pyrite) and the appearance of base metals (sphalerite, galena, chalcopyrite) increase with depth while silicification and quartz/chalcedonic veining occur both within the core and the upper levels of the deposit. The downhole geochemistry confirms that Au is enriched above 100m while As, Sb, Cu and Zn are at anomalous levels below that depth. Antimony closely follows the Au distribution while Pb exhibits a broad dispersion that appears to widen with depth. Manganese clearly exhibits an antipathetic relationship with Au and, along with Cu and Zn, is enriched peripherally to the more intensely altered mineralised zone.

Secondary Geochemistry

Evidence that base metal sulphides commonly occurred in the upper levels of the deposit is lacking based on diamond drill core/RC logging and petrographic data. However, SEM studies have confirmed that trace sulphides as well as Hg, Ag, I and secondary Pb phosphate minerals including native mercury, amalgam, iodyrite and plumbogummite are preserved in quartz breccia veins within the regolith. Chalcophile element (Cu, Zn, Pb and As) depletion within the upper saprolite unit (15 to 35 m), peripheral to the deposit, correlates with a decrease in Fe values. Conversely, the ferruginous saprolite unit (35 to 55 m) is generally enriched in these elements. Primary lithogeochemical trends for Mn, Sb, Pb and Au are demonstrably preserved in both saprolite units.

Geochemical data from shallow exploration (RAB) drill holes were examined using INTERDEX imaging software, confirming lateral element dispersions that mirror primary lithogeochemical trends. Gold is concentrated over the main deposit and broadly distributed along the northwest - southeast structural corridor. Antimony, As and Pb exhibit a broad spatial correlation with Au, while Cu and Zn strongly correlate with Mn and appear to be enriched peripherally to the gold mineralisation.

Soil/LAG Geochemistry

An orientation soil/LAG geochemical sampling programme, conducted over the McKinnons deposit and background areas, comprised five 1000 to 1400 m - long traverses at 200 - 350 m intervals with 50 m stations. Lag and soil samples were analysed by AAS and ICP-OES/MS techniques using total and partial digestion methods, as follows:

- Ao soil samples involving several mesh sizes (-600 + 400 μm, -400 + 200 μm, -200 μm & -60 μm) were digested by a variety of partial (aqua regia and hydroxylamine hydrochloride - Chao, 1984) and total acid digests,
- bulk leach cyanide extraction (BLEG) with Au analysed by AAS/carbon rod plus AAS analyses for Cu and Zn, and
- sampling of non-magnetic lag (LAG) and magnetic - maghemite lag (MAGLAG) material. Pulverised MAGLAG material was subject to similar partial and total acid digests while unpulverised MAGLAG was subject to a partial hydroxylamine hydrochloride digest.

Comparison of the various sampling and digestion methods confirmed the presence of a discrete Au anomaly (450 x 200 m) highlighted by BLEG soils and MAGLAG samples over the McKinnons deposit. However, more extensive multielement anomalies have been achieved from the totally digested MAGLAG and very fine fraction Ao soil samples that exhibit marked similarities with the primary lithogeochemistry. The MAGLAG samples exhibit positive Sb, Mo, Ba and Ag anomalies bordered by an extensive anomalous As halo, as well as negative anomalies for Mn, Cu, Zn, soluble Sn and P over the length of the sampled area (>1 km). The multielement anomalies provide evidence for a potential northerly extension to the mineralised zone below transported cover. The -60 μm Ao soil sample fraction, comprising clays and ferruginous coated grains, does not exhibit the broad dispersion evident in the MAGLAG results, with discrete As, Sb, Ag and Pb anomalies corresponding with the BLEG Au anomaly although negative anomalies for Cu, Zn, Sn, P, V, Fe and Mn would appear to correlated with extent of the hydrothermal system.

Downhole element dispersions coupled with the surface distribution of the maghemite pisoliths may help to explain differences in the MAGLAG and Ao soil geochemistry:

- As, Sb, Cu, Zn, Ba, Mo, Sn, Mn and V are more strongly partitioned into the goethite component in the weathering profile. Bushfires have subsequently converted goethite to maghemite (Anand, et al., 1994) with the potential for the physical transport of the pisoliths, effectively broadening MAGLAG anomalies. Tate (1994) noted that siliceous boulders (30 cm diameter) have apparently been transported up to 200 m away from the deposit.
- Sb, As, Pb and Ag as well as Au (confirmed by the BLEG results) have been retained by fine grained residual vein quartz, residual clays and goethite coatings in the weathering profile resulting in more discrete dispersions for these elements.

Conclusions

The recognition of the epithermal/mesothermal style of mineralisation and attendant primary lithogeochemical haloes at McKinnons has provided the basis for designing and interpreting soil/LAG geochemical exploration programmes in the area. Total acid digestion/ICP analysis of MAGLAG and -60 µm fraction soil samples has produced extensive positive and negative multielement anomalies that are much larger than the target and probably reflect the extent of the mineralising hydrothermal system. The widespread development of maghemite pisoliths in the Cobar area provides a convenient sample medium that has potentially preserved primary geochemical signatures, although local transportation of the anomalies may be expected. Additional controls may be achieved by using traditional BLEG Au soil sampling coupled with multielement analysis of the very fine -60 µm Ao soil fraction. Both the soil and LAG geochemical techniques obviate the need for costly RAB - based, bedrock geochemical programmes as the initial exploration phase in the area.

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An infrared and trace element study of several bore hole samples from the Lakwa and Galeki oil fields, Assam

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Keywords: infrared, trace element, bore hole, oil field, clay shale

Samples for infrared and trace element study were collected from different oil wells from the Lakwa and Galeki oil fields, and from different depths within the Barail, Tipam and Kopili Formations of the Assam Shelf area. The samples were collected from the principal oil producing horizons of Tertiary age, and comprise mainly sandstones and shales. Descriptions of the samples are presented in Table 1. Figure 1 shows the study areas.

The main aim of our study was to determine the clay mineral types present in the samples, the trace element concentrations in those clays, and their relationship to the environment of deposition. Clay size fractions were separated from the collected samples and were analyzed for both infrared and trace element study.

Methods

The samples were analysed to identify the clay minerals using a Perkin-Elmer 883 double beam Infrared Spectrophotometer with Cesium Iodide window. Samples were prepared in Nujol and examined over the frequency range 4000cm^{-1} to 200cm^{-1}. The most useful bands for clay mineral identification are within the regions 3600cm^{-1}, 950-900cm^{-1} and 1125-1000cm^{-1}.

Trace element analyses were carried out for Ni, Ba, Rb, Sr, Mo, V and Ti, with a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer using an air acetylene flame and nitrous oxide flame. The matrix modifiers used for analysis were Potassium Chloride and Aluminium Chloride. The clay size fractions were digested in HF, HNO_3, HCl, and $HClO_4$.

Results

Results from the infrared study indicated the dominant clay mineral in the samples was kaolinite. Illite, montmorillonite, chlorite and mixed layer clays were also identified in some samples. Table 2 shows all the bands ascribed to the clay samples in the infrared spectrograms.

Trace element analyses found Ti to be high in almost all samples. Results of analyses for Ni, Ba, Rb, Sr, Mo, V and Ti vary from 85-1550ppm, 288-125ppm, 166-200ppm, 38-182ppm, 48-163ppm, 248-360ppm, and 2784-6040ppm, respectively. Results of trace element analyses are shown in Table 3.

Sample No.	Unit	Locality	Well No.	Depth (m)
1	Barail Coal Shale	Lakwa	240	3438.84
2	Tipam Sandstone	Galeki	151	2904.00
3	Barail Coal Shale	Galeki	135	3708.52
4	Kopili Formation	Lakwa	141	4490.04
5	Barail Main Stand	Lakwa	155	4121.95

Table 1. Description of the samples studied

Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
3696 S	3696 S	3696S	3696 S	3696 S
3670 M	--	--	--	3670 M
--	--	3660 M	--	3660 M
3650 M	--	3650 M	--	--
3624 S	3624 S	3624 S	3624 S	3624 S
1880 W	1880 W	1880 W	1870 W	1880 W
1820 W	--	1830 W	--	1820 W
1640 W	1640 W	1630 W	1640 M	--
1620 W	1620 W	--	--	1620 W
1190 W	1180 W	--	--	1200 Sh
--	--	1170 W	1170 W	--
1120 W	1120 W	--	--	1120 W
--	--	--	--	1100 W
--	--	1090 W	--	1090 W
1040 W	--	1040 W	--	1040 W
--	1030 W	--	--	--
1000 W	1000 W	1000 W	1000 W	1000 W
--	975 W	980 W	--	--
930 W	940 W	940 W	940 W	--
--	920 Sh	920 W	920 W	--
910 W	--	--	--	910 W
880 M	880 Sh	--	--	880 Sh
--	850 W	--	--	--
--	--	840 m	--	840 W
--	800 S	800 S	800 S	800 S
790 M	--	--	--	--
780 M	780 M	780 M	780 S	780 M
--	--	760 M	--	--
--	--	720 M	--	720 M
700 M	700 W	700 M	700 W	700 W
--	650 W	650 W	--	--
640 M	--	--	--	640 W
--	--	--	620 W	--
605 M	605 M	605 M	605 M	605 M
--	580 W	580 W	--	580 W
--	540 Sh	--	540 W	--
--	--	500 M	500 W	--
490 W	480 W	--	--	490 M
--	450 W	--	--	--
430 W	430 W	430 W	435 W	435 W
--	400 W	400 M	--	400 W
--	390 W	--	--	--
--	370 W	--	360 W	--
350 W	350 W	350 M	350 W	350 M
--	260 M	260 M	--	260 M
250 M	--	--	250 M	--
240 M	240 M	240 M	240 M	240 M

Table 2. Infrared bands ascribed to clay minerals (cm^{-1})
W = Weak; M = Medium; S = Strong, Sh = Shoulder

Sample No.	Sample Location and Description	Values in ppm						
		Ni	Ba	Rb	Sr	Mo	V	Ti
1	4/L-240/CC1 BCS/3438.84m	85	348	198	78	48	248	4242
2	Well No. 155 CC1/TS/2904m	139	298	200	182	62	250	3230
3	Well No. 135/CC2 BCS/3708.52m	210	1253	213	38	86	282	4596
4	4/L-141/CC1 KOP/4490.04m	206	288	166	155	120	344	2784
5	2/L-155/CC2 BMS/4121.95m	1550	328	--	51	163	360	6040

Table 3. Trace element concentrations in clay samples
CC = Conventional Core; L = Lakwa; KOP = Kopili; BMS = Barail Main Sand;
BCS = Barail Coal Shale; TS = Tipam Sandstone.

Discussion

Kaolinite is the most common clay found in all the samples. In sample no. 2, montmorillonite is found along with mixed layer clays and illites. The Tipam Formations are good reservoirs but have permeability problems because of the dense growth of pore lining clay minerals. There is a relationship between expanded clays and hydrocarbon production. Expanded clays retain their pore water to greater depths of burial than do other clays. When hydrocarbons are formed at greater depth, the expanded clays would be the main source of water to carry the hydrocarbons from the shales.

In our study area the Barail Coal Shale, Barail Main Sand and the Kopilli Shale are also major hydrocarbon producing zones. In these units the clay minerals are mainly kaolinite, illite and chlorite.

Titanium was found to be high in almost all the samples, and in samples 5 and 3, Ni and Ba are respectively high.

Trace element assemblages and clay mineral ratios are, in some respects, characteristic of the environments of shale deposition. The dominance of kaolinite in the samples indicates a near-shore environment of deposition.

Acknowledgements

The authors are indebted to Dr I. Haque, Nr N. Sarma, G.C. Bora, N. Barua, Ms B. Barua, and Dr P. Kotoki, for their helpful discussion and co-operation during analytical work. We also wish to thank ONGCL for providing the borehole samples, and the Departments of Applied Geology and Chemistry at Dibrugarh University for providing us with laboratory facilities.

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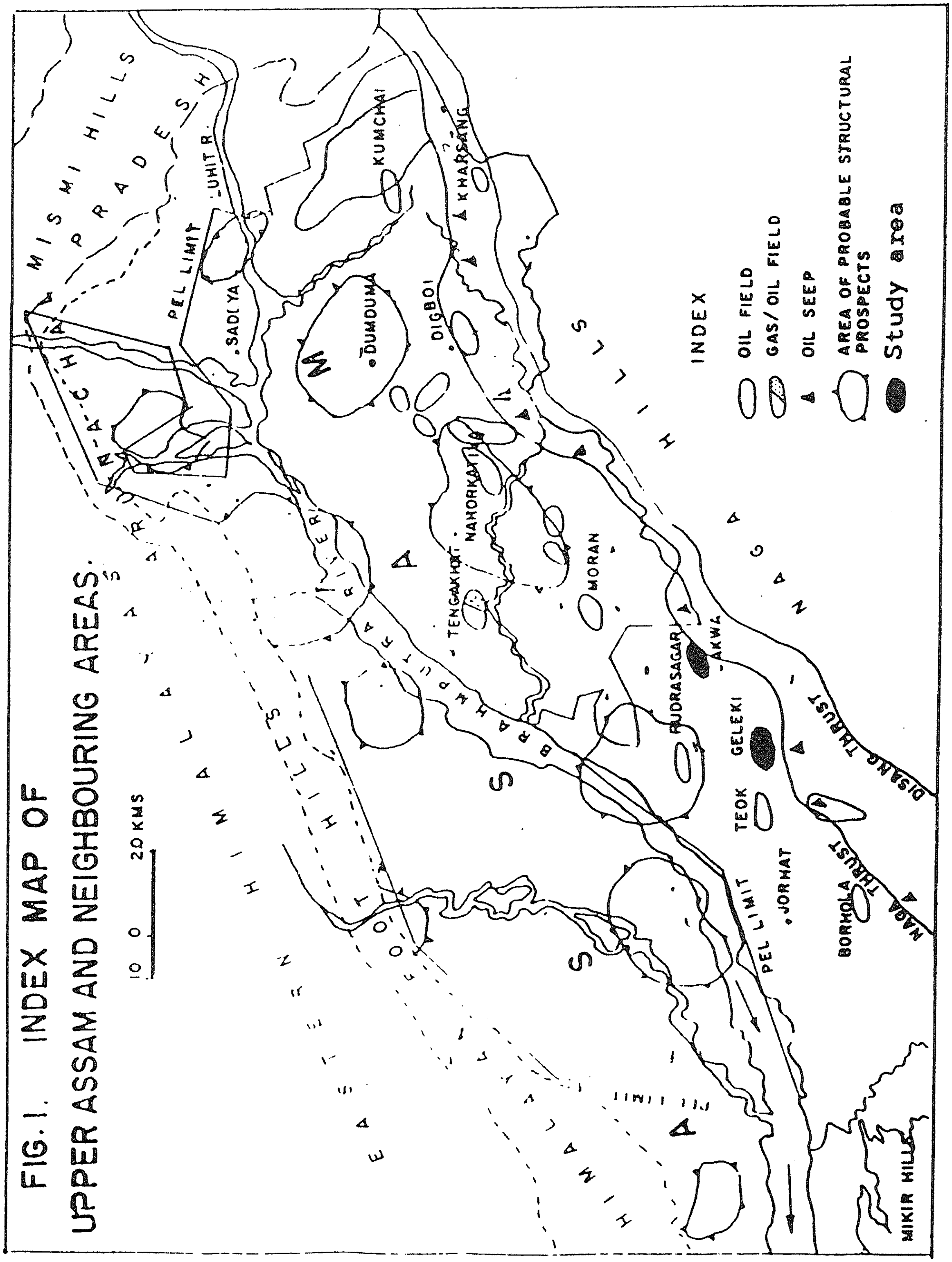

FIG. 1. INDEX MAP OF UPPER ASSAM AND NEIGHBOURING AREAS.

Geology and mineralization of the Ertsberg Skarns, Irian Jaya, Indonesia

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Keywords:

The Gunung Bijih (GB), Gunung Bijih Timur (GBT), and DOM deposits are Cu-Au rich skarns in the Ertsberg district of Irian Jaya. These orebodies all occur in Cretaceous to Tertiary sediments that have been deformed as the northern edge of the Australian continental margin collides with the Pacific plate. Chalcopyrite is the dominant ore mineral in the GB and DOM deposits, whereas bornite dominates the GBT complex. Native gold occurs throughout the district usually intimately associated with copper minerals.

The Ertzberg skarns all occur along the periphery of the Ertzberg intrusive which is a quartz-monzonite to dioritic mass dated at just over 3 million years. The GB deposit is thought to be a roof pendant sitting on top of the intrusive. The DOM deposit and the GBT complex are structurally controlled deposits that lie just off the margins of the main intrusive body.

The GBT complex consists of three distinct deposits which have been broken out for administrative purposes. The GBT deposit proper is the top most zone, and is underlain the by Intermediate Ore Zone (IOZ), and Deep Ore Zone (DOZ) respectively. The GBT complex exhibits a number of vertical mineralogical trends. The bornite to chalcopyrite ratio increases with depth. Garnet decreases with depth; almandine garnets are common in the upper GBT, but have not been observed in the DOZ. Anhydrite occurs throughout the GBT system but is especially abundant at the DOZ, where it is seen to stope out portions of the magnetite/bornite skarns. Copper sulphide and gold mineralization is multi-phase and late stage, apparently associated with the retrograde events.

Differences in mineralization of the various Ertzberg skarns can be attributed to variable composition of the original host rocks. Fossil evidence suggests the DOM and GB deposits are hosted within the more lime-rich Ainod formation. The GBT and upper IOZ are recognized to be within the older Faumai formation. Finally, the lower IOZ and DOZ are thought to be hosted within the more dolomitic and older Waripi formation.

Geochemical dispersion in bedrock and regolith at the Swordfish Prospect, Norseman, Western Australia

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Keywords: gold, copper, Norseman, dispersion

Introduction

The Swordfish Prospect is located about 4 km west of the North Royal mine, under Lake Cowan, and about 7.5 km north of Norseman. The discovery aircore drill hole intersected altered basalt (at 85-90m depth) with anomalous gold (1.98 ppm), bismuth (92 ppm), silver (16.7 ppm), zinc (760 ppm) and copper (7000 ppm). Subsequent drilling has delineated significant Cu, Bi, Ag, As, Zn, Au, Mo, SiO_2 and K_2O anomalies at least 2 km in length and about 400m in width. The mineralisation at Swordfish is unusual for two reasons: (a) the copper-gold association, which is uncommon in Archæan mesothermal gold deposits of the Yilgarn Block; and (b) the mineralisation styles (pyrrhotite-chalcopyrite-pyrite-rich veinlets cutting altered sedimentary units and basalts with chlorite-biotite±magnetite-bearing alteration haloes, and quartz vein breccias) are atypical of most of the mineralisation (in laminated quartz veins) discovered so far in the Norseman field.

Local Geology

The interpreted bedrock geology, based on aircore and diamond drilling, beneath weathered Tertiary sedimentary units and Recent lacustrine gypsiferous sediments, is shown in Figure 1. The main lithological unit is basalt which is considered to belong to the Chinamans Well basalts (the uppermost unit of the Woolyeenyer Formation) west of the Talbot Island ultramafic unit, whereas to the east, the basalts belong to the upper part of the Desirable Pillow Lava Member of the Woolyeenyer Formation. The basalts have been intruded by gabbros which are post-dated by granodiorite and porphyry dykes. The sequence faces to the west.

The basalts between the Swordfish porphyry and the Talbot Island ultramafic unit are predominantly tholeiitic, with interflow cherty sedimentary units. Immediately east of the porphyry is a complex package of pillowed and amygdaloidal tholeiitic and magnesian basalts with cherty interflow units, a mixed sequence of clastic, sulphidic and felsic sedimentary units (which are discontinuous along strike and down-dip), and thin, felsic volcanic units with amygdales. The porphyry (up to 50m thick) thins with depth, is parallel to regional strike (north-south), dips steeply to the west, and is strongly deformed. Tholeiitic and pillowed magnesian basalts occur to the west.

Mineralisation and Alteration

The principal zones of mineralisation outlined to date occur between the two NE-trending faults (Figure 1), both to the west (dominantly auriferous) and to the east (dominantly cupriferous) of the deformed porphyry and locally within it (auriferous). Although the main auriferous and cupriferous zones do not appear to be coincident, the principal auriferous zone contains anomalous copper (up to 1.2%), and the principal copper-rich zones contain anomalous gold (typically 0.5-1.5 ppm).

The mineralised zones are characterised by a relative abundance of sulphides (mainly pyrite, pyrrhotite and chalcopyrite) which may be disseminated, occur along fractures, or form semi-massive to massive clots and veinlets within zones of silicification and chlorite-biotite±magnetite alteration. Quartz±carbonate veinlets commonly occur; they are generally less than 2 cm thick and may contain altered wall rock inclusions. Several generations of veining may be evident; locally, the veinlets have been brecciated with sulphides±magnetite in the fractures. In some instances, the sulphide-rich zones may be fringed (on the hanging wall side) by haloes of disseminated magnetite (including irregular veinlets of quartz and sulphides) up to 5m wide. In some felsic rocks, silicification predominates over quartz veining and sulphides occur as irregular clasts and disseminations, or veinlets.

The alteration assemblages are laterally zoned and are similar to those developed around other Archæan gold deposits of the Yilgarn. In mafic rocks, the outer alteration zones consist of chlorite-calcite-quartz to inner zones dominated by biotite-carbonate-quartz-magnetite-sulphides, with discrete chlorite + biotite selvedges to sulphidic veinlets. Similar assemblages were developed in the chloritic interclast matrix in clastic rocks. Muscovite is well-developed in felsic rocks and some sedimentary units, particularly in deformation zones.

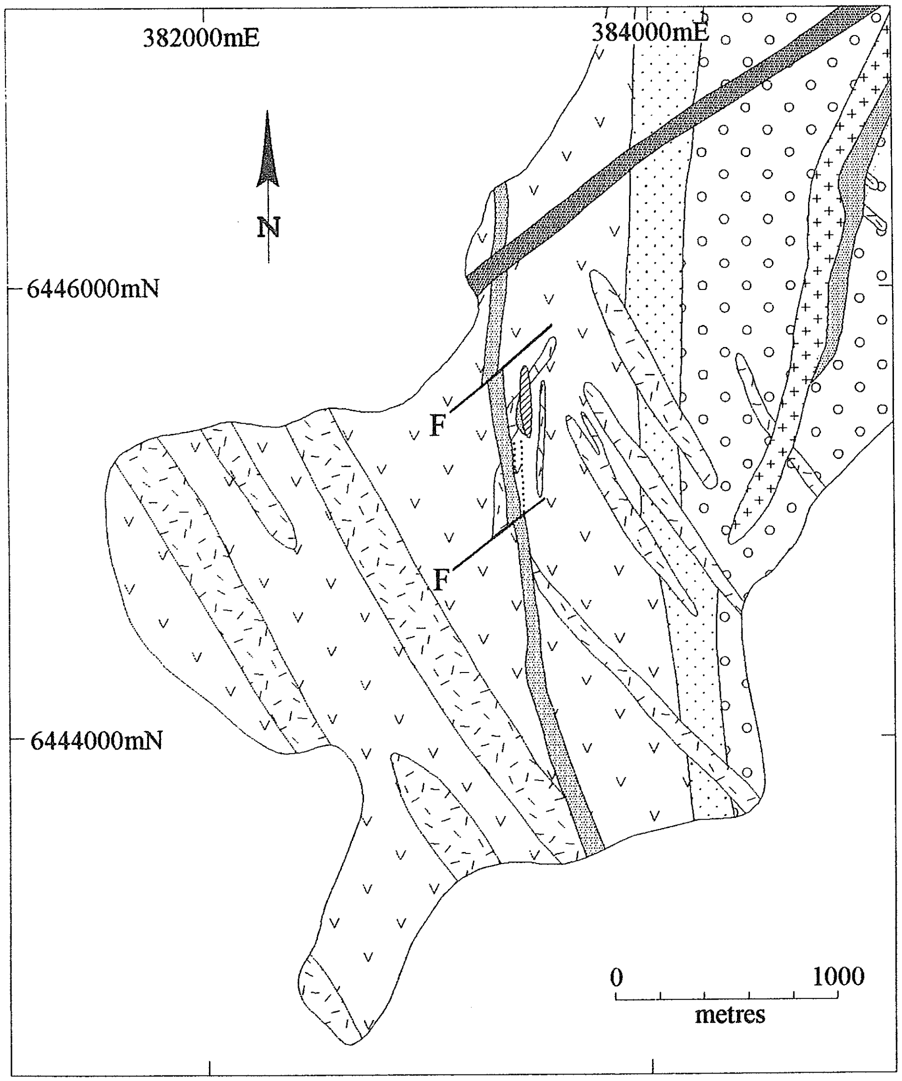
Geochemical Dispersion, Cross Section 6445235N

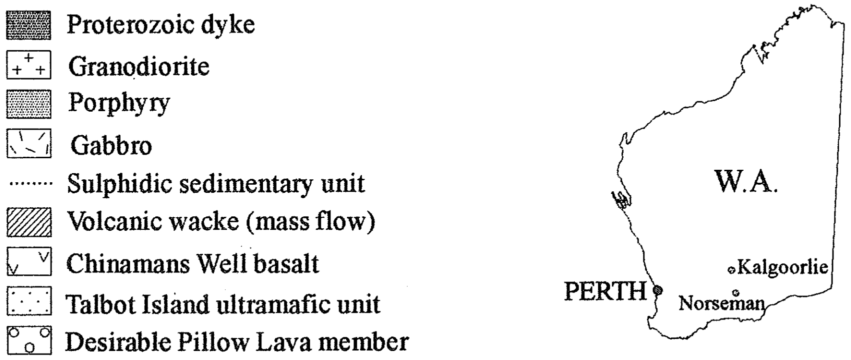
The depth to the base of the Tertiary varies considerably in the Swordfish area (from 25m to over 90m) and much of the regolith has been stripped from the weathered Archæan profile. However, sufficient saprolite (overlying mineralisation) has been preserved on section 6445235N to permit a study of geochemical dispersion within the saprolite. The depth to the base of the Tertiary is 80-85m and to the base of weathering about 95m, with a deepening of the profile (to about 115m) over the interpreted up-dip extension of the mineralisation.

There are two principal zones of mineralisation in bedrock: (a) a lesser upper, western zone with gold around a lens of sheared and altered basalt within sheared porphyry; and (b) a lower, main eastern zone partly within a thin felsic horizon and partly within sheared and altered basalt with gold and copper. The mineralised zones are up to 15m wide and dip 70°-80°W, transgressing lithological contacts (dipping 65°-70°W). In the main (eastern) zone, copper-gold mineralisation is accompanied by anomalous Ag, Bi, Co, Mo and Zn; in the western zone, gold mineralisation is accompanied by anomalous Bi, Cu and As.

Within the saprolite, the broadest part of the gold (>100 ppb Au) and copper (>350 ppm Cu) anomalies lies within the deepening of the weathering profile. Copper and gold concentrations occur towards the base of the regolith and at the top of the preserved saprolite; only the lower layer appears to coincide with a zone enriched in iron. The copper-gold anomalies are accompanied by anomalous Ag, As, Bi, Co, Pb, Sb and Zn. The widths of the dispersion haloes in regolith (up to 50m) exceed the width of mineralisation in bedrock (<20m), and therefore provide potentially larger targets for exploration.

Figure 1.
Interpreted geological plan of the Swordfish Prospect, Norseman, Western Australia.





Application of petroleum surface geochemical and seismic methods as pathfinder tools to detect blind Mississippi Valley Type deposits

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Keywords: iodine, seismic, breccias, Mississippi Valley Type

Introduction

The Mississippi Valley Viburnum and Central Tennessee-Kentucky (CTK) base metal districts, in the Central United States, have been prolific producers of lead and/or zinc for a number of years (Figure 1). In both districts the ore deposits were, and still are, either discovered by surface exposures or located by random drilling. Presented here are petroleum surface geochemical and seismic exploration techniques adapted to detect the location of blind Mississippi Valley Type (MVT) deposits.

Surface geochemical exploration methods identify hydrocarbon accumulations at depth by detecting minor leakage of petroleum that has vertically migrated into the soil and caused secondary chemical reactions there. Within many MVT deposits are various forms of petroleum either as live oil, tar, bitumen or carbonaceous residue. The formation of these MVT deposits may also cause local maturation or generation of petroleum from organics present in the adjacent country and host rock. Regardless of origin, the localized presence of mature hydrocarbons should be detectable through petroleum exploration methods. Analyses of petroleum gases that have leaked into the soil ("soil gas") and the measurement of secondary reaction byproducts, such as the accumulation of iodine in the soil, can be used to target seismic methods to identify MVT breccias.

Seismic methods detect the location of reservoir rock by means of changes in sound waves at rock boundaries. The breccias of the MVT deposits are mappable seismically as a change in velocity of the sound waves between the country rock and the collapse features. In addition, the syncline in which the breccia is found is seismically mappable. Thus seismic methods can be used to detect and delineate the outline and extent of the collapse feature prior to drilling.

General Geology

The geology of each Mississippi Valley District varies, but in general the ore has accumulated in dolomitized breccias or chimneys. The breccias form collapse features that are mappable as structural lows. The synclines tend to be larger than a specific breccia. There can be one of more breccias located in a syncline, but not all synclines are prospective. Dolomitization and subsequent porosity and permeability enhancement are vital for ore and petroleum accumulation in the breccias. The presence of petroleum is thought to be critical to ore formation by providing sulphur and reducing conditions for Zn-Pb sulphide deposition (Anderson, 1991).

A collapsed breccia or dolomitized chimney has only recently been recognized as a reservoir by the petroleum industry. In the CTK province, the reservoir was originally termed "fracturing" but this was due to the lack of any significant data being collected. Recently it has become clear that zinc and petroleum accumulations are found in the same host or reservoir rock and have a common origin of formation (Anderson, 1991). Production of petroleum from these types of deposits in the Central United States has been occurring for a number of years. The two notable examples are the Albion-Scipio Field (155+ million barrels of oil equivalent) found in 1956 in southern Michigan and the Wood-Hancock Complex (21-+ million barrels of oil equivalent) found in 1884 in Northern Ohio (Figure 1). Both fields were discovered by accident. They are dolomitized chimneys or breccia zones encased in lithographic limestones and they produce from Trenton-Black River (Ordovician) strata. Neither field has an obvious structural expression other than a subtle recurring linear low along its length. The breccia or chimney is formed by brecciation and rubblization of rock associated with wrench or strike-slip faulting followed by magnesium replacement of calcium to form dolomite along an elongated (20 to 30 miles) fracture/fault trend that is 1/4 to one mile wide. Reservoir rock varies from approximately a few inches to as great as 800 feet thick. In association with petroleum, a minor but significant amount of Pb-Zn mineralization is found. It was not until the use of surface geochemistry and seismic in concert that additional petroleum fields were discovered, not only in the Michigan Basin, but along the Cincinnati Arch from Ontario to Tennessee. The most spectacular chimney found to date that can be directly attributed to surface geochemical pathfinder methods is the Stoney Point (>8.4 million barrels) field which lies six miles to the east of the Albion-Scipio field and was not discovered until 1983. The field was developed utilizing seismic.

Geological Setting

The presence of MVT deposits in a variety of geological basins has been well documented. Their origin, cause and sequence of formation are part of an ongoing debate. For both the petroleum and mineral industries, we can summarize that the present economic deposits tend to lie near or along basin margins with underlying unconformities and faulting in the Precambrian, and in many cases the deposits overly or are adjacent to Precambrian rift systems.

In the CKT area the Ordovician strata seem to be the primary location of the breccias that contain either producible petroleum or minable zinc. The oldest strata is the Knox Group of Upper Cambrian-Lower Ordovician age. The Knox is composed of the Mascot, Kingsport, Chepultepec and Copper Ridge formations. The section is moderately to finely crystalline dolomite with minor amounts of chert and sandstone. The dolomite, except in areas of brecciation, has low to nonexistent porosity and permeability. Overlying the Knox Group is the Stones River or High Bridge Group (Lower to Middle Ordovician) which include the Well Creek Dolomite; it consists of dolomites, limestones and shales. Above this is a series of formations composed of dolomites and limestones. At the top of this series are the Mud Cave and Pencil Cave bentonite beds. Overlying the bentonite beds is the Nashville Group in Tennessee, or the Lexington, Clays Ferry, Leipers and Cumberland formations in Kentucky, all of Middle to Upper Ordovician age.

The Viburnum Trend has a variety of host breccias, and all are restricted to Upper Cambrian strata, specifically the Bonneterre Formation. The location of the ore deposits is generally in dolomitized and silicified collapse breccias that are related to regional faulting, pinchouts in the Lamotte Sandstone, Precambrian knobs and abrupt facies changes in the Bonneterre Formation.

Surface Geochemistry

Surface geochemistry as applied to petroleum exploration is based on the theory of vertical migration. The theory states that the presence of petroleum in the soil is due to leakage from a hydrocarbon charged reservoir at depth to the surface. The leakage is facilitated by the presence of numerous micr-fracture systems, micro-pores, micro-unconformities and discontinuities in the overlying rock strata. The most notable and visible form of this process has been macroseeps which were a common exploration tool early in the history of petroleum exploration. The macroseeps are the result of a process defined as effusion, and the seepage migrates from the reservoir to the surface along pathways that are essentially megascopic in size. The process is still not clearly understood, and the term effusion encompasses several different concepts (Tedesco, 1994). Microseepage of hydrocarbons is a more subtle and non-visible form of effusion known as micro-effusion that is detected in the parts per million to parts per trillion by surface goechemical methods (Tedesco, 1994).

A petroleum reservoir is usually encased in, or overlain by, a seal of nonporous to slightly porous lithology, usually a carbonate or shale. Historical thinking indicated that the seal was impenetrable as long as geologic conditions remained relatively constant. However, work in recent years suggests that the seal is actually a temporary barrier with numerous flaws such as microfractures, micro-pores, micro-unconformities and disconformities that allow migration to occur through the seal. We can consider the reservoir and geologic beds that allow the migration of the hydrocarbons to the reservoir as a multi-lane highway where fluid flow is easy. When hydrocarbons reach the seal, which can be compared to a small country track, it is nearly impassable but some get through. For example, consider buried gasoline storage tanks. Despite man's best technology at preventing leakage from buried gas tanks, after some years leakage occurs. The earth is unable to produce homogenous materials that are impermeable and restrictive to flow, and will always produce heterogenous materials which contain numerous flaws which allow migration.

The expression at the surface caused by petroleum seepage is either a halo or apical anomaly, depending upon the type of surface geochemical method used. The surface expression is dependent upon a variety of factors, predominantly the microfracture/porosity/unconformity network to the surface which controls the leakage. In addition, the resulting anomaly can be a manmade artifact or a result of the density and layout of sampling pattern. There is almost always no significant displacement of the anomaly away from the petroleum accumulation. The seeping hydrocarbon gases cause changes in the chemistry of the soil, most notably the accumulation of iodine, mobilization and removal of radioactive, trace and metal elements, occasional increases in petroleum-consuming microbes, and changes in the redox potential of the soil. Two methods of petroleum leakage detection presented here are soil gas and iodine.

Seismic Methods

Seismic exploration is based on the variations of sound waves as they travel through the earth. These waves impact on geologic boundaries that send a portion of the sound waves back to the surface; the boundary is called a reflector. Based on the time travelled between the source and the receiver, the relative distance of each reflection in the subsurface can be measured. Thus, a variety of geologic changes and boundaries can be measured so that the subsurface geology can essentially be mapped. However, identifying a potential petroleum reservoir requires a velocity contrast between the trap itself and the surrounding rock. If there is no velocity contrast, then the reservoir cannot be delineated by seismic methods. A velocity contrast is based on two rock units with different speeds at which sound waves travel through them. A simple example is a shale overlying a carbonate which have widely varying velocities. Whereas a dolomite overlying a limestone have similar velocities and would exhibit no contrast in a seismic profile. Based on seismic across several breccias, several velocity contrasts are seen with relations that allow mapping of the collapse area.

Basic Premise

The basic premise for applying petroleum surface geochemical methods to detect MVT deposits is that hydrocarbons have been trapped in, or generated by, the ore body emplaced in brecciated rock, along with lead-zinc mineralization. The presence of petroleum in association with MVT deposits has been well documented (Niewendorp and Clendenin, 1993; Anderson, 1991; Gize and Barnes, 1987; Spirakis, 1985). Further, many researchers contend that MVT deposits are derived from oil field brines and that petroleum may have caused the precipitation of sulfide mineralization (Ballantyne, 1993; Gize and Barnes, 1987; Hoyl et al., 1974). Petroleum trapped with the MVT deposits should undergo the same process of vertical migration to the surface as characterized by other petroleum deposits. Essentially the leakage occurs as a microseep, and it should be detectable at the surface. The breccia, because of its distinct difference from the adjacent country rock, should have a definite seismic characteristic. This contrast and the synclinal nature of the top of the breccia should be detectable by seismic methods. In addition, the nature and formation history of the breccia may be understood by determining its relationship to the geology, structural geology and Precambrian basement.

Two methods were used to test the concept: iodine and soil gas methods. The free-air and head-space gas methods were used to collect soil gases. These are direct detection methods of petroleum gases (Tedesco, 1994). Iodine is an indirect indicator of the presence of petroleum accumulation at depth. Iodine anomalies are caused by reactions resulting from hydrocarbon seepage in the soil (Tedesco, 1994; Alexan et al., 1986; Gallagher, 1984). In the A horizon, a reaction occurs between hydrocarbons and iodine, forming iodorganic compounds. As long as a petroleum seepage into the soil continues, the iodine compounds will continue to form. Iodorganic compounds are only partially stable and are subject to replacement by other halogens and oxygen.

Model

Models were established to determine the viability of both surface geochemical and seismic methods to define a MVT breccia. The models presented here are a recent discovery that was found by surface geochemistry, and an existing breccia from which oil has been produced and, later, from which Zn has been extracted. The models are labelled A and D in Figure 1.

Test of the Concept

Two areas were chosen to test the concept, as stated above, the lead-zinc Viburnum District in Southeastern Missouri (Figure 1, labelled C), and the zinc district of Central Kentucky-Tennessee (labelled B on Figure 1). In the CKT district seismic, soil gas, and iodine methods were used; in the Viburnum Trend only soil gas and iodine were used. The results of the seismic and surface geochemical work over specific breccias in the Viburnum and CKT Districts will be presented here.

Conclusion

The initial results indicate the potential for the use of petroleum surface geochemical and seismic methods as pathfinder tools for locating MVT deposits. The inter-relationship between petroleum and MVT deposits is fairly well established, and therefore methods to detect one should be useful to detect the other. Petroleum, which is volatile and migrates quickly to the surface, can be detected easily. Iodine and soil gas anomalies have led to the discovery of numerous petroleum reservoirs, some of which lie in prospective areas for minerals. Research indicates the viability of applying petroleum surface geochemical methods and seismic for screening areas and targeting other methods for delineating these ore bodies. This would reduce the need for numerous random core holes and reduce exploration costs. In addition, it is possible to delineate the entire areal extent of the breccia prior to drilling with the application of newer seismic and detailed surface geochemical methods. Research could certainly clarify this and possibly determine if a velocity contrast, even if it is subtle, existed between the significant mineralization of the ore body itself and the breccia. The delineation of what were once considered almost undetectable blind deposits by petroleum methods might have a significant economic impact on exploration, and further research is certainly warranted.

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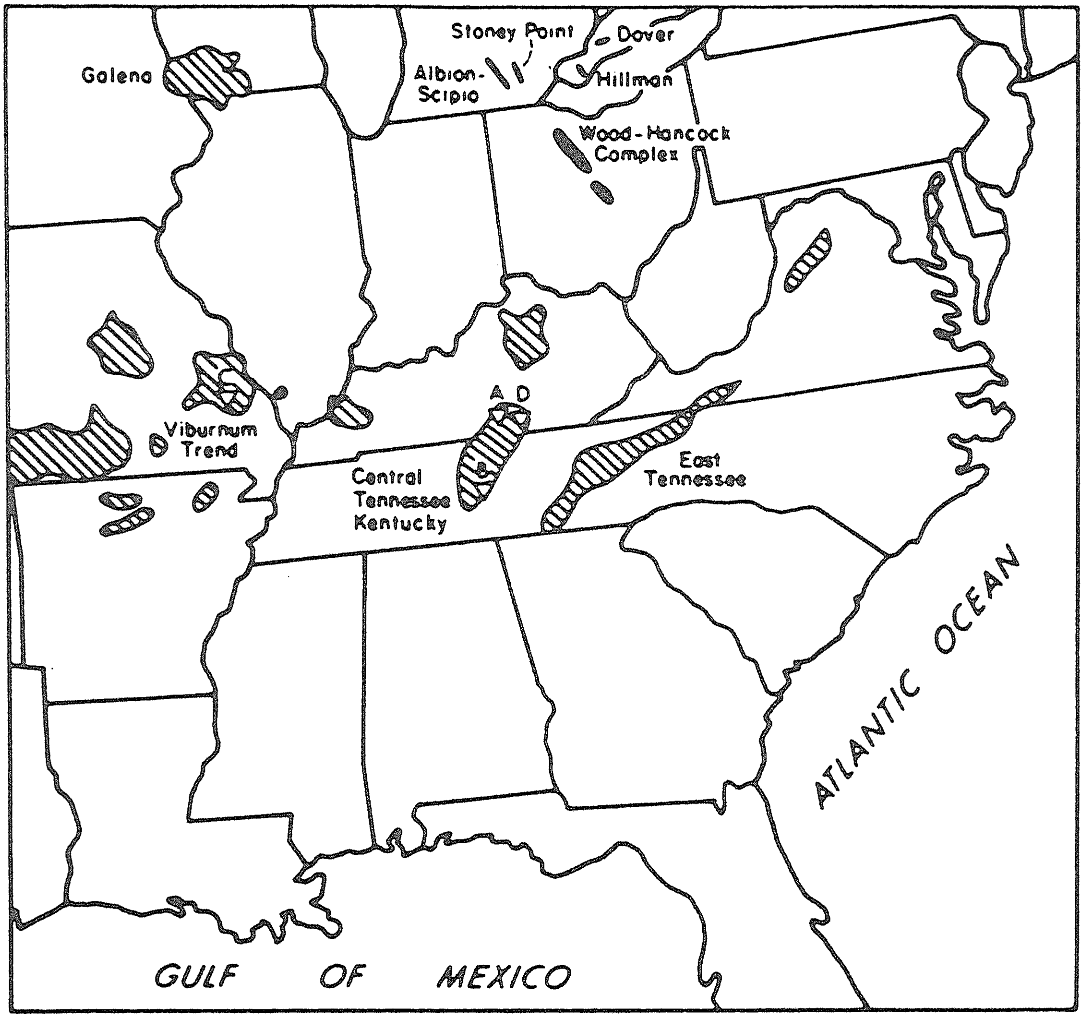

Figure 1. Locations of various MVT deposits and petroleum fields that are considered Mississippi Valley Type deposits. The letters designate the examples used in this paper: A - the Burkesville zinc deposit; B - the Dodson breccia; C - Viburnum Trend; D - the Seventy-Six Oil Field. The Stoney Point Field in Southern Michigan is a breccia that has produced over 9 million barrels of oil and was found by surface geochemistry and seismic methods. The Albion-Scipio, Hillman, Wood-Hancock Complex and Dover are some of the larger breccias. Petroleum production from a breccia is typically 100,000 to 500,000 barrels of oil equivalent per well.

GEOCHEMICAL CHARACTERISTICS OF BENTONITES FROM AMOTAPE (GRAU REGION, PERU).

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Keywords: montmorillonite, cation exhange, Perú.

From Grau to Arequipa regions, in the coastal boarder of Peru, there are abundant bentonite deposits with an enormous amount of potential mineral reserves. The aim of the present work is the study of the geochemical characteristics of five of these deposits -Chapica 2-14 (CH), Mi Vecino (MV), Pituso-1 (PUC), Pituso-4 (P4) and Quebrada Gorda (QG)- located in the Amotape zone of Grau region, northwestern Peru.

The before mentionned deposits of Upper Eocene age, are enclosed in the named Northwestern Structural Zone, within the Talara basin and related to the Chira formation, which is constituted in the area of study by lutites, sandstones, bentonites and volcanic tobes.

Mineralogical composition deduced from x-ray difraction and thermodiferential-thermogravimetrical analyses, allow to stablish three groups of minerals as components of bentonites:
- authigenic minerals: montmorillonite and zeolites.
- inherited minerals: cristobalite, plagioclase and potassic feldspar.
- detritic and supergene minerals: quartz, hornblende, hematite, goethite and gypsum.

With the exception of Quebrada Gorda deposit where montmorillonite rate is lower and cristobalite and zeolite rates are higher, the mineralogical composition of the bentonites in the area of study is homogeneous.

Bentonites chemical composition, obtained from Atomic Absorption Spectrometry, is homogeneous for the whole of the deposits studied, ecepted Quebrada Gorda deposit where TiO_2, CaO, Na_2O, K_2O and P_2O_5 values are higher (table 1). Trace elements analyses in ppm are indicated in table 2. Chemical analysis of bentonites clay fraction (grain size lower than 2 microns), bear relation with the conrrespondant bentonites. In this way montmorillonites from Quebrada Gorda deposit show values of calcium, potassium and sodium, higher than other deposits in the area, corresponding then to bentonites from Quebrada Gorda a total charge higher than others.

Measurements of cation exchange capacity of representative samples of bentonites give values of 96.8 meq/100g for bentonites from Quebrada Gorda deposit, and values from 38.34 meq/100g to 55.3 meq/100g for bentonites from the other deposits.

Geochemical characteristics of representative samples from the mentionned five deposits, allow to think that bentonites from Amotape zone have been formed from an "in situ" alteration of source rocks, which according to their values of Zr/TiO_2 and Nb/Y elemental relations can be correlated with rocks of rhyolitic-rhyodacitic composition. They are sodic bentonites of Wyoming type and their properties of total charge and cationic exchange capacity, which are specially high in samples of Quebrada Gorda deposit, lead to consider these bentonites adecuates as cationic exchangers and their possible applications in the environmental field as heavy metals decontaminating medium for industrial waste water.

Table N° 1 : Chemical Analyses of Bentonites.

DEPOSIT	Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	MnO	LOI
QG	1	69.07	0,14	10,38	2,08	1,04	0,9	1,92	0,9	0,16	0.01	12,7
	2	68.94	0,13	11,04	2,12	1,1	0.87	1,94	0,87	0,15	0.01	12,78
	3	66,77	0,14	11,41	2,38	1,47	0,76	1,93	0,66	0,1	0,01	14,44
	4	69.99	0,12	11,03	2,08	1,09	0,87	1,94	0,93	0,15	0,01	11,77
	u	68,69	0,13	11,12	2,17	1,18	0,83	1,93	0,84	0,14	0,01	12,92
CH	5	65	0,18	13	3,1	1,94	0,33	1,76	0,24	0,03	0,01	14,39
	6	65,63	0,17	12,81	3,05	1,95	0,34	1,81	0,24	0,02	0,01	13,94
	7	64,05	0,18	12,91	3,17	2,08	0,4	1,67	0,25	0,02	0,01	15,23
	8	63,87	0,19	12,76	3,14	2,05	0,42	1,64	0,27	0,02	0,01	15,62
	u	64,64	0,18	12,87	3,12	2	0,37	1,72	0,25	0,02	0,01	14,8
MV	9	64,47	0,18	12,77	2,98	2,24	0,35	2,37	0,26	0,02	0,01	14,3
	10	64,13	0,13	12,76	2,94	2,27	0,32	1,93	0,25	0,02	0,01	15,14
	11	64,06	0,17	12,31	2,81	2,31	0,33	1,96	0,23	0,02	0,01	15,24
	12	64,53	0,16	12,59	2,73	2,28	0,34	1,89	0,23	0,02	0,01	15,18
	u	64,3	0,18	12,73	2,87	2,28	0,34	2,04	0,24	0,02	0,01	14,97
PUC	13	63,97	0,17	13,83	3,46	1,7	0,29	1,76	0,31	0,03	0,01	14,43
	14	64,75	0,18	13,94	3,49	1,74	0,29	1,79	0,33	0,03	0,01	13,45
	15	65,78	0,15	12,3	3,11	1,78	0,2	1,57	0,28	0,02	0,01	14,27
	16	65,26	0,16	13,19	3,16	1,77	0,2	1,6	0,29	0,02	0,01	14,3
	u	64,94	0,17	13,44	3,31	1,75	0,25	1,68	0,3	0,03	0,01	14,11
P4	17	65,71	0,17	12,37	2,84	2,42	0,4	1,79	0,2	0,02	0,03	14,02
	18	65.46	0,17	12,19	2,77	2,45	0,4	1,82	0,2	0,02	0,03	14,45
	19	67,51	0,17	12,6	2,9	2,45	0,38	1,83	0,19	0,02	0,03	11,87
	20	66,54	0,18	12,48	2,87	2,46	0,39	1,93	0,2	0,02	0,02	12,88
	u	66,31	0,17	12,41	2,85	2,45	0,39	1,84	0,2	0,02	0,03	13,31
0		66	0,17	12,51	2,86	1,93	0,44	1,84	0,37	0,04	0.01	14,02

Table N° 2 : Trace Element of Bentonites (p.p.m.)

DEPOSIT	Sample	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba
QG	1	14	15	3	0	5	45	16	163	40	213	17	75
	2	13	13	7	2	4	43	15	164	39	191	17	245
	3	16	47	5	3	7	44	14	115	30	176	14	80
	4	12	12	3	1	5	41	16	173	37	192	13	122
CH	5	12	13	6	3	6	55	10	38	36	241	15	91
	6	11	21	4	5	9	54	11	28	34	231	20	84
	7	20	31	4	2	9	40	12	31	23	152	14	73
	8	18	31	5	3	9	39	12	30	24	152	21	66
MV	9	20	20	4	2	7	42	12	37	19	154	13	112
	10	16	31	5	16	13	45	11	37	22	153	14	115
	11	14	16	4	4	10	41	10	41	24	159	17	138
	12	12	15	5	1	8	38	10	42	23	160	17	106
PC	13	10	16	6	13	7	64	17	25	38	253	24	83
	14	12	11	6	11	7	65	18	25	38	250	14	85
	15	12	13	5	5	7	50	19	22	34	213	20	85
	16	11	27	5	8	7	54	19	22	34	217	22	85
P4	17	8	13	2	2	7	71	11	36	35	238	17	122
	18	6	19	4	2	9	71	10	34	33	240	18	114
	19	8	50	3	4	7	75	10	33	35	245	17	110
	20	9	24	5	4	6	74	10	33	35	243	16	98

Australian Regolith

Characteristics of Magnetic and Non-magnetic Lags in the Cobar Area, N.S.W.

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Keywords: Lags, Cobar, magnetic, non-magnetic

Introduction

In the arid and semi-arid regions of Australia, deep weathering of bedrock, lateritization and varying degrees of overburden transport may result in zones of significant mineralisation exhibiting only a subtle geochemical expression at surface. The use of lags as a sampling media in these environments has received significant attention (Smith and Perdrix, 1983; Dunlop et al., 1983; Taylor et al., 1984; Carver et al, 1987). Lags are composed of weathered and degraded bedrock fragments, quartz fragments and secondary particles derived from accumulations of cemented materials (such as ferricrete, silcrete and calcrete).

Geochemical features are associated with turbiditic sediments of Early Devonian age Amphitheatre Group developed within the trans-tensional intracratonic Cobar Basin of central NSW (Glen, 1992). The basin is host to significant structurally controlled bodies of mineralization containing variable proportions of Cu, Pb, Zn and Au. Locally, the Amphitheatre Group sediments are steeply dipping, thinly interbedded siltstones and sandstones. At one prospect (Mrangelli), the source of the anomalies suggests a variant of Cobar-style Pb-Zn mineralization, with strongly developed silicification. At another site enhanced zinc values are associated with a zone of sporadic quartz-carbonate veinlets.

Topographically, the area has low relief. Deep weathering is wide spread and may extend to depths beyond 100 m to produce quartz-kaolinite rich assemblages. Mottled zones, richer in hematite, are locally preserved. Massive red earths are developed on top of thin colluvial mantles in which an aolian component is present. Calcrete development is wide spread, while silicification is more localised in both basement and the surficial mantle. A landform scheme recognising gradational erosional and depositional domains has been devised by Senior (1992).

A surface lag in the -11+2 mm size range is well developed, with characteristics suggesting derivation from both the weathering profile and the colluvial mantle. Some of the significant characteristics of the lag can also be related to the landform situation. Primary lithic and ferrolithic clasts similar to and directly derived from outcropping bedrock have the primary fabric variably preserved. These are most prominently developed in erosional landforms. Three types of clasts not directly related to the primary lithology are recognised; (i) massive lags formed from aggregates of iron oxide grains with a proportion of sand sized or other clasts, (ii) simple lag pisoids consisting of well rounded, polished fragments with a core of primary or secondary particles and surrounded by single or multiple concentric bands up to 1 mm thick and (iii) composite lag pisoids which are well rounded, complexly rimmed, polished and well sorted. Internally they bear a complex texture and structure. Cores may be composite with cemented smaller clasts of iron oxides and silicates. A system of internal cracks is common in most lag types forming a radial or concentric configuration which is presumably related to episodic dehydration of iron oxides. These cracks may be sites for subsequent accumulation of laminated iron oxides. In secondary magnetic lags, maghemite is mostly present as rims up to 1 mm thick. These lag types are present in both erosional and depositional domains.

Sampling and Analysis

Lags swept from the surface and composited from a number of points within a 20 m radius were collected along with adjacent RAB drill samples. The -11+2 mm fraction was divided into magnetic (ferrolithics and pisolites) and non-magnetic (lithics, ferrolithics, pisolites and vein quartz) fractions. Lithics are weathered fragments or clasts in which primary fabrics are preserved, ferrolithics are similar to the lithics but with a significant proportion of Fe oxides within the clasts and pisolites are composed mainly of iron oxides with no primary fabric preserved. The boundary between these classifications is somewhat subjective. All visible quartz, calcrete and silcrete particles were removed before milling to prevent possible dilution. To limit variations in sample matrices, samples were digested in HF/$HOCl_4$/HCl and analysed by FAAS for As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Magnetic susceptibility was measured on selected sample powders.

Results

The magnetic fraction is dominant in depositional landforms and the non-magnetic fraction on erosional landforms. The magnetic fraction are more highly ferruginised, polished and rounded than the non-magnetic portion, but, unpolished, irregular and rough surfaced magnetic grains are not uncommon. Most of the polished magnetic grains have a distinct skin of maghemite. Magnetic susceptibility (MS) at Mrangelli is about 0.0-0.001 SI units for the non-magnetic and between 0.04-0.07 SI units for the magnetics. The MS/Fe ratio is highly uniform for magnetic and less uniform for the non-magnetic fraction, reflecting uniform and less uniform conversion of iron oxides to maghemite in the fractions respectively.

At Mrangelli both Zn and Cu display higher abundances and greater contrast in the non-magnetic fraction above zones of RAB sample Pb-Zn anomalies. There are spot Pb anomalies in the non-magnetics above mineralization and a weak response in the magnetics. In profile, there is some depletion of Cu and Zn in the top 1.5 m. This may be due, in part, to dilution by calcrete. Fe rarely exceeds 7% in the profile but shows minor relative enrichment along the trend of mineralization. Mn is enriched in the upper part of the profile but depleted in the core of the main Pb-Zn anomaly. All metals show displacement downslope in the lags. Both Zn and Mn are depleted in parts of the profile suggesting oxidation of the stringer sulphides has mobilised the Zn and Mn (carbonates).

At the second site, there is little difference in the Zn anomaly width, continuity and contrast of the magnetic and non-magnetic fractions, with peak values over 500 ppm above local background of 100 ppm. The anomaly pattern is similar for Cu, except that values and geochemical contrast are higher in the non-magnetic fraction (peaks of 100 ppm above background of 40 ppm) than the magnetic fraction (peaks of 70 ppm above background 50 ppm). Background for Cu in the RAB samples and non-magnetic lags are similar. Pb values tend to be higher in the magnetics away from the main Zn mineralization and of similar values in the two fractions above mineralization, with better contrast and anomaly continuity in the non-magnetics.

The extent of the non-magnetic lag Zn anomaly is similar to that of the RAB profiles, where a broad zone of enhanced Zn values is defined. Zn is depleted in the top 3 m of the profile relative to both the lower part of the profile and the lags; this may again be due, in part, to the dilution effect of near-surface calcrete. There are some weak and irregularly distributed Cu anomalies at depth in the profile, but no significant Pb values compared with the lag contents. There are strong Mn anomalies extending through the profile either side of the Zn anomalies. This confirms the pattern of outcrop for Mn-rich carbonate veining which surrounds the main Zn anomaly. Fe contents in the profile rarely exceed 5%, even in the vicinity of the main Zn-Mn-Cu anomalies in the profile. Though only weakly developed, there is a relative depletion of As and Cr in the profile where Mn values are elevated, however this may related to the presence of carbonate rather than Mn itself.

As, Bi and Cr at both sites and Pb at the second site tend to be concentrated in the magnetics, and hence, are strongly correlated with Fe. As bulk Cu and Mn contents increase in the lag samples they are concentrated in the non-magnetic fraction. Cu, Pb and Zn display similar anomaly patterns in the non-magnetics with distinct boundaries at the edge of mineralization indicated by the RAB drilling. The anomalies are more erratic, but wider in the magnetics, especially for Pb.

Preliminary data from sequential 6M HCl leach studies suggests that Pb and other trace metals are preferentially concentrated at the grain rims relative to the cores. The molar ratio of Pb to Fe dissolved decreases significantly from an initial high after 30 minutes of leaching towards a minimum beyond 30 hours. This is especially pronounced in the magnetic fraction and supports the work of Xie (1994) which found that Pb and other metals rapidly migrate to ferruginous grain rims during conversion of iron oxides from goethite to maghemite.

With the exception of Pb at The second site, the correlation between Fe and Cu, Pb, Zn, As and Mn is much stronger in the non-magnetic fraction than in the magnetic fraction. This is the case for local background and anomalous populations associated with mineralization at both targets. Cr and Bi are strongly correlated with Fe in both fractions. Median Cu values are higher in the non-magnetic lags at both sites and Zn is higher in the non-magnetic fraction at Mrangelli despite higher median Fe contents in the magnetics. This implies either the loss of metals from the magnetic lags relative to Fe or accumulation of iron without significant contribution of other trace element to developing lag particles. There is only very weak correlation between trace elements and Fe in RAB samples.

No metals displayed strong correlation with Mn in either the magnetic or non-magnetic fraction at either site. At The second site, manganoan siderite/ankerite veins crop out and Mn values peak in the lag and RAB samples adjacent to the main Cu, Pb or Zn anomalies. This suggests Mn is part of alteration around the core sulphide mineralization or that the carbonates are reducing trace element mobility. There is a depletion of As and Cr in the magnetic fraction where Mn is elevated. If Mn is related to the carbonates then As and Cr are likely to be mobilised in high pH conditions as oxy-anions.

In terms of distributions, beyond the first quartile most metals display a moderate to strong correlation between the magnetic and non-magnetic fractions. Below the first quartiles, As, Bi, Fe and Cr are highly elevated in the magnetic fraction. This may indicate secondary accumulation during weathering or transportation of the lags.

Conclusions

- Elevated metal contents in the lithics could be the result of armouring by silicification and resistance to weathering. An exception to this trend was the tendency of copper to concentrate in apparently unsilicified lithic fractions in spite of presumed easy leaching from the primary material.
- The relationship between Fe and other trace elements is complex, especially in the magnetic lag fractions where the poor correlation between Fe and Cu, Pb and Zn in at the local scale in the areas studied is common. Ferrolithic particles have slightly higher trace element values than the lithics.
- The transition from goethite/hematite to maghemite results in diffusion of metals such as Pb to the edge of the grains, where it my be lost through leaching or abrasion of the grains. Other processes involved in lag development and subsequent weathering effects may also result in loss of trace metals from polished and/or magnetic clasts.
- Trace element anomalies, which can be traced to a bedrock source, are generally more distinct and consistent in the non-magnetic than the magnetic fraction. This reflects the very local origin of the non-magnetics which are dominated by partially ferruginised sedimentary lithic clasts.
- The patterns for Pb and Zn suggest that the magnetic fraction of lags are of more use in reconnaissance exploration and non-magnetics for follow-up work to locating mineralisation and may justify partitioning lag samples in comparable landform situations prior to analysis.

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Regional Regolith Geochemical Mapping in Western Australia: Menzies and Leonora 1:250 000 Mapsheets

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Keywords: regolith, multi-element analysis, Menzies, Leonora

Introduction

The Geological Survey was allocated funds in the 1993 - 94 financial year to enable it to commence systematic regional geochemical mapping of significant parts of the State. Most bedrock and possible mineralization in Western Australia is concealed by surficial products of weathering and degradation (the regolith). In areas with extensive regolith cover regional geochemical mapping is expected to be of use in

- identification of metallogenic provinces and identification of specific areas in the state with potential for undiscovered mineralization
- recognition of underlying or nearby bedrock
- provision of basic geochemical data for use in the agricultural and pastoral activities, and evironmental monitoring and regulation

Regional geochemical mapping is now in common use in various parts of the Northern Hemisphere (Darnley and Garrett, 1990: Davenport, 1993), but there is little recent published work in Australia with the exception of a stream sediment study of the Ebagoola 1:250 000 mapsheet in northern Queensland (Cruikshank, 1994). Most published studies have been carried out in cool-temperate or hot-humid climates, very different from the hot-arid climatic conditions applying through much of Western Australia.

Initial areas chosen for study in 1994 were two adjacent 1:250 000 mapsheets in the Eastern Goldfields region of the Archaean Yilgarn craton, and two mapsheets covering most of the Proterozoic sedimentary Glengarry Basin. This paper presents methods and results from the studies on the MENZIES and LEONORA mapsheets in the Eastern Goldfields region. Samples have been collected from the PEAK HILL and GLENGARRY mapsheets but analysis is not yet complete. Results from each sheet will be released by the Survey in digital form or as maps accompanied by Explanatory Notes.

Geology, Topography, and Mineralization

The MENZIES-LEONORA area is characterised by linear bands of generally north-northwesterly trending greenstone (volcanosedimentary rock) belts, separated by granitic rocks, all of Archaean age. The latter include gneisses and pre-, syn- and post-tectonic granitoids. Surface expression of the greenstone belts is commonly in the form of linear ridges (mainly defined by banded-iron-formations and/or mafic rocks) separated by V-shaped valleys. Surface expression of granitoids is in the form of isolated tors and escarpments (breakaways). The maximum local relief is approximately 100m. The total regional relief amounts to about 240m (594 - 355m ASL). The area is crossed by several well developed (palaeo-)drainages whose sources are in higher ground west of the area, and which trend easterly to south easterly across the sheets. Within these drainages are several major playa lakes, but the drainages only contain flowing water after major downpours such as those generated by collapsing cyclones. The main lakes are commonly coated with salt, and are fringed in places by gypsiferous sands.

Greenstones of the area contain numerous gold deposits and occurrences. Gold mining areas, past and present, include Sons of Gwalia, Harbour Lights, Lawlers, Menzies, Comet Vale, Kookynie, Bottle Creek and Riverina/Mulline. Active exploration for gold continues.. Copper/zinc were mined at Teutonic Bore also on LEONORA. An unexploited nickel deposit is known at Weebo Bore on the northern margin of LEONORA. Mineralization in granitoids is less common, but molybdenite is known in monzogranite at Mertondale northeast of Leonora. Uranium has been previously reported in some of the main drainages (Butt et al., 1977).

Methods

The main sample medium was stream sediment supplemented, in areas where there were no active streams, by consolidated sheetwash and soils. The two last groups were later combined and classified as "soil". Lake sediments were sampled as a separate group and on MENZIES a number of lateritic samples were collected. Sampling density was approximately 1 per $16km^2$ using a basic 4x4 km grid, with specific sample points chosen within each grid unit after consideration of known geology, satellite imagery and topographic data, and aeromagnetics and radiometrics where available.

Larger streams were sampled by trenching. Where the streams were braided a sample was taken from each of the main channels and composited to make a single sample. For smaller streams three subsamples were taken from the streambed and composited into a single sample. At each soil/sheetwash and lake sample site subsamples were taken at the corners of a 50m equilateral triangle and composited. At each site the uppermost 10cm were discarded and material collected from the interval between 10 and 40 cm where possible. Dry samples were sieved on site to between 2 and 0.45mm for chemical analysis, with a second sample of -2mm material collected for archive/research purposes. Wet samples were dried and sieved in Perth. Laterite samples included massive duricrust and/or nodules of varying size. Before analysis all samples were pulverised to a nominal 100 micron size.

Data collected at sample sites included:- the geographic position, the position in the landform, the local regolith, the nature of clasts, any nearby outcrop, and surface coatings on grains/clasts and other relevant information such as nearness to known mine sites, sources of potential contamination, etc.

Samples were commercially analysed using either an alkali-fusion or a "total" (multi-acid, including HF) digest followed by ICP-OES or ICP-MS determination for most elements. Chlorine and F were determined using a selective ion electrode or, where Cl was high, using silver nitrate. Gold, Pt and Pd were determined by fire assay extraction with a graphite furnace atomic absorption finish. In all 47 components were sought; of these Ag and Cd were all below 1ppm with imprecise replications, whilst others such as Be, Bi, Pt, Se and Sn were generally very low so that only the higher values (>5 ppm) could be deemed of significance.

Regolith Units

The regolith was mapped into eighteen basic units, qualified by source material (granitoid or greenstone) where known. The units are based on regolith materials in the context of relict, erosional and depositional regimes. A generalised map for MENZIES is given in Figure 1. The classification is based on, but modified from, that used by Craig and Anand (1993) for the Kalgoorlie area:.

Data Storage and Presentation

Data are stored in an ORACLE database management system and accessed by an ARC/INFO GIS. The data are available as hardcopy maps and in digital form.

Results

Laterite and lake samples constitute well-defined, separate groups. Laterites in general contained highest amounts of Al, Ti, Cr, Ga, V and Zr, whilst lake sediments generally contained the highest amounts of Na, Ca, Mg, Cl, S, Sr and U. Though there are some differences in the patterns displayed by stream sediments and soils/sheetwash, visual inspection and the use of cumulative frequency curves suggest that the variations in composition in these media relate more to source material than the sample type.

Sediments sourced by greenstones are recognisible not only through common elements such as Fe, Ti, Cr, Ni, V, present at the tens of ppm or even percent level, but also through elements such as In and Pd present at the ppb level. Some samples show mafic input even where the main source rock is granitoid. In most cases this can be related to mafic dykes, but there are indications of previously unrecognised mafic enclaves.

Though geochemical patterns relating to greenstone belts are readily distinguishable from those relating to granitoids, individual belts and/or parts of belts display different characteristics corresponding mainly to underlying geology. For example. the general position of ultramafic rocks is shown by high Mg in both soil and stream sediments, even though part of the Mg is now present as magnesite. Concentrations of elements such as Ca, Ni, V and Y help distinguish between different greenstone belts. For example, Ca and V are relatively low in the Ilaara belt on MENZIES and in the Malcolm belt reflecting the higher proportions of felsic and metasedimentary rock in these belts compared with most other greenstones.

It is harder to directly identify sediments sourced by granitoids though many have a high level of K (K_2O>1%). Some of these sediments, for example from the northern margin of MENZIES and the southern and western parts of LEONORA are recognisible as dominated by grus, broken down but only partially leached, rock with K_2O values over 3% and Na_2O over 1%. By contrast, sediments covering granitoids east of the Kalgoolie-Wiluna highway on LEONORA are products of extreme leaching and are comprised largely of sand and clay, with minor iron oxides, and display almost total loss of mobile elements.

Preliminary studies suggest that a few individual granitoids with distinctive compositions can be recognised, but recognition of specific rock groups within the main body of granitoids and within greenstones is possible only in the most general way.

Gold is the main metal of economic interest on the two sheets. Figure 2 superimposes known gold deposits and prospects over the regional Au distribution for the MENZIES sheet. Most known gold-bearing areas, with the exception of Bottle Creek and Twin Hills, are highlighted by values of Au in the regolith above 3 ppb, and the map suggests that gold deposits may be found in other areas, for example, east of Comet Vale. Though no values for Cu or Zn are particularly high, the highest values for these elements (~250 ppm) on LEONORA occur in the vicinity ot the Cu-Zn deposit at Teutonic Bore. The Ilaara and Menzies-Broad Arrow greenstone belts are characterised by relatively high As and Sb in stream sediments and soil, and have potential for containing sulphidic rocks, even though there is little sulphur now present in the sediments.

A few samples contained anomalous amounts of elements of potentially economic interest. Two areas on MENZIES (one extending onto LEONORA) have relatively high levels of Ce and La (maxima of 710 and 450ppm respectively) and are worthy of further investigation.. High Nb (>600 ppm) has been recorded over a granitic shear zone on the eastern part of MENZIES, whilst uranium values up to about 150ppm have been found in main drainages. The latter correspond in part to anomalies recorded by Butt et al (1977).

Chlorine analyses suggest potential for salination of some alluvial plains marginal to main drainages, and provide a warning against overgrazing by stock.

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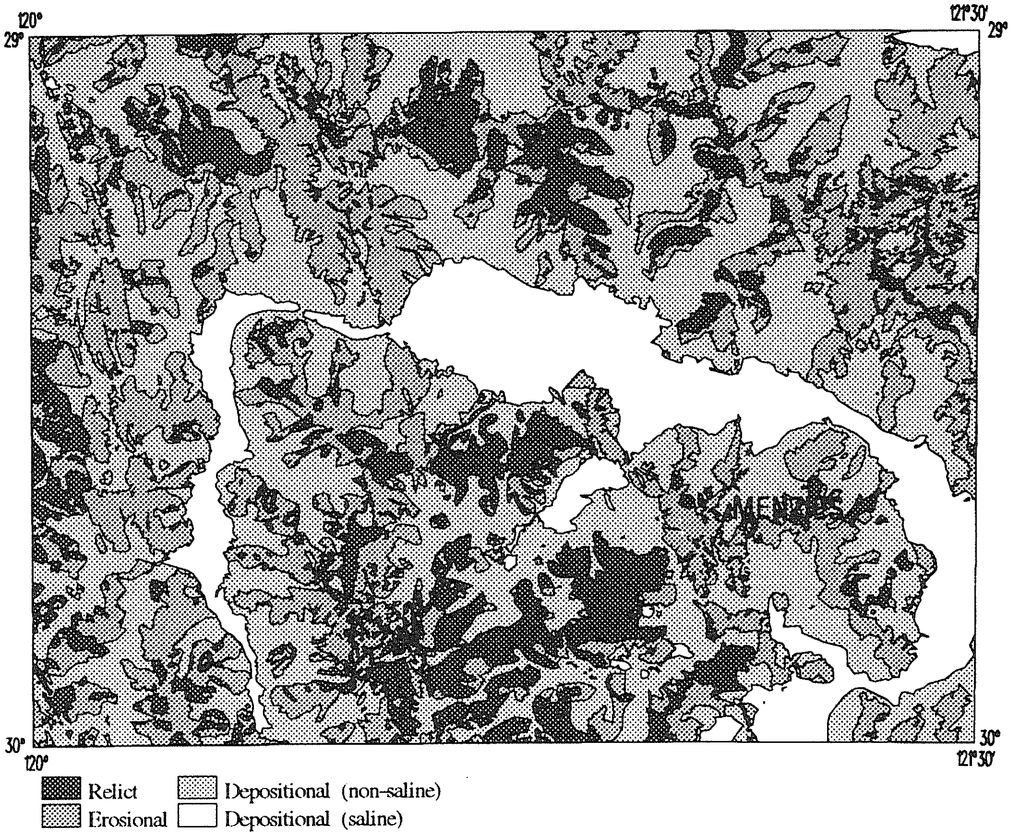

Figure 1. Generalised Regolith map, Menzies area.

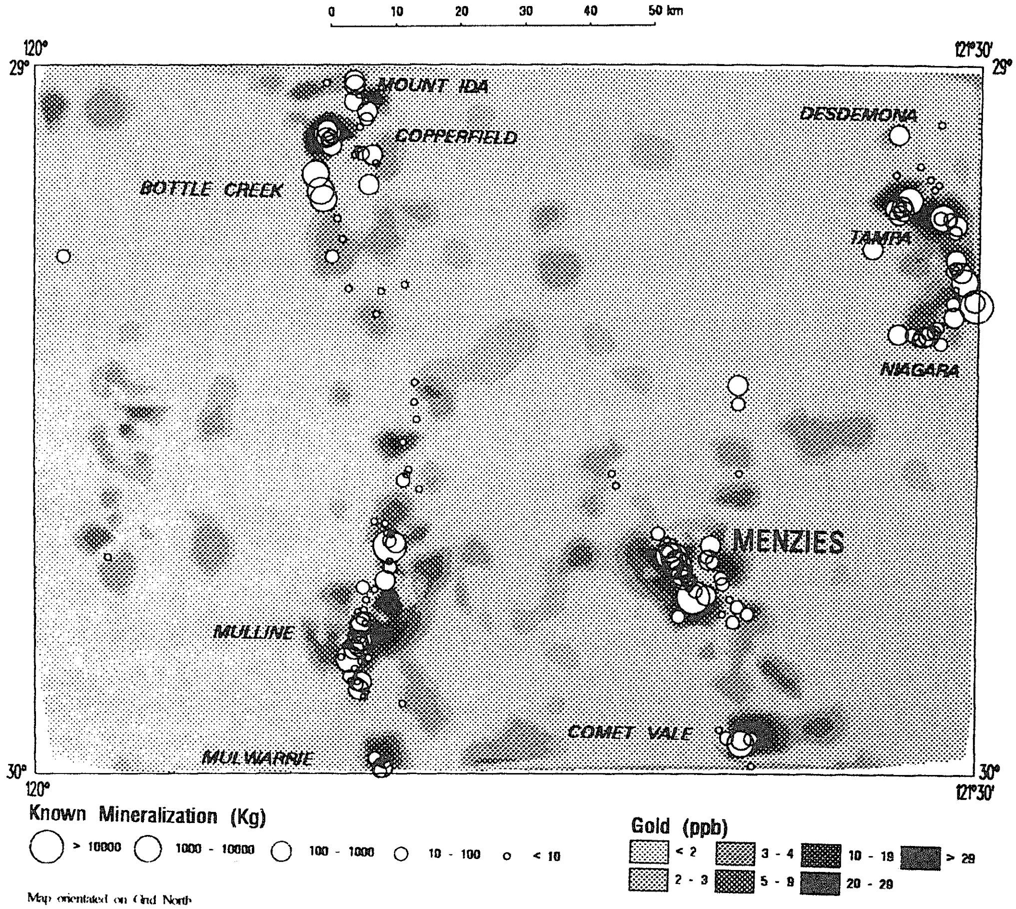

Figure 2. Comparison of gold mines and prospects with regional gold geochemistry, Menzies area.

Interpreting aerial gamma-ray surveys utilizing geomorphological and weathering models

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keywords: aerial, gamma-ray, regolith, modelling, DEM

Aerial gamma-ray surveying is a major tool in the geological remapping of Australia, both at the regional scale (1:250000) and for mineral prospect evaluation (1:25000). The survey measures gamma radiation, derived from the three radioelements K, U and Th (via daughter radionuclides for the latter two elements), which are emitted from no more than the upper 30 cm of the earth's surface. Although broad lithological variations are usually readily "mapped", minor variations in the gamma-ray response within units may be due to lithological variations, weathering, other regolith effects or mineralizing processes. Thus the identification of mineralization signatures requires a detailed interpretation of aerial gamma-ray data that takes into account all these processes.

Our approach to this problem has been to develop an understanding of how radioelement concentrations change during pedogenesis for various common rock types. Studies made in areas throughout Australia over the past 5 years have resulted in a database of weathering responses for a wide variety of rock types, which guides us in modelling the effect of weathering for any particular rock type. Iron oxides and clays have been shown to have an important role in retaining U and, more importantly, Th in weathered material, particularly over mafic rocks. Processed Landsat TM images may be used to determine the iron oxide and clay variation within landscapes.

Geomorphological processes such as erosion and sedimentation may also be modelled, using digital elevation models (DEMs) which can be obtained from stereo SPOT images or topographic contour maps.

In each study area a field examination is made of the landscape, and rock and soil samples are collected for laboratory analysis of radioelements. Finally, the data from the study area and the information in the database are combined into predictive models for radioelement concentrations within prospective lithologies, taking into account the landscape variations. The predicted response is then compared to the observed survey data and residuals examined for significant variations.

The application of this methodology is illustrated by results from two study areas.

Area A is situated near Rockhampton in Queensland. The prospective lithology is Permian basaltic andesite hosting VMS-style base metals. The radiometrics clearly defined the surface extent of the unit and were further examined for evidence of K-enrichment, which has been found associated with the known mineralization. A DEM was created over the area by gridding from AUSLIG contour data constrained by streamlines derived from a georeferenced SPOT panchromatic image. The erosion/sedimentation in the area was modelled using the Universal Soil Loss Equation (USLE) method (Moore et al., 1992). However, in this small study area, many factors such as rainfall, vegetation, soil type and erodibility and cultural effects can all be taken as constant leaving only the length-slope factor to be determined from the DEM. Samples of rock and soils gave median radioelement contents of 0.2 % K, 0.3 ppm eU and 0.5 ppm eTh for outcrop and 0.15 % K, 0.3 ppm eU and 1 ppm eTh for surface soils. (e indicates "equivalent" U and Th as the measurements are made by gamma-ray spectroscopy.) Because of the small variations in radioelement contents between outcrop and soils detailed modelling was not considered justified and the erosion model, the gamma-ray survey data and processed Landsat TM data were combined in a multivariate statistical analysis, controlled by the interpreted geology,. Residuals from the analysis were then examined to look for indications of mineralization.

Area B is situated SW of Bathurst in central NSW. Here the prospective lithology is Ordovician basalts and volcaniclastics which are possible hosts for Au deposits. In the study area these rocks are intruded by the Silurian Barry Granodiorite. The geology of the area cannot be defined from the radiometrics, and field mapping and interpretation of aerial magnetics are required. The gamma-ray survey shows areas of elevated K which may be due either to exposed volcanics or areas of K alteration related to Au mineralization. Extensive field sampling and laboratory measurements are summarized below:

Unit	**Rock**			**Soil**		
	K %	eU ppm	eTh ppm	K %	eU ppm	eTh ppm
Barry Granodiorite	1.8	1.9	7.6	1.0	2.7	8.6
Blayney Basalt	1.4	0.8	1.6	0.8	1.5	5.3
Coombing Formation	1.7	0.6	1.3	0.8	2.0	6.9
Fernside Diorite	0.7	0.1	0.7	0.6	1.5	5.3

These averages show that although the granites and volcanics are dissimilar in radioelement content, the soils are quite similar as a result of different behaviour during weathering. This behaviour also prevents delineation of the units in the gamma-ray survey. A DEM of this area was created from AUSLIG survey data by gridding the spots heights along contour lines (20 m intervals). Field examination showed that rock exposure was a critical factor in determining the surface radioelement distribution. Accordingly a model relating rock exposure to elevation was devised and used to calculate a predicted radiometric response for the area. Comparison with the survey shows that most K-rich areas result from rock exposure but some areas may have undergone K-alteration.

The methods described here are designed to distinguish variations in gamma-ray surveys that may indicate mineralization. As such they are not intended to be applied to regional surveys and a wide variety of lithologies and landscapes. Instead we envisage their application to carefully selected lithologies and areas. Although both approaches shown here require field sampling and laboratory study of representative rocks and soils, it should be possible to derive most of the information required for the modelling from the survey itself using appropriate statistical examination of the selected lithologies coupled with the knowledge of expected weathering behaviour.

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Searching beneath Tertiary alluvial cover

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Keywords: copper, lead, zinc, gold, Charters Towers, Queensland, geochemistry, Campaspe Formation, massive sulphide, RAB drilling

Introduction

The exploration during 1975-85 by Penarroya Australia Pty Ltd in the Charters Towers area, approximately 100km west of Townsville in North Queensland, was quite successful in the search for Volcanogenic Massive Sulphide deposits. The initial discovery of Thalanga 65km west of Charters Towers was followed by the discovery of orebodies at Thalanga East, 2km east of Thalanga and Waterloo, 38km south of Charters Towers. These latter two were found in Cambro-Ordovician basement under 20 to 80 metres of overlying Tertiary Campaspe Formation using the geochemistry of the complete Campaspe profile from RAB drilling. Prior to and at about the same time as the Penarroya work there were a number of RAB programs done by other parties in the area who, with the same objectives, drilled the Campaspe Formation but only sampled bedrock (or what was thought to be bedrock), and relied upon being lucky enough to "jag" the palaeo-outcrop or a significant portion of footwall mineralisation.

Geology

The principal geological components of the areas being discussed are a Cambro-Ordovician acid to intermediate volcanic sequence which flanks the southern edge of the Lolworth-Ravenswood Block of Ordovician to Permian granitoid batholiths. These units are in many places covered by the Tertiary Campaspe Formation, a valley fill unit of poorly consolidated gravels, grits and claystone. The topography of the basement surface is not unlike the topography of outcropping basement units today. This means very rapid changes in the depth of the Campaspe Formation, usually with no surface indications.

Thalanga and Thalanga East are steep dipping Zn-Cu-Pb-Ag VMS deposits with sericite-pyrite-silica altered rhyolitic footwall and unaltered dacitic, andesitic and volcaniclastic hangingwall. Waterloo is a steep dipping Zn-Cu-Pb-Ag-Au VMS deposit with a sericite-(pyrite) altered andesite footwall and a largely rhyodacitic volcaniclastic hangingwall.

Published resources for East Thalanga are not available but are estimated to be of the order of 2M tonnes of approximately 15% Zn+Pb+Cu with palaeo-outcrop dimensions of about 6m wide and 500m long (patchy). Waterloo is 372,000 tonnes of 3.38% Cu, 19.7% Zn, 2.8% Pb, 94g/t Ag, 2.0g/t Au (Hartley & Dash) with a palaeo-outcrop about 300m long and 5m wide.

Palaeogeochemistry

The erosion cycle in North Queensland (and for much of Australia for that matter) probably involved the very rapid erosion during the Tertiary of an existing peneplain. Any outcropping orebody at that time would therefore have been eroded and its subsequent detritus deposited within the sequence as is illustrated in Figure 1. It is obvious therefore, that the mechanical dispersion will occur over a much wider area than the original outcrop and be easier to intercept in RAB drilling.

It became obvious during the exploration at Thalanga and East Thalanga (over 1000 RAB holes), that as well as this mechanical dispersion there is also chemical dispersion towards the surface and along the overlying grit and gravel horizons.

The result of both of these effects was to produce in the Campaspe Formation a "mushroom anomaly" (Figures 2 & 3).

The mechanical dispersion could, with familiarisation, be identifed as chips of gossan etc. during normal logging of drill chips.

Field Procedures

The original drilling was done with a Mayhew 1000 rig (was able to use mud, case easily and do limited coring), using principally rotary air blast (RAB) methods in most cases.

Drilling was done without cyclone collector and cuttings were crudely collected at 3m intervals with trays at the drill collar (2-4kg). An assay sample of 1kg was taken by hand grab or using a tube. A small sample was kept in a chip tray or small plastic bag for geological record. From the end of the hole or somewhere within definite bedrock a collection of larger chips was collected for geological record, alteration studies and petrology as required.

Whilst searching for a VMS deposit assays were only routinely done for copper, lead and zinc, but today one should add gold, arsenic and barium to seek for other styles of gold mineralisation in particular.

It was found from a number of careful orientation studies at Thalanga that lead was the best indicator metal of such mineralisation be it in rock chip, soil or sediment. Zinc values were most erratic and there was the expected very high dispersion. Copper being quite variable in the main orebody was also variable in the sample medium. Lead geochemistry then was used to influence day to day program management although for any element to qualify for a follow up it did require multi-element expression.

The careful plotting of sections, finding "mushrooms" and interpreting their source was a necessary pre-cursor to drilling by RC and/or diamond to intersect any source body. However, the day to day program management (eg where to put infill holes and which direction to chase), was based on a continuously updated surface plan whereby the highest lead value in each hole was the only data plotted, and these were subsequently contoured.

Using such a method it was found that a 400m x 400m grid (or even possibly 400m x 800m) could easily locate bodies which were as small as Waterloo. It was in fact located by drilling on a 400m x 200m grid.

Thalanga East was drilled at 200m x 100m and would probably have been found on a grid of 400m x 800m and certainly on a 400m x 400m grid.

With a background of less than 25ppm, lead anomalies of the order of 100ppm were quite clear and were always meaningful and greater than 400ppm was close to the source and would suggest follow up by RC drilling or such. For copper the levels of significance were 50ppm and 100ppm and for zinc were 100ppm and 1000ppm.

Coupled with this geochemistry of the overlying sediments was not so much the geochemistry of the basement, but it's alteration characteristics. The objective was to keep throwing RAB lines across the perceived horizon of interest defined by the contact between hydrothermally altered footwall (pyrite-sericite-silica) and overlying unaltered rocks. Mostly this could be done with a hand lens, but often in the early days it required petrographic confirmaton. Alteration indices were developed based on whole-rock analyses which were quite useful, but all the best areas were readily defined in the first instance by lead anomalies.

With the very simple sampling required and the nature of the grits and gravels being intersected usually a site geologist can do all the sampling and logging. The key geological features to be logged are:-

(1) Derivation of sediments (volcanomict, granitomict etc. - effecting background values).
(2) Presence of gossan, jasper, etc.
(3) Presence of scavenger minerals such as manganese or iron oxides.
(4) Depth of the bedrock interface.
(5) Bedrock lithology and state of alteration.

Where anomalous geochemistry or gossan chips were encountered in a hole using wide spaced RAB drilling, infill holes were drilled either side until the anomalous source could be defined within 25m. At this point inclined RC or diamond holes could rake the zone within the underlying bedrock in the normal manner.

