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II Brazilian Geochemical Congress

Abstracts

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Foreword

The Rio'89 Organizing Committee welcomes you to Rio de Janeiro and to the combined II Brazilian Geochemical Congress and XIII International Geochemical Exploration Symposium. This is the first time an international geochemical symposium has been held in Latin or South America and represents and ideal opportunity for geoscientists from Brazil and from around the world to compare experiences and exchange ideas. Applied geochemical techniques play a crucial role in effective exploration in Brazilian geologic and weathering environments, and the emphasis placed on geochemical exploration is reflected by the attendance of over 400 geoscientits at the first Brazilian Geochemical Congress held 2 years ago.

The abstracts contained in this volume comprise contributions from 240 authors representing 34 countries and summarize the "formal" presentations for Rio'89. The abstracts provide a useful means for individual delegates to identify other geoscientists with shared interests with whom discussion and exchange of ideas can prove rewarding at the "informal" meetings at lunches, coffee breaks, etc during the event.

The Organization Committee would like to thank the authors for their contributions to Rio'89 and encourages delegates to take full advantage of this opportunity to meet with their geochemical colleagues.

RIO'89
Organizing Committee

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XIII *International Geochemical*
Exploration Symposium

Technical Session
Geochemical Exploration for Precious Metals and Strategic Metals

A MULTI-ELEMENT AND MULTI-MEDIA APPROACH TO GEOCHEMICAL EXPLORATION FOR GOLD IN EASTERN NOVA SCOTIA, CANADA

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Over the past four years gold exploration in eastern Nova Scotia has included the use of several geochemical sample media. Two data sets of similar areal extent (5,000 sq. km), sample density (1 per 8 sq. km), and analytical method (INAA) are appropriate for conducting a comparative study of their element distribution patterns, and their geochemical responses to the presence of gold mineralization. These comprise multi-element data sets from lake sediment and biogeochemical surveys. The combined geochemical patterns for gold and associated elements are of particular use in the identification of anomalous patterns related to gold mineralization. This study demonstrates simple statistical methods of data integration from the two survey media, making use of microcomputer-based systems.

The study area is underlain by Meguma Group (MG) metasediments of Cambro-Ordovician age. A lower turbidite sequence (Goldenville Formation) is conformably overlain by black slates (Halifax Formation). Granitic bodies, locally of batholithic proportions, intruded the MG during the Acadian event (370 Ma), although in the study area most of the intrusions are small in surface outcrop. Deformation during the Acadian Orogeny produced tight to isoclinal , upright folds with accompanying regional greeschist to amphibolite facies metamorphism. A series of northeast-trending anticlines form dome-like structures which are commonly associated with areas of Au enrichment.

Most of the significant Au deposits of Nova Scotia are found within the MG, especially in turbidites of the Goldenville Formation, where typical mineralization is native gold with arsenopyrite and carbonate in quartz veins. Extensive zones of silicic, carbonate and phyllic alteration occur around these deposits and in proximity to large scale shear zones (Kontak and Smith, 1988).

Centre-lake sediment samples of gyttja (organic-rich ooze) were collected from approximately 500 lakes by gravity corers dropped from a float-equipped helicopter (Bingley and Richardson, 1978; Rogers et al., 1985). Samples were air-dried, disaggregated, and sieved to obtain the -200 mesh fraction for analysis. For the biogeochemical survey, the most recent five to seven years growth of balsam fir twigs and needles were collected from almost 600 sites adjacent to available roads and tracks (Dunn, 1988). The samples were air-dried, the needles removed, then the twigs were ashed at 470°C. Both sample suites were submitted for multi-element determinations by instrumental neutron activation analysis (INAA).

Catchment Basin Analysis (CBA) was used to create a model representing lake sediment data (Wright et al., 1988). The lake sediment geochemical model also includes the recognition of hydromorphic and clastic dispersion (Rogers and Garrett, 1987; Rogers, 1988). The biogeochemical data (Dunn, 1988) were interpolated as sample points with a 3km radius of influence assigned to each sample location in order to graphically represet the data. The response of each sampling medium to known mineralization and geologic controls was illustrated by single-element maps and multivariate analysis to identify common associations.