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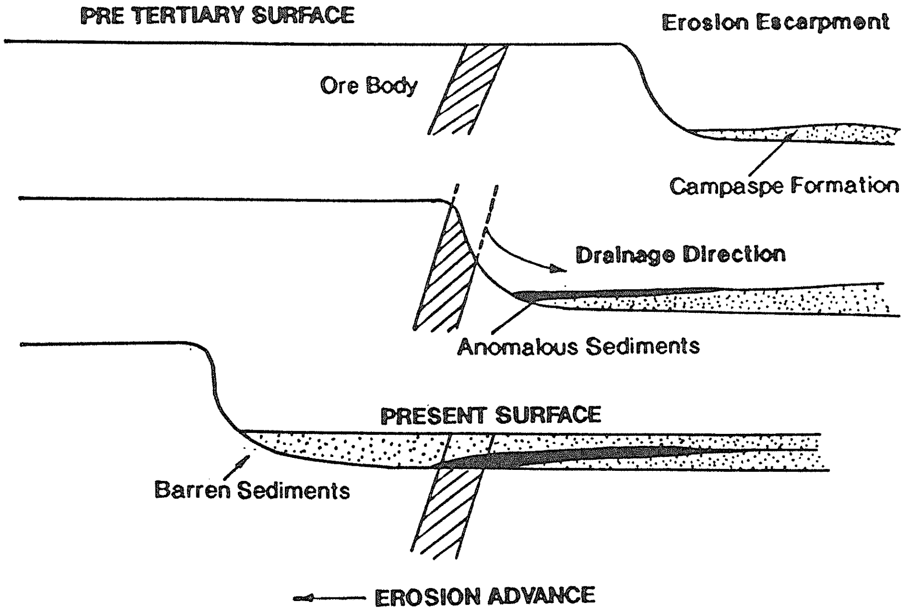
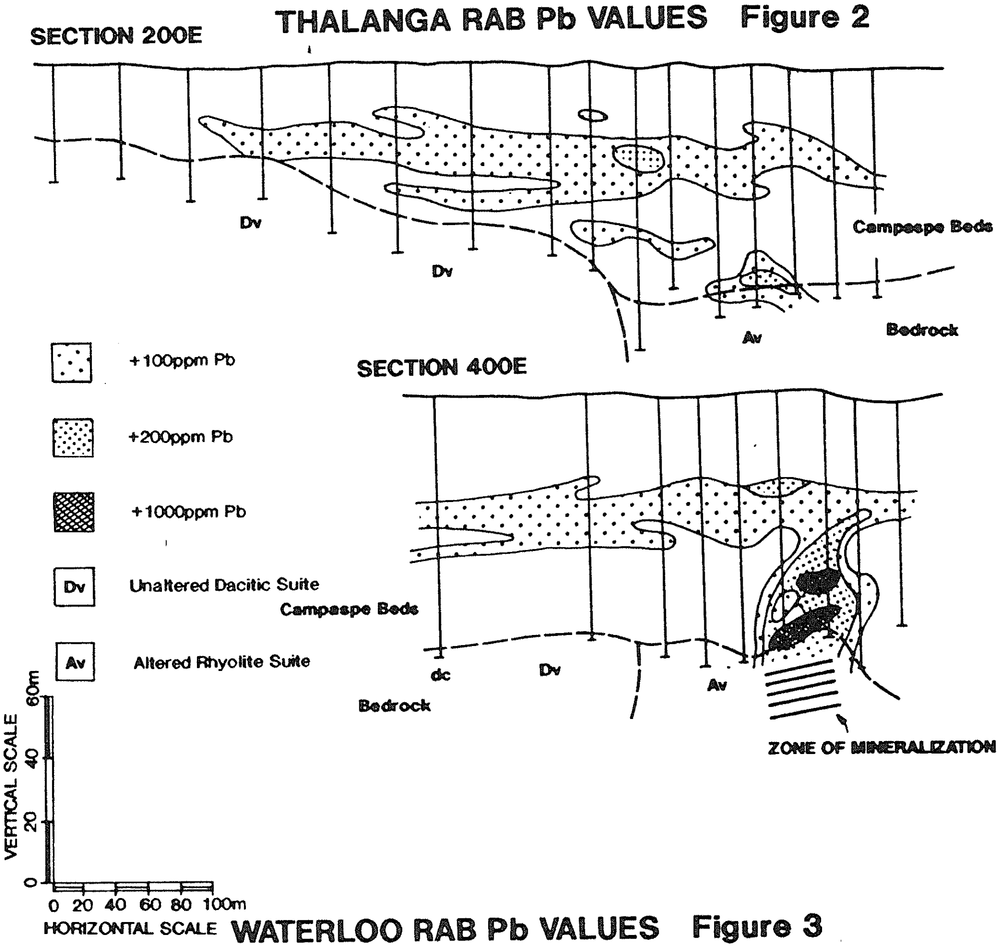
Acknowledgements

We would like to thank Pancontinental Mining Limited, who purchased Penarroya Australia Pty Ltd, for permission to discuss Thalanga and Waterloo. We also thank Gold Mines of Australia Limited and Mt Leyshon Gold Mines Limited for permission to discuss data from the Brolga prospect. We would also like to thank previous fellow workers who helped mould some of the concepts - Fritz Fitton, Les Davies, Peter Gregory and Kevin Wills.

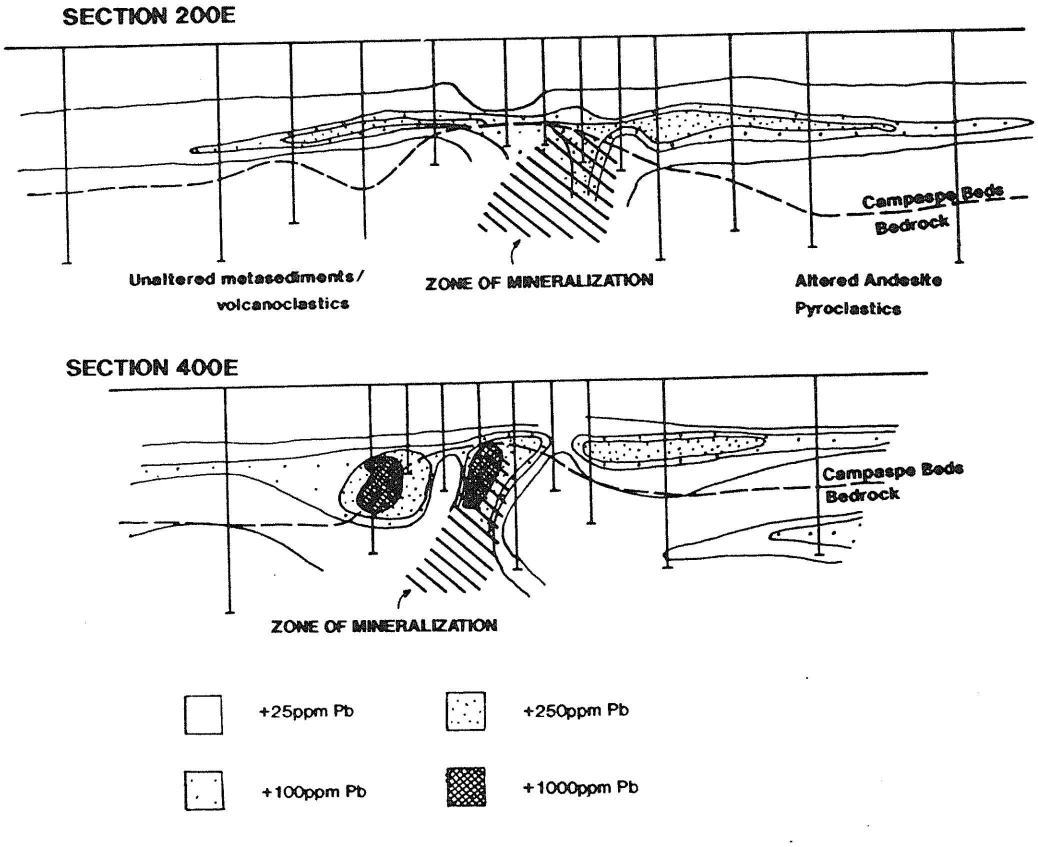


TERTIARY MECHANICAL DISPERSION Figure 1

THALANGA RAB Pb VALUES Figure 2



WATERLOO RAB Pb VALUES Figure 3



Regolith-Landform Evolution and Secondary Nickel Dispersion in the Takashi Ultramafic Belt, Forrestania, Western Australia

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Keywords: nickel, regolith evolution, Forrestania

Introduction

Exploration in the Yilgarn Craton of Western Australia is made difficult by the presence of up to 150m of weathered material, known as the regolith, which overlies fresh rock. To date, however, most studies of this regolith have been related to gold exploration. Smith (1983) estimates that 85% of ultramafic rocks in the Yilgarn Craton with the potential to host nickel sulphide mineralisation are covered by some form of regolith cover. This poster therefore summarises the results of a study of the behaviour of nickel and associated elements during weathering using the Takashi Ultramafic Belt in the Forrestania area as an example. It also presents a proposed model of regolith-landform evolution for this area.

Regional Setting

The Takashi Ultramafic Belt is one of six that trend north-south through the Forrestania Greenstone Belt, located approximately 400km east of Perth, in the Southern Cross Province of the Yilgarn Craton. The Takashi Ultramafic Belt is a steep westerly dipping limb of the Forrestania Syncline of which the fold hinge plunges shallowly to the north. This belt consists of metamorphosed spinifex-textured komatiites and associated olivine cumulate rocks with minor interflow Banded Iron Formation and chert units. The core of the Forrestania Syncline consists of pelitic and psammitic metasediments.

The climate of the study area is semi-arid and characterised by high evaporation (1600 to 1800mm per year). Light winter and occasional summer rainfall averages approximately 300mm per year. Average temperatures range from 17^0 to 34^0C in summer and 4^0 to 16^0C in winter. The vegetation of the Forrestania area is dominated by sclerophyll woodland which covers the heavy soils formed over the mafic rocks. Predominantly mallee, this is replaced by ti-tree and samphire in the low-lying saline areas.

Regolith Distribution and Stratigraphy

Regolith mapping was carried out over an area of 10km x 2km at 1:10,000 scale in order to determine the distribution of regolith units in the study area. In addition, samples from over 300 Rotary Air Blast (RAB) holes were re-examined to determine the regolith stratigraphy. The regolith in this study area is characterised by highly truncated residual profiles that have been partly overlain by at least two phases of sedimentary material. The older sediments are characterised by high quartz and kaolinite contents, were interpreted to be granitic in origin and appear to have been transported from the north-west. These sediments show evidence of lateritisation in the form of mottling and an unconformable contact with the underlying residual profile. Transported pisoliths with polyphase development of cutans were observed in localised depressions at the base of the granitic sediments. These sedimentary units are most obvious in the north-western part of the mapped area and can be up to 15m thick in some RAB holes.

The later sediments are aeolian and show only limited evidence of weathering and soilf formation. It is probable that these most recent sediments were transported in an easterly direction from the granitic rocks on the western margin of the Forrestania Belt by the prevailing winds. Where no sediments are seen, a thin layer of colluvial material overlies the saprolite and mottled zone. Preservation of residual laterite is very poor, except for minor lateritic gravels observed in areas of high relief. Likewise, there is very limited exposure of fresh outcropping rock.

Soils vary greatly over the study area and are heavily dependant on the underlying geology. Dark red iron-rich gravelly clay soils with abundant pisoliths are characteristically developed on relict regimes. Soils developed in erosional regimes have formed directly over mafic saprolite and bedrock. As such these soils are predominantly heavy red iron-rich clays and commonly show "gilgai", (depressions up to 1 metre deep and 5 metres across), due to expansion and subsequent shrinkage of smectitic clays. Soils developed over colluvium in the low lying parts of the study area are generally sandy with varying amounts of quartz sand and lateritic fragments. Over the sedimentary units, the soils contained abundant quartz and kaolinite with minor goethite.

Mineralogy

The residual profile, developed over mafic and ultramafic rocks, shows a characteristic change in mineralogy with increasing depth.

In slightly weathered saprock over ultramafic rocks, the dominant mineralogy is serpentine, amphibole and talc with minor chlorite and Mg-smectite. Increased weathering resulted in the presence of goethite which occurs as a pseudomorph of tremolite in lower saprolite developed over spinifex-textured komatiites. In saprolite over cumulate-textured rocks, silicification and ferruginisation is well developed with preservation of original textures by pseudomorphism. Dominant mineralogy in this silicified ferruginous saprolite zone (sometimes referred to incorrectly as "silica cap") is secondary silica and goethite with minor talc, chlorite and magnetite after mafic minerals. The upper saprolite zone is characterised by dominant smectite and chlorite with well developed goethite staining. Original textures are not well preserved in this zone when compared with underlying units.

At approximately 10 metres depth, a sharp change is seen in the mineralogy which has been interpreted to be a erosional contact between the residual profile over ultramafic rocks and later transported sedimentary material. Above this contact, the dominant mineralogy is quartz and kaolinite with minor goethite and hematite, presumably present as a result of the poorly developed mottling seen in this zone. In the top 2 metres, the effects of soil formation can be seen in the presence of pedogenic carbonate. In addition hematite and goethite, both present in colluvial pisoliths, make up a significant component of this zone.

Geochemical Dispersion

Secondary dispersion was determined by analysis of 100 samples from 3 anomalous and 2 barren RAB holes using X-ray Fluorescence. This analysis confirmed a contact at approximately 10 metres depth as discussed previously. Major oxides such as SiO2 and K2O show marked enrichment in the sedimentary material when compared to lower residual units. Fe2O3, MgO and MnO all showed an opposite trend with higher values in the lower, ultramafic derived, units. Trace elements including Ba, Rb, Sr and Zr are all enriched in the upper units when compared to the saprolite zones. Values for nickel, along with copper, chromium and cobalt are all close to the detection limit in the sediments but are enriched in the ferruginous saprolite zone. Nickel values peaked at approximately 10,000ppm in this zone and showed a high positive correlation with Cu, Cr and Co. The average enrichment in this zone, when compared with bottom of hole values, was 4-5 times for nickel, 2 times for chromium and approximately 10 times for copper. Vanadium and zinc also show enrichment in the saprolite zones when compared to the upper units, also providing evidence for a contact at 10 metres. A summary of down-hole values for several trace and major elements for an anomalous RAB hole, SBR 245, is shown in Figure 2. This figure also shows the dominant mineralogy and a general description of the regolith for the corresponding depth interval.

Analysis of fragments from hole SBR 245 using scanning electron microscopy showed a possible relationship between nickel and Mg-rich secondary minerals such as chlorite and smectite in the lower saprolite. Element mapping with the electron microprobe, however, showed a strong relationship between nickel and iron in the ferruginous saprolite and a negative relationship with magnesium, silicon and aluminium. It therefore appears that initially, nickel copper chromium and cobalt are associated with smectite and chlorite, but become adsorbed onto the surface and incorporated into the lattice of goethite particles with further weathering.

Lateral dispersion is fairly limited in the study area, presumably due to the lack of any major drainage system and is generally less than 100 metres in a south-westerly direction. Surface anomalies of both nickel and copper that relate to underlying cumulate rocks are seen where the residual profile is not covered by transported sediments. The 10 metre thick quartz-rich sediments tend to mask Ni, Cu, Cr and Co in the soil zone, especially in the north-west of the mapping area.

Conclusions and Implications for Exploration

The Takashi Ultramafic Belt shows evidence for at least two phases of weathering. Whether these phases are part of a continuous weathering process or are discreet events is under dispute. Whatever the case, the overlying sediments exhibit little resemblance to the underlying residual profile, either physically or chemically. This has implications for any future soil sampling and/or drilling programmes that may be planned for the area. It is important that soils developed in transported material are distinguished from that developed in residual material by those carrying out the sampling otherwise the results obtained could have little meaning.

Residual silicified ferruginous saprolite is well developed over cumulate textured olivine rocks and shows preferential concentration of nickel, copper, chromium and cobalt. Recognition of this material is therefore important for determining the possible presence of nickel sulphide mineralisation. In addition, the preservation of textures in this material makes it a useful mapping tool for distinguishing ultramafic rocks.

The potential for future nickel sulphide discoveries in Western Australia is probably good based on the large areas that have yet to be explored in any detail, but may be limited by a relative lack of knowledge relating to secondary nickel dispersion processes and regolith evolution.

Acknowledgments

The authors would like to thank Outokumpu Exploration Australia for sponsoring this project and providing logistical and financial support. In addition, several unpublished company reports and confidential reports prepared by the CSIRO for Outokumpu were also made available.

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Geochemical Signatures of Ferruginous Regolith in the Olary Block, South Australia.

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Keywords: Geochemical Prospecting, Gossan, Ironstone, Statistical Analysis, Olary Block

Introduction

The Olary Block (OB) in South Australia comprises one of the inliers of the early Proterozoic Willyama Supergroup. The Olary Block is contiguous with the Broken Hill Block to the east which hosts the giant Broken Hill PbZnAg deposit. The two are separated by a NNE-trending fault and a marked change in aeromagnetic character. The Willyama Supergroup in the OB consists of regionally metamorphosed and deformed sedimentary and minor volcanic rocks which have been intruded by several granitoid types and mafic dykes. Quartzofeldspathic clastic sedimentary and felsic volcanic rocks dominate the lower part of the sequence, followed by finer grained quartzofeldspathic sedimentry rocks, calc-silicate bearing rocks and exhalative chemical sediments. A pelite-dominated sequence terminates sedimentation. Granitoids are widespread and have been emplaced during at least four different periods. Low grade metasedimentary rocks of the late Proterozoic Adelaide Geosyncline unconformably overlie, or are faulted against the OB.

Stratiform, stratabound and transgressive, epigenetic mineral deposits are common in the OB. They include Fe(CuCoAsAu) and Fe(ZnPbMn) sulphide associations of exhalative and possibly diagenetic origin, baritic and manganiferous iron formations of exhalative origin, epigenetic (replacement) ironstones and vein- and shear-hosted CuAu and base metal sulphides. The proximity of the OB to the Broken Hill deposit, and more recent analogies of mineralisation, alteration and deformation with the Eastern Succession of the Mt. Isa Block (Williams and Blake, 1994) continue to drive exploration efforts in the region.

Aims

With 70% of the Willyama Supergroup in the OB covered by Cainozoic sediments, exploration is necessarily becoming directed towards areas concealed by overburden. In this situation, an appreciation of regolith geochemistry is paramount for the evaluation of grab samples, rock chips of ferruginous material obtained by drilling under cover and the selection of areas for follow-up exploration. The aims of this study are to characterise element associations in iron-rich regolith of differing genetic type, and in doing so provide a geochemical framework to determine the parentage and prospectively of samples acquired during routine exploration.

Sample Media

Geochemical data have been collected from iron-rich regolith ranging from gossanous ironstone and banded iron formation, to pisolitic ferruginous duricrusts and lags developed throughout the Proterozoic Olary Block. The surficial iron-rich regolith is derived from, and reflects a variety of parent materials. Prominent among ironstone-forming rocks in the area is the Bimba Suite, a thin (<50m), sulphide-bearing, relatively continuous unit which may be up to 250km in strike length and which has the potential to host stratiform base-metal mineralisation. Sulphides include pyrite and pyrrhotite with minor chalcopyrite, sphalerite, galena, arsenopyrite and cobaltite which occur as disseminations and bedding parallel laminations which grade into rare massive units (Cook and Ashley, 1992). The majority of the outcropping Bimba occurs in the central and northern parts of the area, with considerable strike length inferred by drilling and magnetics to occur to the north along the Benagerie Ridge, where the Olary Block extends under Cainozoic and older rocks (Yates and Randell, 1994). The surface expression of the Bimba varies from prominently outcropping gossanous ironstone in geomorphically immature areas to float and rubble in more degraded situations, especially to the north in areas of low relief. Outcrop is most commonly goethitic with scattered boxwork textures, however, variations include blue-black manganese-rich variants and exotic, solution-precipitated iron oxides in degraded situations.

Syngenetic, finely laminated iron formations (quartz + magnetite ± hematite ± albite ± barite ± pyrite ± calc-silicates) and massive, apparently epigenetic, replacement ironstones (Fe oxides ± quartz) (Lottermoser et al., 1994) also form prominent iron-rich outcrop. Both of these types and the Bimba gossans have shed extensive detritus or "lag" deposits, which were also sampled. The third media type includes ferruginous fragments which form surface veneer deposits in areas of little or no outcrop, ranging in extent from linear features of a few meters in width to hundreds of meters in length, and to blanket deposits of many hundreds of hectares. This group includes both bedrock material which preserves primary fabrics, and loose lateritic nodules and pisoliths. Magnetic and non-magnetic varieties are present. The final media type forms an important, although minor component of the iron-rich regolith present in the area and includes a ferruginous pisolitic duricrust.

Data Analysis

Samples were analysed for 20 elements (Fe, Mn, Cu, Pb, Zn, Ni, Co, As, Ag, Sb, U, Mo, Bi, W, Sn, P, K, Se, Ba, Au) using ICP-MS, ICP-OES and XRF. The elements analysed cover a fairly routine exploration suite in keeping with the aim of the study to determine a practical geochemical framework. The total data set consists of 312 samples. Of these, 225 are derived from Bimba gossans, 11 are pisolitic duricrust, 30 from iron formation and replacement ironstones and 28 are ferruginised fragments of varying types. To capture variability at each location, up to 15 samples were collected from any one occurrence. 35 sample locations are represented in the data. To extract trends and associations from the data matrix, multivariate statistical methods are used including RQ-mode principal components analysis (RQ-PCA) and dynamic cluster analysis (DCA). Prior to multivariate analysis the data are first power transformed to improve normality and multivariate normality is checked with chi-square cumulative probability plots.

Univariate analysis of the raw data indicates all elements except for iron are variably positively skewed. Prior to multivariate analysis it is desirable to improve the skewness of the data to meet statistical assumptions, improve the reliability of statistical results and enhance background element associations. A power transform of the form $(x^{\lambda} - 1)/\lambda$ is applied to transform the raw data to near to zero skewness following the procedure of Howarth and Earle (1979). The transformation is sensitive to outliers, so the top 5% of the ordered data are deleted prior to the calculation of λ. The data set is then reinstated and the transform applied to all the data. Examples of calculated values for λ, together with skewness prior to and after transformation are (λ, S-before, S-after); Cu (0.13, 6.1, 0.0), Ba (0.07, 5.85, -0.04), Ni (-0.06, 7.39, 0.0) and As (0.23, 3.63, -0.05).

To examine relationships between samples and variables RQ-PCA is used as described by Zhou et al. (1983). RQ-PCA is a powerful technique as it allows both samples and variables to be plotted in the same component space, and related groups of samples, together with their associated element behaviour may be determined. RQ-PCA, which uses least squares estimates of dispersion (correlation and covariance), is susceptible to outliers. Zhou (1989) has modified the method to make it robust against multivariate outliers by implementing multivariate trimming (MVT). In the procedure, prior to the extraction of principal components from the covariance matrix, the Mahalanobis distance for each sample is calculated. The Mahalanobis distance is a measure of the distance of an individual sample from the centroid of the data, it follows that outliers will fall the furthest from the centroid and have the largest Mahalanobis distance (Garrett, 1989). A percentage of the samples with the largest Mahalanobis distance are set aside temporarily and new means and covariance matrix calculated. The Mahalanobis distances are recalculated with the trimmed matrices and the procedure repeated. At each iteration the trimmed covariance matrix is converted to a correlation matrix and compared with the previous correlation matrix. When the correlation matrices reach a set convergence level, the procedure stops and the trimmed correlation or covariance matrix is used for the RQ-PCA (Zhou et al., 1989). In this way outliers are not allowed to distort the analysis.

The combined effect of power transformation, and subsequent MVT is to enhance background correlations in the data. Table 1 contains correlation coefficients for the total data set calculated from the raw data (N = 312) and power transformed, 10% MVT data (N=281). Note that the highest correlation in the raw data is Co-Ba, 0.51, but transformation shows this to be due to a gross outlier. The correlation disappears in the modified data. In general, spurious correlations are reduced and real correlations present in the data are enhanced. This has the additional benefit of concentrating more variance into the first few principal components extracted from the data and making the element loadings more interpretable.

Table 1: Selected correlation coefficients calculated from the total data set, before power transformation and 10%MVT (upper right), and after 10%MVT and transformation (lower left).

	Co	Ba	Pb	Zn	Cu	Mo	As	P
Co		0.51	0.07	0.04	0.10	0.02	-0.02	0.02
Ba	-0.03		0.09	0.01	-0.01	0.00	-0.11	-0.01
Pb	-0.02	0.51		0.24	-0.04	0.12	0.03	0.14
Zn	0.09	0.08	0.47		-0.10	-0.01	0.21	0.36
Cu	0.27	-0.34	-0.09	0.06		0.27	0.17	0.09
Mo	0.03	-0.12	0.09	0.20	0.54		0.42	0.06
As	0.04	-0.67	0.16	0.44	0.41	0.72		0.13
P	0.26	-0.05	0.27	0.62	0.48	0.30	0.46	

Results

RQ-PCA of the total data set and subsequent, unsupervised cluster analysis carried out on the principal component scores for all samples identified 12 groups of samples, most of which are contained within the Bimba gossan data. Lag sourced from Bimba gossans was included with the gossans, similarly lag shed from iron formations is included with the iron formation and replacement ironstone samples. Importantly, lags containing ferruginised fragments, nodules and pisoliths from areas of subdued relief and no outcrop cluster as a group, as does the pisolitic duricrust. The average concentration of selected elements for each of the groups is given in Table 2. The Bimba consistently contains anomalous concentrations of Cu, Zn, As and in places Pb, Se, Sb, U, Mo, Co, Bi, Au and Ba. Further RQ-PCA and cluster analysis of the Bimba gossan samples by themselves reveals they may be further subdivided into for example, Cu-Co, Cu-As-Mo-Ag, Zn-Pb-Mn-Ba-As and Zn-As-Cu associations. A notable feature of the entire dataset is the generally high levels of As throughout the area. For example, apart from the iron formations and replacement ironstones, As is generally in the 100-200+ ppm range, even in ferruginised rock fragments and pisoliths. Some pisolitic duricrusts contain Cu-Zn concentrations in the 100-200+ ppm range. In comparison with other base-metals, Pb levels are low throughout the area. The Bimba is not always anomalous with one occurrence containing anomalously low As-Cu-Pb-Zn. This occurrence may result from the weathering of iron-rich calc-silicate and carbonate rocks but with little or no sulphides. The least "anomalous" of the iron-rich regolith material sampled in the area is that derived from the iron formations and replacement ironstones.

Table 2: Mean composition of groups identified during RQ-PCA and DCA. All values ppm.

Sample Type	Cu	Zn	Pb	As	Mn	Ba	Mo	Ag	Co	Ni
Bimba Gossan	1206	649	121	567	3391	1538	70	1.7	106	54
Iron Formation + Replacement Festone	84	61	8	16	2691	1945	7	2.3	57	20
Pisolitic Duricrust	151	110	38	40	235	1298	6	0.9	9	22
Ferruginous frags. & nods.	40	41	56	99	305	5426	11	0.4	7	13

Summary

The regolithic materials considered in this study display varying chemistry which allows the characterisation of most ironstone types. Generally, iron-rich regolith in the OB contains elevated concentrations of As and Ba, and low Pb. The Bimba gossans, including their lags, are consistently anomalous in Cu, Zn, As and in places Pb, Se, U, Mo, Co, Bi, Ba and Au, however, the geomorphic maturity, or level of degradation of the Bimba outcrop does not appear to affect metal contents, implying differential leaching is inhibited by buffering due to the presence of carbonate- and calc-silicate rich rocks at the Bimba stratigraphic level. The iron formations and replacement ironstones are the least anomalous samples from the area.

Some problematic ironstones remain. Samples with low, but still anomalous levels of base metals can be difficult to distinguish from each other as base metals can occur in similar amounts and associations in different media. Further work will be undertaken to determine the mode of formation of some of the more problematic, yet anomalous lags and duricrusts. Further subdivision of the lag material is important so that different geochemical thresholds may be applied to different media, enhancing the sensitivity of the exploration technology to detecting mineralisation.

Acknowledgments

Financial support from North Exploration, the ARC and Mines and Energy South Australia is gratefully acknowledged.

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Kaolin Formation by Tropical Weathering at Weipa, north Queensland

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The Weipa-Andoom kaolin deposit lies on the west coast of Cape York Peninsula in far north Queensland. The deposit overlies Cretaceous marine sediments of the Rolling Downs Formation (Andoom) and Cretaceous-Tertiary fluviatile sediments of the Bulimba Formation (Weipa) below a pisolitic bauxite layer. Four 30 m drill sections were sampled at 0.25 m intervals, and a subset of about 30 samples per core were examined by XRF analysis for composition, XRD for mineralogy, and by AEM for mineral composition.

The kaolin profile shows the classic features of a deep weathering profile: at the bottom of the drill hole is fresh rock, which grades upward to a pallid zone at about 19 m depth, above which is a mottled zone from 7 to 11 m. Above the mottled zone is a zone of ferruginous kaolinite nodules (at about 2 m) which grades into bauxite. Major elements in the profile behave largely as expected: depletion occurs in the order Na>Ca>K=Mg>Si.

Kaolin occurs in all levels of the profile. However, the kaolin formation is rich within the pallid zone, i.e. kaolin deposit, which mainly contains kaolinite (up to 80 wt%) and quartz, with minor or trace minerals of 'mica' (muscovite, illite), smectite, halloysite, Fe minerals (hematite & goethite), Ti oxides (anatase & brookite ?), and amorphous material. Figure 1 shows the variation of mineralogy in Gondol drillhole, Andoom. The Rolling Downs sediments at 30 m depth are quartz glauconite sandstones, becoming smectitic upwards, with kaolin the dominant layer silicate in the pallid zone. Quartz content decreases up hole, from 26 wt% at 30 m to about 3% in the mottled zone. Amorphous materials are about 19 wt% in the sandstone at 30 m, up hole to 5-10% in the pallid zone, and up to 30% in the mottled zone.

The kaolinites mainly concentrate at clay size fraction of 0.5 to 2 μm. Kaolinite plates vary from 0.1 to 15 μm in the ab-plane and from 0.02 to 0.2 μm in thickness. It seems that kaolinite crystals are more euhedral shaped and well sorted in the mottled zone than those in the pallid zone.

AEM examination shows that the kaolinite of the mottled zone has a higher structural Fe content (about 2-3% Fe_2O_3) than kaolinite of the pallid zone (Fe_2O_3<1.5%). Rare halloysite has the same composition as associated kaolinite. Goethite Al-content is less than 13 mol%. High-resolution TEM (HRTEM) study reveals the structural details of kaolin. One or two 2:1 layers (possible smectite layers) were found as a surface layer on one side of some kaolinite particles from the pallid zone. Transformation of mica (muscovite or illite) into kaolinite by topotactic alteration was demonstrated in samples from the pallid zone. HRTEM studies show some 'amorphous' materials may be crystalline but about 10 nm in size.

The formation of the Weipa kaolinite is believed to be of in-situ origin, which formed from recrystallization of previously transported kaolin, solution reacting with other minerals, and topotactic alteration of other sheet silicates. The kaolinite in the bedrock is mainly of transported origin.

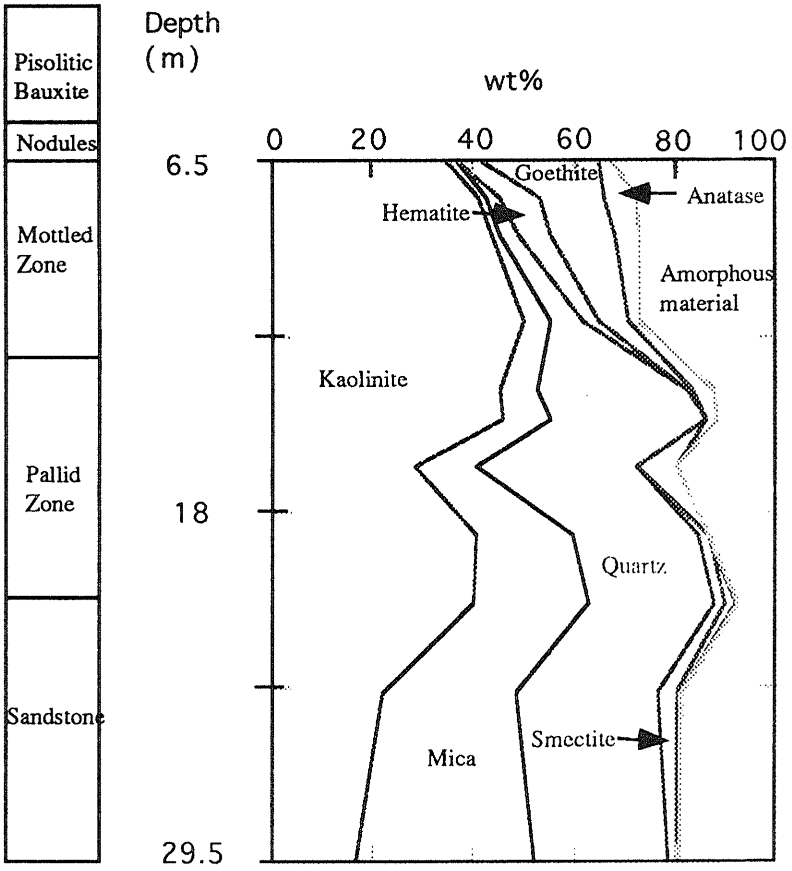

Figure 1 Mineral distribution in Gondol drillhole, Andoom.

Use of the isocon technique to monitor element mobility during basalt weathering: examples from semi-arid and wet tropical North Queensland.

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Keywords: weathered basalt, graphical isocon technique, element mobility

Introduction

Most commonly used weathering indices rely on the comparison of mobile elements versus a relatively immobile index element (Reiche 1943, Roaldset 1943, Ruxton 1968, Vogel 1975, Nesbitt and Young 1982, Chittleborough 1991, Brimhall et al. 1992). However, often it is difficult to assess how immobile the index element really has been during the chemical and physical processes of weathering. One solution to this problem is to make the comparison relative to more than one immobile element, as in the graphical isocon technique (Gresens 1967, Grant 1986, Huston 1993). This provides an internal check as all index elements must occur in the same ratio (weathered rock / unweathered protolith) as each other to be truly considered immobile.

The graphical isocon technique, formerly used in studies of metamorphic and metasomatised rocks, has here been used to interpret the geochemical data of weathered basalts of the Nulla, McBride and Atherton provinces, North Queensland.

Method

When scaled chemical data for weathered rocks are plotted versus similarly scaled data for unweathered protolith, relatively immobile elements (e.g. Al, Ti, Zr, Y, Nb) plot on a straight line called the "isocon". The steepness of the isocon indicates the degree of mass loss/gain for a weathered sample. If there has been a mass loss in the weathered material, the isocon will lie above the 1:1 line of fresh basalt, but if the isocon lies below this line, then there has been a mass gain. Data points falling in the fields above and beneath the isocon represent elemental mass gains and losses respectively.

Results and Discussion

Calcium and strontium partition very similarly in primary basalt minerals, hence are released at the same time during the weathering of basaltic glass, plagioclase feldspar and to a lesser extent ferromagnesian silicate minerals. These cations are readily leached from the profile although small amounts of strontium may be adsorbed onto secondary products causing slight fractionation. However, generally the two elements show a similar strong depletion pattern early in weathering. Secondary enrichment of calcium as a result of precipitation of carbonate or zeolite (e.g. chabazite) minerals from percolating fluids is not always associated with secondary enrichment in Sr.

Because potassium-bearing phases (e.g. alkali feldspar, mica) are not common in basalt, the total concentration of potassium in fresh basalt is relatively low. Potassium is released early in weathering during the devitrification of basaltic glass and the breakdown of plagioclase feldspar. Rubidium has similar chemical properties to potassium and shows similar behaviour during weathering.

Although magnesium and sodium are released from different phases in the basalt, both also show a strong depletion early in weathering. Both elements may be released from basaltic glass, but magnesium is mobilised principally from weathering olivine and pyroxene. Sodium is released during the dissolution of plagioclase feldspar.

Silica is not as strongly leached from the profile as calcium, strontium, potassium, rubidium, magnesium and sodium. Although silica is mobilised during the breakdown of basaltic glass and silicate minerals, it is also incorporated into neoformed clay and other secondary minerals. For this reason, silica shows a progressive depletion with increase in weathering, rather than rapid early depletion.

Copper may show a small relative enrichment early in weathering but thereafter shows relatively strong depletion. Copper is present in basalts in very low concentrations. Minor amounts may be enclosed in ferromagnesian minerals but often copper is present in very fine grained disseminated copper-sulphides (chalcopyrite) in basalts. Initially these minerals are enclosed in other phases and hence are not released until the host mineral breaks down. Once sulphides are released into an oxidising environment, copper is mobilised. Copper appears to be strongly adsorbed onto iron oxyhydroxides in the weathered material, and may be relatively enriched, until, with increased weathering copper is depleted from the profile.

Zinc and vanadium both show enrichment early in weathering because they are largely enclosed within relatively resistant phases (e.g. magnetite). This enrichment occurs due to the concentration of resistant phases as a result of the reduction in mass (and volume) during the weathering of basalt. Eluviation of these resistant phases may result in their concentration in fractures and voids within the weathering profile. As weathering proceeds, the break down of resistant iron oxides allows slow depletion of zinc and vanadium.

Chromium and nickel are both released during the dissolution of olivine which occurs early in basalt weathering. Chromium is predominantly enclosed within the olivine in fine grained blocky grains of chrome-spinel, while nickel is present in the silicate. Cr-spinel may be lost from one part of the profile and concentrated elsewhere as a result of eluviation, a process similar to that effecting resistant iron-oxides. Nickel may be taken into or adsorbed onto secondary products (e.g. hematite, goethite). Hence chromium and nickel are usually enriched in moderately weathered basalt. Later in weathering, the elements show a small but progressive decrease in abundance.

Total iron (Fe) concentration maintains a relatively constant value, but when mass changes for FeO and Fe_2O_3 are compared FeO shows strong early depletion and Fe_2O_3 shows strong early enrichment. This reflects the oxidation of Fe^{2+} to Fe^{3+} during weathering, and the consequent fixing of iron in the weathered material.

Manganese (Mn) is released from ferromagnesian silicates during weathering, and in basalts most of the manganese is present in olivine, an early weathering phase. Manganese may be progressively leached from the profile if it is in the mobile form Mn^{2+} but it may oxidise to Mn^{4+}, which is relatively insoluble, and hence precipitate within the weathering material. This manganese precipitation frequently takes the form of a black manganese-rich coating on exposed surfaces, indicating that the manganese-oxide has precipitated from the weathering fluids.

Cerium is released during the dissolution of apatite and to a lesser extent from the break down of pyroxene, olivine and plagioclase feldspar. Because cerium may be fixed in the profile during weathering as a result of the oxidation of Ce^{3+} to Ce^{4+}, it is believed to behave similarly to manganese, and is sometimes associated with manganese coatings in the weathered material. However, cerium may show strong anomalous enrichment, and in samples where this occurs manganese does not show similar enrichment. The oxidation of cerium during weathering may fractionate this element relative to other rare earth elements, which are generally readily leached from the profile.

In samples where cerium shows significant enrichment lanthanum also shows anomalous enrichment, and in some cases lead is enriched, but to a lesser degree. These elements can combine with phosphorous released from the weathering of apatite, to form secondary resistant phosphates of the plumbogummite group.

In the majority of samples lanthanum and lead are relatively readily leached during weathering, although small amounts may be adsorbed onto secondary clays and iron or manganese oxyhydroxides. Phosphate is principally derived from the dissolution of apatite and is present in basalts in very small quantities. In general phosphate is relatively rapidly depleted during weathering. Because the dissolution of apatite in acid fluids is more rapid, there is a correlation between kaolin rich deeply weathered profiles (acidic krasnozems) and the strong depletion of phosphate.

Barium shows anomalous enrichment in a number of samples similar to the enrichment observed for cerium, lanthanum and lead. This may be explained by the presence of fine grained $BaSO_4$ in incipiently weathered basalt.

Thorium and uranium are released during the weathering of apatite, and later in weathering may be released from metamict zircon. Th may show relatively strong enrichment in moderately weathered basalts, mostly as a result of incorporation into secondary weathering products. Uranium, in contrast, appears more readily leached than thorium. A small enrichment in some relatively strongly weathered samples may be attributed to the presence of a resistant Th and U bearing phase, probably zircon.

Conclusions

Because we can monitor the change in element concentration at different levels within a profile, observations can be made regarding progressive element concentration or depletion with weathering, that is, map progressive change in concentration of a given element, or group of elements within a profile. This also enables assessment of the assemblages of secondary minerals which are most likely to host certain economically significant element concentrations.

An understanding of the physicochemical conditions that lead to concentration of elements, and at what level this occurs in the profile has important economic significance. It is also important to have some concept of what concentration or depletion trends are "normal" for a given rock type in a particular climate regime, so that anomalies might be recognised. Some enrichment as a result of weathering may lead to high concentrations of an element in the weathering profile in localities where the protolith is not specifically enriched with respect to this element. This technique may enable the exploration geologist to predict which elements are likely to be concentrated at different stages of weathering and which phases will be preserved in the most weathered portions of the profile.

The graphical isocon technique, although used in the past primarily in the study of metamorphic and metasomatised rocks, is an appropriate technique to use in evaluating element enrichment and depletion and mass loss as an indication of degree of weathering, in weathered rocks. However, careful petrographic work and where possible, X-ray diffraction must be carried out to enable correct interpretation of the graphs produced. The graphical isocon technique is superior to other weathering indices in that it provides an internal check on the degree to which "immobile" index elements have remained immobile. The use of this technique has enabled better understanding of element mobility in weathering basalts and hence may be used to interpret likely element pathways in other rock types.

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Ferruginous lag geochemistry on the Yilgarn Craton of Western Australia; practical aspects and limitations

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Keywords: lag, gold, surficial geochemistry, multi-element
geochemistry, regolith, Western Australia

Introduction

Lag is a surface veneer of diverse fragments that includes, in deeply weathered terrain, ferruginous concretions. Ferruginous lag is common in the Yilgarn Craton and is particularly abundant over mafic and ultramafic rocks, where it concentrates by residual accumulation caused by landscape reduction, having been brought to the surface by churning or bioturbation and dispersed laterally, largely by sheet wash. Thus, lag may represent either the underlying material, largely-removed laterite or other cover. It has been used extensively and successfully as a geochemical sample medium in the search for Au and base metals (Carver *et al.*, 1987).

The geochemistry and other attributes of lag-covered surfaces above the Bottle Creek, Beasley Creek and Lights of Israel Au deposits were studied as parts of CSIRO/AMIRA Projects 240, 241, 240A and 241A, prior to mining. The study sites provided a range of lag-covered regolith situations. Bottle Creek has a complex terrain with a relatively complete, though partly obscured, laterite profile at the Emu Au deposit, grading to areas stripped to saprolite and buried beneath sheetflood colluvium-alluvium and fluvial gravels at the VB-Boags deposits. A partly-truncated profile at Beasley Creek, complete with a partly preserved lateritic duricrust and upper saprolite, protrudes through surrounding sheetwash colluvium-alluvium. Drilling and mining also revealed a palaeo-channel, filled with Permian glacial debris. Most truncation has occurred at Lights of Israel, where the lower saprolite is partly covered by fluvial gravels and all is mantled by a thin, calcareous soil. Beasley Creek lies well to the north of the Menzies Line (Butt *et al.*, 1977), Bottle Creek lies very close to this important environmental dividing line and Lights of Israel is located to the south.

Lag characteristics related to regolith and bedrocks

The outward appearance of lag gives clues to the nature of the underlying regolith. Where the lag consists of light brown to yellow-brown nodules, granules and pisoliths, complete with cutans, the underlying regolith is probably lateritic duricrust. Where the lag consists of brown ferruginous saprolite and dark, hematite- and goethite-rich nodules and granules, there is probably underlying saprolite. Both these lag types are monomictic. Where the lag is polymictic, the underlying regolith is probably transported (Anand, 1993).

Internal fabrics of lag fragments at all three sites have been shown to have potential for recognition of underlying rocks, although interpretation of lag fabrics is complicated by saprolitic and pedogenic retexturing of various kinds (Robertson, 1994). In general, fine lag (1-10 mm) is closely related both texturally and geochemically to the coarse soil fraction (>1 mm), from which it was derived.

Chemical and mechanical dispersion

Chemical dispersion of Au and other elements took place in the upper ferruginous horizons of the residual regolith before these ferruginous materials were incorporated in lag. Gold and As in particular were dispersed this way and anomalies in lateritic residuum and mottled zone will reflect this prior to further, physical dispersion as lag.

Once lateritic nodules have reached the top of the saprolite or the lateritic duricrust, by downward weathering of the landscape, they are either directly weathered out on the surface as a lag or are incorporated in soil, hardpan and calcrete.

Vertical, mechanical dispersion takes place in the soil by erosion of fine particles by wind and water, by the burrowing action of ants, termites and larger animals, by the plucking action of tree roots and by clay eluviation. Lateral dispersion of lag at the surface takes place by the action of wind and water; the finer lag fractions being more widely dispersed.

Significance of magnetic and non-magnetic components

Some particles of fine lag are in part magnetic due to a variable content of maghemite, probably largely generated by heating from bush fires. Magnetic separation of this material in the field or laboratory yields a very consistent ferruginous material which has *analytical* advantages by providing a consistent matrix. This practice was assessed to determine if there were any *exploration* advantages in using complete, magnetic or non-magnetic lag materials.

Petrographic examination of material from Beasley Creek showed that the magnetic material, which makes up about 20-40% of the lag, consists of dark, compound granules of hematite and maghemite with minor goethite. The largely non-magnetic material (maghemite-poor) consists of hematite and goethite granules, red-brown and yellow-brown granules of hematite- and goethite-stained clay, fragments of quartz and calcrete. Close to mineralisation, a very small but geochemically very important component of cellular gossan may occur in the lag; *this is entirely non-magnetic.* Gossan fragments from Bottle Creek were also non-magnetic.

Geochemical analyses of materials from Beasley Creek showed that, for Au, there is little difference between the magnetic and the non-magnetic materials. However, for the important pathfinder elements (As, Sb, Cu, Se, Zn), the anomaly is contained almost exclusively in the non-magnetic fraction. The gossanous material contains these elements in elevated proportion. These elements showed a slightly improved signal to noise ratio in the non-magnetic samples compared to the complete lag. As the non-magnetic component made up about 60-80% of the total sample, only a slightly improved performance would be expected by analysing it separately. Thus, it seems there is nothing to be gained and much to lose by using magnetic lag fractions in geochemical exploration in the Yilgarn.

Exploration significance of lag size fractions

Both coarse and fine lag are effective sampling media but the very nature of the coarse lag (10-50 mm) invites representativeness problems, unless very large samples are taken. Coarse lag tends to have lesser lateral dispersion, due to its resistance to aeolian and sheetwash action. If the representativeness issue can be minimised, by collecting several kg of sample, which is tedious and may not be possible at all sites, it could be used for follow-up work. At Beasley Creek, spikes of up to 12 ppm Au closely defined the location of the ore subcrop in the coarse lag. Generally, fine lag is to be preferred.

Regolith-landforms, anomaly sizes and sampling strategy

Lag sampling on a 1 km triangular grid, covering a broad region around Emu and VB-Boags at Bottle Creek was effective in detecting a large (>300 m) As and a smaller (>150 m) Au anomaly in areas underlain by lateritic residuum and very thin colluvium around Emu. These anomalies are truncated by areas of colluvium-alluvium covered plains and alluvium-filled drainages, despite the presence of the VB-Boags deposits in these areas. Slightly more detailed sampling on a 0.5 km triangular grid produced very similar results. It was only very detailed sampling on a 0.1 km pattern or less that was able to detect very small anomalies that occurred where the colluvial-alluvial cover was locally particularly thin (0.1-0.5 m) over VB-Boags. Very restricted Au anomalies were also found in lag at Lights of Israel, where there has been considerable stripping of the regolith.

Lag geochemistry is effective in relict regimes, particularly where the lateritic duricrust subcrops beneath a thin, stony soil. In contrast, the effectiveness of lag geochemistry is severely limited in depositional areas, by the thickness of the transported veneer and the ability (or inability) of bioturbation to bring geochemically anomalous material to the surface. This is made more difficult where the layer of colluvial-alluvial sheetflood debris has been silicified. Sporadically, where this transported veneer is extremely thin, the lag shows a few indications of mineralisation. Where saprolite is overlain by narrow channels, filled with fluvial gravels, geochemical signals are completely prevented from becoming incorporated in the lag.

Influence of orebody pathfinder suites

The success of multi-element lag geochemistry is very dependant on a useful pathfinder element suite characterising the primary mineralisation. Some orebodies are very rich in pathfinder elements (Beasley Creek (As, Cd, Cu, Mo, Pb, Sb, W, Zn), Bottle Creek (As, Sb, Pb)); in contrast, others are particularly poor (Lights of Israel).

Implications for exploration

- Lag sampling is very effective in areas of relict regimes, particularly where lateritic duricrust subcrops beneath a very thin soil. It is also effective where there has been regolith stripping.

- The scale of a lag sampling pattern needs to be adjusted to suit the degree of regolith preservation; use broadly spaced samples where the regolith profile is complete or nearly complete and close-spaced sampling where there has been significant regolith stripping.

- The success of lag sampling in areas of colluvial cover is highly dependent on a very thin cover and on the ability of soil turbation processes to bring anomalous material to the surface; it is therefore not recommended and should be replaced by sub-surface sampling.

- Fine lag may be swept from the surface or the equivalent coarse fraction of the soil may be sieved on site, where lag is not well developed. If coarse lag is used, sufficient sample needs to be collected to ensure representativeness; fine lag is to be preferred.

- Multi-element analysis for at least As, Au, Bi, Cd, Cu, Pb, Sb, W and Zn of complete lag is recommended. Use of a magnetic fraction is not recommended, particularly if any reliance is to be placed on pathfinder elements other than Au. The complete lag is to be preferred.

Acknowledgements

The support of the sponsors of CSIRO/AMIRA projects 240, 240A, 241 and 241A is acknowledged. In particular, Aberfoyle Resources Ltd, Western Mining Corporation and North Exploration are thanked for access to their properties at Lights of Israel, Beasley Creek and Bottle Creek respectively.

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Geochemical dispersions in the deep regolith at Beasley Creek, Reedy and Mt Percy

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Keywords: Gold, weathering profile, dispersion, multi-element geochemistry, regolith, Western Australia

Introduction

The lateral and vertical distributions of gold and a wide range of other elements in the regolith close to Au mineralization were investigated at Mt. Percy (Butt, 1991), Beasley Creek (Robertson 1991) and Reedy (Robertson *et al.*, 1990). Duplicates of grade-control samples were obtained from Mt. Percy, spot samples were taken from the pit wall at Reedy and a drill fence was sampled at Beasley Creek.

Geology, geomorphology and primary geochemistry

Mt Percy is situated relatively high in the landscape, in a region showing only a few tens of metres of relief. An almost complete lateritic regolith is capped by duricrust. Bedrocks consist of chlorite talc carbonate rocks and porphyries with strong fuchsite-carbonate alteration along their contacts. Beasley Creek typifies a partly truncated regime, with a partly preserved duricrust and upper saprolite protruding through a blanket of sheetwash colluvium-alluvium. Drilling and mining revealed a palaeochannel filled with Permian glacial debris. Bedrocks consist of a relatively steeply dipping phyllite host in amphibolitic mafic-ultramafic wallrocks. The Rand pit at Reedy lies on a stony, erosional plain, from which the ferruginous upper horizons of the regolith have been stripped. Upper saprolite is thinly covered with a veneer (<1 m) of ferruginous, gravelly colluvium-alluvium. Bedrock consists of near vertical Au-bearing mica schists set in metamorphosed mafic-ultramafic schists, with minor carbonaceous schists intruded with quartz-porphyry pods.

Reedy and Beasley Creek lie well to the north of the Menzies Line. Mt Percy is located to the south of this important environmental dividing line (Butt et al., 1977).

The pathfinder elements, As, Ag, Sb and W, accompany Au mineralization in differing abundances at each site. Copper, Pb, Zn, Mo, Bi and Sn occur sporadically, perhaps regionally associated with sulphide mineralization; Te is present at Mt. Percy. Increased abundances of K and Rb reflect muscovite (or fuchsite) in alteration zones but also occur in unmineralized rocks. Although most deposits are enriched in Ba, so too are other rocks such as felsic porphyries.

Gold

At Mt Percy, where the profile is mostly complete, there is a widespread zone of Au enrichment close to the surface, within lateritic duricrust and gravels and in overlying residual soil. This has been mined as as 'lateritic ore', although much of the Au is associated with pedogenic carbonates. Where the lateritic horizon has largely been eroded (Beasley Creek and Reedy), remnant gravels retain the enrichment as an anomaly detectable by lag sampling.

A leached zone, depleted in Au (<100 ppb) is present in the upper, clay-rich zones of the regolith developed over primary mineralization. This is most evident at Mt. Percy as a 5-10 m thick zone beneath the ferruginous horizon. Depletion is less evident at Reedy, possibly due to Au preserved within quartz, and at Beasley Creek. Such depletion is an important feature of the regolith over much weathered Au mineralization in Western Australia, in places extending to 40 m depth. If the possibility of its existence is not recognised, it can cause a substantial barrier to exploration.

Supergene enrichment has occurred within the saprolite over the primary mineralization and wallrocks at Mt. Percy but not at Beasley Creek and Reedy. Most Au in the saprolite is secondary, indicating remobilization and homogenization of Au.

Elements associated with mineralization: S, Ag, Te, As, Sb, W, Tl, Ba, K, Rb

Each element behaves differently during weathering and none has a distribution similar to that of Au. Sulphides are readily weathered and S is deeply leached, except where present as barite or concentrated as secondary alunite and gypsum. Silver and Te are also generally strongly leached and abundances are commonly too low for dispersion patterns to be detected. However, Ag appears to be retained through much of the profile at Beasley Creek (0.5-1 ppm), possibly with some depletion in the upper saprolite and dispersion into the mottled zone and the hanging wall duricrust. Secondary Ag halides occur in the lower saprolite at Mt. Percy.

Arsenic becomes homogenised and concentrated in the regolith, particularly in Fe oxides, and is dispersed laterally in lateritic gravels, duricrust and lag. Antimony and W, which have low abundances at Reedy, are residually concentrated within the regolith over the mineralization and alteration zones, with anomalies extending into barren wall rocks high in the profile. Antimony, W and As are retained in the Au-depleted zone and are important pathfinders where leaching is extreme. Thallium was determined only at Reedy, where it seems to discriminate both ore and porphyry pods, with some lateral dispersion in the top 5 m of the regolith.

Barium, K and Rb are commonly, but not exclusively, associated with alteration zones around Au mineralization. Each is hosted by resistant secondary barite (Ba) and primary muscovite (Ba, K, Rb) that persist through the regolith, only being partly destroyed in the ferruginous horizon. They may provide a geochemical and mineralogical indication of a primary mineralized system, even within the depleted zone. In contrast, K and Rb, hosted by weatherable minerals such as biotite and feldspar, are leached deep in the profile.

Alkaline earth elements: Mg, Ca, Sr, Ba

Magnesium, Ca and Sr are all strongly leached at the onset of weathering, particularly where they occur as primary carbonates, and are almost totally depleted from some upper horizons. In places, these elements are concentrated at or close to the surface as pedogenic calcrete. In contrast, Ba reprecipitates as secondary barite when released from primary minerals and is relatively enriched through most of the regolith. Magnesium in the saprolite is commonly more resistent to weathering than Ca and Sr, due to occurrence as relatively resistant minerals such as chlorite and, particularly, talc.

The distributions of Ca and Sr at Mt. Percy are characteristic of semi-arid parts of the southern Yilgarn Craton. They have particular significance given the association between carbonate alteration and mineralization in many Archaean Au deposits and the enrichment of gold in horizons containing pedogenic carbonate. Such carbonates are absent at Reedy and only patchily developed at Beasley Creek although, here, some carbonate has also accumulated in the upper saprolite.

Base metals: Cu, Zn, Pb

There is no consistent enrichment of base metals with primary Au at any of the sites studied. The Pb abundance is greatest at Beasley Creek and a narrow zone of high values (100-150 ppm) in the surficial mottled and clay zones extends laterally for over 400 m down slope to the west. This dispersion is reminiscent of that at Teutonic Bore (Greig, 1983), although this was at 20 m depth.

Rare earth elements: Y, La, Ce, Sm, Eu, Yb, Lu

The distributions of these elements have a number of general characteristics in common, with some variations corresponding to whether they are "light" (*La, Ce, Sm*) or "heavy" (*Eu, Yb, Lu* *and Y*). These variations probably relate to the relative resistance to weathering of primary host minerals having different REE signatures. Discrimination between lithologies, using REE abundances is maintained in the lower saprolite, but light REE, in particular, are strongly depleted in the upper saprolite and clay-rich horizons. This depletion continues to the surface at Reedy and Beasley Creek but, at Mt. Percy, where the lateritic profile is essentially complete, there is some concentration of the REE in the lateritic duricrusts and gravels. Nevertheless, this concentration is greater for the heavier REE elements, particularly in the massive duricrust over the talc chlorite ultramafic rocks. Lateral dispersion and enrichment of REE is possible at Reedy.

All REE at Mt. Percy are enriched in the lower saprolite, where there is an increase in hardness and porosity. Maximum enrichments (80-110 ppm La, 80-130 ppm Ce, 10-22 ppm Sm and 2-5 ppm Eu) occur in the weathered porphyries and extends laterally into the weathered ultramafic wallrocks. The ore host rocks at Beasley Creek are indicated by high concentrations of La and Ce, which might constitute pathfinders for these units. However, there is no obvious relationship between REE and mineralization.

Implications for exploration

These multi-element dispersion patterns have exploration implications for Au and other commodities. At local to sub-regional scales, Au is one of the best indicators of Au mineralization, despite (or perhaps because of) its chemical mobility during weathering. However, it is vital that sampling takes account of the distribution of Au in the regolith; in particular, the accumulation of gold in calcareous and ferruginous surface horizons and its probable depletion for 5 to 20 m below them. Thus, sampling must be accurately directed and data interpretation depends on the horizon sampled. Other pathfinder elements commonly confirm Au mineralization but they become essential where Au has been depleted, is patchily distributed or where samples have been derived from an alteration zone rather than from mineralization.

Primary and supergene Au mineralization are indicated by broad Au anomalies in lateritic duricrusts and in lag and soil derived from them. These anomalies are comprised of (i) primary and (mostly) secondary Au associated with Fe oxides and presumably accumulated during lateritic weathering and (ii) principally in the south of the Yilgarn Craton, secondary Au associated with pedogenic carbonates and accumulated during recent aridity. Mineralization is also indicated by high concentrations of other ore-associated elements in these surface horizons, principally W, As and, less commonly, Sb, but only As may have wider or more consistent dispersion haloes than Au. Barium, K and Rb contents give a surface expression to alteration zones, commonly wider targets than mineralization itself; K also offers potential for detection by radiometric surveys. However, these alkalis are not exclusively associated with mineralization.

The "depleted zone", present over most Au deposits in the Yilgarn Block, commonly occurs in the mottled, plasmic clay zone and upper saprolite. The location and thickness of the depleted zone varies, so that, in some deposits, one or more of these horizons may be depleted whereas, in others, they may be enriched. At Mt. Percy, the Au content of the mottled zone is depleted and the upper (clay) saprolite is enriched, contrary to the situation at Boddington (Davy and El Ansary, 1986). At sites where the regolith has been truncated and the ferruginous horizon is absent, the depleted zone commonly outcrops, or subcrops, beneath transported overburden. The depleted zone is not well developed everywhere (Beasley Creek) but its common occurrence demands that care must be taken to avoid sampling within it. The Au contents are generally <<100 ppb, even where quartz veins host mineralisation, and give little or no indication of the underlying mineralization. However, it is important to note that the other ore- and alteration-associated elements (Sb, W, K, Ba and, to a lesser extent, As) remain throughout the depleted zone; they would be expected to be anomalous in soils developed from Au depleted material in truncated regoliths, even if Au contents are near to background. If pedogenic carbonates are present, Au depletion may be offset by surface enrichment.

Gold in the saprolite beneath the "depleted zone" is generally present at abundances similar to or greater than those in the fresh rock. Lateral dispersion and concentration of secondary Au commonly occurs at one or more levels, enhancing the weathered expression of the primary mineralization and, commonly becoming an exploitable resource in its own right. The abundances of elements associated with Au mineralization are very variable, so that there are no universal 'threshold' values. Compared to the primary mineralization, element distributions (including Au) in the saprolite are more homogeneous, due to dispersion and reprecipitation by weathering. In general, dispersion and increase in size and coherence of secondary anomalies over primary distributions are:

$$S > Ag, Te >> As > Sb > Au > W > Ba, K, Rb$$

Arsenic, Sb and W may give wider expression to mineralization in saprolite zones in which Au has not been dispersed, whereas Ba, K and Rb indicate the broader target of an alteration zone. Silver, Te and S are very mobile and are generally leached to background abundances.

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EDUCATING EXPLORATIONISTS IN A REGOLITH DOMINATED CONTINENT

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Keywords: Regolith, Education

Introduction

How many exploration geologists learned anything of soil science, geomorphology or hydrogeology as part of their undergraduate degree? Who studies weathered rocks in their course? Few or none! What does a typical geology undergraduate degree program in Australia contain (and most other places as well)? What, particularly in Australia where regolith dominates our landscapes, should it contain in the way of Earth Science training? See Table 1 for the answers!

Table 1

Year/ Semester	Traditional program[1]	Future program[2]
1/1	Geology IA	Earth Dynamics & Materials
		Chemistry
		Mathematics
		Biology
1/2	Geology IB	Landscapes & Materials
		Physics
		Statistics
		Scientific Communication
2/1	Mineralogy	Mineralogy and Petrology
	Petrology 1	Soil Science
	Sedimentology 1	Sedimentology, Facies & Stratigraphy
		Geomorphology
2/2	Structural Geology I	Tectonics and Structural Geology
	Palaeontology I	Resource Geology
	Economic Geology I	Engineering & Hydrogeology
		Geochemistry
3/1	Petrology 2	Applied Geochemistry
	Sedimentology 2	Mineral Deposits
	Coal & Petroleum Geology	Remote Sensing
	Australian Stratigraphy	Ecology
3/2	Invertebrate Palaeontology	Exploration in the Regolith
	Tectonics & Continental Evolution	Australian Landscapes & Regolith
	Ore Deposits	Australian Stratigraphy
		Industrial Minerals
Hons.	"The Geology of the Area" **OR** "Cleavage types in an old alluvial gold mine at Woop Woop"	Work on a project with the exploration industry, CSIRO or Soils etc. - Applied and professional.

Some examples; real and imaginary

Because of the nature and complexity, as well as because of our general lack of knowledge about it, any regolith undergraduate program should cover a wide range of topics to equip the new (and older)

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[1] This program is fictitious but of the ilk.
[2] Also fictitious, but wouldn't it be lovely!

practitioner with sufficient background to "think regolith", tussle with problems, and exploit opportunities.

Northparkes

At its Northparkes project North has recently begun to mine porphyry copper gold hosted in intermediate Ordovician volcanics. The deposits are buried beneath a variable thickness of regolith but in places it is up to 30m. Initially, the company collected and analysed samples from RAB refusal depth to locate mineralisation and obtain information on bedrock lithology and alteration. All the samples from the surface to RAB refusal were retained in storage.

Later, on re-examination of the samples, it was discovered that many geochemical anomalies defined by the RAB drilling were also present in the brown earth soils of the transported overburden. The overburden consists of several to ten metres of fine-grained alluvium often containing well rounded quartz granules. With the excavation of the open pits the whole regolith sequence was exposed, revealing a few previously unexpected features including the channel-like feature shown in figure 1.

Some of the many questions which arise from this example are:

1. how do we determine whether the channel-like body is a channel or a fault slice of weathered bedrock? Both fill and weathered bedrock seem to consist of the same materials;
2. how is it possible that, if the channel-like feature is indeed a channel, it too is deeply weathered, for in appearance it is clearly is weathered an intensely as bedrock;
3. if the overburden is transported (and it contains quartz granules) how is it possible that it reflects geochemical anomalies in the fresh bedrock?

To answer question 1 we need to know some geomorphology, sedimentology, structural geology and about weathering; to answer 2 we need to know about weathering and the formation of new minerals as bedrock is altered, and for 3 a knowledge of alluvial processes, soil science, plant ecology and functioning, plant nutrient cycling and chemistry are essential.

For those who are asking "well what's the answer", here are a few hypothetical ideas for testing:

1. although the material is very similar, derived mainly from weathered volcanics, the channel fill contains a small proportion of silt-sized quartz, therefore it is unlikely to originate entirely from the volcanics. These channels are probably part of the northward drainage in to the Eromanga Basin during the Mesozoic prior to the downwarping of the Murray Basin, abandoned as the Murray Basin to the south was depressed;
2. there have either been two phases of deep weathering in response to climate change as suggested by McGowran (1994), or weathering has been continuous, but the removal and filling of the channel took time and weathering going on on the adjacent bedrock profile is not represented in the channel (Taylor 1994); and,
3. the presence of quartz granules and small pebbles in the overburden clearly shows it to be alluvial, derived from other than the local bedrock. The most likely way for anomalies to be reflected is by bio-pumping. Pit face exposures strongly suggest this when palaeo-watertables show clear cones of depression, probably related to large trees using the water during an arid climatic phase. This process has brought trace elements from the saprolite to the transported overburden.

Another interesting aspect of undertaking geochemical studies in the upper regolith (soil) is illustrated well by the red-brown earth soils which occur around Parkes. Figure 2 demonstrates one characteristic of these soils formed in the transported overburden; pH increases dramatically down profile. This change in pH through the profile will have an effect on the parts of the soils you would sample for different elements.

Surficial stratigraphy

This an hypothetical example, but it illustrates some of the reasons that an understanding of sedimentary, geomorphic and geochemical processes, and the interpretation of surficial stratigraphy (many would say Quaternary terrestrial stratigraphy) are important tools in exploration.

In figure 3 three valleys exit an escarpment and deposit alluvial fans which coalesce to form a wedge of fan deposits (bajada) along the escarpment foot. Assume that the middle valley is transporting traces from an ore body exposed in that valley but not the others. Which stratigraphic units of the sedimentary pile will be worth investigating and which not? Or if the traces have been found from downstream stream sampling how can the number of samples to be analysed be reduced by an understanding of the surficial history/stratigraphy (figure 4)? Identification of stratigraphic units 1A & B in the sediment pile will potentially save large exploration dollars. To achieve this a detailed knowledge of surficial depositional processes and stratigraphy, and soil stratigraphy and formation will be necessary.

Mineralogy & Petrology

How many students get training in clay mineralogy? Most can optically identify lawsonite or andesine and tell a shonkinite from a syenite, but can they describe and name clays, Fe^{3+} oxides and describe systematically a weathering profile? No! While not denying the need to understand primary mineralogy and petrology, few of the extreme details taught are ever needed. Any course on mineralogy and petrology must teach the mineralogy and petrology of the regolith. Most of the crust is made up of about 10-15 major minerals which when combined make up a limited range of rocks, so perhaps there is an argument to reduce the 'traditional igneous and metamorphic petrology taught and increase the amount taught about the part of the Earth we see; the regolith.

Most would agree that we think we understand the chemistry of weathering reasonably well, but equally important is the understanding of the physical transformations which occur during weathering if we are to understand in any meaningful way the processes of trace element release and mobility. Recent work in the Centre for Australian Regolith Studies at ANU has clearly shown how important some of these physical processes are important. When many silicates weather they dissolve, form an amorphous phase which in turn crystallises to produce the new-formed regolith minerals we see. It is also during this process that trace-elements are released, mobilised and perhaps concentrated. Feldspars for example weather by dissolving, forming a gel of different composition to the original and this gradually crystallises to form clays of a different composition again (figure 5). The implications for this in terms of understanding the release and mobilisation of elements during weathering are obvious. As this research progresses opportunity will exist to understand better where, in varying chemical environments, to search for particular elements.

Discussion

Obviously the proposed future program is broader, more applied and has fewer elective subjects than the traditional, but it does give a firm grounding in the basic sciences required for professional practice if not the depth the more traditional course does. It is clear that in both cases postgraduate experience is required, whether that is achieved through professional experience or formal education or training. It has been that graduates "learn on the job" much of what is required to practice. A problem with this approach arises when it comes to landscapes and regolith evolution and chemistry. Few in practice currently have the knowledge to assist new graduates learn on the job. The option is formal courses and research at postgraduate level, and I suspect that as major ore deposits become more difficult to locate and regolith geology becomes increasingly important, which is happening to some extent, more students will undertake postgraduate education before practicing and more in practice will undertake more formal training in these areas. Until our knowledge and skill levels increase substantially there are few options.

Conclusion

If the scenario I outline is true then there needs to be a major rethink and shift in the basic education of Earth Scientists. This is hard work for the educators and so there is and will continue to be inertia, consequently change must be demand driven, which leaves the ball in the court of practitioners and managers of exploration programs. Having painted this scenario I think there is still room in the system (20+ universities) for the more traditional courses to continue being taught as we need some of the skills they impart to the profession, but not *everyone* needs them. Australia needs both at present.

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Figure 1

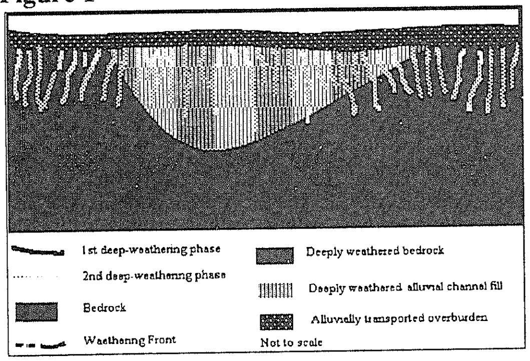


Figure 2

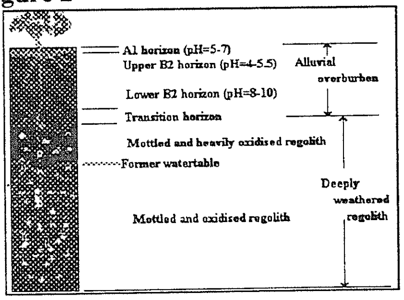


Figure 3

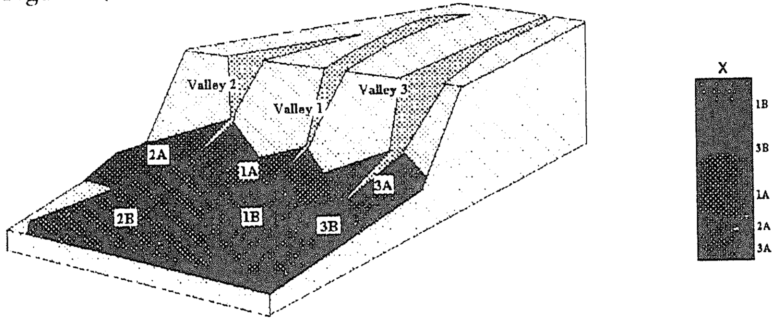
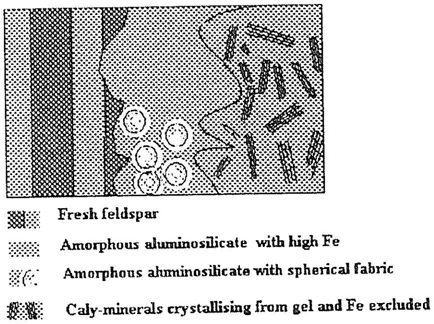


Figure 4

Figure 5



Advances in the interpretation of regional stream sediment geochemical data: Ebagoola, a case study

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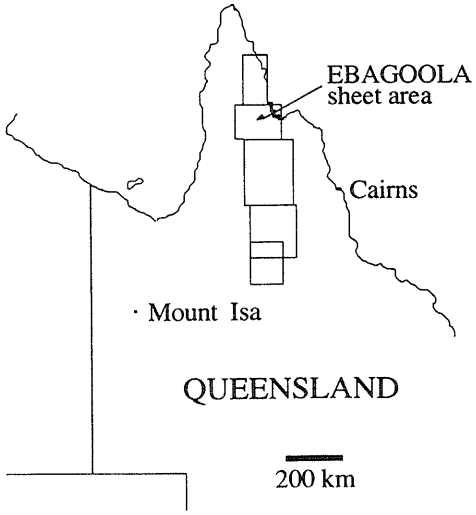
Keywords: geochemistry, stream, regolith, rock, GIS, Queensland

The Australian Geological Survey Organisation (AGSO) has been carrying out multi-disciplinary geoscientific mapping with the Queensland Geological Survey (GSQ) in Cape York Peninsula since 1990. Disciplines involved include geology, whole-rock geochemistry, geophysics (airborne magnetics and gamma-ray spectrometry), regolith mapping (regolith processes and landforms) and multi-element stream sediment geochemistry. Geochemical mapping activities concentrated on the Proterozoic-Palaeozoic igneous and metamorphic rocks of the Coen, Yambo and Georgetown Inliers in areas covered by the CAPE WEYMOUTH, COEN, EBAGOOLA, HANN RIVER, WALSH and RED RIVER 1:250 000 map sheet areas. A total of 3200 samples were collected from an area of approximately 47,000 km^2, and analysed for 40 elements.



The EBAGOOLA 1:250 000 sheet area (744 samples from 12,500 km^2) covers the centre of the Coen Inlier, including the Hamilton Gold and Mineral Field. The initial interpretation of the stream sediment geochemistry (Cruikshank, 1994; Cruikshank and Butrovski, 1994) was made using univariate and multivariate statistics and gridded images of the distributions of unprocessed element values and of statistically derived parameters such as factor scores, residuals (element values corrected for lithochemical contributions) and additive indices (Eggo et al, 1995). Overlays of geology (Trail et al, 1995), mineral occurrences and regolith landforms (Pain et al, 1994) were also used in the interpretation. Variability in the data can be explained by 7 factors with the most important being due to accumulation of resistant minerals such as monazite and xenotime in the sediment lode (Factor 1), Fe minerals in the bedrock and/or scavenging by hydrated Fe-oxides in the secondary environment (Factor 2) and the weathering of K-rich minerals in granites (Factor 3). Residuals for Cu, Pb, U and Zn, estimated by removing lithochemical contributions, have been calculated and show areas which are anomalous and may be prospective for economic concentrations of these elements. Similarly, additive indices derived from standardised values for elements characteristic of known styles of mineralisation have been estimated for gold, base metals, heavy minerals, porphyry copper, platinum and uranium mineralisation and show additional areas that may be prospective. The greatest potential appears to be for gold, base metals and tin, and several areas potentially prospective for these commodities have been delineated. The source of several tin anomalies was not obvious since they occurred over sedimentary rocks to the west of the inlier, which itself did not appear to contain any high-tin granites. However, some of the anomalies occurred near paleodrainage channels. Removal of the lithochemical Factor 1 high-lighted areas of high mobility U near known minor uranium mineralisation and an area draining a high-uranium granite.

The large amount of information generated in a study of this size and complexity (maps, images, etc) now is being managed and integrated in the Geographical Information System (GIS). The EBAGOOLA GIS has been developed as a test bed for the region, wherein spatially related datasets are being integrated and analysed to develop predictive models of regolith chemistry and lithochemistry to assist in the identification of mineralisation related geochemical features (Wilford et al, 1995). The GIS contains coverages for basement and general geology, whole-rock geochemistry, regolith type and landform, erosional activity and soil loss index, in-situ and transported regolith, drainage, airborne geophysics (as images) and stream sediment geochemistry as both images and drainage basin polygons. This is one of the most comprehensive geoscientific datasets of its type available for northern Australia.

Combining regolith-landform and geochemical data for mineral exploration is well established. In particular, CSIRO Division of Exploration and Mining has developed successful methods for selection of sample media at the prospect or mine site scale (e.g. Anand and Smith, 1993). It is clear that knowledge of regolith-landform environments (regimes in CSIRO terminology) can aid considerably in the interpretation of geochemistry at that scale. There are also suggestions that more regional information about landforms can assist mineral exploration (e.g. McFarlane, 1981). Our work extends these procedures to regional scales (1:250 000), and to other data sets in addition to geochemistry, regolith and landforms.

The stream sediment geochemistry data represent catchments of 10-15 km^2 (Cruikshank, 1994). The regolith-landform map (Pain et al, 1994) provides information about the nature of the regolith in each catchment (e.g. in place or transported, residual material or saprolite, degree of weathering). It also provides information about landform types which can be related to regolith-landform environments. Gamma-ray imagery, when combined with the regolith-landform and bedrock maps (Trail et al, 1995), can be used to assess the relative contributions of weathering and transported sediment to the surface materials of each catchment. With the addition of slope angles from digital elevation data, relative geomorphic activity can be estimated for each catchment. This in turn allows a more informed interpretation of the stream sediment geochemistry, and the potential of relating particular elements in stream sediments to particular parts of the source catchment.

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A Global Geochemical Database for Environmental and Resource management: recommendations for International Geochemical Mapping

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A report, describing the "why and how" of geochemical mapping, the reasons why a comprehensive quantitative database is urgently required, and why a global reference network is a necessary foundation, was published in January 1995 by UNESCO, Paris, as Earth Sciences Report No. 19. This report will be widely distributed to government agencies and academic institutions in most countries.

The report reviews the present status of geochemical mapping in all countries of the world, and the inadequacies and problems associated with existing databases. This review leads into a series of interlinked recommendations, which are developed around the establishment of a global network of geochemical reference samples; sample collection and preparation specifications; analytical requirements and standards; gamma radiation methods applicable to natural and man-made radioelements; and data management procedures. The final chapter considers the practical administrative and funding requirements which are implicit in the implementation of the recommendations on a global scale. An appendix contains information to assist readers in developing countries who may not have easy access to supplementary technical literature. Application of these recommendations will make it possible to assemble geochemical baseline data for all non-gaseous elements on a systematic global basis. A world geochemical atlas will be one of many possible products which can be derived from these data.

The following requirements summarise the essential prerequisites for a global geochemical database:

- commonly available representative sample media, collected in a standardized manner;
- continuity of data across different types of landscape;
- adequate quantities of the designated sample media for future reference and research requirements;
- analytical data for all elements of environmental or economic significance;
- the lowest possible detection limits for all elements;
- determination of the total amount of each element present, and
- tight quality control at every stage of the process.

The authors of this report believe that a Global Geochemical Database is a necessary and exigent investment for mankind. The cost of establishing the proposed reference network is estimated to be in the range of US$300-400 million, about equal to the cost of launching one Space Shuttle flight, of which there are seven or eight each year. This comparison indicates that, although establishing the reference network is expensive, it is not inordinately so with respect to other global monitoring activities. Acceptance of the project is primarily a matter of establishing its priority relative to other global data collection projects.

A summary of the principal recommendations will be open for discussion in an Australian context.

Removal of background processes controlling trace element variablity in -80# stream sediment geochemical data, Georgetown Region, Northeast Queensland, Australia

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Keywords: Image processing, NE Queensland, statistical methods, stream sediment geochemistry.

Extended Abstract

This poster session presents some results of a geochemical research programme undertaken by CRA Exploration Pty. Limited in collaboration with the Australian Geological Survey Organisation (AGSO, formerly BMR) with the aim of developing improved methods for managing and interpreting stream sediment geochemical data (Eggo, *et. al.,* 1990). The study utilised a total of 4,568 -80# stream sediment samples collected by AGSO over the Georgetown region, NE Queensland. The data comprise analytical results for As, Bi, Co, Ce, Cu, Fe, Mo, Ni, Nb, Pb, Rb, Sn, Th, U, W, Y and Zn.

Stream sediment geochemical surveys were undertaken by AGSO (then BMR) in the Georgetown region (Fig. 1) during 1972-73, 1974, 1976 and 1980 as an integral part of their Georgetown Project which was designed to aid metallogenesis and resource-potential studies in the area.

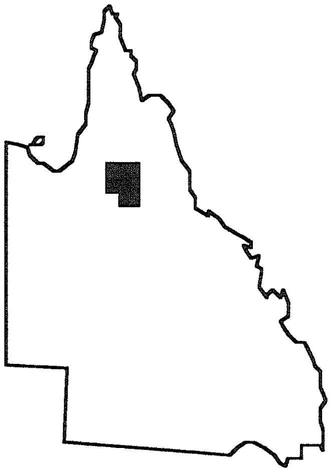

Fig. 1 Location diagram for the Georgetown region -80# stream sediment survey.

Orientation studies were discussed by Rossiter (1975), and survey parameters and techniques by Rossiter & Scott (1978). Raw geochemical data have been published by AGSO in map form (Georgetown, Forsayth, Gilberton 1:100,000 Sheet areas), microfiche tables (Georgetown, Gilberton, North Head-Forest Home, and computer tapes - all areas). A preliminary interpretation of the Forsayth data appeared in Rossiter & Scott (1978), and research by CSIRO into more advanced data manipulation and presentation techniques using the Forsayth data was reported to AMIRA (Craig & Green unpubl. 1982, 1983, 1984).

The initial steps in data analysis were undertaken by AGSO and included amalgamation and levelling of the data from the four individual surveys (Forsayth, 1974; Georgetown, Gilberton, 1976; and North Head-Forest Home, 1980), determination of what were termed "anomalous" levels for the consolidated dataset based on arithmetic and geometric means and standard deviations, and the manual plotting of "anomalous" drainage basin maps for each element at 1:250,000-scale. The areas thus defined were compared with the geological map and simple

interpretations of the observed relationships noted. Although elementary the data treatment was considered an important first step in indicating the range of information available from these data.

Utilising CRAE-developed procedures background concentrations for each element for the Georgetown survey were established using robust statistical techniques (*Trimmed, Hampel & Biweight* estimates) which are superior to traditional measures of central tendency when the data depart significantly from a gaussian distribution (Ellis & Steele, 1982). Highly anomalous maximum concentrations for many ore and pathfinder elements were identified in the data set and included (times background in brackets): 33ppm As (33x), 18ppm Bi (18x), 2490ppm Ce (26x), 286ppm Co (29x), 393ppm Cu (25x), 23ppm Mo (23x), 192ppm Ni (16x), 3210ppm Pb (128x), 742ppm Rb (7x), 924ppm Sn (314x), 2720ppm Th (118x), 93ppm U (23x), 81ppm W (27x), 905ppm Y (23x), and 3740ppm Zn (69x).

Multivariate statistical techniques employed to quantify inter-element relationships included correlation studies (Pearson, Spearman and Kendall) and principal components factor analysis. An association of Th, Ce, Y, U, Nb and W (Factor 1) is considered to represent uraniferous accessory minerals shed from acid igneous rocks and granitic lithologies and other heavy minerals such as scheelite. Cobalt, Ni, Fe, Cu and Zn (Factor 2) are strongly correlated and are related to the distribution of basic igneous rocks and to secondary iron enrichment. Factor 3, dominated by Rb, Pb and Zn, is tentatively considered to represent potential Pb-Zn mineralisation. An association of As, Bi, Sn, W and Nb is suggestive of epithermal-style gold mineralisation, possibly related to deep mantle magmatism.

Removal of background control on trace element abundances was accomplished by regressing the element of economic interest against factor scores interpreted to represent lithochemical or secondary environmental effects. The procedure yields residual geochemical values which reflect known mineralisation more effectively than the raw data. Confirmation of the statistical model was provided from geochemical images prepared using gridding & interpolation techniques developed at CRA Exploration Pty. Limited optimised to handle the highly skewed distributions and relatively random sampling pattern characterising stream sediment geochemical data sets.

Patterns for raw geochemical values are seen to be dominated by gross lithochemical variations in which subtle signatures related to known mineralisation are masked. Analysis of factor score maps and the residual data maps confirms that the derived variables reflect background processes and known mineralisation more effectively and identifies prospective areas that are not apparent in the raw data. It is therefore concluded that this generation of geochemical maps is most important for geochemical interpretation.

The advantage of using this approach is exemplified by a comparison of the geochemical maps prepared for raw Zn and corrected or residual Zn. Residual Zn, which has been corrected for lithology and scavenging, suppresses noise, enhances features related to known mineralisation and clearly identifies highly anomalous prospective areas which also coincide with structurally favourable zones.

An alternative approach is to standardise the data with respect to mapped geology by thresholding to local background levels. However, comparison of geochemical data from the Georgetown region corrected to local geological backgrounds with the regression-derived residuals shows the latter to be superior. It is concluded that correcting geochemical data with respect to mapped geology does not adequately account for samples with mixed geological provenance, fails to recognise secondary processes not related to mapped geology (e.g. scavenging) and tends to over-emphasise moderate geochemical values sampled from geological units that have inherently low geochemical backgrounds.

Reliable interpretation of multi-element geochemical data demands a multivariate approach. Principal component factor analysis, which allows identification of complex inter-element relationships in an efficient and quantitative manner, has been successfully applied to the Georgetown survey. The procedure allows recognition of distinctive geochemical associations, or factors, which are interpreted to be related to gross lithochemistry, secondary environmental processes and mineralisation.

Removal of geochemical variability resulting from background processes using principal component factor analysis followed by multiple regression yields residual geochemical values which are considered by the authors to reflect known mineralisation more reliably than raw element concentrations.

In the Georgetown region a number of target areas prospective for a range of mineralisation styles were recommended for follow-up work. Assessment was based on favourable geology, extensive geochemical dispersion patterns, coincident multi-element geochemical anomalism and "unexplained" concentrations of the ore elements as indicated by their high residual values computed from the regression studies.

The Georgetown study demonstrates that sophisticated statistical modelling of geochemical data successfully enhances geochemical trends and associations suggestive of mineralisation. In the Georgetown region, where there is good geological control, these techniques appear to be superior to traditional methods of interpretation. In other areas, where geological knowledge and control is poor, factor analysis followed by calculation of residuals using regression techniques is considered to have increased importance as a tool for interpretation.

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The uses of high resolution Digital Elevation Models in geochemical exploration and landform analysis

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A recent innovation is the computer generation of very high resolution digital elevation models (DEMs) by 'soft photogrammetry'. This increase in resolution (sub-metre precision), and areal coverage, has significant impact on geochemical sampling programmes and landform analysis.

In soil geochemical sampling programmes in very flat terrains, such as the Eastern Goldfields of Western Australia, the DEMs allow accurate estimation of slope and hence dispersion directions even in sheetwash areas. In stream geochemical programmes available software can be used to automatically generate stream networks and flow accumulation giving accurate measures of stream orders. Drainage divides of a given size can also be calculated and displayed along with the creek intersections i.e. likely sampling sites. This facilitates rapid and systematic coverage of stream sediment programmes.

Automated and supervised landform classification schemes have been developed using both the simple statistical transformation (SST) and the gray level co-occurrence matrix (GLCM) methods. The small pixel size (0.5-1.5 metres on the ground) of the DEM means that small scale landforms can be identified at 1:5000 and 1:10,000 scale.

The resulting classified maps can be used in conjunction with the height data from the DEM to reconstruct palaeo-surfaces and quantify the amount of incision and/or deposition.

Comparison of numerical methods applicable for identification of anomalous and background areas in geochemical exploration

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Keywords: geochemical exploration, geostatistics, gnostical theory, geognostics

Introduction

Geochemical data consist of two different components - spatial location (coordinates) and values of measured variables (eg. concentrations). The approach to the spatial component of the data follows from the theory of regionalised variables (TRV) (Matheron, 1963). Sample positions are reflected in the modelling of the variability of the data by way of, for example, the correlation function or semivariogram. They are then used in whatever weighting system is subsequently employed in the estimation process. Data anisotropy may be accounted for in such practice (gridding, kriging). The approach to the estimation of values of the studied variable follows from some form of information theory, for example statistics. Combination of both approaches builds a complex theory, which in the case of the TRV and statistics results in geostatistics.

The *Gnostical Theory of Uncertain Data* (GT) (Kovanic, 1986) has brought a new view of a datum which results in two main approaches to data treatment. New methods are based either on the *gnostical global distribution function* (GGDF) and are characterised by robustness; or they are based on the *gnostical local distribution function* (GLDF) and then they are flexible identifiers of local subsets.

Gnostical Theory Of Uncertain Data

GT was developed, because of a need for sensitive and/or robust algorithms for data treatment of small and disturbed data sets, for which other methods fail. Unlike statistics, GT grows from the theory of an *individual datum.* The starting point was discovered in the theory of measurement. Data are understood as products of a process, called *quantification*, where influences of the *ideal value* of datum and the *uncertainty* are involved. The reverse process to the quantification is the *estimation* and it is realised during data treatment.

Data understood thus are then composed of two elements and represented by a couple number. However, there is no essential difference between the mathematical structures representing the ideal value and the uncertainty, because the decision (what is the disturbing influence and what are we looking for?) depends on the aim of measurement. Thus, the full description of a datum requires a square matrix of the datum couple and its dual couple. These matrices are isomorphous with similar matrices which describe mass points in the special theory of relativity (Kovanic, 1986).

The analysis of the mathematical properties of data couples leads to significant results. The quantification process is described by operators belonging to the Riemann geometry. The estimation process is controlled by operators on the Euclidean geometry. It allows definition of substantial characteristics of an individual datum: *weight, irrelevance, distribution function, entropy growth and information loss.* All characteristics of individual data which have their parallel in statistical characteristics are consistent with them for small values of uncertainty. Studies of extremes of these characteristics proved the utility of the *ideal gnostical cycle*, which defines the theoretical minimum of information loss and entropy growth in the cycle - quantification and estimation. The ideal gnostical cycle has its parallel in the Carnot cycle of thermodynamics.