Gold in balsam fir twig ash ranges from <5 to 170ppb. Most of the twenty gold districts recognized in the study area outlined by balsam for samples from several sample sites that contain gold concentrations greater than the 90th percentile of the data set. Several new areas of gold enrichment are indicated, especially near the margins of the eastern granites along major shear zones. As yet unexplained anomalous Au values are also found over the Carboniferous rocks in the north of the study area. Arsenic, with concentrations from <1 - 72 ppm, shows similar distribution pattern to the gold of local enrichment and exhibits a marked spatial correlation with known gold deposits. Zones of weak W enrichment are apparent near some Au deposits and adjacent to some of the granitic bodies.

The lake sediment Au response is positive for most of the known deposits, with concentrations up to 525 ppb. Arsenic also highlights the Au districts and is an important pathfinder element for precious metal mineralization. For the other elements the lake sediment response is generally flat, especially for Th, W, Rb and Sb. Uranium and Th highs occur over some granitic bodies, especially in the eastern half of the area. In general, W and Rb have a similar response, and relatively high concentrations outline the granitic bodies. Wright et al. (1988) describe multivariate element patterns in lake sediments of the study area by three content (Zr-Rb-Ti-Th-Nb-F), the second to scavenging (Cu-Pb-Zn-As-Sb), and the third to gold mineralization (Au-W). In addition, the lake sediments have two main multi-element associations related to lithology: a lithophile response over granitoids (F-Li-Nb-Rb-Sn), and a siderophile association of Au-Sb-As over the metasediments (Rogers et al., 1987).

The spatial relationship between elements common to both data sets were modelled by sampling the lake catchment basin map to capture any biogeochemical point locations within each catchment basin. This study compares the patterns of As, Au, Rb, Sb, Th, W and Rb in the two sample media. The Au and As patterns are very similar for both media anomalous concentrations are spatially related to the known gold districts. The advantage of integrating the data sets is that anomalies can be stacked, and low order anomalies exhibited by a single sample medium can be ascribed a lower exploration priority. On a reconnaissance survey scale, both media respond well in detecting known Au deposits and also in detecting new anomalous areas. The biogeochemical data also clearly outline important shear zones which act as a loci for Au mineralization in Nova Scotia.

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ANTIMONY AND ARSENIC AS PATHFINDERS TO PRECIOUS METALS ASSOCIATED WITH METASEDIMENTARY-HOSTED MINERALIZATION AT MORRO DO BULE, QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRAZIL

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Simultaneous determinations of arsenic, antimony, bismuth and tellurium and single element determinations of selenium (all by ICPAES/ hydride generation) in addition to gold, mercury and multielement determinations were carried out in rock, soil and stream sediment samples from the Morro do Bule area, near Cachoeira do Campo, Quadrilátero Ferrífero, Minas Gerais State, eastern Brazil.

Lithogeochemical results show that antimony is the principal indicator element of the Morro do Bule Zn-Pb-Sb vein mineralization as an ore constituent in its own right. Antimony is well correlated with arsenic, base metals, silver, gold and mercury. SEM/EPMA studies carried out on vein samples show that antimony is present in the ore suite as stibnite, copper and lead sulfantimonides and secondary antimonates. EDS analyses confirm the presence of silver in the lead sufantimonides (jamesonite, zinkenite and fuloppite) and gold in secondary lead antimonate. The detailed surveying of a section of itabirites and quartzites immediately southwest of the vein mineralization confirm the high values of arsenic, antimony and base metals detected in previous work, though suggesting that enrichment tends to occur preferentially in either ferruginous quartz veins or metapelitic lenses or manganiferous impregnations. Mineralogical data from goethite-rich quartz veins indicate that the high arsenic and antimony values relate them to the presence of sulfides. However, the concomitant presence of grains of platinum-iron alloy also raises prospects for the itabirite to host platinum-group elements. On a border scale, both antimony and arsenic are enriched in the rocks of the region, with antimony predominanting over arsenic in the vein-hosting dolomites and arsenic exceeding antimony in itabirites, phyllites and quartzites. Bismuth, selenium and tellurium appear to relate better to phyllites than any of the other lithologies.