For description of the whole data set the characteristics of individual data have to be "combined." The gnostical composition law was inspired by the following features:

- matrix data structure is isomorphous with relativistic structure;
- quantification and relativistic phenomena operate in the same type of geometry (Riemannian);
- composition of data, errors and squares of errors in statistics is isomorphous with the composition of energy and motion in classical Newtonian physics and uses the same geometry (Euclidean);

- composition law in the special theory of relativity is represented by the law of conservation of energy and momentum.

Statistics grows from Euclidean geometry and Newtonian physics. GT respects that consistency between sciences as a new generation of information theory related to the relativistic paradigm. The result of additive composition of the weights and the irrelevances (equal to the law of energy-motion conservation) is the GGDF. This function is robust against outliers and external clusters. It is useful for robust estimation of data set location (central value), quantiles of expectation and testing of data set homogeneity. The GGDF has no parallel in statistics.

Another way of composition is allowed by the properties of the distribution function of an individual datum, which has the properties of Parzen's kernel. The GLDF is flexible and allows identification of local subclusters. At the same time it is robust at each point in respect to the data from other subclusters. This function has parallel in Parzen's non-parametric estimates.

Geognostics

In the above paragraph it was shown that GT closes the square built by Newtonian and relativistic physics and statistics. Statistics is parallel to Newtonian physics. The relativistic physics represents a higher generation of Newtonian physics. GT thus represents a parallel to the relativistic physics and a higher generation of information theory (compared to statistics). Similar ideas motivate an upgrade of geostatistics by a substitution of existing statistical characteristics by GT in the TRV. This approach to spatial data is sometimes called "*geognostics*".

Estimation Of Spatial Model

The most common task in the estimation of spatial models in exploration geochemistry is the interpolation of surfaces. The data from the soil survey in the Riverland (Brooker et al 1993) are used in three examples of possible methods. Samples were taken on an almost regular grid 75m x 75m. The analysed variable is the depth of the topsoil layer (Fig. 1). The examples are presented in the form of matrices of data, which can be consequently processed by an appropriate software package into contour, surface, and coloured/shaded maps.

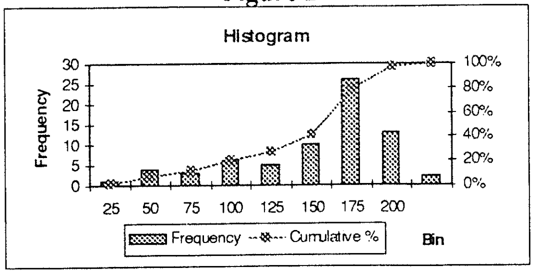
Figure 1

160	160	160	160	160	160	160	160	85	50
170	180	180	210	190	180	170	140	35	110
100	150	170	110	180	200	80	60	60	120
110	90	175	180	110	150	170	170	100	55
30	90	130	150	170	170	160	170	170	170
15	170	180	180	210	150	180	150	160	130
50	135	170	180	180	150	160	170	170	180

Data Analysis With Consequent Spatial Interpretation

The simplest approach leads to division of data into subsets of particular interest and plots and compares the locations of various subsets in the studied space. The most illustrative data presentations in statistics are the histogram and in GT the gnostical data density function (the first derivative of the gnostical distribution function).

Figure 2



The histogram (Fig. 2) shows that the sample is not homogeneous. The usual classifications on the base of quantiles of the normalised normal distribution is shown (Fig. 3). The integer values, the number of the standard deviation away from the arithmetic mean, are displayed. The arithmetic mean is equal to 143 and the standard deviation is 46.

Figure 3

1	1	1	1	1	1	1	1	-2	-3
1	2	2	2	2	2	1	-1	-3	-1
-1	1	1	-1	2	2	-2	-2	-2	-1
-1	-2	1	2	-1	1	1	1	-1	-2
-3	-2	-1	1	1	1	1	1	1	1
-3	1	2	2	2	1	2	1	1	-1
-3	-1	1	2	2	1	1	1	1	2

The GGDF of the sample (Kovanic, 1986) is not acceptable because it fits to the sample in less than 1% of all cases (Kolmogorov-Smirnov test (KST)). The gnostical local data densities (GLDD) for various values of the scale parameter (Kovanic, 1986) are plotted on Figure 4. The GLDDs for scale parameters (S) equal to 0.773, 0.5, 0.25 and 0.1 identifies 1, 1, 3 and 9 clusters. The GLDD for S=0.773 passed the KST at a

Figure 4

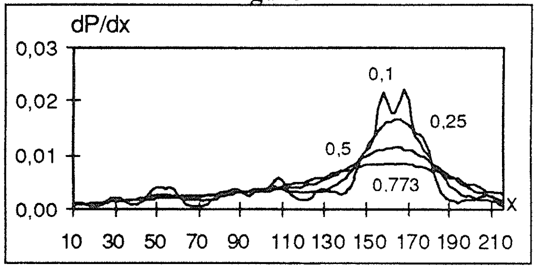
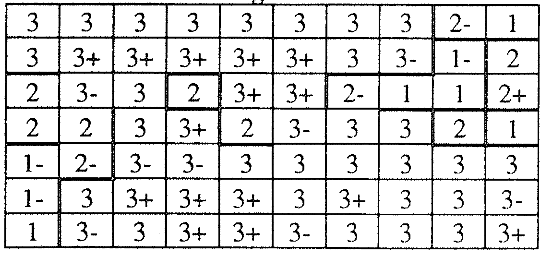


Figure 5



3	3	3	3	3	3	3	3	2-	1
3	3+	3+	3+	3+	3+	3	3-	1-	2
2	3-	3	2	3+	3+	2-	1	1	2+
2	2	3	3+	2	3-	3	3	2	1
1-	2-	3-	3-	3	3	3	3	3	3
1-	3	3+	3+	3+	3	3+	3	3	3-
1	3-	3	3+	3+	3-	3	3	3	3+

significance level of 1%, the others are in good fit on at least 50%, but the case of misfit occurs in at least 5% of such data samples. The GLDD for S=0.25 has three clusters with locations 55, 108 and 166. The intervals of typical data (ITD) are ⟨44, 65⟩, ⟨97, 118⟩ and ⟨ 158, 175⟩, respectively. Two minima divide the three clusters: 74 and 122.

The GLDD for S=0.25 is used in the division of data in Fig. 5. The numbers represent data from the related ITD. If a number is followed by a sign, it means that the corresponding value does not belong to the cluster, but is from an interval between the boundary of the ITD and the minimum of the GLDD. Any further decision about that data needs deeper analysis. However, overlapping of the ITDs and values in neighbouring cells allows recognition, if the data are from strictly different sets (lines between cells on Fig. 5). Such a feature defines discontinuities in the interpolated surface (faults, ruptures). No similar instrument in geostatistics exists.

Analysis Of Profiles

The approach with the next level of complexity involves one spatial coordinate and accepts data as a set of profiles (double line frame at Fig. 1). In the three examples the profile was filtered by a moving window method with width of the window equal to 5 cells. Data are plotted as boxes.

Figure 6

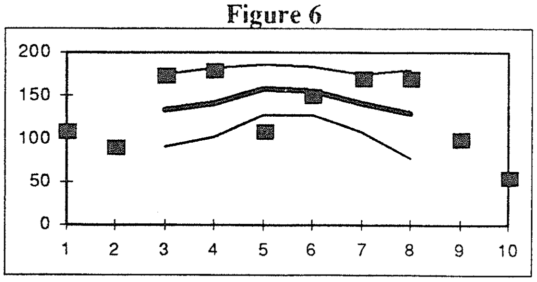


Figure 7

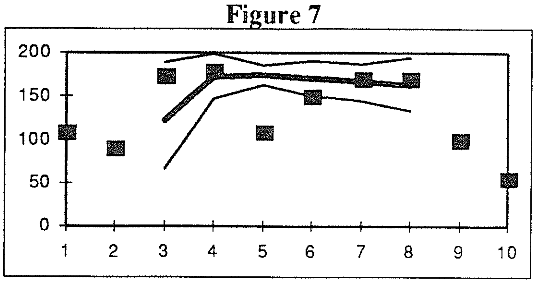


Figure 8

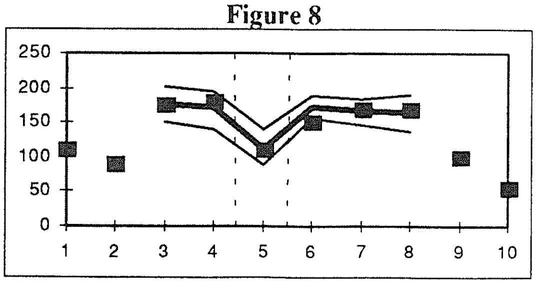


Fig. 6 shows the arithmetic mean (bold line) and the belt given by values of the arithmetic mean plus/minus one standard deviation (slim lines). It is seen that the estimates do not follow the data well.

Fig. 7 shows the location parameter for the gnostical global data density (GGDD) (bold line) and the ITD (slim lines). The estimate is close to the majority of data in the window. The belt is narrower and outluing data have low influence on the estimate. That is, the estimate is robust against outliers.

Fig. 8 shows similar result to the above for GLDD. Results are plotted only for those subcluters, which contain the value of the central cell from particular windows. Other subclusters are not displayed. The location parameter closely follows the data with a very narrow ITD. Distant data belongs to separated clusters. Comparison of neighbouring ITDs allows a unique classification. The point 5 has an ITD which does not overlap the neighbouring ones. Thus this point is isolated by two discontinuities (dotted lines) from the continuous profile sections of other points on LHS and RHS.

Figure 9

151 38	152 41	148 42	139 47
150 47	154 43	153 43	146 46
142 47	151 41	155 36	150 40

Figure 10

164 151 135	179 154 129	175 159 144	189 148 107
196 159 122	188 164 139	188 162 136	185 154 124
184 152 120	180 161 141	182 163 144	180 159 138

Figure 11

116 109 101	175 169 156	176 169 162	117 83 74
182 175 168	117 110 103	180 173 167	178 171 165
182 154 145	178 172 166	177 171 166	177 152 146

Evaluation Of Cell Value

The most usual method of geochemical data treatment in two dimensions is an estimation of values at points of a regular grid (composed from rectangular cells) by a moving window algorithm. It can be divided into two steps - selection of the data in the window and estimation of the interpolated parameter. In the following examples the size of moving window was 7 cells by 5 cells (dotted at Fig. 1). Result are plotted in 4×3 matrices as mentioned at Fig. 1.

Gridding (Fig. 9) employs the arithmetic mean (upper number) and standard deviation (lower number) for estimation of the cell value. The quality of the estimated surface is affected by window size (too smooth) and non-robustness of statistical moments (high deviation caused by data with extreme values).

Estimates with a minimum of error variance can be discovered by kriging. Here it can be mentioned, that estimation variance of central block is 12.2 cm (Brooker et. al., 1993).

Fig. 10 shows result of interpolation of location parameter (middle number) and ITD (upper and lower numbers) for GGDD. The result has again greater robustness and narrower interval of calculated parameters.

Fig. 11 represents the same results as in Fig. 10 calculated for GLDD. The surface has a very narrow ITDs and location parameter closely follows data values. Comparison of ITDs again allows determination of surface discontinuities (bold boundaries between cells).

Conclusion

Substitution of GT into algorithms for spatial data treatment brings improved robustness of estimates (for estimates derived from GGDF) and flexible detection of clusters in data (for estimates derived from GLDF). If data are composed from more clusters, each cluster is identified individually.

ITDs are characteristics of a homogeneous cluster, which do not contain data of neighbouring clusters and are not affected by them. Thus the intervals are narrow and contain variable parts of the distribution. However, intervals based on quantiles (mean ± deviation = 68%) can contain inhomogenous data. Of course, robust detection of quantiles is possible, because all GT results are derived from distribution functions. The major difference between geostatistics and geognostics lies in this advantage of GT. Where geostatistics is only able to identify anomalous behaviour, or quantifies such a phenomenon with some level of significance, the GT in such a situation quantifies the phenomenon in detail or quantifies it with much higher level of accuracy.

Comparison of neighbouring clusters allows detection of discontinuities in the interpolated surface. This feature has no simple parallel in geostatistics.

The possibility of estimation of data distributions with a minimum of error variance, similar to kriging in geostatistics, also exists, but this problem exceeds the scope of this paper.

Geognostics is thus particularly useful for treatment of highly disturbed and inhomogeneous data sets so typical in exploration geochemistry. Peripheral clusters are related to anomalies, major trends to background. Discontinuities in interpolated results identifies faults and boundaries.

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A further verification of threshold level by the graphic technique

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Keywords: log-normal, prospecting, coefficient of deviation

The log-normal distribution pattern depending on the mean value and the character of value distribution, appears to be most applicable to the results of trace element studies of geological materials in geochemical prospecting for mineral/ore deposits, and accumulations of oil and natural gas. The two important parameters, background value and coefficient of deviation, can be calculated statistically to evaluate the threshold level above which the values are considered as anomalous. The absence of anomalous distribution generally indicates an absence of mineralisation. An attempt has been made to calculate the threshold level statistically, and a further verification is done graphically, using probability-log graph paper. The sample set consists of 349 soils samples, from the Bozy Dar area in Czechoslovakia, analyzed for zinc by XRF. The threshold level was found to be almost identical by both methods.

During the preliminary orientation work it became apparent from a number of methods applied to the investigation, that zinc is especially important. The work was, therefore, concentrated on this element, and other methods were used only as supplementary, and to verify some regularities established. This suitable selection of methods made it possible to investigate zinc-bearing sediments over a large area in a relatively inexpensive way.

Concentration clarke value and regional concentration coefficient used in stream sediment surveys

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Keywords: concentration clarke value, concentration coefficient, stream

One of the main subjects in regional geochemical mapping is to estimate regional dispersion and enrichment of elements in stream sediments. Traditionally, concentration clarke value(KK) that means the ratio value between the average content value of one element in stream sediment in one region or one geological unit and its crustal clarke value for some regional geochemists is to be used to evaluate the degree of dispersion and enrichment of the element in the region or geological unit relative to the crustal clarke value. The ratios, however, can not be sufficient clear to reflect the regional geochemical distributions of different elements because the results may be divorced from its geochemical background of tectonic region and/or metallogenitic provence by this method.

The main problems that affect concentration clarke value to be successfully used for stream sediment survey involving:(1). the Clarke values are mostly calculated on the basis of the analytical data obtained in 1960's-1970's. Limited in the level of analytical technique and the sample representativity at that time, it is over-high or -low for the Clarke values of some elements to be estimated. (2). Because different geochemists have used different global crust model and calculating method and range to calculate their crustal clarke values, the clarke values for the same one element supported by different authors have bigger differences. (3). Compared crustal clarke values (Vinogradov, 1962; Taylor and McClennam, 1985; Li Tong, 1976) with regional geochemical anomaly thresholds (Xie and Yin, 1993) for Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cu, F, Fe, Hg, La, Li, Mn, Mo, Nb, Ni, P, Pb, Sb, Sn, Sr, Th, Ti, U, V, W, Y, Zn, Zr, Si, Al, K, Na, Ca and Mg, it shows that the Clarke values of major ore elements such as Ag, Cd, Cu, Mo, Nb, Pb, Sn, W and etc. are closed to their thresholds, and even some of them are higher than the thresholds such as Au and Hg. (4). The crustal clarke values of elements were calculated with the element contents in primary rocks in the light of a certain assumption pattern. They represent original average contents of elements in crust which have not been affected by any endogenesises and supergenesises. However, stream sediments are naturally composed of materials in the catchment of upper reaches. The element contents in stream sediment can be affected by the concentration decay of stream transportation and the reconcentration and dilution of elements in secondary environment.

Therefore, it is very clear that the traditional concentration clarke values used to study enrichment and impoverishment of different elements in different geological units and dealt with the metallogenitic regularity is not reasonable in geochemical mapping. In order to overcome the drawbacks of KK value mentioned above, a new method for calculating regional concentration coefficient (RCC) has been advanced in which geochemical regional average background values of different elements in stream sediment are used instead of their crustal clarke values.

Regional spatial distribution patterns of elements from stream sediment survey carried out in Xinjiang and Shanxi province have been studied with RCC values of Au, Ag, Hg, Cu, Pb, Zn, Sn, W, Be, Sb, Bi and Mo, and meanwhile compared to their KK values. The results show that KK values of the elements can not effectively and correctly reflect their regional distributions and mineralizations. On the basis of their RCC values, however, the regional distribution patterns of those elements in different geological units have been revealed clearly, and the distribution tendency of different elements are coincident with their anomaly distributions and mineralizations.

In regional geochemical mapping, the traditional KK values used to study distributions of elements may be not sufficient. Using KK values the distributions of elements either be reflected unclearly or can not be found, and even have us make error estimation. However, RCC value presented in the paper have more advantages than KK value to do so. Not only is it possible for revealing regional spatial distributions of elements and showing the favourable geological units, but it can also be important for us to identify major ore elements and to preliminarily evaluate the mineralized possibility of those elements rapidly.

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Integration and modelling of stream sediment geochemistry using GIS: Ebagoola, a case study

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Keywords: stream, rock, regolith, radiometrics, integration, GIS, Queensland

Multi-element stream sediment geochemical survey data collected as part of the National Geoscience Mapping Accord (NGMA) over the Ebagoola 1:250 000 map sheet area in North Queensland are integrated and modelled with other datasets including: digital elevation models, airborne gamma-ray spectrometry, regolith-landforms, Landsat Thematic Mapper (TM), bedrock geology, rock geochemistry, regolith chemistry, mineral deposits and drainage patterns using a Geographic Information System (GIS) with the aim of:

1) producing integrated and derivative maps of stream sediment information with complementary data for more effective and informative displays; and

2) understanding relationships between stream sediment geochemistry, regolith, bedrock and geomorphic processes to develop more effective stream sediment geochemical models for mineral exploration.

Stream sediment geochemical data can be displayed in the form of contour lines, images or as points with variable size symbols indicating the relative abundance of each element (Cruikshank, 1994). Image geochemical data can be manipulated and enhanced using image processing software prior to being incorporated into a GIS. Once in the GIS, the contour, image and point displays can be integrated with a number of other datasets to underpin advanced modelling and display operations (Plant, et al, 1987). A number of these integrated displays are discussed. Firstly, combinations of stream sediment geochemical data with digital elevation models (DEM), Landsat TM and drainage lines are displayed enabling interpretions to be made in a geomorphic framework. Secondly, combinations of stream sediment geochemical data are displayed with regolith, bedrock geology and gamma-ray spectrometry. This allows interpretations to be made in a weathering and geochemical framework. Stream sediment catchment boundaries overlain on regolith and bedrock geology polygons and mineral deposit locations provide displays that aid interpretation and visualization of complex relationships between the stream sediment data and other inter-dependent datasets.

Relationships between the stream sediment geochemistry and regolith, bedrock geology and gamma-ray spectrometry for Ebagoola were assessed by using catchment polygons as areas of interest to perform statistical analyses. The influence of regolith and bedrock geochemistry and percentage area occupied by different regolith/bedrock types in each catchment can be analysed and compared with sediment geochemistry. Choosing catchments with similar bedrock composition but with different regolith types effectively isolates the bedrock influence enabling relationships between sediment geochemistry and regolith to be evaluated. Regolith units map and describe different types of weathered materials; including in-situ and transported materials (Pain et al, 1994). The influence of weathering on sediment geochemistry is determined by combining and analysing regolith unit attributes with the stream sediment data.

Gamma-ray imagery shows the distribution of transported material including the sediment provenance and different styles of weathering which complements and aids the interpretation of stream sediment data (Wilford, 1992). Relationships between gamma-ray data and stream sediment data are assessed by comparing mean gamma-ray values for potassium, thorium and uranium in each catchment with the stream sediment chemistry. Once the gamma-ray response of the bedrock and regolith is understood gamma-ray data and slopes derived from the DEM are used to estimate relative geomorphic activity (ie process rates) in the landscape. Combining catchment boundaries with the derived 'geomorphic activity map' enables relative activity to be calculated for each catchment. The impact of catchment activity on stream sediment chemistry can then be studied.

This type of data analysis contributes to our understanding of the distribution and mobility of particular elements from within different bedrock, regolith and geomorphic regimes (results in Cruikshank, 1995, this vol). Knowledge gained from this type of analysis is used to develop more robust geochemical models. Refined geochemical models can then be used to produce weighting factors on particular elements to assess more effectively the economic potential of a region.

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Environmental Geochemistry

Impact of mining on the trace element geochemistry of sediments from the Coeur d'Alene River, Idaho, USA

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Keywords: geochemistry, sediments, mining impact, Coeur d'Alene River, Idaho

Introduction

The Coeur d'Alene mining district, located in the panhandle of northern Idaho, has been a source of metal pollution for nearly 100 years. The discovery of Pb, Zn and Ag during the 1880s led to active mining in this area. Mining and milling wastes were discharged directly into the South Fork of the Coeur d'Alene River since the onset of mining. It has been estimated that about 115 million tons of mine and mill tailings were generated during mining operations and that over 60% of this material probably entered the South Fork and the Coeur d'Alene River system (Javorka, 1991). The presence of heavy metals in mine tailings throughout the Coeur d'Alene River is a potential long term source of heavy metal pollution in the valley. In 1983, a 54 square kilometer area at Kellogg and Smelterville Flats was designated as the Bunker Hill Superfund site by the U.S. Environmental Protection Agency.

Recently Horowitz et al. (1993, 1994) carried out detailed investigations on the effect of mining and related activities on the trace element geochemistry of surface and subsurface sediments from Lake Coeur d'Alene. These studies suggest that most of the sediments in Lake Coeur d'Alene are substantially enriched in Ag, As, Cd, Cu, Hg, Pb, Sb and Zn relative to both unaffected sediments from within the lake and to uncontaminated sediments from the St. Joe River. Although a number of studies on a few enriched metals in the Coeur d'Alene River sediments have been conducted over the last few decades at different locations along the river, it is apparent that a detailed geochemical study of the entire river is overdue. The main purpose of this study is to investigate in detail the lateral and vertical distribution of 23 major and trace elements in the mining and pre-mining sediments of the Coeur d'Alene River and to compare these data with the background sediments.

Sampling and analytical methods

Six cores were obtained along the flood plain of the Coeur d'Alene River between Enaville and Lake Coeur d'Alene. In order to compare the concentrations of major and trace elements of the Coeur d'Alene River sediments with the background concentrations, one core was obtained from the St. Joe River. The cores varied in length from 72 to 261 centimeters. A total of 65 samples from 7 cores were selected for this study. Examination of the cores revealed two distinct periods of sediment deposition: 1) pre-mining sediments, represented by clay-rich fine sand and silt occasionally rich in organics; 2) mining sediments, characterized by laminated mottled orange-brown fine sand and silt generally poor in clay.

Each sample was sieved through 20 mesh screen to remove large material and then pulverized to minus 200 mesh. Aliquots of 250 mg were digested with a combination of HF-$HClO_4$-HCl-HNO_3 in teflon beakers; the resulting salts were dissolved in 2 ml of 1:1:2 of HCl:HNO_3:H_2O and diluted to 25 ml with 1N HNO_3. Samples containing high concentrations of Ag were digested with aqua regia and the salts were dissolved in 2N HCl. The determination of As, Ba, Be, Cd, Co, Cu, Mo, Ni, Sb, Sr, Th, Tl, U and V was made by inductively coupled plasma mass spectrometry (ICP-MS), whereas Al, Ca, Fe, Mg, Mn, Ti, Pb and Zn were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Silver was determined by flame atomic absorption spectrometry (AAS). Samples containing low concentrations of Ag, Pb and Zn were analyzed by ICP-MS. All the analyses were performed in the Geochemistry Laboratory, Eastern Washington University.

Results

The minimum, maximum, mean and median concentration of 23 major and trace elements in the Coeur d'Alene River sediments are presented in Table 1. The mean concentrations of mining, pre-mining and background sediments are also shown for comparison. A total of about 300 sediment samples from 40 sites are being studied under a U.S. Geological Survey-Eastern Washington University cooperative program. The data presented in Table 1 are based on 65 samples and will be modified as more data become available.

Table 1
Statistical data for major and trace elements in sediments from Coeur d'Alene River and St. Joe River (Al, Ca, Fe and Mg in wt. %, all other elements in ppm)

Element	Coeur d'Alene River Sediments (n=60)*				MS (n=36)	PMS (n=24)	Background (n=5)
	Minimum	Maximum	Mean	Median	Mean	Mean	Mean†
Ag	0.06	115	10	12	17	0.30	0.07
Al	2.9	6.6	4.6	4.5	4.0	5.5	5.8
As	3.1	384	104	74	170	5.8	7.4
Ba	344	755	540	534	575	487	495
Be	0.96	2.0	1.5	1.5	1.3	1.7	1.8
Ca	0.10	0.46	0.20	0.17	0.20	0.20	0.52
Cd	0.11	330	19	11	30	2.6	0.19
Co	3.5	18	8.7	8.3	11	5.4	8.6
Cu	11	360	113	120	140	73	31
Fe	1.7	14	7.0	7.4	10	2.3	2.9
Mg	0.32	0.75	0.51	0.51	0.46	0.58	0.73
Mn	95	13770	5365	5670	8745	302	368
Mo	1.3	72	11	8.0	8.7	14	2.1
Ni	10	112	16	14	18	14	17
Pb	28	41050	3445	3130	5680	89	22
Sb	1.2	228	36	42	58	1.8	0.74
Sr	21	82	43	43	38	51	66
Th	5.9	14	8.6	8.1	7.5	10	8.3
Ti	760	2570	1490	1495	1180	1955	2830
Tl	0.41	0.78	0.54	0.55	0.52	0.56	0.44
U	1.5	4.6	2.6	2.5	2.3	3.0	4.0
V	23	55	37	38	32	46	53
Zn	84	13600	2140	1750	3255	459	79

n=number of samples; MS=mining sediments; PMS=pre-mining sediments
*Minimum, maximum, mean and median concentrations in both the mining and pre-mining sediments of the Coeur d'Alene River
†Mean concentrations in the St. Joe River sediments

Discussion

The data obtained in this study indicate that the surface and subsurface mining sediments of the Coeur d'Alene River are significantly enriched in Ag, As, Cd, Cu, Fe, Mn, Mo, Pb, Sb and Zn relative to the sediments from the St. Joe River (Table 1). The highest observed concentrations in the sediments are 115 ppm Ag, 384 ppm As, 330 ppm Cd, 360 ppm Cu, 14% Fe, 13,770 ppm Mn, 72 ppm Mo, 41,050 ppm Pb, 228 ppm Sb and 13,600 ppm Zn. Enrichment factors calculated for the metals relative to the background concentrations (St. Joe River) are: Ag 240, As 23, Cd 160, Cu 4.5, Fe 3.5, Mn 24, Mo 4.1, Pb 260, Sb 78 and Zn 41. Strong positive correlations exist among the enriched metals as well as between the metals and Fe and Mn which is suggestive of the presence of enriched metals in oxyhydroxides phases of Fe and Mn rather than in sulfides.

The spatial distribution of metals within the Coeur d'Alene River sediments indicates that they are uniformly distributed within the river sediments. The slight variation of certain metals is attributed to changes in physico-chemical conditions within the river as well as to mobilities of certain metals. The vertical distribution of metals shows a considerable variation in their concentrations, especially the mobile metals. There is evidence of mixing of mining and pre-mining sediments at the contact, but a large number of metals show a sharp decline in their concentrations below the contact. Some of the enriched metals (Ag, Cd, Mo, Pb, Sb and Zn), however, show a slight to moderate enrichment in the pre-mining sediments when compared with the background sediments (Table 1). It is interesting to note that Mo is enriched more in pre-mining sediments than in mining sediments. The slight to moderate enrichment of Ag, Cd, Mo, Pb, Sb and Zn in pre-mining sediments may be attributed to mobilization of some of these metals from mining sediments and reprecipitation in the pre-mining sediments.

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Gutter Trap Sediments - Analogues of Stream Sediments for Use in Urban Environmental Geochemical Baseline Surveys

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Keywords: Baseline surveys, lead, gutter trap, road dust, Sydney

Introduction

For the majority of urban areas, the relationship between land use and ambient trace metal concentrations in dusts, sediment and other particulate matter is poorly understood. Limited data on the mode of occurrence and factors controlling variation in background contents of contaminants such as chrome, lead and arsenic creates significant problems in assessing the effect of various land uses (including mining and mineral processing) on contaminant levels, establishing targets for contaminated site remediation and in formulating environmental planning policies. Without reliable data on baseline metal distributions it may be difficult to locate sources of contamination.

Geochemical baseline values (local background) are influenced by background metal contents of local rock and soil types, the composition of exotic materials such as dusts and anthropogenic contributions. Diffuse sources for metals include vehicle emissions, leaking sewage systems, pesticides and fertilisers; point sources may include industrial site emissions and the remnants of vehicle collisions. Van Alphen (1994) lists over 120 potential sources of lead contamination in urban areas.

Previous baseline geochemical contaminant studies in urban areas have tended to concentrate on lead and provide limited information on the form of contaminants, optimum sampling media, the extent and causes of site and seasonal variations (Duggan, 1984; Davies *et al*, 1987, Skacel and Pekarek, 1992; Ferguson and Kim, 1991). Such studies have, however, demonstrated the capacity of low-density sampling surveys to provide indications of regional contaminant trends and isolate anomalous areas (Birke and Rauch, 1993; Davenport, et al, 1993).

A key problem in baseline contaminant surveys is selecting the appropriate media. Such material must be principally of local origin, exposed to contaminant sources, representative of ambient metal contents in the area from which is collected and display a high degree of sub-sample homogeneity to ensure consistency of geochemical patterns. Various options for sample media and site types in urban areas are summarised by Barratt (1990). Residual soils are generally representative of only a limited source area, unless in contact with migrating groundwaters. Dust samples collected directly from either air or surfaces may be dominantly exotic and contaminant levels are likely to be affected more by the characteristics of the source area than the local environment where the dust is deposited (Thornton, 1988). The use of artificial concentrating techniques, such as brushing or vacuuming of external surfaces, produces highly variable data (Schwar *et al.* 1988). Stormwater may not be available and many of the trace metals are adsorbed or bound to suspended particulate matter.

Reconnaissance geochemical exploration surveys, based on the fine fraction of stream sediments, have proven highly successful in establishing regional trends in metal distributions and identifying anomalous samples or areas at sampling densities lower than one sample per 5 km^2 (Beeson, 1984; Baxter and Dunlop, 1988). This material has the capacity to pre-concentrate most trace elements, grain size and mode of transport tend to produce homogeneous samples at the site scale and metal concentrations are generally correlated with the size and intensity of anomalous sub-areas in the catchment. The analogue of stream sediments in urban environments is the sediment which collects in roadside stormwater sediment traps (gutter traps). These sediments include material washed off roofs, roads, gardens and exposed soils. This study has investigated their use in urban geochemical baseline studies

Description of Study Areas

Strathfield Municipality, in inner Sydney, and Kings Langley, in the north western part of Sydney, are dominantly residential areas with commercial and industrial establishments. Both areas are crossed by major transport links. Strathfield was divided into four areas; Area 1 is a medium-density residential houses bounded on the north by commercial and industrial establishments. Area 2 is low density residential housing bounded by parks on the south and industrial establishments on the west. Area 3 contains medium density residential housing. Area 4 encompasses major roads bounded by some commercial and industrial establishments. Kings Langley was divided into two areas; Area A is low density residential and Area B a major arterial road. Both regions are situated on weathered shales which overly the Hawkesbury Sandstone. Both areas are services by stormwater drainage systems with 0.3 to 3 m deep sediment traps located at regular intervals along streets.

Sampling and Analysis

51 sediment samples from sites at Strathfield and 16 sample from Kings Langley were collected from gutter traps or depressions at the side of roads. Samples represented individual traps or composites from several gutter traps. Some of the samples were also taken from grass verges adjacent to the gutter traps and up to 1 m through the soil profiles. Samples were wet sieved to -180 µm and -570+180 µm. Orientation samples from Strathfield were digested by three methods; cold extraction by nitric acid, partial digestion in hot (165° C) 20% HNO_3 and total digestion by hot $HNO_3/HClO_4/HF$. Samples from Kings Langley were digested by hot HNO_3. Solutions were analysed for Cu, Pb, Zn, Cd, Co, Cr, Ni, Mn and Fe by FAAS and samples from Kings Langley were also analysed by trace XRF.

Results

Mean concentrations and standard deviations of the two fractions analysed for the various residential and industrial areas are presented in Table 1. With few exceptions, the -180µm fraction displayed significantly higher metal concentrations than the -570+180 µm fraction.

Compared with variance within sub-regions, variance between analytical sub-sample duplicates and site duplicates was relatively low for Cr, Co, Zn, Mn in both fractions and Cu in the -180µm fraction. Most of this variation was attributed to sample processing and analytical error. The variance between analytical sub-samples for Ni, Pb and Cu in the coarse fraction was high and primarily caused by a few large differences between replicates at higher metal concentrations.

The mean Pb and Cu values of both fractions were higher in the industrial areas and along major roads than the residential areas. There was also asignificant variation in metal values between adjacent residential areas. In Strathfield, there was a consistent trend towards elevated metal concentration in ethe residential area bounded by industrial establishments (Area 2) compared with the medium-density residential areas (1 and 3). Zn values in Area 2 exceeded those for the industrial areas and major roads and may be explained by the output from adjacent industrial areas. Average Ni and Cu in soils from 20 to 120 cm depth along nature strips were similar to road dusts levels. Zinc levels were 3 times higher in the gutter traps/road dusts than the soils and average Pb values 20 times higher.

The form of the metals is still under investigation. Metallic particles, especially lead, have been found in heavy liquid separates. At a number of sites Pb wheel balance lugs, displaying the effects of being run over on repeated occasions, were present. At Kings Langley Ni, Cr and Cu in the -180µm fraction were closely correlated with Fe, yet Pb and Zn were poorly correlated with Fe. The level of extraction of Cu, Cr, Zn and Ni was similar for cold HNO_3 and hot $HNO_3/HClO_4/HF$, whereas more Pb and Mn were release by the second leach. Only Ni returned higher XRF values than hot HNO_3/AAS analyses.

Table 1. Comparison between mean metal values (ppm) of different sieve sizes for gutter trap sediment from residential and industrial areas in Strathfield and Kings Langley, Sydney.

	Residential				Major Road/Industrial	
	S'field 1	S'field 2	S'field 3	K.L. A	S'field 4	K.L. B
Cu 1	77 (24)	85 (13)	72 (33)	33 (29)	233 (133)	78 (41)
2	59 (43)	42 (7)	43 (23)		150 (138)	
Ni 1	42 (33)	54 (28)	37 (27)	7 (11)	57 (39)	17 (8)
2	23 (16)	37 (16)	25 (13)		33 (20)	
Zn 1	548 (242)	1575 (1905)	1096 (1386)	344 (390)	926 (546)	974 (749)
2	310 (160)	828 (1263)	523 (534)		608 (548)	
Pb 1	573 (257)	618 (255)	427 (385)	164 (167)	2420 (1835)	2295 (2257)
2	484 (273)	440 (191)	328 (204)		1656 (1314)	
Cr 1	90 (40)	103 (32)	75 (31)		103 (47)	
2	60 (31)	94 (48)	55 (36)		86 (57)	
Co 1	19 (5)	23 (6)	17 (6)		27 (7)	
2	10 (2)	14 (4)	10 (4)		18 (8)	
Mn 1	525 (193)	537 (160)	423 (224)		633 (237)	
2	295 (120)	423 (120)	407 (370)		405 (211)	

Figures in brackets denote standard deviations. Cu 1, Cu (ppm) in-180 µm fraction; Cu 2, Cu (ppm) in -570+180 µm fraction, etc. S'field, Strathfield; K.L., Kings Langley.

Conclusions

- Gutter traps sediment chemistry reflects the significant variations between ambient metal distributions in residential areas, main roads and industrial areas. The samples represent material accumulated from a range of surfaces (roads, roofs, gardens) and incorporate material ranging from dusts and vehicle emissions to fugitive coins.
- Metal concentrations are similar for samples within individual sub-catchments suggesting the sediments represent an "averaging" of particulate materials washed off surfaces into the storm water system. There is significant variations between trace metal concentrations in residential and industrial areas and between major and minor roads indicating a dominantly local source of the sediments.
- The finer fraction (-180 µm) generally displays higher concentrations than the corresponding coarse fraction (+180-570 µm), although peak values tend to occur in the coarser fraction. High variation between analytical sub-sample duplicates may be related to the presence of coarse particulate materials. A comparison between sample digestion methods indicates the majority of Cu, Cr and Zn is chemically adsorbed to dust particles or present as readily dissolved metals, whereas a significant proportion of the Pb and Ni appears to be particulate.
- Trace metal concentrations in the gutter trap sediments are an order of magnitude higher than adjacent residual soil below 20 cm depth (except for Ni and Cr) indicating the main source of metals to be anthropgenic.
- Peak Pb contents of road dust and gutter trap sediments in residential sections of the Municipality of Strathfield and Kings Langley exceed most intervention levels set by environmental regulatory authorities for soils by an order of magnitude, and are close to marginal ore grade in some mines.

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Mobilization of U isotopes on waste disposal area of sand mining activities at Analândia (SP)

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Keywords: uranium, isotopes, groundwaters, sand mining, water quality

The isotopic compositions of dissolved uranium in groundwaters have been extensively investigated and documented in several papers. The U content and U-234/U-238 activity ratio (A.R.) data have found applications to an appropriate evaluation of some hydrologic problems or for the prospection of concealed uranium deposits. For instance, the waters of the Carrizo Sand formation of South Texas, United States of America, exhibit a pattern of changing across reducing barrier reported by Cowart and Osmond (1977) where, in general : the samples from the outcrop area and shallow aquifer are characterized by relatively high U concentrations and low AR's; the samples from downdip show much lower U concentrations and higher AR's.

A similar tendency was reported by Toulhoat and Beaucaire (1991) on studying groundwaters in a drill hole from the Lodève uranium deposit located in the southwestern prt of the French Massif Central where, according to the progressive evolution of the chemistry with depth in the aquifer: higher U concentrations and lower AR's characterize the oxidizing upper part of the aquifer (between 50 and 100 m deep); lower U concentrations and higher AR's characterize the more reduced lower part of the aquifer (between 100 and 150 m deep).

This investigation was carried out in an area of treatment and waste disposal of sand mining for industrial purposes located around the Analândia municipality, which is situated nearly in the center of São Paulo State at about 22°10'S and 47°45'W. The area belongs to C.R.S. - Mineração Indústria e Comércio Ltda., where anthropogenic activities are taking place for the last 3 years.

The hydrologic environment around the waste disposal area was studied on sampling groundwaters from three boreholes drilled for investigating the character of the subsurface flow and surface waters from Veado stream that receives most of the area drainage. The aquifer system was developed in the weathered cover over Pirambóia Formation, which consists predominantly of clayey sandstones whose grain sizes vary between medium and very fine. Quartz is the main mineral of these sediments: its abundance is about 95% (Wu and Soares, 1974).

Groundwater samples for U isotopes analysis were collected from two boreholes in December 1991 on using a 1-m long, 5-cm diameter polyvinil pipe with a ball-point-valve closed at the bottom. The samples were stored in polyethylene bottles and were filtered through a 0.45µm Millipore membrane. Dissolved oxygen, pH, Eh, conductivity and temperature were measured in situ and other parameters were evaluated in laboratory. Several techniques were used for obtaining the composition of the waters, for example, potentiometry, flame photometry, Ar induced plasma, specific ion electrode, alpha spectrometry, etc. The results of the measurements are reported in Table 1.

The chemical data obtained for the surface and groundwaters were compared with the maximum permissible concentration limits in drinking water, and it was verified that the present concentrations don't reflect any environmental impact related to the sand mining activities. The low values of total dissolved solids measured for these waters probably reflect the composition of rainwater with small amounts of potassium, calcium and silica added from contact with the aquifer; they are not much amenable to plotting on a standard Piper diagram because there is a lack of the preponderance of typical anions and cations. The Eh-pH field indicates they are reducing in character. The CO_2 partial pressure evaluated by Henry's law on using total dissolved CO_2 content and 0.033 mole per liter atmosphere as constant (Brownlow, 1979) is about 0.1 atm. The Eh-pH field for uranium species under this condition of pressure shows that the mobilization of this element is occurring as $UO_2{}^{2+}$. When the chemical data are used to study stability relations of mineral phases in the systems K_2O-Al_2O_3-SiO_2-H_2O, CaO-Al_2O_3-SiO_2-H_2O and Na_2O-Al_2O_3-SiO_2-H_2O (Garrels and Christ, 1965) it is found that these groundwaters fall into the kaolinite field of stability. The use of X-ray diffraction in the identification of mineral components in samples from the weathered cover developed over Pirambóia Formation confirmed this possibility, because kaolinite was identified as the second mineral phase in abundance.

The results of the isotopic compositions of dissolved uranium obtained in this work showed that lower U concentrations and higher AR's characterized the more reduced part of the aquifer, according to the data reported by previous investigators (Cowart and Osmond, 1977; Toulhoat and Beaucaire, 1991). However, the direction of the flow-through water in the studied hydrologic context is from the deeper part of the aquifer up to the shallower zone, which is opposite to that already referred and involves the tendency of generating values of higher U concentration and lower AR.

Acknowledgements

The author would like to thank the Director of C.R.S. - Mineração Indústria e Comércio Ltda. for his permission to publish this paper and also is grateful to E.G. Oliveira for his contribution during the activities of sampling.

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Environmental geochemical research on the ecological effects of Se-enriched geology

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Keywords: Se, enrichment, ecology, Ankang

Aim

This paper presents the results of environmental geochemical research on the ecology and geology of naturally occurring Se-enriched areas in the Ankang district, Shaanxi Province, China. The aim of the research is to determine the reaction of naturally occurring Se with geological and ecological materials.

Methods

Environmental geochemical samples were taken from three areas: a Se-enriched area, a Se-poisoned area, and a coal mine. Field stations were set up; rocks, soils, waters, plants and animals were sampled at each station. These were crushed and processed by specialised methods, and each sample was analysed by two banded atomic fluorescence spectroscopy with a detection limit of 0.01 ppm.

Geological Setting

The Ankang area lies on the northwest margin of the Yangtse Platform, Shaanxi Province, China. Throughout the area there are bone coal-bearing strata of the Cambrian Dong He Group. The coal-bearing strata consist of bone coal, silver coal, cabonolite and carbonaceous shale.

Results

Case Study 1: Bone Coal Mine

The bone coal mine is located on the north bank of the Pinling River, Dragon Village, Pinling County, Shaanxi Province, China. The mine is abandoned now. The Se-enriched unit is a bone coal layer containing 96 ppm Se. The Se content of soil near the abandoned mine is high, ranging from 27 ppm to 29.5 ppm Se. Water from the mine adit has a pH of 3. *Amorphophallus Konjac K. Koch*, a chinese herb, contains 4.92 ppm Se.

Case Study 2: Shan Li Yia Area

A sample of bone coal from the Shal li yia coal mine contained 48ppm Se. Most of the bone coal is covered by other rock units and soil, and soil in the Shan li yia area has Se contents ranging from 0.85 ppm to 2.81 ppm. Selenium is enriched in weathered materials overlying the bone coal layer, with values of 64 ppm Se occurring in a calcareous sinter, and 64.8 ppm Se in native sulphur. The content of Se in edible plants is high, e.g. Se in the Shan li yia tea plant ranges from 0.24 ppm to 2.81 ppm.

Case Study 3: Se Poisoning Area, Shuang An, Zi Yang County

The soil in Shuang an, Zi yang county, contains 3.7 to 34 ppm Se, although selenium contents in cabonolite and carbonaceous shale range from 11 to 30 ppm. Bedrock outcrops consist partly of carbonate and calcareous units. Edible plants contain high selenium, for example, 1.3 ppm Se in corn, 0.89 ppm Se in beans, and 0.275 ppm Se in tea. Selenium contents in the Zi yang tea ranges from 0.122 to 3.83 ppm.

Discussion and Conclusions

The data show that soils in the Ankang district contain high selenium. The Se-enriched soil in the area comes from bone coal-bearing strata which are widespread in the Ankang distict. Edible plants grown in the soil contain high Se, and indicate that the reaction of Se in the environment is obvious in numerous forms.

From field observations and analysis of the data, a picture emerged indicated the significant provenance of selenium is the bone coal-bearing strata occurring in the area. The overlying calcareous sinter and native sulphur have formed by oxidation of the pyrite and carbonate units in the bone coal-bearing strata. After groundwater infiltrated the bone coal-bearing strata, Se in a mobile form was removed from the strata, and transported towards the surface soil by acidic groundwater. These processes resulted in a soil with a high Se content.

Some principles of anthropogenic component discrimination in geochemical mapping and monitoring of the environment

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In view of the global scale of anthropogenic transformations of surface environments, and the disappearance of primary environments, discriminating anthropogenic from natural conditions using geochemical mapping and monitoring data is one of the fundamental problems in current applied geochemistry. Some principles of anthropogenic component discrimination were formulated based on the results of environmental monitoring and geochemical mapping of different media (stream sediment, surface water, soil, vegetation, snow cover) on several scales (1:1 000 000, 1:500 000, 1:50 000), of the Baikal polygon, Irkutsk region, Siberia. Components of the study and summarised results are given below.

- *A direct analysis of the correlation between the geochemistry of the environment and land use.*

This is illustrated by the correlation between snow pollution and technogenic load intensity calculated for the land use map. Another example is the differences in the typical element associations in overbank sediments and waters from the industrial zone of the city of Irkutsk (Ag, Cu, Zn, Pb, Hg, Ni, Cr), to the zone around the Shelekhov aluminium plant (F, Be, Cu, Mo, Pb, Cr, U), and the agricultural zone (Ni, Co, Ti, V, P,F, U, Mn, Hg).

- *A comparative analysis of geochemical associations deduced from mapping and monitoring of the environment and reference associations of typical natural and anthropogenic settings.*

The disturbance of typical natural distributions of chemical elements, and an emergence of the specific technogenic components, are clear signals of anthropogenic transformation of the environment. This is the most generally applied approach to the problem of discriminating anthropogenic effects.

- *A study of the mode of occurrence of elements in different environmental media.*

The study of seven partial extracts from soils showed remarkable enrichment of the mobile and biologically consumable modes of heavy metals in polluted soils. ^{137}Cs and benz(a)pyrene in soils and stream sediments, and benza(a)pyrene in snow are typical examples.

- *A comparative study of conjugate media.*

The comparison of geochemical maps obtained from bedrock, soils, stream waters, stream sediments and snow, reveal different sensitivity of the media to anthropogenic pollution. The broad haloes of F (Shelekhov aluminium plant) and U (the chimneys of Irkutsk) mapped from snow are lower, with less contrast, in stream sediments, and are practically undetectable by the methods used for soil analysis.

- *A comparative study of facies and fractions of the same medium.*

The variations in element distributions within a medium are exemplified by four types of element distributions in a 50km soil transect through the Irkutsk-Shelekhov industrial area. The anthropogenic element associations show background levels in the soil parent material, but are strongly anomalous in the upper horizons of the soil, and in vegetation.

- *Bioindication and biotesting.*

Both quantitative and species changes in micro-organism communities, along with the accumulation of heavy metals in micro-organisms, were discovered in the soils of polluted areas. Anaerobic fermentation is also depressed in these polluted soils.

- *An assessment of the disturbance of the balance of natural chemical elements in biological objects.*

This is the geochemical equivalent of bioindication. The comparative study of macro-nutrients (e.g. K) and toxic elements can be informative. The accumulation of pollutants may cause reduction in nutrient uptake by plants.

- *A study of substance flow dynamics with time.*

This is especially essential for hydrogeochemical investigations.

This preliminary overview of approaches to the assessment of the anthropogenic component of geochemical anomalies showed that these approaches require further formalisation and qualitative expression.

200 years mining activities at La Paz/ San Luis Potosí/ Mexico - Consequences to environment and geochemical exploration.

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Keywords: environment, soil, heavy metals, arsenic, Mexico

Introduction

The Ag-Pb-Zn-Cu-Au mining district of Santa María de La Paz is located approximately 500 km north-north-west of Mexico City and 5 km west of the small Town of Matehuala/San Luis Potosí. It occurs at the western margin of the Sierra Madre Oriental on the eastern slopes of the small mountains Sierra del Fraile which were formed as upset anticline. The deposits of La Paz are part of a 1600 km long northwest-trending belt of carbonate-hosted high temperature (>200°C) hydrothermal mineralizations (MEGAW et. al.,1988). The majority of these deposits, including the La Paz mineralization, have taken place in Jurassic-Cretaceous platform carbonates. By a fault at the eastern fringe of Sierra del Fraile, this deposit is divided in to different types of mineralization : The eastern part consists of hyrothermal Ag-Pb-Zn veins, the western part of Cu-Au- skarn mineralization.

The mine district of La Paz has been extensively exploited for approximately 200 years. In 1992, work on the eastern veins was ceased due to the low market prices. The mines in the skarn deposits (Cu-Au) are still in production. For more than 60 years the ores have been treated in the ore-dressing plant of La Paz. Until ~1960, the ores were refined in a smelter at the northern side of Matehuala.

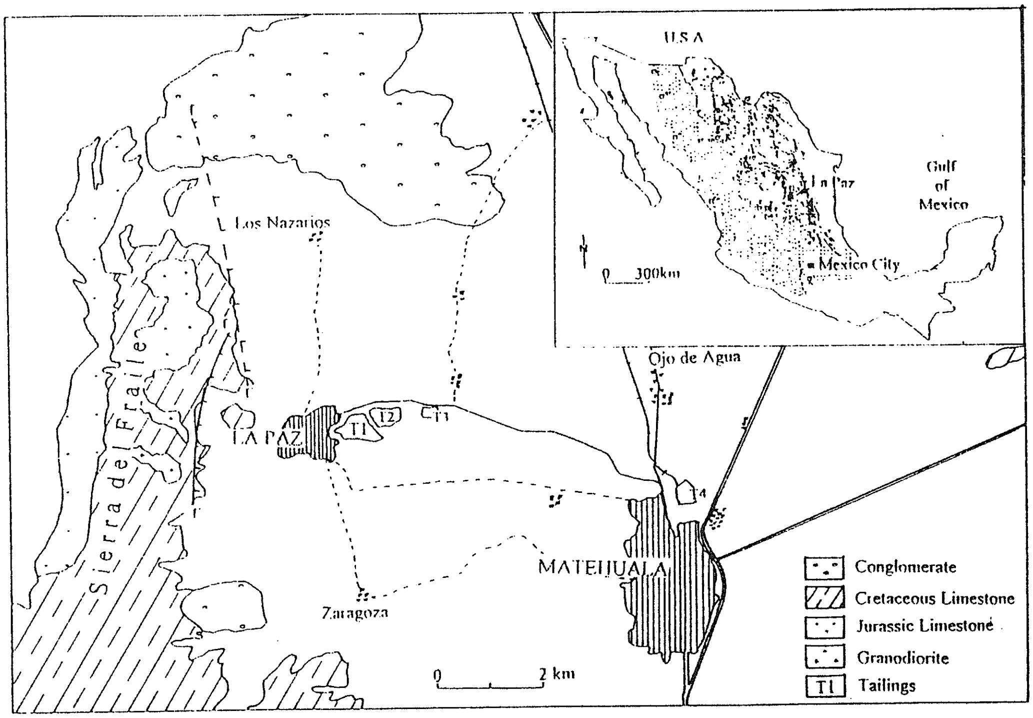

Fig. 1: Sketch map of the La Paz mining district showing locations of tailings. Locations T1-T4 are refered in the text.

Consequence of these activities are several deposits of tailings which are completely insecure. The biggest of these dumps (T1) has a volume of 8 m tons with arsenic concentrations of approximately 3000 mg/kg.

Since the climate is arid and the dumps have no protective cover, material in the dumps is dispersed by strong winds. It is also washed out during seasonally strong rainfalls. By these processes, dump material is dispersed in the environment resulting in a widespread contamination of the surrounding soils. Most of the minewaters (4.5 m^3/min; pH= 7-7.5) is used in the flotation plant but a part is used for agricultural irrigation without any pretreatment.

The mine is therefore the main source for environmental pollution, allthough some industrial sources can not be neglected.

As a result of the mining and industrial activity a variety of anomalies of different origin (geologic and anthropogenic) exists in the area of La Paz:

- geologic from subsurface mineralizations
- anthropogenic-geologic from the recent and abandoned mining activities
- anthropogenic from ore dressing and the resulting dumps
- anthropogenic from ore refining and other industrial sources, e.g. recycling of lead from batteries

The aim of our work is to discrimate between the different types of anomalies and contamination and to estimate the consequences for geochemical soil exploration and for food production in this region. It therefore represents a case study for the effects of extensive mining in arid environments.

Sampling and sample preparation

More than 200 locations have been sampled in an area of approximately 100 km^2. The soil samples were taken by an earth auger designed by Dr.Pürckhauer. At most of the locations, three horizons were sampled (0-20; 20-50 and >50 cm). To study the vertical transport in the soil column, some soil profiles were sampled in detail. The soils are in general calcic to gypsic xerosols with a "caliche" layer that begins in a depth of approximately 50- 100 cm. Sample locations were selected with respect to main wind directions and drainage systems. The wind direction in this area is SSE, flow direction of drainage systems is from Sierra del Fraile in the west into the Matehuala valley. Groundwater flow is the north-west to the south east. In the La Paz Area, the undisturbed groundwater level occurs 120 m below surface. Due to the mining activities, the level has been lowered to a depth >450 m below surface. Therefore contamination of the groundwater flow does not therefore appear. Consequently, sampling focussed on the area north of the big dump Sta. María de La Paz (T1) (main wind direction) and south of this dump, where mining waters are used for agricultural irrigation. In addition the area the north of the old refining plant (T4) (main wind direction) and the drainage system starting at the big dump into the Matehuala valley were sampled. This area was flooded, during heavy rainfalls 5 years ago, by waters containing dump material. Background samples have been taken from the eastern slope of Matehuala valley out of an area not affected by wind- or water transport of material from dumps, mines or industrial activities. From agricultural areas, samples of corn (Zea mays L.) and chili-plants were also taken to estimate the transfer of toxic elements into the food chain.

Soil samples were air dried and screened to -2 mm, an aliquot of this material was used for pH determination, the remnants were finely ground for chemical analysis. The plant material was dried at 105°C and ground.

Analytics and data processing

All soil samples were analysed by energy dispersive X-ray fluorescence for 13 elements including Cu, Zn, As, Cd, Sn, Sb and Pb. For verification and to obtain information about additional elements including Au, 21 soil samples and 7 samples from the dump were analyzed by instrumental neutron activation. Plant samples were dissolved in HNO_3 by microwave digestion and analyzed by ICP/MS. Exchangeable heavy metals for the 0-20 cm horizon of 40 sample locations was determined by 1 M NH_4NO_3 extraction and ICP/MS. Details of the analytical procedures are given in KRAMAR, 1984; KRAMAR & PUCHELT,1982 and NÖLTNER et. al., 1990. The analytical data were now evaluated by uni- and multivariate statistically methods.

Results and discussion

Tailings of Sta. María de La Paz (T1) can be regarded as the biggest contamination source in the La Paz area. Samples taken at the dump from different locations show average concentrations of 400 ppm Cu, 2000 ppm Zn, 4000 ppm As, 30 ppm Cd, 3000 ppm Pb and 0.7 ppm Au. Whereas Cu, Zn, Cd, and Pb are approximately equally distributed to the different grain size fractions (200-600 µm, 63-200 µm and -63 µm), arsenic is greatly enriched in the finest fraction with concentrations of up to 5%. Due to the high concentrations in the fine fraction and its high mobility under oxidising and neutral to slightly basic conditions, arsenic can be more easily released from the dump compared to the heavy metals. Residual salts at the base of the dump showed As- concentrations in the order of 10%.

The soil samples of the surrounding of the big dump (T1) show greatly increased values for heavy metals and arsenic in the upper horizons. Along a south-north traverse starting 200 m north of the big dump, the concentrations for Zn, Pb and Cd decrease approximately exponentially with distance from the dump. Zn decreased from >1000 ppm to 200 ppm at a distance of 4 km in wind direction from the dump and to 100 ppm at 5 km distance. Pb decreases from 390 ppm to 30 ppm and Cd from 16 to ~ 1 ppm. Cu and As show a completely different pattern. Up to 2 km distance from the dump the behaviour of Cu and As concentrations is equivalent to Zn, Pb and Cd. Then Cu and As concentrations increase again to 550 ppm Cu and 300 ppm As. At this point, the traverse crosses the slope of Sierra del Fraile draining the area of the Cobriza copper-gold mine.

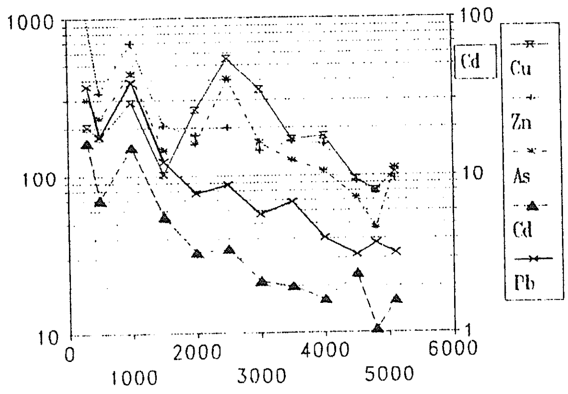

Fig. 2: Copper, zinc, arsenic cadmium and lead concentrations in top soils along a 5 km traverse starting at dump T1 to the north.

The area south of the dump (T1) are used for domestic purposes and agriculture. Contamination of this area can be expected by wind transported material from the dump and from mine waters which are used for irrigation. Figure 3 shows notched box-plots, minimum and maximum values for Cu, Zn, As and Pb of the 0-20 cm (A) and the >50 cm (C) horizon of the sampling grid.

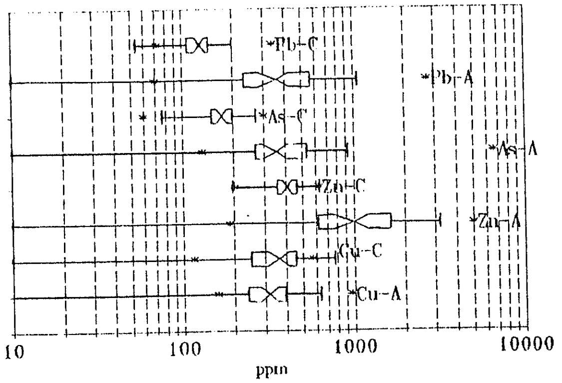

Fig.3: Variation of Cu, Zn, As and Pb in 0-20 cm and > 50 cm horizons from agricultural fields south of dump T1.

Zn, As and Pb are enriched in the top soils up to 5000 ppm Zn, 6600 ppm As and 2700 ppm Pb. These high values can not only be explained by contamination with dump material. Especially at greater distances from the dump the ratio As:Zn:Pb is shifted in favour of As and Zn. Since lead is nearly immobile under oxidizing and neutral to slightly basic pH conditions, Pb is not much transported by mine waters. The ratio shift can be used as an indication for contamination from mine waters. Corn plants of this area showed concentrations up to 20 ppm As in leaves, which are also used for fodder.

Cu shows the same general trend as Pb for a part of the profiles, but at several locations Cu concentrations increase with the depth. This can be regarded as indication for geologic anomalies.

Approximately 100 m north of the small dump (T3) a Pb-recycling plant was running for several years. Soils from the vicinity of this plant show clearly elevated values for Cu, Zn, As and Pb. Compared to material from the dump the concentration of Pb has increased relative to Zn,As and Cu. This pattern can be interpreted as a mixture from the two potential contamination sources, the dump and the recycling plant.

North of Matehuala two types of contamination can be observed: Runoffwater and material from the dumps washed out during heavy rainfalls flooded the area north and east of Matehuala 5 years ago. The runoff waters had percolated in the central Matehuala valley east of the town Matehuala. Drainage sediments show up to 10% As. Soils of this area are contaminated with several hundred ppm As, Cu, Zn and Pb.

The halo of the polluted air from the smelter (T4) can be traced several kilometres to the north by elevated concentrations of several hundred ppm Cu, Zn, As and Pb (at ~ 3 km distance from the smelter ~ 150 ppm Cu, 250 ppm Zn, 200 ppm As and 400 ppm Pb). At 6 km distance the concentrations of these element have decreased to backgroundlevel. The area directly north to the smelter (up to ~500 m distance) was flooded by runoff waters from the big dump 5 years ago. In this area, concentrations of Cu, Zn, As and Pb fluctuate between 200 and 2000 ppm each.

Conclusions

In the vicinity of the La Paz mining district, an area of approximately 100 km² has been affected by the mining activities. By far the most important contamination source is the big dump of Sta Maria de La Paz. Water transported material from these tailings cause significient contaminations of soils in the central Matehuala valley in 10 km distance. Windblown material can be traced for more than 5 km to the north and to lesser extent, to the south. The most critical effects on the food chain occur in the areas, irrigated by mine waters. It is therefore highly recommended to cover at least the biggest dump and to avoid the use of unpretreated mining waters for irrigation.

Using the multielement data set in conjunction with adequate multivariate statistical methods it is possible to discriminate between different contamination sources and geologic anomalies for most of the locations.

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Rapid following-up and evaluation of regional gold anomalies in stream sediment in heavy mining contamination areas

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Keywords: following-up, gold anomaly evaluation, rock survey, mining contamination

In the recent ten years, rapid following-up and evaluation of Au anomalies in the stream sediment areas have being laid stress on in the geochemical exploration of China. The geochemists have contributed their great efforts for the reseach of the measures, and extreme success has been abtained. However, a effective method to eliminate the artificially imposed contamination produced in the mining activity from ancient times to the present has not been found, which made a lot of following-up and evaluation of geochemical anomallies get half the result with twice the effoert, even fall short of success for lack of a final effort.

There are hundreds of gold mineral and mineralized points in the northern slope of Wutai mountain in Shanxi province, China, but only three small gold deposits were found in the area until now. a 84 square kilometer of Au anomaly (Ping AS-26 Au anomaly) found by regional stream sediment geochemical survey in the area atract geoscientists much attention to the region (Cui Binhua et al., 1987). For over three hundreds years, due to mining activity for gold in the region by folks, natural geologic evironment has been strongly destroyed and stream sediment been greatly contaminated. Therefore, the selection and the confirmation of regional Au anomalies of stream sediment measure were enormously disturbed and the predicted aim of verifying the regional Au anomalies was not achieved.

Based on our study for over three years, the reasonable methods for rapid following-up and evaluation of Au anomaly sources in the heavy contaminated geologic environment areas were conducted: (1) a hydrochemical sample of 2.6 square kilomenter is substituted for 8 stream sediment samples of 1 square kilometer of conventional survey, which can remove the artificial contamination of stream sediment from mining activity, indicate objective geochemical features and outline the macroscopic targets quickly; (2) thorough the study of comparing the hydrogeochemical results with stream sediment results, the targets for further detailed exploration can be rationally selected; (3) onventional point-line geochemical survey is improved into "Areal" rock geochemisty with multiple sub-sample combination in 250 x 250 meter grid or geologic-geochemical profile with multiple sub-sample combination within 50 meter area, which can not only eliminate the contamination effect of waste residue by artificial mining but also follow rapidly up regional Au anomalies and outline favorable targets for exploring gold deposits.

We carried out test survey in Ping AS-26 Au anomaly with above new technology, which saved much more working expenses as well as determined more rapidlly and effectlly detailed prospecting sectors than conventional geochemical measure. For example, in a detailed target of 20 square kilometer, 204 working days of one group were needed to collect 7160 samples with the conventional measure, even two samples were conbined into one laborary sample, 3580 sample would be tested by conventioal survey; however, 12 working days of one group completed the sample collection of 80 units in the same area by using the "Areal" rock geochemical survey.

The test results of "Areal" rock geochemistry in above Au anomaly showed that the mineralization related to intermediate acid gray rock of Yansan age on the formation and the geochemical anomalies formed circled contribution model from the centre of the rock. The element composition of anomaly from centre to outside is : Mo, Cu, Au-Cu, Pb, Zn, Au-Au, Ag and Pb, which indicated the features of porphyry copper mineralization, contact-metasomatic mineralization and post-magmatic hydrothermal mineralizaton.

The result of the test detailed survey from Zhengou to Huangchao showed a multiple element anomaly of Au, Ag, As, Sb, Cu, Pb, Zn, Hg and W about 5 square kilometers in No: 1 anomaly distribution area. The anomaly center was very clear, its Au concentration area greater than 200 ppb is 1.5 square kilometer, average Au value 3985.2 ppb, maxium 12.20 ppm; and the anomaly located at a triangle zone crossed by many group faults with the features of strong hydrothermal activity and several kinds of wallrock alteration. Above evidences showed that the area was potential for prospecting mineral deposits, especially for mining gold bodies on the surface. The deduction was confirmed by folk mining last year, the very rich gold ores, in which the maxium Au grade was greater than 1000g/t, were mined in the Au concetration centre of No: 1 anomaly.

The reseach was a part of the key problem project for gold geology and scientific technology of China. The authors are grateful to Shanxi geological bureau for their assistance and financial support and to Zhou Changyi, Zhao Chuandong, Cheng Hangxi and Wang Yinxiu for their work in the reseach.

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The incorporation of heavy metals into coral skeletons as a result of metalliferous mining and smelting in tropical areas: a laser ablation microprobe (LAMP) ICP-MS study of *Porites lutea* from Ko Phuket, Thailand.

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Keywords: Coral skeletons, annual bands, heavy metals, reef stress, laser ablation, tin smelting

Abstract

Mining, dredging and smelting operations are among the most important sources of heavy metals to the tropical marine environment. Such activities are widespread in tropical coastal regions, for example marine mining for Cu, Zn, Ag, Cd, Pb and other sulphides occurs in the Caribbean and the Red Sea (Yanchinski 1981, Mustaffi and Amann 1978) marine dredging for placer deposits of Sn is carried out in Thailand (Chansang *et al.* 1983) and the smelting and refining of metalliferous ores takes place in both Thailand (Sn, Cu, Zn and Fe) and Queensland Australia (Ni) (Brown and Holley 1986, Carey 1983). Furthermore as concern grows regarding the long term availability of terrestrial mineral resources the importance of shallow and deep sea mineral extraction will also increase. In addition to the metallurgical industries, extensive and diverse coral reefs also exist in these areas, and still relatively little is known about the effects of heavy metals on reef corals.

Annually banded corals have been used for the past two decades to provide records of both natural and anthropogenic environmental change. They are suited to this for a variety of reasons: they are abundant, fast growing (0.5-2.0cm year^{-1}) and long lived, their prominent annual bands (revealed by x-radiography or long wave UV light) provide long and detailed chronologies, coral communities are sessile and their skeletal structure, growth and chemistry are dependant on ambient environmental conditions. The trace element and heavy metal chemistry of coral skeletons are of particular interest as they may reflect changes in sea water chemistry that can be related to natural and/or anthropogenic processes. Previous studies have tended to focus on bulk analyses of elements bound within the lattice of *pure* skeletal aragonite. Such analysis has allowed more detailed understanding of ocean upwelling and advection . (Shen *et al.* 1987, Lea *et al.* 1989, Tudhope 1994). Changing levels of ocean pollution have also been studied using Pb and Pb isotopes (Shen and Boyle 1987), Cd, V, Cu, Zn and Sn (Brown 1987, Guzman and Jimenez 1992, Howard and Brown 1984) However still very little is known about the binding mechanisms of heavy metals in coral skeletons and it would seem that there is much information to be gained from studying the phase associations of skeletal trace elements.

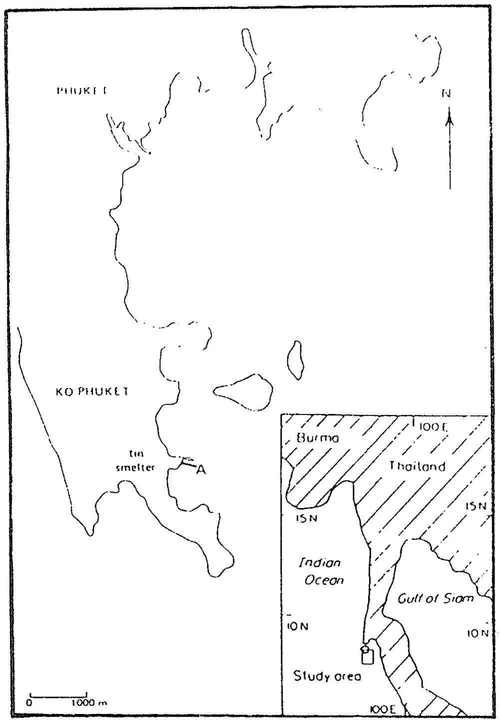
Recent work by Brown *et al.* (1991) on corals from Thailand has highlighted a possible mechanism for the incorporation of Fe in to coral skeletons from Ko Phuket, Thailand. These corals are regularly subjected to elevated concentrations of both dissolved and particulate Fe (up to 29 mgl^{-1}) from a near by tin ore-processing plant, and they display visible orange Fe-bands in their skeletons. The mechanism they propose is as follows: in response to

environmental stress (fluctuations in temperature, salinity or levels of pollutants) tissue retraction occurs, which exposes skeletal spines. In addition the production of copious protective mucus causes the precipitation of Fe-oxides on to the exposed skeletal spines. Subsequent tissue recovery incorporates the Fe-oxides within the skeleton. It is likely that in the case of both the Ko Phuket corals and those from less Fe-rich waters, production of mucus as a response to stress may cause the precipitation of many metal ions other than Fe (Carpenter 1927). Clearly the detailed study of non-aragonite bound heavy metals, and particularly those associated with mucoproteins/ Fe-oxides may provide valuable records of *reef stress*.

Previously the detailed examination of metal phase-associations in coral skeletons was not possible. However, the recent application of analytical techniques such as ion probe (Allison and Tudhope 1992) and LAMP ICP-MS (Lidiard et al. 1995a) to coral skeletons, has highlighted considerable micro-scale heterogeneity of minor and trace elements. LAMP ICP-MS in particular has manifold advantages for this type of research. It is well suited for the rapid sequential determination of a wide variety of elements and it is possible to achieve exceptional temporal resolution (spot sizes from 3-25μm are possible). Accurate positioning of the laser beam allows direct and detailed analysis of microscopic structures. Direct sample analysis ensures the minimum of sample contamination and it has the advantage of being virtually non destructive. This allows the use of complementary techniques including ED analysis, SEM and FT-Raman spectroscopy (Lidiard 1995b) for the detailed determination of associated metal binding ligands.

These techniques are *currently* being applied to sections of *Porites lutea* collected from the intertidal reef flat on a fringing reef in Ko Phuket, South Thailand (courtesy of A.W. Tudhope 1994). The reef is located close to a tin ore-processing plant, and tin smelter (Figure 1). The corals were covered by pools of Fe-rich ore washing effluent at low tide, and displayed visible Fe-banding when sectioned. Corals in this area are also likely to have been subjected to increased levels of suspended particulates as a result of local dredging. LAMP ICP-MS combined with SEM, ED analysis and FT-Raman spectroscopy promise to provide further insights in to the incorporation of heavy metals into coral skeletons in areas of significant metal mining and smelting. The results of this work will be presented.

Figure 1. Location of sample *Porites lutea* in relation to the tin ore-dressing plant and tin smelter (A) at Ko Phuket, South Thailand (after Brown *et al.* 1991)



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The role of biogeochemical processes in minimising uranium dispersion from a mine site

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Keywords: environment, biogeochemistry, humic, iron oxyhydroxides

The pre-mining condition of natural dispersion from ore bodies involves erosion of the exposed parts of them and transfer of uranium in groundwater which seeps from the surface. The evidence for this is taken from studies undertaken at Ranger uranium deposits, Alligator Rivers Region (ARR), and the floodplain downstream from those deposits. The dominant mechanisms in the transfer step of the biogeochemical cycle of uranium are :

(i) complexing of uranium in solution by carbonate/bicarbonate in groundwater at the interface with the surface; and
(ii) complexing with humic substances and adsorption on iron oxyhydroxides, which may themselves be coated with organic matter.

After a pH change at the interface, induced by the hydrolysis of the iron oxide complexes, the dispersion mechanisms are confined to :

(i) mechanical erosion, i.e. as clastic particles; and
(ii) transport as attachments to colloidal particles in suspension.

Prior to the commencement of mining at Ranger One, uranium dispersion to surface waters and sediments had been observed from both Orebody 1 and Orebody 3 (Sherrington et al. 1983). Where uranium mineralisation intersects the land surface, weathering results in elevated uranium concentrations in groundwater (Giblin et al. 1983). Enrichment of uranium in plants and the overburden at Orebody 3 was observed by Cruikshank and Pyke 1986. The near-surface soil pH above this orebody is between 4 and 5 due to the presence of humic acids, rainwater and hydrogen ion from the formation of hydrated ferric oxides. Following degradation, uranium in biota may easily be transferred from soil at Ranger Orebody 3 to the nearby Magela Creek and transported downstream. The high concentrations of uranium found at and near Georgetown Billabong may be attributable to dispersion from Ranger One Orebody 1, via erosion of the regolith and expression of groundwater at the surface (Davy and Conway 1974).

A materials budget for the Magela Creek Floodplain showed that 30 kg U was transported to it during the 1982-83 Wet season (Hart et al. 1987a). The nett deposition to the floodplain (total input-output) was 48 kg U, although the error bars are half an order of magnitude. A study of two floods during the 1984-85 Wet season examined the variation of ^{238}U concentration, together with other radionuclides in Magela Creek water (Johnston et al. 1988). No peak ^{238}U concentration was observed in either unfiltered or filtered water. Transport of uranium by creek water was associated with the filterable or fine colloidal material and not with the suspended matter (>0.45 µm) which follows the hydrograph (Hart et al. 1987b). This indicates that surface runoff is not the main source of uranium in Magela Creek water. Data for uranium in unfractionated Magela Creek and Magela Floodplain sediments (Noller and Hart 1993) and deposition of radionuclides including ^{238}U (Johnson et al. 1987), show generally similar concentrations of uranium in floodplain sediments compared with upstream creek sediments. The uranium concentrations are, however, greater in the <20 µm sediment fractions taken from the upstream backflow billabongs around the Ranger deposits and at the downstream Magela Floodplain sites. The most likely hydrological uranium transfer process firstly involves relocation from the exposed orebody via groundwater, with subsequent transfer in dissolved and colloidal forms via Magela Creek.

Data for sediment carbon content show an association of high values with the finer fractions of suspended material transported by Magela Creek (Noller and Hart 1993). This is supported by results for organics in fractions of particulates collected during the 1985-86 Wet season (Hart et al. 1987b). It was found that the coarse (>0.45 μm), fine (0.1-0.45 μm) and colloidal matter (0.015-0.1μm) respectively, had mean concentrations of 21%, 60% and 83% organics.

Several studies have shown that adsorption of uranyl ion on organic matter, including humic acids and particularly in the pH range 4 to 5, is an important uranium transfer mode e.g. Ho et al. 1985, Shanbhag and Choppin 1981. Uranyl ion showed greater selectivity of fixation with organic matter for a pH range 2 to 4 than all other heavy metal ions examined, including cupric ion. Fixation is by interaction between the cationic uranium species and anionic carboxylate groupings and is independent of the amount of the cationic species fixed with regard to the cation exchange capacity of the organic matter and existence of a pH effect (Disnar 1981). A pH range of 3 to 5 was found for uranyl ion adsorption on peat (Van Der Weijden and Van Leeuwen 1985).

The presence of humic acid, together with pH, influences the adsorption of cationic uranium species onto other surfaces such as haematite. In the absence of humic acid at low pH (4.30), uranium uptake, as uranyl ion, is low and only weak interactions occur between uranyl ions and haematite surfaces (Ho and Miller 1985). Addition of humic acid increases uranyl ion uptake in haematite, with greater adsorption occurring at pH 4.3 compared with pH 6.36. Further, they showed that, at pH 6.36, $(UO_2)_3\,(OH)^{5+}$ is the predominant uranium species and shows high adsorption onto haematite surfaces which decreases abruptly when humic acid is added. The haematite surface becomes saturated with humic acid and complex formation occurs between unbound humic acid in solution and the cationic uranium species. Bicarbonate ion complexing prevents uranium adsorption onto haematite and Ho and Miller (1986) showed that uranium is adsorbed by haematite in bicarbonate solution as the $(UO_2)_2\,CO_3\,(OH)_3^-$ species for pH 6.5 to 8.0 In the pH range 6.5 to 9.1, they showed that several dissolved uranium species exist in solution, of which $(UO_2)_2CO_3(OH)_3$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$, are the dominant species at $25^{\circ}C$. Shanbhag and Choppin (1981), demonstrated that, in natural waters, including seawater at pH 8 and carbonate ion at 10^{-5}M, the uranyl ion exists entirely as the carbonate complexes and humate cannot compete with carbonate as a complexor of uranyl ion. In natural waters of lower pH, as are present in Magela Creek (pH<6.5), the above may not be the case. At pH 6 and a carbonate concentration 10^{-7}M, together with a humate concentration 10^{-4} M, it was shown that uranyl ion will be complexed predominantly by humate-containing material (ibid.). Passage of groundwater through insoluble humate-containing material should lead to strong adsorption of the uranyl ion, including on colloidal particles. Thus the presence of humic acid plays an important role in the transfer of uranium species from groundwater to the upper regolith.

Organic loams are commonly found in shallow depressions on the Magela floodplain (Bettany et al. 1981). Organic matter in the floodplain surface ranges from 3.2% to 16.8% carbon (Noller and Hart 1993). Other sediments in the ARR contain similar carbon percentages. A plausible mechanism for uranium transport to the floodplain is for uranyl ion to be adsorbed on humic-containing particles. This is supported by the fact that appreciable uranium was found in the 'fine silt+clay' fraction of sediment from the Magela floodplain, together with high levels of organic carbon, relative to levels in the channel billabongs and creek.

The Ranger Uranium Mine generated larger quantities of waste rock materials than were able to be returned to the mined out pit, because only a small fraction of the ore (0.3%) is removed from the site. By the time Orebodies Nos. 1 and 3 are mined out circa 2012, the combined mass of uranium mill tailings, waste rock and subeconomic grade ore remaining will be approximately 175 MT, which may form an artificial landform with an area of some

4 km^2 and a height of about 17 m (East et al. 1994). The uranium tailings have special containment requirements because of their radioactivity, which is associated with the presence of residual long-lived isotopes, particularly ^{230}Th and ^{226}Ra ($t_{1/2}$ 80 000y and 1600y respectively). Above-ground structures for containment of tailings are required to have an engineered structural life of 1000 years, over which time the tailings should be isolated from the environment. A major difficulty in designing such long lived structures in the ARR is the provision of rock and earth slopes with sufficient resistance to erosion. There is great potential for high erosion rates on disturbed or engineered slopes in the ARR, which has a seasonally wet tropical climate with a long dry season, and a wet season with high intensity rainfalls. Undisturbed natural slopes nearby, however, have great resistance to erosion, even at gradients over 30 degrees.

Erosional monitoring trials of waste rock slopes at Ranger, comprising both highly weatherable massive chlorite and a more weathering resistant chlorite schist, show removal of both suspended matter and soluble constituents during and following rain events (ibid.). The water derived from this runoff is dominated by magnesium and sulfate ions with some bicarbonate. The last is from dolomite, which dissolves in acidic waters. Data for runoff from waste rock at Ranger Mine over several years shows that moderately alkaline waters of about pH 8 result from this interaction. The presence of bicarbonate allows solution of uranium from the waste rock and gives a final concentration in the emanating water of about 50 ppb uranium.

Release of the waste rock runoff water is permitted each year once sufficient flow is achieved in the nearby Magela Creek. The preferred pathway at Ranger Mine is to release overflow waters from a sedimentation pond (RP4) via the backflow Djalkmara Billabong, adjacent to Magela Creek. Studies on the fate of the constituents in RP4 water, which included uranium, show that its concentration rapidly decreases once the water enters the billabong. In contrast, the major ions are not attenuated and their concentrations are only reduced by dilution. At the end of the 1992-93 wet season, data for uranium concentration and conductivity showed almost complete removal of uranium from the water column (<0.5 ppb (filtered) and 900 µS/cm, representing remnant major ions. This situation prevailed for the duration of the 1993 dry season.

During and following mining, uranium is released by chemical weathering from the waste rock dump in oxidised form, i.e. as the hexavalent uranyl ion. The dispersion of this soluble uranium is limited over ground by the humic matter and sesquioxides inherent in the soil and in surface waters by the passage through natural billabongs, which contain high amounts of organic matter and therefore act as wetland filters. That water which does not not pass through such billabongs, is not cleaned up as well and is the source of the inorganic solids and solutes contained on and in the floodplain. Aquatic plants thus play a key role in minimising the dispersion of the colloidal particles which otherwise might be transported there. The aquatic plants contribute the "bio" to the biogeochemical cycle.

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BENTONITES FROM AMOTAPE (GRAU REGION, PERU), AS EXCHANGE MEDIUM FOR HEAVY METALS IN INDUSTRIAL WASTE WATERS.

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Key words: bentonite, cation exchange, copper, cobalt, nickel, zinc,

In Grau region, province of Paita (northwestern Peru), there are abundant and important bentonite deposits of tertiary age, in proximity to Amotape village. These deposits consist of beds of 1.30 to 2.50 metres thickness, interbeded with lutites and sandstones related to the Chira formation (Upper Eocene).

The bentonite, essentially composed of montmorillonite and related minerals of the smectite group, have a good cation exchange capacity. This property is due to the presence of interlayer cations as Ca^{++}, Na^{+}, K^{+}, etc., compensating the negative charge deficiency of the silicate layers.

The aim of the present work is to investigate the properties of bentonite from Amotape zone, as cation exchanger of heavy metals, and their possible application for the decontamination of industrial waste waters.

Representative clay mineral samples of two deposits (Quebrada Gorda and Pituso-4) from the mineralized area, have been used for study. Selected deposits represent two different types of bentonites differing in the total charge, what involves different geochemical behaviour with regard to their cation exchange capacity. Physical, chemical and mineralogical characterization of these bentonites is represented in table 1. Measurements of cation exchange capacity (CEC) of bentonites have been carried out for representative samples: Quebrada Gorda deposit (96.8 meq/100g) and Pituso-4 deposit (55.3 meq/100g).

Laboratory experiments consisting of mixtures of bentonite with prepared monometallic solutions of some heavy metals (copper, cobalt, nickel and zinc) in the form of sulphate, have been realized. Solutions containing two or more of the mentioned heavy metals have been used as well. The sorption grade have been stablished for variable experimental conditions of metallic concentration, pH, ionic strength, bentonite amount and granulometric size, mixing time, agitation and temperature.

The solutions have been analysed for copper, cobalt, nickel and zinc, by atomic absorption spectroscopy. The ionic strength effect has been evaluated by addition of sodium and potassium sulphate into solution. Anyway the presence of organic and inorganic added ions as AEDT, Ca^{++} and Cl^{-} in solution, has been considered.

In bentonites from Amotape zone, the sorption of heavy metals as results of cation exchange in interlayer spacings of the montmorillonite show some important characteristics:
- Sorption is accordint to Freundlich isotherm model.
- Under same experimental conditions, rates of retained heavy metals decrease in the order: Cu-Ni-Zn-Co.
- The exchange grade of heavy metals appears to be pH-dependent, increasing with pH values, and showing a minimum for pH values around 2.5.

Sorption rate of heavy metals in bentonites is very high for low concentrations of heavy metals in solution, decreasing when metal concentration increases. The effect of increasing ionic strength is a decreasing of the sorption rate of heavy metals.

The granulometric size of bentonites is very important for its comportment as exchange medium of heavy metals, and sorption rate increases with decreasing of bentonite grain size. Sorption is specially high for grain size lower than 2 microns.

As conclusion, and from the actual state of the research, can be drawn that bentonites from Quebrada Gorda deposit exhibit higher cation exchange capacity than Pituso-4 deposit, which is according to their different geochemical characteristics. Then bentonites from Amotape zone have good properties as exchange medium of Cu, Co, Ni and Zn from contaminated solutions; and under the laboratory experimental conditions, in the particular case of copper, their sorption rate can arrives up to 99.6 %.

TABLE Nº 1

Physical Characterization

Deposit	Density (g/cc)	Bulk Density (g/cc)	Porosity (%)	Swelling (c.c)	Specific Surface (m^2/g)
Q.G	2,41	2,17	9,76	10	52,4
P.4	2,49	2,20	12,07	7	62,5

Chemical Characterization

Deposit	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	MnO	LOI
Q.G	68,7	0,13	11,1	2,17	1,18	0,83	1,93	0,84	0,1	-0,01	12,7
P.4	66,3	0,17	12,4	2,85	2,45	0,39	1,84	0,37	0,02	0,03	11,9

Mineralogical Characterization

Deposit	Smectite	Cristobalite	Feldspar	Plagioclase	Zeolita	Hornblende	Quartz	Hematite	Goethite	Gypsum
Q.G	70,21	25,09	0,3	0,72	2,17	0,12	0,74	0,18	0,48	0,12
P.4	83,20	14,08	0,13	0,74	0,15	0,06	0,46	0,05	0,31	0,03

Q.G : Quebrada Gorda
P.4 : Pituso Nº 4

Objective and significance of ecosystem prediction and geochemical mapping[1]

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Keywords: geochemical map, ecosystem prediction

Ecosystem prediction and geochemical mapping derived its inspiration from a research program sponsored by Natural Science Fundation of China (NSFC): "Investigation on localizing the areas with high incidence of diseases by using multi-element distribution map and searching for the pathogeny". This paper seeks to find out and identify the health or disease patterns and make ecosystem comparison by presenting them in the form of geocartography, a method which best suits its purpose. The work is based on the finding of "the multi-element distribution maps" and " regional geochemical prospecting" conducted by the Ministry of Geology and Mineral Resources, surveys on regional correlation in ecosystem and long-term observations made by departments of agriculture, forestry, husbandry, environmental protection and medical science as well as other related data and statistics. It also draws on the advanced experience, theory and methodology of exploration geochemistry, ecology, prospective medicine, geography and other disciplines, and by consulting the multi-element distribution maps to localizes the hyperendemic domain and then investigate the pathogenic agents. Hence the title of this research program is "Ecosystem Prediction and Geochemical Mapping".

The traditional "ecosystem mapping" and "disease distribution map" refer to a description of the regional correlation survey on botanical ecology (namely, the biomorphous state) and the symptoms and traits of population. In such a map, the prevalence rate, mortality rate and other statistical treatments and morphological descriptions are plotted in exact positions by appropriate means of specific types and geoecotype of animals and plants as well as the map of disease distribution among human groups can in no way indicate the time distribution of the disease, nor the distribution among different groupings of humans (or among different ecospecies). Without a clearly defined pathogenic background, it would be very difficult to trace the root cause to the distribution of elements, or to describe the special features of different types of environments in terms of ecology and epidemiology. Therefore, the traditional approach has its limitations.

This research program is meant to conduct a multi-disciplinary experimental study by making use of the Provisional Geochemical Atlas of Northwestern Jiangxi province, and the data collected on the distribution of diseases of an ecological and geochemical character in the district. Its purpose is to explor a standardized working method and a mapping pattern by the concerted efforts of various institutions so as to pave the way for future drawing of a formal "Ecosystem Prediction and Geochemical Mapping". Geochemical environmental diseases refer to endemic diseases, public nuisance diseases (mainly non-contagious and non-hereditary diseases) which respond to the treatment by compounds and chelates of various elements and are liable to be effectively protected against.

Ecosystem Prediction and Geochemical Mapping is based on prolonged observations of the dynamic state of human groups and biological colonies. All the statistical data indicating the state of health (evolution), disease (regression) and measurements of frequency (such as fatality rate, prevalence rate, high quality rate and etc.) are patternized by computerization geographical simulation modelling. By referring and comparing to the multi-element distribution maps and the geographical environmental background maps, it localized the adaptive state, namely the generative causes of health (evolution) or disease (regression), and the trend of development, calculate the benefited area (or the victimized area), and explores the relationship between

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[1] The project supported by National Natural Science Foundation of China (NSFC)

diseases whose pathogenic causes are yet unknown and the distribution of elements in the soil and water. In this way it aims to provide a basis for the use of chemical elements for the treatment and control of the diseases and their prevention. The differentiation between health and disease means the difference between the normality and abnormality of the various criteria while the differentiation within diseases refers to the difference between the criteria of symptoms and signs.

The suitability of floodplain sediment as a global sampling medium: evidence from China

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Keywords: floodplain, sediment, representativity, coverage, geochemical, mapping

The objective of the International Geochemical Mapping (IGM) project is to compile surface geochemical maps of the earth as tools in the search for new resources and solution to environmental problems. It is likely, however, that we will have to wait one or two centuries to see such maps, which will only be feasible after completion of a large number of separate national geochemical mapping projects (Xie, 1993).

Research undertaken by IGCP259 (Darnley et al., 1994) leads to the conclusion that wide-spaced sampling is crucial to the concept of IGM, as it appears to provide the only practical way to obtain a relatively rapid (10-20 year) overview of global geochemistry. Thus it is important that IGM demonstrate the validity and usefulness of wide-spaced sampling.

In 1982-93, geological teams in Zhejiang province (south of Shanghai) conducted a very extensive 40-element survey of stream sediment over the entire province. In 1993-94, a supplementary survey was carried out on the basis of the provincial survey. Most of the 100,000 km^2 was divided into 15 super-catchment basins (SCBs) of 1000-10,000 km^2 each in area. From each SCB 3-11 stream sediment samples, each representing a component catchment basin of 100-1000 km^2 within the SCB, were taken; also gathered were one surface floodplain sediment sample from a depth of 5-30 cm, one deep floodplain sediment sample from a depth of 80-120 cm, and one steam sediment sample (this latter representing the entire SCB). Thus three levels of data were available, permitting a hierarchical evaluation of the samples.

Thus far the 120 stream sediment samples (including 15 composite samples from the 102 samples representing 102 component-catchment basins) and 30 floodplain sediment samples have been analysed for 46 elements, using the muti-element multi-method analytical system devised for China's Regional Geochemistry-National Reconnaissance (RGNR) project. The standard reference samples GSD 1-8 (Xie et al., 1985a;1985b;1989) were used for quality control. Detection limits achieved were the same as those recommended for the IGM (Xie, 1994).

Floodplain sediments show good suitability as a global sampling medium. Contents of individual elements in floodplain sediments in a SCB of 1000-10,000 km^2 agree with the average values derived from RGNR data. Preliminary statistical tests also demonstrate that the values for elements in the component catchment basins and SCBs are not significantly different from RGNR results.

Geochemical maps of Sb, Na_2O, Sn, Ag and 40 other elements show that there are strong similarities in distributions and trends among the three levels of data.

Two geochemical provinces of F and Ag have been outlined by means of 15 floodplain sediment samples, these are in surprisingly coincidence with RGNR maps.

Wide-spaced sampling can be utilized to monitor environmental change and also to predict environmental hazards in the making. Heavy Hg pollution has been detected in several areas of Zhejiang province thanks to data collected for this investigation. Maps predicting the scale and extent of Hg pollution in Zhejiang in the year 2044 have been drawn up on the assumption that the speed with which pollution spreads in 1994-2044 will equal that observed in 1944-1994. The map indicates the existence of a potential chemical time bomb.

Many thanks to the Shen XiaChu, Gu Tixin and Gu Jinqiu for their assisting with field works, Wang Zhongmin assisting with statistic tests work. We benefited from discussion with Dr. R. Garrett regarding the interpretation of methods. We would like to express our cordial thanks to Dr. W. White for his help in editing the manuscript.

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The importance of mobile forms of chemical elements for decision of exploration and environmental tasks

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Keywords: mobile forms, exploration, environmental

New geochemical methods have been developed lately with results being highly effective for solving of many applied tasks. Among the most perspective ones are as we are sure the methods of investigation of mobile forms of chemical elements.

As mobile forms of chemical elements we treat those ones that are thermodynamically stabile in water under varios physical-chemical conditions of the environment and the forms that are easily transferred from minerals and rocks into water solutions and can easily migrate to large distances.

In the first case we have used stability of various forms of chemical elements in water to work out hydrogeochemical method of exploration with preliminary thermodynamic analysis and in the second case - geochemical method of exploration by superposed haloes of chemical elements (methods of exploration by mobile forms of chemical elements in soils).

It has been established that transference of mobile forms of chemical elements from ore bodies to the surface can take place by capillar uplift, diffusion, free filtration and other processes. Reaching the surface they are sorbed and form syperposed haloes. These haloes form geochemical anomalies even above blind ore bodies covered with thick layers of sedimentary rocks.

Geochemical anomalies of mobile forms of chemical elements are recognized by extraction of that quantity of chemical compound (element) which came from ore body (was sorbed) taking to account kinetics and dynamics of sorbtion-desorbtion process.

High effectivity of method is proved during exploration for fluorite, polymetals rare and scattered elements and other mineral deposits.

The use of mobile forms of chemical elements are very important for solving of environmental tasks. Ecological-geochemical maps, plotted in most cases by data of spectral analysis reflect total content of chemical elements and toxic compounds in soils.

However behaviour of chemical element in trophic line water - soil - plant - animal - man is determinated by its forms and their migrational ability. That's why we consider that only ecologic-geochemical maps of mobile forms of chemical elements give ecologic estimation of the territory and may be the basis of scientific forecast of the environment.

Geochronological Studies of Weathering

Use of light stable-isotopes in the exploration of the regolith

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Keywords: Oxygen isotopes, carbon isotopes, sulphur isotopes, geochronology, palaeovegetation, mineral exploration

The isotopic ratios of several of the light elements can be used to trace the conditions of formation of the regolith. In this presentation three applications are considered. Firstly, the use of $\delta^{18}O$ (a measure of the $^{18}O/^{16}O$ ratio) of weathering minerals, particularly kaolinite, to define past Earth-surface temperatures. Such measurements can also be used to investigate tectonic uplift (eg. for Papua New Guinea, Chivas et al., 1984) and, in the case of a rapidly translating continent like Australia, used as a chronometer for regolith formation since the Permian.

The second medium for investigation is carbon-bearing regolith materials, such as calcrete or iron nodules where $^{13}C/^{12}C$ ratios can provide information about palaeovegetation patterns. Here the distinction between the past presence of C_3 plants (trees and shrubs) and C_4 plants (typically, warm-growing-season grasses), and their mixtures can be made.

The final example is the use of $^{34}S/^{32}S$ ratios to firstly understand the origin of surficial sulphate on the Australian continent and secondly to apply this to the detection of anomalous sulphur sources related to economic mineralization by sampling the regolith directly or by sampling groundwaters.

Oxygen-isotope compositions are expressed as a normalized ratio between the minor isotope, ^{18}O, and the more common isotope, ^{16}O. Typically the $^{18}O/^{16}O$ ratio is ~1:500, and such ratios are compared to that in a standard material; in this case, V-SMOW (Vienna Standard Mean Ocean Water). The normalized ratio is multiplied by 1000 to produce a value, termed $\delta^{18}O$ ("delta O-18") that can be readily compared with similarly calculated values for many materials. $\delta^{18}O$ values, by virtue of the multiplier of 1000, are therefore expressed in parts per thousand, or per mil units (‰). The equation describing the definition of $\delta^{18}O$ is:

$$\delta^{18}O_{\text{V-SMOW}} \text{ (in ‰)} = \left[\frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{V-SMOW}}}{(^{18}O/^{16}O)_{\text{V-SMOW}}} \right] \times 1000$$

$\delta^{18}O$ values are small numbers of the form X.X that may be either positive or negative. The $\delta^{18}O$ value of the V-SMOW standard itself is zero. Similar expressions for the isotopes of hydrogen ($^2H/^1H$), carbon ($^{13}C/^{12}C$), and sulphur ($^{34}S/^{32}S$) can be elucidated as δD values (D = ^2H, or deuterium), $\delta^{13}C$ values and $\delta^{34}S$ values, respectively. The standards for $\delta^{13}C$ and $\delta^{34}S$ are Pee Dee belemnite (PDB) and Cañon Diablo troilite (CDT), respectively.

$\delta^{18}O$ in clays

The oxygen- and hydrogen-isotope compositions (expressed as $\delta^{18}O$ and δD values) of a mineral are related to its temperature of formation and the isotopic composition of the water from which it crystallized. For minerals formed near the Earth's surface during weathering, the water is typically groundwater, or meteoric water (i.e. water in isotopic equilibrium with the atmosphere). As the isotopic composition of meteoric water varies principally as a function of the temperature of rainfall condensation at the time of recharge of groundwaters, both rainfall and unevaporated groundwaters have $\delta^{18}O$ and δD values related to global mean temperatures. Thus there is a regular relationship between latitude/altitude and isotopic values.

During weathering, this same variation in isotopic composition as a function of temperature is preserved in newly-formed minerals that are precipitated in equilibrium with groundwater. This relationship holds true for a variety of weathering minerals but is most easily demonstrated for the clay minerals, where it has been shown that the $\delta^{18}O$ values for kaolinite are retained for up to 240 Ma. Thus gross distinction between cold-climate and warmer weathering is readily made.

Tectonic movement of weathered cratons either by translation or uplift can also be detected by comparison of the preserved $\delta^{18}O$ values in kaolinite with those calculated for the present situation from the isotopic composition of modern rainfall. Conversely, if the rates of motion of such plates are known, the interpolated ages of weathering can be deduced. A broad conclusion of this work is that cold-climate weathering is a common event, but not so well preserved at current high latitudes owing to Quaternary glaciation. The presence of deep weathering profiles in the geological record should not be necessarily taken to indicate past "tropical" conditions or latitude.

The above methodology is ideally suited to the study of clays from both deep-weathering and reworked-sedimentary environments in the Gondwanaland continental fragments. For example, oxygen-isotope results from clays in Australia and India demonstrate the expected substantial climate shifts related to continental translations since the Permian. Isotopic results from South America, where continental drift was less during the Cretaceous and Tertiary periods show only minor changes with time. The existence of the Australian Eastern Highlands since the Cretaceous is also strongly supported by isotopic results on surficial clay minerals (Chivas and Bird, 1995).

Weathering profiles from eastern Australia, still at the Earth's surface and currently exposed at a variety of elevations (0 to 1200 m) along the Eastern Highlands may be dated by their stratigraphic relationships, particularly by reference to dated basaltic outpourings. Such basalts span the range from 70 Ma to a few thousands of years old. Weathering profiles of five demonstrable age ranges are recognized (1) Early Permian, (2) pre-Late Mesozoic (?ie. Triassic-Jurassic), (3) Late Mesozoic-Early Tertiary, (4) post-mid-Tertiary, and (5) Tertiary and recent from monsoonal northern Australia. The $\delta^{18}O$ values of kaolinite separated from these profiles show a progressive increase for successively younger profiles (Bird and Chivas 1988a, b; Bird et al. 1990). This is in keeping with the continental drift history of Australia to progressively lower latitudes, and implies much lower sea-level air-temperatures in the Late Cretaceous-Early Tertiary (5°C cooler than today), and in the Mesozoic (10 to 17°C cooler). The Permian clays, have the lowest $\delta^{18}O$ values ever measured for a weathering clay and imply weathering under the influence of glacial meltwaters (Bird and Chivas, 1993). By contrast, the presence of kaolinite of weathering origin has previously been taken as an indicator of a warm climate in Australia during the Permian (Loughnan 1991).

The generalized $\delta^{18}O$ versus time trend can be used as a crude geochronometer to date weathering profiles of unknown age using the $\delta^{18}O$ value of their kaolinite (Chivas 1983). Such application (Bird and Chivas 1989) reveals the widespread occurrence of low-^{18}O kaolinites in Australia and the implication that much of the Australian landscape developed during the Mesozoic Era and under relatively cold conditions.

$\delta^{13}C$ in calcretes

Recent studies have shown that the $\delta^{13}C$ value of soil carbonates is determined by the $\delta^{13}C$ value of the plants that grew at the soil site during pedogenesis. Most plants fall into three distinct groups with respect to their carbon isotopic compositions (Smith and Epstein, 1971; Bender *et al.*, 1973). C_3 plants average -27‰ in $\delta^{13}C$ (PDB) and include nearly all trees and shrubs, and those grasses favouring cool growing seasons. C_4 plants average -13‰, and include grasses adapted to warm growing seasons, and a few shrubs. A third group called CAM plants, which include cactus, yucca, and many epiphytes, are not important in the Australian ecosystems. Plants produce large amounts of CO_2 as they respire and decay. In soils where the plant respiration rate is high, soil carbonate will be 14 to 17‰ enriched in ^{13}C compared to coexisting plant organic matter. Thus, soil carbonate formed in the presence of pure C_3 and pure C_4 biomasses will have average $\delta^{13}C$ values of -12 and +2‰, respectively. In soils where soil respiration rates are lower, such as in deserts, $\delta^{13}C$ values of carbonate can be further enriched in ^{13}C by several per mil due to mixing with atmospheric CO_2.

Recent analyses of soil carbonate (Quade et al., 1995) and carbon in iron nodules (Bird et al., 1994) in Australia demonstrate that (palaeo)vegetation information is preserved in both media. Incidentally there is little to no relationship between the $\delta^{13}C$ values of regolith minerals and underlying rock types nor distance from the ocean (ie. the marine aerosolic transport of HCO_3^- is swamped by the atmospheric CO_2 contribution).

The $\delta^{13}C$ technique can be used, in favourable circumstances, to distinguish, in the regolith, between pedogenic carbonate and non-atmospherically-related carbonate precipitates (ie. tufa, sinter and spring deposits), particularly if the $\delta^{13}C$ values of co-existing organic matter is measured. This may be important if putative calcretes are being directly analysed during geochemical exploration.

$\delta^{34}S$ in the regolith

The $\delta^{34}S$ values of gypsum and alunite from playa lakes and regolith outcrops and of dissolved sulphate in groundwater (Chivas et al., 1991) produce a pattern of values that is related to modern coastlines. Highest values ~+21‰, occur near the ocean, with values decreasing to ~13% in central Australia. In humid areas, eg. southeastern and southwestern Australia, bacterial sulphate-reduction is common and the $\delta^{34}S$ pattern for residual sulphate can be perturbed to higher $\delta^{34}S$ values (~+30‰).

The continent-wide patterns relate to the delivery of atmospheric sulphate via precipitation. The ultimate sources of the sulphate are inorganic marine sulphate ($\delta^{34}S$ ~21‰) and plankton-produced dimethylsulphide ($\delta^{34}S$ ~15.6 ± 3.1‰, Calhoun et al., 1993). The regular pattern of $\delta^{34}S$ values for Australian 'surficial sulphate' provides a baseline against which to search for anomalous $\delta^{34}S$ values associated with base-metal or gold mineralization.

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Application of U-series Geochronology for Surficial Geochemistry and Landscape Evolution

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Keywords: U-series geochronology, Quaternary, landscape, silcrete, calcrete

Understanding weathering and landscape processes in the design, collection and interpretation of geochemical data sets used to locate drilling targets in deeply weathered terrains is of paramount importance in mineral exploration. Many geomorphological models suffer from the lack of chronological control that is essential for quantitative modelling of landscape evolution. Improved resolution of the Quaternary history is essential for the development of better constrained geochemical models for regolith development. This improved understanding will have a major impact on the identification of potential blind mineral targets thereby increasing the success rate and lowering the total cost per discovery.

Our ability to constrain time during the Quaternary has recently been revolutionized with the development of mass spectrometric techniques for the precise measurement of U-series isotopes. The new technologies of high abundance sensitivity thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS) allows the accurate dating of earth processes during the last half million years with precision currently not readily obtainable in Australia (± 5 a in 0.2 ka and ±1 ka in 150 ka, to ± 20 ka in 500 ka). Age resolution at this scale is critical to our understanding of the time scales in natural processes.

The ^{238}U and ^{235}U decay series isotopes (^{234}U-^{230}Th-^{226}Ra and ^{231}Pa) are particularly useful in providing age information about the timing of crystallization in igneous rocks that are too old to be dated by ^{14}C methods and too young for K-Ar or ^{40}Ar/^{39}Ar. The U-series daughter isotopes are typically determined by measuring activities using α-spectrometry. Unfortunately, this technique imposes severe limitations to ^{238}U-^{230}Th geochronological studies of igneous rocks and minerals because: (1) the large sample size (1 to 5 g) required to yield *ca.* 1 mg of ^{238}U; (2) long analysis times are required, depending on the ^{238}U content; and (3) poor precision is generally achieved in determining the ^{230}Th/^{232}Th ratios 3-5% (2σ).

Developments in thermal ionization mass spectrometers (TIMS), and analytical techniques by a number of groups over the last decade have revolutionized Quaternary chronological studies of marine carbonates, speleothems and volcanic rocks (Edwards *et al.*, 1986/87; Williams *et al.*, 1992; Cohen *et al.*, 1992; Palacz *et al.*, 1992; Ludwig *et al.*, 1992). Determination of ^{230}Th/^{232}Th ratios by TIMS has the advantage of: (1) direct measurement of ions of elements; (2) achievement of significantly higher precision measurements 0.3% (2σ); (3) the ability to analyse smaller amounts of Th (50 to 100 ng), which is particularly important in mineral isotopic studies; and (4) rapid analysis times (hours rather than days). Although ^{230}Th/^{232}Th atomic ratios of 10^{-3} to 1 can be measured in marine carbonates by conventional single focusing TIMS, the precise and accurate measurement of ^{230}Th/^{232}Th ratios in volcanic rocks and minerals is significantly more difficult. This is due to the poor ionization efficiency of Th, the fact that these ratios are typically in the range 140,000 to >500,000, and the presence of a sloping tail from ^{232}Th under mass ^{230}Th. At the present time the TIMS at UQ is the only instrument in Australia with the proven ability to yield high precision ^{230}Th/^{232}Th in volcanic rocks (Collerson *et al.*, 1995). It is also ideally suited for the somewhat less onerous task of measuring ^{230}Th/^{234}U ratios in carbonates.

The timing of crystallization of igneous rocks can be obtained using ^{238}U-^{232}Th disequilibrium by the internal isochron method or by measuring the decrease in excess ^{230}Th in whole rocks with time. Chronological information for igneous rocks can also be obtained using ^{226}Ra-^{230}Th disequilibrium and ^{235}U-^{231}Pa disequilibria, using precise isotope ratio measurements by TIMS. Age resolution in the range 0 - 8 ka has been demonstrated with ^{226}Ra-^{230}Th disequilibrium techniques (e.g. Rubin and Macdougall, 1990). With ^{235}U-^{231}Pa disequilibria chronology, ages of

0 - 130 ka (with an accuracy of ±1-7 ka) have been reported (e.g. Goldstein *et al.*, 1993).

Absolute dating of silcretes and laterites will provide valuable information about the climate and geochemical environment prevailing during the formation of landscape surface deposits. Although some laterites have been successfully dated by K-Ar and Ar/Ar analysis of supergene managanese oxides, the absence of these phases in silcretes prevent us from using these same methods. One common and unique feature of silcretes is their unusual enrichment in the elements Zr and Ti. Although the precise phase hosting Zr is poorly known, Ti in silcretes is commonly hosted by anatase. Because anatase displays essentially the same mineralogical and crystal chemical characteristics of rutile, it is theoretically possible to date this phase by the U-Pb, Pb-Pb, and U-decay series methods (in Quaternary anatase). Preliminary microprobe analysis of anatase from weathering profiles in Brazil indicates a high U content and relatively lower Th content, confirming the suitability of anatase for U-series dating. U-series dating method has the potential to address youg silcretization events or the recrystallization of older silcretes in the recent past.

The application of these methods in dating silcretes have not been successfully developed because it requires a combination of detailed crystal chemical and high spatial resolution, low blank isotopic studies of supergene Ti oxides. It also requires the application of U-Pb, Pb-Pb, and U-decay series in the same study in order to address all the possible processes, ancient and recent, which may have promoted the precipitation or recrystallization of supergene Ti oxides.

U-series techniques for dating carbonates (calcretes) and speleothems and their application to the study of landscape evolution will also be reviewed.

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Weathering history of the Australian regolith: the evidence from K-Ar and $^{40}Ar/^{39}Ar$ dating of supergene K-Mn oxides and alunite-jarosite minerals.

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Keywords: Australia, weathering, cryptomelane, alunite-jarosite, K-Ar, $^{40}Ar/^{39}Ar$

Under particular climatic conditions, tetravalent K-Mn oxides and alunite-jarosite minerals ($KAl_3(SO_4)_2(OH)_6$ - $KFe_3(SO_4)_2(OH)_6$) can be formed during terrestrial chemical weathering of rocks. The presence of potassium in the structure of these minerals makes them useful for dating chemical weathering utilising the decay of ^{40}K to radiogenic argon ($^{40}Ar^*$). Here, we present the results of K-Ar and $^{40}Ar/^{39}Ar$ dating of weathering-related K-Mn oxides (mainly cryptomelane $(K,Ba)Mn_8O_{16}.xH_2O$) from supergene Mn deposits in northern Australia (Groote Eylandt Manganese Deposit), northwestern Australia (the Pilbara and Peak Hill Mn Provinces) and from many scattered occurrences of K-Mn oxides found in deeply weathered rocks in Western Australia. In addition, the results of K-Ar dating of weathering-related alunite and jarosite minerals are compared with those obtained on K-Mn oxides.

Cryptomelane-hollandite minerals appear to be the most promising tetravalent K-Mn oxides for dating by the $^{40}Ar/^{39}Ar$ method. In order to investigate the argon release characteristics of these minerals in vacuum, two irradiated samples of pure cryptomelane with banded texture were subjected to incremental stepwise heating experiments. The argon release spectra of both samples are very similar and show that almost 80% of the atmospheric argon was released at or below 600°C. On the other hand, radiogenic and nucleogenic argon ($^{40}Ar^*$, ^{39}Ar, ^{38}Ar, ^{37}Ar) are released predominantly between about 700 and 900°C. All radiogenic and nucleogenic isotopes have remarkably similar release patterns suggesting that these isotopes occupy similar structural positions.

The Arrhenius plot shows that the diffusion of argon from cryptomelane between 300° and 1400°C is not controlled by a single diffusion law, but that laboratory heating in vacuo causes major changes in release mechanisms at temperatures around 420°, 680°, 820° and 1000°C. These temperatures correlate with the thermally induced phase transformations of cryptomelane into bixbyite (Mn_2O_3), hausmanite (Mn_3O_4) and cubic Mn oxide with a spinel structure, respectively. The largest proportion of argon was liberated in connection with the phase transformation between 820° and 830°C, which can be correlated with the formation of hausmanite.

Good agreement between the conventional K-Ar ages and the $^{40}Ar/^{39}Ar$ total fusion ages for both samples indicates that no significant loss of ^{39}Ar has occurred as a result of recoil in the reactor. The results of our step-heating experiments compare well with the results of other similar studies (Vasconcelos et al., 1994a, Vasconcelos et al., 1994b).

Thus cryptomelane seems to be amenable to isotopic dating by both the K-Ar and the $^{40}Ar/^{39}Ar$ methods. In ideal circumstances, such ages will reflect the time since formation of this regolith mineral. However, the use of K-Mn oxides for determining the age of weathering by the $^{40}Ar/^{39}Ar$ and K-Ar dating methods may be complicated by: (1) admixture of mica inherited from bedrock and (2) mixing of several different generations of weathering-related minerals. These problems can cause the K-Ar age measured on an impure weathering-related mineral to not accurately record the time of its formation. To correct for admixture of inherited mica a two-stage K-Ar dating technique was applied. This method uses a material-balance approach to correct for radiogenic ^{40}Ar contributed from inherited mica.

Some samples of cryptomelane have finely banded and colloform textures, and therefore may represent several generations, thus prompting the need to investigate age differences on a microscale. The combination of microsampling and laser microprobe $^{40}Ar/^{39}Ar$ dating allowed us to date thin overgrowths, groups of adjacent growth bands and thin veinlets that traverse the matrix.

Total fusion age determinations of several groups of growth bands of a Late Oligocene densely layered cryptomelane from the Woodie Woodie manganese deposit (NW Australia) suggest an averaged growth rate of 0.8 ± 0.3 mm/Ma. However, the growth rate calculated for much of

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the overall band sequence is 1.5 mm/Ma, which is five times greater than 0.3 mm/Ma calculated for the remaining youngest group of bands. The development of this banded concretion appears to have occurred at an uneven rate. The small growth rate might be the result of very slow growth of cryptomelane, and/or the presence of hiatuses in cryptomelane precipitation. The fact that the relative probability graph of total fusion ages from the banded cryptomelane shows several peaks (25, 26.5, 28-28.5 and 29.5-30 Ma) supports the latter idea.

Total fusion ages measured on void filling banded and colloform cryptomelane in samples from a vertical profile through a mesa-like deposit near Horseshoe (NW Australia) show peaks at 48-52, 43-44, 39-40, 35, and 29-30 Ma. In addition banded overgrowths of cryptomelane-manjiroite were deposited at about 7.5 Ma ago in the lowermost part of the profile. This evidence is interpreted as reflecting an episodic history of weathering-related product formation over a remarkably extended period related to alternation of more humid and drier climatic periods during the Tertiary in Australia.

The results from this study compare favourably with the results of similar studies from Brazil, indicating the existence of relatively globally widespread periods of weathering-related manganese oxide formation in the Tertiary, recording humid climatic conditions.

The K-Ar ages of alunite and jarosite in the western Australian regolith corrected for inherited mica range from essentially the present to ~14 Ma (Early Miocene). This coincides with intensification of climate aridification in Australia, which commenced in the Miocene. Alunite-jarosite minerals from the western Australian regolith yielded much younger ages than K-Mn oxides from the same broad area. We suggest that alunite and jarosite in the regolith are essentially evaporitic minerals, the formation of which marks the cessation of intense chemical weathering and onset of drier climatic conditions. The onset of generally drier climatic conditions in Australia is responsible not only for the precipitation but also for the preservation of alunite and jarosite in the regolith profiles.

This initial work is of a reconnaissance nature, but serves to amply demonstrate the possibilities of utilising the potassium argon isotopic dating system in studies of regolith formation, climatic history and geomorphologic evolution of the landscape in Australia.

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Laser oxygen isotope analysis of weathering goethite from the lateritic profile of Yaou, French Guiana: Paleoweathering and paleoclimatic implications

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Keywords : goethite, oxygen isotopes, laterites, paleoclimate, Amazonia, French Guiana

The results of an oxygen isotope study of goethite from the lateritic profile of Yaou, French Guiana, illustrate 1). the usefulness of the newly developed laser-based extraction techniques to measure the isotopic composition of lateritic goethite and 2) the potential of oxygen isotopes as tracers of paleoclimatic changes in continental environments. The analytical approach used in this study permitted to determine the $\delta^{18}O$ value of individual grains of goethite and investigate grain-to-grain variation within a single sample (or horizon) as well as vertical variation with depth. Without the availability of the laser-based extraction technique analysis of uncontaminated sample of goethite may not have been possible.

Geological and Pedological Context

The lateritic profile of Yaou is located in the western part of French Guiana near Maripasoula. It presently lies near the equator at an elevation of 140 m under hot (T=25°C) and humid (P=2400 mm/year) equatorial climatic conditions. The bed rock is a gold-bearing tonalite containing disseminated hydrothermal pyrite of macroscopic size. The overlying weathering profile is about 28 meters thick. It is essentially composed of a thick saprolite ($\approx$24 m) formed in-situ at the expense of the underlying tonalite. The top part of the saprolite has been truncated by recent erosion and an ochre ferralitic soil (latosol), typical of Amazonian rain forest areas, has developed above it. The mineral assemblage in the saprolite is dominated by smectite, kaolinite and goethite in association with variable amounts of relictual primary minerals (quartz, mica, feldspar). The overlying latosol is essentially composed of quartz, kaolinite, goethite and traces of hematite and gibbsite. The very top part of this soil shows a thin (0.5 m) brown humic horizon rich in organic matter.

At the weathering front between the tonalite and the saprolite, the pyrite is rapidly pseudomorphically replaced by goethite. The goethite pseudomorphs generally preserve the cubic shape of precursor pyrite and range in size from 0.1 to 1.5 mm. Electron microprobe analyses and X-ray diffraction (XRD) data indicate that the goethite is essentially devoid of Al (<0.86 % Al_2O_3). Upward in the profile, the cubes of oxidized pyrite are progressively degraded by dissolution of the goethite. In the latosol, they usually exhibit abundant intragrain microporosity and vugs which are often filled with a neoformed microcristalline plasma of kaolinite mixed with a second generation of goethite, especially in the rim of the pseudomorphs.

Oxygen Isotope Compositions

As a preliminary test, goethite pseudomorphs from one sample (C44/5.1) were segregated by sieving-hand-picking and cleaned by ultrasonic agitation in order to measure their oxygen isotopic ratio. In spite of repeated ultrasonic treatments, a majority of goethite grains could not be totally freed of their microcristalline kaolinite coating. XRD analysis of a powdered aliquot of the goethite concentrate revealed the presence of 5-10% kaolinite. Oxygen isotope analysis of this contaminated aliquot using a conventional fluorination technique yielded a $\delta^{18}O$ value of 3.5 ‰ SMOW. Kaolinite being significantly enriched in ^{18}O compared to goethite, this value can only be considered as a maximum value for the pure goethite end member. Because of the small number of goethite grains available and because of potential isotopic exchange we preferred not to use chemical treatments to remove selectively the contaminating kaolinite. Instead, we performed oxygen isotope analysis of individual grains from the goethite concentrate using a laser-based extraction line.

From the same sample, four grains exhibiting visible kaolinite coatings and four grains apparently free of any kaolinite were selected and analysed. Grains with residual kaolinite coatings yielded $\delta^{18}O$ values between 1.8 and 2.7 ‰ while clean grains yielded lower and more consistent $\delta^{18}O$ values, ranging from 1.0 to 1.4 ‰ and averaging 1.2 ±0.1 ‰. The latter values (1.0 to 1.4 ‰) are considered representative of the pure goethite. In order to verify the internal consistency of the data the isotopic composition of the pure kaolinite was independently measured after removal of the iron by standard chemical treatments. An average $\delta^{18}O$ value of 19.5 ±0.2 ‰ was obtained. Using end member values of 1.2 ‰ for the goethite and 19.4 ‰ for the kaolinite, mass balance calculations indicate that the bulk concentrate would contain 8.5 % kaolinite. This is in good agreement with XRD data and suggests that $\delta^{18}O$ values measured on clean grains are valid. The small scatter in the data for clean grains may represent limited grain-to-grain natural variation and/or small amounts of micaceous inclusions which have been observed under the SEM to be present in some pseudomorphs. However, the scatter remains within analytical uncertainty (±0.3 ‰).

Laser oxygen isotope analyses of goethite pseudomorphs from fourteen samples located at different depths within the profile of Yaou were carried out. Four samples come from the latosol and ten come from the saprolite. Only grains visibly free of any kaolinite coating were analysed. Goethite pseudomorphs from the latosol yielded highly variable $\delta^{18}O$ values ranging from 0.8 to 3.2 ‰. In addition significant grain-to-grain variation is also observed within a single sample. In the underlying saprolite, goethite pseudomorphs exhibit rather consistent $\delta^{18}O$ values ranging from 1.0 to 1.8 ‰ (average 1.3 ±0.2 ‰) between 4 and 18 m depth, and from 2.5 to 3.3 ‰ (average 2.9 ±0.2 ‰) in the lowermost part of the profile between 23 and 28 m depth. In contrast to goethite pseudomorphs from the latosol, the pseudomorphs from the saprolite show no significant grain-to-grain variation within a sample.

The $\delta^{18}O$ value of the water in equilibrium with goethite at 25°C was calculated for each sample analysed using the fractionation equation of Yapp (1990) and compared with measured $\delta^{18}O$ values of local groundwater, soil water and rainfall. $\delta^{18}O$ values are plotted as a function of depth in figure 1. In the saprolite, the lowermost samples (23 to 28 m) appear to be in isotopic equilibrium with the groundwater with which they are in contact. In the middle and upper parts of the profile (3 to 18 m) the calculated equilibrium water is $\approx$1.5 ‰ depleted with respect to present groundwater and 1.5 to 4.5 ‰ depleted relative to soil water and rainfall. In the latosol, the calculated $\delta^{18}O$ values of the goethite-forming water are scattered from $\approx$-5 to $\approx$-3 ‰, i.e., similar or lower than $\delta^{18}O$ values for present rainfall and soil water.

Paleoweathering and Paleoclimatic Implications

These results suggest that in the 5 m interval at and immediately above the weathering front, goethite pseudomorphs may be forming today or formed in the recent past under weathering-climatic conditions similar to present conditions. Because the shift in the equilibrium water $\delta^{18}O$ values (around 20 m depth) does not coincide with the present position of the top of the groundwater table (around 10 m depth), the possibility that the goethite pseudomorphs from the lowermost depth interval may have formed anciently and, subsequently, reequilibrated their oxygen with present groundwater is ruled out.

The goethite pseudomorphs from the middle and upper saprolite (3 to 18 m), which are not in isotopic equilibrium with present groundwater, soil water or rainfall, must have formed in the past under weathering-climatic conditions different from today's conditions. Their lower $\delta^{18}O$ values are unlikely to reflect a climatic temperature higher than today. Indeed, the necessary increase of temperature in order to explain a 1.5 ‰ shift would be 14°C, which would bring the climatic temperature up to 39°C. Consequently, it is most likely that the old goethite pseudomorphs from the middle and upper saprolite formed in the presence of paleogroundwater that was depleted in ^{18}O (by $\approx$1.5 ‰) relative to present groundwater. Essentially two causes may be invoked. It has been suggested that pre-Miocene, i.e., pre-glaciation, oceans may have been depleted by up to 1 ‰ with respect to modern oceans (Sheppard, 1986). If this concept is correct, our data could be explained by assuming a pre-Miocene age for the goethite and, thus, for the middle and upper saprolite. Alternatively, in the absence of a depleted ancient ocean, our data may simply reflect a more intensely monsoonal character of past climate as suggested by Bird et al. (1993) for lateritic profiles from Amazonia. This latter hypothesis agrees with the model of soil development in Amazonia proposed by Nahon et al. (1989) and Lucas and Chauvel (1992) on the basis of pedological observations. The latosol, forming at the expense of the underlying saprolite, would be in equilibrium with the present equatorial humid climatic

Table 1 - Characteristics of the boreholes and chemical analyses of groundwaters around the sand mining activities at Analândia (SP)

PARAMETER	UNITS	BOREHOLE No.1	BOREHOLE No.2
Diameter	mm	75	75
Altitude of the top	m	711.5	685.0
Total length	m	16.0	5.5
Water table depth	m	13.2	1.6
Temperature	°C	25	26
Dissolved oxygen	mg/l	7.5	4.5
pH		5.2	4.6
Eh	mV	+183	+217
Conductivity	µS/cm	50	40
Total dissolved solids	mg/l	40	32
Silica	mg/l	3.00	3.30
Bicarbonate	mg/l	2.90	1.00
Sulfate	mg/l	<2.00	<2.00
Chloride	mg/l	1.20	0.30
Nitrate + Nitrite	mg/l	0.03	0.02
Fluoride	mg/l	0.06	0.04
Ammonium	mg/l	<0.20	<0.20
Phosphate	mg/l	<0.10	<0.10
Sodium	mg/l	0.80	0.30
Potassium	mg/l	0.50	0.20
Calcium	mg/l	1.60	0.40
Magnesium	mg/l	0.10	<0.10
Boron	mg/l	<0.02	<0.02
Aluminum	mg/l	<0.10	<0.10
Barium	mg/l	0.02	0.02
Total iron	mg/l	<0.02	<0.02
Total chromium	mg/l	<0.05	<0.05
Manganese	mg/l	<0.02	<0.02
Zinc	mg/l	0.02	0.02
Nickel	mg/l	<0.02	<0.02
Copper	mg/l	0.02	0.02
Cadmium	mg/l	<0.02	<0.02
Lead	mg/l	<0.10	<0.10
Uranium	µg/l	0.05	1.35
U-234/U-238 Activity			
Ratio		1.32	0.80

conditions. The saprolite, for the most part, would represent the remains of an older lateritic profile capped with a ferricrete and developed under tropical contrasted wet and dry climate. The observed shift in the δ^{18}O values of goethite pseudomorphs in the saprolite at $\approx$20 m depth might, therefore, record the onset of climate change and latosol development. If this true the lowermost 5-10 m depth interval over which goethite is in equilibrium with present groundwater would represent the amount of saprolite that was generated since the climate changed to present conditions. An approximate average rate of weathering of 1.7 cm/1000 y has been estimated for the entire profile of Yaou on the basis of the hydrogeochemical budget of the watershed (Farah, 1994). If this estimate is representative of recent conditions, then, the lowermost part of the saprolite, and the latosol, would have developed in about 600000 years or less.

The scatter in the data from the latosol may nor represent natural variation. Because goethite pseudomorphs in the latosol are partially replaced by a microcrystalline plasma of kaolinite + goethite that fills intragrain microporosity, they are expected to be more difficult to clean. It is therefore most likely that some or all of the scatter in the δ^{18}O values of goethite pseudomorphs from the latosol arises from undetected contamination with kaolinite (not visible at the surface of the grains). In contrast, no intragrain kaolinite was observed within the pseudomorphs from the saprolite. Alternatively, the scatter may represent the coexistence of two different generations of goethite. Conceivably, the lowest δ^{18}O values could correspond to the unweathered old goethite pseudomorphs, such as those encountered in the upper and middle saprolite, while the higher values may represent goethite pseudomorphs recrystallized under present conditions and i isotopic equilibrium with soil-rain water. Petrographic evidence, however, do not support this latter hypothesis.

Conclusions and Future Work

Recently developed laser-based microanalytical techniques for oxygen isotopes analysis allow a new scientific approach in the study of weathering processes. The results of the present study illustrate that δ^{18}O values of weathering goethite do vary significantly within a the profile of Yaou. They also indicate that goethite pseudomorphs in ancient saprolites may preserve their original oxygen isotopic composition, acquired at or close to the weathering front between bedrock and saprolite. Lateritic goethite may therefore be used as indicators of paleoweathering-paleoclimatic conditions. Investigations are underway to determine whether similar variations are recorded in the δ^{18}O (and δD) values of the associated kaolinite, which forms the bulk of the pedological horizons.

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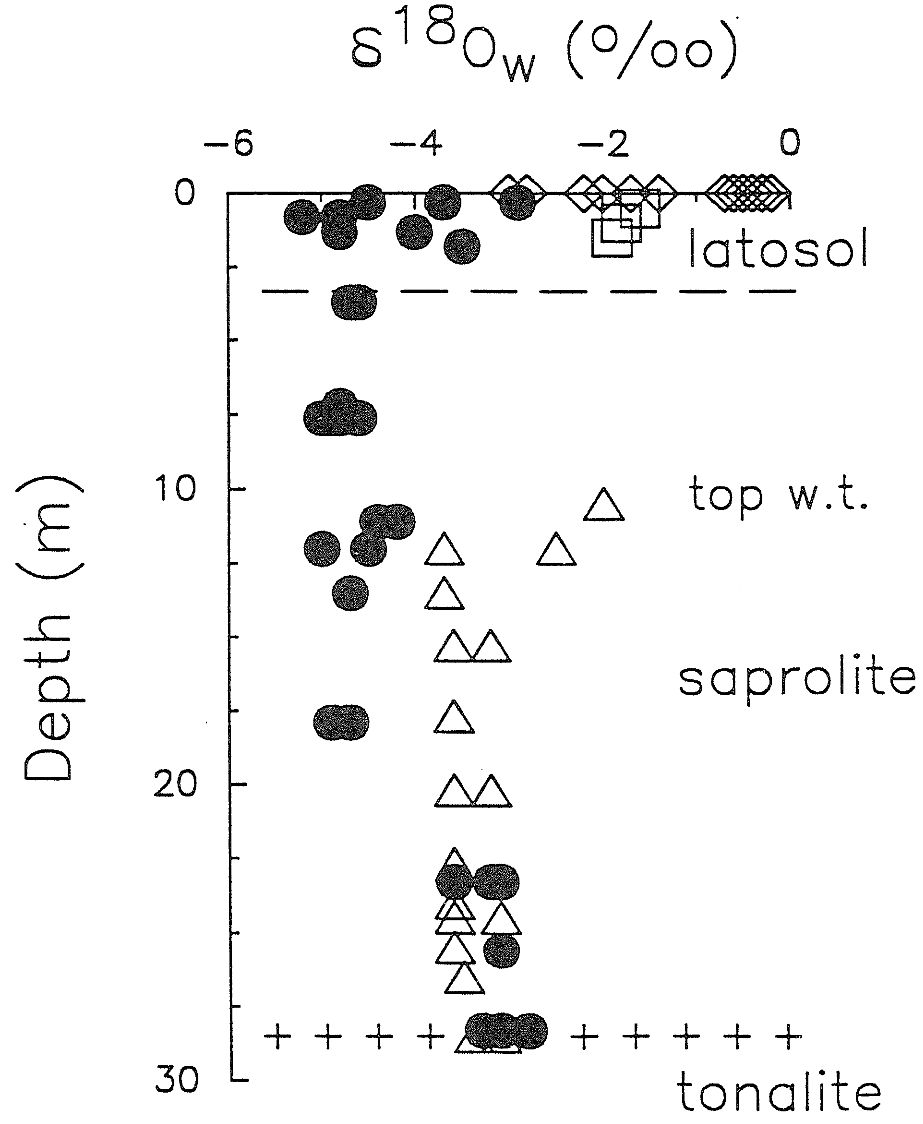

Fig. 1 : Calculated $\delta^{18}O$ values of waters in isotopic equilibrium (at 25°C) with goethite pseudomorphs (filled circles) and measured $\delta^{18}O$ values of groundwater (open triangles), "soil water" (open squares) and rainfall (open diamonds) as a function of depth in the lateritic profile of Yaou. The position of the top of the water table (i.e., the boundary between the unsaturated and the saturated zones of the profile) is indicated as top w.t..

Exposure dating, continental erosion and regolith dynamics with cosmic-ray-produced isotopes

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Keywords: Cosmogenic isotopes, exposure dating, erosion, regolith

Cosmic ray bombardment of the atmosphere and earth's surface produces a variety of rare isotopes, whose accumulation and dispersal can be exploited for exposure dating, measurement of erosion and sedimentation rates and the study of surficial transport and mixing processes. Isotopes produced *in situ* (within mineral grains) are ^{10}Be ($t_{1/2}$ = 1.5 Ma; measurable in O-rich minerals such as quartz), ^{26}Al ($t_{1/2}$ = 0.7 Ma; measurable in quartz) and ^{36}Cl ($t_{1/2}$ = 0.3 Ma; produced in K- and Ca-rich minerals such as feldspars and calcite). Production of these isotopes decreases exponentially downwards from the surface, by a factor of two every ~ 50 cm. Comparatively large amounts of ^{10}Be are also produced in the atmosphere and deposited by rainfall, subsequently binding strongly to mineral surfaces ($K_D \sim 10^5$). Surface residence ages are obtained by comparing cosmogenic isotope concentrations with their production or delivery rates, which are currently known to ~ ±10%. Transport processes can be studied by comparing the spatial distribution of an isotope, both laterally and in depth profiles, with its source distribution. Cosmogenic isotopes typically accumulate to concentrations on the order of 10^6 - 10^9 atoms/g (i.e. 10^{-7} to 10^{-4} ppb) and must therefore be measured by ultra-sensitive accelerator mass spectrometry (AMS).

Exposure dating

Build-up *in-situ* of an isotope in a rock surface provides a measure of exposure age. Surfaces to be dated must have been produced by an identifiable event, and excavated from more than a few metres depth (to avoid prior exposure). Simple examples include landslide surfaces, fault scarps and glacial pavements. In the absence of erosion, isotopes accumulate to saturation — the point at which production is balanced by radioactive decay — in 3 - 4 half-lives. Applicable timescales are thus ~1 Ma for ^{36}Cl, 2 -3 Ma for ^{26}Al and ~5 Ma for ^{10}Be.

Erosion and sedimentation rates

Erosion generally imposes a limit on exposure dating before isotopic saturation is reached. Erosion dictates the depth-time history of material reaching the surface, and therefore its cosmogenic isotope concentration. High erosion rates transport material rapidly through the zone of cosmogenic isotope production, resulting in low isotope concentrations when the material reaches the surface. Conversely, low erosion rates result in material spending a long time in the production zone, leading to high concentrations. Sedimentation results in a conceptually similar relationship between isotopic concentration and burial rate, since the production rate in a sample decreases as sediment cover builds up. Sedimentation in deep water (> 5 - 10 m) removes material from the cosmic ray flux, so burial times and sedimentation rates can be determined by the use of isotopic decay (if the initial isotope concentration is known) or by measurement of a second isotope of different half-life (if the surface production ratio is known).

Different scales of erosion are addressed by different measurements and sampling strategies. Measurements of *in situ* isotopes on hard-rock samples give erosion rates at the outcrop scale. These can be extended to the drainage basin scale by using representative sediment samples. In the regolith, erosion rates can be estimated from soil inventories of meteoric ^{10}Be, since the inventory represents the balance between delivery (in rainfall) and removal by erosion and radioactive decay. The ^{10}Be flux carried by river sediment provides another means of estimating erosion at the drainage basin scale.

Tracing sediment mixing and dispersal

Cosmogenic isotopes are introduced into the regolith with simple, well-defined source functions — in a static regolith profile, the vertical distribution of an *in-situ* isotope should follow its exponential production profile, that of meteoric ^{10}Be should show a strong surface accumulation with some leakage downwards due to slow leaching. Vertical mixing processes disrupt these depth distributions. Profile measurements therefore offer a method for measuring rates of eluviation and overturn by shrink-swell churning, precipitation of secondary minerals, burrowing and root penetration. Rates of lateral dispersal by sheetwash and downslope creep can also be determined where these processes lead to vertical redistribution of the tracer isotopes. Cosmogenic isotopes should be of use in distinguishing residual from transported regolith and also in identifying (and dating) lag deposits above eroding profiles. Comparison of ^{10}Be inventories in the regolith with concentrations of *in situ* isotopes in underlying saprolite should provide a powerful means of dating and quantifying regolith stripping events within the past few million years.

Preliminary results from Australia

Because of its low relief and ancient landforms, the Australian continent offers limited scope for straightforward exposure dating. However, it should be possible to use cosmogenic isotopes to measure erosion rates and study dispersal and concentration processes within the Australian regolith. As yet, only a few such measurements have been made. Hard-rock erosion rates in arid areas of central and western Australia are found to be on the order of 1 - 2 m/Ma. Catchment-scale rates for small, low relief catchments in northern Australia are ~ 2 m/Ma. The concordance between these results is surprising and needs to be investigated with much wider sample coverage. Comparisons between outcrop and regolith surface erosion rates at individual sites will be particularly important, since these bear on whether present-day outcrops are long-term or transient features of the land surface, and on the stability of both surficial and buried topography. Erosion rates have been measured on limestone surfaces from sites around Australia characterised by a wide range of environmental conditions. As might be anticipated, erosion rates correlate strongly with precipitation, ranging from ~ 3 m/Ma in central and western Australia, through values of ~ 15 - 30 m/Ma in the eastern highlands, to ~ 150 m/Ma in Papua/New Guinea. As the majority of the sites lie below ridgelines of more resistant rock, these are not representative denudation rates; in fact measurements (in progress) on surrounding lithologies will indicate current rates of relief development. Combined ^{26}Al-^{10}Be data for samples of aeolian quartz from Australian dune fields indicate complex histories of exposure and burial, far exceeding depositional ages. Minimum erosion rates calculated for the source regions of these sands are again on the order of ~1 m/Ma. Transport histories are inferred to have included ~ million-year burial times, suggesting prior periods of residence in slowly-cycling sedimentary environments such as riverine flood plains. Characterisation of quartz from different sedimentary environments, and derived from catchments differing in size and relief, is in progress.

The study of landscape and regolith evolution with cosmogenic isotopes has barely begun. There is vast scope for innovative developments at all scales from reconnaissance survey to detailed, quantitative, site-specific problem solving.

Acknowledgements

All results described are part of a collaborative effort involving the Accelerator Mass Spectrometry group in the Department of Nuclear Physics, and faculty and students of the Research School of Earth Sciences, at the Australian National University.

Lithogeochemistry/Primary Dispersion Haloes

On the albite-enriched granitoids at Um Ara area, Southeastern Desert, Egypt.
I. Geochemical, Ore potentiality and Fluid inclusion studies

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Keywords: amazonitization, albitization, rare metals, apogranites, fluid inclusions

A radioactive and metasomatically albite-enriched microgranite (apogranite, 556 Ma) stock is emplaced at the northern contact of the Um Ara monzogranite pluton (589 Ma), Southeastern Desert, Egypt. The rock-fluid interaction within the apogranite is well displayed as petrographical and geochemical zonal patterns, resulting in a lower unaltered miarolitic alkali-feldspar microgranite zone, a middle zinnwaldite amazonitized (K-feldspathized) microgranite zone, and a roof zone of zinnwaldite albitized (Na-feldpathized) microgranite. Locally, extreme Na-metasomatism has resulted in patchy and erratically distributed albitite rock.

The rock-fluid interactions have been characterized by XRD, XRF, EPMA, wet chemical analyses, mass transfer calculations and fluid inclusion studies. The metasomatic reactions commence with K^+, Rb^+ and Pb^{2+} (amazonitization), followed by Na^+ (albitization), and finally with Mn- and Fe-oxides on joints and fracture surfaces. A gradual and gross enrichment of Nb, Y, Zr, Li, Zn, and F occur from the K-metasomatism zone to the Na-metasomatism zone, however, in albitite rock the concentrations of these elements are sharply decreased. Although the Na-metasomatic zone shows an enhanced level of U (76 ppm average) the uranium mineralization occurs as lemon-yellow gossan of essential uranophane on later fracture and joint surfaces, in both the K- and Na-metasomatized zones.

For exploration geochemical purposes, it is suggested that the 10000*Ga/Al and log ($K*Mg*Sr/Rb^2*Li$) ratios are good indicators for distinguishing granitic rocks associated with postmagmatic alteration and cogenetic rare metal mineralization of Zr, Nb, Y and U.

The microthermometric study of fluid inclusions in quartz of amazonitized and albitized microgranites indicates that high to moderate temperatures, highly saline, exsolved fluids interacted with the solidified microgranite cupola in the early metasomatic processes. Fluid inclusions in the K-zone homogenize in the range of 285-425°C, with salinities of 7-22.1 wt% NaCl equivalent, whereas those in the Na-zone homogenize in the range of 240-365°C, with salinities of 6.3-20.8 wt% NaCl equivalent. The inclusions in the later fracture and joint-filling quartz veins and fluorite veinlets homogenize in the range 190-310°C, with salinities of 2-5.1 wt% NaCl equivalent. The Fe- and Mn-oxide alteration might prevail at temperatures of 145-240°C and salinities of 1-6 wt% NaCl equivalent. It is clear that the presence of K^+, Na^+, and F^- in the ore fluids is essential to stabilize the complexes of the rare metal elements during extraction and transportation. In contrast, contemporaneously decreasing temperature and salinity, the loss of CO_2, and increasing pH due to pressure release, are considered to be essential factors for the deposition of disseminated Zr, Y, Nb and Th, and gossans of U mineralization on fractures, in the apical parts of the Um Ara apogranite stock.

Cu-Au and Pb-Ag-Zn Metallogenesis in the Cloncurry District (Mount Isa Eastern Succession), NW Queensland

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Keywords: Copper, Gold, Lead, Proterozoic, Cloncurry, NW Queensland

Introduction

The Cloncurry district (Mount Isa Eastern Succession) has recently emerged as a globally-significant metallogenic terrain following the discoveries of the world class orebodies at Cannington (47 million tonnes at 10.7% Pb, 4.6% Zn and 470g/t Ag, discovered in 1990) and Ernest Henry (132 million tonnes at 1.2% Cu, 0.6 g/t Au and ≈0.06% Co, discovered in 1991). Prior to these finds the district had seen far less research than the western part of the Mount Isa Block and the nature and geological context of the deposits were poorly understood. Recent work undertaken at James Cook University which has been designed to address the metallogenic problems in the district whose deposits appear to have stronger affinities with Broken Hill, NSW (Pb-Zn-Ag) and Olympic Dam (Cu-Au-Fe oxide) style mineralization than with deposits in the western Mount Isa Block. This abstract summarizes some of the preliminary findings of the project.

Regional Setting

Both Cu-Au and Pb-Ag-Zn deposits are essentially restricted to deformed and metamorphosed 1785 - <1670Ma supracrustal rocks in the vicinity of the ≈1500Ma Williams-Naraku batholiths (Blake, 1987; Page, 1994). Cu-Au deposits occur throughout the stratigraphy and in rocks exhibiting metamorphic grades from greenschist to upper amphibolite facies. With the exception of the geologically-distinct Dugald River Zn deposit, significant Pb-Ag-Zn mineralization is restricted to amphibolite facies metasiliciclastic rocks in the southeastern part of the district.

Nature and Possible Metallogenic Significance of the Batholithic Granitoids

The Williams-Naraku batholiths contain a variety of intrusive rock types many of which, at least in part, contain a tectonic foliation. Magma mixing and mingling features are commonly observed and provide evidence for bimodal mafic and felsic magmatism. The geochemistry of many of the granitoids is typical of A-type granites described elsewhere in the Proterozoic. Although there is a strong spatial and temporal association between granites and mineralization in the region the ore-forming potential of individual suites has yet to be fully explored.

General features of Cu-Au Deposits

Several different styles of Cu-Au mineralization are present but exhibit consistent features including epigenetic mineralization controlled by faults, common association with silicification, and sulphides that overprint geochemically fertile host rocks. The latter include magnetite ironstones (e.g. Starra, Osborne W), mafic silicate alteration (e.g. Eloise, Mount Elliott, Osborne E) and carbonaceous metasediments (e.g. Mount Dore). A growing body of evidence suggests that at least some of the magnetite ironstone hosts are not metamorphosed iron-rich sedimentary rocks but rather products of metasomatic replacement (Williams, 1994; Blake, 1994; N. Adshead, unpub. data; J. Rotherham unpub. data).

Fluid inclusion data from Mount Dore (Beardsmore, 1993) and Osborne (Adshead, 1994) reveal roles played by high temperature (> 500° C), extremely high salinity (up to > 70 wt. % salts) and geochemically complex fluids during Cu-Au mineralization. The origin of these fluids remains unclear with limited light stable isotope data from Mount Dore (Beardsmore, 1993) suggesting they were either metamorphic or significantly modified magmatic fluids. Additional fluid inclusion

Data Processing and Manipulation

evidence from Osborne (N. Adshead, unpub. data) indicates that this deposit formed at unusually great depths for hydrothermal Cu-Au mineralization at pressures in excess of 200MPa.

Osborne Cu-Au Deposit

High grade Cu-Au mineralization at Osborne (36Mt at 2% Cu & 1 g/t Au including a mining resource of 12Mt at 3% Cu & 1.3g/t Au) is hosted by massive silicification. The deposit is strongly anomalous in Co, Se, Mo, Ag, Sn, Bi and Hg but has only very low concentrations of Pb and Zn. It is developed in a sequence of upper amphibolite grade metasedimentary and meta-igneous rocks intruded by pegmatites. The earliest metasomatic rocks include banded magnetite-quartz-apatite ironstones in the west and Ca-Mg amphibole-biotite rocks in the east. The silicification and associated Cu-Au mineralization occur in, and around this older alteration.

Eloise Cu-Au-Ag Deposit

The Eloise deposit (3.2 Mt at 5.8% Cu, 1.5g/t Au, 19 g/t Ag) is hosted by amphibolite facies metasedimentary and metabasic rocks. It is controlled by late to post regional D2 shear zones developed parallel to the N-trending subvertical S2 foliation (Baker, 1994). Mineralization is distinctly zoned. Subeconomic magnetite-pyrite dominated mineralization occurs in the southern zone whereas the main lode zone is dominated by pyrrhotite-chalcopyrite, varying to pyrrhotite rich in the north. The periphery zone is characterized by weak pyrite-chalcopyrite mineralization. Six distinct alteration events have been recognized. An early quartz-albite alteration is overprinted by hornblende-biotite-quartz. The mafic alteration subsequently formed the locus of the mineralizing stage. Later alteration was associated with brittle faults.

Starra Au-Cu Deposit

The ironstones hosting Au-Cu mineralisation at Starra (5Mt at 5 g/t Au and 2% Cu) show many similarities to the Early Proterozoic giant iron ore systems of the world such as Kiruna in northern Sweden (Blake, 1994). In both regions the ironstones are dominated by magnetite, and typically display a broadly tabular or elongate form parallel to the regional strike; these bodies occasionally appear to bifurcate at depth. The ironstones are typically associated with marginal strained breccia zones, in which magnetite and iron silicates form the matrix to variably strained albitized rock clasts, whose morphology and attitude mimics the ironstone bodies. Alteration assemblages include an early, widespread sodic alteration followed by the introduction of magnetite and amphibole, the latter as vein infill and pervasive replacement breccias. At Kiruna this is the result of a high–temperature (>500°C), magmatic–hydrothermal fluid and preliminary stable isotope results from Starra suggest that the magnetite there crystallized in equilibrium with a ≈500°C metamorphic or magmatic hydrothermal fluid.

General features of Pb-Ag-Zn Deposits

Deposits within the metamorphosed siliciclastic sedimentary rocks of the "Maronan supergroup"/Soldiers Cap Group" in the southeastern part of the district exhibit a consistent paragenesis in which high temperature Fe-Mn-Ca skarn alteration is overprinted by hydrous silicates and ore minerals (Newbery, 1991; Williams and Heinemann, 1993; Pendergast, 1993; Chapman, 1994). The skarn minerals themselves commonly occur as veins and replacements in late metamorphic brittle structures and the Pegmont deposit is enveloped by a late metamorphic, initially high temperature potassic (K feldspar-biotite-muscovite) alteration system. This reflects the action of a complex ultrasaline fluid (Pendergast, 1993) broadly similar to that implicated in the Cu-Au mineralization at Osborne and Mount Dore.

Cannington Pb-Ag-Zn Deposit

Cannington is hosted by pyroxene-pyroxenoid-garnet-quartz alteration in sillimanite-K feldspar grade gneisses. Sulphides occur in a retrograde paragenetic association superimposed on this alteration and a significant proportion of the potentially economic resource is present as vein and breccia mineralization. Alteration associated with the main economic resource in the southern part of the deposit occurs as two discontinuous stratabound zones that form sharp contacts with host rocks, extend 600m laterally and vary in thickness from 5 to 100m. Earliest anhydrous (graphite stable) alteration includes silicification that is peripheral to, and overprinted by the Mn-bearing anhydrous assemblage hedenbergite, pyroxferroite-pyroxmangite, and calcic almandine with quartz and apatite. Hydrous Fe-K-Cl rich alteration characterized by hornblende-biotite is a widespread overprint which itself preceded sulphide-magnetite-fluorite mineralization.

Directions for Future Research

Future research will document the composition of ore fluids and conditions of Cu-Au mineralization throughout the district, constrain the source(s) of the fluids, and provide a comprehensive geochronological framework for the thermal evolution of both Cu-Au and Pb-Ag-Zn ore systems. A comparison of these features between the two deposit-groups will be used to investigate whether they are genetically and temporally-related or whether the Pb-Zn-Ag deposits reflect a separate and much earlier metallogenic event as has previously been supposed.

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Geochemically distinct volcanic rocks associated with volcanic-hosted massive sulphide deposits, Iberian Pyrite Belt

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Keywords: massive sulphide deposits, lithogeochemistry, zinc, copper

The massive sulphide deposits of the Pyrite Belt of southern Portugal and south-west Spain are hosted by a felsic-dominated volcanic sequence. Rocks of intermediate and mafic compositions constitute a relatively small proportion of the sequence, although these may be locally abundant. The volcanic package rarely exceeds one kilometre in thickness.

The mineralogy and geochemistry of the volcanic rocks of the Pyrite Belt have been affected by district scale hydrothermal metasomatism. Geochemical investigations of the felsic rocks, in particular, have to rely heavily on those elements which are less mobile in alteration and metasomatism (Ti, Nb, Y, Zr, rare earth elements, etc.). These elements display considerable variations in abundance levels in the felsic rocks across the Belt, as do the normalised rare earth element patterns. These element associations and variations suggest that the Pyrite Belt can be divided into sub-terrains on the basis of the geochemistry of its volcanic rocks.

High abundances of Nb, Y and Zr are present in the host rocks to massive sulphide mineralisation at several of the massive sulphide deposits. For example, at Aguas Tenidas in the northern sector of the Spanish Pyrite Belt, these rocks are restricted to approximately the central third of the total volcanic pile, and the two massive sulphide-bearing horizons occur within their development. Rocks of similar composition, for which data is available, also host the massive sulphide mineralisation at Aljustrel, Sotiel, San Telmo, and Neves Corvo. However, not all massive sulphide deposits are hosted by rocks of this composition, for example the Sao Domingos deposit in Portugal.

The geochemically distinctive rocks also occur in some areas with no known significant mineralisation. From the analytical data available such locations are on the northern and southern margins of the outcropping Pyrite Belt. However, in the majority of these areas rocks with high abundances of high field strength elements make up only a small proportion of the total as, for example, on the northern margin of the Pyrite Belt near the Spanish/Portuguese border. In summary, the majority of the rocks with high abundances of Nb, Y and Zr identified to date occur in close proximity to known massive sulphide deposits.

Rocks of distinctive composition do have potential, therefore, to be used as an exploration criterion for volcanic-hosted massive sulphide deposits in the Iberian Pyrite Belt, although they also occur in apparently non-mineralised sequences. Consequently, lithogeochemistry, including analysis of selected less mobile elements, should be included in reconnaissance exploration programmes in the region to assist in defining target horizons and areas.

Primary and secondary element and mineral dispersions in the Wagga Tank polymetallic deposit, New South Wales, Australia

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Keywords: base metals, precious metals, lithogeochemistry, mineralogy, prospecting, New South Wales

The Wagga Tank Zn-Pb-Cu-Ag-Au deposit lies about 27 km northwest of Mount Hope and 130 km south of Cobar, in western New South Wales, Australia. This deposit was studied to identify both minerals and major and trace elements that are (1) related to local geologic units and to the mineral deposits, (2) related to fresh and strongly weathered rocks, and (3) best suited for prospecting for similar polymetallic mineral deposits in the Cobar region.

The study area is located in the Lachlan Fold Belt Structural Province, which consists of a thick sequence of clastic sedimentary rocks of the Lower Devonian Mount Kennan Volcanics, a part of the Cobar Supergroup. Macroscopic and microscopic examinations of drill core and cuttings from the Wagga Tank deposit indicate that these sedimentary rocks include an older volcaniclastic unit containing interbedded slate, siltstone, sandstone, conglomerate, and felsic tuff, and a younger turbidite unit consisting of alternating siltstone and slate beds that are locally carbonate- or pyrite-rich. Both the contact between the two units and the bedding within each unit are nearly vertical. Primary sulfide-mineral deposits consist of irregular massive lenses of pyrite, chalcopyrite, galena, and sphalerite that average 3-5 m in width and are locally accompanied by quartz veins and by siderite, white mica, and chlorite gangue. The lenses are generally present along the contacts between the two lithologic units but are more commonly within the volcaniclastic unit. A well-defined zone of strongly weathered rocks is present throughout the area to depths of about 100 m. Locally, the effects of weathering extend to depths of as much as 180 m. A 1- to 30-m-thick layer of overburden covers most of the study area, including the parts of the area that contain near-surface, weathered sulfide lenses.

For this study, we collected 247 core or cuttings samples from 17 drill holes, most of which penetrated sulfide lenses, oxidized-sulfide lenses, or both. The core samples were composited from typical material in a 5-m run. These core samples were analyzed for 34 elements (Ag, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, La, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Sn, Sr, Te, Ti, Tl, V, W, Y, Zn, and Zr). Selected samples were also analyzed for their mineralogy by X-ray diffraction. In addition, some gangue minerals were analyzed for selected elements using an electron microprobe.

The chemical and mineralogical data were evaluated (1) graphically on cross-sections, and (2) statistically, using means, percentiles, and R-mode factor analysis. These evaluations indicate that, below the zone of strong weathering, Ag, As, Au, Bi, Cd, Cu, Fe, Hg, Mo, Pb, Sb, Te, Tl, W, and Zn, as well as alunite-jarosite-group minerals (plumbogummite, hinsdalite, and beudantite), siderite, and chlorite, are positively associated with sulfide minerals, whereas B, Ca, Cr, Ga, La, Mg, Na, Sc, Ti, V, and Zr, as well as dolomite, seem to be negatively associated. In this zone of fresh rock, anomalous concentrations of many of the positively-associated elements extend laterally as much as 70 m beyond the outer limits of massive-sulfide deposition. Microprobe analyses show that hydrothermal chlorite associated with the sulfide lenses is Fe-rich and contains as much as 0.2% F and 770 ppm Zn.

In the strongly weathered zone, anomalous concentrations of the sulfide-related elements Ag, As, Au, Cd, Cu, Mo, Pb, Sb, Te, Tl, and Zn were observed, particularly in the lowermost 10-50 m. These anomalies are deemed to be related to supergene enrichment. The As, Sb, Te, Tl, and Zn anomalies often extend to the top of this zone, indicating that these five elements were not as strongly affected by weathering and are therefore useful for shallow prospecting.

Alunite-jarosite-group minerals, where found in the oxidized shallow parts of sulfide lenses, may extend laterally for at least 100 m. Secondary siderite is present near the base of the zone of strong weathering. Microprobe analyses show that hematite, goethite, and Pb-rich alunite-jarosite-group minerals in this zone are the most significant accumulators of base metals. The Fe oxides are particularly important accumulators of base metals and may contain as much as 1.0% Pb, 1.3% Cu, 0.73% Zn, and 0.79% As.

Plots of B, Ba, Cr, Ga, La, Ni, Sc, V, and Y concentrations show that differences in the concentrations of these elements can be used to discriminate between the two major geologic units, even in the strongly weathered zone. The distributions of these elements should thus be useful for geologic mapping in this area.

The wide haloes of Ag, As, Pb, Sb, Te, Tl, and Zn are the most effective for locating lenses of sulfide minerals in both fresh and strongly weathered rocks at Wagga Tank. The information obtained from this study should be useful in prospecting for similar polymetallic deposits in the surrounding region.

Application of immobile-mobile element geochemistry to characterisation of a primary alteration halo in a sedimentary environment.

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Keywords: alteration halo, sedimentary rock, Abra, Western Australia

Introduction

Chemical changes induced in rocks during hydrothermal alteration may be monitored by using immobile element techniques, such as those devised by MacLean (1990) and MacLean and Barrett (1993), which allow quantitative assessment of chemical variation and mass changes within an alteration zone. Most examples of the application of mobile-immobile element geochemistry to the identification and characterisation of alteration halos have used ore deposits hosted by volcanic sequences (e.g., Finlow-Bates and Stumpfl, 1981; MacLean and Kranidiotis, 1987; Barrett and MacLean, 1991). In these examples, the parent rock is either homogeneous or has a characteristic fractionation trend, in which case the effects of hydrothermal alteration on volcanic rocks can be readily identified using highly immobile high field strength elements such as Zr, Ti, Al, Nb and Y that are also incompatible in igneous processes.

This contribution presents the results of an investigation of immobile-mobile element geochemistry of an hydrothermal alteration halo in sedimentary rocks. The same criteria that have been devised for a chemically homogeneous parent rock (i.e., a single precursor system of MacLean and Barrett, 1993) have been applied to evaluation of the alteration halo to a large Proterozoic sediment-hosted epithermal deposit at Abra, about 220 km north of Meekatharra and 180 km southwest of Newman, Western Australia. The Abra alteration halo is a good test of this method in sedimentary rocks that do not have the same predictable homogeneity or systematic variation as volcanic rocks.

Geological setting

The Abra deposit is hosted by sedimentary rocks at the eastern end of the Jillawarra sub-basin, a 60-65 km long, east-west trending, fault-bounded basin in the central Bangemall Basin (Muhling and Brakel, 1984). There are two main sedimentary units within the Jillawarra sub-basin, the Gap Well and the West Creek Formations, which accumulated during the initial rifting phase that led to formation of the larger Bangemall Basin (Collins and McDonald, 1994).

The Gap Well Formation consists of ~1000 m of laminated to thinly bedded dolomitic siltstone, shale and arkose, with minor interbedded massive dolomite that accumulated in a subtidal - supratidal terrestrial environment. At the top of the Gap Well Formation is a siliciclastic grit - fine pebble conglomerate (up to 40 m thick) with finely laminated ferruginous and jaspilitic bands, and stromatolites and evaporitic textures in argillaceous interbeds within the conglomerate. The conglomeratic member, referred to as the Abra beds, locally is overlain by a 1.5-2 m thick unit of fine-coarse rhyolite pebble conglomerate. The rhyolite pebbles are derived from the Tangadee rhyolite that crops out 15 km east of Abra and is the only confirmed felsic volcanism within the Bangemall Basin. The Tangadee rhyolitic volcanism preceded accumulation of the West Creek Formation and has a maximum age of about 1.63 Ga (Collins and McDonald, 1994) which is similar to a Pb model age of about 1.64 Ga for galena from the Abra deposit (J.R. Richards, pers comm.).

The Gap Well Formation is conformably overlain by the West Creek Formation (~1000 m thick) which typically is a coarser grained siliciclastic arenaceous turbiditic sequence that accumulated in a near shore, shallow marine environment.

Mineralisation

Epithermal-type mineralisation at Abra was coeval with accumulation of clastic sediments (Abra beds) in the upper parts of the Gap Well Formation and had concluded before subsidence and accumulation of the West Creek Formation. Although there are no volcanic rocks in the host sequence it is likely that a deep-seated sub-volcanic felsic intrusive body associated with the nearby coeval Tangadee rhyolite volcanism was emplaced beneath Abra and that this has caused a convective hydrothermal system resulting in two main styles of mineralisation: an upper layered hematite-magnetite-barite stratabound zone that is capped by a funnel-shaped vein stockwork zone (Boddington 1987, 1990; Vogt and Stumpfl 1987; Collins and McDonald, 1994). Abra has an indicated a resource of about 200 Mt at 1.9 % Pb, 0.18 % Cu, 6 % Ba and 5 g/t Ag (Boddington 1987). Sulphide mineralisation is dominated by galena, chalcopyrite and pyrite, with minor tetrahedrite and traces of scheelite, but there is a paucity of sphalerite.

The stratabound zone consists of variably banded red hematite-barite-chert-carbonate-magnetite mineralisation above banded magnetite-grey hematite-chert-carbonate-barite mineralisation that are referred to as the red and black zones, respectively. Both assemblages are locally interleaved and coeval with the host conglomeratic and siliciclastic sediments, but have replaced the underlying arenaceous and pelitic rocks.

A northwest-southeast trending stockwork zone underlying the stratabound mineralisation consists of veins of crustiform and colloform banded quartz-carbonate-barite±galena that has infilled fractures and cavities and replaced adjacent host rocks. The veining is perpendicular to the palaeosurface and served as a feeder to the stratabound surface mineralisation. At depth (up to 400 m below the palaeosurface), the veins have infilled brittle fractures and breccias whereas nearer the palaeosurface there is more replacement of adjacent host sediments where the hydrothermal fluids probably have percolated through unconsolidated sediment and overlying laminated hematitic chert or ferruginous siliceous sinter.

Alteration halo

All of the rocks of the Gap Well Formation are altered to varying extent. The stockwork system, beneath the stratabound zone in the Abra beds, is enclosed within a pervasive chlorite-siderite alteration envelope. This is accompanied by quartz and barite, commonly in small veinlets, with disseminated magnetite in deeper intersections.

A significant hiatus between the Gap Well and West Creek Formations has meant that there was no leakage of late stage hydrothermal fluid into the overlying sediments and hence there is no hangingwall alteration halo.

Alteration geochemistry

Sampling and chemical analysis

As the Abra deposit does not crop out, the geochemical sample set used for this study is derived entirely from exploration drill core. This study is restricted to the chlorite-siderite alteration halo within that part of the Gap Well Formation that is below the Abra beds and hence potentially was a more homogeneous protolith. Twenty-one samples of altered Gap Well Formation and three samples of unaltered Gap Well Formation have been analysed for 60 major and trace elements by a range of analytical techniques. As sampling of the Gap Well Formation is controlled by the orientation and distribution of drill holes, altered samples are spread over a palaeodepth range of some 500 m, but extend only up to ~50 m laterally from the stockwork system. Unaltered samples of the Gap Well Formation have been collected from a drill hole about 1 km northeast of Abra because all drill hole intersections at the Abra deposit are within the alteration halo. The unaltered samples are from the equivalent stratigraphic level as most of the altered samples, but do not extend to the same palaeodepths. All key incompatible and immobile elements (e.g., Zr, Ti, Al, Nb, Y, REE) that are used to identify mobility and immobility during hydrothermal alteration have been analysed by XRF and NAA.

Alteration lines and homogeneity

Most of the highly immobile elements that have been used to characterise alteration halos in volcanic settings have also been found to be immobile during alteration of the Gap Well Formation. For all 24 samples of the Abra data set, the best positive linear correlation is between TiO_2 and Al_2O_3 (Fig. 1) with a correlation coefficient of 0.97. Most of the altered samples are depleted in TiO_2 and Al_2O_3, relative to unaltered samples, but all are confined to an 'alteration line' that passes through the origin.

A number of other immobile element pairs have similar, highly correlated linear trends ($r > 0.90$) with alteration lines that pass through the origin, including Al_2O_3 - Zr, TiO_2 - Hf, and TiO_2 - Sc. For other combinations of immobile elements, the correlation is not as good, but all are positively correlated and have linear regression lines that intersect or are close to the origin. These include TiO_2 - Ce, TiO_2 - Sm, TiO_2 - Th, Zr - Ce, Zr - Nb, Zr - Yb, Zr - Sm and Zr - Th, all of which

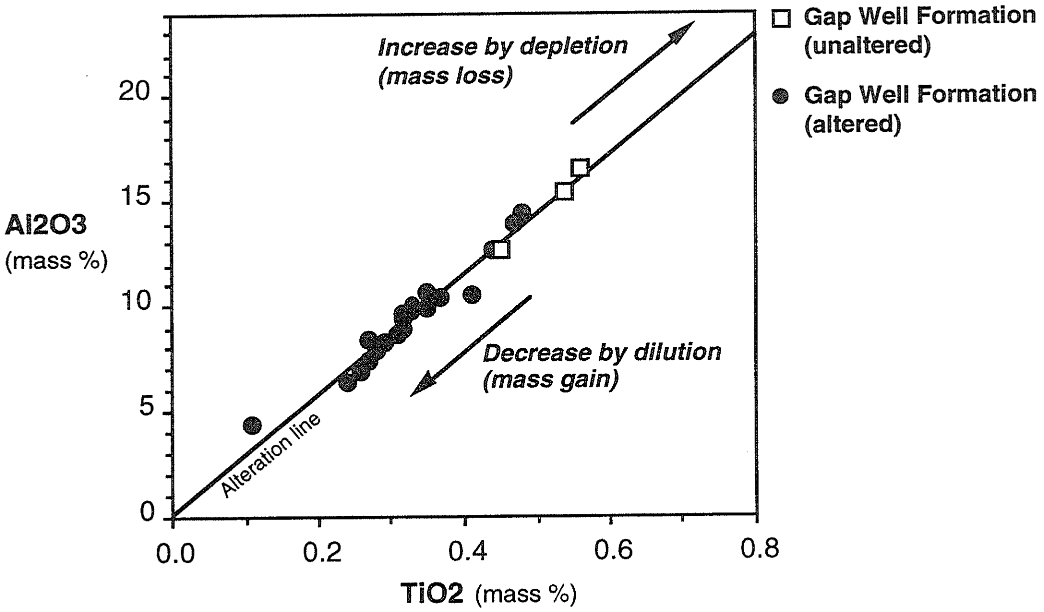

Figure 1 Al_2O_3 - TiO_2 plot of unaltered and altered sedimentary rocks from the Abra deposit with all samples plotting along the same 'alteration line'.

have correlation coefficients in excess of 0.80. Yttrium, one of the key immobile elements in altered volcanic sequences, does not show the same degree of correlation in sedimentary rocks.

Most other elements, including mobile elements, are poorly correlated when plotted against immobile elements, whereas some pairs of the more compatible elements have very high degrees of correlation (e.g., for K_2O - Rb, $r = 0.91$; and for Zr - Hf, $r = 0.96$).

Spatial variation of mobile elements

The high correlation of most immobile elements indicate that the Gap Well Formation may be considered as an homogeneous unit for the purposes of evaluation of the alteration halo. Minor systematic variation of immobile elements with palaeodepth (e.g., TiO_2) can be attributed to mass gain during alteration rather than to changes in chemistry of the Gap Well Formation during accumulation of sediment. Most other elements, including mobile elements, also do not exhibit systematic trends that may indicate significant changes in chemistry of the unaltered Gap Well Formation, and systematic variations with palaeodepth may therefore be attributed to hydrothermal alteration.

The alteration envelope that encloses the stockwork zone at Abra is expressed chemically by a general enrichment in Si, Fe and Ba and depletion in Ca, K, Rb and Pb when compared with the protolith. A number of mobile elements exhibit systematic depletion (e.g., SiO_2) or enrichment (e.g., Fe_2O_3, MgO) with increasing palaeodepth, whereas some show depletion then enrichment with proximity to the palaeosurface (e.g., Ba). Several elements, such as Ca, Zn and Cu, do not show any systematic variation that may be attributed to hydrothermal alteration nor to changes in chemistry of unaltered Gap Well Formation.

Mass gain ~ loss

The distribution of immobile elements along the alteration line and their displacement towards the origin indicate a relative decrease in concentration by dilution, which is attributed to mass gain in altered rocks (Fig. 1). Estimates of the extent of this mass gain in altered Gap Well Formation, using methods devised by MacLean and Kranidiotis (1987), MacLean (1990) and others, ranges from about 10 % to in excess of 100 % when compared with unaltered Gap Well Formation.

Mass gains in excess of 100 % may be attributed to crystallisation of hydrothermal minerals in poorly lithified sediments that may be able to 'absorb' additional material precipitated within pore spaces. In this case, the alteration halo is not due entirely to replacement of the host rock, but mostly to addition of minerals to unconsolidated sediment. At greater palaeodepths, where veining in brittle fractures indicates a more lithified rock, then more of the chemical variation in the alteration halo is attributed to replacement of the Gap Well Formation, as normally expected during metasomatism and hydrothermal alteration.

Discussion

Correlation coefficients in the range 0.90 to 0.99 are considered highly significant for altered volcanic sequences (MacLean and Barrett, 1993). As sedimentary host rocks are not necessarily as homogeneous, nor have the same predictable fractionation trends, as volcanic sequences then highly correlated immobile element pairs ($r > 0.9$) in the Abra data set clearly indicate immobility of Al_2O_3, TiO_2, Zr, and some REE's during hydrothermal alteration of the Gap Well Formation. This may be extended to include elements such as Nb, Th, Ce, Yb and Sm which also show a high degree of correlation for the Abra data set, considering the heterogeneity expected in host rocks that are of sedimentary origin.

Such good correlation between immobile element pairs indicates that immobile element techniques can be applied to quantitative assessment of chemical variation and mass changes within alteration halos in sedimentary rocks. The successful application at Abra may be attributed to the pelitic nature of most of the Gap Well Formation, but it may not be as effective in sedimentary sequences that are dominated by less uniform arenaceous-rudaceous rocks because of the potential for greater variation in mineralogy and chemistry of the protolith.

Conclusions

Mobile-immobile element techniques that have been devised for quantitative assessment of primary alteration halos in volcanic sequences may also be used in the evaluation of hydrothermal alteration halos in sedimentary rocks.

Acknowledgments

This research project is supported by North Exploration Ltd (formerly Geopeko).

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Primary geochemistry of slate-belt gold deposits

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Keywords: lithogeochemistry, gold, slate-belt, Victoria, Juneau

Introduction

Of the 110,000 tonnes of gold that have been mined, over 75 percent has come from primary gold deposits. The remainder has come from placer deposits, largely eroded from these "gold-only" deposits, and from base metal - bearing mineral deposit types in which gold is a co-product or bi-product. The gold-only deposits include the Archaean Witwatersrand deposits of South Africa (45,000t), the Archaean greenstone gold deposits (25,000t), slate-belt deposits (ca 5-10,000t) and some relatively localized epithermal vein / porphyry deposits.

The slate-belt gold provinces have been under-represented in exploration during the 1980's global gold boom and, with notable exceptions, under-represented in research for much of this century. The common poor exposure and extensive erosion of source lodes in tectonically active host provinces are typical difficulties in the evaluation of slate-belt gold systems. Nevertheless, several of the larger past and present lode producers indicate that these systems make outstanding exploration targets.

General features of slate-belt gold provinces

Slate-belt gold provinces are concentrated in oceanic sedimentary units that have been deformed along continental margins. The more productive examples include those within the Tasman fold system (Victoria, Queensland), Appalachian - Caledonian belt (Great Britain, Meguma of Nova Scotia, Carolina slate belt of USA), the Hercynian orogen (Massif Central, Bohemia Massif, Murantau), and the Cordilleran orogen (Mother Lode, Klamath Mountains, Klondike, Alaska).

The classical distinguishing features of slate-belt gold provinces are widespread, auriferous quartz veins hosted in medium metamorphic grade, clastic metasedimentary rocks that display a slaty to phyllitic texture.

The greenschist facies host sequences can be both pelitic and psammitic. Many deposits are preferentially developed in these slate-belts within relatively competent zones, commonly within older felsic to mafic igneous bodies. The predominance of metasedimentary rather than metavolcanic rocks provides distinction from Archaean greenstone gold deposits.

In any exploration geochemistry programme for slate belt gold deposits, knowledge of four parameters will influence sampling design, the selected sample media, and the chosen analytical methods. These parameters are the distribution of deposits within a province, the geometry of individual deposits, the distribution of elements within those deposits and their adjacent wallrocks, and any later supergene processes that affect the deposits. This study examines the first three of these parameters, with much of the discussion focussed on relatively well-known Victorian deposits of southeast Australia, and the Juneau gold belt of southeast Alaska.

Distribution of deposits in a slate-belt

Gold occurrences are concentrated in greenschist facies rocks, compatible with substantial fluid generation at the greenschist / amphibolite facies transition. Many of the more productive Phanerozoic lodes have developed adjacent to major, deep crustal structures, some of which are terrane - bounding faults developed during plate collision (e.g. Juneau). Competent lithologies within a few kilometres of the faults may impose structural traps for ore deposition, and/or relatively carbonaceous metapelites may provide chemical sinks for destabilization of gold complexes. Intrusive bodies located within 10-20 km of many deposits and broadly coeval with the ore systems are common in many productive slate-belts. The igneous activity is further evidence of tectonothermal events with the potential to drive ore fluid convection.

The Victorian gold province (Phillips, 1991) comprises up to 7000 mines of which 164 have produced over 0.1 t Au. The largest goldfields are Bendigo (700 t), Ballarat (390 t), Castlemaine (130 t), Stawell (82 t), Walhalla (68 t), Maldon (54 t), Woods Point (52 t), Creswick (47 t), Clunes (47 t) and Chiltern (30 t). These figures are derived by combining gold from quartz reefs plus related placer and palaeoplacer accumulations. These larger deposits are not distributed evenly across the exposed Palaeozoic of Victoria, but are concentrated in a 10,000 sq km area around Ballarat - Bendigo, and between Woods Point and Walhalla. In the Ballarat - Bendigo area major lodes are near but slightly removed from major structural features (Cox et al., 1991).

Tertiary gold deposits of the Juneau gold belt (Goldfarb et al., 1993) have yielded ca 215 t of gold, with at least an equal amount of remaining reserves. Gold-bearing quartz veins are all within a few kilometres of two steeply-dipping thrust faults that separate a series of accreted terranes. More than 95 percent of the known ore occurs in veins that cut metagabbro and monzodiorite located adjacent to the faults. Emplacement of a major continental margin batholith occurred 10 km to the east and was simultaneous with vein formation.

The presence of major structural controls to concentrate large fluid fluxes may be significant for exploration in slate-belt gold provinces. Where major flow networks are not strongly channelized along large structures, widespead relatively low tonnage gold systems will result during regional uplift. Examples include Otago (New Zealand), Chugach and Kenai Mountains (south-central Alaska), and Nome (northwest Alaska). Such systems may be eroded to form productive placers, but may not be favourable lode targets. Syntectonic plutonism within a slate-belt is commonly a good indication of the presence of a thermal event that may have concentrated gold in nearby veins. However, in some cases, there is little evidence for such activity and simply a high geothermal gradient may have led to ore formation. The Klondike district in westernmost Canada is such an example where several hundred tonnes of placer gold were derived from Early Cretaceous lodes that lack any spatially associated coeval plutons (Rushton et al., 1993). Finally, recognition of a slate-belt with high background concentrations of gold may indicate a leachable source capable of assisting formation of a major gold deposit. The more than 4000 t of gold at the Murantau deposit in Uzbekistan (Berger et al., 1994) is located in a greenschist facies metapelite that averages at least 10 ppb Au.

Geometry of specific major deposits

A feature of the Victorian gold deposits is their relatively small surface area and their substantial depth continuity. The surface area of the entire Bendigo goldfield is about 5 km by 25 km, and mining continued to depths of 1.5 km. The mafic intrusions that host Woods Point and Walhalla are tens of metres thick and 100's metres in length, but continue to one kilometre depth. Auriferous veins at Bendigo occurred along and near several parallel anticlinal axes and less commonly in reverse faults. At Woods Point, classic ladder veins cut mafic dykes.

Gold grades in the major deposits of the Juneau gold belt are also consistent over large vertical extents. Ore-bearing veins at the three largest deposits, Alaska-Juneau, Treadwell and Kensington, continue down-dip for more than 1 km. At the surface, the metagabbro-hosted Alaska-Juneau deposit consists of a dense network of brittle-ductile fissure veins that continue for more than 6 km along strike and occur in swarms 50-300 m wide. Individual veins are up to 4 m thick. At the Treadwell and Kensington mines, much of the monzodiorite-hosted ore occurs within intricate stockwork systems.

At Murantau, most ore is contained in extremely thin veinlets and widespread silicification that extends for 20 km and to depths of at least 2.5 to 3 km. The geometry of these types of slate-belt systems likely reflects more ductile and slightly higher temperature conditions of ore formation.

From an exploration viewpoint, large deposits can represent a relatively small surface target with great depth extension. Within any given province, such deposits can develop in quite varied lithologies and it is thus difficult to rule out any one lithology type as being unlikely to host ore.

Primary geochemistry of specific slate belt gold deposits

Quartz is consistently the major vein constituent, but lesser amounts of carbonate minerals are usually present. Veins typically contain less than 2-3 percent sulphides along with gold. Arsenopyrite and/or pyrite are commonly the major sulphide phases in metapelitic-hosted veins, with pyrite being common where veins cut igneous rocks. Pyrrhotite, sphalerite, galena, chalcopyrite, stibnite, loellingite, tellurides, and scheelite are subordinate metallic phases. Chlorite, muscovite, fuchsite (Cr-mica), albite and tourmaline are less common silicates.

Alteration around major slate-belt gold deposits can be rather subtle, especially in metasediments. Where igneous rocks host ore in the slate-belts, alteration assemblages are better developed. Carbonate alteration, white mica and Fe-bearing sulphides are the most common minerals in slaty host rocks, but even close to quartz veins such alteration does not necessarily change the appearance of the host rock substantially. Rarely do economic gold grades continue far outside the veins, in contrast to the Archaean greenstone belts where much ore is in altered wallrock.