The major feature in soils over the mineralized zone is their much stronger expression of mineralization than rocks as a result of supergene processes taking place on the dolomites where the veins are hosted. Effective weathering is reflected by well-developed soils with intensive iron and manganese accumulation. Antimony and arsenic are preferentially accumulated in the B horizon. Geochemical and SEM data indicate that antimony occurs in the major secondary forms: (1) as secondary antimonates admixed with iron and manganese; (2) as co-precipitates with or absorbates onto Mn and Fe oxides. Arsenic also appears to occur co-precipitated with or absorbed onto both Mn and Fe oxides. A noteworthy feature in soils outside the mineralized zone, i.e. over phyllites, quartzites and itabirites, is the absence of significant enrichment for the majority of elements in relation to bedrock. This seems to lie on the acid soil pH whereby strong leaching takes place with only moderate iron fixation.

Stream sediment data show that the mineralized vein is mapped by an antimony signature that extends for approximately 1km downstream from the source. The association of antimony with manganese and iron in soils and with manganese in stream sediments suggests that antimony is partly mobilized in admixture with secondary hydrous oxides. Antimony is also present in the drainage as secondary antimony minerals. These findings indicate that the drainage dispersion of antimony at Morro do Bule is predominantly mechanical. The arsenic pattern, on the other hand, does not relate itself to the vein, but instead, to the itabirite lithology due to persistently higher values upstream from the vein. The persistently higher values of lead, zinc and copper upstream from the veins, in addtion to those of arsenic, could either indicate the existence of another sulfide mineralization at a different stratigraphic level than the dolomites or the presence of a wider, though less intense halo. Like antimony, arsenic is thought to occur predominantly present in admixture with iron and manganese oxides in drainage sediments.

The aforementioned results highlight the masking effect that the itabirite contribution produces on drainage patterns and the resulting difficulty identifying mineralization from stream sediment geochemistry in this type of terrain. Therefore future surveys in areas similar to Morro do Bule should entail a careful examination of the suite of the elements employed regarding its content in the local lithologies and in source of mineralization.

ARSENIC, ANTIMONY, BISMUTH, SELENIUM AND TELLURIUM AS PATHFINDER ELEMENTS TO GRANITE-HOSTED VEINTYPE AND DISSEMINATED GOLD MINERALIZATION AT CERRITO DO PIRES, RIO GRANDE DO SUL, BRAZIL

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Multielement tecnhiques featuring the determinations of arsenic, antimony, bismuth, selenium and tellerium by ICPAES/hydride generation were carried out on rock, soil and stream sediment samples from the Cerrito do Pires area, located on the Lavras do Sul Granitic Complex, Rio Grande do Sul state, Southern Brasil.

Lithogeochemical results indicate that arsenic, antimony, selenium and tellurium are enriched in the main vein at Cerrito and that their distributions, as well as those of gold and base metals, are associated with fracturing and hydrothermal alteration. The presence of major As, Sb, Te and Se anomalies and minor Bi anomalies on the northern half of the sampling traverses, reflect the existence of other veins in addition to the central main vein. Arsenic is the most abundant pathfinder element and the one that displays the largest extension over mineralization. Antimony behaves similarly to arsenic, though at much lower concentrations and contrasts. Tellurium and selenium appear preferentially distributed in fractures, either associated with the main vein or located on the northern sections of the traverses. Bismuth shows a less pronounced signature than the other four pathfinder elements. SEM and EPMA studies, conducted on rock specimens, indicate that: (1) arsenic is mainly present as arseniferous pyrites and sulfarsenides; (2) antimony occurs as sulfantimonides of lead, silver and copper; and (3) tellurium is found in the form of silver-gold tellurides. The mineralogical forms of selenium and bismuth could not be ascertained.

The results from soil analyses incate that arsenic, again, is the pathfinder element that represents the underlying gold mineralization most consistently. Tellurium and antimony show good soil patterns, but, unlike arsenic's, their patterns do not always reflect the mineralization underneath. A comparison between the average concentration of elements in soils and in rocks shows no significant enrichment for the majority of elements in soils relative to the underlying bedrock.

The major geochemical feature in stream sediments is the high concentration of many elements along the stream profile. The levels of concentration of antimony, bismuth, copper, silver and lead in stream sediments largely exceed those found in bedrock and soils along the sampling traverses. Potassium, aluminium, iron, arsenic, tellurium, manganese and zinc also present in higher amounts. During a field inspection conducted in early 1984 it was observed that most of the stream samples runs over a rocky channel enclaved in what appears to be a fracture in the granite, in apparent aligment with the fault hosting the main vein at Cerrito. This led to speculation that the stream could be running along a mineralized fracture, a southwestern extension of the main vein. On the basis of the data and of recommendations of the senior author, the Companhia Brasileira de Cobre sited an inclined borehole at the southern margin of the stream, transecting the subsurface underneath the stream. This borehole intersected an 85m-thick section of hydrothermally-altered granite containing disseminated gold mineralization.