Broad zones of sulphide and carbonate alteration provide the best lithogeochemical indications of ore. Also, arsenic anomalies distal to the veins are useful pathfinders for ore in slate-belts. At the Clunes deposit, Binns and Eames (1989) indicate carbonate alteration and anomalous arsenic extend for as much as 0.5 km from auriferous veins. At Bendigo, there is little strong alteration adjacent to veins, but throughout the district disseminated sulphides and carbonate spots are common. At the Alaska-Juneau deposit, formation of secondary pyrite, pyrrhotite, titanite and calcite occurs up to 1 km from the ore zones, whereas rutile, ferroan dolomite, tourmaline, arsenopyrite and biotite develop in narrower haloes (Newberry and Brew, 1988).

The behaviour of minerals and elements during gold mineralization can be explained in terms of the bulk rock composition of the host rock and the low salinity of the ore fluid. The low salinity of the fluid leads to limited mobility of the major elements and base metals that might normally be transported as chloride complexes. As a result, the volume of base-metal bearing sulphides in the veins is minimal and the metals are generally poor pathfinders for slate-belt gold deposits. Reduced sulphur is the major complexing agent, so soft acids are readily transported. This results in strong enrichment of As, Au, Sb and rarely Hg compared to base metals and Ag. As, Au and Sb provide the best metal dispersion patterns in wallrocks. In addition, sulphur and carbon dioxide enrichment provide useful visual dispersion haloes for exploration, and may extend hundreds of metres.

Summary

Slate belt gold deposits are small-sized targets that may contain substantial amounts of gold. They are inherent products of continental margin orogenesis where devolatilization, particularly at the greenschist / amphibolite facies boundary, can produce significant volumes of high temperature, sulphur-bearing fluid. If these fluids migrate into major conduits that cut the slate-belt, gold bearing vein systems will develop. Enrichment of CO_2, S, As and Au in adjacent wallrocks will typically provide the best evidence of nearby ore zones. Where ore-related structures continue to shallower and cooler parts of the crust, the predominance of sulphur as a complexing agent would result in near surface Sb and Hg lithogeochemical anomalies.

Acknowledgements

We thank the organizers of the 17th International Geochemical Exploration Symposium for the invitation to present this paper, particularly Dr Pat Williams who also commented on the abstract. Dr Martin Hughes is thanked for his close collaboration in a study of Victorian gold, and both authors acknowledge the contribution of colleagues and students towards the respective components of this contribution. Australian Research Council (large grant scheme) and National Key Centre In Economic Geology support for research is acknowledged.

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Geochemistry of ironstones and barite-rich rocks in the Proterozoic Willyama Supergroup, Olary Block, South Australia

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Keywords: ironstone, barite, Willyama Supergroup, South Australia

Introduction

The early Proterozoic Willyama Supergroup in the Olary Block comprises upper greenschist to amphibolite grade metamorphosed sedimentary and minor igneous rocks. It has been interpreted to have formed in an intracontinental rift setting with a sequence dominated by clastic and chemical sediments, with the latter including evaporites and exhalites (Cook and Ashley, 1992). Modern analogues for the setting may include the Salton Sea-Gulf of California, Red Sea and East African Rift Valley settings. The aim of this contribution is to present field and laboratory data of iron-formations, ironstones and barite-rich rocks which are distinctive minor rock types in the Olary Block. Their petrological and geochemical characteristics point to a distinct exploration potential for syn-metamorphic, stratabound Cu-Au and stratiform base-metal mineralisation. Included in the sequence are several ironstones which are defined herein as rocks containing Fe>15wt% (Kimberley, 1989). On the basis of field evidences ironstones have been subdivided into syngenetic and epigenetic types. Epigenetic ironstones show gradual replacement of quartz-albite, Fe-oxide-quartz and quartz-rich host rocks by magnetite-hematite-quartz veins, as well as local breccia textures. Finely laminated ironstones (quartz+magnetite±hematite±albite±barite±pyrite±calcsilicates) are present as distinct stratigraphic units and are termed syngenetic iron-formations following the generalised nomenclature of Kimberley (1989), who described "iron-formation" as a mappable stratigraphic rock unit which contains Fe>15wt%. The iron-formations grade into, or are associated with carbonate, silicic and especially baritic facies (barite+quartz+magnetite±hematite ±CuFe-sulphides). These rock types occur as lenses and thin bodies to thick masses and as a sequence of discontinuous, stacked horizons which are concordant to S_1. Barite-rich rocks, ironstones and iron-formations of the Quartzofeldspathic Suite (a unit dominated by clastic rocks of felsic igneous derivation and evaporites) are dominant, whereas manganiferous iron-formations (magnetite+quartz±Mn-Fe-garnet±amphibole±olivine±apatite) of the Pelite Suite (a unit dominated by fine-grained clastics) and alkali, Fe^{3+}-rich iron-formations (albite-hematite-clinopyroxene-quartz±amphibole±andradite±K-feldspar±apatite±phlogopite) of the Calcsilicate Suite are only of local occurrence.

Samples and Methods

Samples were taken from surface outcrops and included ironstones, iron-formations, and barite-rich rocks. All samples were split in two parts, the first being used for petrographical descriptions and optical microscopy. Major and trace elements were analysed by X-ray fluorescence of fused discs and pressed powder pellets on a Siemens SRF300 spectrometer in the Department of Geology and Geophysics, University of New England. Selected REE (REE: rare earth elements, La to Lu; LREE: light REE, La to Sm; HREE: heavy REE, Gd to Lu) and additional elements (Ag, As, Au, Br, Cd, Co, Cs, Hg, Hf, Ir, Mo, Sb, Sc, Se, Ta, Te, Th, U) were determined by instrumental thermal neutron activation analysis at the Becquerel Laboratories Pty. Ltd., Lucas Heights, Australia. Sulphur isotope measurements were conducted on barite samples at the Centre for Isotope Studies, CSIRO, North Ryde, Australia.

Barite-rich Rocks of the Quartzofeldspathic Suite

Geochemical analyses of the barite-rich rocks generally show low Mn, Pb, Zn, As and Sb concentrations, and elevated Cu and Au values (up to 1.27ppm Au, 0.3wt% Cu). Compared to the associated ironstones, the barite-rich rocks possess higher Sr, Cu and Au values, lower Co, Ga, Sc, V, Zn, and Zr contents, and lower total REE concentrations (ΣREE <30ppm). Mineralised rocks with high Ba, Cu and Au and low Fe concentrations generally exhibit large positive Eu anomalies on their chondrite normalised REE patterns. Unmineralised samples with low contents of Ba, Cu and Au and elevated values of Fe possess chondrite normalised REE patterns characterised by negative Ce and positive Eu anomalies. Low total REE contents, LREE enrichments (La/Lu >1), positive Eu anomalies and REE patterns unlike the North American shale composite (NASC) point to a hydrothermal origin of the barite-rich rocks. REE patterns of mineralised barite-rich rocks are similar to high-temperature (>230°C), acid (pH <6), chloride-rich submarine hydrothermal vent waters from the Salton Sea, East Pacific Rise, and Mid-Atlantic Ridge and pure hydrothermal barite precipitates formed on the sea-floor (cf. Michard, 1989; Barrett et al., 1990). Also, unmineralised barite-rich rocks with low Cu and Au values possess REE distributions identical to those of hydrothermal barite precipitates from the Southern Explorer Ridge of the northeast Pacific (Barrett et al., 1990) and thus barite-rich rocks from Olary are regarded as synsedimentary hydrothermal precipitates. The presence of both negative Ce and positive Eu anomalies within unmineralised barite-rich rocks indicate that barite precipitation did not occur in response to simple conductive cooling of a high-temperature hydrothermal fluid (>230°C). In contrast, the presence of negative Ce anomalies shows that convective mixing occurred between the high-temperature (>230°C), acid (pH <6) hydrothermal vent fluid and an oxidised water column. Sulphur isotopic compositions of barites (+6.5 to +16.3 per mill) are similar to the $\delta^{34}S$ values that characterise early Proterozoic seawater (+10 to +18 per mill; Strauss, 1993), and thus barite precipitation occurred as a result of convective mixing with seawater.

Iron-formations of the Quartzofeldspathic Suite
The iron-formations are characterised by low As, Au, Cu, Mn, P, Pb and Zn concentrations and very rarely possess elevated Cu and Au values (up to 0.65ppm Au, 0.2wt% Cu). Olary Block iron-formations generally have geochemical compositions similar to those of iron-formations documented from elsewhere (cf. Morey, 1992). However, in contrast to these documented rocks the Olary Block iron-formations are characterised by distinctly lower Mg values reflecting the absence of carbonates. Iron-formations containing no albite generally exhibit low Al, Ti, Na, K, Cr, Hf, Nb, Ta, Th, Y, and Zr contents. These elements are indices of detrital and volcanic sediment contributions indicating that such iron-formations were formed by predominantly chemical precipitation processes. Correlation of Al, Zr and Ti was used by Ewers and Morris (1981) to define the pyroclastic component in the Brockman iron-formation in Western Australia. For the Olary iron-formations there is a positive correlation (>+0.8) of Al with Ti, Na, K, Hf, Nb, and Zr, reflecting some clastic or volcanic inputs to these chemical sediments. Chondrite normalised REE patterns for the iron-formations show that most are enriched in LREE, depleted in HREE with either no Eu anomaly or a negative one. LREE enriched, Eu depleted REE signatures are similar to those of low-temperature, neutral to alkaline hydrothermal fluids (e.g., Michard, 1989), and to those of exhalites distal to Broken Hill-type base-metal deposits (Lottermoser, 1989). The strong similarities of the REE patterns of the iron-formations with the REE patterns of recent hydrothermal fluids compounds the notion that these horizons gained their REE from hydrothermal solutions. Thus in comparison with the associated barite-rich rocks the iron-formations precipitated from solutions characterised by a higher pH and lower temperature. Some iron-formations display chondrite normalised negative Ce and Eu anomalies. Such REE distributions are also found in modern seawater, in ferruginous oxidised submarine hydrothermal precipitates from the Romanche fracture zone (Bonatti et al., 1976), and in umbers from the Troodos Massif, Cyprus (Robertson and Fleet, 1976). The umbers' REE patterns were interpreted by these authors to originate from a seawater source involving incorporation of the REE into ferruginous sedimentary oxyhydroxides. Thus some Olary iron-formations may have gained their REE signatures from the overlying seawater column after hydrothermal precipitation.

Genetic Processes
Field data, petrology and REE geochemistry indicate that barite-rich rocks and iron-formations precipitated from an oxidised hydrothermal fluid which developed from high-temperature acidic, to low-temperature alkaline conditions. These changing parameters led to the successive precipitation of barite, silica and Fe-oxide-rich metalliferous sediments. The increase in pH is likely a result of the injection and mixing of the acidic hydrothermal fluid with alkaline waters of a playa lake (cf. Cook and Ashley, 1992), or more likely, a sabkha of an early Proterozoic soda ocean (cf. Kempe and Degens, 1985) as indicated by the sulphur isotope and REE geochemistry. The chemical composition of ancient and recent metalliferous sediments has been interpreted by various authors to reflect contributions from seawater, hydrothermal, biogenic and detrital sources. Pure hydrothermal sediments are enriched in elements such as Si, Mn and Fe. Addition of detrital or volcanic material dilutes hydrothermal elements and enriches detrital elements, such as Ti and Al. Major element discrimination diagrams (Fe/Ti versus Al/(Al+Fe+Mn); SiO_2 versus Al_2O_3) show that the original chemical sediments necessary for the formation of most barite-rich rocks and iron-formations were pure hydrothermal products and contained only insignificant detrital or volcanic material. In addition, hydrogenous and pelagic sediments accumulate sufficiently slowly to incorporate Th from the overlying water column, whereas pure hydrothermal precipitates scavenge

U from the hydrothermal fluids. Thus hydrothermal, hydrogenous and pelagic sediments exhibit distinctly different U/Th ratios. Olary iron-formations have low U/Th ratios similar to those of hydrogenous sediments whereas barite-rich rocks possess higher U/Th ratios similar to those of pure hydrothermal deposits. Iron- and sulphate-rich oxidised hydrothermal precipitates occur stratigraphically above and in strike extension of numerous massive sulphide deposits. They represent the more oxidised hydrothermal facies of the sulphide ore bodies. Characteristic features of the Kuroko ores is that the REE contents of the sulphide ores and anhydrite-rich rocks are lower than those of the associated Fe-oxide quartz rocks (Shikazono and Matsumoto, 1989). High total trace element contents within the Fe-oxide quartz precipitates have been interpreted as the result of long-term exposure to seawater and associated scavenging of elements (Shikazono and Matsumoto, 1989). The Olary iron-formations and barite-rich rocks exhibit total REE distributions identical to those of the Kuroko chemical sediments whereby the iron-formations possess distinctly higher total REE contents (ΣREE 10-250ppm) than the barite-rich rocks (ΣREE <30ppm). Thus low total REE and Th contents of Olary barite-rich rocks reflect rapid accumulation rates and rapid burial in the volcano-sedimentary pile, whereas relatively high total REE and Th contents in the iron-formations of the Quartzofeldspathic Suite are due to long-term exposure to the overlying water column, subaqueous oxidation and associated pronounced scavenging of REE and Th.

Epigenetic Ironstones

Massive ironstones comprising magnetite±hematite occur as replacement products of quartz- and feldspar-rich host rocks, as isolated outcrops and as pods and lenses within laminated iron-formations. The massive ironstones possess geochemical compositions identical to the laminated iron-formations including elevated Cu and Au values and these ironstones cannot be distinguished from the syngenetic iron-formations on geochemical grounds. Albite-rich samples have variable Al_2O_3 and Na_2O contents and the highest HFSE concentrations, reflecting variable abundances of albite, and thus different degrees of replacement of feldspar-rich host rocks by magnetite-hematite-quartz veins. Studies on Olary Block calcsilicate-hosted breccias and alteration zones (Yang and Ashley, 1994) indicate significant mobilisation of Fe^{3+}. Thus the origin of these ironstones and their elevated Cu and Au values are attributed to the mobilisation of Fe, Cu and Au by hot, saline, oxidising fluids during diagenesis and/or regional metamorphism and subsequent precipitation of these elements in suitable structural sites (shear zones, dilatant zones in zones of competency contrast) and host rocks (pre-existing iron-formations, feldspar-rich rocks) thereby forming massive ironstones and local Fe^{3+}-rich calcsilicate assemblages.

Exploration Significance

The occurrence of stratiform barite deposits and ferruginous chemical sediments in the Proterozoic Willyama Supergroup would suggest a potential for massive sulphide deposits as these rock types are commonly found in zones peripheral to, or overlying, sulphide ores (e.g., Meggen, Germany; Gamsberg, South Africa). However, the barite-rich rocks and iron-formations of the Quartzofeldspathic Suite lack the geochemical and mineralogical characteristics typical for rocks associated with massive sulphide ores. They possess low Mn contents, an oxidised assemblage of magnetite-hematite-barite-chalcopyrite-bornite-pyrite, and a REE and trace element geochemistry implying subaqueous oxidation and low-temperature, oxidised hydrothermal fluids. However, epigenetic ironstones with elevated Cu-Au values were formed by hot, saline, oxidising diagenetic/metamorphic fluids indicating a distinct potential for stratabound Cu-Au mineralisations similar to those found in the Mt Isa Eastern Succession. In contrast to the iron-formations of the Quartzofeldspathic Suite, iron-formations of the Pelite Suite possess elevated As, Au, Mn, P, U, and Zn concentrations (up to 5.83wt% MnO, 1.60wt% P_2O_5, 238ppm As, 627ppm Zn). They also exhibit LREE and Eu enrichments similar to those of high-temperature hydrothermal fluids (>230°C) and of exhalites proximal to Broken Hill-type base-metal deposits (cf. Lottermoser, 1989). In addition, the manganiferous iron-formations are associated with stratiform MnFe-garnet-rich rocks. Discriminant diagrams using major (Fe/Ti versus Al/(Al+Fe+Mn); SiO_2 versus Al_2O_3) and trace (U versus Th) element data point to a pure hydrothermal origin of both rock types. Such manganiferous iron-formations and garnet-quartz rocks are commonly associated with massive sulphide, gold, scheelite and stibnite deposits (e.g., Wonder et al., 1988).

Conclusions

Included in the Quartzofeldspathic Suite of the Proterozoic Willyama Supergroup in The Olary Block are several occurrences of barite-rich rocks and associated iron-formations. The presence of the barite-rich rocks as lenticular horizons, lateral and vertical gradations into carbonate, silicic and Fe-oxide facies and enclosing quartz-albite rocks, and the stacking of iron-formations and barite-rich rocks are interpreted as facies changes in the original sedimentary environment, competing volcanogenic and chemical sedimentation and multiple hydrothermal fluid events resulting in the deposition of different hydrothermal products. Apparent epigenetic ironstones may have developed from oxidising, saline hydrothermal fluids causing Fe^{3+} remobilisation in breccias and calc-silicate alteration zones at various times up to and including the D3 retrograde event. Hot spring activity leading to the precipitation of the iron-formations and barite-rich rocks involved oxidising fluids and potential for massive sulphide deposits is only likely in adjacent, more reduced environments. However, elevated Au and Cu values of both rock types indicate a distinct potential for stratabound, syn-metamorphic Cu-Au mineralisations in the Olary Block similar to those found in the Mt Isa Eastern Succession. In addition, localised manganiferous iron-formations and quartz-garnet rocks are similar to base-metal ore associated banded iron-formations and garnet quartzites in the Broken Hill Block and point to the possible presence of massive sulphide ores in the lower part of the Pelite Suite.

Acknowledgements

Funding for this study was provided by the Australian Research Council.

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The potential use of retrograde schist zones for detecting geochemical leakage in the Broken Hill Block, N.S.W.

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Keywords: Exploration, lead-zinc deposits, lithogeochemistry, Pb isotopes

Introduction

Extensive surface exploration of the Broken Hill region over a period of more than 100 years has discovered numerous small occurrences of Broken Hill type mineralization, but has failed to detect any large or medium sized orebodies, other than the Broken Hill deposit itself. This suggests that any large deposits that might exist are deeply buried or blind and are thus unlikely to show detectable geophysical or secondary geochemical signatures at the surface. One approach to detect such blind deposits would be to search for leakage geochemical anomalies along suitable channelways and then follow these back to their source (e.g. Koksoy, 1978).

Retrograde Schist Zones

Retrograde schist zones occur widely throughout the regionally metamorphosed Broken Hill Block. These are planar or curviplanar zones with a well-developed schistosity, defined by retrograde and hydrous minerals. They have fulfilled the function of faults under conditions of ductile deformation and typically displace units which they intersect by a combination of folding, attenuation and transposition. Some also contain major faults which appear to post-date the initial formation of the schist zones (Vernon and Ransom, 1971; Stevens, 1986). The zones are up to 2 km wide and up to 60 km long and a number of major and minor zones have intersected Broken Hill type mineralization (e.g. the British, De Bavay, Globe-Vauxhall, Main and Thackaringa-Pinnacles shear zones). Evidence for fluid activity and element mobilisation within the retrograde schist zones and associated faults suggests that they are potential leakage channels for elements sourced from Broken Hill type orebodies which they may have intersected or interacted with.

It is clear that there have been a number of stages of retrogression in the Broken Hill area and also in the retrograde schist zones. Field relationships, structural studies and K-Ar and Rb-Sr dating indicate that at least some retrograde schist zones existed at about 1600-1570 Ma, soon after prograde metamorphism and possibly even following the regional D_2 deformation, and that further activity extended up to 520 Ma (Stevens, 1986; Barnes, 1987). The zones generally contain a lower amphibolite facies mineral assemblage, dominated by quartz-biotite-muscovite, although some faulted and brecciated zones contain low greenschist grade rocks with chlorite and clay minerals (Vernon and Ransom, 1971). Some zones show domainal retrogression at the microscale and others retain disequilibrium assemblages indicating multiple retrograde stages and fluid activity.

Evidence for Element Mobility During Retrogression

In metamorphic environments fluid flow is commonly guided by active deformation zones and it is therefore likely that the retrograde schist zones were important in focussing fluids. Under the higher grade conditions fluid movement accompanying ductile deformation was most likely via grain boundaries and microfractures (cf. Bell and Cuff, 1989). At lower grade conditions brittle deformation would have allowed fluid flow via through-going, interconnected fractures. The nature of the permeability in these zones would thus have varied throughout their history.

The activity of fluids and concentration of U and B in hydrous alteration phases during early retrograde metamorphism at Broken Hill has been demonstrated by Ahmad and Wilson (1981). They suggested that fluids may have originated from dehydration reactions accompanying granulite facies metamorphism or from granites and pegmatites that post-date the high grade metamorphism. There is also evidence to confirm element mobility along the retrograde schist zones themselves, including K metasomatism and base metal enrichment. Edenborough (1969) reported elevated metal contents (Pb, Zn, Cu, Ag and Cd) in retrograde schists and overlying soils. Lawrence (1968) described vein-type galena and siderite mineralization in the British retrograde schist zone where it cuts the main Broken Hill lode. The lead in this vein has isotopic characteristics approaching those in Thackaringa type mineralization (Cooper, 1970). Both (1978), on the basis of Pb and S isotopic data and the close spatial relationship between Thackaringa type galena-siderite rich veins and retrograde schist zones, suggested that this type of mineralization formed by partial remobilization from earlier Broken Hill type mineralization during retrograde metamorphism. Many of the Thackaringa type veins are developed along faults which cut the schistosity of the retrograde schist zones and some veins cut later granitoids, pegmatites and dolerite dykes, indicating that any remobilization involved in forming these veins probably occurred late (between 520 and 280 Ma; Stevens, 1986). Barnes (1987) has also suggested that hydrothermal activity associated with retrogression and confined to the retrograde schist zones, at least in the later stages, was responsible for a range of vein-type mineralization including the Thackaringa type deposits.

Isotopic Data

Lead isotope data indicate that the different styles of mineralization in the Broken Hill Block have significant differences in their Pb isotope characteristics (Russell et al., 1961; Russell and Farquhar, 1970; Cooper, 1970; Reynolds 1971; Gulson et al., 1985). Broken Hill type deposits have "primary" Pb isotopic ratios which are distinct from those in Thackaringa vein-type deposits, which are more radiogenic. The Thackaringa type deposits are commonly associated with retrograde schist zones and Both (1978) has suggested that addition of radiogenic Pb to Pb remobilized along these zones from Broken Hill type mineralization could explain the isotopic ratios of the Thackaringa deposits. These ratios could also be explained by mixing of disseminated stratiform Pb and radiogenic Pb.

It may be possible to use Pb isotope ratios within the retrograde schist zones to determine proximity to major Broken Hill type mineralization. Lead remobilized along retrograde schist zones from a nearby Broken Hill type orebody might be expected to consist of a mixture of "primary" Pb and more radiogenic Pb formed from U and Th in the country rocks and fluids. The relative importance of the "primary" type Pb would decrease with reduced influence from a Broken Hill type source. Data from the Browne shaft mineralization, which occurs within the British retrograde schist zone near the Broken Hill orebody, indicate less radiogenic Pb than in typical Thackaringa and other vein-type deposits and lend support to this suggestion. Lead isotopic analysis of galena remobilized locally (possibly by mechanical processes) along fractures (<3 m) and into the Main Shear retrograde schist zone (<15 m) indicates that over these distances mineralization retains the "primary" Pb isotopic characteristics (McQueen, unpubl. data).

Testing the Concept

The concept of using geochemical leakage along retrograde schist zones to detect mineralization could be further tested by:

1. Detailed underground sampling of retrograde schist zones around the Broken Hill orebody to determine the nature and degree of ore element remobilization along the zones in the immediate vicinity of the deposit.
2. Further examination of element remobilization utilising samples from drill core through retrograde schist zones at greater distance from the Broken Hill orebody.
3. Surface sampling of major retrograde schist zones which have intersected the Broken Hill orebody to determine if any evidence of remobilization is preserved in weathered material.

Likely problems and complications would include:

1. Complexities related to the likely prolonged history of fluid movement through retrograde schist zones. It would be necessary to establish a clearer understanding of the structural sequence and history of fluid activity in the various retrograde schist zones.
2. Difficulties in interpretation due to the initial, probably low level, dispersion patterns being overprinted by chemical weathering effects in the regolith. This could be overcome by

RAB sampling of bedrock or by utilising elements or element and isotope ratios that have not been significantly affected by secondary processes (e.g. Pb isotope ratios).

3. Complications related to the development of Pb-Zn veins of Thackaringa type within some retrograde schist zones. This may be overcome by examining trace element associations (e.g. Bi, Cu and Zn and mobile elements such as As, F and Sb, associated with or more abundant in the Broken Hill type sulphides) and using Pb isotope discrimination techniques. Sequential leaching methods could be applied to extract Pb for isotopic analysis from minerals formed at different stages in the history of the retrograde schist zones.
4. The difficulty of determining fluid and element flow directions within the retrograde schist zones, necessary to trace the source of any leakage anomalies.

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Regional geochemical models of plate tectonic for the Jungger plate in Xinjiang, China

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Keywords: regional, geochemistry, plate tectonic, Jungger, China

Western Jungger of Xinjiang, China lies at the collision belt between Siberia and Jungger plate. Stream sediment survey covered about 15700 km^2 has been carried out in 1987-1990. Therefore, the regional geochemical models of deep faults and suture line could have been discovered, and then the gaps in geochemistry about plate tectonics of this area were filled in for the first time.

Multi-element anomaly belts of Fe, Mg, V, Ti, Co, Cr, Ni and Mn are closely related to the deep faults. The distributions of the positive and negative composite anomalies of those elements are linear and regular. The positive composite anomalies occur alternating with or inlaying with the negative composite anomalies in space. The positive anomalies are generally distributed around their negative composite anomalies. Overall, there appear to be 3 linear and continuous belts of positive and negative composite anomalies coinciding with basic and ultra-basic volcanic rocks. 3 deep faults are revealed.

Multi-element geochemical high background areas of two groups of elements can reflect the suture line between Siberia and Jungger plate. One group of the elements are Fe, Mg, V, Ti, Co, Cr, Ni, Mn, Cu, Sr, P and Al. All of their high background areas are mainly distributed on the upper half part of the area. Another group of the elements are K, Y, Be, Sn and Bi. Their high background areas are dominantly occurred on the lower half part of the area. It is interesting that those two groups of elements of high background areas or belts can be put together or inlaid with side by side along the suture line.

Therefore, large scale of regional geochenmical data derived from stream sediment survey can be utilized to study the boundary of plate tectonics. The regional distribution models of background areas and anomalies of single- and multi-element may be the departure point of studying and resolving the problems of regional structures and tectonics using regional geochemical data. The regional tectonic framework in an area can be effectively revealed by the changement tendency of the geochemical dispersion patterns of various elements. It can be concluded that beads-shaped distributions of positive and negative anomaly belts of Fe, Mg, V, Ti, Co, Cr, Ni and Mn can reflect the deep faults in this region. The belt along which two different groups of multi-element high background areas can be put together side by side may corresponds to the suture line.

Integrated Thermoluminescence Radiometrics in the Location of Producer Oil Wells, Helez Field, Israel

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Keywords: oil, exploration, thermoluminescence, radiometrics, Israel

Aim

This study was designed to evaluate integrated thermoluminescence (TL) radiometrics as a method to complement geological and geophysical data in targeting spud-in sites for the initial drilling of oil wells in a prospect or for stepout production in existing oil fields. It is predicated on the hypothesis that uranium is present in the reducing environment of an oil trap; further, the premise is made that there is vertical migration of gaseous daughter products from the decay of uranium through the overlying geological column. Radioactive signals registered in soils at the surface should be related spatially to petroleum accumulation in the subsurface.

The research area is the Helez Oil Field, Southern Coastal Plain, Israel. Gilboa et al (1990) show production is from depths between about 1480 and 1600 m in Lower Cretaceous sandstone and porous Jurassic carbonates. They describe the Helez field as a combination stratigraphic-structural trap located on a northeast-southwest trending faulted anticline (Late Cretaceous-Early Tertiary) that is tilted gently to the east and downfaulted to the west. During Neogene events, transverse faults divided the Helez Field into several blocks. On the basis of biomarkers and stable isotopes, Bein and Sofer (1987) proposed that the oil originates in Jurassic limestone.

Past studies on the use of TL in oil exploration have shown that integrated TL radiometric measurements can be useful in lowering front end costs (Siegel et al., 1989, 1993, Wang et al., 1993; Sun and Zhu, 1993). This was done by taking a large area prospect and using integrated TL radiometric measurements to identify smaller areas within it with a greater probability of containing petroleum and natural gas. At the Shengping, China oil pool, for example, 35% of the >110 km^2 prospect was targeted as likely to contain petroleum. Drilling stepout wells on the basis of TL data and the complementary geology and seismic analysis resulted in an increased production area of 6 km^2 (p.c. to FRS from Wang and Qin, 1993).

Methods

LiF:Ti,Mg thermoluminescent dosimeters (TLDs - 3.2x3.2x0.9 mm) were prepared for the study by cleaning them with methanol, heating them at 400°C for 1 hour and then, after cooling, heating again at 100°C for 2 hours. They were kept out of light and two or more dosimeters were put in labeled plastic containers for burial. Upon recovery, the dosimeters were kept in the dark until radiometric measurements were made.

Dosimeters were buried at 67 sites in about a 14 km^2 area. These included 24 wells which had been or still are oil producers. Pits 20 cm in diameter were hand dug to a depth of 50 cm. The dosimeters were buried in plastic containers at this depth and the pit was filled with the soil taken from it. After about 3 to 4 months, the TLDs were recovered and kept out of light until radiometric measurements were made. The accumulated radioactivity dosage was measured using a Harshaw Thermoluminescence Dosimetry Reader. Radiometric readings were normalized to 100 days to be able to compare readings between measurement sites.

Main Results

Values for accumulated dosages normalized to a 100 day burial period ranged from 72 to 201 nanocoulombs for 60 sample sites. The mean accumulated dosage was 134 nanocoulombs. Reproducibility of replicate samples was 3.4%.

Dosimeters were recovered from 18 of the 24 producer well sites where they had been buried. Four plastic containers were not found and two had been breached during recovery digging and the dosimeters lost.

For the 18 of 24 oil producer sites where dosimeters were planted and recovered 14 had low radiometric values (< 130 nanocoulombs) which, with existing geological and seismic data would have prioritized them as drilling targets. Of 11 oil producer sites on the anticlinal structure bounded by faulting to the W, the SW, and the NNE, 8 had low radiometric values.

Discussion and Conclusions

Transient radiometric measurements as have been used in petroleum exploration have not been consistently reproducible since they are subject to interferences from changes in ambient conditions such as in barometric pressure, differences in temperature during the day, and others. As such, integrated radiometric measurements made during an extended period of time would alleviate the influence of these environmental interferences and provide reproducible data (Siegel et al. (1982).

We used TLDs to measure radioactivity at the Helez Oil Field, Israel, with the aim of investigating the relation between integrated radiometric measurements and the location of former and existing oil producer wells. The results were encouraging. Drilling based on numerically sequential values from the low TLD values to higher values, show that the first eight (8) wells (integrated radiometric values ranging from 97-118 nanocoulmbs) drilled would have been completed as oil producers (including the field's discovery well). It should be emphasized that geological and geophysical data must support a decision to spud-in a well and that TL radiometric data alone does not warrant such a decision.

In theory, if an anticlinal structure is being drilled, low value radiometric measurements can be expected where the trap is sealed by secondary deposits (carbonate, sulfate, sulfur) which are not as permeable to gas escape compared to the lateral areas. This can result in an annular distribution of higher value measurements farther away from the trap where the seal is missing or breached due to strain fractures. A combination of stratigraphic-structural traps such as present at the Helez field complicates the geometry of the surface radiometric signal distribution. At the Helez field, five (5) of the initial eight (8) lower radiometric value drilling sites were on the anticlinal structure bounded by downfaulting to the NE and SW. Higher values presented a partial annular pattern to the E.

If, with further testing, integrated TL radiometrics is shown to be reliable in locating spud-in sites for petroleum and/or natural gas wells or for stepout production in context of the geological and geophysical information, exploration efficiency for petroleum and natural gas can be increased.

The use of integrated TL radiometrics may be useful in exploration for mineral deposits as well. For example, the largest known uranium deposit in the world, the Jabiluka II body in the Alligator River Province, Australia is essentially blind to all methods not involving drilling. The Jabiluka II body would be an ideal place to test the buried TLD technique for uranium prospecting. Similarly, gold and uranium deposits in quartz-pebble conglomerates and associated coarse-grained arenites of lower Proterozoic age where the Phanerozoic and upper Proterozoic covers have not been stripped away might be detected using the integrated TLD method.

Acknowledgements

We would like to acknowledge the assistance of Lapidoth, Israel Oil Prospectors, Ltd., which allowed us to carry out this study.

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Geochemical characterization of tungsten bearing granites from Rajasthan, India.

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Keywords: Tungsten, granites, geochemistry, exploration, Geochemical Characterization Index, Rajasthan.

ABSTRACT

Tungsten deposits are generally found associated with acid igneous rocks. Number of granitic rocks associated with various mineralization have been studied in recent years in order to establish criteria useful in finding targets for detailed prospecting of that particular mineral (Flinter et al.,1972; Tauson and Kozolov 1973; Tischendorf,1977; Ohlander, 1985; Horbe et al.,1991). However additional work is required for establishing geochemical characteristics of granites related with the tungsten mineralization.

The objective of the present paper is to investigate if there is any correlation between the geochemistry of granitic rocks and tungsten mineralization in order to discover possible geochemical criteria for regional exploration and to delineate areas with tungsten potential. The area chosen for the study is Rajasthan (North-Western India), because of its rich potentiality in tungsten mineralization. Bhattacharjee et al. (1993) have suggested a possible 500 km long tungsten belt running from Balda in Rajasthan to Tosham in Haryana which cover all the tungsten occurrences of Rajasthan.

To achieve the above objective the geochemical results for the granites associated with tungsten mineralization (tungsten granites) and those which are not related with any mineralization (barren granites) in the same or near by areas from Rajasthan, are compared to investigate the possible geochemical parameters for exploration of tungsten prospects.

Tungsten mineralizations in Rajasthan are genetically related with the granites of Precambrian age emplaced on the western margin of Delhi Fold Belt (Bhattacharjee et al., 1993). Greissenization of the host granites is found to be intensely associated with these mineralizations (Srivastava and Sinha, 1994). This might be resulted by action of the volatile rich mineralizing fluids, derived from the parent magma during late stage of their evolution, on the host granites.

Tungsten granites are found enriched in SiO_2, total alkalies and are depleted in CaO, FeO, TiO_2 and MgO. The number of atoms for Na+K is varying from 180 to 240 with mostly more than 200 for tungsten granite while for barren granites it ranges between 130-200. The similar difference was found in the south China tungsten fields (Liu and Ma, 1993). It is also inferred that the tungsten granites of Rajasthan are highly differentiated and fall

under S-type granite category. The tungsten granites are showing in general a higher concentration of W than the barren granites. They are also enriched in Rb, Li, Sn, Nb, B, Be and are depleted in Ba and Sr. The study suggest that the higher values of Rb/Sr, Li/K and Ba/Sr and lower values of K/Rb, Ba/Rb and Mg/Li for granites are the most significant discriminators for identifying tungsten granites from barren granites.

A Geochemical Characterization Index (GCI) is proposed using the trace elements discriminators as –

$$GCI = \log_{10} \frac{Rb^3 * Li * 10^4}{Mg * K * Ba * Sr}$$

for ostracizing tungsten granites and barren granites, where the values for elements are taken in ppm. GCI has possitive values for the tungsten granites while the barren granites are represented by negative values. The Index has been positively tested for the granites of India and also in some parts of world as shown in fig.1.

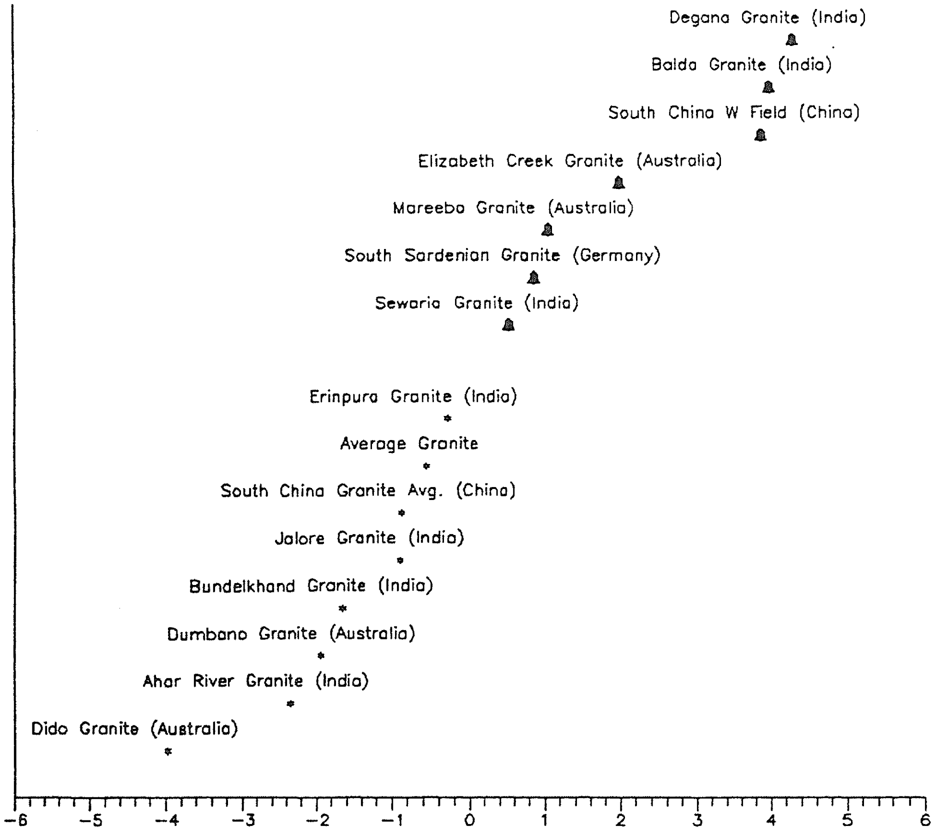

Fig.1. Geochemical Charecterization Index for different Tungsten granites (▲) and Barren granites (*). (Data computed from Biste, 1982; Bhattacharjee et al, 1993; Eby and Kochhar,1990; Liu and Ma, 1993; Rahman and Zainnudin, 1990, 1993; Sheraton and Black, 1973; Turekian and Wedephol, 1961 and author's work)

It may be concluded that the proposed Geochemical Characterization Index is useful in delineating the granites genetically and spatially associated with tungsten mineralization and hence it can be used as an exploration parameter.

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Investigating lithogeochemical variations using a Pearce element ratio strategy without a conserved element assumption

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Keywords : lithogeochemistry, mass balance, Pearce element ratios

Introduction

Valid approaches to investigate compositional variations in rocks avoid the effects of closure, a mathematical constraint that requires geochemical concentrations to sum to unity (100 %). The effects of closure are evident when, for example, SiO_2 is added to a rock (perhaps precipitating in its pores), causing the SiO_2 concentration of the rock to increase. Unfortunately, it also causes the concentrations of every other element in the rock to decrease, even though these other elements were not removed, to ensure that the sum of all concentrations equals one. This discrepancy between the action and manifestation of material transfer is caused by closure and is the primary motivation for using numerical approaches to eliminate these numerically-induced variations that obscure the real geological material transfer-induced variations (*e.g.*, igneous fractionation or hydrothermal metasomatism). Numerical approaches in common use that circumvent closure in lithogeochemical data include those of Akella (1966), Gresens (1967), Pearce (1968) and Grant (1986). Unfortunately, all of these approaches rely on an assumption of either element, mass or volume conservation to perform the calculations that mitigate closure. These assumptions significantly limit the application of these methodologies to those geological environments where the assumptions are valid.

General Element Ratio Diagrams

An alternative strategy, the general element ratio (GER) diagram (Stanley, in review), avoids the effects of closure and thus also allows quantitative investigation of compositional variations in rocks. Unlike the conventional techniques, above, this approach does not rely on associated restrictive assumptions. The GER methodology uses a diagram composed of axes of molar ratios with a common denominator. Thus, the diagram is similar to a Pearce element ratio (PER) diagram; however, it lacks a conserved denominator. The ratios have numerators and denominator made up of linear combinations of elements, such that the effects of specific material transfers affect where samples plot onto the diagram in predictable ways. Lithogeochemical data plotted on the diagram then can be used to test whether the hypothesized material transfer process could be responsible for the observed variations.

Depending on the GER diagram axes, material transfer can cause rock compositions to be displaced : (i) toward a specific node on the diagram that is the projection of the mineral(s) undergoing material transfer or a net metasomatic exchange, or (ii) along a predictable vector on the diagram defined by the mineral(s) undergoing material transfer or a net metasomatic exchange (in a manner analogous to PER diagrams). Alternatively, material transfer may have no effect on the diagram because it is a projection from the mineral(s) undergoing material transfer or the net metasomatic exchange.

GER diagrams are topologically equivalent to ternary diagrams. Thus, the amount of material transfer responsible for any observed compositional difference between two rocks can be calculated because : (a) a weighted lever rule applies to 'phases' projecting as nodes on the diagram, and (b) distances between samples on the diagram are proportional to the amount of material transfer of 'phases' defined by vectors on the diagram. These attributes ensure that the amount of material transfer calculated can be expressed in terms of the modal mineralogy or net metasomatic exchanges that have affected a suite of rocks.

Examples - Diagram Design

GER diagrams may be used to investigate, and quantify, the compositional variability of a given suite of rocks. The petrography of the rocks is used to design the diagram. For example, a fresh clinopyroxene-phyric basalt will probably exhibit several varieties of compositional variation caused by different effects : (1) variable amounts of clinopyroxene crystal sorting (fractionation or accumulation within a melt of probable constant composition), and (2) variable compositions of the clinopyroxene undergoing crystal sorting (ranging from diopside to hedenbergite). With no other information, we can design a simple GER diagram that is unaffected by variations in the composition of the clinopyroxene by using the molar sum of $Fe+Mg$. All clinopyroxene compositions on this diagram (Figure 1) plot at the point (1/2,1/2) - the 'clinopyroxene node'. However, the composition of the basaltic melt plots at another location on the diagram $(x/z,y/z)$ - the 'melt node'. Because the basalt is a mixture of melt and clinopyroxene, all basalt compositions will lie on the tie-line that passes through these two nodes. If this is not true, either the rocks are not derived from a common parent melt or another material transfer process has operated to produce additional compositional variability. In Figure 1, basalt samples that have accumulated clinopyroxene will plot between these two nodes, and those that have fractionated clinopyroxene will plot on the far side of the melt node from the clinopyroxene node. In both cases, the lever rule may be used to quantify the proportions of melt and clinopyroxene in any sample that plots on the tie-line.

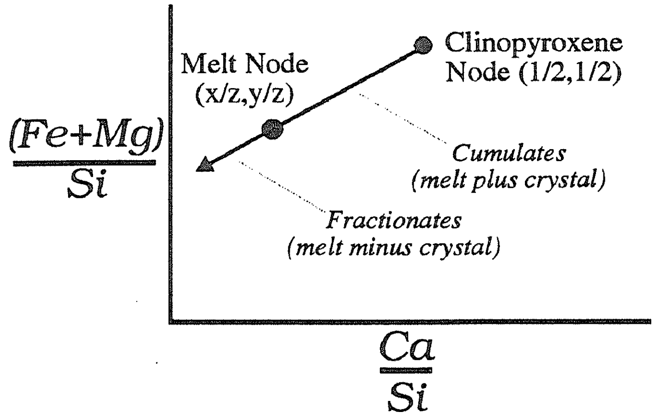

Figure 1 - GER diagram investigating compositional variations in a clinopyroxene-phyric basalt. All clinopyroxene compositions (diopside ↔ hedenbergite) plot at (1/2,1/2). The melt composition determines the slope of the line describing the material transfer effects of crystal sorting within the basalt. See text for further discussion.

In essence, the GER diagram can eliminate (or project from) several types of compositional variation so that other types can be quantified. At the same time, because the diagram is formed from ratios, the GER methodology avoids the obscuring effects imposed by closure. As such, GER diagrams may be used to remove sources of noise (closure and other material transfer process-induced variations) that prevent geochemists from quantifying specific material transfer effects of interest (e.g., hydrothermal alteration and metasomatism).

Whereas the above example may appear trivial and intuitive, more realistic petrologic hypotheses may require very complicated GER diagrams. A diagram analogous to Figure 1 designed to investigate the compositional variability in a hornblende-phyric andesite would have $(2Si+9Al+9Fe^{+3}+9Na+9K)/16$ and $(-4Si+9Al+9Fe+9Mg)/13$ as abscissa and ordinate numerators divided by a common $(-Si+9Ca)/2$ denominator. This diagram accommodates several more varieties of compositional variation than Figure 1, and thus is more powerful and has more complex axes ratios. All hornblende compositions constrained by the five principal solid solutions that occur in Na-Ca amphibole (ferro-magnesian exchange - $FeMg_{-1}$, tschermak exchange - $Al_2Mg_{-1}Si_{-1}$, edenite exchange - $NaAlSi_{-1}$, ferri-alumina exchange - $Fe^{+3}Al_{-1}$ and soda-potassic exchange - KNa_{-1}) will plot at (1,1) on this diagram. As a result, this diagram leaves only the compositional variations due to hornblende crystal sorting manifest, allowing its quantification using the lever rule.

Determination of the linear combinations of the numerators and common denominator in the axes ratios of GER diagrams are made using a matrix methodology that utilizes the relationship between : (i) the composition of the constraining minerals or exchanges, (ii) the axes numerator and denominator coefficients, and (iii) the behavior of material transfer on the diagram (Stanley and Russell 1989). Thus, GER diagrams may be tailored to the specific petrology of a compositionally diverse suite of rocks. In a lithogeochemical exploration context, diagrams can be designed that eliminate, or restrict, the 'background' compositional variations of a mineral deposit host rock (*e.g.*, sedimentary or igneous fractionation variations), allowing additional compositional variations imposed during deposit genesis (hydrothermal alteration and metasomatism) to be manifest and quantifiable.

Examples - Quantifying Metasomatism

For example, compositional variations within a pyroxene diorite reflecting magmatic sorting of plagioclase, clinopyroxene, magnetite and apatite will not influence the GER diagram of Figure 2. However, subsequent potassic alteration of this diorite will displace rock compositions toward the tie-line through the quartz, potassium feldspar and biotite nodes. The weighted lever rule may then be used to determine how potassically altered each rock is. The displacement direction of an altered sample from the diorite node constrains the actual metasomatic material transfers that produced the altered rock and the resulting alteration mineral mode, allowing formulation of a balanced reaction describing the net hydrothermal alteration effects.

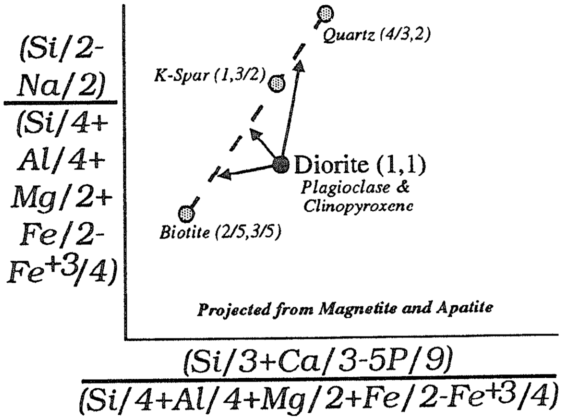

Figure 2 - GER diagram for investigating compositional variations in a fractionating pyroxene diorite that has been potassically altered. Compositional variations due to differential sorting of clinopyroxene, plagioclase, magnetite and apatite, and all of their solid solution effects, will not displace unaltered rock compositions from the point (1,1) because it is the plagioclase and clinopyroxene node, and the diagram is a projection from magnetite and apatite. The effects of potassic alteration of this diorite to an assemblage of quartz, potassium feldspar and biotite will displace rock compositions toward the tie-line through the collinear nodes of these three minerals. The distance from the diorite node (1,1) to a potassically altered sample, relative to the distance from the diorite node to the tie-line, is a measure of how potassically altered the diorite is and may be a useful exploration parameter when quantified using the lever rule.

Because the GER methodology uses petrological constraints, rather than volume, mass or element conservation assumptions to avoid closure and quantify material transfer, it may be used in a variety of geological systems that have proven to be intractable to date using conventional approaches (Akella, 1966; Gresens, 1967; Pearce, 1968; Grant, 1986; *e.g.*, magmas undergoing both fractionation and assimilation, and coarse clastic rocks exhibiting sedimentary fractionation and hydrothermal alteration). Figure 3 depicts a diagram that addresses one of these more complex systems where the 'background' variations (imposed by sedimentary fractionation between the base and top of a turbidite bed) cannot be completely eliminated. Instead, the variability can be constrained to lie on a line segment so that residuals from that line segment can be used to quantify an additional source of variability (tourmalinization associated with the genesis of a sediment hosted massive sulphide deposit; Figure 3).

Tourmalinization effects can be removed by subtracting *4B/3* and *B/3* from the abscissa and ordinate numerators, respectively, of Figure 3. This will displace the tourmaline node to the point (2,3), the mica node, causing the effect of tourmalinization to be indistinguishable from primary sedimentary fractionation. This allows further investigation of other material transfer processes, such as an overprinting chloritization (which on this modified diagram would displace rock compositions along a vector with a slope of three, assuming an ideal clinochlore composition). Thus, the residual from a chloritized sample to the turbidite tie-line along a line with slope of three on this modified diagram would be a quantitative measure of how chloritized a sample is relative to other samples.

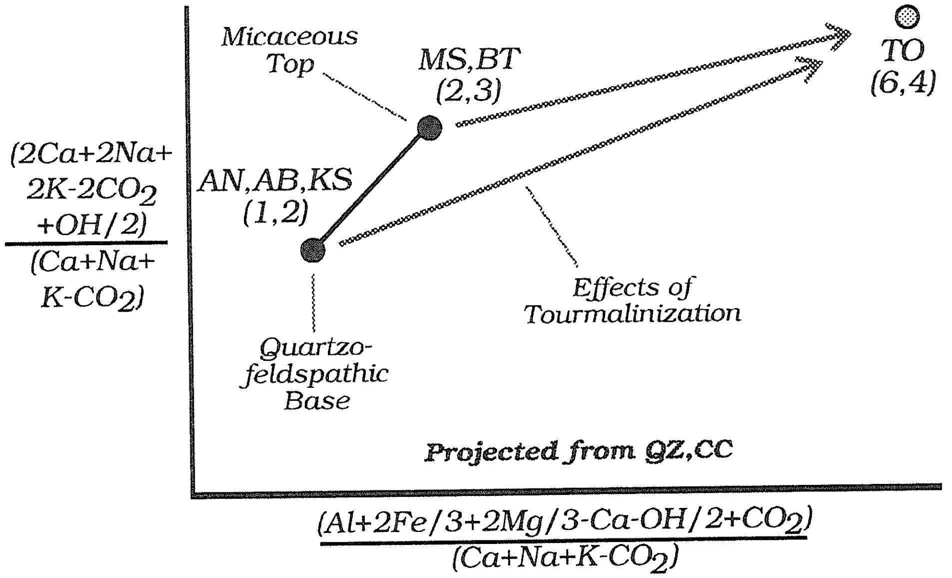

Figure 3 - GER diagram for investigating compositional variations in a metamorphosed turbiditic greywacke that has undergone tourmaline (TO) alteration as host to a sediment hosted massive sulphide deposit. The sediment is composed of quartz (QZ), plagioclase (AN,AB), potassium feldspar (KS), muscovite (MS), biotite (BT) and calcite (CC). Background rock compositions will plot on the (1,2) ↔ (2,3) line segment. Rocks that have been tourmalinized will have their compositions displaced from this line segment toward the tourmaline node. The lever rule may be used to quantify this tourmalinization, a potential exploration parameter.

General element ratio diagrams provide geochemists with the ability to investigate complicated geochemical hypotheses in rock systems that are not amenable to investigation by conventional material transfer methodologies. This expands a geochemist's ability to perform material transfer calculations in systems that could not previously be quantitatively studied. Specifically, the ability to investigate specific lithogeochemical variations in these complex rock systems allows the geochemist to quantify hydrothermal alteration, a potential exploration parameter.

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Lithogeochemical exploration for hydrothermal mineral deposits using Pearce element ratio diagrams

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Keywords : lithogeochemistry, hydrothermal mineral deposit,
massive sulphide, Pearce element ratios

Introduction

Chemical reactions between mineralizing fluids and host rocks commonly produce large zoned mineralogical and geochemical haloes about hydrothermal mineral deposits that are ideal intermediate exploration targets. Lithogeochemical data treatment procedures to identify these haloes commonly fail because the variations observed in the altered host rocks to hydrothermal mineral deposits are the result of : (i) metasomatism associated with the deposit genesis, (ii) closure, a mathematical constraint that requires the sum of all element concentrations in a rock to equal unity (100 %), (iii) rock-forming processes (*e.g.,* igneous fractionation, sedimentary fractionation, *etc.*), and (iv) other material transfer processes that also modify the chemistry of the rocks (*e.g.,* sea-water metasomatism, metamorphism, diagenesis, weathering, *etc.*). As a result, the response to hydrothermal metasomatism associated with ore genesis is only one component of the compositional variability in the lithogeochemical data. Other sources of variability introduce noise that masks the anomalous response, making it difficult to investigate hydrothermal metasomatism. Lithogeochemical data treatment procedures that avoid these other influences provide significant advantages when investigating hydrothermal alteration zones.

Pearce Element Ratio Analysis

A number of lithogeochemical data treatment procedures have been devised to avoid the problem of closure and, thus, to quantify material transfer (*e.g.,* igneous fractionation, hydrothermal metasomatism, *etc.*; Akella, 1966; Gresens, 1967; Grant, 1986). All of these approaches rely on an assumption of either element, mass or volume conservation to perform the calculations that mitigate closure. Pearce element ratio (PER) analysis (Pearce, 1968; Russell and Nicholls 1987; Russell and Stanley 1990a) uses molar ratios with a 'conserved' denominator (one that did not participate in the material transfer that caused compositional variability in rocks) in order to avoid closure. Thus, it differs significantly from the other mass-based methodologies, providing a significant advantage because its molar format allows straightforward examination of simple petrologic processes (Figure 1). Linear combinations of PER's may be plotted against each other to model compositional variations in rocks that overprint those cause by metasomatism.

For example, compositional variability in an olivine-phyric picrite may be due to differential sorting of olivine within a presumed homogeneous melt. If this is the only source of compositional variation, other than closure, then a Si/Z (abscissa) *versus* $(Fe+Mg)/Z$ (ordinate) PER diagram can be used to model the compositional variation. The effect of olivine addition or loss will displace rock compositions up or down a line with slope of two on this diagram. Thus, cumulate picrites will plot above fractionated rocks along the line. The linear combination $(Fe+Mg)$ in the ordinate numerator is used to remove the effect that different olivine compositions can impose, and this made easily done because the diagram is composed of molar ratios.

One assumption required by PER analysis (and all other material transfer approaches) is that the rocks under investigation be derived from a common homogenous parent. In the case of PER's, unlike the others, this composition need not be known. The assumption can be supported by geological observation (*i.e.*, stratigraphic correlation) or by examining conserved element ratios. Conserved element ratios are constant, given measurement error, in rocks related to a common parent that was at one time homogeneous (Stanley and Madeisky 1993; Figure 2A). This requirement is geologically reasonable when considering igneous melts, and pelagic/hemipelagic sediments (Barrett 1992; Stanley and Madeisky 1993). Thus, before utilizing any material transfer approach to determine *how a suite of rocks are related*, one must verify *whether the rocks are related* (Russell and Stanley 1990). Examination of possible conserved element ratios to test whether rocks are related allows identification of a conserved element for use in PER denominators. Thus, PER's provide an additional means to resolve complicated stratigraphic relationships (*i.e.*, chemostratigraphic correlation), a useful attribute in volcanic environments.

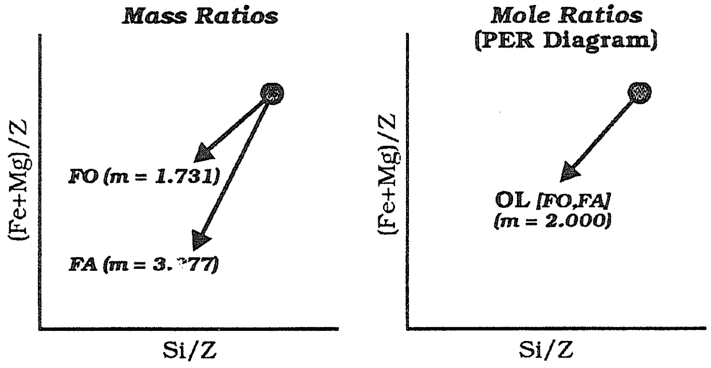

Figure 1 - Comparison of molar and mass PER-type diagrams. The effects of olivine fractionation differ on a mass ratio diagram as a function of olivine composition due to the different atomic weights of *Mg* and *Fe*. In contrast, olivine fractionation effects on a molar (Pearce element) ratio diagram will be identical, regardless of olivine composition. The denominator in these diagrams (*Z*) is any conserved element.

Background Compositional Variation Models

In order to address more complex fractionation scenarios (such as that of olivine, clinopyroxene and plagioclase in mafic volcanic rocks), a matrix equation developed by Stanley and Russell (1989) may be used to design the linear combinations for the axes numerators of PER diagrams that satisfy specific graphical constraints (commonly exhibiting material transfer effects along lines with unit slope). Differential sorting of olivine (OL), plagioclase (PL) and clinopyroxene (CP; augite), of any composition in any proportion, will cause samples related to a common parent to plot on the PER diagram of Figure 2B along a line with unit slope. Clearly, the numerator coefficients of Figure 2B are neither intuitive nor simple, but are the numerical consequence of the OL, CP and PL chemical formulae and the desired material transfer effect.

These minerals are probably responsible for most compositional variation in fresh basalts, basaltic andesites and primitive andesites. As such, the PER diagram of Figure 2B represents an important tool for modeling fractionation in mafic volcanic rocks. Similarly, an *Al/Z versus (Na+K)/Z* PER diagram represents an important tool for modeling fractionation in felsic volcanic rocks. On this diagram, alkali feldspar material transfer causes compositions to be displaced along a line with unit slope; quartz fractionation does not displace lithogeochemical data across the diagram. These two minerals are probably mostly responsible for the observed, petrologically controlled compositional variations observed in rhyolites and rhyodacites.

Quantifying Metasomatism

Because petrologic models for pre-existing compositional variation in volcanic rocks can be developed using PER's, other material transfer processes, such as metasomatism associated with the genesis of a hydrothermal mineral deposit can be investigated without the interference imposed by compositional heterogeneity of the host lithology. Thus, metasomatism may be rigorously quantified if a geochemist : (i) develops a petrologic model for the background lithogeochemical variability of un-altered host rocks using the PER method, (ii) recognizes as altered samples that do not conform with this 'background' petrologic model, and (iii) quantifies the additional (metasomatic) material transfer effects in these samples by calculating residuals from the fractionation model. In this way, the background variations in the host rocks are eliminated and a better measure of the amount of metasomatism is obtained (Stanley and Madeisky 1994). Thus, the PER methodology may be used to identify, discriminate between and quantify the different types of metasomatism and hydrothermal alteration. In this way, exploration vectors can be developed toward higher grades of metasomatism. Results allow unimpeded observation of metasomatic reactions and thus provide a better understanding of the processes that lead to mineral deposit genesis. All of these aspects enhance a geologist's ability to use lithogeochemical data to explore for hydrothermal mineral deposits.

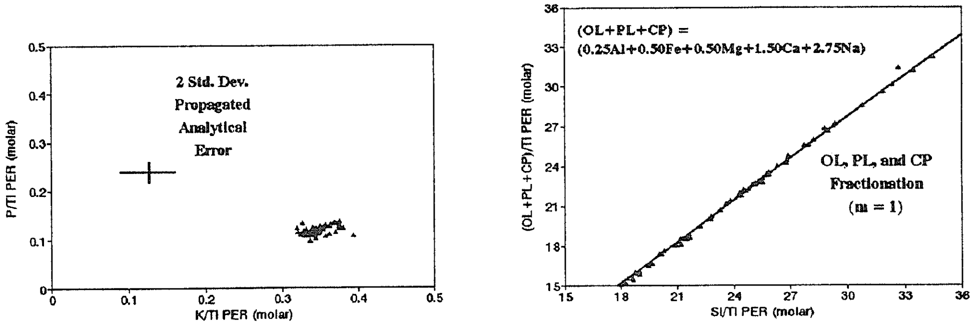

Figure 2 - Olivine-, plagioclase- and clinopyroxene (augite)-phyric lavas from the 1959 summit eruption of Kilauea volcano, Hawaii (Russell and Stanley 1990b) are plotted on a *K/Ti versus P/Ti* PER diagram (A). The data at a single point, given measurement error, and thus we conclude that these rocks are derived from a common homogeneous parent, and that these three elements are conserved. The same samples have also been plotted on a *Si/Ti versus (Al/4+Fe/2+Mg/2+3Ca/2+11Na/4)/Ti* PER diagram (B). Given measurement error, these ratios plot on a single line with unit slope, indicating that the observed compositional variability is solely due to closure and crystal sorting of these phenocrysts. Six major elements are involved in this fractionation model and three others appear to be conserved (from A). Thus, this fractionation model appears to explain all of the compositional variability in the major oxides observed in these rocks.

Two types of alteration measures may be used to quantify metasomatism using the PER approach. These are illustrated using lithogeochemical data from the quartz- and feldspar-phyric rhyolite footwall to the Eskay Creek massive sulphide deposit (Figure 3; Bartsch 1993). Data representing fresh and metasomatized rock compositions are plotted on this diagram. Relatively fresh rocks plot along a line with a unit slope. Variations along this line describe the different amounts of feldspar fractionation each sample has undergone. Altered rocks generally plot below this line due to the net loss of alkali elements. The distance an altered sample lies below the feldspar fractionation line (the vertical residual) is a measure of the absolute amount of (*metasomatic*) alkali loss. An alternative metric for quantifying *alteration* is to use the slope of a line from an altered sample to the origin. If the slope equals 1/3, then we conclude that the rock has been completely sericitized (in muscovite, *(Na+K)/Al* = 1/3). Similarly, if the slope equals 0, then the rock is interpreted to have been completely chloritized (for chlorite, *(Na+K)/Al* = 0). Equations can be developed relating the slope to the extent of sericitization or chloritization.

Conclusions

Application of PER analysis in to studies of metasomatism utilizes a 'components of variance' philosophy, stripping off interfering components to allow direct observation of the variance of interest. Its molar format provides a direct relationship between lithogeochemical data and mineral formulae, chemical reactions and material transfer processes. It also does not require the assumption that rocks be homogeneous before metasomatism took place, allowing study of and exploration in rocks that exhibited fractionation-induced variability before mineral deposit genesis. As a result, PER analysis offers significant advantages in lithogeochemical exploration because it accurately quantifies the effects of metasomatism and alteration.

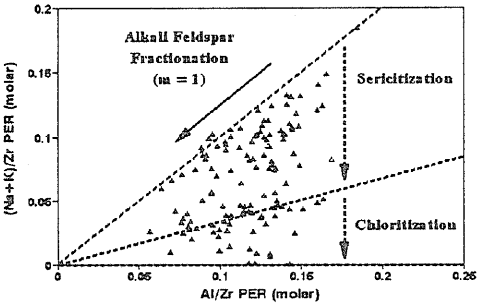

Figure 3 - Quartz- and feldspar-phyric rhyolite footwall volcanic rocks to the Eskay Creek VHMS deposit, British Columbia (Bartsch 1993) are plotted on an *Al/Zr* versus *(Na+K)/Zr* PER diagram. See text for discussion.

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Lithogeochemical discrimination of Archaean mafic intrusives ('dolerites') at Kalgoorlie, Western Australia.

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Keywords: lithogeochemistry, dolerite, Kalgoorlie, Western Australia

Introduction

Mafic intrusives, traditionally termed 'dolerites', are significant hosts for gold mineralisation throughout the Eastern Goldfields of Western Australia, particularly in the Kalgoorlie area where the giant Golden Mile deposit and Mt Charlotte deposit are hosted by the Golden Mile Dolerite (e.g., Clout et al, 1990). At Kalgoorlie, these dolerites generally have been documented as part of the stratigraphy and most workers have considered that there are two major dolerites: the Golden Mile Dolerite and the Williamstown Dolerite (Travis et al, 1971; Keats, 1987). However, in a recent study of the Kalgoorlie goldfield, Clout et al (1990) proposed that there are five separate dolerite intrusives within the Kalgoorlie sequence: the Williamstown, Eureka, Federal, Golden Mile and Aberdare Dolerites, each in different stratigraphic and structural positions (Fig. 1).

The purpose of this investigation has been to test the concept of five different dolerite intrusives for it has implications on the structure of the Kalgoorlie sequence, and on exploration for Golden Mile and Mt Charlotte style gold mineralisation in the Kalgoorlie area. Much of the Kalgoorlie sequence has been pervasively altered and the primary mineralogy and textures of some of the dolerites are not well preserved. Therefore considerable reliance has been placed on geochemistry for testing of the five dolerite concept, and to develop diagnostic lithogeochemical parameters for identification of these dolerites during geochemical exploration.

Geological setting

The Kalgoorlie sequence consists of a 3-4 km thick succession of ultramafic to mafic volcanic rocks of the Hannans Lake Serpentinite, Devon Consols Basalt and Paringa Basalt, with minor intercalated sedimentary units (Kapai Slate), and a number of strikingly concordant differentiated 'dolerite' sills (Fig. 1). This is overlain by a 1 km thick pile of sedimentary and felsic volcanic rocks of the Black Flag Beds (Fig. 1). All rocks are of Archaean age and have been subjected to several phases of deformation and greenschist facies metamorphism.

The Williamstown Dolerite (~250 m thick) has been emplaced between the Kapai Slate and overlying Paringa Basalt. The Eureka and Federal Dolerites have been emplaced within the Paringa Basalt, but apparently at different stratigraphic levels. The Eureka Dolerite (50-220 m thick), to the east of Kalgoorlie, previously has been interpreted as stratigraphically thinned Golden Mile Dolerite on the east limb of the Kalgoorlie Anticline (Travis et al, 1971). The Federal Dolerite (84-100 m thick) is on the west limb of the Kalgoorlie Syncline, to the west of the Mt Charlotte mine.

The Golden Mile Dolerite (600-940 m thick) and Aberdare Dolerite (600-700 m thick) have been emplaced at the same stratigraphic level between the Paringa Basalt and overlying Black Flag Beds (Fig. 1), but in different(?) structural positions. The Aberdare Dolerite abuts the Golden Mile Dolerite across the Adelaide Fault. Although Clout et al (1990) consider this a separate body, the Aberdare Dolerite previously was interpreted as part of the Golden Mile Dolerite in the closure of the Kalgoorlie Anticline (Travis et al, 1971).

Petrology of the dolerites

The five major dolerites in the Kalgoorlie sequence are differentiated sills, each with a number of distinct lithological units. The Williamstown Dolerite has two major units: an upper subophitic and granophyric gabbro that is subdivided into three units and a lower cumulate-textured ultramafic unit which includes sub-units of pyroxenite and peridotite.

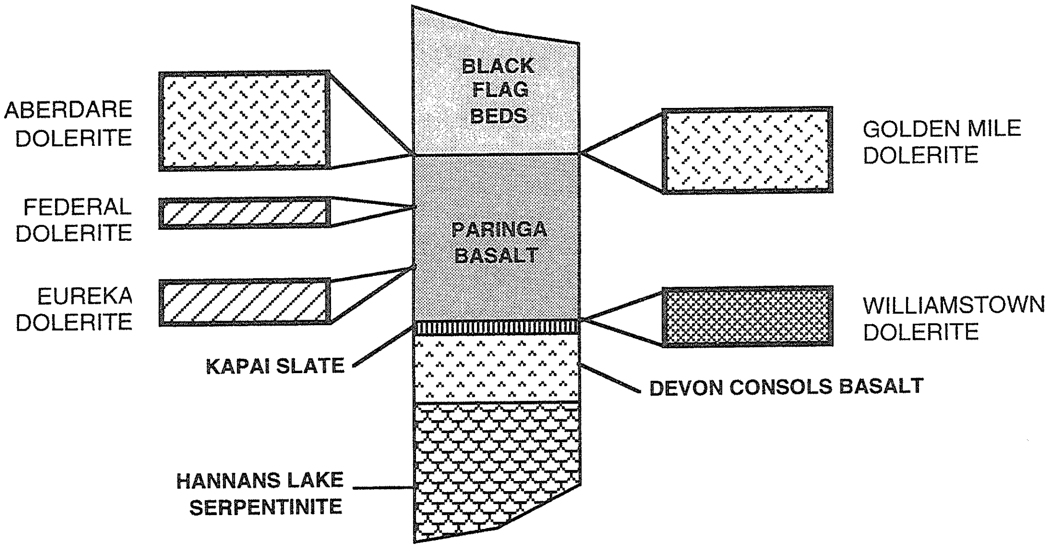

Figure 1 Structural relationships of the Williamstown, Eureka, Federal, Aberdare and Golden Mile Dolerite sills within the Kalgoorlie sequence (after Clout et al, 1990).

The Eureka Dolerite is a differentiated sill with seven identifiable units including upper and lower chilled margins and subophitic gabbroic units on either side of a central quartz gabbro. The Federal Dolerite is a weakly differentiated sill that also has seven identifiable units but appears to be of more uniform composition than the Eureka Dolerite. It has chilled margins at the top and base of the sill and at least two gabbroic units on either side of a granophyric gabbro in the central portions of the sill.

The Golden Mile Dolerite has been subdivided into ten lithological units (Travis et al, 1971): a lower and upper chilled margin (units 1 and 10, respectively), an ultramafic layer (unit 2), a gabbroic unit with clusters of tabular pyroxene (3), a pyroxene-phyric gabbro with aggregates of skeletal oxides (4), a gabbroic unit with bladed plagioclase laths and sparse skeletal oxides (5) a subophitic and granophyric gabbroic unit (6) a subophitic microgabbro (7), a central granophyric quartz gabbro (8) and a thick subophitic and granophyric gabbroic unit (9) which is equivalent to and mirrors units 2 to 7 in the upper parts of the sill. Geochemical data indicate that units 2 and 8 may be further subdivided into two subunits.

The Aberdare Dolerite is a weakly differentiated sill also with ten units, but not as well defined as in the Golden Mile Dolerite because of pervasive alteration. It has fine grained chilled margins with an ultramafic(?) unit at the base of the sill and seven medium to coarse grained subophitic and granophyric gabbroic units.

Lithogeochemisry

Sampling and chemical analysis

As the aim of this project is to identify lithogeochemical discriminants for each dolerite, then geochemical samples have been collected from locations as remote as possible from mineralisation and associated hydrothermal alteration. All samples collected for this study are from drill core as the only 'outcrop' is in mine workings which are unsuitable because of alteration and deformation. As most drilling is targeted on mineralisation, the number of suitable drill holes is limited and there are few complete intersections of dolerite sills. Of the 94 samples of Kalgoorlie dolerites analysed, 37 are from the Golden Mile Dolerite, with the rest from the Williamstown Dolerite (12 samples), Eureka Dolerite (12), Federal Dolerite (14), and Aberdare Dolerite (18).

All samples have been analysed for 55 major and trace elements by a range of analytical techniques, but all key incompatible and immobile elements that are used to identify lithogeochemical parameters have been analysed by XRF and NAA. Quality control has been monitored through the use of duplicate samples and two tertiary standards, and the only elements that show significant variation are those associated(?) with hydrothermal alteration (e.g., Pb, Mo, Cd, Ba, As, Sn) and gold (ppb levels).

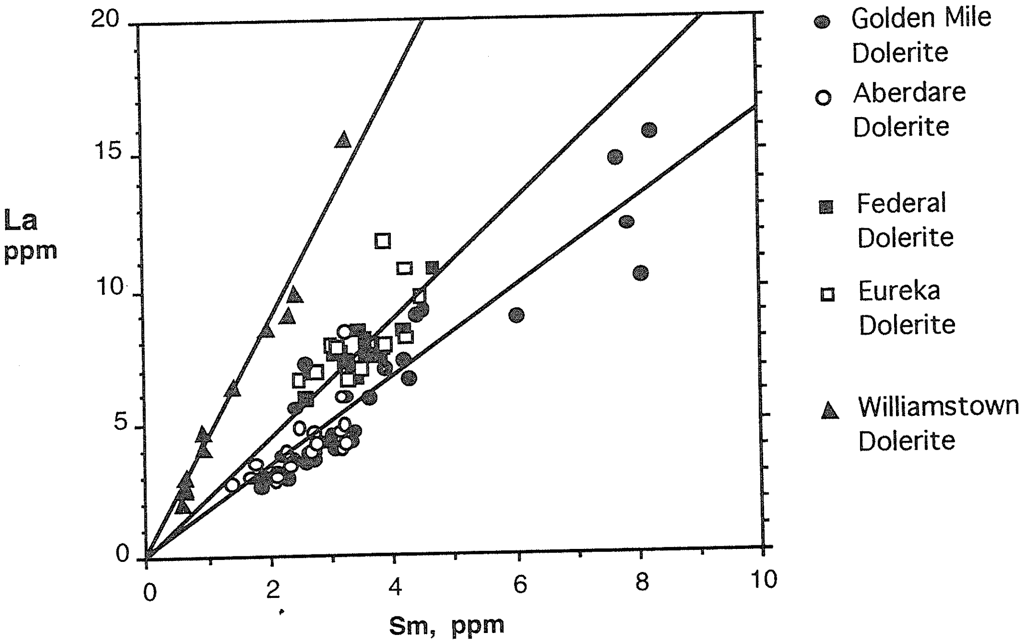

Figure 2 La - Sm diagram for Kalgoorlie dolerites, showing similarity of the Golden Mile and Aberdare Dolerites, and Federal and Eureka Dolerites distinction between these groupings and the Williamstown Dolerite.

Petrogenesis

The Eureka, Federal, Aberdare and Golden Mile Dolerites all exhibit similar tholeiitic affinities. The Williamstown Dolerite is markedly different to the other dolerites, and may have formed from a separate magmatic event, possibly with two intrusive events preserved within this dolerite. The upper gabbroic units in the Williamstown Dolerite exhibit affinities with high-Fe tholeiite and the lower ultramafic units have komatiitic affinities. Rare earth element (REE) data indicates that the parental magma(s) for Kalgoorlie dolerites was derived from both partial melting and fractional crystallisation processes: partial melting being the more prominent process for the lower ultramafic units of the Williamstown Dolerite, whereas fractional crystallisation is the dominant process for the upper gabbroic units of the Williamstown Dolerite and for the other four dolerite sills.

Lithogeochemical characteristics

The Golden Mile and Aberdare Dolerites geochemically are similar and have comparable differentiation trends, best expressed by variation in MgO and mafic index. This reflects the petrological subdivision, including a mafic unit with a high-MgO content at the base of each sill, though a unit equivalent to unit 9 in the Golden Mile Dolerite has not been identified in the Aberdare Dolerite. The two dolerites have markedly similar flat REE patterns and probably are co-magmatic.

The Eureka and Federal Dolerites also are geochemically similar, but their characteristics are different to the Golden Mile and Aberdare Dolerites. The Eureka and Federal Dolerites have comparable differentiation trends, best expressed by variation in SiO_2 and mafic index, which reflect the petrological subdivision into seven units in each sill. They each have similar REE patterns with slight enrichment in light rare earth elements (LREE), and probably are from the same magmatic event.

The Williamstown Dolerite is characterised by enrichment in MgO and a weak positive Eu anomaly in the ultramafic units, depletion if TiO_2 and markedly different REE patterns which show strong enrichment in light rare earth elements (LREE) compared with only a slight enrichment of LREE in other dolerites.

Lithogeochemical discriminants

Rare earth elements provide the most effective means of discriminating between the Williamstown Dolerite, the Eureka and Federal Dolerites, and the Golden Mile and Aberdare Dolerites. As well as the different REE patterns, the dolerites are readily distinguished by ratioing light and heavy REE, particularly using La/Sm ratios (Fig 2). Similar trends are apparent for ratios of other elements such as Ce/Sm, Sm/Yb and Gd/Yb. Major elements and most trace elements are not useful in discriminating between the Kalgoorlie dolerites because of the pervasive alteration prevailing throughout the area.

Conclusions

Although, structurally, there may be five dolerites in the Kalgoorlie sequence, lithogeochemical data indicates that there are only three magmatic units. The Golden Mile and Aberdare Dolerites are co-magmatic, and so too are the Eureka and Federal Dolerites. The Williamstown Dolerite is markedly different to the other dolerites and may have formed from two separate intrusive events.

Rare earth elements are the most effective parameters for discriminating between dolerites in the Kalgoorlie area, and the same technique of ratioing REE data could be applied elsewhere to solve similar problems.

Acknowledgments

This research has been sponsored by Kalgoorlie Consolidated Gold Mines Pty Ltd. Theingi Swe was the recipient of a scholarship awarded under the Australian Development Cooperation Scholarship Scheme of the Australian International Development Assistance Bureau.

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The Studies of the Mesozoic K-Rich Calc-alkaline and Shoshonite Series and Related Copper (Gold), Iron and Nonmetal Deposits, Lishui, Jiangsu Province, China

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The Lishui Mesozoic volcanic basin is located in the Lower Yangtze fault depression which is an important metallogenic province of copper (gold), iron and some nonmetal deposits in eastern China. The Cretaceous volcanic sequences from bottom to top in the Lishui basin include the Longwangshan, Yunheshan, Dawangshan, Guanshan and Jiashan formations. Among them the Yunheshan formation represents the sediments of volcanic inactive period. Other formations are the products of four volcanic cycles respectively. In the K_2O-SiO_2 diagram (after Peccerillo, et al., 1976), most rocks of the Longwangshan cycle are located in a transitional area between calc-alkaline series and high-K calc-alkaline series. Thus they are named for K-rich calc-alkaline series in the present study. Most of rocks of the Dawangshan and Guanshan cycles fall into the field of shoshonite association, they (including the rhyolite of Jiashan cycle) are classified as shoshonite series. Petrochemically, typical features of the Lishui shoshonite series are high in total alkaline (Na_2O+K_2O=5.31-13.69 wt%), K_2O/Na_2O ratios (0.82-2.87), Al_2O_3 (14.14-20.77 wt%), Fe_2O_3/FeO ratios (0.67-3.50) and are low in TiO_2 (0.21-1.21 wt%) and Fe. In contrast, K-rich calc-alkaline series in the Lishui basin have lower K_2O, Na_2O and Fe_2O_3/FeO ratios, but are rich in Fe (zhou, et al.,1994).

The iron deposits in the Lishui basin are related to the K-rich calc-alkaline rock series. The germanium deposits are hosted in the Yunheshan formation (formed in volcanic inactive period). Other deposits, such as those of copper, strontium, bentonite, are related to the shoshonite series (Zhou, et al. 1994; Wu, et al., 1981).The iron deposits are of pneumatolytic metasomatic-filling type.The ore-body occurs at the top of basaltic porphyry within conduct of the Dong Gang caldera. Albite, scapolite, diopside, and chlorite alterations in the basaltic porphyry are directly associated with the iron mineralization. Ore minerals are mainly magnetite with less amount of pyrite and chalcopyrite. Temperatures measured by decrepitation method for magnetite and chalcopyrite are 350-500 °C and 255 °C respectively. δS^{34} values for pyrite and chalcopyrite are -3.9 to 6.5 per mil. The copper (gold) deposits occur within or outside the Guanshan caldera, as a hydrothermal infill vein type with moderate temperatures. The wall rocks of the Guanshan caldera include banakitic and trachytic lavas and pyroclastic rocks. The Conduit of the Guanshan caldera is filled with banakitic porphyry. Twelve Cu (Pb)-bearing lodes distribute along ring and radial faults around the the conduit. Six Au (Ag,Te)-bearing lodes occur outside the Guanshan caldera in Jinjushan. It appears that gangue quartz related to Au mineralization shows bimodal thermoluminescence curves, with maximum thermoluminescence temperatures of 215-220 °C and 260-295 °C respectively. Whereas gangue quartz related to Cu (Pb) mineralization exhibits unimodal thermoluminescence curves with maximum thermoluminescence temperatures of 215-230 °C.

A large strontium deposit is hosted in banakitic, high-K dacitic ignimbrites of Dawangshan cycle in Aijingshan of Lishui. The deposit is a hydrothermal vein type, with low to moderate temperatures and containing mainly celestite with less amount of kaolinite, barite and pyrite. The formation of the strontium deposit is related to the quartz porphyry of Jiashan cycle. Both celestite veins and related quartz porphyry veins are controlled by NW-trending faults.The temperature measured by decrepitation method for celestite is 259 °C. δS^{34} values for celestite and associated pyrite are 20.9-28.5 per mil and 7.2-9.5 per mil, respectively. A large benstonite deposit is hosted in rhyolites of the Jiashan cycle. It occurs as layered orebody and extends about 1800 meters along strike with 200 meters wide and 8-14 meters thick. The alteration of rhyolite to montmorillonite and less commonly to illite, cristobalite, K-feldspar, beulandite and pyrite was caused by volcanic pneumatolytic hydrothermal activities. Three small germanium-iron deposits of volcanic-sedimentary type are hosted in the Yunheshan formation. Three germanium-bearing layers exist in a orebody in Hongshishan. From bottom to top these are hematite layers, ferromanganese rock layer and silicon and iron-bearing rock layer.The hematite layer, grade at 58.21 g/t with the highest up to 140 g/t germanium, is a main germanium-bearing layer which extends about 165 meters along strike with 3 meters thick and up to 62 meter wide. Microprobe analyses and other studies indicate that germanium is concentrated in hematite in the form of adsorption.

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Supergene
Deposits

Gold, wolframite, tourmaline-bearing lateritized gossans in the Amazon region, Brazil.

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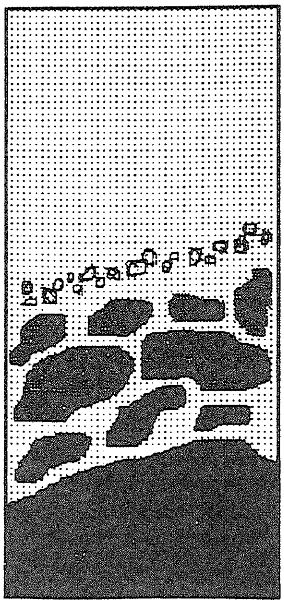
Keywords: gold, laterite, gossan, crust, Amazon, Brazil

Several important supergene gold occurrences have been recently discovered in the Amazon region, representing an great impulse for the mineral exploration in north Brazil (Costa, 1993). This progress follows what have already happened in the 80's in lateritic environments of West Africa and Australia.

These occurrences present ubiquitously the following important characteristics:

1. Primary related sulphide mineralization;
2. Upper oxidation zone (gossans) disturbed by lateritization and tropical pedogenesis → **lateritized gossans**;
3. Wolframite and tourmaline occurrences as resistate minerals (besides elevated Sn values) in the ferruginous horizons.

The general structuration of the upper part of these profiles can be summarized as follow:



Latosols: predominantly yellow, reddish-brown over the gossans; Kaolinite, Al-goethite, gibbsite, hematite, quartz.

Stone-lines: representing pre-existing surfaces

Lateritic iron crust: brecciated, with gossan fragments; goethite > hematite.

Gossan: generally massive, magnetic; hematite dominant.

Several studies have been conducted in these profiles in order to characterize the gold distribudion in the different supergene horizons besides their mineralogical and geochemical associations. Mean gold contents generally increases from the parent rocks toward the gossans, diminishing slowly to the lateritic crusts and abruptly to the latosols. SEM-EDS analysis in isolated grains from the ferruginous zone reveal a high heterogeneity in gold composition, specially in Ag contents, representing the presence of both primary grains and supergene/lateritic gold (higher fineness).

The present knowledge shows that lateritization processes that took place in the Amazon region since early Tertiary times superimposed pre-existing gossans and gave rise to a breccia-like iron crust, with a new dispersion of gold and other elements. The final products are the wide distributed yellow loose clay latosols (tropical pedogenesis) that invariably cover and mask these profiles and weaken gold signals. The ferruginous horizons (gossans, lateritic crusts, stone lines, etc.) are thus the better sampling media for gold geochemical exploration. The occurence of coarse-grained tourmaline and wolframite minerals can be an important auxiliary tool in the exploration, acting as true pathfinder minerals and also in distinguishing different iron crusts occurrences and infering the probable primary parent rocks.

Costa, M.L., 1993. Gold distribution in lateritic profiles in South America, Africa and Australia: applications to geochemical exploration in tropical regions. In: F.W. Dickson and L.C. Hsu (Editors), Geochemical Exploration 1991. *J. Geochem. Explor.*, 47:143-163

The weathering of platinum-group minerals: implication for the redistribution of platinum-group elements in laterite (New Caledonia ophiolite)

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Keywords: platinum-group elements, platinum-group minerals, ophiolite, laterite, remobilization

Ophiolite does not normally contain Pt concentrations of economic interest. Nevertheless, some complexes, such as the Shetland ophiolite (UK) or the Acoje ophiolite (Philippines), present interesting and unusual concentrations of platinum-group elements (PGE) other than the Os, Ir and Ru classically found in ophiolitic chromitite. Such is also the case for the New Caledonia ophiolite, where unusual Pt concentrations are known mainly in placers. Thus, in 1991, within the framework of a research project on natural resources, BRGM decided to re-investigate the possibility of PGE mineralization in relation with the New Caledonia ophiolite.

The New Caledonia ophiolite, which forms a discontinuous nappe that was obducted during the Late Eocene, is composed mainly of mantle rocks (lherzolite, harzburgite and dunite, with chromitite concentrations) with in the south of the island, cumulate rocks (dunite, wehrlite, pyroxenite and rare gabbro) constituting the base of the crustal sequence. Primary magmatic mineralization includes large chromitite bodies and very minor base-metal sulphide concentrations in the mantle peridotite.

BRGM began its investigation for PGE with a geochemical stream-sediment survey in selected areas based on a sample density of about 4 samples per km^2. The -125 µm fraction of the stream sediments, alluvial heavy-mineral concentrates and samples from selected laterite profiles were analysed for Pt and Pd. The result of this first campaign was positive in that several Pt anomalies were identified in the stream sediments. The best of these anomalies in terms of Pt content was in the "Pirogues" area and has been followed up in detail. Through geochemical controls it was possible to define its extension and rapidly find its origin. The source of the Pt (controls made on sediments for the other PGE were negative) appears to be 1) stratiform chromite concentrations in dunite and wehrlite at the base of the cumulate series, and 2) chromite concentrations in pyroxene-rich dykes cutting these cumulate rocks. The highest Pt content, obtained from a chromitite, is 36 ppm (Figure). Detailed study of the mineralized area confirms that the primary mineralization is systematically associated with chromitite concentrations; the Pt content of the surrounding rocks nowhere exceeds 50 ppb. In the model recently proposed by Augé and Maurizot (submitted) for this mineralization, the platinum-group minerals (PGM) precipitated directly from the melt following magma mixing that increased the fO_2 and decreased the FeO content of the PGE-bearing magma and thus provoked the sudden crystallization of PGM. The chromite crystallization (provoked by the same event) occurred later and "fossilized" the Pt mineralization.

Mineralogical study of the Pt-rich chromitite confirms that the PGM form inclusions (average size varying between 10 and 40 µm) trapped within chromite crystals and, in rare cases, in their silicate matrix. Detailed investigation reveals two types of minerals: primary PGM belonging to the magmatic mineral assemblages and secondary PGM, resulting either from weathering of the magmatic PGM or from PGM neogenesis (Table). Secondary PGM have been found in most of the chromitite samples, even those with an apparent low degree of weathering.

The Pirogues area has undergone strong laterization with the weathering profiles in the mineralized area as much as 20 m thick. Chromite layers in the laterite appear well preserved and relatively undisturbed, which suggests only a minor volume reduction due to weathering. Analysis of these chromite layers shows the same PGE distribution patterns as in the fresh chromitite. More surprisingly, analysis of chromite-free laterite revealed, in places, a strong Pt enrichment compared to fresh chromite-free peridotite: 4.4 ppm Pt was obtained from a laterite containing only 2.5 wt.% Cr_2O_3 (Figure). The absence of Pt in the fresh chromite-free cumulates suggests that the source of the Pt in the laterite is the chromite-bearing rocks. This involves a mechanism whereby Pt is remobilized from the chromite-rich facies, redistributed and locally reconcentrated in the laterite. Study of apparently unweathered Pt-chromite ore provided a good illustration of this phenomenon: grains showed the migration of Pt from weathered PGM through fractures in the chromite crystals. The weathered grains, presumably original Pt-Fe-(Cu) alloys, are now relatively enriched in Pd and Ni and impoverished in Pt; they are also probably oxidized. Other examples show the migration of Pd as Pd-Hg from a weathered PGM.

Because of the discontinuous character of the primary mineralization, the spatial relationships between the chromite-Pt mineralization and the Pt enrichment in the Cr-free laterite are difficult to establish. A study of several weathering profiles has shown a Pt content in the laterite generally above 200 ppb, with a strong decrease towards the upper part (iron crust) of the profile. The Pt-rich samples do not seem to occupy any particular position in the profiles, nor do they seem to be accompanied by other mineralogical or geochemical anomalies.

A study of the Pt carriers in the Pt-rich laterite has recently been undertaken to try and determine the mechanisms involved. Although the results of this study yet are not available, a partial answer can be obtained from studying PGM in the alluvium. The PGM collected from the alluvium in the Pirogues area are presumed to derive from the primary chromitite mineralization (after liberation of the grains trapped in the chromite crystals) and from the secondary Pt-rich laterite. Five types of PGM are recognized in the concentrates: 1) euhedral or slightly rounded grains (mainly different Pt-Fe-Cu alloys) obviously corresponding to the primary magmatic mineralization, 2) porous grains of various compositions, and grains presenting corrosion and dissolution features, 3) rounded grains commonly showing a complex internal texture (most of these grains have been interpreted as complex Pt, Pd, Fe, Ni, Cu oxides; Augé and Legendre, 1994), 4) Pt-Fe grains resulting from pseudomorphism of a hexagonal mineral 5) Pt-Fe alloys presenting an unusual fibrous-lamellar texture. The last four categories are interpreted, on the basis of their composition and texture, as derived from secondary processes related to weathering (Table).

The presence of weathered PGM in the chromitite suggests that remobilisation occurs relatively early in the weathering process. Oxidation must have played a major role since many of the PGE alloys have been altered to oxides. Several problems still remain unsolved at this stage of the study. The form of the Pt in the Cr-free laterite has not been directly determined. The unusual textures, such as concretions or fibrous minerals, probably correspond to neogenic minerals developed in the laterite, such development having already been observed in other contexts (Bowles, 1986). The coexistence of PGE oxides and alloys probably reflects two stages in the process of Pt migration and precipitation.

The conclusion that we can draw from this relatively early stage of the study is that, under certain circumstances, laterite should be considered as a target for PGE exploration.

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	primary mineralization	supergene mineralization
isoferroplatinum Pt3Fe	●	●
tulameenite Pt2FeCu	•	
undetermined PtPdFeNiCu		⬤
tetraferroplatinum PtFe	●	●
cooperite PtS	⬤	
iridium IrOsRu	●	
osmium OsRuIr	●	
erlichmanite OsS2	•	
laurite RuS2	⬤	
unnamed Rh5S4	•	
bowieite-kashinite (Rh,Ir)2S3	•	
irarsite IrAsS	•	
malanite (Cu,Fe)(Pt,Rh)2S4	●	
cuprorhodsite (Cu,Fe)(Rh,Ir)2S4	●	
unnamed Pt-Fe oxide		⬤
unnamed Pt-Ir-Fe-Rh oxide		•
unnamed Ir-Fe-Rh oxide		•
unnamed Fe-Rh-Pt oxide		•
unnamed Ru-Mn-Fe		•

Table - Mineral assemblages attributed to primary magmatic and secondary supergene mineralization. Symbol size reflects relative abundance of the mineral.

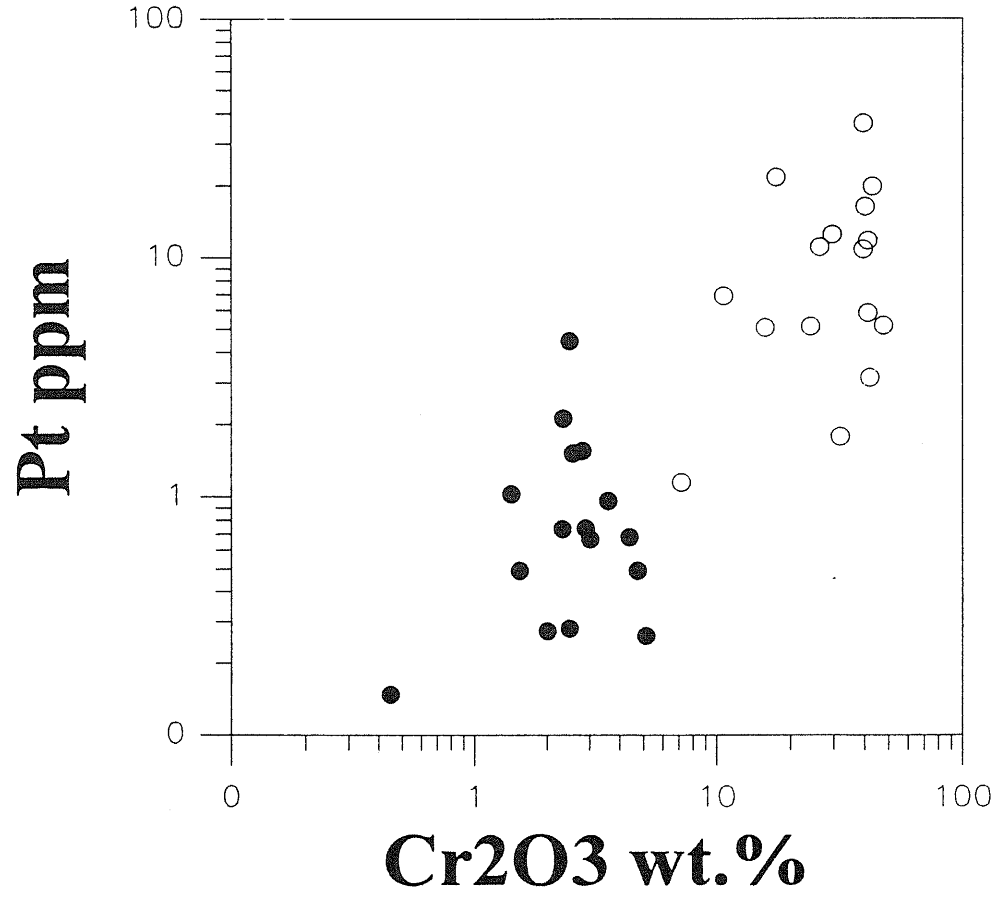

Figure - Correlation between the Pt (ppm) and Cr_2O_3 (in wt.%) contents in chromitite (open circles) and chromite-free laterite (filled circles).

Secondary dispersion at the Redeemer gold deposit, Eastern Goldfields Province, Western Australia.

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Keywords: gold, bismuth, soil, dispersion, supergene, Western Australia

Abstract

The Redeemer Gold Mine lies 1 km south-west of the old Agnew township within the northern part of the Norseman-Wiluna Greenstone Belt of the Eastern Goldfields Province. The orebody was discovered by the Exploration Division of Western Mining Corporation Limited (WMC) in 1985 after identification of Au anomalous soil along southern extensions of the Emu shear zone. The Redeemer Gold Mine has a pre-mining resource of more than 1.6 Moz of Au as at June 1994.

The major lodes are hosted by a shear zone within a thick mafic conglomerate close to the unconformable basal contact between sediments of the Scotty Creek Formation and ultramafic flows of the Lawlers Greenstones. The mafic rocks in the Agnew area have mineral assemblages indicating upper greenschist to lower amphibolite facies metamorphism.

Gold in the main orebody occurs as free grains (<100μm) or in intimate association with chalcopyrite and various bismuth minerals and sulphotellurides. Molybdenite and scheelite also occur in high grade zones. The alteration mineral assemblage of randomly oriented biotite, actinolite and magnetite occurs only within the immediate vicinity of the ore. The elements associated with the mineralisation are Au, Bi, Mo, Te, Se, K, W, Sb, Ti, S. A very strong correlation between Au and Bi in the primary ore has been used to distinguish primary ore from ore remobilised chemically or mechanically during weathering.

The main Redeemer orebody was covered variably by soil, minor iron rich material, alluvium and a channel filled with glacial tillite. A small part of the main orebody was covered by only thin (<5 m thick) alluvium. A channel filled with Permian glacial sediments next to and partly above the main orebody contains significant amounts of Au. The weathering front is about 50 m below the present land surface.

WMC explored the area using surface soil sampling. The samples (<6 mm fraction) were analysed for Au and As. The soil Au anomaly over the deposit is about 450 m x 100 m at 0.025 ppm Au. Recent alluvium probably subdued the concentration of Au in these soil samples. There is a regionaly extensive As anomaly in the soils around the deposit (about 1500 m x 600 m at 50 ppm As). This As anomaly is enigmatic, because As is associated with the mineralisation in only a small part of the deposit.

The Au has been remobilised during weathering by three distinct processes. The first was mechanical dispersion during the Permian, the glacial channel being filled by debris which included ore material. The second process acted less than 15 m below the present surface; gold was leached from the orebody and deposited either below or laterally. The third process occurred at a depth exceeding 30 m from the present surface. Here Au and Bi were dissolved probably at or close to the air/water interface. Subsequently they were precipitated away from the ore zone producing a blanket anomalously rich in Au and Bi that transgresses rock boundaries. During the formation of this secondary dispersion blanket the Bi was more mobile than Au and its spread indicates the ground water flow was generally towards the tillite-filled channel.

Acknowledgments

We would like to thank Western Mining Corporation for their permission to publish the material included in this paper. Acknowledgement is also made to the geological staff at the Redeemer Gold Mine with particular thanks to the geologists N. Aoukar for help during the sampling program and J. L. Dugdale for his excellent geological reporting on the deposit.

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Two generations of laterite profiles in the Amazon region and their ore potential: rock and ore display.

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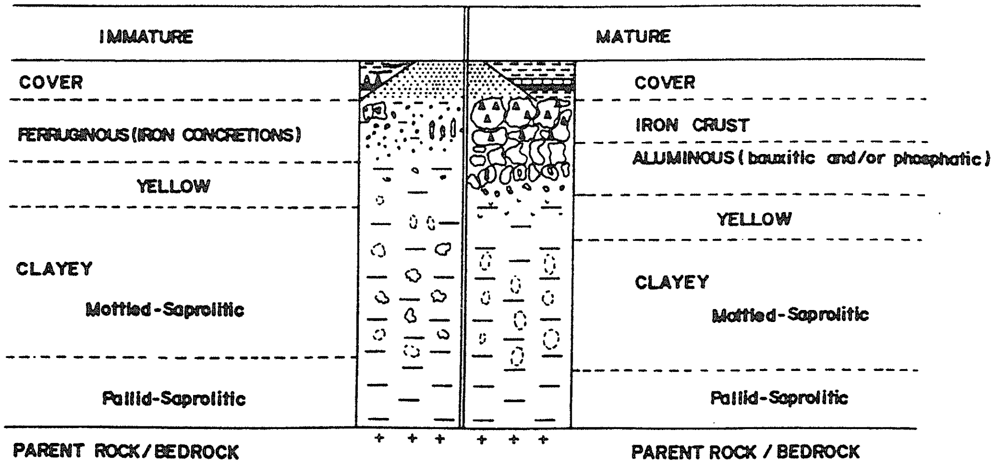
Keywords: laterite, mature, immature, crust, Amazon, Brazil

The landscape of the Amazon region, northern Brazil, has been developed over widespread lateritic cover and younger sedimentary sequences, which are restricted to its southwestern part. This landscape is represented by two different domains: (a) flat lowlands and (b) prominent plateaus surfaces, sculptured over old laterite formations. The lowlands evolved from both younger laterite formations and terrestrial sedimentary sequences.

In this scenery, two main important types of laterite profiles can be distinguished, after their evolution degree and relative age: the **mature profiles** and the **immature profiles**. There are many contrasts between these two types of profiles, mainly related to horizon structuration and succession, textural aspect, rock cohesion, mineralogy and chemistry, besides relative age and general landscape. The mature profiles are deeper, older, better horizon-structurated and describe the plateaus, displaying more diversified mineralizations in comprison with the immature profiles (Figure 1).

The majority of the ore deposits in the Amazon region have been found historically in the mature laterite profiles, for example: iron, manganese, gold, copper, nickel, titanium, niobium, bauxite (aluminium), kaolin and Al-phosphates.

This rock display will present slabs of rocks which constitute the main horizons of both mature and immature profiles, as well as slabs of the indicated ore rocks together with maps and photos from the respective deposits. The displayed material may allow to identify the main characteristics of the laterite formations and their ore potential, in order to compare the Amazon laterites under presently equatorial conditions with laterites under semi-arid to arid conditions, as for example the Australian laterites and their ore deposits.



Application of multielement geochemistry in gold- and phosphate-bearing lateritic crusts in the identification of parent rocks (Serra do Pirocaua, Eastern Amazon region, Brazil)

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Keywords: gold, laterite, crust, phosphate, Brazil, Amazon

The Serra do Pirocaua is located in the interfluve of the Gurupi and Maracaçumé rivers close to the boundary between the states of Pará and Maranhão (eastern Amazon Region, Brazil). The exploration for gold in this area dates from the time when first European adventurers arrived soon after the discovery of Brazil. Jesuits mined for gold early in 17th century employing Indian labor force. During the 30's of the present century, gold was mined with advanced implements for that time. In the 60's and even after 1970, the area was the target of an exploration program for phosphate and manganese. During the 80's, a new influx of miners took place in the area and new basic research was performed by then. The irregular extraction of gold continues up to the present day in that region without support of a systematic geological research.

Historically, in this region, the gold was first mined in marine placers until this century. The mining phase of the 30's was supplemented by mining of gold in quartz veins and quartz-rich zones. In the last decade exploitation encompassed the horizons of the lateritic profiles and colluvial deposits hosting gold mineralizations.

Taking into account the historic background of mining in the region, which is favorable for gold, the extensive occurrence of laterite, including those phosphate- and manganese-bearing varieties, as well as tourmaline occurrences, a systematic mineralogical and geochemical survey was carried out in the lateritic plateau of the Serra do Pirocaua. This plateau remains still unmined despite gold has been extracted around it. The main objective of this research is to identify the nature of the underlying rocks (parent rocks), based on multielement geochemical analysis of either outcropping crust or soils on the plateau. Further more, one intends to study the primary geological environment and the possible primary gold mineralizations, since these rocks do not crop out and they have not even been reached by drill holes down to 50 m. This work also aims to investigate the distribution pattern of the elements and their geochemical associations in the lateritic crust, which are not well-known yet.

The field works encompassed mapping and cartography of the lateritic crusts and soils as well as the sampling of these materials. The sampling was performed following a 100x200 m regular net, giving a total of 66 samples which were pulverized to less than 200 mesh for mineralogical analyses by XRD and chemical analyses (SiO_2, Fe_2O_3, Al_2O_3, P_2O_5, TiO_2, Ba, Y, Nb, Zr, Ga and Sc by XRF; Pt, Pd, and Rh by optical spectroscopy after pre-concentration; REE by ICP; Ni, Co, Cr, Cu, Mn, V, As, and Bi by atomic absorption spectrometry; and Au by fire assay) comprising a total of 34 analyzed elements. The mineralogical composition was determined on the basis of chemical analyses. The mineralogical and chemical data were statistically treated with the help of suitable IBM microcomputers for use of such softwares as Geoquant System (developed by USGS from STATPAC and adapted by CPRM), Golden Software, and Microsta. These programs made possible univariant and multivariant treatments of data, evaluation of the anomalies, and preparation of geochemical maps.

Both chemical and mineralogical compositions of lateritic crusts and soils are practically equal, being characterized by high contents of Fe_2O_3 (48.96 and 40.51 wt %, respectively in the crust and soils) and Al_2O_3 (19.47 and 22.84 wt %, respectively in the crust and soils), very high contents of P_2O_5 (11.85 and 15.5 wt %, respectively in the crust and soils), while TiO_2 contents are within the common range of lateritic crusts (2.96 and 2.54 wt %, respectively in the crust and soils). Silica is present in very low levels (1.04 and 1.93 wt %, respectively in the crust and soils). The variation of the contents of these elements compared with the average is greater for P_2O_5 and SiO_2. This chemical composition reflects a mineral assemblage made up mainly of hematite, goethite, crandallite-goyazite, senegalite, augelite, gibbsite, and anatase. Dravite tourmaline is found locally as restricted concentrations. The phosphates and also kaolinite are slightly more abundant in soils, whereas hematite, goethite, and anatase are more enriched in the crust. Among the trace elements, which present significant concentrations, Sr (0.82 wt % in the crust and 1.30 wt % in the soils), As (188 in the crust and 273 ppm in the soils), Ba (153 in the crust and 205 ppm in the soils), Sc (117 and 111 ppm, respectively in the crust and soils), Cu (109 in the crust and 118 in the soils), Cr (1235 in the crust and 1542 ppm in the soils), and V (1411 and 1125 ppm, respectively in the crust and soils) are outstanding. Despite Sr contents are considered very high, they are similar to those of Al-phosphates-rich laterites. By means of cluster analyses and correlation matrixes, two large geochemical associations were identified in either crust or soils: the associations Fe_2O_3-V-Ga-Ni-Cu-Cr-As and P_2O_5-Al_2O_3-(TiO_2)-Sr-Y-Zr-REE-(Ba). The former represents the iron minerals while the latter represents chiefly the phosphates of the crandallite group. The above-mentioned mineral group - crandallite group - has been described often in lateritic profiles, with several examples in Amazon Region. The first association spreads over almost all the area of the plateau top, without distinction between crust or soil covers, where its trace element contents define anomalies of first and second order related to tourmaline concentrations as well as anomalous values of gold and platinum. The anomalous values of the second association, mainly Sr, Ba, REE, and Y are found in the periphery of the plateau which is in part covered by the soils.

Gold was detected in 13 samples (detection limit of 50 ppb) and averages 0.2 ppm, showing a maximum value of 1.01 ppm. The areas where the anomalous gold-contents occur present a direct correspondence with those which exhibit anomalous concentrations of As, Cr, Cu, Ni, and tourmaline. These areas, mainly in the south of the plateau, have an elongated shape suggesting the presence of gold- and tourmaline-bearing quartz-rich zones. Quartz may have been dissolved, as it is common in lateritic environments, and tourmaline remained due to its resistance to this conditions of weathering. Moreover, gold- and tourmaline-bearing quartz veins crop out near the plateau crosscutting intensively weathered layered rocks.

The mean Fe, Al, Ti, Cr, Ni, Cu, Zr, Y, and Ga contents in both laterites and overlying soil cover suggest they evolved from rocks of mafic composition, and the anomalies of Au, As, and tourmaline must reflect the existence of portions modified by hydrothermal activity or even constituted by hydrothermal products. This typical association of hydrothermal environment remained in the lateritic crust and also shows that it did not undergone physical significant displacement, since the dispersion was not extensive and its shape still suggests the existence of a former elongate zone, what is a common feature in hydrothermal environments. Gold anomalies - some times in economic level - occur hundreds of meters away from the plateau, thus confirming the assertions above. That is, although the lateritic plateau of Serra do Pirocaua has not been mined yet, it covers probably volcanic rocks of mafic composition hosting hydrothermal products as tourmaline-bearing quartz veins. The high P_2O_5 contents of these surface laterites also suggest that these rocks were rich in primary phosphates which, however, must have no relationship with magmatic events, since concentrations of trace elements such as Ba, Sc, Y, Zr, and REE are relatively low for phosphatic laterites derived from magmatites with influence of carbonatite and/or alkaline rocks - the typical magmatic environments of phosphates. This chemical composition suggest that the bed rock of Serra do Pirocaua have a sedimentary or volcano-sedimentary nature, where the volcanics are basic in composition. The bed rock of Serra do Pirocaua also bears phosphates which are sedimentary in origin.

Gold mobility in latosols of the Amazonian rainforest: example of the Yaou deposit

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Keywords: supergene gold, lateritic weathering, Amazonia, French Guiana

Introduction

Gold in tropical zones shows various contrasted behaviors depending on the type of lateritic profile (Freyssinet, 1994). The aim of the present study is to characterize the gold distribution of the Yaou deposit (western French Guiana) in terms of pedologic horizons, mass balance calculations and selective extractions.

Geologic setting of the Yaou area

The country rocks surrounding the Yaou deposit are mafic to ultra-mafic schists of the Precambrian Paramaca series composed mainly of serpentine, chlorite, biotite, carbonates and quartz.

The Yaou-A orebody corresponds to a subvertical trondhjemite intrusion within the mafic schists. A late phase of hydrothermal alteration developed a fine mineralized quartz-carbonate-pyrite stockwork in which gold is present mostly as native gold in the intergranular pores and also as microinclusions within the pyrite. As the gold is evenly distributed within the mineralized body, it is possible to estimate the gold mass balance within the entire profile.

Morphopedologic setting

Yaou is situated in the rainforest of western French Guiana where the morphology is of a "half-orange" type. The tops of the hills are generally capped by a thick nodular horizon containing boulders of ferricrete that bear witness to preexisting lateritic plateaus covering the ancient landscape. The slopes have been truncated by recent erosion at the top of the saprolite , and an ochre-colored ferralitic soil, typical of Amazonian yellow latosols (Lucas and Chauvel, 1992), is developing under the present humid climate.

The Yaou-A orebody, located on a slope of a lateritic "half orange", is covered by a 24-30-m-thick weathering profile composed of a thick saprolite (20-25 m) capped by the yellow latosol (figs. 1 and 2). The saprolite at the base of the weathering profile preserves the structure and texture of the parent rock. Moving up the profile, the primary mineral such as chlorite, biotite and microcline become weathered and altered to kaolinite and goethite; only quartz and muscovite remain unweathered up to the top of the saprolite.

The overlying yellow latosol is composed of three main horizons: transition, ochre and brown humic. The transition horizon (≈1 m thick) still shows remnants of the primary textures, but is characterized by a pale-orange color due to the presence of a new clayey matrix of small (< 1 μm) goethite and kaolinite crystals developed at the expense of the large kaolinite booklets derived from weathering of the primary minerals. The ochre horizon (2-3 m thick) is characterized by the strong development of this fine kaolinite-goethite clayey matrix which here forms a homogenous loose material; the primary muscovite is strongly weathered at that level. The brown humic horizon (0.5 m thick) at the top of the weathering profile contains fragments of organic matter associated with the fine clayey matrix which is here ferruginized at the expense of the small kaolinite crystals and shows traces of gibbsite.

Gold mass balance in the weathering profile

A regular grid of vertical drill holes through the regolith and numerous drill cores in the primary mineralization have enabled a good evaluation of the 3-D distribution of gold. The soil anomaly above the primary mineralization shows an average content of 9.1 g/t Au with maxima of 12 g/t Au, although the saprolite only contains 5.0 g/t. Lateral dispersion is restricted to only a few meters. Calculation of the gold mass balance using the methodology defined by Brimhall and

Dietrich (1987) shows an absolute enrichment of +64 per cent in the yellow latosol with respect to the average content in the saprolite.

In detail the gold mass balance of the soil profile shows a regular enrichment from the saprolite to the ochre horizon, followed by a tendency to decrease in the brown humic horizon. Gold seems to accumulate in the transition horizon or at the base of the ochre horizon where total porosity is at a minimum and where macroporosity (>50 µm diameter) disappears (fig. 1).

The gold mass balance calculated for the whole profile with respect to the primary mineralization shows that about 40-50 per cent of the initial gold stock is leached in the saprolite (fig. 2) with the dissolution process occurring at the weathering front. Leaching does not increase in the higher part of the saprolite, although a local enrichment is seen between 12 and 17 m depth associated with an Mn-oxide enrichment close to the present water table. The global mass balance calculation for the Yaou gold deposit shows no residual enrichment, and a loss of gold of about 40 per cent compared with the primary stock.

Morphology of gold particles

Gold particles collected through careful micropanning were systematically studied under binocular and sweeping electron microscopes. The average particle size increases from 140 µm in the saprolite to a maximum of 240 µm between 0.5 and 1.0 m depth at the top of the ochre horizon, then decreases to 165 µm in the brown humic horizon. These variations mostly concern residual primary particles and the relative increase of coarse particles seems to be due to a vertical translation process of heavy grains within the macroporosity from the brown humic horizon to the ochre horizon as mentioned by Colin *et al.* (1993).

The morphologic study shows that a corrosion process develops in the latosol with maximum intensity in the brown humic horizon where 82 per cent of the primary particles show etched surfaces (fig. 3a) as compared with 45 per cent at the top of the saprolite.

The etching of primary gold particles in the latosol is associated with the precipitation of secondary gold microspherules (0.5-4.0 µm) within the kaolinite-goethite matrix. Coarser secondary gold particles (100-200 µm) made up of agglomerated microspherules are observed at the base of the ochre horizon where the absolute accumulation of gold is at a maximum (fig. 3b).

Selective extraction of gold

Selective extractions were made in order to evaluate the gold contents in the organic and mineralogical phases (Table 1). Sodium hypochlorite, acidified hydroxylamine hydrochloride and a solution of Na-citrate, Na-bicarbonate and Na-dithionite (CBD) were used respectively to dissolve the organic matter, the Mn-oxides and the Fe-oxides.

The data show that organically bound gold constitutes up to 30 per cent of the total gold in the brown humic horizon of the mineralized weathering profile. This proportion decreases with depth, passing from 10 to 4 per cent in the ochre horizon. In the saprolite 6 per cent of the total gold occurs in the organic fraction even though there is no detectable organic carbon. These results are in good agreement with the values given by Bowell *et al.*, 1993 for the Ashanti lateritic profile in Ghana. In the brown humic horizon of the dispersion halo, the organically bound gold fraction is strongly predominant.

Table 1 : Relative proportions of gold in the different selective extraction solutions.

	No. of samples	Total Au content (ppb)	TOC. (% Au)	Na-hypochlorite (% Au)	Hydroxylamine hydrochloride (% Au)	CBD (% Au)	Solid residue (% Au)
Dispersion halo							
Brown humic horizon	2	200	1.20	84.7	0.0	0.0	15.3
Mineralized profile							
Brown humic horizon	3	3370	1.00	30.1	0.5	0.7	68.8
Upper ochre horizon	3	5330	0.06	10.7	0.0	0.1	89.1
Lower ochre horizon	4	4480	<0.01	4.2	0.0	0.0	95.7
Transition horizon.	2	4500	<0.01	4.4	0.0	0.1	95.6
Saprolite	3	4230	<0.01	5.7	0.0	0.0	94.3

Discussion - conclusion

The gold mass balance of the weathered part of the Yaou deposit is negative with respect to the primary mineralization. The loss is around 40 per cent and occurs only at the weathering front, suggesting that the remobilization process is controlled by the weathering of primary minerals such as sulfides producing thiosulfates. Leaching does not increase in the higher part of the saprolite, probably no available ligand in the groundwater of the upper saprolite. The process is thus due to regolith formation and could be relevant for most of the gold deposits that have been subjected to lateritic conditions. The mineralized Yaou profile also shows postlateritic phenomena, such as trapping by Mn-oxides, which may give rise to local gold accumulations in the saprolite.

The recent yellow latosol pedogenesis at the surface has led to a significant surface gold enrichment in the brown humic horizon and, more especially, in the underlying ochre horizon. A small amount of residual enrichment occurs due to the translation of gold particles, but this process is restricted to the macroporosity developed in the top meter of the soil. The presence of secondary particles in the latosol from 0 to 3 m depth suggests that the gold enrichment is mostly dominated by a chemical process.

Selective extractions show that gold complexation in the brown humic horizon occurs mainly as organically bound gold, probably as fulvate complexes. The proportion of exchangeable gold is related to the organic carbon content of the horizons; organic acids being rapidly destroyed in rainforest soils, organically bound gold reprecipitates as native secondary gold and is not scavenged by Fe or Mn oxides in the latosol. Gold migration appears to be a vertical process related to the presence of macropores, with subsequent precipitation being controlled by the breakdown of macropores between the latosol and the saprolite. The dramatic decrease in macroporosity strongly reduces the permeability with the result that the percolating water may temporarily stagnate at the interface of the ochre horizon and the saprolite, creating more reducing conditions and thus permitting reprecipitation of native gold.

Under equatorial conditions, therefore, the gold accumulation effect in rainforest soils must be taken into account when selecting exploration targets from geochemical soil survey results.

Acknowledgments

BRGM and BHP-UTAH International Minerals are gratefully acknowledged for their help in the fieldwork and access to data. Drs J.L. Lasserre, Head of the Yaou Project and P. Skipwith are respctively thanked for help on the field and the improvement of the english manuscript. The study was carried out as part of BRGM Scientific Project MA01.

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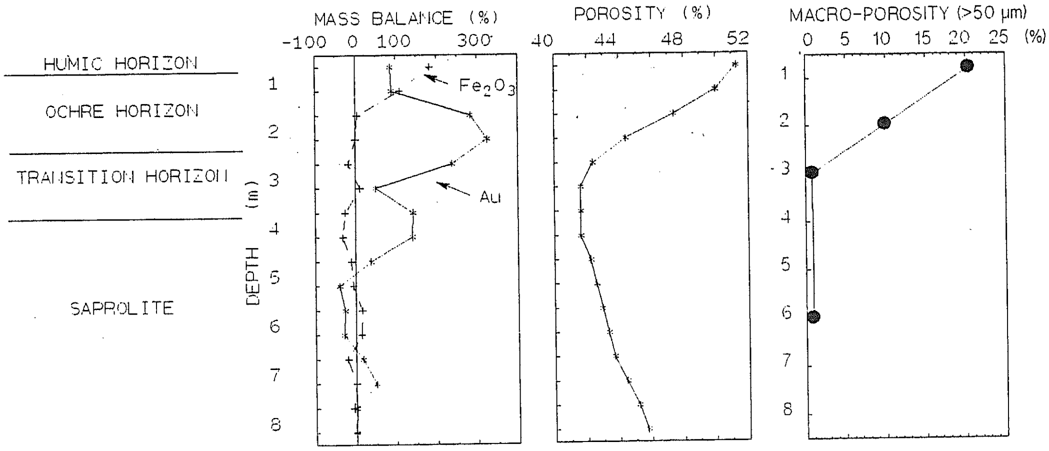

Fig. 1 : Gold and Fe_2O_3 mass balance in a a top profile at Yaou using the average content in the saprolite as reference. Relationship with total porosity and macroporosity (> 50 µm diameter).

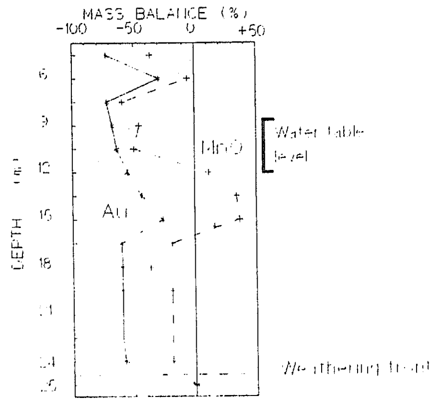

Fig. 2 : Gold and MnO mass balance in the saprolite using the primary mineralization content as reference.

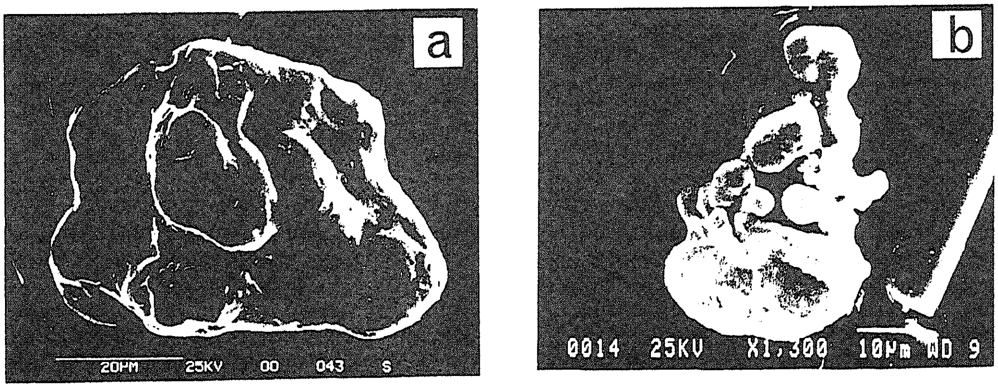

Fig. 3 : (a) Primary gold particle strongly etched in the humic horizon. (b) Secondary gold particle constituted by an agglomerate of spherules.

Speciation of platinum and palladium in lateritic regolith, Ora Banda Sill, Western Australia.

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Keywords: PGE, geochemistry, regolith, selective extraction, Western Australia

Introduction

Exploration for platinum group elements (PGE) in Western Australia requires an understanding of the geochemical behaviour of Pt and Pd in the lateritic regolith. The speciation (*i.e.*, the physical location) of Pt and Pd has been investigated [#], at the Ora Banda sill, Western Australia, one of a number of highly differentiated sills in the Norseman-Wiluna Greenstone Belt known to contain anomalous concentrations of PGE. The lower, ultramafic units of the sill have been deeply weathered and have given rise to lateritic enrichments of PGE similar to those of gold. These were explored by Carbine Gold N.L. during 1987-1990 at their Ora Banda and Mt. Carnage prospects south and west of Ora Banda, respectively (Menzies, 1988a,b). The region has moderate relief with variable preservation of lateritic regolith. PGE contents in the regolith increase steadily towards the surface, with a total enrichment of three- to five-fold in the lateritic, ferruginous zone. The maximum concentrations are up to 2000 ppb total PGE in clay-rich duricrusts at Mt. Carnage. The accumulations appear to be residual and are of the same order as other elements such as Cr, Zr and Cu that also appear to be immobile.

Regolith mineralogy

The regolith stratigraphy and mineralogy in hole MC 24, from Mt. Carnage are shown in Figure 1. The various zones are:

a. *Ferruginous zone (lateritic, mottled and plasmic clay horizons)*, 0-13 m. Ferruginous, clay-rich, poorly indurated duricrust and ferruginous clays, characterized by abundant goethite and hematite and moderate kaolinite.
b. *Saprolite*, 13-39 m. Soft and clay-rich throughout, becoming harder with depth. The clays are green, but strongly oxidized (brown, purple-red), especially above 23 m, in the clay saprolite. The saprolite is dominated by saponite, with minor kaolinite at 23-27 m and above 16 m. Primary talc and tremolite occur below 17 and 23 m, respectively. There are only minor Fe oxides. Manganese oxides are abundant at the base of the clay saprolite (20-23m).

Selected analytical data for hole MC 24 are shown in Figure 1. The lateritic, ferruginous zone has mean concentrations of 45% Fe_2O_3, 20% SiO_2, 16% Al_2O_3 and 0.2% MgO, reflecting the dominant mineralogy (Fe oxides, kaolinite, minor quartz), destruction of primary and secondary magnesium silicates and severe leaching of alkalis and alkaline earth elements. In comparison, the saprolite has mean concentrations of 21% Fe_2O_3, 45% SiO_2, 4% Al_2O_3 and 12% MgO, with the high Mg content due to the presence of saponite and relict primary minerals. The lateritic horizons are also enriched in Cr and Cu, especially at 10-13 m, and depleted in Mn and Ni compared to the saprolite. The clay saprolite has similar Si and Fe contents to the saprolite, but Al and Mg contents are intermediate between those of the saprolite and ferruginous zone, corresponding to the change from dominant saponite to dominant kaolinite. The clay saprolite is also enriched in Mn, Ni, Co and Zn relative to the other horizons, and in Cr and Cu relative to the saprolite. Maximum concentrations of all these elements, except Cr, occur in the transition to saprolite at 20-24 m. This transition, which is marked by Mn oxide precipitation, may mark a past redox front or water-table. Zirconium and Ti concentrations increase upwards through the profile, doubling from clay saprolite to ferruginous zones.

[#] This study was part of CSIRO/AMIRA project 252 and the support of the sponsors is acknowledged.

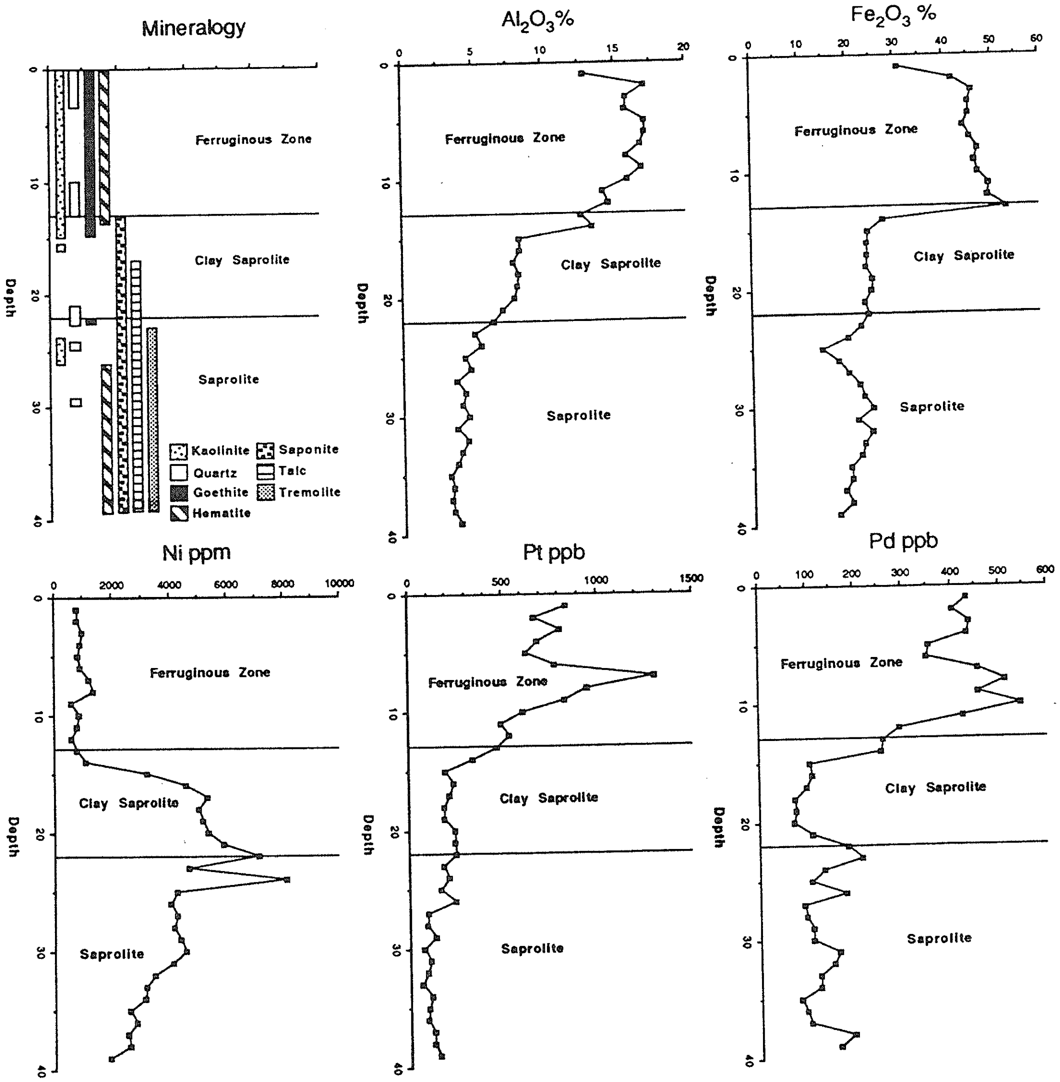

Figure 1: Mineralogy and distributions of selected elements in the regolith, MC 24, Mt. Carnage.

Attempts by SEM examination of panned concentrates and magnetic concentrates, and electron microprobe examination of chromites and other minerals to isolate individual PGE minerals at Mt. Carnage were unsuccessful. Analyses of Mn oxides occurring as a cobble at surface and separated from 22 m in hole MC 24 showed both to be enriched in Pt and Pd, respectively:

	Pt (ppb)	Pd (ppb)	Mn (%)	Ni (ppm)	Ba (ppm)	Cu (ppm)	Co (ppm)
Cobble	1750	170	26	23400	17400	15600	35100
MC24 - 22 m	380	2950	nd	nd	nd	nd	nd

nd: not determined

The cobble consists of manjiroite (cryptomelane group), with minor barite and cerianite, and has Cu, Ni and Co contents similar to those of Mn oxides in profiles on dunites. Such Mn-rich zones (*e.g.* at Mt. Keith; see Butt and Nickel, 1981) are also enriched in PGE. A chromite-magnetite concentrate from 22 m was also slightly enriched in Pd (560 ppb Pt, 1080 ppb Pd).

Particle Size Distribution

The particle size distribution of Pt and Pd were determined. Platinum is primarily located both in the 2 - 20 µm and < 2 µm fractions in the ferruginous zone. This does not necessarily mean that Pt in the fractions greater than 2 µm is in minerals with crystal sizes greater than 2 µm, as this fraction could contain mineral aggregates (such as commonly observed for Fe oxides) that were not dispersed by the separation method. In contrast, Pd is dominantly in the < 2 µm fractions. The small particle sizes for Pt and, particularly Pd, explain why attempts to investigate the mineralogy of PGE by scanning electron microscopy have been unsuccessful.

Selective Extraction

Because of the small particle size of the minerals containing Pt and Pd, selective extraction techniques were used to investigate the speciation of these elements. The extraction schemes used are described below.

1. *Easily extractable phases:*
   - (a) exchangeable cations [1 mole/L (M) ammonium acetate, pH 7]
   - (b) pH 5 extractable cations [1 M ammonium acetate, pH 5]
   - (c) Mn oxides [0.1 M hydroxylamine hydrochloride / 0.01 M nitric acid]
   - (d) 'Amorphous' Fe oxide [0.25 M hydroxylamine hydrochloride / 0.25 M hydrochloric acid]
   - (e) Crystalline Fe oxides (*i.e.*, hematite and goethite) [0.3 M ammonium citrate + solid sodium dithionite (CD), though insufficient for total dissolution].

Minor proportions of the Pt (0 - 25%), but virtually no Pd, were dissolved by reagents (c) and (d), *i.e.*, those extracting Mn oxides and amorphous Fe oxides. As significant proportions of Pt and Pd were dissolved with CD, this extraction method was further investigated.

2. *Citrate-dithionite (CD):*

This involved dissolution of the Fe oxides over five steps, so that the rate of dissolution of Fe, PGE and other metals could be tested, followed by aqua-regia extraction to dissolve other resistant phases. Up to 60% of the Pt was dissolved (Figure 2a), with similar kinetics to that of Fe. In contrast, Pd solubility was considerably lower (0 - 30%), with very different dissolution behaviour to Fe.

3. *Citrate-thiosulphate (CT):*

In order to test that the citrate-dithionite was dissolving PGE associated with Fe oxides, rather than a separate phase PGE mineral, a "blank" extraction for Pt and Pd using citrate-thiosulphate (CT; which will have a similar, or greater affinity for PGE as CD, though little ability to dissolve Fe) was also done. The blank extraction dissolved only small amounts of Pt and Pd (shown for Pt in Figure 2b), indicating that the PGE dissolved by CD are contained in Fe oxides.

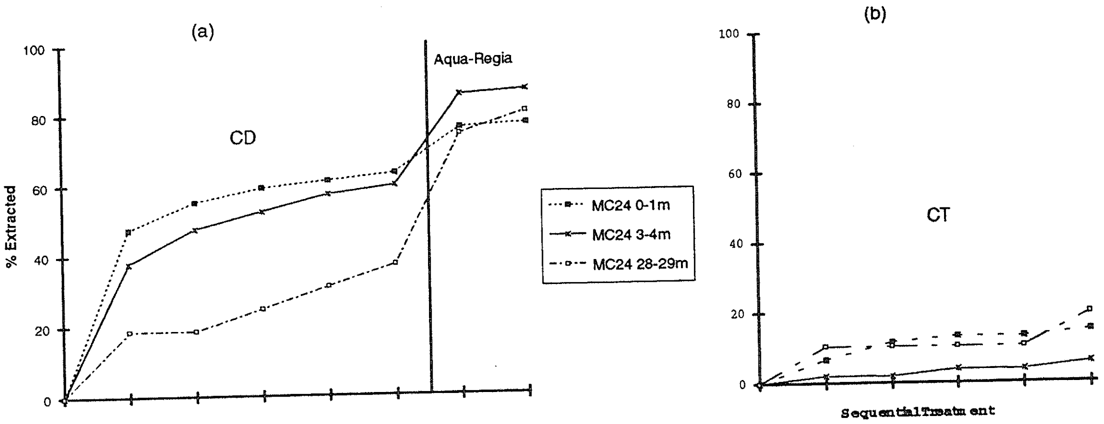

Figure 2: Sequential extraction of Pt from MC24, using (a) CD, and (b) CT.

4. *High gradient magnetic separation / differential XRD:*

The location of PGE in Fe oxides was also tested by enhancing the concentration of the Fe oxides in the solid prior to extraction, by using high gradient magnetic separation (HGMS) on < 2 µm fractions, followed by Tamm's acid oxalate (TAO; for amorphous Fe oxides) and CD extractions. Total Pt (Figure 3) was enhanced to a similar degree to total Fe, whereas total Pd was only slightly enhanced, supporting the hypothesis that most of the Pt and only some of Pd is contained in the Fe oxides. The comparative concentrations of hematite and goethite were calculated by differential XRD. The enhancement of extractable Pt concentration by HGMS approximately matched the enhancement of hematite, suggesting that the Pt may predominantly occur in hematite, whereas Pd associated with the Fe oxides tended to occur with smaller Al-rich goethite.

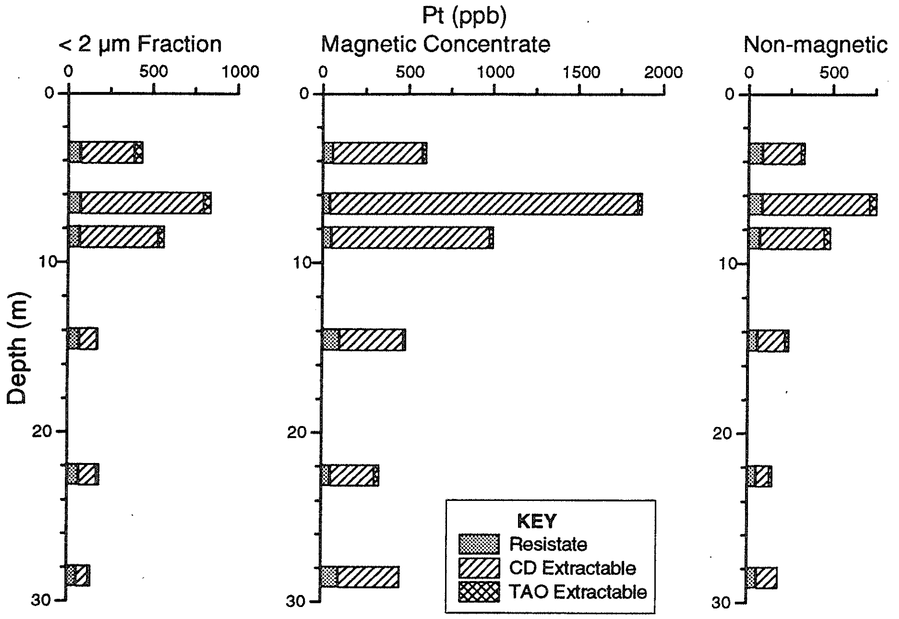

Figure 3: Selective extraction results for Pt, from HGMS fractions of MC 24 samples.

Summary and Discussion

It appears that most of the Pt is contained in Fe oxides, possibly dominantly in hematite. Nevertheless, up to 40% of total Pt is non-extractable, apparently in minerals greater than 2 µm, that could represent primary resistant Pt, with the resistance to weathering possibly due to larger particle size. Most Pd occurs in the < 2 µm fraction, *i.e.*, in very small grains; generally less than half is associated with Fe oxides. This Pd appears to be associated with different Fe oxides to Pt: specifically with the Fe oxides poorly concentrated by HGMS, *i.e.*, fine Al-rich goethite. This major difference in the mineralogies of Pt and Pd, despite the similar chemistry of these two elements, probably reflects different weathering histories. Hematite is commonly formed via aggregation and dehydration of poorly crystalline Fe oxides (Schwertmann and Murad, 1983). Thus, if Pt was released during early weathering, when Fe is initially precipitating in poorly crystalline forms, it will be incorporated with these Fe oxides, and then ultimately into hematite. In contrast, goethite forms by slow crystallization of Fe oxides. Given the initially low Al abundance in these rocks, aluminous Fe oxides are presumably late-stage, authigenic minerals. It appears that about half of the Pd remains insoluble, with the remainder incorporated into Al-rich goethite. It is possible that this represents a very late release of Pd from its primary form, followed by accumulation into late-stage goethites.

In conclusion, the distributions of Pt and Pd appear to be fundamentally controlled by the affinity of these metals for Fe oxides and their initial mineralogy, which in the case of Pd, may still be partially controlling the chemistry close to the regolith surface. Once incorporated into Fe oxides, the mobility of Pt and Pd will be controlled by Fe oxide stability. There appears to be a tendency for Pt to be incorporated into larger hematitic Fe oxides, and for Pd to be incorporated into smaller Al-rich Fe oxides.

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Supergene gold deposits in Siberia

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New complex gold-arsenic deposits have been discovered in Siberia (Olympiadinsk), and Au, As, Sb, W, Hg, Ag, Zn and Pb are extracted from the ores.

The Olympiadinsk deposit is characterised by gold-arsenic mineralisation along tectonic zones, accompanied by carbonaceous metasomatic alteration of the rocks. The main sulphide minerals within the ore zones are pyrite and arsenopyrite containing finely dispersed gold. Vein-hosted gold mineralisation is typical of carbon-bearing terrigenous strata.

High concentrations of gold occur in deposits with a lateritic weathering crust. The geochemistry of the supergene alteration and acid leaching of the quartz-sulphide veins and massive ores can be determined.

Within the zone of oxidation the ore bodies and sulphide-bearing enclosing rocks are bleached, and partially leached of metals. Some metals remain in relatively insoluble forms, for example, Pb as lead sulphate.

Gold mineralisation was discovered by mapping horizontal zones of oxidation from the surface down:

- a zone of disintegration;
- a zone of supergene enrichment;
- a zone of total oxidation;
- a zone of leaching;
- a zone of cementation and secondary sulphides; and
- a primary sulphide zone.

The finely dispersed gold in the groundmass of the ores is soluble and easily dissolved into solution. Supergene Fe and Mn minerals, and kaolinite, are extensively developed in the upper zones of the supergene profiles due to the action of acid fluids.

During the weathering of ore-bearing rocks and quartz-veins, W, As, Sb and Hg accumulate in the weathering zone, coinciding with an abrupt increase in rare metal concentrations associated with clays and supergene Fe minerals.

Gold transported and deposited during weathering has characteristic morphological features. Gold particles are typically spheroidal, from 0.1 to 0.25 mm in size, and have a finely shagreen surface. Gold fineness is high (960-990). Gold grades vary, depending on the grade of the primary mineralisation.

Gold deposits formed by supergene processes can be difficult to define, as the gold is typically irregularly distributed. It can therefore be useful to use indirect geochemical indicators, and identify the anomalous haloes of associated elements.

Geochemistry of trace elements in bauxites

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Keywords: bauxites, trace elements, geochemistry

The main aim of this research is to describe, in relatively full detail, the trace element geochemistry of bauxites. Both published and author's data on trace element distribution in bauxites, from more than 140 deposits throughout the world, are summarized. These data also contain information about the rock-forming minerals and elements, the underlying rocks, and the age of the bauxites. The list of publications from which these data have been extracted has been published (Mordberg, 1993a). The statistical methods used in analysing the data include the calculation of distribution parameters, and correlation and factor analyses. Results from studies of concrete bauxite deposits have been taken into account.

The distribution and behaviour of trace elements in bauxites are controlled by the factors described below.

Composition of the Parent Rocks

Bauxites after acidic rocks are generally relatively enriched in felsiphile elements. In contrast, iron-rich bauxites after ultrabasites contain high amounts of femaphiles. Bauxites after alkali metasomatites (e.g. Timan, Russia) and carbonitites (e.g. Chadobets, Russia) contain very high Th (up to 800 ppm), Nb (up to 0.27%), Zr (up to 0.19%) and certain other elements. Karst bauxites after mixed source material can be enriched in both femaphiles and felsiphiles.

Physical-Chemical Conditions of Bauxite Formation

These conditions include pH, Eh and drainage intensity, and have a significant effect on the mineral composition and geochemistry of bauxites. Different mineralogical and chemical types of bauxites vary in their trace element contents. The amount of iron in bauxites is directly proportional to the Zn and La contents, and inversely proportional to the Li, Ga, Mo and Nb contents. Certain elements (Y, Ni, Co, Cu and Zn) rarely accumulate in gibbsitic bauxites, but have accumulated in boehmitic and diasporic bauxites. Plots of these elements can be used to discriminate the mineralogically different bauxites. The variations in mineralogy and geochemistry probably reflect different mechanisms of bauxite formation.

Mineralogy of Parent Rocks

The same element can be concentrated in relatively insoluble accessory minerals, and also dispersed in the main rock-forming minerals. The behaviour of the element during bauxitic weathering will be determined by the relative proportions of these different mineral phases. However, Patsukhova et al. (1984) showed that some relatively immobile elements can form new mineral phases during bauxitic weathering. Movement of Zr and Th within bauxite profiles was observed in Carboniferous bauxites of the East European Platform (Mordberg, 1991).

Chemical Properties of Elements

Properties such as solubility, pH of hydroxide precipitation, and the possiblity of complex formation, can have an effect on element mobility during bauxite formation. Sometimes relatively mobile elements, such as Pb and Y, can become immobile, as was observed in bauxites of the North Onega Basin in Russia (Mordberg and Nesterova, 1995). In these cases, the elements can be used as indicators of bauxite genesis.

Diagenetic, Epigenetic and Recent Transformations of Bauxites

The supply and redistribution of certain elements varies during geological time. For example, Sr and Ba are present in higher amounts in ancient bauxites, particularly Paleozoic bauxites.

Carbonate Footwalls

A carbonate footwall plays an important role, acting as a geochemical barrier preventing the removal of certain elements which could form hypergene carbonates, or other minerals, within a bauxite profile.

Chemical Composition of Magmatic Rocks and Regional Metallogeny

The composition of rocks on a regional scale can influence the trace element contents of bauxites formed in sedimentary rocks (Mordberg, 1993b). For example, the Late Devonian bauxites of the South Urals, and the Cretaceous bauxites of Provence, are the richest in Pb and Zn (apart from bauxites that have formed directly from mineralized lithologies). Within both regions, the bauxite deposits are spatially associated with base metal deposits. Another example is the Devonian bauxite deposit of the Middle Timan, where later hydrothermal activity has led to the formation of galena mineralization, not only in surrounding rocks, but also within bauxites with high porosity.

For mineralogically distinct bauxites (e.g. gibbsitic, diasporic and boehmitic), the trace element content generally does not depend on the age of the bauxites. However, as boehmitic and diasporic bauxites were more widespread in the Paleozoic and Mesozoic, and gibbsitic bauxites were widespread in the Cenozoic, we can observe a total decrease in the content of certain elements in younger bauxites. The mechanism of gibbsitic bauxite formation seems to favour the removal of elements, in comparison to the mechanisms leading to formation of boehmitic and diasporic bauxites.

Schroll (1979) referred to Ga, Zr, V, Nb, Cr and Mo as bauxitophilic elements. Bardossy and Aleva (1990) concluded that only Cr, Ga and V are enriched in all types of lateritic bauxites. However, it seems that only very special conditions can lead to the depletion of certain elements during bauxite formation. It is probable that, in addition to the elements listed by Schroll (1979), Th and Pb could also be included in the group of bauxitophilic elements.

Acknowledgements

The research described in this publication was made possible in part by Grant No. NSW000 from the International Science Foundation.

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Distribution and behaviour of cesium during lateritic weathering of alkali metasomatites on Timan (Russia)

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Keywords: cesium, geochemistry, bauxite

The distribution and behaviour of Cs in bauxitic profiles has not been well studied for two reasons: the low clarke of this element in the Earth's crust, and its great mobility during lateritic weathering. This latter property usually leads to the total removal of Cs from the weathering profile. Lateritic bauxites after rocks rich in Cs are relatively rare. Therefore, a bauxite profile formed in Cs rich rocks was ideal for the study of this element.

Geology

The Devonian bauxite deposits are situated on the Middle Timan (Northern East of the the East-European platform) within the Chetlass orogen structure. The northern deposit was formed after Rifean alkali metasomatites, which are widespread in this region, together with carbonatites and other alkali rocks. The parent rocks are Rifean carbonate strata strongly altered by Vendian alkali metasomatism. Rock-forming minerals are dolomite, calcite, microcline and orthoclase. Minor plagioclase, aegerine, biotite and sericite are present locally. Rare-metal mineralization can also be observed. The laterite profile attains a total depth of 100-120m.

The following mineral zones were distinguished conditionally from the bottom to the top of the deposit:

- a zone of carbonate leaching, consisting mainly of feldspars with variable amounts (2-11%) of iron oxides and hydroxides;
- a zone of partial kaolinization, containing feldspars and kaolinite after feldspars;
- a kaolinite zone, with 3-26% hematite;
- an allite and bauxite zone, characterized by the presence of free aluminium minerals. The boehmite content can reach as high as 93%, diaspore is found locally, and kaolinite and hematite also typically occur within this zone;
- a resilification zone of a few meters thickness, characterized by increasing silica content and strong kaolinization, formed as a result of the influence of the overlying rocks.

Thin layers (10-20cm), which consists mainly of $2M_1$ muscovite, with minor kaolinite, are present in various parts of the section.

The profile has a complicated mineral zonation because of selective weathering: the same section is often represented by repeated alternation of different zones as a result of substratum heterogeneity.

Methods

Samples for investigation were taken from drill core and, after grinding, were analysed for Cs (flame photometry) and major elements (X-ray analysis). A few sections were studied by electron microprobe. Correlation analysis of Cs and major elements was also used.

Geochemistry

It was found that the underlying metasomatites exhibit geochemical zoning of, in particular, Cs. The highest Cs was found only in the north ore body and in the underlying fresh rocks. The distribution of Cs and some rock-forming oxides, in a profile of the north ore body, is presented in Table 1.

Table 1. Vertical distribution of Cs and some rock-forming elements within the lateritic profile

Zone	n	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	Na_2O %	K_2O %	CaO %	Cs ppm
VI	7	2.45	52.17	28.26	<0.15	0.06	0.88	49
V	11	30.85	34.65	19.38	<0.15	0.10	0.30	231
IV	15	37.41	32.2	14.93	<0.15	0.59	0.23	159
III	3	43.90	29.30	11.46	<0.15	4.15	0.44	270
II	11	57.41	18.72	5.79	0.19	13.77	0.33	1310
I	2	23.55	6.75	2.60	<0.15	5.98	19.40	850

n = number of samples; Zone I = fresh rocks; Zone II = feldspar zone; Zone III = partial kaolinization zone; Zone IV = kaolinite zone; Zones V and VI are interbedded bauxites and bauxitic rocks: Zone V = bauxitic rocks; Zone VI = bauxites.

Microcline from parent rocks contains from 600-2200ppm Cs. Unaltered microcline from the lower zones of the weathering profile has the same Cs content. Because of carbonate leaching, the average amount of Cs in the lowest zone (1310ppm) increases relative to the underlying rocks (850ppm). In the kaolinite zone the Cs content decreases to 159ppm; in this zone Cs is irregularly distributed, varying from < 10ppm to 500ppm. Cesium values such as these are also found in the upper parts of the section in allites, and even in bauxites. However the amount gradually decreases upwards in the section, and rocks in the upper 20-30m of the weathering profile contain less than 10ppm Cs. This part of the profile is not geochemically characterized in Table 1. There is no correlation between Cs and major elements within the zones, however a strong positive correlation between Cs and K is observed for the bauxitic rocks as a whole.

To the south, metasomatites contain less than 10ppm Cs. However, it is is interesting that within the weathering profile, rocks that are rich in feldspar, kaolinite and muscovite, sometimes contain Cs in amounts up to 35ppm.

Discussion and Conclusions

Bronevoy et al., (1985) estimated the average Cs content of bauxites to be 1.4ppm. Kronberg et al., (1987) point out Cs accumulation in moderately to highly leached rocks, and found depletion of Cs in Amazonian bauxite. The data considered here are in agreement with their conclusions.

The model of Cs behaviour during weathering seems to be as follows: at the stage of carbonate dissolution and feldspar accumulation, Cs was retained in the feldspars. With the replacement of feldpars by kaolinite, Cs lost its host mineral; sorption of Cs by kaolinite is an important factor in preventing its removal. Deep bauxitic weathering, with the formation of boehmite and hematite, led to total removal of Cs, although it was partially retained by kaolinite in the lower zones during vertical transport. Thus, the combination of carbonates and cesium-rich feldspars in parent rocks allowed the accumulation of this element at the first stages of weathering, and the inheritance, in relatively large amounts, during following weathering stages.

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The Sulphur Springs volcanic-hosted, base-metal sulphide gossan, eastern Pilbara, Western Australia

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Keywords: volcanic-hosted, base-metal, sulphide, gossan

Setting

Archaean volcanic-hosted massive sulphide mineralization at Sulphur Springs in the Panorama district of the eastern Pilbara, Western Australia, about 35km west of Marble Bar, was discovered in the 1980's by prospectors tracing a trail of iron and magnesium sulphates up a drainage system to an outcropping gossan. Subsequent drilling has indicated significant Fe-Zn-Cu sulphide mineralization with identified resources of 3.3 million tonnes (Mt) @ 11% Zn and 2.9Mt @ 4% Cu (Sipa Resources Quarterly Report, April 1994). The primary mineralization mainly comprises pyrite, sphalerite, chalcopyrite, barite and quartz as lenticular bodies with typical upward zonation from Cu to Zn and Pb. A zone of stockwork or stringer sulphide mineralization (mainly pyrite-chalcopyrite) occurs beneath the sulphide lenses. Mineralization is hosted by a succession of metamorphosed and deformed Archaean volcanic and sedimentary rocks (greenstones).

The Archaean granite-greenstone terrain of the eastern Pilbara has experienced a similar history of weathering and erosion to the Hamersley Ranges recording a change from early lateritization to dissection and desiccation. Much of the weathered mantle has been removed at Panorama and the Sulphur Springs gossan outcrops in partly weathered volcanic rock on a relatively steep slope beneath a ridge capped by laterite developed over silicified, fine-grained, sedimentary rocks (Figure 1). Ironstone is developed over pyritic black shale in this sedimentary unit at Bledisloe ~1 km north west of Sulphur Springs.

Figure 1. Schematic cross section illustrating landscape characteristics of rock and gossan types at Sulphur Springs.

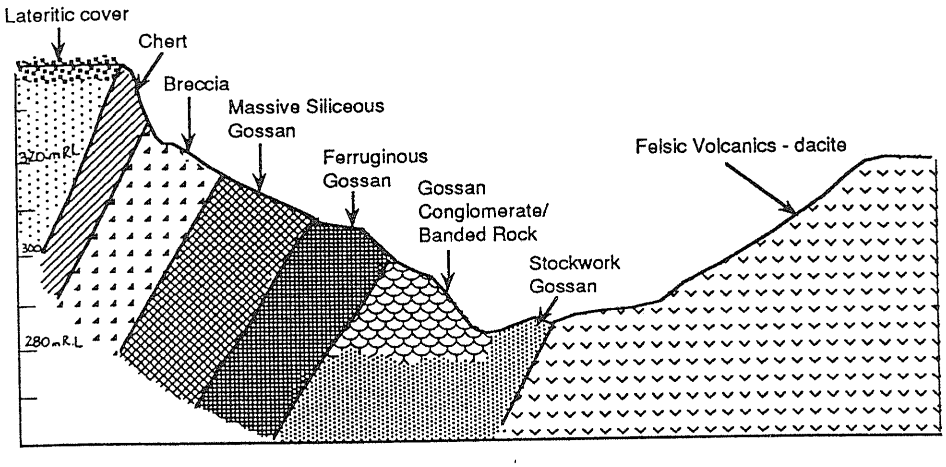
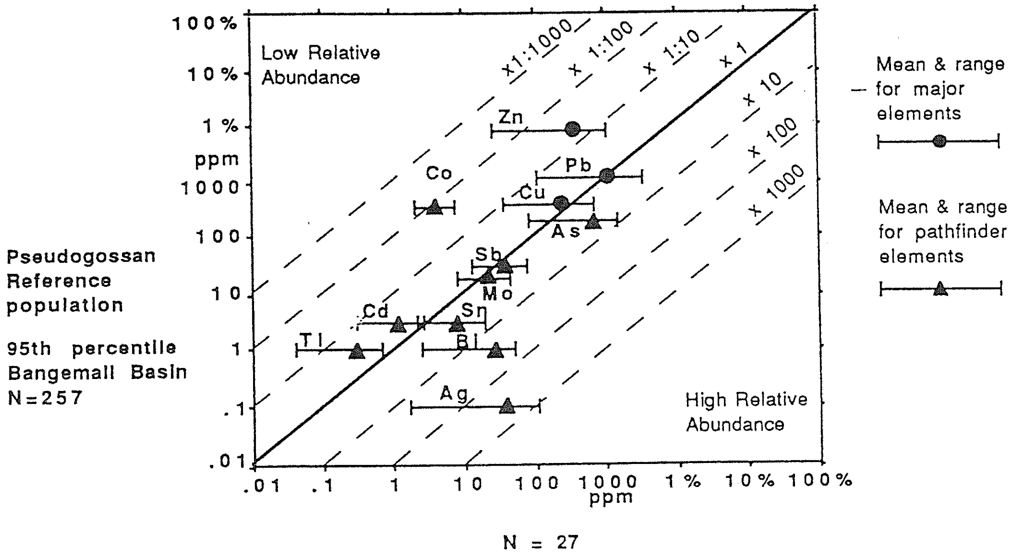
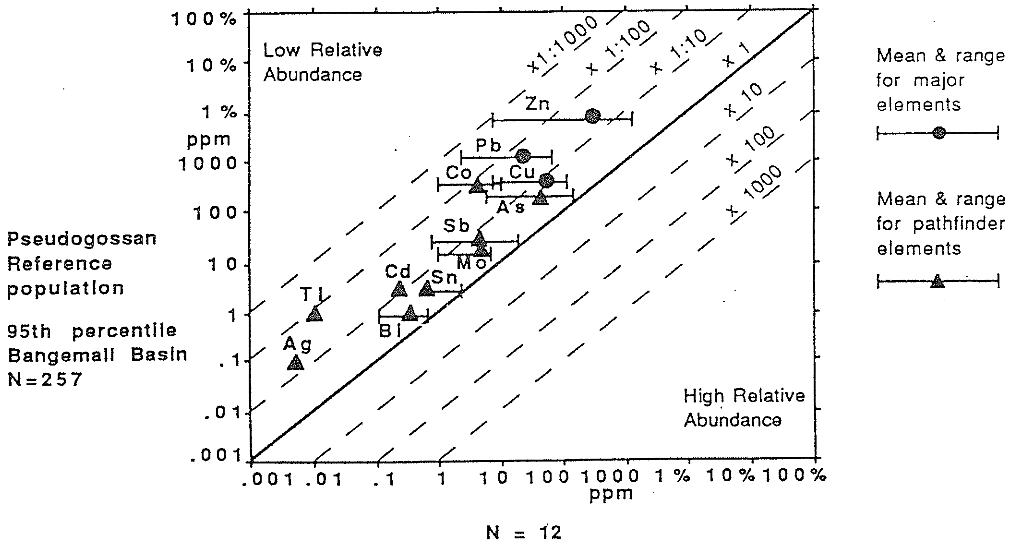


Figure 2. Geochemical display diagrams for (A) Sulphur Springs gossans and (B) Bledisloe pseudogossans. Compared to 95th percentile of Smith's (1979) reference ironstone population from the Bangemall Basin.



Sulphur Springs base metal sulphide gossans



Bledisloe pseudogossans

The Sulphur Springs gossan

Gossan types at Sulphur Springs (Pickard, 1993) include gossans after pyrite-chalcopyrite stockwork, ironstones after massive pyrite-chalcopyrite mineralization and highly porous siliceous gossans after sphalerite mineralization as well as conglomerates and breccias containing gossan fragments. The distribution, textures and geochemistry of different types of gossan broadly reflect the zonation, textures and geochemistry of the primary sulphide deposit. However, the conglomerates and breccias formed as alluvial and fluvial deposits during formation of the weathering profile (Figure 1).

Gossan outcrops have undergone almost complete leaching, with quartz and iron oxides the dominant minerals. Diagnostic boxwork textures except those of pyrite are not well developed due to the fine grainsize of primary mineralization and low pH during weathering which in combination resulted in the formation of large solution cavities and empty pyrite moulds. Verification that some of these cavities reflect original sulphide-quatrz intergrowths can be based on the recognition of textures reflecting the difference in free energy between sulphide and quartz. However, many samples also contain relict sulphide inclusions (sphalerite, chalcopyrite and pyrite) or resistant minerals such as cassiterite.

Geochemistry

Although leached and depleted in target and pathfinder elements relative to the sulphide body, the surface gossans are geochemically anomalous. An increase in Zn/Cu ratio from the stockwork gossans to siliceous gossans reflects the primary geochemical zonation within the sulphide body. Gossan geochemistry is typified by high Pb values compared to the other target elements indicating a well-developed mature weathering profile. Of the pathfinder elements high As, Ag, Bi and Ba are the most diagnostic. In comparison a suite of pseudogossans developed at Bledisloe over pyritic shales have distinctly different geochemical characteristics. Although having higher than background values for some elements associated with VHMS mineralization (in particular Zn), they have consistently lower values for most pathfinder elements than the Sulphur Springs gossans (Figure 2).

Acknowledgments

The Sipa Resources - Outokumpu Australia joint venture is thanked for their generous logistic and financial support of ALP's BSc (Honours) project. Particular thanks go to Bruce Uren for his help in the field and to Mike Doepel and Nick Archibald for their help.

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Mineralogy, morphology and chemistry of gold in the Posse Stone Line Lateritic Profile, Central Brazil

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Keywords: gold, laterite, stone line, Brazil

Introduction

This study examines the modifications to the mineralogy, morphology and chemistry of the gold grains from the stone line lateritic profile overlying the Posse gold deposit, and contributes to the understanding of gold behaviour under tropical weathering conditions.

The Posse deposit is hosted in a Precambrian meta-volcanic sequence in a seasonal tropical region with a history of lateritic weathering. The profile is dominated by a saprolitic zone, with a stone line horizon near the surface containing ferruginized quartz and iron crust fragments. Under the present regime lateritization is not taking place, but remnants of iron crust accumulated in the stone line indicates that it is now being degraded (Lecomte, 1988).

Investigation Methods

Primary gold ore mineralogy was characterized by SEM-EDX analyses on drill core samples. Four hundred and sixteen gold grains, recovered from representative pan concentrate samples from each weathering zone, were analyzed with the binocular microscope and SEM-EDX. Corresponding samples from each weathering zone were wet sieved into six granulometric fractions for gold analysis by AAS.

Results

More than 80% of the gold in the primary ore at Posse occurs associated with frohbergite ($FeTe_2$) at silicate grain boundaries. Results of gold grain size measurements across the profile show that in the stone line and top soil the grains are larger. At all levels of the profile gold is enriched in the coarse fraction (425-2000μm). However, individual gold grains of that size are not present, and therefore this gold must be attached to coarser particles. The concentration of gold in lateritic fragments such as pisoliths is low (0.15 ppm). It can be deduced that gold in the coarse fraction occurs on the surfaces of particles, where it is deposited by chemical reprecipitation.

Seven main morphological classes of gold grains could be identified, including gold crystals (Figure 1). Grains with regular shapes and smooth surfaces dominate in the saprolite and ferruginous zones, while crystals and rugged and irregular grains predominate in the stone line and top soil.

Examination of those grains under the SEM shows that they often contain limonitic cavities, the frequencies of which are plotted according to grain class in each weathering horizon (Figure 2). Limonitic cavities become more frequent as the grains become more irregular and rugged. SEM observation of polished gold grains show fine telluride mineral inclusions characteristic of primary gold. The frequency with which these inclusions were observed in each grain class shows a coincident trend with that of limonitic cavities (Figure 2). This suggests that the limonitic material is a residual feature derived from frohbergite oxidation. Grains lacking limonitic cavities and telluride inclusions are generally more regularly shaped and smooth and, like the gold crystals, are thought to result from chemical reprecipitation. Gold crystals from the saprolite tend to show sharp edges and flat faces whilst those from above the saprolite show dissolution features such as corrosion cavities or rounding of crystal angles (Freysinnet et al., 1989). This suggests that the saprolite is a zone of gold precipitation above which gold is partially dissolved.

EDX analyses on primary gold grains show low and heterogeneous Ag concentrations, with a fineness ranging from 938-1000. X-ray Ag maps produced on gold crystals from the saprolite and stone line, and on grains from classes E and F, show a characteristic homogeneous Ag distribution, with a similar fineness to gold from the primary ore. This shows that the process of gold reprecipitation in the profile is one which does not lead to a fineness increase. Reprecipitation of gold and silver takes place homogeneously in the same grain, and with a similar level of silver concentration as is found in primary gold grains.

Discussion and Conclusions

Despite the dominance of primary gold in the profile, the size of the gold grains tends to increase toward the top, even though chemical dissolution features are present. Colin and Vieillard (1991) showed that primary gold grains in stone line profiles of equatorial Africa become smaller upwards in the profile as a result of chemical dissolution. These contrasting results probably reflect the different morphoclimatic conditions of the two areas: compared to equatorial rainforest, Posse is less humid and less vegetated (typical savannah) and the role of surficial erosion is probably stronger. This results in the preferential removal of fine grained gold and the relative concentration of the coarser grains at the surface.

Gold dissolution in the saprolite is minimal. Porto (1991) showed that the groundwater has a neutral pH and low S concentrations ($3\mu g/l$), a condition which does not favour gold dissolution as chloride or sulphur complexes (Mann, 1984; Webster, 1986). The reprecipitation of gold in the profile does not lead to a fineness increase, implying again that the role of chloride complexes is negligible (Mann, 1984).

At the top of the profile, where gold dissolution is evident, the environment is organic and iron rich and highly oxidizing, and gold mobilization is probably more influenced by organic complexes and colloids (Bowell et al., 1993a), and hydroxy-complexes (Bowell et al., 1993b; Krupp and Weiser, 1992; Colin et al., 1993). The enrichment of gold in the coarse granulometric fraction may be due to the adsorption of gold complexes and various colloids on to iron oxides which occur coating the coarse particles.

Acknowledgements

The authors wish to acknowledge CNPg and Western Mining Co. for financial support and permission to publish this work.

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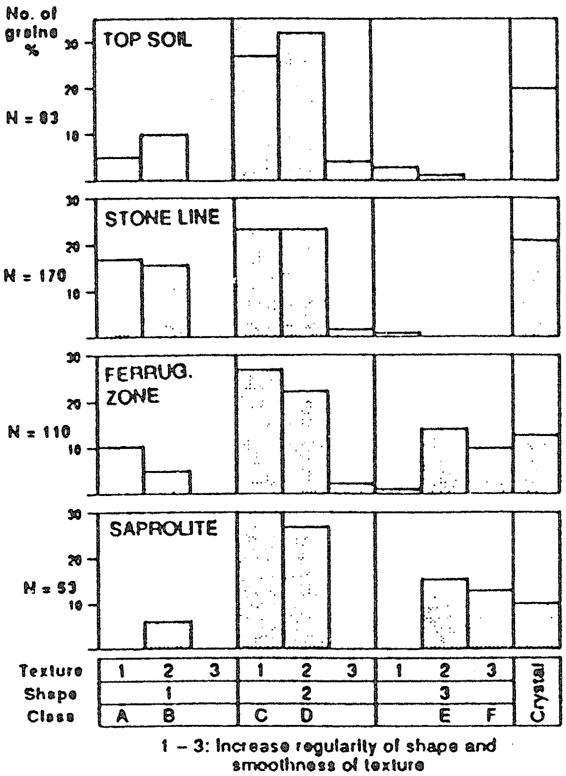

Figure 1. Morphological classification of gold grains

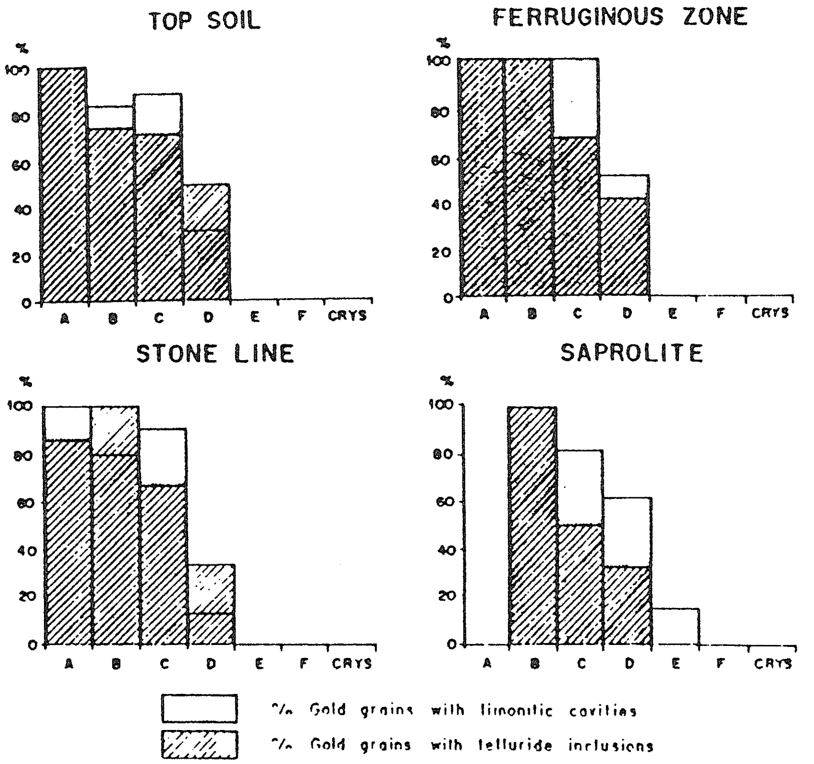

Figure 2. Frequency plots of gold grain classes in each weathering horizon

Supergene gold concentration related to massive sulfide weathering in the Red Sea Hills (Sudan)

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Keywords: gold, supergene deposit, Sudan

Introduction

The Ariab district, which lies within a Proterozoic volcanosedimentary belt on the Sudanese side of the Arabian-Nubian Shield, contains several gold deposits localized in the oxidation zone of massive polymetallic sulfide bodies: Hassai, Hadal Auatib, Oderuk, Baderuk, Talaiderut, Addassedak, Ganaet (Cottard *et al.*, 1986, Cottard *et al.*, 1993). The economic gold potential of these deposits, estimated within the top 50 m below the surface, represents several tens of tonnes of gold with average ore grades of 7 to 40 g/t Au. At the surface, the gold is concentrated in siliceous and silico-baritic rocks intercalated within gossans that are commonly more than 1 km long and as much as several hundred meters wide.

A gitologic, mineralogic, and geochemical study of the Hassai deposit (6.2 t of gold at 8.2 g/t) has enabled us to evaluate the role of supergene processes in (a) the formation of the gold-bearing siliceous and silico-baritic rocks and (b) the economic concentration of the gold within these formations from an essentially pyritic massive sulfide orebody containing on average 2% Cu, 0.5% Zn, 7.4 g/t Ag and 1.4 g/t Au (Récoché, 1993).

The Hassai deposit

Surface gossans and siliceous facies at Hassai form an E-W-trending monoclinal lenticular structure, 1800 m long and 5-40 m wide, dipping 50-70° S. At depth the Hassai sulfide ore forms massive decimeter- to meter-thick lenses, concordant with the enclosing hydrothermalized chlorite schist, lava, and silicic pyroclastites. The mineralogic association comprises dominant pyrite with variable amounts of chalcopyrite, sphalerite, and quartz, and subordinate tennantite, galena, carbonate, barite, (Pb, Bi, Ag, Au) tellurides, and gold. Micron-size native gold is rare, but gold tellurides such as calaverite-petzite are common as inclusions in the pyrite and its cementing chalcopyrite and galena.

Weathering of the massive pyritic orebody and its volcanic host rock has developed an oxidation profile at present more than 120 m deep. This profile shows a characteristic vertical mineralogic zoning with, from the top down:

- an upper oxidation zone, 60-90 m deep, characterized by siliceous and (or) oxide facies;
- a lower oxidation zone, 20-40 m deep, with amorphous silica and sulfates (jarosite, alunite, gypsum, anhydrite) showing a lateral zoning;
- a zone of active cementation with covellite which marks the lower limit of the oxidation profile overlying the protore.

Mineralogic studies of the oxidation zone

A mineralogic study carried out on samples collected at the surface and from drill holes in the oxidation zone shows that the siliceous and silico-baritic facies form microbreccias composed mainly of quartz showing cubic imprints of dissolved sulfides. The cement of the microbreccias in the upper oxidation zone consists of variable proportions of microcrystalline quartz, syntaxial quartz overgrowths on the imprinted quartz, (Fe, Ti, Sb, Sn) metal oxides, and euhedral to pseudoeuhedral barite that can make up as much as 55% of the rock. In the lower oxidation zone the cement is composed of jarosite, amorphous silica and rare barite. The microbreccias represent the residual product from supergene alteration of the underlying pyritic sulfide orebody with which they are in geometric continuation within the oxide zone. The economic concentration of gold essentially localized in these formations. The gold is micron sized and forms individual grains and strings included, depending on the oxidation zone, within the metal oxides, the jarosite or the euhedral barite crystals.

In the upper oxidation zone these formations are contained in banded or schistose gossans which appear to be weathered volcanites with a secondary enrichment of iron oxide and other mobile elements (Cu, As, Bi, Pb) leached from the massive orebody during its supergene alteration.

Geochemistry

A geochemical study was made of the results from the ICP multi-element analyses and AA gold analysis. This study, combined with the mineralogic study, involved 214 spot samples collected from the surface and in cores, and 53 continuous samples representing each meter along a vertical drill hole that intersected the different zones of the oxidation profile. By geochemically identifying each petrographic facies in relation to the weathering zone in which it occurs, it has been possible to determine the geochemical exchanges between the ore and its host rock during the development of the oxidation profile.

The trace-element geochemistry of the complete oxidation zone provides a broad distinction between the gold-bearing siliceous microbreccia with an Au, Pb, Ba, Sb, Sn, Ag Sr signature, and the enclosing silicified or oxidized (gossan) banded volcanites with a Fe, V, Cr, As, Bi, P, Mo signature. The ore and the host rock both contain stable or poorly mobile elements by which they can be characterized throughout the oxidation profile: Au, Sb, Sn, Pb, Ag for the ore and Cr, V for the country rock. In contrast, the very mobile elements such as Zn in the ore and Mn and Mg in the host rock are scavenged at the base of the profile (cementation zone) where sphalerite is totally leached and phyllosilicates are reduced to silica skeletons. Among the other mobile elements, certain migrate and reprecipitate within the same formation - e.g. Ag and Au in the ore, and Ti (oxides), Al (alunite), Ca (carbonate, gypsum) in the country rock. Other mobile elements become fixed in the neighboring formation - e.g. Fe, Cu, As, Mo, (Bi) which migrate from the ore and become fixed in the host rock as secondary minerals (oxides, sulfates, carbonates, native elements) after complete leaching of all the sulfides at the oxidation front. Conversely, the leaching of baritic micas from the host volcanites apparently releases the Ba^{++} ions necessary for the formation of the supergene barite that characterizes the gold ore in the upper oxidation zone.

Apart from a slight decrease close to the surface, the gold concentrations are fairly homogeneous with no significant increase in depth within the mineralized formation. This tends to indicate that the gold concentration involves neither major migration nor accumulation within the profile.

In detail, the elements apparently showed different behaviors during the formation of the different zones of the oxidation profile. For example, the Ba and Sr signature that characterizes the ore in the upper oxidation zone, where barite precipitated exclusively and massively, is not as distinct in the lower oxidation zone where barite, which is rare in the ore, occurs commonly as micro-inclusions in the silica skeletons of the micas leached from the host rock. Similarly K, Ca, Al, which are not present in the upper oxidation zone, are indicators of the leached host rock in the lower oxidation zone which is where jarosite, alunite and gypsum are precipitated. The Ag signature of the gold ore is only really apparent in the lower oxidation zone.

Interpretation

The supergene alteration of the pyritic sulfide ore grading 1.4 g/t to a gold-bearing silico-barite ore grading 8.2 g/t is the result of several stages of development in both time and space. The alteration begins in the cementation zone with the replacement of chalcopyrite by covellite and digenite and the leaching of sphalerite and phyllosilicates. At the oxidation front a complete leaching of all the sulfides, thus pyrite, causes a significant drop in pH with solubilization of the iron to ferrous sulfate. This acid leaching results in the progressive formation of large sulfide solution cavities that host accumulations of dismantled residual minerals such as imprinted quartz, rare barite, and silica skeletons of phyllosilicates. These microbreccia components are then cemented by stable secondary minerals according to the physicochemical conditions of the ambient environment; e.g. jarosite, amorphous silica, and rare barite in the lower oxidation zone and quartz, metal oxides, and barite in the upper oxidation zone.

Acid leaching of the massive ore sulfides also gives rise to a solubilization of associated gold compounds. It is generally accepted that under such conditions the gold remobilizes as thiosulfate complexes. However, thiosulfate is not stable in an acidic milieu with the alteration of pyrite; it oxidizes rapidly to sulfate which becomes the major sulfur species in solution. Gold remobilized in this form will precipitate practically "on site" at the oxidation front, at the same time as the secondary minerals (jarosite, barite, Fe-Ti-Sb-Sn oxides), whereas most of the other metals (Cu, Zn, As, Fe) are leached towards the host rock (tab. 1). The economic concentration of gold in the siliceous and silico-baritic microbreccias at Hassai thus appears to represent a residual supergene concentration for which the coefficient ($F = 6.3$) can be assessed in relation to the proportion of quartz and sulfide in the initial sulfide ore.

The specific mineralogic and geochemical characteristics of each facies in the different oxidation profile zones also indicate a superposition (with time) of two oxidation profiles formed under different paleoclimatologic and paleogeomorphologic conditions. The upper oxidation zone would represent the base of a paleo-oxidation profile developed during a period, probably pre-Cretaceous, of tectonic stability (peneplanation) under a semi-arid climate with alternating dry and wet periods. Such conditions would have enabled a remobilization of silica with reprecipitation of quartz, an intense leaching of iron and copper towards the host rock, and a large addition of barium favoring the precipitation of supergene barite rich layers. Recent tectonic activity related to the opening of the Red Sea at the end of the Tertiary and the onset of an arid climate would have led to an abrupt lowering of the water table and continued alteration in the lower oxidation zone. The solutions, receiving little supply under these conditions and thus more concentrated in silica, cations, and impurities, would have precipitated amorphous silica. These conditions would also have favored the precipitation of iron sulfates and a weak migration of the barium in the profile. The area is today relatively flat with a desert climate, and the oxidation front appears to be at the present groundwater table. With no large fluctuations of the hydrostatic level, the profile is slowly deepening. The desert climate also favors an accumulation of soluble salts through evaporation, enabling the remobilization of gold close to the surface as chloride complexes; this may explain the gold concentration recorded at this level.