BEHAVIOUR OF GOLD AND OTHER HEAVY MINERALS IN DRAINAGE SEDIMENTS – SOME IMPLICATIONS FOR EXPLORATION GEOCHEMICAL SURVEYS

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Geochemical anomalies for elements, such as Au, dispersed in drainage sediments as a major constituent of a rare heavy mineral are typically extremely erratic and difficult to confirm. This results partly from the statistical problems of sampling for rare grains. However, detailed studies of free gold, W in scheelite and Sn in cassiterite have shown that their anomalies in stream sediments have important features in common. For example, (i) there can be considerable variations in metal concentrations between adjoining sites on a stream bed (ii) their greatest concentrations are usually found in sediments from "high energy" environments, (iii) difference in metal concentrations between adjoining sites decrease with decreasing grain size of the heavy minerals, and (iv) heavy mineral concentrations at a single site can show systematic variations with time.

The field relationships are shown to be consistent with stream (hydraulic) processes that result in either selective deposition of the heavy mineral grains or the winnowing of lighter minerals to leave a heavy mineral lag deposit. Implications of the model for design and interpretation of stream sediment and heavy mineral surveys are discussed in relation to when, where and what to sample and how to present the data.

DEPOSITION AND SUPERGENE ENRICHMENT OF THE GOLD KING-DAVIS EPITHERMAL PRECIOUS METAL LODE, SILVERTON CALDERA, SAN JUAN VOLCANIC FIELD, SOUTHWESTERN COLORADO, USA.

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The epithermal Gold King-Davis precious metal vein system is a caldera-hosted, bonanza-type gold telluride vein deposit. It is peripheral to a low grade porphyry copper-gold system of Tertiary age. These and numerous additional precious and base metal deposits are located within and near the Silverton caldera, a Tertiary collapse-caldera in the San Juan Volcanic Field, sothwestern Colorado. Thin Paleozoic and Mesozoic strata had been largely eroded from the apex of the San Juan dome when Tertiary volcanism began at the Silverton volcanic center. Thus at that time the Proterozoic basement was exposed and became part of the roof of the Silverton caldera.

Earlier research revealed the following understanding of the regional geology. The Silverton caldera collapsed asymmetrically toward the southwest and thereby formed a hinged, half-graben structure at about 27.5 Ma. Resurgent volcanic activity occurred along the southern margin of the caldera, where the Silverton quartz-monzonite was dated at 25.1 Ma. The Red Mountain porphyry, which is the youngest resurgent stock of the caldera was intruded at about 11-10 Ma in the northwestern part of the caldera. It probably supplied the heat source for the hydrothermal system that formed the Gold King-Davis gold lode deposit. The apical Eureka Graben subsided between 27.5 and 22.5 Ma and today transects the Silverton caldera, strinking northeast-southwest. In the northeast this graben terminates at the margin of the 22.5 Ma Lake City caldera. This graben structure and caldera-related concentric and radial faults, provide the dominant structural control for emplacement of base metal and gold ores. The Gold King-Davis gold telluride veins are near the Red Mountain stock in the north central part of the Silverton caldera. There, west-northwest-striking hinge faults that are related to the collapse of the caldera intersect northeast-trending faults of the Eureka Graben.

This research comprises the Gold King-Davis vein system and its geological and geochemical setting. The Gold King-Davis veins are up to 5m wide and follow steeply southeast and northwest-dipping structures of the Eureka Graben. Subsidiary veins, which are up to 1 meter wide branch off the main lode. These veins strike northeast and are termed "flat veins" because of their shallow dip of 45 to 50 degrees toward the northwest. The roof of the caldera consists of Proterozoic basement rocks that are unconformably overlain by Tertiary caldera fill of rhyolitic ash-flow tuffs, followed by latitic flows and flow breccias. These, in turn are covered by andesitic lahars, and lapilli and crystal tuffs. The Gold King-Davis deposit is hosted by latitic flows, and flow-breccias of the Burns Formation.