The supergene gold mineralizations of the Ariab district constitute a particular type of supergene deposit which could be found in similar metallogenic and paleoclimatic contexts. The discovery in Saudi Arabia of similar deposits in the oxidized zone of massive sulphides deposit from the Wadi Bidah and Wadi Schwas belts (Cottard et al. 1993) demonstrates the regional potential of this kind of gold concentration.

Acknowledgements

The Geological Research Authority of Sudan and Ariab Mining Company are gratefully ackowledged for their assistance in the field work and the access to data. The study was carried out as part of BRGM scientific project M13.

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Table 1 : Global geochemical signature of the mineralization and its hostrock in the oxidation profile

	MINERALIZATION	HOSTROCK
	massive sulphide in the protore than silica (barite) microbreccias in the oxidation profile	volcanite in the protore than banded silicified or oxidized (gossans) facies in the oxidation profile
Upper oxidation zone	Au Sn Ba Pb Sr	Cr V Fe Cu Ti As P Mo Bi
Lower oxidation zone	Au Sn Ba Pb Ag Sb Ti	Cr V As K Ca Al
Cementation zone	Au Sb Mo Pb As Cu P	Cr V P Ti Sr Al Ca Cu
Protore	Fe Cu Pb Zn Au Ag Bi Mo As Sb (Ba) Sn (P)	Si Ca Ti Mg Mn V Cr Sr Ba (P)

The bauxitisation of a ferruginous-kaolinite mottled horizon: an explanation for the evolution of the Weipa bauxite deposit

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The bauxitic pisoliths of Weipa may be divided into two main groups. Over 95% of pisoliths are single and average 5mm in diameter. The remainder are compound; that is roughly elliptical hollow bodies, 20 to 50mm in diameter, with single pisoliths inside. The majority of compound pisoliths form by the bauxitisation of ferruginous-kaolinite nodules. The present-day distribution of compound pisoliths provides a key to understanding the evolution of the weathering profile.

Weathering of the kaolinitic sands of the Bulimba Formation at Weipa probably commenced soon after their deposition, during the early Tertiary. In the 50 million years which followed deposition it is probable that the evolving weathering profile was affected by similar episodic and periodic climatic changes as those recorded elsewhere in the world. Under conditions similar to that of today, ferruginous-kaolinite mottles and nodules formed by the epigenetic replacement of kaolinite with hematite. Under a more equable climate with perhaps higher rainfall, desilicification and deferruginisation dominated, resulting in the formation of bauxite.

The mass change associated with the bauxitisation of ferruginous-kaolinite nodules was calculated to explain the structure of compound pisoliths. Before bauxitisation, an idealised ferruginous-kaolinite nodule has a mineralogical composition of 86 wt% kaolinite, 7 wt% hematite, 7 wt% goethite, and a density of 2.25 gcm^{-3}. Deferruginisation and desilicification of the nodule results in a net loss of 1.08 gcm^{-3}. This loss in mass is not evenly distributed throughout the bauxitised nodule but is greatest in the core where a chamber is formed. Surrounding the chamber, aluminium hydroxide crystallises to form a gibbsitic shell. If an opening is present into the inside chamber, single pisoliths may fall into and occupy the cavity.

The material which surrounds ferruginous-kaolinite nodules and mottles is dominantly kaolinitic. During conditions associated with bauxitisation, aluminium migration occurs to sites richest in kaolinite. Here, the epigenetic replacement of kaolinite with bauxite minerals such as eta-alumina (η-Al_2O_3), tohdite ($5Al_2O_3.H_2O$), boehmite and gibbsite occurs, leading to the development of aluminous nodules. The progressive inward rehydration of the more dehydrated phases results in the formation of concentrically banded cortices around pisoliths.

Techniques

Thermal setting of the Cadjebut Zn-Pb deposit, Western Australia

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Keywords: apatite fission track analysis, Mississippi Valley-type Pb-Zn ore deposits

Introduction

By definition, hydrothermal ore solutions are inferred to transport heat as well as metals of economic interest. Whether or not thermal alteration is detectable within the vicinity of a hydrothermal ore deposit depends on a variety of factors, including the temperature, duration and rate of fluid flow, the temperature and thermal conductivity of the country rock, and whether the area was heated either prior to or following ore deposition. Viable exploration targets have been delineated on the basis of thermal anomalies but the absence of a thermal halo may also have important implications for genetic theories that can benefit regional exploration strategies.

Thermal indicators in common use can be subdivided into three categories depending on whether they involve inorganic materials such as conodont colour alteration (CAI), organic alteration such as vitrinite reflectance (R_o), or thermochronological methods such as apatite fission track analysis (AFTA). These specific techniques are examples of a wide range of methods, many of which are routinely used in the petroleum exploration industry. All three categories of thermal indicator allow the discrimination of relative temperature differences as well as an estimate of peak temperatures. In addition, thermochronological methods allow an estimate of the timing of peak temperatures. The technique used also depends upon the availability of suitable material; Cambrian to Triassic carbonate rocks for conodonts, coal or black shale for vitrinite, sandstone or igneous/metamorphic rocks for apatite.

A thermal history investigation of the eastern Lennard Shelf (Figure 1) was undertaken using apatite fission track analysis to extend the area covered by a previous study (Arne et al., 1989). While that study provided a framework for the regional thermal history for the Lennard Shelf, only Pb-Zn prospects were examined in a systematic fashion. The present study was undertaken to test the conclusions of this earlier investigation on the Cadjebut deposit.

Thermal Setting of Mississippi Valley-Type (MVT) Ore Deposits

The thermal setting of MVT deposits has been summarized by Arne (1992) and Sangster et al. (1994). Based on apatite fission track data from four MVT ore districts (Southeast Missouri, USA; Pine Point, Canada; Gays River, Canada; Lennard Shelf, Australia), Arne (1992) concluded that major MVT ore districts were generally associated with regional heating. A similar conclusion was also reached by Sangster et al. (1994) based on a comparison of CAI values with fluid inclusion homogenization temperatures for 12 North American MVT districts. Eight of the ore districts examined by Sangster et al. (1994) were found to be in thermal equilibrium with their host rocks. However, Arne (1992) and Sangster et al. (1994) differ in their explanations for regional heating. Whereas Arne (1992) suggested that deep burial of host sequences may play an important role in regional heating, Sangster et al. (1994) invoked the migration of hot brines through MVT ore districts. No doubt both mechanisms, burial and advective heat transfer, are contributing factors.

Geological Setting

The Lennard Shelf forms the northeast margin of the Canning Basin, Western Australia (Figure 1). It is comprised mainly of Devonian carbonate and clastic rocks that either rest unconformably on, or in faulted contact with, Precambrian basement of the Kimberley Block (Playford, 1980). Devonian carbonate rocks host a number of base metal deposits and prospects (Murphy, 1990), including the Cadjebut deposit. Arne et al. (1989) inferred peak temperatures during Late Devonian/Early Carboniferous burial, at which time they suggested Pb-Zn mineralization may have occurred, and identified a major phase of regional cooling at ca. 200 Ma. This thermal framework was subsequently used by McManus and Wallace (1992) to constrain a phase of Late Devonian/Early Carboniferous sulphide mineralization within a regional cathodoluminescent cement stratigraphy. Arne et al. (1989) also concluded that base metal prospects on the Lennard Shelf (Narlarla, Wagon Pass, Blendevale) were in thermal equilibrium with their host rocks, a conclusion previously reached by Lambert and Etminan (1987) on the basis of CAI data. Tompkins et al. (1994a) subsequently disputed the timing of sulphide mineralization on the Lennard Shelf inferred by Arne et al. (1989) and McManus and Wallace (1992) and instead proposed that base metal mineralization occurred during the mid-Carboniferous.

A reliable estimate of the temperature of ore formation at Cadjebut from fluid inclusion data is lacking due to the very fine-grained nature of the sphalerite. Etminan and Hoffmann (1989) reported preliminary homogenization temperatures of ~90°C for the Cadjebut deposit and also noted on the basis of biomarkers in fluid inclusions that the ore fluid migrated from a region of higher organic maturity than that exhibited by rocks in the vicinity of the deposit.

The Cadjebut mine began production in 1988 with total reserves of ~3.8 Mt averaging 17% combined zinc and lead (Tompkins et al., 1994b). It is hosted by Givetian dolostone at the base of the Pillara cycle where it forms two essentially strata-bound replacement orebodies. Massive ore of lens 2, or the lower lens, is separated from a basal arkose unit by an oolitic horizon generally less than 10 cm in thickness. This basal arkose contains detrital apatite grains which were recovered from five diamond drill cores in the mine area (Figure 1). Three samples of the arkose were obtained from directly beneath the Cadjebut orebody (ID-225, 317 and 328) and two samples were collected up to 1 kilometre away on the north side of the Cadjebut Fault (ID-32 and 53). Precambrian basement and a basal sand were sampled from two drill cores at least 2.5 km to the west of the Cadjebut deposit on the south side of the Cadjebut Fault (ID-12 and 16).

Methods

Apatite fission track analysis is a radiometric method of thermal history reconstruction that exploits the thermal instability of damage tracks formed from the spontaneous decay of trace ^{238}U in the apatite crystal lattice. Fission tracks are formed continuously through time at a rate controlled by the spontaneous decay rate of ^{238}U and the total concentration of uranium in the mineral grain. Apatite fission tracks are progressively shortened at temperatures between 20 to 150°C for time periods in the range 10^9 to 10^5 years in a process referred to as track annealing. As track lengths are reduced, the measured track density on an etched, internal grain surface is also reduced, resulting in a lowering of fission track age. Since each track forms at a different time, each undergoes a unique time-temperature history and is shortened in response to the maximum temperature to which it was exposed. Therefore, a cumulative time-temperature history is preserved in the distribution of individual tracks lengths confined within the apatite grain that, when coupled with the measured fission track age, can be used to test predictions from forward thermal models. In sedimentary basins where heating times are on the order of 10^6 to 10^8 years, paleotemperature control is provided over the more restricted range of ~60 to 120°C. Above ~120°C, the precise value depending on the heating rate and apatite composition, fission tracks in apatite are totally annealed in the sedimentary basin environment.

Results

Apatite fission track data from the nine samples are summarized in Figure 1. Analytical procedures and calibration results are described in Arne (1989). All uncertainties quoted in Figure 1 are at the 2 sigma level and are typical of apatite fission track data (i.e. ±~10%).

The three samples from beneath the Cadjebut deposit at depths between 81 and 250 m give apatite fission track ages of 359 ± 44 Ma, 370 ± 74 Ma, and 394 ± 44 Ma for a weighted mean of 375 ± 27 Ma. The two samples from north of the Cadjebut Fault away from the deposit at a depth of ~120 m give apatite fission track ages of 424 ± 42 Ma and 369 ± 60 Ma that are indistinguishable from age data from directly beneath the Cadjebut deposit.

Two samples were obtained from each of two drill cores located to the south of the Cadjebut Fault (Figure 1). The two samples from ID-12 give apatite fission track ages of 242 ± 36 Ma and 276 ± 22 Ma for the basal sandstone and Precambrian basement, respectively, at a depth of ~640 m that are significantly younger than those obtained from samples north of the Cadjebut Fault. The two samples from ID-16 give apatite fission track ages of 303 ± 38 Ma and 375 ± 32 Ma for the basal sandstone and Precambrian basement, respectively, at a depth of ~325 m that are significantly different from each other. The fission track age of the basal sandstone is significantly less than those obtained from north of the Cadjebut Fault.

All samples have mean track lengths of around 12.4 μm and relatively broad to negatively skewed track length distributions. Thus the track length data also fail to show evidence for greater thermal annealing as the Cadjebut deposit is approached.

Interpretation of Thermal History

All fission track data from the Cadjebut mine area show evidence of annealing after deposition of the host sequence. This is particularly evident for the four samples south of the Cadjebut Fault which give apatite fission track ages significantly less than their Precambrian and inferred Ordovician ages of formation. Individual apatite grains in both basal sandstone samples show a significant spread in fission track age compatible with heating to temperatures in the range 90-110°C prior to cooling at ~200 Ma (Arne et al., 1989). These samples show a greater degree of fission track age reduction compared to samples close to the Cadjebut deposit, possibly because they were obtained from a greater depth. The interpretation of data close to the Cadjebut deposit is less obvious as the apatite fission track ages overlap the inferred Givetian age of the basal arkose. However, these five samples all show a degree of track length reduction incompatible with their present day position close to the surface and so are inferred also to have been hotter in the past following deposition. How hot these samples may have been and how these temperatures compare to the estimated temperature of sulphide mineralization at Cadjebut remains to be determined.

Conclusions

Apatite fission track data from the vicinity of the Cadjebut Zn-Pb deposit, Western Australia show no direct evidence for thermal alteration associated with mineralization. Rather, all data show evidence for regional heating although a direct comparison with the temperature of ore formation is not yet possible. A review of thermal data from numerous MVT ore districts suggests that evidence for regional heating is common, and that this can be used as a regional exploration guide.

Acknowledgments

This research was supported by the New Pinnacles BHP/Billiton joint venture, the former Australian Bureau of Mineral Resources, and the Australian Institute of Nuclear Science and Engineering. The author was funded by a Melbourne University Postgraduate Scholarship while undertaking this study and received assistance from Geotrack International and LaTrobe University.

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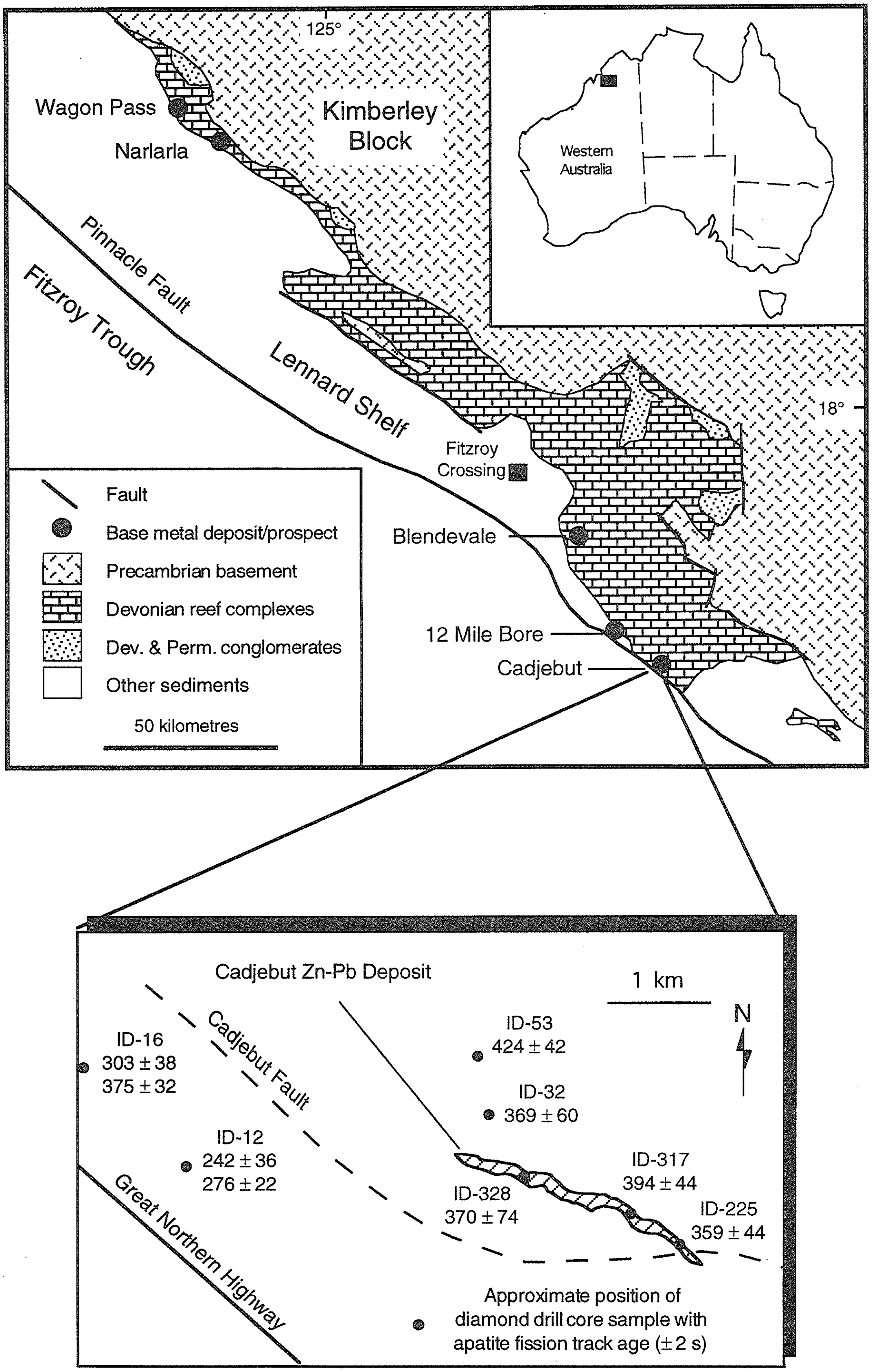

Figure 1: Simplified geology of the Lennard Shelf and location of apatite fission track samples in the Cadjebut mine area (modified from Playford, 1980 and Tompkins et al.,1994).

INNOVATIVE ENZYME LEACH PROVIDES COST-EFFECTIVE OVERBURDEN PENETRATION

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Keywords: deposit, overburden, analysis, desert, glacial, soil

Introduction

Layers of glacial till and glaciolacustrine sediments cover large areas of the Canadian Shield, and much of the bedrock in the Basin and Range Province of United States and Mexico and much of the Atacama Desert of Chile and Peru have been buried by basin fill and volcanic rocks. The problem, when trying to perform geochemical exploration in terrains that are covered by transported overburden, is that the overburden is usually exotic to the bedrock that it covers. In some regions, intense weathering has stripped the surficial material of the original chemical signature of the parent rock. Conventional chemical analysis would reveal only the composition of the overburden and would not give any indication of the underlying bedrock. Total methods of analysis and stronger-leaching techniques produce results that are dominated by the overburden signature, and random variations in this signature suppress any anomalous chemistry emanating from underlying mineralization. In the past, drilling has been the only means of collecting useful geochemical samples in areas of extensive overburden. An inexpensive means is needed for detecting subtle geochemical dispersion through transported or deeply weathered overburden and providing some indication of the chemistry of the bedrock.

Trace elements released by weathering of mineral deposits in the bedrock will migrate up through overburden by such means as ground water flow, capillary action, or diffusion of volatile compounds. However the amount of these bedrock-related trace elements is typically a very small component of the total concentration of these elements in the overburden. The goal is to determine the amount of a trace element that has been added to the overburden rather than the total amount in the overburden sample. Upon reaching the near surface environment, many of the trace elements migrating through overburden will be trapped in manganese oxide and iron oxide coatings, which form on mineral grains in the soils. One of the most effective traps for trace elements migrating toward the surface is amorphous manganese dioxide, which is usually a very small component of the total manganese oxide phases in the soil sample. Not only does amorphous manganese dioxide have a relatively large surface area, but the irregular surface and the random distribution of both positive and negative charges on that surface make it an ideal adsorber for a variety of cations, anions, and polar molecules.

A selective leach has been developed that employs an enzyme reaction to selectively dissolve amorphous manganese oxides. When all the amorphous manganese dioxide in the sample has been reacted, the enzyme reaction slows, and the leaching action ceases. Because the enzyme leach is self limiting, there is minimal leaching of the mineral substrates in the sample. Thus, the background concentrations for many elements determined are extremely low and the anomaly/background contrast is dramatically enhanced. Typically, three types of geochemical anomalies are found with the Enzyme Leach: 1. Mechanical/hydromorphic dispersion anomalies; 2. Oxidation halo anomalies; 3. Apical anomalies. In terrains where the bedrock is buried by glacial overburden, mechanical/hydromorphic anomalies are the most common type found (although all three types of anomalies are observed in soils developed on tills). Mechanical dispersion trains were formed in the basal till as mineralized bedrock material was smeared down ice during glaciation. Gradual weathering of this mineralized material releases trace elements into the ground water flowing through the till. Vegetation with roots tapping into either the mineralized till or anomalous ground water picks up trace elements which are eventually shed to the forest floor in plant litter. Anomalous trace elements are often relatively quickly leached from the *A*-soil horizon and trapped in oxide coatings in the *B* horizon. In essence the *B*-soil horizon often acts as a long-term integrator of vegetation anomalies (J.R. Clark, 1993). The Enzyme

Leach has been used to detect very subtle mechanical/hydromorphic anomalies related to mineralized bedrock in a number of glacial overburden situations, including areas where the glacial till is blanketed with glaciolacustrine sediments. Subtle hydromorphic dispersion anomalies in stream sediments have also been detected with the Enzyme Leach. Trace element suites comprising mechanical/ hydromorphic-related soil anomalies commonly reflect at least part of the chemical signature of the bedrock source. Anomaly contrast in soils developed on glacial till often range from 2-times to 10-times the background concentrations for the elements forming the anomaly.

Oxidation halo anomalies are produced by the gradual oxidation of buried reduced bodies. Any reduced body (an ore deposit, a barren body of disseminated pyrite, a buried geothermal system, a petroleum reservoir, etc.) can produce one of these anomalies. Once these anomalies are found it is up to the geologist to make a geological interpretation based on all the information at hand, including Enzyme Leach data, as to what the source of the anomaly might be. These anomalies are characterized by very high contrast values for a suite of elements, the "oxidation suite," which can include Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U, and Th. Often, rare-earth elements and base metals will be anomalous in the same soil samples, but with reduced contrast. Evidence indicates that the oxidation suite migrates to the surface as halogen gases and volatile halide compounds. These elemental gases and compounds would tend to form under the acid/oxidizing conditions of the anode of an electrochemical cell. The low contrast base-metal anomalies coinciding with oxidation-suite anomalies may result from the gradual migration of cations away from these anodes along electrochemical gradients. Less commonly, enzyme-soluble Au and enzyme-soluble Hg will be found in the area of these anomalies. Metallic Au and Hg are not soluble in the enzyme leach. These low-level Au and Hg anomalies often appear to form as a result of the oxidation of these elements in the soil by the subtle flux of oxidizing gases passing through the soil. Oxidation anomalies often form an asymmetrical halo or partial halo around the buried reduced body, and that body underlies part of the central low within that halo. The trace element suite in oxidation anomalies, although often enriched in many types of metal deposits, is not typically representative of the composition of the buried reduced body. For example, essentially the same suite of elements forms halos around petroleum reservoirs as is found around porphyry copper deposits, epithermal gold deposits, buried geothermal systems, and barren pyritic bodies. Sometimes, the low contrast base metal association in the halo can be somewhat indicative of the composition of the source. Oxidation anomalies can form above reduced bodies that are covered by either overburden or barren rock. The depth of detection for oxidation anomalies is often too great for the mineralized body to be of economic interest. In arid climates, anomaly-to-background ratios for the oxidation suite commonly range between 5:1 to 50:1, and sometimes anomaly contrast exceeds 100-times background. Oxidation anomalies tend to have more subdued contrasts in humid climates.

Apical anomalies detected with the Enzyme Leach occur directly over the source of the anomaly rather than forming a halo around the source. Often these anomalies appear to form as the result of diffusion of trace elements away from a highly concentrated source. That source can be the actual source of the anomalous trace elements, or it can be a structure such as a fault that facilitates the movement of trace elements to the surface. Simple apical anomalies that lie directly over a buried mineral deposit will not show dramatic halogen contrast, as is typically found with oxidation anomalies. A fault-related anomaly will occur almost directly over the subcrop of the fault. The suite of trace elements represented in the anomaly will often be indicative of the chemical composition of the ultimate source of those trace elements. However, where a deeply buried reduced body is intersected by a fault, an oxidation suite of elements, including one or more halogens, can form an extremely-high-contrast anomaly directly over the trace of the buried fault. Otherwise, apical anomalies usually exhibit a diminished contrast above background, compared to oxidation anomalies. Fault-related anomalies commonly contain very-high-contrast concentrations of zirconium and other supposedly "immobile" elements.

Sample Collection

Although the Enzyme Leach can be used as a partial-analysis method for virtually any surficial geological material, the sample media most commonly analyzed with this method is *B*-horizon soils. Research to date indicates that amorphous MnO_2 in soils is most abundant in the *B* horizon.

This horizon is the most chemically active part of the soil, with regard to the formation of oxide coatings on mineral grains. Studies in both arid and humid climates indicate that the sampler should be careful to collect soil samples from the *B* horizon.

The following information is based on observations from studies in glacially-buried terrain in northern Minnesota and Canada, desert pediments in Nevada, areas of extensive overburden in South America, test sites in the Colorado Front Range, and over oil fields in western Wyoming and southeastern Texas. Soil horizons vary in appearance and depth, even within relatively small areas. It should be emphasized that the samplers should be collecting material from a consistent soil horizon, rather than a consistent depth. Samplers should be encouraged to expose the soil profile whenever they encounter soil zoning that varies from previous observations. Before beginning, it is a good idea to observe soils profiles in ditches and trenches in and near the area to be sampled. The best potential sample sites are those that appear to be undisturbed and that have mature vegetation growing on and around the site. Samples collected from trenches and pit cuts are also good, as long as a fresh surface is scraped on the face of the soil profile to be sure that you are collecting freshly exposed material. Ditch banks, on the side away from infrequently used roads, under most circumstances can also be good sample sites, after scraping the bank to expose fresh material. The sampler should observe the conditions at such sites and make a judgement about the potential for contamination or of excessive disturbance. Road fill (new or old) is not usable sample material. Also, roads are often contaminated with a variety of pollutants that can linger for centuries. Plowed fields can provide usable samples, if an undisturbed site is not available. It is better to move a sample site a relatively short distance rather than to use a bad site just because it is at the specified spot.

Desert-Pediment Soils. There is an adage to the effect that desert soils are not zoned (azonal). In many cases this is not true. The appearance of the horizons is different from soils in humid climates, but they are still frequently zoned. The current surface on many desert pediments is more than one million years old, which is more than sufficient time for soil horizons to develop. Relatively little organic matter is found in *A*-horizon soils in desert climates. The *A* horizon is typically a light-gray to light-grayish-tan, loose, fine sand to silt. Descending through the soil profile, the *B* horizon begins where the soil is more cemented and slightly darker in color, often becoming slightly more brown than the overlying loose material. The brown color often becomes darker farther down into the *B* horizon, but in other cases, the color difference between the *A* and *B* horizons is almost imperceptible. Where the color changes are minimal, a key criteria is that the cementing of the grains in the *B* horizon often produces a weak blocky fracture that is absent in the *A* horizon. In areas that have a history of previous mining activity, the upper centimeter of the *A* horizon can be highly contaminated with many trace elements. Rarer elements, such as gold, can be enriched by as much as 10- to 100-times background. The *A* horizon should be scraped from the area around the spot to be sampled for a radius large enough to prevent this contaminated material from trickling into the sample material. In areas of extreme aridity, such as the Atacama desert of South America, the sampler often will not find soil horizons. At most locations in that region the best level to sample is 25 cm to 40 cm beneath the surface. All the Enzyme Leach studies performed to date have used *B*-horizon soils collected above the caliche layer. Do not sample from the caliche layer or immediately beneath it. Caliche will produce extremely erratic Enzyme Leach data. Where caliche comes too close to the surface to collect a sample, move the sample site a short distance or abandon it. In the Atacama desert a reddish layer will often be encountered just above the caliche layer. This reddish color results from selenite that has formed in the soil. The presence of granular selenite in the soil does not detract from the results.

Humid Climate Soils. Sample sites with the best developed soil horizons are usually found in groves of trees. In northern climates, aspen groves are the best. The *A* horizon consists of an upper humus layer, a dark layer of mixed organic and mineral matter, and there may be a bleached mineral layer at the bottom. The bleached layer results from the reducing action of the overlying organic-rich layers, which dissolves oxide coatings on mineral grains. The top of the *B* horizon is the point below which there is no organic matter and where oxide coatings are found on mineral grains. Iron oxide coatings typically give *B*-horizon soils colors that are some shade of brown or red (dark brown, medium brown, light brown, brick red, tan, orange, etc.). Where the *A* horizon is quite thick, such as around bogs, there is often a faintly gray layer beneath the bleached layer of the *A* horizon. The faint gray color is due to manganese oxides, and this material is usable *B* horizon, if a darker colored *B*-horizon layer is not available. In a humid, forested area all the material comprising the *A* horizon of the soil (decaying leaf litter, humus, and organic-rich mineral layers) should be scraped away to reveal the *B* horizon. The sample is collected from 10 to 30 centimeters into the top of the *B* horizon. *A*-horizon contamination of *B*-horizon samples should be avoided as much as possible.

Mountain Soils and Glacially Scoured Terrain. Due to the rapid rate of mechanical weathering in mountainous areas, there are localities where the soil is truly azonal. Also, during Pleistocene glaciation, the regolith was completely removed in many areas and a chemically mature soil profile has not had sufficient time to redevelop. In such cases the sampler should dig deep enough to obtain soil material that is as free of organic matter as possible.

Sample Handling

Samples should consist of about 100 to 200 grams of material depending on the fineness of the soil. Coarser soils require more material to assure adequate sieved sample material for analysis. If at all possible, the sample should be air dried. If circumstances require the use of a drying oven, the temperature should not exceed 40°C, and the drying time should not be longer than is necessary to dry the sample. Too high a drying temperature alters the chemistry of the amorphous manganese dioxide coatings and drives out the volatile halogens and halide compounds. If in doubt, let the laboratory perform the sample preparation. They know which sieve sizes to use, and what steps must be followed to maintain the geochemical integrity of the sample material. Pulverized samples and samples that have been "cooked" are not suitable for analysis with the Enzyme Leach.

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Neutron activation analysis in the tropics - the role of total analyses

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Keywords: Neutron activation analysis, pan concentrates, gold, multi-element geochemistry, stream sediment sampling

Introduction

Large areas of the tropics have been subjected to deep weathering which has removed most of the mobile elements from the regolith, and only the more resistant minerals are preserved. Minerals that are resistant to weathering can also be resistant to dissolution in the laboratory, and it will only be possible to recognise their geochemical signatures with confidence if appropriate analytical schemes are adopted. Gedeon et al (1977) found that when lateritic samples from Western Australia were analysed by a variety of acid digests, both perchloric and nitric/perchloric digests left residues which could contain goethite, haematite, serpentine, talc, muscovite, chromite and other minerals, depending on the starting material. Acid digests which included hydrofluoric acid proved to be more successful but they were still incapable of dissolving all minerals in the test samples. Neutron activation analysis (NAA) does not require sample dissolution and provides total analyses, even for highly refractory samples. As such it is well suited to analysis of samples from the tropics, either in combination with other methods of analysis or as a stand-alone technique.

Neutron activation analysis in combination with other methods

While Gedeon et al (1977) were interested primarily in achieving total analyses, an alternative approach is to compare results from a total analysis technique such as NAA with analyses on the same samples by another method where extraction of elements may not be total. The differences between the two sets of data may yield useful information which is not apparent from either if viewed in isolation. Figure 1 shows the result of such an exercise where soil samples were analysed both by NAA and by ICP-OES using an aqua regia/perchloric/hydrofluoric attack. This is often referred to as a 'total acid digest' but it will not dissolve all minerals, and elements such as Ba,Cr,Hf,Nb,Sn,Ta,Te,Ti,V,W,Y and Zr may be undervalued. In this case NAA invariably reported higher chromium content than was measured by acid digest/ICP-OES analysis. The most plausible explanation for this would be that the acid attack was not dissolving any chromite in the samples and the differences between the two sets of values could then be taken as a measure of the chromite content of those samples. Such information may be useful in, for example, platinum exploration, since there is often a close association between platinum group elements and chromite.

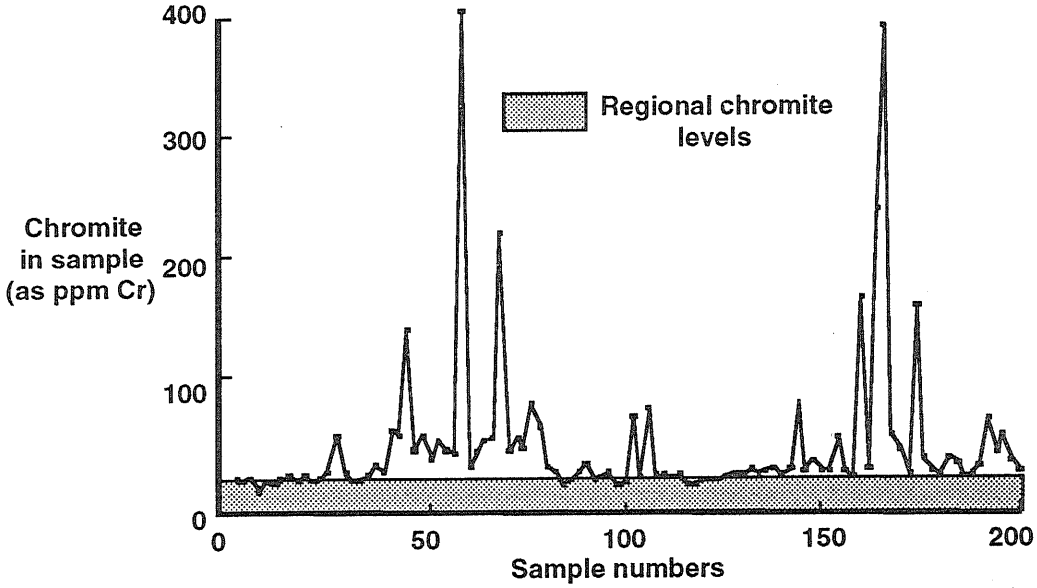

Fig.1. Estimated relative chromite contents of soil samples from Papua New Guinea, derived by plotting the amount by which NAA total chromium values exceeded ICP-OES acid-soluble chromium values for each sample.

Neutron activation analysis as a stand-alone technique

If the regolith in the tropics is deeply weathered and contains a large proportion of resistant minerals then stream sediments derived from weathering of such material are likely to contain an even higher amount of refractory material. Heavy mineral concentrates derived from these stream sediments are likely to be even more resistant. Such concentrates are often analysed for gold alone by fire assay. Alternatively they may be subjected to a partial extraction, using an aqua regia leach, which allows determination of both free gold in the sample and also a range of other elements, so long as they are not occluded by silicates or other resistant minerals.

Since NAA delivers a total multi-element analysis regardless of mineralogy it offers a viable alternative to these techniques, and may highlight element associations which had not been anticipated at the start of the survey. Figure 2 summarises element associations in pan concentrates collected in the region of an epithermal gold deposit. Gold is shown to be more closely correlated with barium than with the more usual pathfinder elements such as antimony or arsenic, perhaps because barium was present as detrital baryte while antimony and arsenic were not preferentially concentrated into the heavy mineral fraction. Baryte is difficult to dissolve and a total analysis by NAA is therefore more likely to detect this relationship.

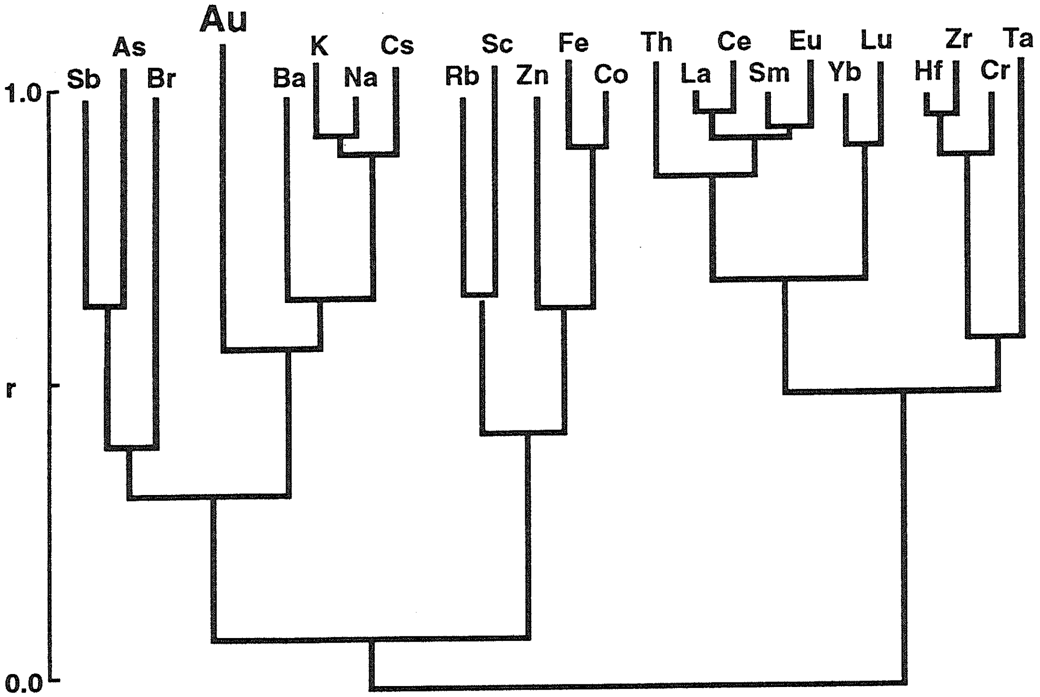

Fig. 2. Element associations in pan concentrates from an epithermal gold region, Papua New Guinea (Garnett and Waldron, 1991). r = Spearman rank correlation coefficient.

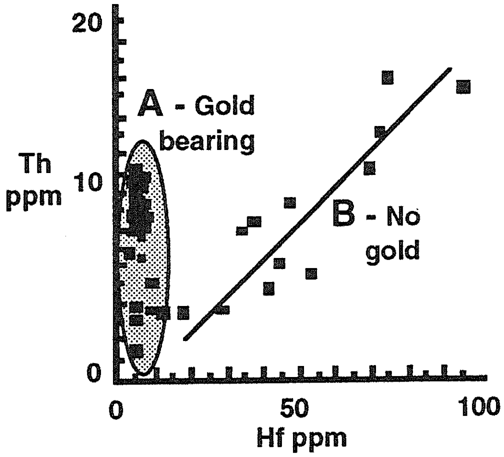

Fig. 3. Hafnium / thorium patterns for the same data as Fig. 2. Group A is dominated by samples with elevated gold values, trend B is dominated by samples with no detectable gold.

Hafnium and thorium, from the same data set which formed the basis for Fig. 2, provide a further example of the value of a total analysis (Fig. 3). Two groups of samples can be recognised.

Samples containing no gold (trend B) show a strong hafnium/thorium correlation which probably reflects presence of variable amounts of zircon in the samples. In contrast the gold-bearing samples (group A) contain little hafnium and, given the close association shown in Fig.2 between thorium and the rare earth elements (REE), it is possible that the thorium is present in a mineral such as monazite. Such differences in mineralogy may be important in that they can give clues to the nature of the source rocks associated with the mineralisation. Both monazite and zircon are resistant to acid digests and a total analysis by NAA offers the greatest certainty of recognising such patterns.

The refractory nature of zircon can also be exploited in order to provide a more realistic ranking of gold anomalies in stream sediments. Gatehouse (1990) argued that since hafnium is always present in zircon it can be used as a measure of the zircon content of a sample. This in turn provides an independent measure of hydraulic activity at a sample site: increase in hafnium in a sample can be taken to reflect a higher energy environment which therefore also has a greater potential for concentration of gold. Thus, absolute amounts of gold in a sample need not be taken as the sole criterion for anomaly definition, and a high gold:hafnium ratio can also be considered to be favourable (Fig.4). Fletcher and Day (1989) found considerable variation in gold content of heavy mineral concentrates between high and low energy environments, while Fletcher and Wolcott (1991) showed that gold was only transported under certain hydraulic conditions. Any measure of hydraulic activity at the sample site must be of value and the ability of NAA to analyse both gold and refractory minerals such as zircons in the same sample provides one possible means of doing this. Equally clearly such relationships should not be viewed too simplistically since variations in hafnium content of sediments can also be the result of variations in the geochemistry of source rocks in different catchment areas.

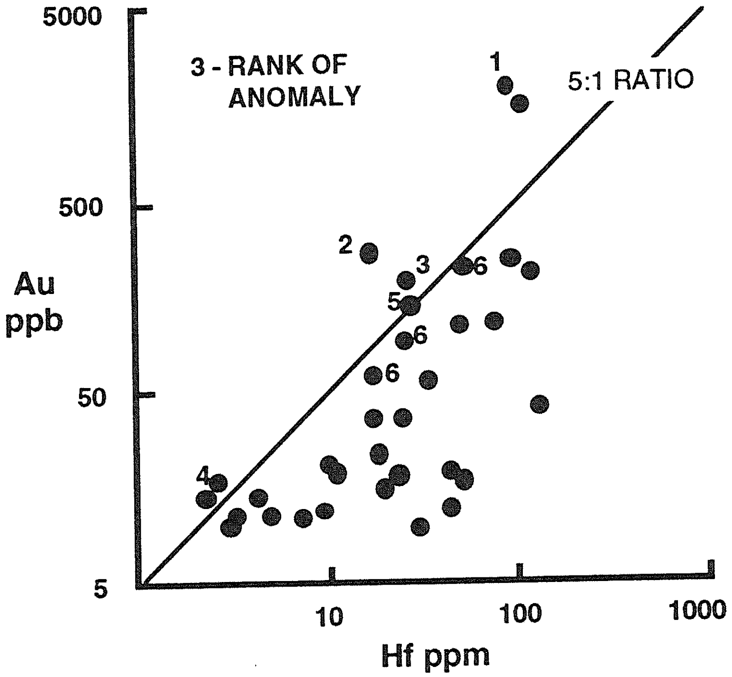

Fig. 4. Gold / hafnium interrelationships in -200 mesh Tasmanian drainage sediments. After Gatehouse (1990). Hafnium, in zircons, is used as an independent measure of hydraulic activity and gold anomalies are ranked taking this into account. The result of this is that sample sites in low-energy environments, with consequent low potential for gold concentration, may still be ranked as a higher priority than higher energy sample sites if their Au:Hf ratios are higher. For example, the anomaly ranked 4, above, is rated as being more important than anomalies ranked 6, even though the latter represent samples with up to ten times the amount of gold in them.

Discussion

Total and partial analyses need not be mutually exclusive. Just as partial extractions can be used to measure loosely bound elements dispersed in solution, or even in a gaseous form, so total analyses can be effective in identifying resistant minerals that have been preserved in deeply weathered tropical profiles or have been dispersed mechanically. Some of these may be of direct economic interest e.g. gold, wolframite, osmiridium, while others may be associated with mineralisation e.g. chromite, baryte. Many more, such as apatite, garnet, zircon, monazite, have the potential to reflect changes in geology which may be valuable in helping to understand the regional setting of mineralisation. The choice of analytical technique comes down to the specific needs of the exploration program, and a combination of both total and partial analyses may well provide a large body of useful, cost-effective information.

Acknowledgement

Placer Pacific are thanked for making available the data originally quoted in Garnett and Waldron (1991).

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Groundwater Geochemistry In Australia - An Exploration Window To Concealed Ore Deposits

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Keywords: groundwaters, exploration, gold, base-metals, Australia

Many areas of Australia have been repeatedly explored for the same metallic ores throughout the last half century. For successful new discoveries, the mining industry will need to explore deeper into the earth in its search for ores. Such deposits are likely to be too deep to be sensed by traditional surface geochemical and/or geophysical exploration technologies. Hence the role of groundwaters as geochemical samples of deeper zones that may contain concealed ore deposits.

The exploration value of all aqueous geochemical samples derives from their reactivity with rocks and soils, and their physical mobility. Products of these reactions in groundwaters therefore reflect the geochemistry of extensive rock volumes that represent a much greater proportion of local lithologies than do conventional solid samples. Groundwaters are also relatively easy to sample, and modern analytical techniques, with low detection limits, provide a sensitive geochemical description of concealed rocks that have contacted the groundwater. Experience gained through CSIRO-industry collaborative research has also produced logistically feasible methods for groundwater sampling within Australian field exploration programs, appropriate analytical procedures and interpretation techniques based on observations at established deposits, theoretical solution chemical models and multivariate statistical methods of data handling .

The overall package is becoming a cost-effective robust addition to the exploration armoury that is timely for an industry in which only 1 in 1000 exploration prospects currently develop into major mines. Exploration successes are not only new mines. Reduced expenditure on the other 999 represents a huge potential cost saving to the mining industry.

Groundwater constituents that can be used as exploration indicators.

1. *For base metal deposits* - groundwater acidity, content of reduced iron, high concentrations of sulfate compared to other anions and base metal abundances assessed in terms of a locally relevant solubility model, can all constitute valid indicators of mineralization.
2. *For gold deposits* - groundwater concentrations of gold and associated trace elements such as As, Sb, Bi and Cu.
3. *For deposits targeted on the basis of a specific host lithology or alteration system* - elements generically associated with the host. These provide groundwater signatures diagnostic of proximity to giant systems in which mineralization is potentially amenable to deep mining. Application of this technology should open new exploration opportunities within and beyond the concealed margins of established major mineral provinces. Examples include mafic hosts that are identified by groundwaters with high relative concentrations of Mg and locally anomalous Ni, Co and Cr, zones of potassic alteration in which groundwaters contain enhanced concentrations of Rb, Cs and locally increased K/Na ratios.
4. *For deposits hosted by sub-surface extensions of mineralized blocks beneath the margins of adjacent sedimentary basins* - the contrast between the major element (Ca, Mg, Na, K, Cl, SO_4 and total carbonate) compositions of basin groundwaters and those from the target crystalline basement.

Appropriate analytical techniques

Two stages of analysis are required, immediate field measurements at the sample site for parameters that are unstable when the sample is removed from the natural environment, and subsequent laboratory analyses that are sufficiently robust to handle waters of widely varying salinities.

Useful field parameters are pH, relative redox potential, salinity(conductivity), dissolved O_2, reduced Fe and temperature. These contribute to assessments of proximity of sample sites to : chemically reducing environments where base metal sulfides would be preserved;, chemically oxidizing environments with evidence of present day sulfide oxidation; field evidence for aquifer variation and locations of high heat flow. In addition, pH and redox potential measurements are important in assessing what values of trace elements are indicative of the presence of potentially economic mineral sources of these elements. This is a major difference between solids and waters as geochemical exploration samples. Interpretations of waters must take account of the constraints of solution chemistry on the solubility of the least soluble solid containing that constituent. By contrast solid samples have no ceiling on constituent concentrations and statistical appraisals are appropriate.

Important requisites for field measurement equipment are - portability, robustness, ease of maintenance and capacity for rapid measurements with adequate precision and accuracy. Several good multi-parameter water testing sets are commercially available for pH, conductivity(salinity), dissolved oxygen and temperature and experience has proved the Horiba U7 to be reliable. For Eh, combined redox probes based on Pt, Ag-AgCl couples are also available that can be used with portable pH meters. In the long term separate Pt and reference electrodes, the latter being a glass refillable type rather than the commonly available gel filled epoxy body type, will be more cost-effective. Reduced Fe is easily determined using a simple colour comparison with standard abundances of FeII reacted with 2-2' dipyridyl.

For a laboratory analytical technique to be appropriate for assessing groundwaters as geochemical exploration media, it needs to - be able to provide high quality data at appropriate levels of precision and accuracy, be able to process large numbers of samples with a speedy throughput to interact with exploration field planning, provide detection limits that relate to solubilities of solids that control solution concentrations and be cost effective in the context of the overall exploration program. Advances over recent years in technologies that fulfil these criteria have prompted the wider use of groundwater geochemistry in mineral exploration among those explorers who keep up with such developments.

The CSIRO-industry collaboration has considered a wide range of groundwater constituents as potential exploration indicators. Similarly, a specific exploration program should make a preliminary orientation study involving a similar range of variables. From them a subset of the variables that are sensitive to the ore target can be selected for the bulk of the program.

Results from the CSIRO-industry collaborations have demonstrated that the following analytical protocol is effective using the direct sample, centrifuged if necessary to remove suspended material -

- ICP-AES analyses of the major cations and Al, B, Ba, Be, Fe, Li, Mn, P, S, Sr, Sc, Si, Ti, V, Zn.
- ion chromatography for Cl analyses,
- specific ion analysis for F,
- a procedure for As in which it is converted to a hydride prior to quartz furnace AA analysis,
- total carbonate analyses using an instrument that releases all carbonate species as CO_2 into a cell where its concentration is measured from changes in thermal conductivity.

Additionally, ICP-MS analyses are made for a series of trace elements using an aliquot of the direct sample, acidified with ultra pure HNO_3 and diluted to a concentration of total salts suitable for ICP-MS instruments. Determinations of Cu, Cd, Co, Cr, Ni, Pb, Rb, Cs, Mo, U, La, Y, Th, Tl, Yb, Ga and Ge are calibrated with a mixed standard. Other elements, Ag, W, Hg, Zr and Sb, are unable to be included in the mixed standard due to solubility incompatibilities. These are determined using a semi-quantitative ICP-MS technique based on internal spikes of In and Lu.. A separate mixed standard allows a full set of rare earths to be determined when required. Measurements of Pb and Ni are sometimes unsatisfactory and are checked using electrochemical methods. Analytical quality is controlled by inclusion of standards as every 10th sample, and matrix effects by replicates of 5th, 15th etc samples spiked to 5ppb concentrations of appropriate standards.

Measurement of gold in groundwaters has been very successful using an analytical technique copied from the 'Carbon In Pulp' gold processing technology. In the field, immediately after collection, a 1 litre sample is dosed with lime (10g) and Na or KCN (1.2g) and a small nylon sachet containing approximately 1 g of activated charcoal. Back in the laboratory, after 8-10 hours on a bottle roller the sachet is recovered, washed in distilled water and the contents submitted for analysis of Au by Neutron activation analysis (NAA). Reagent blanks and extraction efficiency of the charcoal are checked by inclusion of a blank and a range of three standards in each batch. This procedure has allowed a groundwater detection limit of 1ng Au/l which readily allows identification of groundwaters that have contacted rocks or soils with anomalous Au concentrations.

Interpretation of groundwater geochemical exploration data.

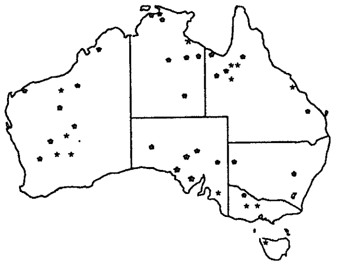
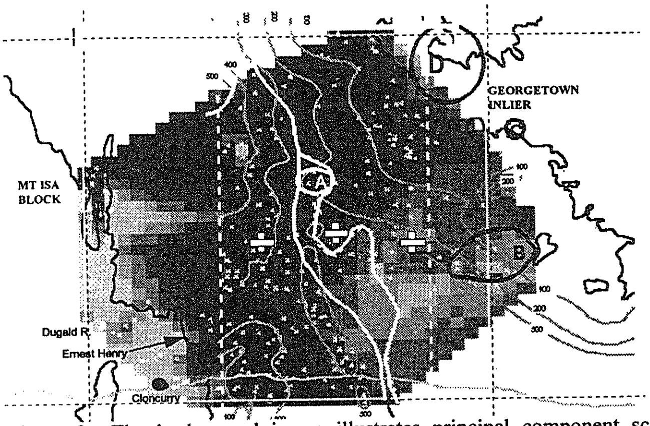


Figure 1 Locations of CSIRO-Industry groundwater geochemistry study areas.

Figure 1 is a map of study areas that illustrates the extent of data on Australian groundwaters generated by CSIRO-industry collaboration over the last 15 years. Coverage and quality of the data are variable depending on collection periods. For example, trace element data collected by ICP-AES 10 years ago, at detection limits of 50ppb, would lack the subtlety available today with the low detections available from ICP-MS, NAA and updated batch scale electrochemistry. Nevertheless the major element data are reliable throughout, and the following example illustrates its value.

The possibility that the margins of sedimentary basins, may overlie prospective extensions of adjacent mineralized blocks provides new exploration targets. This type of exploration target requires a technique that can identify basement lithologies at sufficiently shallow depths for associated ore-deposits to be mineable. The essence of this is a technique that can distinguish crystalline basement from basin sediments. Many examples have been recorded in CSIRO-industry studies of using the major element chemistry of groundwaters to reflect variation among aquifer lithologies in exploration leases.

In the example portrayed in Fig 2, major element compositions were recorded for more than four hundred groundwaters, from locations distributed across a region incorporating a portion of a large Mesozoic basin and the margins of adjacent Proterozoic basement blocks. The study was motivated by the possibilities of locating sub-surface extensions of the adjacent mineralized blocks and the existence of magnetic and gravity features that suggested the basement topography was far more structured than previous interpretations implied. The surface terrain to be explored comprised featureless Mesozoic sediments (depth varying from 0 - >300m.) with scattered and sparse outcrops of basement.



.Figure 2 The background image illustrates principal component scores derived from the concentrations of Ca, Mg, Na, SO_4 and HCO_3 for all samples. Increasing depth of shading depicts the transition from dominant Ca, Mg and SO_4 to dominant Na and HCO_3 groundwaters. White * - sample locations; white lines - geophysical boundaries; observed or inferred intrusions - A,B,C,D; and gravity highs - +.

Consideration of the Ca, Mg, Na, SO_4, HCO_3 content of each groundwater indicated that major ions in waters in the deep part of the basin were predominantly Na-HCO_3, whereas groundwaters from the adjacent mineralised blocks were predominantly Ca-Mg-SO_4. Variation between these extremes was clearly expressed by values of a principal component score derived from the concentrations of Ca, Mg, Na, SO_4 and HCO_3 for all samples. This score is then a variable that quantifies the contributions from each major lithology to the composition of each groundwater. The image illustrates a strong contrast between groundwaters located within the two adjacent basement blocks, and those of intervening basin sediments. Crystalline basement rocks are apparently better sources of Ca-Mg-SO_4 dominant groundwaters than are deep basin sediments. This contrast is illustrated in the image by clear depiction of basin margins coincident with the boundaries of the two blocks, and also at some locations within the basin that could reflect shallow basement concealed by basin sediments. In some cases these accord with sub-surface structures or basement variation previously identified by geophysics, in others they suggest concealed features not otherwise recorded. Because prospectivity will relate to depth of younger sedimentary cover, a next step will be to calibrate basement depths in terms of principal component scores.

Ore related trace elements were also determined for each sample and elevated levels of these enhance prospectivity of certain zones where they coincide with either groundwater or geophysical postulated basement highs. Elevated concentrations of other trace elements can be related to alteration processes or unusual lithologies. For example zones of elevated Cs coinciding with gravity anomalies suggest associated potassic alteration.

Groundwaters have great potential in Au exploration programs, due mainly to the very low concentrations of Au that can be detected. Different styles of Au mineralization are expressed in groundwaters by different combinations of groundwater variables. For example, applications of groundwater geochemistry to exploration for primary Au ores include the establishment of a groundwater geochemical signature for previously discovered deposits in the region. In addition to Au concentrations, the signature would be based on abundances of trace elements such as Mo, As, Cu, Rb and Ni, and major element relativities. If regional groundwaters are channelled into palaeodrainage systems, down-flow Au values (as illustrated in Fig. 3), can operate as geochemical drainage samples, in the same way as do stream sediments. In addition to known deposits indicated in Fig 3, one Au value suggests the presence of a presently unknown deposit.

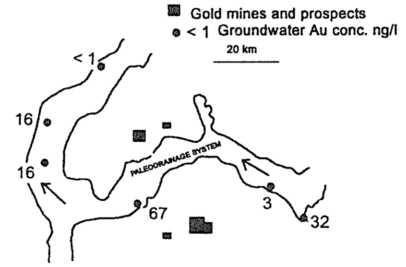


Figure 3 Concentrations of Au in groundwaters down-flow in a palaeodrainage channel.

Groundwaters can also detect secondary, placer or deep lead deposits of Au in palaeo-channels. These can be recognised in groundwaters by high concentrations of Au, but low concentrations of As and other trace elements that often accompany primary Au deposits. This style of deposit implies that Au is moved in solution or as very small particulates through the channel by traversing groundwaters. In exploration for this style of palaeochannel hosted deposits, important exploration indicators relate not so much to Au transportation but rather to locating sites of deposition. Deposition of a mineable Au deposit would require a change in channel chemistry that causes the Au to be immobilised. If this process is still occurring, deposition sites could be identified from local changes in groundwater chemistry. For example, applying similar groundwater interpretations, as were developed for roll front uranium deposits, reducing zones in the channel path could be prospective. These are recognised from groundwater indications of sulfides including high values of reduced Fe and increased groundwater acidity.

These are only a few examples among many, but they were chosen to emphasise the potential and special possibilities of groundwaters compared with other geochemical exploration media if high quality data is available. The most important point to emphasise is that it is essential to evaluate overall groundwater chemistry when interpreting results. Absolute abundances of single elements may be both misleading and meaningless.

CHIM Method
Revealing deep-seated deposits from quick ions in the Earth

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Keywords: aureoles, deep-seated deposits, CHIM, quick ions, jet migration

1. Revealing of deep-seated deposits is one of the critical issues of prospecting geochemistry. Prospecting by means of traditional geochemical methods is limited by thickness of overlying deposits of the first metres. At the same time, vast areas (approximately 6-70%) of the Earth's surface are overlain by cover deposits of hundreds or more metres thick. Significant means and time are spent to prospect such areas, including the cost of drilling deep wells.

2. New potential for prospecting deep-seated deposits are associated with the discovery of the phenomenon called long-range chemical jet migration of elements. These works were greatly contributed by Yu. Ryss, L. Antropova, Yu Saet, G. Vostroknutov, B. Sudov, N. Voroshilov. Above ore deposits, in places where they are overlain by later deposits of any lithological composition, including impermeable clayey sequences, for instance, cover effusives, which were earlier regarded as screens, soils and other surface formations are regulations and ubiquitously noted for shows of superimposed dispersion haloes of heavy metals including gold, other rare elements, corresponding to the composition of subsurfaces orebodies. The discovery of such aureoles made it possible to conduct from the surface geochemical prospecting of both ore deposits and oil fields if the thickness of overlying deposits reached hundreds of metres.

3. One of such methods registrating orebodies is the geoeletrochemical method CHIM. Distinguishing of aureoles from deposits in CHIM method is accomplished by means of electromobile occurrence forms of metals with their selective electrochemical extraction directly in the Earth. In surface deposits a constant electric field is created using a system of element-receivers operating as combined feeding and receiving electrodes installed along profiles or on area and other electrodes operating as an infinity.

   The regime in each point is set on the basis of field intensity, tone and time which ensure a selective extraction of electromobile occurrence forms of metals in element-receivers.

   Solutions from element-receivers are analysed for elements characterising the composition of presumed objects of prospecting.

4. Anomalous concentrations of electromobile occurrence forms of metals are characterised by certain specific features:

   - Anomalies of metals show up directly above the face of orebodies and occupy an area, corresponding to the projection of exposure of the orebody on the day surface.

   - Their position is independent of geological structure, lithological composition of rocks and tectonics.

   - Intensity of the anomalies of metals is independent of the occurrence depth of the orebody.

- Concentration of mobile forms of metal occurrence is quite low. Preliminary calculations enable to evaluate their concentration as being four or five orders below the clark (total bulk concentration of metals in rocks).

Such specific features of shows of metal anomalies above deep-seated orebodies point to unusual properties of mobile occurrence forms of metals migrating from orebodies to the surface at such a low level of concentration.

5. As far back as 1926 V.I. Vernadsky was the first to presume, that elements in a dispersed state has high movement velocities at low levels of concentration. Theoretically this assumption ensues from, the probability theory on the basis of which Maxwell deduced the law of molecule distribution based on velocities for gases. Maxwell's distribution curves for molecules based on velocities have a clearly expressed maximum, are symmetrical, i.e. shifted towards high velocities.

A similar distribution of gas particles in terms of velocities was obtained by Boltsman. He considered the non-equilibrium state of the system. Inthe process of equilibration such as gas, due to collisions of molecules, by itself passes into the state with Maxwellian distribution.

The process of attaining equilibrium by means of mass transfer from one part of the system to the other, resulting from thermal motion of particles (molecules, atoms, ions etc.), was considered by Finn and received the name of diffusion. As is known, the diffusion equation holds true for the behaviours of particles both in gases, and in liquids. However, commonly, when the motion of particle sin liquid is assessed, only average velocities are considered.

The law, following which the system attains equilibrium according to Finn's equation looks as follows:

$$d\ Ci/dt = -\ D\ d^2Ci/dL^2.$$

where Ci is concentration of i component; t, time; L, distance, D, diffusion factor. The solution of this equation for one of the simplest cases, i.e. diffusion of matter from a thin layer with the constant concentration into an infinite half-space looks as follows:

$$Ci/Co = 1 - efr\ (1/2\ {}^{L}/\ V\triangleleft t)$$

From this equation mean velocities of components (V_m) can be determined by differentiating Ci/Co =f(t) dependence in time and changing to coordinate to V_m) = Lo /t. The graphic analysis of this equation shows, that the curve has an asymmetric character, the predominant share of components has the velocity corresponding to the mean one. To the right of the mean velocity there is an area of quick ions. Their share is markedly reduced with increasing velocity. As compared to ions which have the mean velocity, the amount of ions moving with the velocity which is five times higher is an order less, than that of the first ones, whereas the number of ions moving with the velocity 10 times higher is 30 times less. No value of the maximum attainable movement velocity of components in the solution is deduced from the equation. Theoretically, it can reach the free path velocity. However, their share should be negligible.

6. Experimental research conducted under laboratory conditions on diffusion and electromigration of copper and uranium ions confirmed the existence of quick ions in heterogeneous media and the possibility of their registration. Particularly,

the curve showing distribution of uranium ions in experiments on electromigration within the velocity range from 0.5 cm/h (mean velocity) to 12 cm /h was obtained. The recorded motion velocity of quick ions in this particular case exceeds the mean value 24 times.

8. "Quick ions" in the Earth are highly informative and can be used not only for solving prospecting tasks, but also to study the processes connected with earthquakes, for solving different environmental problems and other natural phenomena.

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Geoelectrochemical Systems within the Earth - Their Geological and Exploration Significance

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Keywords: geoelectrochemical systems, mobilisation, deposits,
prediction, prospecting estimation

A. The formation of an ore deposit requires a process (or processes) which convert the ore material from a disseminated state to a more concentrated form. This transition may be described as a dynamic process of compressing the "ore atmosphere". This means that if the basic elements of the lithosphere (O,Si,Al,Ca,Mg,Na,K,C) are considered solvents, then the heavy metals ("ore material"),which are present in rocks as admixtures, may be considered dissolved substances. From the point of view of general thermodynamics such an admixture may be regarded as a quasi-gas and will exhibit properties of compression and tension.

B. Compression of the "ore atmosphere" is realised only at energy expenditures and is manifested in the form of work. The greater the work:

- the greater the mass of concentrated metal
- the higher the tension degree of the "ore atmosphere" presented by the metal.

C. The processes of compression/expansion is a polar one which must exist within the limits of a volume which is conceptually separated from a specific space (which corresponds to a thermodynamic system.) The space, which is external to the system is characterised as environment. The ability to do the work by the system above the environment (medium) or by the environment above the system is determined through potentials. Clearly, when the potentials are equal, i.e. at the equality of the outer action and inner counteraction, the possibility of processes proceeding within the system is excluded.

D. Conventional thinking in relation to the formation of ore deposits considers three forms of energy: thermal, mechanical and chemical.

However it is known that within the earth, as within any thermodynamic system (q.v. first law of thermodynamics), other forms of electromagnetic energy also exist. These are generally not taken into account when considering the formation of metallic mineral deposits.

E. A wide spectrum of electrical energy forms has been revealed within the earth, and they manifest themselves as fields associated with both regional and local sources. From the viewpoint of concentrating minerals static electrical fields are of most interest. The sources of these vary:

- the flow of natural waters (surface and ground): filtration electrical fields;

- the contact of media interfaces: diffusion-absorption electrical fields associated with sulphides, graphitic formations and galvanic electrical fields.

The depth at which these sources of electrical fields occur can vary enormously from the surface down, and the duration of their existence may be extensive (equivalent to geological periods). The energy they generate is comparable to other energy forms.

F. Within these electrical fields a geoelectrochemical system originates and together with the electrical parameters (potential gradient) this system is characterised by definite thermodynamic attributes - thermal, mechanical and chemical.

G. Within the limits of such systems, under the action of the energies mentioned, including electrical,the electrochemical extraction of ore elements, their polar redistribution and generation of the regions of compression (ore substance concentration) and regions of depletion of these metals are achieved. It was stated experimentally that the degree of electrochemical extraction ( ) of elements from rocks (the relation of the mass of the element extracted to the mass of this element within the original rock) is inversely proportional to their concentration.This relation accounts for obtaining higher concentrations of ore elements during their extraction. At the same time other (deep seated) sources of metals are not excluded at substance geoelectrochemical mobilisation.

H. The redistribution of components, ore elements included, within the system and their concentration is accompanied by the physical and chemical transformation of geological medium. These changes are monitored by special methods of analysis as well as on the basis of known data (materials) processed by special methods.

I. Between the dimensions of geoelectrochemical systems and concentration of metals, direct quantative dependencies have been revealed. They enable, on the basis of theoretical and experimentally proven data, to give the quantitative estimation of ore objects of corresponding ranks. Prospecting for deposits is carried out by means of subsequent compression of the prospective area over several stages, for the purpose of isolating targets of various ranks within the system (ore provinces, ore regions, ore deposits and then individual ore bodies).

J. Depending on the increase of electrical energy sources and geological formation of the area, the structure of electrochemical systems might grow, as will the contents of various cations in zones of concentration. The overall view of geoelectrochemical structures, considering dipoles, bipoles and tetrapoles, as applied to gold ore targets, and models of such formations, can be seen on fig.1.

Electrical observation for gold has found a polar Au zone, as well as elements in the iron group (Ni, Co, Cu, Mu, Cr). Reasons for these connections require special discussion.

K. Application of geoelectrochemical exploration procedures is rapid and does not require highly sophisticated (and hence expensive) technologies.

Large exploration tenements can be quickly appraised leading to the early recognition of prospective targets, whose size, composition and location can be estimated. By minimising the need for more expensive and time-consuming procedures in early exploration, and by optimising their application in later phases, geoelectrochemical exploration techniques have a wide sphere of application in all geological environments.

The implementation of the ISGS strategy involves a complex of new Geoelectrochemical methods such as CHIM, MPF,TMGM etc. as well as conventional geochemical and geophysical methods with interpretations based on conceptions of geoelectrochemical systems.

L. The most effective implementation of the ISGS strategy is achieved through consistent exploration over several stages. This considerably reduced the chance of mistake in choice of area for exploration. The aims of procedures to reduce exploration from regional to local follows.

(i) **Initial Prediction Stage**

After choosing the area for prediction, the minimum amount of geological information is used. Special methods of geoelectrochemical analysis are used to determine the distribution of heavy metals and some other elements in surface deposits and an analysis of fine changes in the structure of physical fields on the basis of the available geophysical evidence is conducted.

(ii) **Further Prospecting Stages**

In addition to the ones mentioned above, but on a scale corresponding to the deposits, specific geological settings can be supplemented with other data.

(iii) **Final Stage of Evaluation**

Results of observation on the basis of special geoelectrochemical methods, including CHIM, are used to localise an ore deposit.

Distribution of gold in drill-hole water around disseminated gold deposits in northern Nevada—a potential exploration tool for buried deposits

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Keywords: gold, ground water, drill holes, Nevada

Ground-water samples were collected from drill holes near the Lone Tree, Pinson, Summer Camp, and Twin Creeks disseminated gold deposits in northern Nevada (fig. 1) to study the distribution and mobility of gold and ore-associated elements such as arsenic, antimony, and tungsten. The gold in these deposits is hosted primarily in siliciclastic sediments, volcanics, and limestones of Upper Cambrian and Lower Ordovician age (Kretschmer, 1984; Parratt et al., 1989) and generally occurs as submicron-size particles of native gold. Other minerals often present with these Carlin-type gold deposits include orpiment, realgar, and stibnite.

Ground-water samples were collected during active drilling and from exploration drill holes several years old. The samples from the new drill holes were taken from reverse-circulation rotary drill rigs at 40- to 100-ft intervals during drill-pipe changes immediately after water in the drill hole had been purged. No drilling mud was used in any of the drill holes sampled and little, if any, injection water was added. The water samples from the older drill holes were collected at and below the water table using a custom-built double-check-valve bailer with a maximum volume of 1.25 L. The bailer was manually lowered into the drill holes using nylon cord to sampling depths as great as 550 ft below the ground surface. The check-valve system of the bailer enabled water samples to be trapped and retrieved from any desired depth below the water table.

The samples were analyzed for several constituents including gold at the 1-part-per-trillion (ppt) level using anion-exchange, graphite-furnace atomic-absorption spectrometry (McHugh, 1986). The relative redox potential of the ground-water samples was approximated by determining the concentrations of the arsenic species, arsenite [As(III)] and arsenate [As(V)], using ion-exchange, graphite-furnace atomic-absorption spectrometry (Ficklin, 1983).

Background concentrations for gold in the ground water up-gradient from the buried deposits was less than 1 ppt; near the deposits, the gold values ranged from 6 to 400 ppt; and in drill holes penetrating mineralized rock, concentrations of gold in the ground water were as high as 4,700 ppt. Highest concentrations of gold were found in ground-water samples where the relative concentrations of arsenic species indicated oxidizing redox potentials. Similarly, arsenic, antimony, and tungsten concentrations in the ground water near the deposits were significantly enriched relative to concentrations in the ground water up-gradient from the deposits. In general, however, the highest concentrations of arsenic, antimony, and tungsten were found in ground-water samples where the distribution of arsenic species indicated reducing conditions.

Results of this study demonstrate that gold is being mobilized from the concealed disseminated gold deposits in this area of Nevada and is being dispersed into the local ground-water systems. The pH of the ground water in this area is neutral to alkaline and does not appear to have a controlling influence on the hydromorphic mobilities of ore-related metals. However, the redox potential of the ground water near the buried deposits appears to affect mobilities. Significant mobilization of gold was found under oxidizing conditions, whereas mobilization of antimony and arsenic was generally enhanced under reducing conditions. The resulting hydromorphic dispersion anomalies (in a "down-gradient" direction) of gold and ore-related elements in the ground-water systems associated with these gold deposits present a much larger drilling target than the mineralized bedrock source. Results of this study illustrate the potential use of drill-hole hydrogeochemistry as an exploration tool for concealed disseminated gold deposits in this part of Nevada and in similar environments.

Acknowledgments

The authors extend appreciation to FirstMiss Gold Inc., Pinson Mining Co., and Santa Fe Pacific Gold Corp. for permission to sample water from drill holes and for sharing their time, expertise, and drill-hole logs. We are grateful to A.L. Meier and M. Malcolm of the Branch of Geochemistry, U.S. Geological Survey, for providing the ICP-MS analysis of the water samples.

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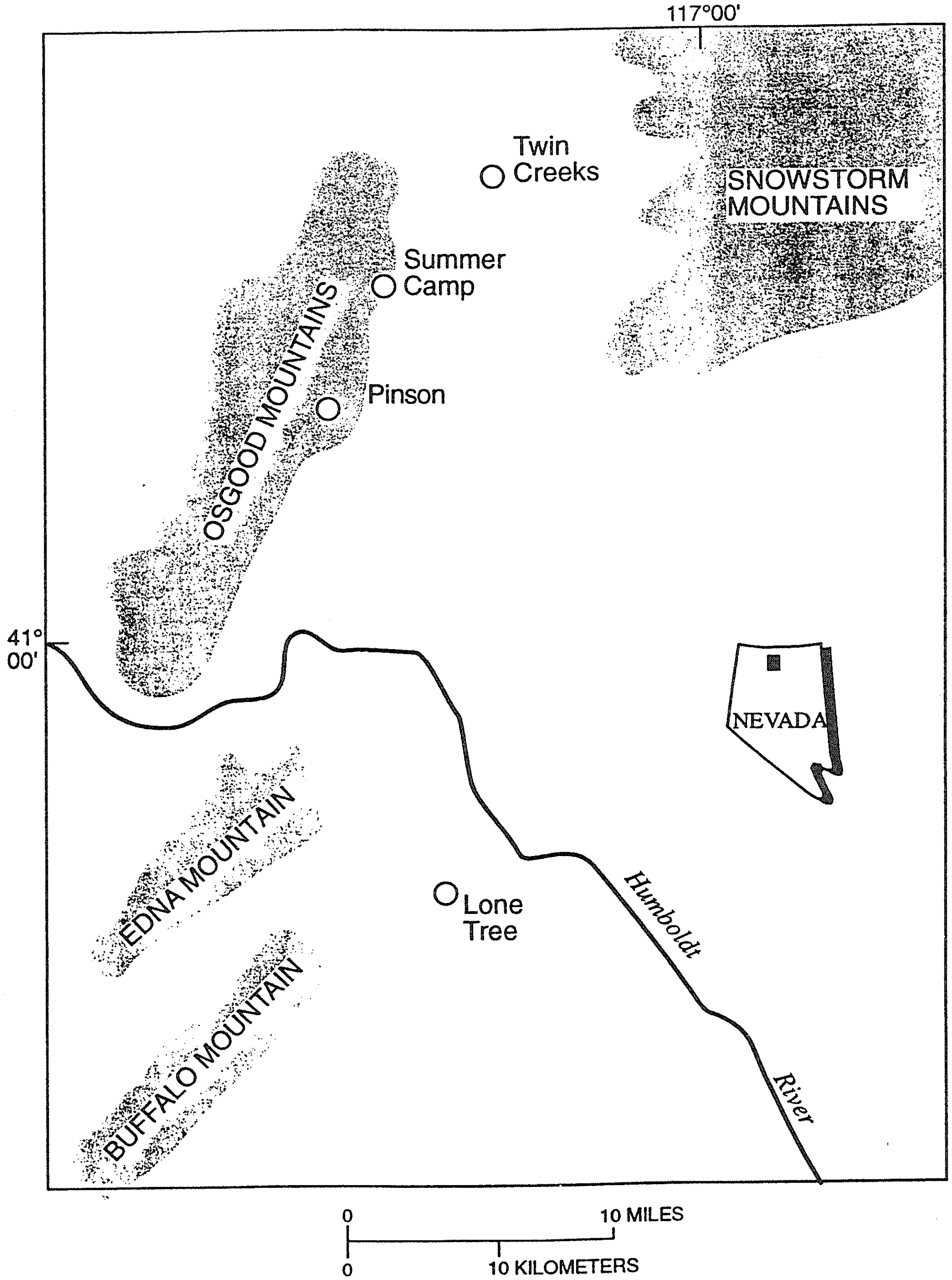
Figure 1. (Grimes and McHugh). Index map showing the location of the Lone Tree, Pinson, Summer Camp, and Twin Creeks disseminated gold deposits.



New progressive technologies for mineral exploration

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The discovery and successful exploitation of economic supergene deposits of metals requires the use of new technologies which involve multi-level investigations (e.g. geochemical, mineralogical), in conjunction with drilling, ore reserve estimation, and mining.

Gases

One of the new technologies involves the detection of gases associated with the mineralisation; a wide range of gases can be used for a variety of geochemical tasks. Gases of geochemical interest include mercury and halogen vapours, sulphur compounds, and radon. These gases diffuse rapidly and need to measured close to the surface to be of use. In the supergene zone of ore bodies, gases related to the oxidation of the ore minerals may also be formed. Thus, gases of different genesis and composition can be related to deposits during various stages in deposit evolution. Endogenous and exogenous gas aureoles around deposits can be used as highly sensitive geochemical indicators, and also for structural mapping.

Mercury

Mercury is an important indicator element for certain deposit styles and, unlike other indicator elements, forms not only lithogeochemical and hydrogeochemical haloes, but also atmochemical haloes, which can be detected using modern technology. Several forms of mercury compounds are generally present within ore bodies; these forms can be distinguished by the temperatures of thermal decomposition. Samples from the ore bodies and enclosing rocks are subjected to differential thermal analysis using an Atomic Fluorescence instrument "Flur-2". The following temperature intervals, representing the thermal decomposition of mercury-bearing compounds, can be clearly distinguished in thermograms:

1. 190-230°C
2. 260-280°C
3. 320-340°C
4. 400-440°C
5. 550-620°C.

This technique confirms the presence of a variety of mercury-bearing compounds in mineralized rocks.

Artificial Sorbents

The use of artificial sorbents for detecting mineralisation makes use of hydrogeochemical prospecting methods. Synthetic ion exchange resins, and other sorbents, are used to concentrate significant quantities of migrating elements in known chemical forms. The artificial sorbents fix the mobile forms of the elements being investigated; the concentration of some metals on the sorbents (e.g. Zn, Cu) can be several times the background values.

Phase Analysis

Studies of dispersed haloes around deeply buried ore deposits in tropical areas indicate that phase chemical analysis can be used for exploration purposes in these areas. Identifying the elements and phases associated with the deposits allows the identification of both mineralogical and geochemical haloes. In the haloes around copper deposits, the copper can occur in a variety of mineralogical forms, including as secondary sulphides, native copper, carbonates, halogens, oxides (± Fe), silicates, phosphates, and primary sulphides. Around deposits of nickel ore, nickel can occur as silicates, oxides (+ Fe), sulphides, and as water-soluble salts.

Fluorine and Chlorine

Geochemical exploration for gold mineralisation can be carried out using a variety of analytical methods for the determination of fluoride in stream waters, stream sediments, and soils. Experimental studies have shown that the fluoride adsorption capacity of soils depends on time, electrolytes, and the nature of the clay minerals. The use of neutron-activation methods to determine fluorine contents is advised.

Selective chloride ion electrodes are useful tools for determining water-leachable chloride in rock leach solutions; the procedure is simple, rapid and reliable. The electrodes operate well, even under the adverse conditions presented by turbid and gritty sample solutions.

Electrogeochemical methods

Attempts have been made to apply electrogeochemical methods to exploration for ore mineralization, using selective extraction techniques to isolate and analyze the mobile forms of the elements (Goldberg and Russ, 1978; Voroshilova, 1982). The techniques that have been used are briefly described below.

1. The MPF method, which is based on the extraction of metal-organic acid compounds from soils. Studies of the method have shown it can detect mineralization up to 500m below surface.

2. The thermomagnetic method (TMGM) uses secondary Fe and Mn complexes of the elements. The TMGM method is based on the selective extraction of bedrock related metals associated with Fe and Mn oxides and hydroxides. The TMGM method has been successfully applied in the exploration for polymetallic tungsten-gold mineralization beneath up to 100m of unconsolidated overburden, as well as for mineralization covered by up to 500m of bedrock.

3. The CHIM method involves partial extraction of the elements, and identifies haloes of the electromobile forms of elements in surface soils and rocks (Goldberg and Russ, 1978). The CHIM method is now being used in the exploration for a variety of deposits, including copper-nickel, gold, tin, and molybdenum deposits. It is used for locating deposits buried beneath unconsolidated overburden in excess of 150m, and bedrock in excess of 400-500m.

In the search for ore mineralization it is advisable to combine both geochemical and mineralogical techniques. Heavy concentrate geochemical sampling of alluvial sediments and bedrock can aid in identifying secondary and primary haloes of minerals and elements. Black interbedded oxides and hydroxides of Mn occur on the border between oxidizing and reducing conditions, and can serve as an indicator of intensive weathering and as possible evidence of prospective supergene gold mineralization.

Combining various exploration techniques maximises the chances of deposit discovery, and of identifying deep and buried mineralization and extensions to known mineralization.

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Lithobiogeochemical haloes of precious metals in the mountain pinery landscapes of the Transbaikal

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Keywords: silver, platinoids, gold, lithobiogeochemistry, pinery, Zabaikal'e

Aims

The main aim of our eleven year study was to investigate exploration and prospecting methods for precious metals in a zone of deep-seated faults, and to evaluate the effectiveness and reliability of the various methods. The region studied had been an old mining district several centuries ago, however there are no records now. It is situated in a landscape of dry pineries, close to asphalt roads (4-12 km) and a railway station (15-30 km).

Methods

Work conducted from 1984 onwards included biogeochemical, geobotanical, phytopathogenic, resonance biogeophysical, geophysical, soil-geochemical, loose cover and primary haloes, weathering, leaching, secondary enrichment, technological, analytical, geoethnic and geoarchaeological investigations.

Results

It was established that the most effective techniques in the region are nontraditional - nonbarrier biogeochemical exploration (NBE) and nonbarrier biogeochemical prospecting (NBP) methods, which are the author's NOW HOW. The effectiveness of these techniques were confirmed when most of the various precious metal ore bodies and mineralized zones were missed after four detailed 1:10,000 scale exploration programmes from 1971 to 1985. These programmes combined a variety of traditional methods: soil geochemistry, geophysics, geological mapping, pitting and trenching.

Up till the present, in addition to one occurrence of silver mineralization discovered by geophysics and soil geochemistry in 1971, our investigations of 24,000 samples have revealed 160 local (1-8m wide) supposed ore biogeochemical anomalies (SOBA) of silver, more than 100 intensive (10 x background and higher) biogeochemical anomalies (IBA) of the six platinoid elements, many tens of IBA of gold, hundreds of IBA of Pb, Cu, Zn, Cd, Hg, and many hundreds of statistically trustworthy biogeochemical anomalies of Li, Rb, Cs, Sr, Ba, Sc, Y, Yb, La, Ce, Zr, Ge, Sn, Nb, As, Sb, Bi, Mo, W, Mn, F, Cl, Fe, Co, Ni.

Thirty-nine silver SOBA, defined by 70-3000ppm silver in the ash of rotten stumps of pine (*Pinus silvestris*) and larch (*Larix dahurica*), were trenched. Twenty-four trenches revealed 34 silver ore bodies in syenites, and rarely in diorites. The ore bodies were 0.4 to 11 m wide, bearing 20 to 6200 ppm silver. In addition, the trenching revealed more than 100 silver-bearing zones with silver contents of 1 to 15 ppm (local background values are around 0.05 ppm silver). The trenches also revealed more than 100 platinoid-bearing local mineralized zones (LMZ), 0.2 to 2.0m wide, tens of gold-bearing LMZ, some lead-bearing ore bodies, and tens of lead-bearing LMZ.

A significant characteristic of these ore bodies and LMZ is the spatial incompatibility of various precious metals. For example, in a 320m long trench, 72 LMZ of Au, Ag, Pt, Rh, Os, Pd (Ir and Ru were not analyzed) were revealed; only eight of these were bi-metallic: Au+Pt (2), Au+Os (2), Ag+Pt (1), Ag+Rh (1), Pt+Pd (1), Os+Pd (1). In other trenches, Au+Ag LMZ are typical.

It is considered the precious metal mineralization forms linear stockworks some hundreds of metres wide, with tens to hundreds of LMZ inside and outside of the stockworks. In an area of three square kilometres, nine complex stockworks were exposed and partially contoured. Six of these are silver ore, with 51, 35, 19, 16, 12 and 9 SOBA of silver occurring in localities of 200 to 400 x 150 to 300m in area. There are considered to be close to one hundred of such stockworks in the contoured prospective region of 300 square kilometres.

From the trenching of 39 SOBA of silver it was found :

1. three main geochemical and mineralogical types of gold, silver and platinoid LMZ: lead-rich (5-50% Pb), low-lead (1-5% Pb), and leadless (<1% Pb);

2. five main types of silver ores: massive or embedded galena without quartz, massive or embedded galena with quartz, quartz-galena veins, quartz-galena veinlet-bearing brecciated zones, and low-sulphide brecciated zones with native silver to 20μm and locally native gold to 200μm;

3. four main types of platinoid mineralization: stockworks in hybrid syenites, LMZ, xenolith of altered rocks, hydrogenic blankets and pockets of secondary enrichment in the weathering crust.

In one intensively studied uncontoured stockwork more than 320m wide, these types of mineralization show the following zonation: quartz-free galena-silver ore bodies and LMZ are located in the centre; flanking these, to the east and west, are quartz-galena veinlet-bearing silver LMZ; in the narrow ends of these stockworks are located low-sulphide gold-silver LMZ. All these silver ore bodies and silver-bearing LMZ are flanked by LMZ of platinoids and/or gold. Within this stockwork, silver forms five zones of 22 to 40 m width, with 5 to 11 silver ore bodies and LMZ of 1 to 2 m width; silver values are greater than 1 ppm (background level is 0.05 ppm). Trenching of this stockwork revealed six ore bodies with 50 to 2000 ppm silver, including three ore bodies with 500 to 2000 ppm silver.

Conclusions

The investigations have shown that a combination of non-traditional methods with the main one - lithobiogeochemistry, resulted in the discovery of a deep-seated fault zone containing complex precious metal mineralization. The discovery of platinoid mineralization was unexpected, and resulted in the definition of four new mineralization types. The most prospective of these new types are the local hydrogenic blankets and pockets of secondary enrichment in the weathering zones of syenites.

Analysis of all our data shows that the most effective techniques were our NOW HOW: NBP and NBE. These techniques provide valuable exploration and prospecting data relating to numerous veined precious metal ore bodies and mineralized zones: their positions, their probable resources, their probable geochemical, mineralogical and technological types, and about the complex inner structure of the ore deposits. Other methods have important but subsidiary significance. The most important are portable X-ray analyzers, which have the potential to exclude mass lithogeochemical sampling, and speed up biogeochemical analysis by measuring biogeochemical samples ashed in the field. Analyzers of this type can, in one day, measure up to 1,000 ashed biogeochemical samples, or outcrops or drill core.

All platinoid and gold results so far collected are preliminary. Close to 24,000 biogeochemical and lithogeochemical samples were collected between 1984 and 1994; these require reliable and costly analyses. An international programme, incorporating modern western analytical technology, is needed for this analytical programme. The author invites anyone who is interested, and who has the financial and technical capability, to take part in the investigations of precious metals in Transbaikal.

Scintillation Emission Spectral Analysis (SESA) for precious metals

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Keywords: analytical methods, gold, silver, platinoids, arsenic, lead

Scintillation emission spectral analysis (SESA) registers the lines produced by elements due to emission from their separated particles. SESA provides analytical results with a sensitivity of 3-30 ppb, and can analyse samples of 0.2 to 2.0g.

SESA, without chemical preparation of the powdered samples, was used to determine Au, As, Ag, Pt, Ir, Os, Pd, Rh, Ru, Nb, Ta, Ti, Zr, Pb (Prokopchuk, 1986, 1990, 1994). For some of the later analyses, our SESA apparatus was automated, and results registered digitally. Three selected elements with 2 to 5 sizes of particles are determined by SESA simultaneously. After determining the quantity and sizes of the particles, the SESA registers the coincided impulses of two or three elements. These data may be used to determine the quantities and sizes of mineral particles containing two or three analyzed elements.

The various possibilities of SESA method have been explored by geologists and geochemists for more than 15 years and, in later years, by mineralogists also. SESA may also be used in environmental chemistry to determine particles of chemical elements in smoke, dust, soil and plants. Over 16 years we have analyzed gold and the platinoid elements in more than 150,000 samples, including around 20,000 samples of plant ash.

SESA is not used in western and developing countries, but from our experience we recommend SESA for wide use in geochemical and mineralogical analysis for all eight precious metals: Au, Ag, Pt, Ir, Os, Pd, Rh, Ru, and their most important indicators: As, Sb, Bi, Pb, Cu, Zn, Cd, Hg, etc. From the 1970's, SESA has been used for gold analyses (Kovalevskii and Prokopchuk, 1978, 1990, 1993; Prokopchuk, 1986, 1994). In 1990 SESA was elaborated for analyzing Ag, As, Pt, Pd (Prokopchuk, 1994), and in 1993 for Ir, Os, Rh, and Ru (Kovalevskii and Prokopchuk, 1993; Prokopchuk, 1994). In 1993 the first stage of SESA expansion for analysis of all eight precious metals, and As, was completed.

SESA can be of particular use for analysis of biogeochemical samples 0.2-2.0 g in weight (Kovalevskii, 1979, 1987; Kovalevskii, 1991). The technique is relatively quick and inexpensive for the analysis of Au and the platinoids, as other techniques providing equal sensitivity require 20-200g samples.

Our programme of SESA analyses currently includes the simultaneous automatic determination of five precious metals, along with their most important associated indicator elements and interfering elements (e.g. the simultaneous analysis of Pb with Ir; Kovalevskii and Prokopchuk, 1993). The technique is highly productive, with the analysis of 100-200 samples/day/analyst, and economical, costing 10 to 100 times less than methods requiring chemical preparation of samples. Our research is aimed at further improvements of the techniques, and one of our objectives is to increase the sensitivity of SESA as, currently, clarke content levels of Au, and the six platinoid elements, can generally not be determined by this technique.

There is necessary an international effort to promote the wide applications of this new and very prospective technique for analyzing mineral forms of precious metals.

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Advances in energy dispersive X-ray fluorescence

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Keywords: analytics, trace elements, X-ray fluorescence

Introduction

X-ray fluorescence (XRF) spectrometry is one of the most widely used methods for the routine analysis of geological samples. XRF- spectrometry is suitable for the determination of most of the major elements as well as a large number of geochemical important trace elements. A wide range of trace elements can be determined at the ppm level. One of the main advantages of XRF, compared to other methods (except instrumental neutron activation analysis INAA), is the capability to analyse solid samples, usually prepared either as powder pellets, or glass discs, but the analysis of bulk powder samples is also possible.

Two types of instrumentation have been evolved. Since the early 1960's wavelength dispersive (WD) instruments are widely adopted to geochemical applications. Today WDXRF-systems are common instruments in geochemical laboratories. The development of solid state detectors in the early 1970's was the precondition to discriminate the X-ray lines of different elements by their energy. Since the mid-1970's are instruments available, which are based on the energy-dispersive (ED) registration of X-ray spectra. The major advantage of these instruments is the capability for the simultaneous determination of 10-30 elements. Compact EDXRF-systems can be easily adopted to mobile laboratories (Kramar, 1984). Today EDXRF- systems are well known for their capability extremely rapid and semiquantitative analysis. Their capability for the quantitative determination of major and trace elements is often underestimated (Potts and Webb, 1992). For many elements the sensitivity of EDXRF systems is equivalent to WDXRF systems.

The principal factor, limiting the sensitivity of XRF is the peak to background ratio. During the last years two new EDXRF instruments, with considerable improved peak to background ratio, were developed. Total reflection XRF (TXRF) (Schwenke and Knoth, 1982) was designed to analyse extremely small sample amounts. An instrument, using polarised X-rays (P-XRF) for excitation (Brumme, 1990), is designed to reduce Compton-scattered background in spectra of bulksamples. The features of both methods are very interesting for geochemical applications, but they are relatively unknown in geoscience. Therefore the aim of this study is to compare the performance of these methods with common WDXRF and EDXRF methods.

Total reflection XRF (TXRF)

TXRF combines the capability of microanalysis with a very high analytical sensitivity and flexibility. In TXRF the sample is prepared as a thin film on a well polished quartz block. In conventional thin film methods the characteristic lines of elements in the film are excitated, but excitation and Compton scattering occurs within the material of the sample support as well. In TXRF the geometry is arranged to provide a grazing incidence of the primary X-ray beam.

At very low incident angles (< 2 mrad), the primary beam is totally reflected at the sample support. By total reflection of the primary beam interaction with the material of the sample support is efficiently reduced. Double reflection of the beam is used to cut off the high energy bremsstrahlung of the tube (Figure 1).

Using TXRF, detection limits < 5 pg can be achieved for the elements K - Sr, J - Gd and Os - Bi. In practical applications an 50 µl aliquot from a sample solution or slurry is pipetted onto the surface of the sample support and evaporated to dryness. An 50 µl aliquot from aqua regia digestion of 3g sample/ 100 ml (DIN 38414) contains the extract from 1.5 mg sample powder. Theoretically relative detection limits of <5 ppb referred to the solid sample can be achieved, practically 50-100 ppb seem to be more realistic.

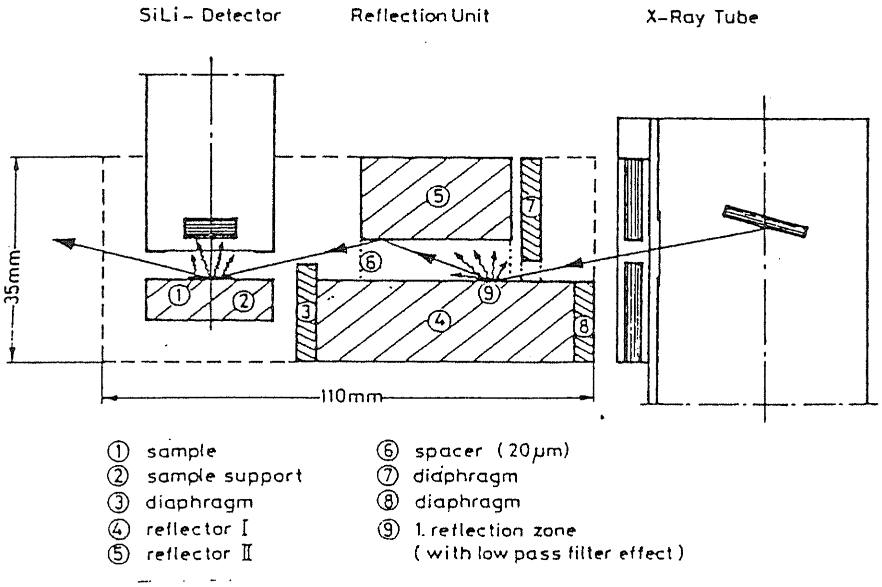

Fig. 1: Schematic design of an TXRF spectrometer (after Schwenke and Knoth, 1982).

Compared to conventional WDXRF and EDXRF methods detection limits are clearly improved. The advantage of conventional XRF methods to analyse solid samples without or after a minimum of sample preparation is lost. Compared to ICP/MS the consumption of sample solution is very low and measurement is non-destructive i.e. the sample can be used for multiple measurements.

The highlight TXRF is the capability of microanalysis. Even in a 10 µg sample detection limits at the ppm level are possible. This offers the possibility to analyse single mineral grains without time consuming mineral separations.

Polarised X-ray fluorescence (P-XRF)

Polarised X-ray fluorescence improves the detection limits for the analysis of bulk samples.

In polarised X-ray fluorescence systems, a BARKLA scatterer is irradiated by the primary beam. Under orthogonal conditions the scattered irradiation is highly polarised. The polarised irradiation is used to excitate the characteristic X-rays of the elements in the sample. The secondary radiation is measured in orthogonal geometry to the polarisation plane. Under these orthogonal conditions incoherent scattered radiation is at a minimum. The peak to background ratio is efficiently increased. Intensity decreases by 4-5 magnitudes. Therefore the advantage of EDXRF to use low power X-ray sources (radionuclides or air-cooled X-ray tubes) is lost. Detection limits for geological samples are improved approximately by a factor 3. Thus sensitivity and accuracy is equivalent (K - Mo, Hf - U) or better (Ag - Nd) than obtained by WDXRF. Therefore the P-XRF combines the capability of non-destructive multi-element analysis with low detection limits and a minimum of sample preparation.

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A study of a "dipole" extraction in tracing and interpreting ore-induced secondary epigenetic haloes

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Keywords: epigenetic halo, buried deposit, partial extraction, element-collector

Background

A feasibility of the conventional surface geochemical techniques, such as soil geochemistry, is limited in exploration for mineral deposits covered with thick overburden layer. In order to solve this problem, a number of phase geochemical (partial extraction) methods have been developed in the last two decades. They allow the detection of buried deposits by tracing their secondary epigenetic haloes in the surface sediments (Antropova et al., 1992). These haloes are represented exclusively by poorly bound modes of elements and are famous for their strikingly high mobility (up to 600 - 800 m upwards from the source).

One of the fairly successful phase geochemical techniques is the CHIM (Russian acronym for "Partial Extraction of Metals") (Shmakin, 1985). It includes an *in situ* selective extraction of the electromobile modes of elements (e. g., ions) with the direct electric current into the element-collectors (ECs), chemical analysis of the extract, and interpretation of the analytical data. The ECs are comprised of cylindrical polyethylene vessels with semi-permeable diaphragm as a bottom, filled with certain electrolyte where solid electrode is dipped. These units are embedded in the surface sediments along an explored profile and connected to a current source as either anodes or cathodes. A common auxiliary electrode is positioned in "infinity" and represented by a metal bar(s) (Bloomstein, 1990).

The main disadvantages of the current CHIM version are:
- the extraction is carried out on either anions or cations while in most cases both modes are informative (Hoover and Leinz, 1994);
- the measured parameter is not a concentration of a certain element in sediments in a sampling point but its extracted mass in an EC.

The setting

Recently, a new electrogeochemical technique has been proposed by ExploTech Ltd. The proposed technique is derived from the CHIM-method and is based on a simultaneous extraction of positively and negatively charged mobile modes of the pathfinder elements in each measurement point (Levitski, 1993). In the extracting "dipole", both anode and cathode are represented by the ECs (Fig. 1), and spacing between these is negligible as compared to a distance between the adjoining measurement points. Such setting allows attribution of the extraction data to the geometrical center of a dipole.

The processed volume

Two-dimensional experiments have shown that an electric field in this geometry is concentrated within a "dipole" and in its close vicinity. Theoretically, the processed volume (V_o) up to a certain moment may be considered as conditionally secluded. An accuracy of this assumption could be proven while comparing the ion speed within V_o, where the process is represented by both diffusion and electromigration, and outside of it (pure diffusion):

$$V_\Sigma / V_D = 1 + \alpha E, \quad (1)$$

where: V_Σ - net ion speed (migration and diffusion), cm/h; V_D - diffusion ion speed, cm/h; α - constant, cm/V; E - electric field intensity, V/cm.

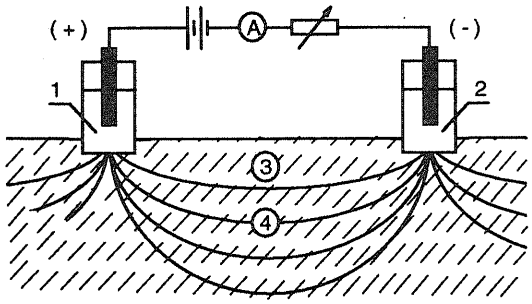

Fig. 1. The "dipole" setting. 1 - anion-collector, 2 - cation-collector, 3 - surface sediments, 4 - current flow lines.

For the majority of potentially indicative elements, such as Cu, Pb, Zn, Co, Ni, α =0.7-0.9. While the overage value of E is kept at 5-10 V/cm, an extraction from V_o into the ECs will proceed 4-9 times faster than influx into this volume from outside.

Experimental data

The laboratory experiments were conducted sequentially in two reservoirs filled with water-saturated quartz sand, 12 liters and 180 liters by volume. The spacing between anion- and cation-collector measured 25 cm, stabilized current (I) - 200 mA, voltage drop on a dipole (U) varied in different experiments from 70 V to 200 V. By using specific EC-filling electrolytes and electrode materials, and by observing certain electric parameters, almost pure Faradaic process was established. An electrolysis was carried out for 5-6 h with sampling of ECs each 40 minutes. An analysis for Cd was performed by means of Stripping Voltammetry.

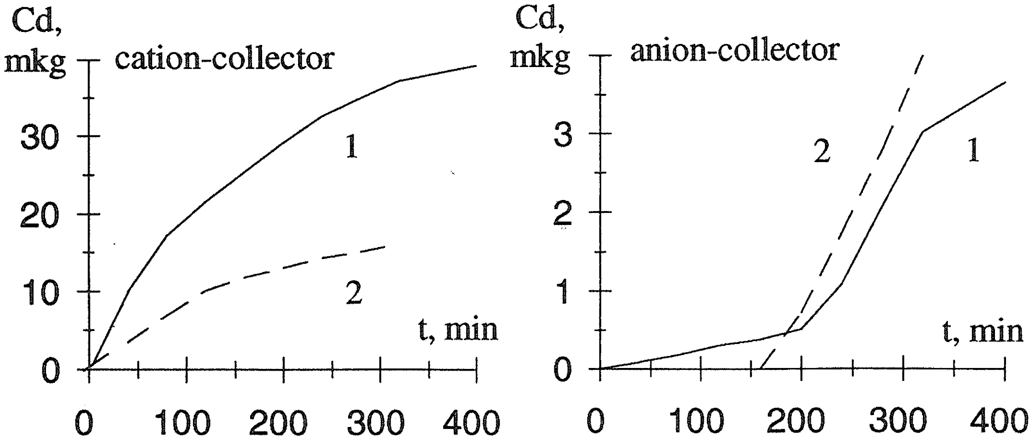

Fig. 2. Experimental hodographs of the "dipole" setting. Spacing between the ECs is 25 cm, I=200 mA, U=100 V. 1 - reservoir volume 12 liters, 2 - reservoir volume 180 liters.

Typical hodographs (extracted mass versus time) are given in Fig. 2. Two major observations could be made concerning these data:

- even a definite cation such as Cd, in an environment free of organic matter creates certain amount of negatively charged modes;
- while the volumes of the reservoirs differ by 15 times the extracted masses of Cd in the anion-collectors are of the same magnitude in both reservoirs, and in cation-collectors differ just by 2-2.5 times.

Preliminary conclusions

The study performed leads to the following conclusions:

1. The "dipole" setting allows to collect more complete information about the distribution of electromobile modes of elements.

2. The closeness of the extraction level in bigger and smaller reservoirs confirms our idea of "seclusion" of the processed volume in the "dipole" setting.

3. When considering the processed volume conditionally secluded, the "dipole" extraction process for a certain i-element may be described by the following equation:

$$M_i(t) = C_i V_0 [1 - e^{-Kt}], \quad (2)$$

where: M_i - an extracted mass of i-element (mkg) , C_i - concentration of i - element in electromobile forms in V_0 (mkg/cm^3), V_0 - conditionally secluded volume (cm^3), t - time (h), K - constant (depends on spacing between electrodes, diaphragm area, electric field intensity, etc.).

4. While using formulae (2), a quantitative M_i - C_i transfer could be performed. That would enable the determination of the concentration of the pathfinder elements in each measurement point. Then, all the interpretation methods of the conventional geochemistry may be applied to the field data, including determination of the halo-inducing object value and depth.

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Study of the geoelectrochemical extraction method in the search for hidden ore deposits

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The geoelectrochemical method or prospecting for metals was developed more than 20 years ago in the former Soviet Union. Russian investigators extensively researched the method, which they called CHIM, and developed many improvements. During the early 1980's experimental research on CHIM began in China.

The CHIM method is used for prospecting for hidden orebodies by exciting and extracting metallic ions in overburden and in the surrounding rocks (i.e. in haloes) using an artificial electric field.

Halo-Forming Mechanisms

Ions within ionic haloes develop from the dissolution of minerals. Dissolved metallic ions form ion haloes in dynamic equilibrium around orebodies, due to action of forces such as geoelectronic fields, concentration gradients, and groundwater circulation. Dissolution caused by oxidation mostly occurs in shallow ore bodies, and electrochemical dissolution chiefly occurs in deep ore bodies. Electrochemical dissolution of an ore body occurs mainly because of the different electrode potentials of the various minerals within the ore body, resulting in the continual electrochemical dissolution of the ore body through the action of micro- and macro-batteries. The potential values of various metallic sulphides and gold, under different oxidizing-reducing conditions, have been determined, as has electrochemical dissolution by batteries in different sulphides.

The Action of an External Electric Field

Ionic mobility may be accelerated by the application of an external electric field. Metallic ions will migrate towards the cathode at the surface and, with time, ions moving towards the surface are replaced by ions from below. As long as a sizeable ionic source (ore body) exists at depth, within the range of the external electric field, ions can continually move towards the cathode at the surface. The application of an external electric field can change the state of metallic elements in the soil, can accelerate dissolution and the formation of new minerals, and can accelerate chemical reactions.

True and False Anomalies

Geoelectrical anomalies are based on concentrations of metallic ions, however, whether these concentrations result from deep seated ore bodies is not always clear. In the author's experience, true anomalies can be distinguished from false anomalies by the shapes of the time-scale curves.

Extraction Methods and Extraction Electrodes

Both deep and shallow extraction methods can be used, depending on the power of the external electric field. The methods can be combined to provide a comprehensive survey.

Extraction electrodes are divided into solid and liquid electrodes. Liquid electrodes are being researched for future exploration; solid electrodes have been studied and used by the author in prospecting for a variety of commodities, including Au, Cu, Pb, Zn, Sn, and As.

Prospecting Results

A large number of electrochemical prospecting programmes have been carried out in more than ten provinces in China, searching for deposits of Au, Ag, Cu, Pb, Zn, Sb, Sn, As and Hg. The electrochemical technique have proven effective and, after testing by drilling in five areas, has a discovery rate of 70%.

Biogeochemical exploration for gold in tropical rain forest regions of Papua New Guinea

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Keywords: biogeochemistry, Papua, rain forest, exploration, gold, Lihir

Introduction

Biogeochemical prospecting has been used as an exploration method for mineral deposits worldwide, particularly in boreal forests and semi-arid regions. The lure of giant Au-Cu porphyry deposits in volcanic regions of the south Pacific, and particularly in Papua New Guinea (Lihir, Bougainville, Ok Tedi and Porgera) has increased the level of mineral exploration activities in previously unexplored rain forest regions. Although stream sediment and soil geochemistry surveys remain the vanguard of the explorationist in these areas, these exploration methods can be complicated and expensive undertakings due to terrain and climate difficulties. This paper describes the results of biogeochemical exploration research field trials which were conducted in high relief terrain on the volcanic islands of Simberi and Lihir islands, Papua New Guinea.

Geology of ore deposits and conventional exploration methods on Simberi and Lihir Islands

The volcanic-hosted gold deposits on Simberi and Lihir Island are of epithermal origin and post-date active volcanism. The Simberi deposits are bulk-tonnage disseminated types, hosted in volcanic or hydrothermal breccias. Occasional high-grade zones were created where lithologic contacts and extensional structures concentrated hydrothermal fluid flow. The Ladolam deposit is hosted in volcaniclastic rocks within an active geothermal field. Visible gold is rare on Simberi and absent on Lihir. Gold is predominantly contained as micron to submicron size inclusions in pyrite, arsenian pyrite and marcasite (Davies and Ballantyne, 1987).

Observations in the field on the difficulty of reconnaissance scale soil sampling prompted an investigation into the use of biogeochemistry surveys as an effective reconnaissance scale exploration method. Post-mineralization volcanic deposits (ash, lahars, alluvium and colluvium) are known to have buried mineralization beyond the reaches of soil sampling techniques. In addition, interpretation of soil survey data in rain forest laterite conditions can be difficult due to groundwater dissolution and dispersion of metals. For example, studies of gold distribution in laterite terrain indicate that supergene Au enrichment occurs at the interface of the B and C soil horizons (Webster and Mann, 1987), often below the level of penetration obtainable using conventional soil sampling procedures.

In an attempt to make accommodations for this penetration problem, soil surveys on Simberi Island require collection of large volume samples (1-2 kg) at consistent depths of either 1 or 2 m, in order to obtain as representative a sample as possible of laterite soil with fine grained (5-10µm) secondary Au. The difficulty in transporting the cumulative weight of high volume soils over high relief terrain with dense vegetation makes soil sampling an inefficient and expensive process when compared to bark sampling, even in areas where labour costs are low. Moreover, soil samples, particularly those from high rainfall areas, require special preparation (drying, crushing, sieving) processes prior to analysis which can prolong reconnaissance exploration programs and reduce the economic viability of exploration in tropical environments.

Biogeochemistry has the potential of overcoming the problems posed to Au exploration using conventional soil survey techniques because: (1) tree roots penetrate deeper and sample larger volumes of soil, (2) tropical trees cycle large volumes of groundwater and its dissolved constituents daily, and (3) rapid sampling and preparation techniques combine to produce a quicker turnaround time for exploration results and thus a better cost-effectiveness.

Topography, climate and vegetation of the study area

Simberi and Lihir islands are located in equatorial Papua New Guinea, and are covered by dense, primary evergreen rain forest except along the sparsely populated coastal regions. Topography varies from 0 to 700 m with moderate to steep slopes. The climate is hot and humid with rainfall exceeding 2.5 m per year. The drier season occurs in July and August. The vegetation of the Tabar-Lihir-Tanga-Feni island chain is of the mixed lowland tropical rain forest type. Approximately 85% of the areal extent of New Britain, New Ireland, Bougainville, Solomon Islands and 40% of mainland Papua New Guinea are covered by this rain forest type (Johns, 1972).

Remobilization of metals by low temperature aqueous solutions (e.g.. $AuCl^{-}{}_{4}$, $Au(S_2O_3)^{3-}{}_{2}$, $Au(CN)^{-}{}_{2}$) makes groundwater an effective vector for their incorporation into plants. If the roots of a plant cannot discriminate and actively exclude dissolved metals, they will readily intake these metals at a rate proportional to availability in the substrate. Biogeochemical exploration methods are therefore particularly suited for tropical regions because a constant daily intake of soil moisture by the rain forest is necessitated by high measured evapotranspiration rates. Calculations combining evapotranspiration rates and annual rainfall values indicate that large trees recycle as much as 300 l of water per day to the atmosphere. Under these conditions, metals dissolved in groundwater may be concentrated in plant tissue.

Soil sampling and processing procedures

During the Simberi biogeochemical survey, soil samples were taken at the base of the tree for comparison purposes. Auger samples of 1 kg soils were taken from 1 m and 2 m depths. The average time required to take 1 m auger samples was 15 minutes, whereas 2 m samples took 21 minutes. In areas where soil sampling or exploration drilling had previously been conducted, that data was used. Moisture content of tropical soils can make up 25 to 45 weight % of a 1 m deep soil sample (Windsor, 1990), and soil samples require several days of drying in a copra shed at 80°C before processing can begin.

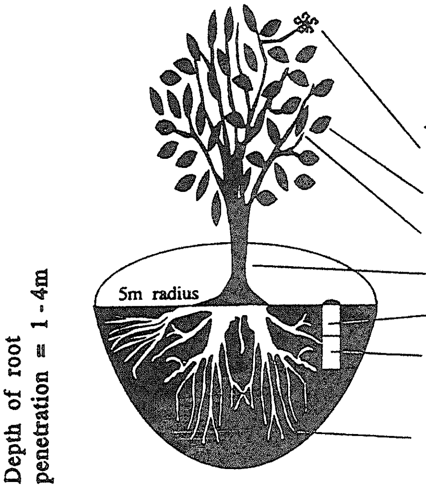
Vegetation sampling and processing procedures

Biogeochemical surveys were conducted on Simberi Island over an area covering the Sorowar, Pigiput, Samat and Botlu prospects. The Lihir survey was conducted within the Luise caldera over the Kapit, Minifie, Lienitz and Coastal zones. A total of 99 soil samples and 242 vegetation samples were taken during the Simberi Island survey and 190 vegetation samples were taken during the Lihir survey.

After investigation of several plant species, a small- to moderate-size tree species was chosen for sampling because it is abundant and has a widespread distribution. *Astronidium palauense* (although many species of the genus *Astronidium*/*Astronia* may be useful) is present throughout the southwest Pacific region bordered by Sumatra and the Malay Peninsula, Philippines, Marshall Islands east to Fiji and Tahiti, south to New Hebrides and throughout Papua New Guinea and the Solomon Islands. Density of this species is approximately 1/100 m^2 on Simberi and varies between 1/20 m^2 and 1/300 m^2 on Lihir Island. It may not occur at elevations greater than 1000 m, although *Astronidium novo-guineense*, a species very similar to *A. palauense* has been identified as high as 2150 m. The tree is easy to identify by the distinctive parallel venation of the leaf. The bark is loosely attached and easily removable with a knife and therefore is easy to sample.

Figure 1 demonstrates that the concentration of Au in bark most accurately represents that of Au at low, medium and high soil concentrations. The loose, outer bark was also the most efficient organ to collect. The average time required to collect a bark sample and record data was 6 minutes per site. The bark was then dried in open aluminum trays in on-site copra drying sheds for two days at approximately 80°C. Approximately 50 g of bark was placed in an aluminum tray and ashed for 12 hours in a conventional pottery kiln at 470° C. Ashing the sample was necessary to comply with customs restrictions on importing plant material into Australia. Because Melastomataceae genera are seldom cyanogenic, Au volatilization during ashing is unlikely (Dunn, 1986; Brooks, 1983). The ash yield ranged from 5 to 20% and averaged 10.5%. Vegetation analyses are quoted on an ash weight basis.

The final stage of sample preparation involved accurately weighing 0.8 - 1.0 g of ash into a small polyethylene vial suitable for instrumental neutron activation analysis (INAA). A standard (V2) and a sample duplicate were analyzed with every batch of 20 samples to provide statistics on accuracy and precision. Accuracy was 13.8 ± 2 ppb for Au and 1.9 ± 0.2 ppm for As (n=10), which are considered to be acceptable values for V2. Precision was determined using duplicate analysis. Relative error on Au determination ranged from 0 to 94% and averaged 17%, whereas relative error on As determinations ranged from 0 to 47% and averaged 13%. An indication of reproducibility can be obtained from Sample 4 on Figure 1, where variation in Au and As content in ashed bark sampled in two different years was 1% and 17%, respectively.



AU CONCENTRATIONS (PPB IN ASH/SOIL)

SAMPLE #	1	2	3	4	5	6
FLOWERS	3	5	-	8	-	-
LEAVES	3	7	2	8	4	16
TWIGS	3	2	6	15	8	5
BARK	0.5	4	19	248*	562	140
1m SOIL	18	11	123	544	3230	1430
2m SOIL	14	5	70	816	1230	4180
ROOTS	7	-	-	-	-	-

EQUIVALENT SOIL VOLUME SAMPLED ≡ 100m^3

* **1988 sample = 255 ppb Au**
1989 sample = 248 ppb Au

- not sampled

Figure 1. Soil and vegetation profiles for Au and As concentrations at six different Simberi Island sample locations representing low, medium and high Au concentrations in soil.

Vegetation sampling results and data analysis - Simberi Island and Lihir Island
Gold and arsenic results of Lihir and Simberi vegetation have lognormal distributions, and statistical analysis of logarithmically transformed data sets was conducted as recommended by Brooks (1983). The range of Au and As in ash from the Ladolam survey is 2-207 ppb and 1-86 ppm, respectively. The corresponding ranges for the Simberi samples are 2-562 ppb Au and 1-77 ppm As. Although the range of Au and As values is similar, the geometric means and mean standard deviations of the log Au concentrations for Lihir (1.25±0.30, n=189) and Simberi (0.93±0.56, n=162) *A. palauense* populations are significantly different as indicated using the *F* test of variability. Cumulative frequency plots also indicate a stronger Au enrichment on Lihir (Ladolam 50th percentile = 15 ppb c.f. Simberi 50th percentile = 7 ppb) whereas the percentiles for As at Ladolam is similar to those at Simberi. At Lihir, only 23% of the samples contain background levels of gold (<10 ppb), while 39% were anomalous (between 10 and 20 ppb) and 38% were highly anomalous (>20 ppb). This compares with 54% below background, 21% between 10 and 20 ppb Au and 25% highly anomalous (>20 ppb Au) samples from the Simberi survey.

The greater dispersion of Au prospects on Simberi Island resulted in more trees sampled over barren ground, more closely representing a reconnaissance scale exploration program than does the Lihir survey. Background values for Au and As were determined to be 10 ppb Au and 5 ppm As, based on correspondence with the >0.2 g/t soil anomaly, considered to be soil background.

Highly significant statistical correlations exist between Au and As concentrations in vegetation and Au in soil (Table 1), indicating that biogeochemical surveys can be used to predict anomalous concentrations of Au in mineralized soil. Biogeochemistry anomalies on Simberi Island are most strongly developed over areas of deep Au mineralization in rock and were successful in identifying the Sorowar, Pigiput, Botlu and Samat prospects. Extensive Au-As biogeochemistry anomalies were identified over the Ladolam deposit on Lihir Island. Post-mineralization deposits of colluvium and alluvium appear not to have formed a barrier to sampling buried mineralized rocks by the root systems of *A. palauense*.

Table 1. Correlation coefficients for the relationship between Au, As, Sb and Te concentrations (logarithmic values) in soil and *A. palauense* bark on Simberi and Lihir Islands, Papua New Guinea.

x	y	n	r	P	Level of Significance
Ausoil-1m	Ausoil-2m	62	0.75	<0.001	S**
Aubark	Asbark	163	0.73	<0.001	S**
Ausoil	Aubark	109	0.54	<0.001	S**
Ausoil	Asbark	109	0.46	<0.001	S**
Ausoil	Sbbark	109	0.20	0.05	S
Ausoil	Tebark	109	0.04	>0.10	NS

n = number of pairs of observations
r = Pearson correlation coefficient
P = probability that a relationship does not exist

Level of significance as specified by Brookes et al. (1966):
S** = very highly significant, H_0(null hypothesis) very confidently rejected
S = significant, H_0 rejected with reservations
NS = not significant

Conclusions

The anomalous concentration of Au and As in *Astronidium palauense* over mineralized areas on Simberi and Lihir Islands indicates that biogeochemical prospecting can be used successfully as a cost-effective mineral exploration technique in tropical rain forest regions. Ease of identification, sample acquisition and widespread distribution of *A. palauense* makes biogeochemical exploration applicable throughout the southwest Pacific. An added benefit of these surveys is that the biogeochemical data can be used as baseline environmental surveys, providing an indication of the natural metal concentrations of living organisms prior to mine development.

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The PIMA II: a field-based tool for alteration mapping

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Introduction

The mineral exploration industry is increasingly aware of the importance of tying in mineralogical data with geochemical results. However, until recently, the cost and time constraints of most techniques for mineral identification have precluded detailed alteration studies. These impediments have been reduced by the introduction of the Portable Infrared Mineral Analyser (PIMA II). The PIMA is ideally suited to field-based alteration mapping and over recent years, this technique has been effectively applied to mineral exploration and characterisation of alteration suites in Australia, USA, South Africa, Chile and Europe.

In using the PIMA, exploration geologists gain a significant advantage in,

- delineating alteration systems,
- understanding alteration-mineralisation relationships,
- targeting significant regions,
- identifying overburden/bedrock boundaries.

This paper is an introduction to the PIMA and the uses of spectral analysis in mineral exploration and prospect development.

The PIMA II

The PIMA II is a fully field-portable infrared spectrometer, which measures the reflectance spectra of rocks and minerals in the short wavelength infrared (SWIR), from 1300-2500nm. The PIMA measures the reflected radiation from the surface of a sample using an internal light source producing laboratory quality spectral data of minerals. Aside from mineral identification, the spectra recorded by the PIMA also permit the determination of fine spectral details, such as crystallinity variations and elemental substitution. Each measurement requires no sample preparation and takes 30-60 seconds, allowing the rapid collection of a large number of analyses.

Measurements can be made of all types of samples including diamond drill core, RC and RAB chips, outcrop and soil samples and selective measurements may be made of *in situ* veins, breccia clasts and small-scale alteration zoning. Given these unique advantages, the PIMA has considerable potential for practical application at all phases of mineral exploration and mine development.

Mineral Analysis Using Infrared Spectrometry

Mineral identification

The major application of PIMA technology is in mapping mineralogical variations within alteration systems, either at the surface from measurements of outcrop and soils, or at depth from analyses of percussion and drill core samples. In this context, SWIR infrared spectrometry is a useful technique for mineral identification because many alteration minerals have characteristic spectral absorption features at these wavelengths.

The spectral absorption features observed in the SWIR are the result of combinations and overtones (or harmonics) of fundamental lattice vibrations that occur at longer wavelengths, which are the result of bending and stretching of molecular bonds. The bonds giving rise to absorption features in the SWIR include those in hydroxyl, water, carbonate and ammonia and between Al-OH, Mg-OH, and Fe-OH. These molecules are found as major components in phyllosilicates (including clay, chlorite and serpentine minerals), hydroxylated silicates (such as epidotes and amphiboles), sulphates (alunite, jarosite and gypsum) and carbonates. Examples of various mineral spectra are shown in Figure 1.

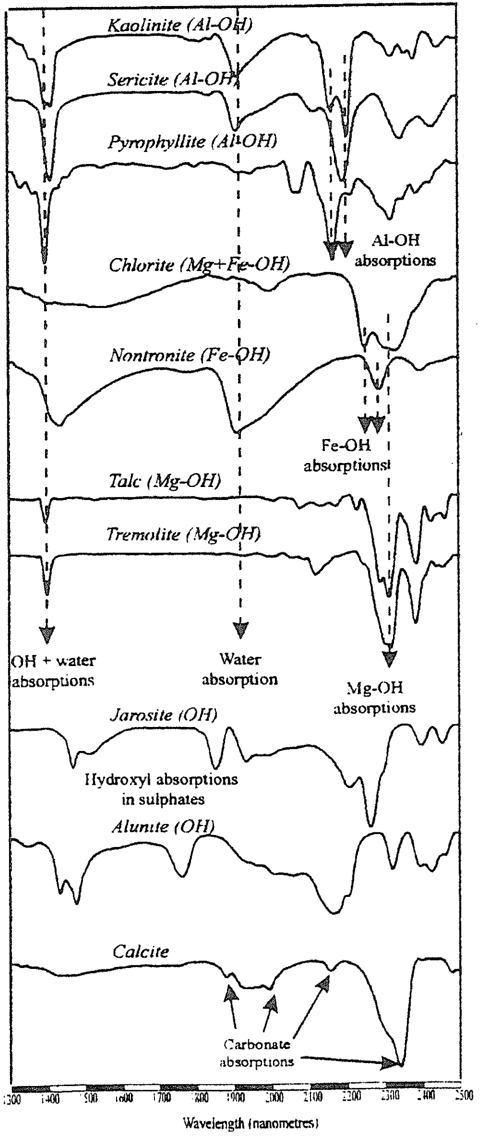

Figure 1: Examples of mineral spectra

The majority of the spectral absorption features that distinguish different silicates in the SWIR are due to vibrational transitions associated with hydroxyl and water producing absorption features near 1400nm (OH and water) and 1900nm (water). Other important and diagnostic spectral absorption features occur at or near 2200nm, 2250nm and 2330nm and are related to the bending and stretching of the bonds between Al-OH, Fe-OH and Mg-OH, respectively.

Sulphates, such as alunite, jarosite and gypsum, also have diagnostic OH absorptions that are easy to distinguish from the silicate absorptions. In addition, carbonates have characteristic spectra associated with the carbonate ion including a strong diagnostic feature between 2300-2350nm.

Crystallinity Variations

In addition to mineral identification, the PIMA spectra can also provide information on the degree of crystallinity of a mineral. For example, clay minerals, such as muscovite, illite and kaolinite, display variations in crystallinity that may be detected spectrally, and which can permit the delineation of temperature and chemical zoning in an alteration system or distinguish weathering- from alteration-related clays.

Generally, variations in crystallinity are reflected by variations in the shapes of the diagnostic absorption features. The absorption features typically increase in sharpness with increasing crystallinity, which is a function that may be parameterised in a similar way to the crystallinity indexes used in XRD. This application of spectral data was illustrated by Fraser *et al* (1990) in their study of alteration at Mount Leyshon, in North Queensland. Crystallinity indexes from the spectral data have also been used by Kruse and Hauff (1991) to characterise illite crystallinity in disseminated gold deposits in the USA, and to map proximity to ore.

Compositional Variations

Spectral analysis with the PIMA can also be used to discriminate compositional variations within mineral groups, which is significant as mineral composition may vary systematically in an alteration system as a function of the temperature and composition of the altering fluids and with proximity to zones of mineralisation. Mapping these variations can allow field geologists to evaluate mineralisation/alteration relationships and to position themselves within an alteration system. Compositional variations are typically represented by shifts in the wavelength positions of diagnostic absorption features, with the overall characteristic spectral signature of the mineral remaining unchanged. Typically, minerals such as chlorites (McLeod *et al*, 1987), carbonates (Gaffey, 1986) and sericites (Post and Noble, 1993) display distinct wavelength shifts in their diagnostic absorption features associated with compositional variations.

Application Of Spectral Analysis In Mineral Exploration

The versatility of the PIMA provides a rapid, effective and low cost indication of mineralogical, crystallinity and compositional variations in a suite of samples that on many occasions can replace XRD methods, with the significant advantage that the analysis may be made in the field and that no sample preparation is required. Given these unique advantages, the PIMA has considerable potential for practical application in mineral exploration and geological mapping.

When using the PIMA for carrying out routine spectral analysis of outcrop or soil, the results of the spectral data may be represented by an alteration map delineating the spatial distribution of the alteration zones. Figure 2 shows an example of 'bullseye' alteration delineated from a PIMA study of 58 outcrop samples along two traverses across an alteration system. Both traverses define a clear, apparently concentric, zonation in the alteration system, from weakly altered biotite-amphibole rich outer margins, through zones of sericite of increasing crystallinity to a more silicified clay-poor zone in the centre.

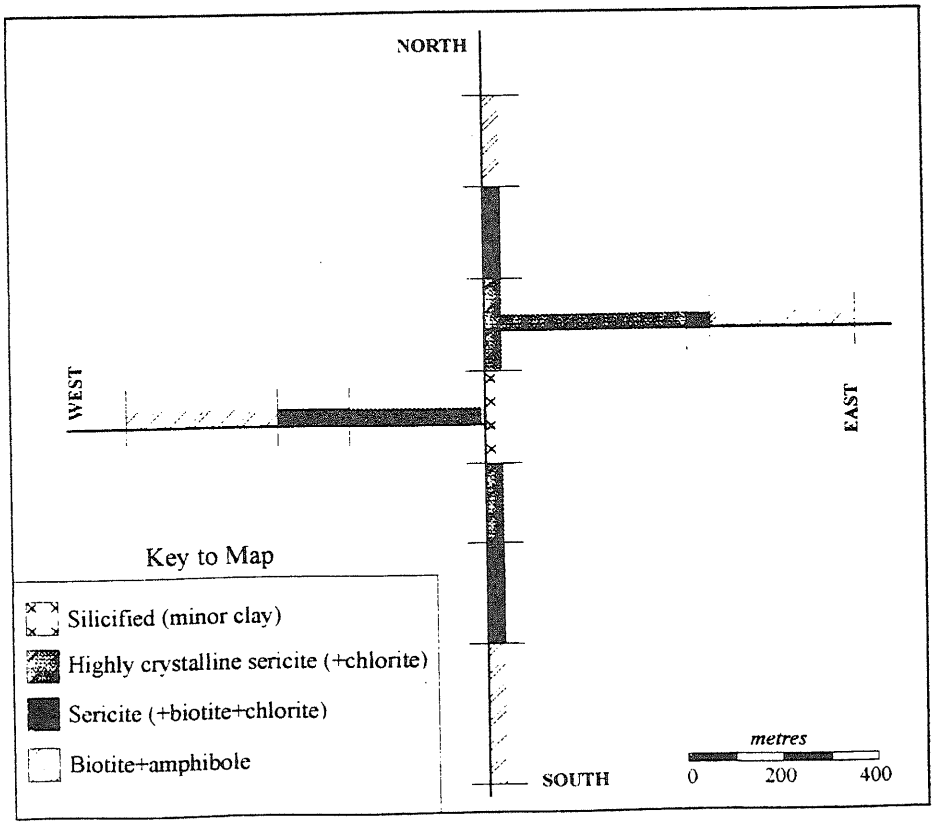

Figure 2: Example of a 'bullseye' alteration pattern delineated from a PIMA study of outcrop along two traverses

Aside from alteration mapping, the PIMA spectral data can also be reduced to a small number of significant values, that may represent variations in mineral assemblage, crystallinity and/or composition in a suite of samples. The resultant data can be plotted as line graphs to represent variations in these mineralogical parameters relative to other data, such as geochemical data, and/or treated in the same way as geophysical data and be gridded, contoured and entered to 3-D mine modelling packages.

Figure 3 illustrates an example of such an application from the Fosterville Gold Mine, Victoria. Prior to the spectral survey, no data existed relating sample mineralogy to proximity to mineralisation at Fosterville. Although superficially the Fosterville spectra appear similar, comprising illite and kaolinite, subtle variations within the diagnostic illite and kaolinite absorption features correlate closely with variations in gold grade. Figure 3 compares the wavelength of the

AlOH absorption near 2200nm in these spectra and the gold grade of samples from three RC holes. At Fosterville the wavelength of this absorption feature near 2200nm represents the relative proportions of kaolinite and illite in a sample. For example, as the proportion of kaolinite and illite changes, the wavelength typically shifts towards 2208nm in kaolinitic samples and towards 2202nm in more illitic samples. These data indicate that at Fosterville high gold grade is associated with increased proportions of illite.

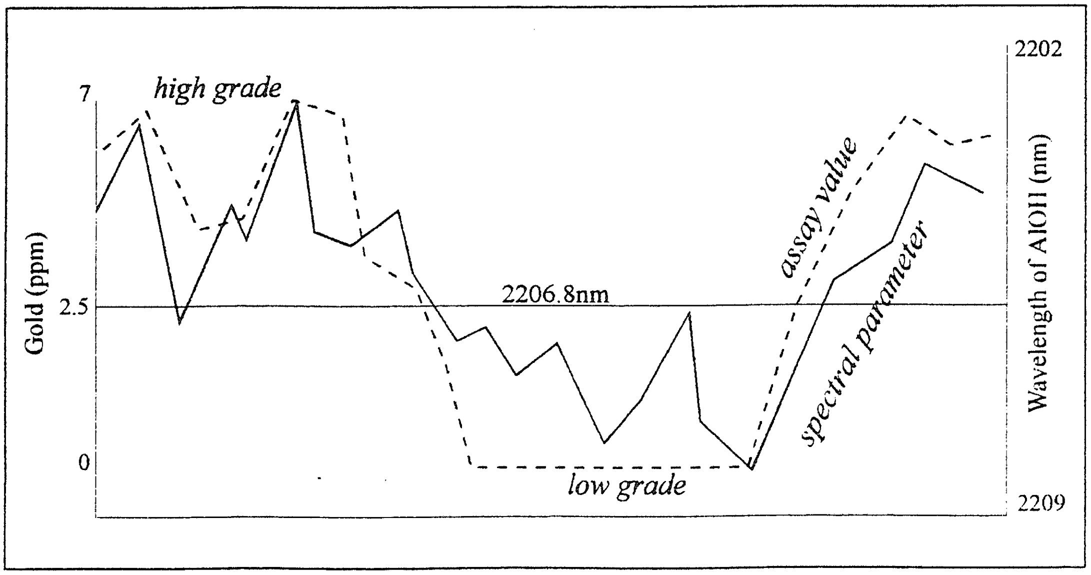

Figure 3: Correlation of gold grade and spectral parameter data for Fosterville

Conclusions

These applications demonstrate that the PIMA II spectrometer, can provide valuable additional information in cases where alteration minerals are either unfamiliar to field geologists or are bleached by alteration or weathering. These data may be used for targeting altered ground and homing in on and identifying alteration zones. Moreover the potential exists to use the spectral data to map proximity to zones of mineralisation. This Australian-developed technology is increasingly being taken up by exploration companies and mapping agencies as an additional weapon in their exploration armoury.

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A case-hardened, low contamination ring mill for multi-element geochemistry

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Keywords: sample preparation, contamination, mill, multi-element geochemistry

Introduction

Contamination of samples is inherent to most geochemical analyses because grinding contributes some of the mill material to the sample. This can be reduced by using hard mill materials such as tungsten carbide (WC) or partially stabilised zirconia (PSZ). Although a few analytical techniques use the complete sample, without preparation (e.g., bulk leach extractable gold (BLEG) analysis and some cases of instrumental neutron activation analysis (INAA)), and so avoid this contamination, most analytical techniques need small aliquots, thus, sample size reduction and pulping are essential to preserve sample representativeness.

There are two ways of minimising sample contamination during laboratory preparation :-
i) To use mill components made of materials that are not to be determined (e.g., WC or PSZ milling followed by Au analysis only).
ii) To use mill components composed of elements that are abundant in the samples, thus effectively camouflaging the contamination (e.g., some steels and agate).

Use of WC mills, which contribute W and Co with some Ta, Sc and Nb (Hickson and Juras, 1986), or PSZ mills, which add Zr, Hf and REE to the sample, cannot be used for most multi-element geochemistry as these elements are all important pathfinders or lithological indicators. The best approach is (ii). Agate mills (which add Si and some Fe) are fragile, slow and expensive. These mills generally have a low capacity, and are notoriously difficult to clean. Steel mills are more rugged, cheaper and milling times are short (about one minute), but they may contribute significant contamination to abrasive samples. Typical contaminations to silcretes and quartz sand are given in Table 1 (Smith and Butt, 1983):-

TABLE 1
CONTAMINATION OF QUARTZ SAND
BY GRINDING IN STEEL MILLS
- DATA IN PPM

Cr Steel		*Ketos Steel* [1]	
Fe	1000 - 10 000	Fe	10 000
Cr	100 - 1000	Mn, W, Cr, Cu	10 - 100
Ni, Zr, Cu	10 - 100	Ni, Mo	1 - 10
V, Mn, Mo	1 - 10		

The CSIRO/AMIRA geochemical projects 240 (Laterite Geochemistry) and 241 (Weathering Processes), initiated in 1987, required a large throughput of reliable, research-quality geochemical analyses. This, and the advent of low detection limits of some elements in the low- to sub-ppm range, provided by some multi-element analytical packages (e.g., ICP/MS and INAA), made it necessary to reconsider sample preparation techniques and to mill to well-understood specifications for a wide range of elements. One of the products of this review was the mill described below, first constructed in 1988, and which has since had considerable use.

Mill design and manufacture

A mild steel was selected with the least abundance of alloying elements. Initial steel hardness was not a criterion as the completed mill was to be case hardened. Various configurations of a puck and one or two rings were considered and later tried, but the configuration shown in Figure 1 was selected as the most successful.

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[1] Ketos steel is a product of Comsteel Co Ltd, its nearest equivalent is AISI 01 (American Iron and Steel Institute).

The mill was machined from a billet of K1045[2] steel. An 'O' ring groove was machined in the lid and radii were provided at the base of the bowl interior and the outside lower corner of the outer ring to make the mill easier to clean. The radius on the outer ring is slightly larger than that on the inside of the bowl to minimise interference. Care was taken to match the dimensions of the base and top of the mill to the mill shaking and clamping mechanism. All of the complete mill components were case hardened, using a conventional salt-bath technique, to 61-62 Rockwell C, and their hardnesses were confirmed by hardness tester. Penetration of the case hardening to greater than 1 mm has since been confirmed by monitoring hardness on a worn mill and comparing its dimensions with those of the original specification.

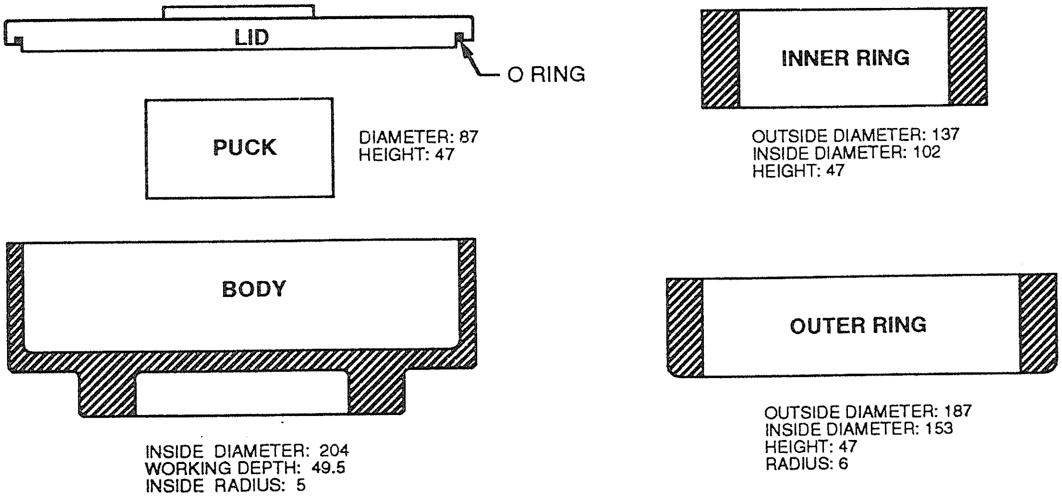

Figure 1. The K1045 Swing Mill. Dimensions in mm.

The abundances of many critical trace elements are not included in the steel manufacturer's specification, which is restricted to C, P, Mn, Si and S contents. Consequently turnings, produced during the manufacture, were collected and analysed. The results are given in Table 3. K1045 steel is a Mn steel with small quantities of Cr, Cu and Ni and traces of Mo and Nb.

Mill performance

The performance of the mill was assessed using three materials, white vein quartz, kaolinitic saprolite and pisolitic gravel. All these are typical components of sample media used in geochemical exploration in Western Australia. These materials were pre-crushed in a jaw crusher, with case-hardened K1045 plates, to less than 12 mm. Separate 100 g charges were milled for intervals which increased by 10 second increments and each milled charge was brushed through a 75 µm sieve. The greater than 75 µm fraction was weighed and the percentage of less than 75 µm was determined by difference and plotted against milling time. The times taken to achieve 90% and 95% less than 75 µm (common specifications) were determined from the graphs (Figure 2). Vein quartz, which is highly abrasive, is a severe test and needs more milling than most materials commonly encountered. The only exception is pisolitic gravel, consisting of Fe-oxides and silica, its fabric giving it a surprising degree of toughness.

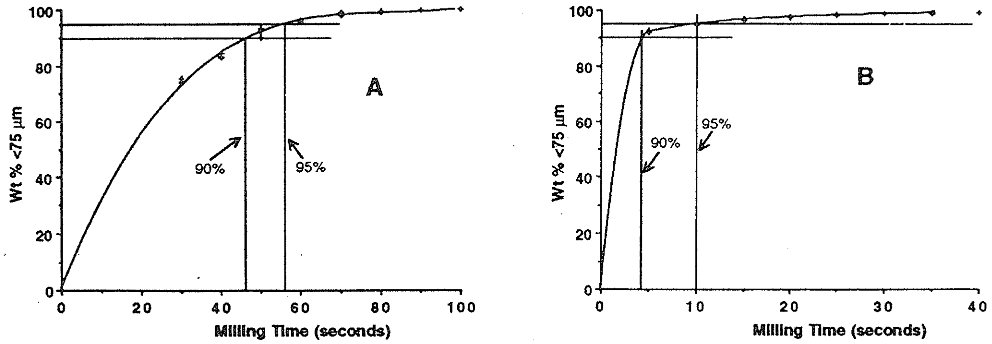

Figure 2. Milling performance curves for quartz (A) and kaolinitic saprolite (B).

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[2] K1045 steel is described in Australian Standard 1442.

TABLE 2
MILLING TIMES TO SPECIFICATION

	Mill time (seconds) to <75 µm 90%	 95%
Quartz	46	56
Kaolinitic saprolite	4	10
Pisolitic gravel	77	123

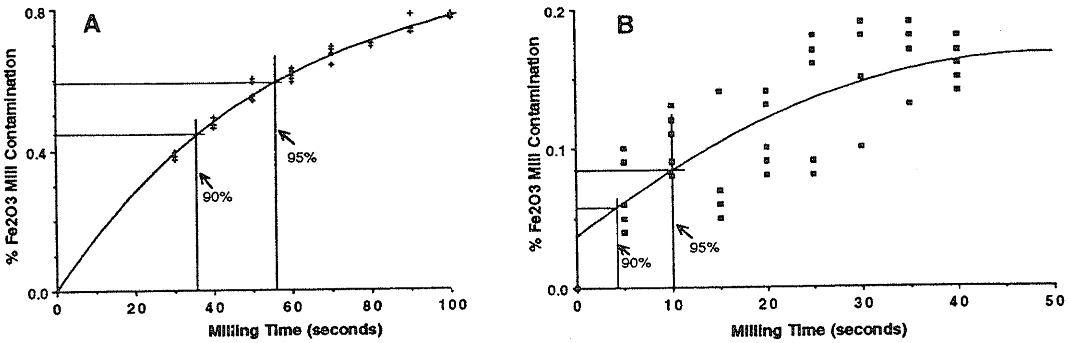

Figure 3. Iron contamination curves for quartz (A) and kaolinitic saprolite (B).

TABLE 3
TRACE ELEMENTS IN STEEL AND CALCULATED CONTAMINATION OF MILLED QUARTZ AND KAOLINITIC SAPROLITE SAMPLES

Trace Element	Steel ppm	ppm in Quartz 90% <75 µm	 95% <75 µm	ppm in Kaolinitic Saprolite 95% <75 µm	 90% <75 µm
Ag	<10	<0.0318	<0.0416	<0.0040	<0.0059
As	5	0.0159	0.0208	0.0020	0.0030
Ba	<20	<0.0636	<0.0832	<0.0080	<0.0119
Bi	<10	<0.0318	<0.0416	<0.0040	<0.0059
Cd	<2	<0.0064	<0.0083	<0.0008	<0.0012
Co	71	0.2259	0.2955	0.0283	0.0422
Cr	795	2.5299	3.3083	0.3169	0.4726
Cu	850	2.7049	3.5372	0.3389	0.5053
In	<5	<0.0159	<0.0208	<0.0020	<0.0030
Mn	6592	20.9775	27.4321	2.6280	3.9189
Mo	260	0.8274	1.0820	0.1037	0.1546
Nb	220	0.7001	0.9155	0.0877	0.1308
Ni	620	1.9730	2.5801	0.2472	0.3686
Pb	20	0.0636	0.0832	0.0080	0.0119
Sb	25	0.0796	0.1040	0.0100	0.0149
Sn	80	0.2546	0.3329	0.0319	0.0476
Ta	<100	<0.3182	<0.4161	<0.0399	<0.0594
Ti	45	0.1432	0.1873	0.0179	0.0268
V	40	0.1273	0.1665	0.0159	0.0238
W	<20	<0.0636	<0.0832	<0.0080	<0.0119
Zn	30	0.0955	0.1248	0.0120	0.0178

Trace element contamination

Iron contamination of the quartz charges was determined by XRF analysis of the milled material. This was compared to agate milled material. The true Fe contamination was determined by difference. The results are shown for quartz for different milling times below and gave very consistent results (Figure 3). A similar determination on the kaolinitic saprolite was more difficult to interpret due to a greater variance in the initial Fe content (Figure 3). It was not possible to determine Fe contamination of the milled pisolitic gravel due to its very high Fe content and Fe variance.

If the iron contamination produced by milling various materials (quartz and kaolinitic saprolite) to selected degrees of fineness is known, it is easy to calculate the trace element contamination that the mill will produce under a given set of conditions, if the composition of the mill steel is also known (Table 3). This is far more accurate and reliable than milling quartz and analysing the sometimes vanishingly small quantities of trace elements with which it has been contaminated.

Conclusions

The milling time required for quartz is about a minute. Kaolinitic saprolite requires about 10 seconds and pisolitic gravel requires 1.5 - 2.0 minutes. Most of the sample is pulverised in the first few moments of milling. It is concluded that tough materials, such as pisolitic gravels, require longer milling times than very hard materials (quartz), so 80 g charges[3] or smaller are recommended in comparison to 100 g for quartz and clay-rich materials.

Iron contamination by the K1045 mill increases non-linearly as milling time increases for both hard and soft materials. The majority of the contamination occurs in the initial stages of the milling. Once a significant amount of the sample has been pulverised, the fines cushion the mill, reducing mill wear but also reducing the rate of comminution. As material hardness increases, iron contamination from the K1045 mill also increases.

The contamination produced by the K1045 mill is significantly less than that from a conventional Cr-steel by one or two orders of magnitude and is generally superior to a Ketos mill by half to one order of magnitude. The maximum expected abundances of a wide range of contaminating elements is firmly established for a quartz charge. Also it was possible to quantify what has been long suspected, namely that mill contamination is reduced by about an order of magnitude on passing from quartz to clay-rich samples.

Acknowledgements

M. I. Krencej was involved in the initial formulation of mill parameters. M. Willing (CSIRO Division of Mineral Products) analysed steel turnings and M.K.W. Hart analysed Fe contaminated quartz by fused disc XRF. C.R.M. Butt, R.E. Smith and D. Garnett provided critical comment. All this is acknowledged with appreciation.

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[3] Our research has also shown that extended milling times significantly increase contamination by mill steel. It is generally preferable to reduce the mill charge and resort to multiple charge but rapid milling of a large sample than to over fill the mill. Such multiple charges require tumble mixing to a single aliquot prior to analysis.

Probing ore forming fluids using the Scanning Proton Microprobe

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The study of ore forming fluids trapped as fluid inclusions in minerals is the key to understanding fluid flow paths at the time of ore formation, and to predicting the location of ore bodies within large-scale magmatic hydrothermal systems. Large penetration depths and the predictable nature of MeV proton trajectories, PIXE yields and X-ray absorption, and high spatial resolution and sensitivity, make the proton microprobe ideally suited to non-destructive, *in situ* analysis of these inclusions. Major progress has been made in recent years in the calculation of PIXE yields from intact fluid inclusions using a layered yield model, and in the modelling of the complex 3D geometry of the beam-inclusion interaction, in order to develop a standardless, quantitative analysis method (Ryan et al., 1993, 1995).

This paper reports on recent developments to increase the accuracy of quantitative analysis by improving the modelling of the internal inclusion structure, which typically contains a vapour bubble and daughter crystals, and through the use of beam-scanning techniques to provide a uniform beam-dose distribution across each inclusion (Ryan et al., 1995). The method has been tested using specially prepared synthetic fluid inclusions in quartz. Inclusions at depths of 2-15 μm were selected by optical microscopy and analyzed using the proton microprobe; the depth was later determined from the PIXE spectrum to ± 1.5 μm using the Cl K_α/K_β X-ray intensity ratio (Ryan et al., 1991). The fluid composition results from the analysis of the individual synthetic inclusions demonstrated an accuracy of ~10-15% for heavy elements and ~20-30% for Cl, with detection limits as low as ~40 ppm in the fluid.

The method has been successfully applied to analyze natural fluid inclusions to study ore-forming fluids associated with granite-hosted tin deposits (Heinrich et al., 1992, 1993a), massive sulfide deposits (Zaw et al., 1994), porphyry copper-gold deposits (Heinrich, et al., 1993b) and metamorphic gold deposits, and in experimental studies of precious metal mobility (Ballhaus et al., 1994).

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New insights into partial extraction methods

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The exploration for base- and precious-metal orebodies is becoming increasingly competitive and costly as geologists must now search for deeply buried or blind deposits under exotic transported overburden. Geochemists are pursuing methods of detecting mineralization through exotic overburden where more conventional methods have failed. In contrast to conventional techniques, which attempt to determine the total metal in soils, partial extraction procedures have been developed to preferentially extract weakly adsorbed and absorbed ions from organic and sesquioxide soils particles; the extracts are subsequently analyzed for a variety of elements. The selective nature of partial extractions reduces the contribution of other mineral phases (eg. humin, carbonates, silicates) thereby improving anomaly contrast and facilitating the identification of anomalies undetectable by conventional methods.

Previous research has focused on finding more selective partial extractions methods or making existing methods cost effective (Chao, 1984). Although such laboratory investigations are essential, little emphasis has been placed on field-oriented research to evaluate where and why partial extraction methods succeed or fail in detecting mineralization under exotic overburden. Research is currently underway at Queen's University to compare the effectiveness and reproducibility of certain partial extraction procedures relative to less expensive conventional methods. The extreme sensitivity (ppb) of some methods also prompted an evaluation of the impact of sample processing on partial extraction results.

Seven orientation surveys were carried out in Canada and two in South America over known base-metal mineralization covered by variable thicknesses and types of exotic overburden. The soil profiles encountered varied according to the nature of the parent material and climate which included glacial overburden in a temperate climate (Canada) and alluvial pediment gravels in an arid climate (South America).

In Canada, soil samples were collected at intervals of 25 meters over background areas and 12.5 meters adjacent to mineralization. Humus and B-horizon soils were collected in higher, well drained areas whereas peat and C-horizon silts were sampled under swampy poorly-drained areas. In South America, an organic horizon was not available for sampling but caliche and calcareous silty sand matrix from gravels were collected at 50 or 200 meter intervals.

Humus samples (-250 micron fraction) were submitted for humic/fulvic acid extraction using a sodium pyrophosphate leach and total extraction by aqua regia leach. Solutions were analyzed by ICP/AES for 31 elements at the ppm level. The pyrophosphate leach extracted 20 to 30% of the element concentrations reported by aqua regia with the exception of zinc (80 to 95% extraction).

B-horizon soil, silty sand, and caliche samples (-250 micron fraction) were submitted for the amorphous manganese-selective enzyme leach (Clark et al., 1990) and/or the amorphous manganese/iron "enhanced" enzyme leach. The enzyme solutions were analyzed by ICP/MS for 46 elements at the ppb level. The same samples were also leached with aqua regia and analyzed by ICP/AES analysis for 31 elements at the ppm level. In comparison to the metal extracted by aqua regia digestion, the enzyme leach extracted about 1% whereas the enhanced-leach removed up to 5%.

An experiment was undertaken to test the effect of drying temperature and the degree of contamination during sample processing on the amount of an element extracted. The less sensitive aqua regia and pyrophosphate leaches were not effected by sample processing but drying temperature and contaminants had a profound effect on results of the more sensitive enzyme leach. It was found that drying B-horizon samples at temperatures above 45 °C increased the levels of base-metals and halogens substantially. Sources of contamination affecting the manganese-selective enzyme leach were kraft paper bags, which added up to 2000 ppb zinc to samples during drying, and brass sieves that added similar levels of both copper and zinc.

Duplicate samples were collected within a 10 meter radius of sample sites to assess sampling variability whereas analytical variability was evaluated by analyzing samples in duplicate and the replicate analysis of reference soil samples. The greatest variability in element concentrations typically occurred between samples taken 2 to 10 meters apart whereas less variability was found within any individual sample. The variability contributed by the analysis was minor compared to the sampling variability. The precision of a specific element analyzed by pyrophosphate and aqua regia leaches of humus varied from 10 to 100% (95% confidence level) but in general was less than 50%. The precision was slightly lower for pyrophosphate-leached humus possibly due to the removal of inhomogeneous humin from samples. The precision for both types of enzyme leach was typically greater 50% (95% confidence level) for most elements and commonly approached 100% for manganese. In contrast, the precision shown by aqua regia leach of B-horizon samples was generally less than 40%.

The pyrophosphate, enzyme, "enhanced" enzyme and aqua regia leaches were all effective in outlining base-metal mineralization covered by less than 4 meters of basal till. Anomaly contrast for a specific element commonly exceeded sampling variability allowing the identification of anomalies. For humus samples, the aqua regia leach provided better anomaly contrast than the pyrophosphate leach. Both types of enzyme leach showed better anomaly contrast in copper and zinc than aqua regia and also revealed marked responses in chlorine and bromine directly over mineralization.

For the most part, there were no clear indications of anomalous concentrations associated with base-metal mineralization covered by deep (> 10 meters) glacial overburden by any of the methods tested. Element profiles for humus and B-horizon samples were generally "noisy" making threshold values very difficult to determine. In some cases, single sample anomalies were spatially associated with mineralization but it was unclear whether the anomalies reflected bedrock or overburden sources.

In South America, the sampling variability associated with calcareous silty sands was also high but typically lower than anomaly contrast allowing the identification of anomalies. On one property, the enzyme leach revealed multi-element, multi-sample halogen and base-metal anomalies over a porphyry copper deposit buried by 30 to 150 meters of gravel.

The reasons for the extreme sampling variability associated with partial extraction analyses of soils developed on deep glacial overburden are, as yet, unknown. The variability could reflect:

(1) soil forming processes acting on heterogeneous parent materials resulting in variable amorphous manganese oxides around sample sites,

(2) surface contamination, and/or

(3) the non-specific nature of the enzyme leach

However, it is clear that the sample representativity problem will have to be addressed before attempting to interpret "noisy profiles" with low anomaly contrast. Finer grain size fractions will be analyzed by partial and conventional extraction techniques to test the influence of grain size on reproducibility.

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The use of PIXE/PIGME and EPR as an exploration method in highly weathered terrain: Broken Hill, NSW.

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Keywords: EPR, ion-probe, PIXE/PIGME, gossan, weathering, acid insoluble residue, Broken Hill

Electron paramagnetic resonance spectroscopy (EPR) of quartz has been used in gold exploration since the mid seventies, and in Australia for a decade. Chemical analysis by the ion probe techniques PIXE and PIGME indicated moreover that quartz associated with a variety of gold deposits is invariable very impure.

The application of electron paramagnetic resonance was extended to characterise instead of quartz siliceous rocks associated with volcanic hosted massive sulphide deposits, particularly Rosebery. In order to avoid interference from carbonates and sulphides the rock pulps had to be carefully cleaned by acid prior to EPR analysis. The chemical composition of the acid insoluble residue of the rock pulps was again determined by simultaneous PIXE/PIGME analysis. The hostrock at Rosebery is characterised by enrichment in Al, Ti, Mn, Fe, Zn, Rb, Ba, Tl and Pb and depletion in Na and Sr (Aung Pwa et al., 1992).

In a parallel development, rock pulps instead of quartz from gold-bearing and barren jasperoids from Carlin, Nevada, were analysed by these same techniques. The mineralised samples were characterised by high Li, F, Al, K, Ti, Rb, V, Y and Zr values and by significantly higher Rb/Al and V/Al ratios in particular. Significant differences in EPR intensity exist between mineralised and barren jasperoids (van Moort et al., 1995). An important result of the Carlin study was that the EPR signal remained unaffected by weathering such that the composition of acid treated gossanous samples did not vary markedly from the composition of fresh samples.

Because of the success of applying the method to the sometimes highly weathered rocks at Carlin the use of an integrated EPR and PIXE/PIGME technique was recently tried out on a large number of samples from the oxidised lode at Broken Hill, collected by Swensson in 1977. The outermost layer of the original lode consisted of a veneer of plumbic-manganiferous limonite, which was underlain by an unusual gossan of dense black rocks. The latter consisted of intergrown aggregates of botryoidal lead manganese oxides and altered rock fragments, with some quartz and goethite. The gossans are more siliceous towards the top, full of cracks and vugs filled with oxide botryoids and stalactites and, towards the base, inreasingly exhibited cracks and scattered masses of cerussite and pyromorphite. Van Moort and Swensson (1982) reported coronadite, pyrolusite and psilomelane in addition to goethite, limonite and lepidocrocite. Geochemically these gossans are characterised by an extreme enrichment in manganese and lead. Significant features of the oxide gossan at the surface are the Pb/Fe ratio of about 1 or more and a Pb/Mn ratio of 1-2 or greater, even when free of lead carbonate. These mineralogical and chemical characterisics may serve to distinguish from gossans along the lode line, and elsewhere, which are not underlain by ore at depth.

The aqua regia acid insoluble residue of the Broken Hill material consists of quartz, some chalcedony and minor amounts of residual minerals like sphene, anatase, rutile, garnet, zircon, barite and occasionally potash feldspar, mica and xenotime. The acid insoluble residue, rarely more than 10% of the original sample weight, gives an EPR signal which correlates positvely with its Mn content and which is reminescent of synthetic Mn containing silica. The same signal is encountered in quartz from hostrock and footwall of the VHMS deposit at Rosebery. Quartz from the oxidised zone at Silverpeak, on the lode line 7 km NE, and from a unrelated ferric gossan at Wolseley 15 km NW of Broken Hill shows only a very weak EPR signal.

The acid insoluble residue of all the Broken Hill material contains substantial amounts of Ca, K, Ti, Pb, Zn, Y and Zr related to the presence of sphene, rutile etc. The Mn and F content of the samples and the Mn x F product can be used as indicators of mineralisation, as they are high at the gossans or locations where the orebody exists at depth and low above barren sections like at Silver Peak or Wolseley. These indicators appear to be more reliable indicators of mineralisation at Broken Hill than the previously used Pb, Zn and Mn content or elemental ratios like Pb/Fe of the bulk gossan and appear also to be more suited to locate deeply buried deposits.

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The influence of organic matter on determining As, Sb, Bi by hydride-generation atomic fluorescence spectrometry in soils and sediments

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Keywords: arsenic, antimony and bithmuth analysis, organic matter, soil and sediments

Arsenic,antimony and bismuth are important pathfinder elements of selected 39 elements in China's Regional Geochemistry-National Reconnaissance Project (RGNR). To meet the requirement of the detection limits of As (1 ppm), Sb(0.2 ppm) and Bi (0.1 ppm) and analysis of a great number of samples in the Project, hydride-generation, atomic fluorence spectrometry (HGAFS) was chosed for for analysing these elements because of its high sensitivity, high efficiency and low cost since the problem of bismuth interference had been solved (Zhang et al., 1984; Guo, 1989).

In routine analysis of the elements in soil and stream sediments in RGNR Project, samples were digested by 1+1 aqua regia (Zhang et al,1984). Great difficulties might be encountered for analysing As,Sb,Bi in organic-rich soil and sediments by using this procedure though there is no problem for organic-poor samples.

As part of the RGNR project, regional geochemical mapping by collecting mainly organic stream sediments (peat) has been carried out in most of the forest-swamp regions of northeastern China. For the organic-rich samples, however, no special attention has been taken in the procedure of digesting them by analysers yet. Our reseach is to understand the influence of organic matter on determining As, Sb, Bi in organic-rich soils and sediments by hydride-generation atomic fluorescence spectrometryand evaluate the previous data determined by this method in the RGNR project.

Sample processing and analytical procedures

60 organic-stream sediment and 32 soil samples were collected in forest areas from a polymetallic mineralization in Da Hingan Mts. and a porphyry copper deposit in Xiao Hingan Mts., northern Heilongjiang. The samples were airdried, siezed with retention of the minus 0.2 mm fraction and seperated into two aliquots of 50 g (few samples are less than 50 g weight because of shortage of sample material) . One 50 g sample was directly pulverized to a minus 0.076 mm in a ball mill. The other 50 g sample was placed in a 200-ml beaker, heated to 200^{o}C to smoke in an oxidized atmospher about 2 hours and then heated to 450 ^{o}C over a period of half an hour, whence it was held at this temperature for over 5 hours until organic matter was completely oxidized. After cooling to room temperature the percentage weight loss was determined. The ignited sample was also pulvirized to a minus 0.076 mm in a ball mill.

The ignited and non-ignited samples were digested in aqua regia and HNO_3+$HCLO_4$ at heating plate respectively and analysed by HGAFS for As, Sb, Bi. To compare the results, the As in the ignited and non-ignited samples were determined by XFS.

The results

The range of LOI in organic stream sediments is 10-65%(organic carbon 4-20%) and most of them are between 20-40%. LOI in the soil of A horizen is 15-25% (OC 2.5-6%) and LOI in the soil of B horizen is less than 10% (OC <1%). To be comparable, the results of As,Sb,Bi after ignition were multiplied by 1-LOI.

For organic stream sediments and soils in Ah horizon, the As, Sb and Bi determined by HGAFS following aqua regia digestion are much lower than that by the same procedure after ignition and by HNO_3+$HClO_4$ digestion with no ignition. the As and Bi analysed by HGAFS show a simple linear relationship, whereas the Sb show no simple linear relationship between the results by different procedures although, the results of Sb after digestion of HNO_3+$HClO_4$ or ignition are much higher than that with no ignition(Fig.1,2 and 3). The As determined by XFS show a simple relationship between ignited and non-ignited samples and is comparable to the As determined by HGAFS with digestion of aqua regia after ignition and HNO_3+$HClO_4$ digestion (Fig.2).

For soils in B+C horizon, As and Bi except Sb determined by HGAFS show a simple linear ralationship between the results by different procedures(Fig.3).

Discusion

Organic stream sediments or valley peats were main sampling media in the China's RGNR project and follow-up surveys in the past in forest-swamp area (more than 400 000 km^2), northeastern China. Although that for these organic-rich samples foaming in the generator might affect the results was recognized by some analysists when conducting routine measurements using HGAFS after digestion of aqua regia, no much attention was taken to change the standard procedures because most of measurements were not done by academically trained workers. It is obvious that the previous data of As, Sb, Bi determined by HGAFS after digestion of aqua reiga are marked low and hard to be used as basic data to select targets for follow-up or detailed survey.

Conclusion

Organic matter can greatly influrence the results of As, Sb, Bi determined by HGAFS following aqua regia digestion and the influrence can be eliminated by igniting the samples or by a wet ashing in perchloric acid. Lower Sb values by HNO_3+HCl_4 digestion compared to aqua regia digestion following ignition may demonstrate loss of antimony chlorides at higher temperature place(Boyal and Jonasson,1984).

To better use previous data in the RGNR project of China, the collected samples should be reanalysed by pretreating or changing digestion procedures.

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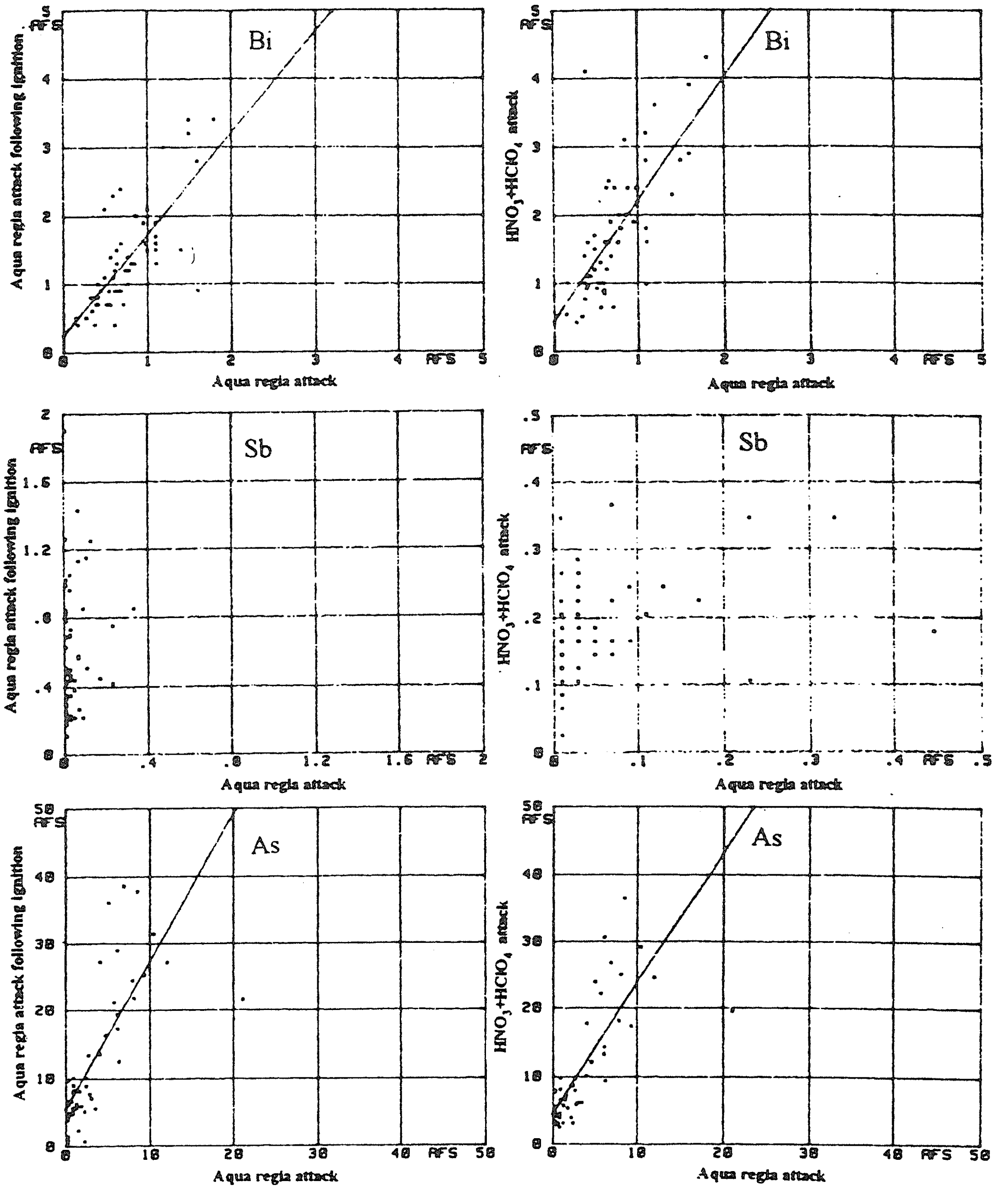

Figure 1. Relationship between the results determined by hydride generation atomic fluorescence spectrometry following different processing procedures in soils (in ppm).

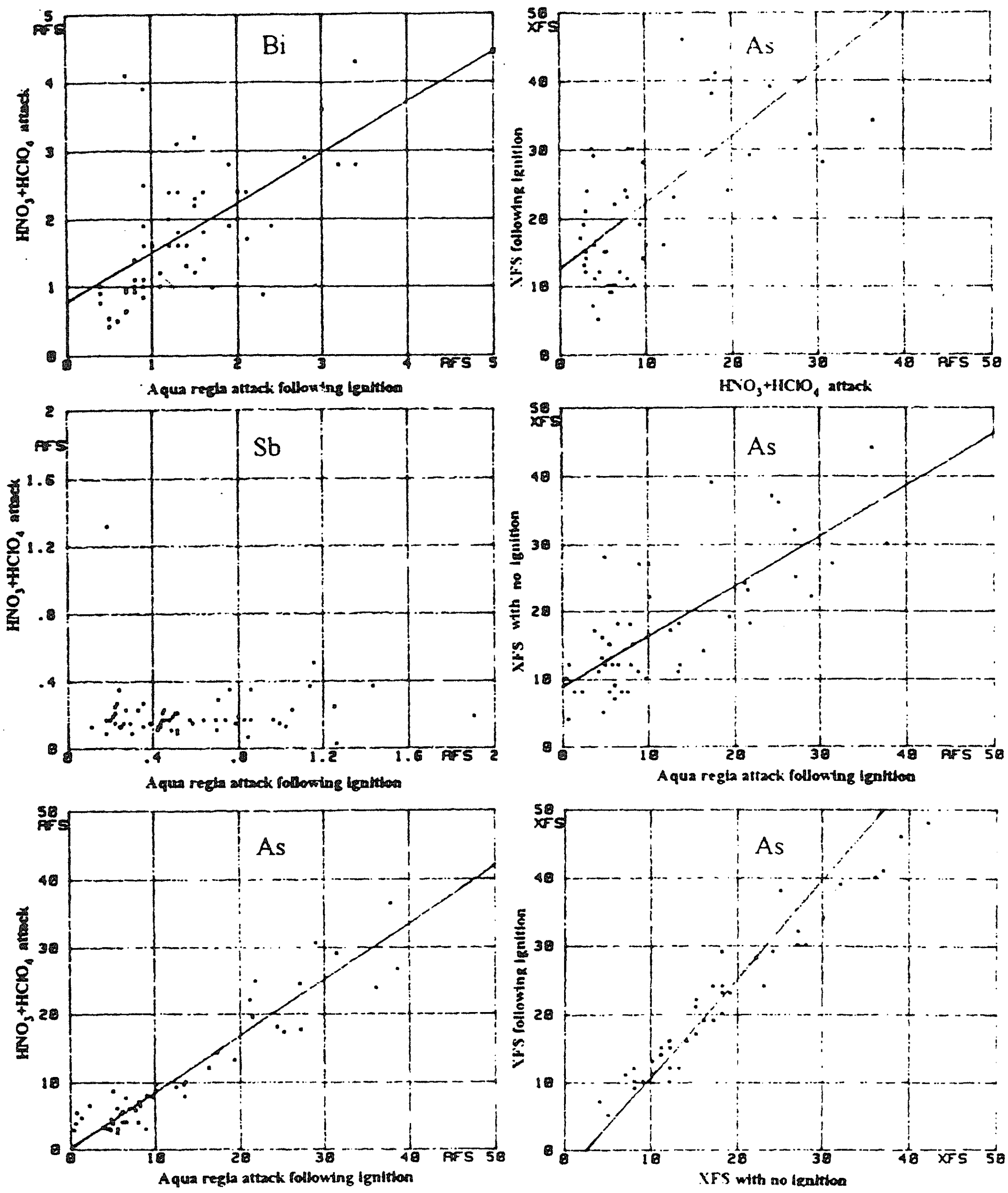

Figure 2. Relationship between the results determined by different analytical procedures or methods in organic stream sediments (in ppm). AFS = hydride generation atomic fluorescence spectrometry; XRF = X-ray fluorescence spectrometry

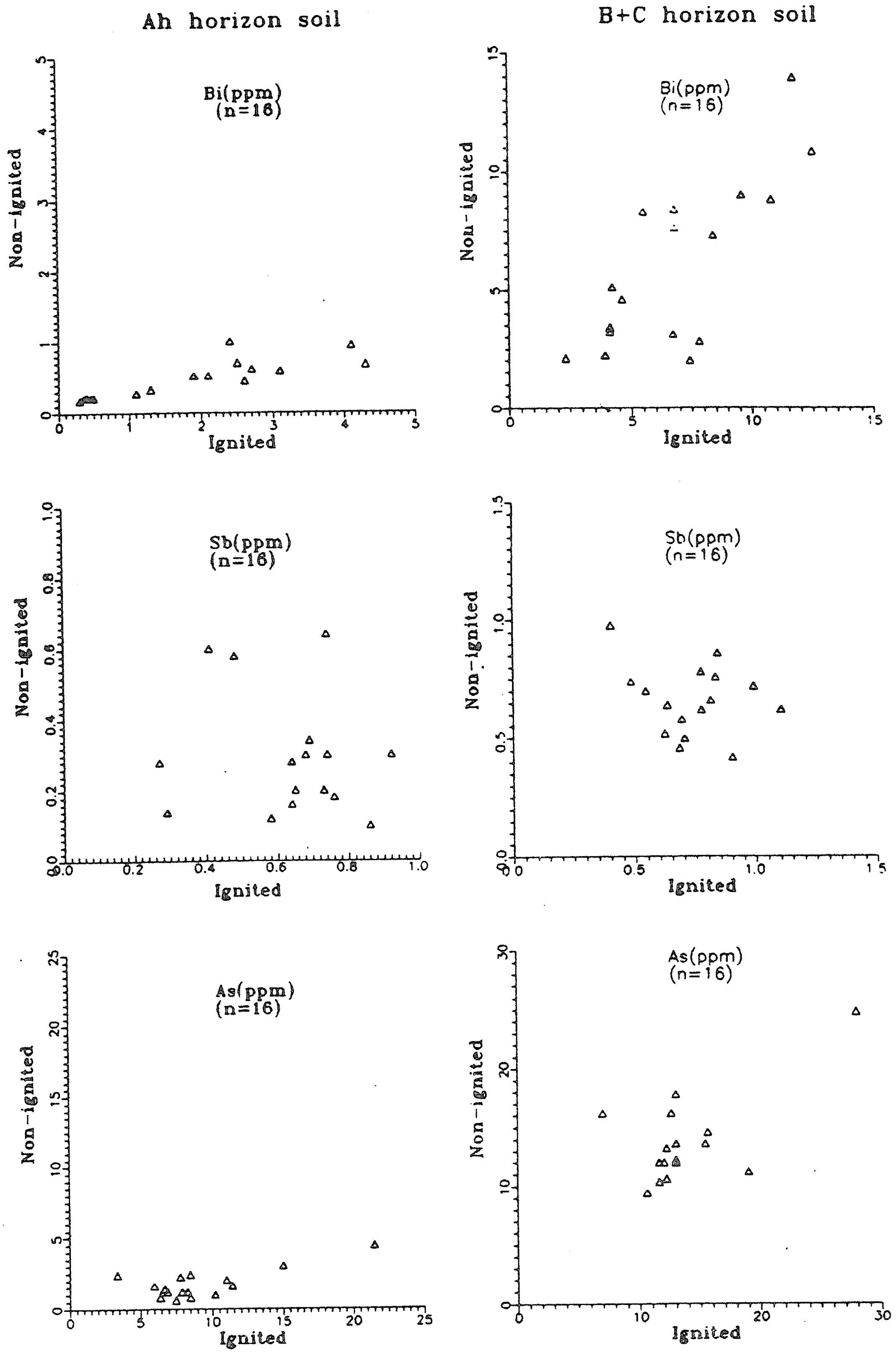

Figure 3. Relationship between the results determined by different analytical procedures in organic stream sediments (in ppm). AFS = hydride generation atomic fluorescence spectrometry.

GEOGAS AND DETECTION OF SUPERIMPOSED MOBILE FORMS OF ELEMENTS FOR REGIONAL EXPLORATION IN TRANSPORTED OVERBURDEN AREAS

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keywords: GEOGAS, DESME, regional, exploration, overburden

In China geochemical methods have played an important role in the discovery of minerals. However, selection and location of drilling targets for new deposits in areas covered by transported overburden are becoming more difficult. In response to these problems, a series of new techniques of dynamic collection of geogas (GEOGAS) and detection of superimposed mobile forms of elements (DESME) have been developed and have been successfully used in the search for buried deposits in the past 5 years. Recently, these two methods are being used in regional-scale geochemical surveys in areas where bedrock or mineral deposits are buried beneath deeply weathered or transported overburden.

These techniques are based on the consideration that gases generated at depth continuously migrate upward, when they pass through mineral deposits, trace elements (a variety of ions, molecules or ultrafine particles) released from the mineral deposits will be absorbed on the surface of the gas bubbles and transported upward to the overburden. Upon reaching near surface environment, part of the amount of trace elements is still in gases and part of it will be transformed into other mobile forms trapped in manganese and iron oxide coatings, organic matter or in clay minerals.

To find anomalies built up in this way, GEOGAS and DESME techniques are used. GEOGAS is obtained by pumping soil gases through the collector with special sorbing material. Trace elements will be absorbed on the material and then analysed by INAA and LSAD (Single Atom Detection with Laser). It generally takes 5-10 minutes to collect a sample at each sampling site.

Regional GEOGAS and DESME were first tested in the total area of 160000 square kilometres in Shandong province where there are the largest gold deposits in China. Most of the area is covered by transported overburben. The thickness of overburben generally ranges from several meters to two hundred meters. The principal rocks consist of Archean metamorphites and Mesozoic granites. The gold mineralization veins are controlled by NS-trending altered fault zones. Gold occurs in zones of silicic and phyllic alteration and quartz veins.

The sampling density is 1 site per 800 square kilometres. At each sampling site, two kinds of composite samples, gas and soil, were collected.

Gas samples were analysed for Au, Ag, Cu, Pb, Zn, Fe, Mn, As, K, Na etc. , by INAA and LSAD. Soil samples were analysed for Au, Ag, Cu, Pb, Zn, Fe, Mn in water-soluble phase, clay minerals, organic matters and Fe-Mn oxides by using sequential extraction and the elements were determined by AAS.

The pilot results show that very large regional anomalies of Au in gas and Au, Ag, Cu, Pb, Zn, Fe and Mn in water-soluble phase, clay mineral phase, organic phase and Fe-Mn oxide phase were delineated over and around the gold deposits. The anomalies have greater contrasts and size for many trace elements than with other methods tested. The strongest anomalies exist over the gold deposits and tend to follow the buried altered fault zones, suggesting that areas may have potential for new gold deposits.

Current research and tests using GEOGAS and DESME are being conducted in Kizilkum desert, one of the world's largest gold ore province, in Uzbekistan and in Takeramakan desert, having potential of gold deposits, in Xinjiang, China.

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