Two hydrothermal events affected the Silverton volcanic center and are both represented within the Gold King-Davis vein system. The propylitic alteration acompanied a period of base metal mineralization at 23-22.5 Ma. A younger, 11-10 Ma event introduced the distinct and localizated gold tellurides with associated argillic and acid-sulfate alteration which are characterized by sericite, kaloinite, and alunite. Sericite-kaolinite alteration accompanies elevated gold grades and gold ore-carrying structures, whereas alunitized wall rock yields only traces of gold.

Supergene enrichment of the precious metal assemblage resulted in metal tenors as high as 3.016g/t gold and 1.088g/t silver. The veins contain electrum (95/5 weight% Au/Ag), hessite, petzite, sylvanite, krennerite, altaite, tetrahedrite/tennantite, bismuthinite, with or without pyrite, chalcopyrite, and sphalerite. These minerals were precipitated together with quartz from hydrothermal solutions. Homogenization temperatures of 280 to 300 degress C for the precipitation of the vein quartz that is the main component of the gold telluride-bearing veins. Characteristically, ore-forming solutions appear to have been predominantly of meteoric origin and were of relatively dilute nature, with fluid inclusions showing an average salinity of 1.6 wt% NaCl equivalent.

These auriferous solutions penetrated rocks of the caldera roof that include thick Proterozoic olivine and tholeiitic basalts, ferruginous sedimentary rocks, and minor iron formation. Worldwide, these rock types are thought to be relatively enriched in, and therefore favorable source rocks for gold deposits. Other research into lead isotopic data from base metal deposits in the San Juan Volcanic Field support a Proterozoic source for the lead. Thus, by implication, gold too may have been leached from rocks of the Proterozoic basement below the Tertiary caldera fill.

From the local geologic setting and characteristics of these ins the following interpretation is suggested: Meteoric water-dominated hydrothermal solutions generated by the Red Mountain stock ascended through intensily fractured, ferruginous Proterozoic formations and overlying Oligocene rocks of the caldera fill. These solutions were funnelled into the open fracture system, there causing vein emplacement with the sequence of phyllic, argillic, and acid-sulfate alteration.

This took place under physico-chemical disequilibrium with water to rock ratio, > 1 and slightly alkaline conditions that resulted in potassic alteration and the generation of adularia at depth. Gold that was probably derived from rocks of the Proterozoic basement was transported in hydrothermal solutions, which ascended along major fractures, particularly the caldera collapse faults and/or bounding faults of the Eureka Graben. These fractures served as channels along which physico-chemical equilibrium was established between the rising solutions and the wall rocks. The breakdown of gold bisulfite complexes and precipitation of native gold thus resulted from boiling and decreased temperature, as well as from decreased pH and increased log f02 in hydrothermal solutions near the paleo-surface.

Other precious metal deposits of the central and southeastern San Juan Volcanic Field show geological and geochemical settings, which are similar to those of the Gold King-Davis vein system. At Creede and at Summitville too, precious metal-bearing veins are structurally controlled and, like the Gold King veins, also occur in volcanic rocks of latitic composition. These deposits too, resulted from physico-chemical changes in hydrothermal solutions as these approached the paleo-surface.

From this research the following guides are suggested for precious metal exploration in the San Juan Volcanic Field:

1) Proximity to both, Proterozoic basement and Tertiary stocks, 2) structural control, 3) distinct lithologic control, and 4) characteristic alteration pattern that indicate specific changes in hydrothermal solutions near the paleo-surface.

GENESIS OF PLATINUM MINERALIZATION AT THE GIBELLINI Mn-V-Ni DEPOSIT, EUREKA COUNTY, NEVADA.

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Anomalus platinum mineralization has recently been detected at the abandoned Gibellini Mine workings in the Fish Creek Range, Eureka County, Nevada. At this occurrence, hydrothermal Mn-V-Ni mineralization of possible Miocene age is hosted by Devonian Devill's Gate Limestone. Platinum-group element (PGE) mineralization is dominated in surface samples by platinum (400 to 600ppb) with weak palladium and rhodium mineralization (approximately 30ppb).

Archive samples from seven other Nevada manganese occurrences and one sample from New Mexico were analyzed for their PGE content. None of these samples contained greater than 10ppb platinum or palladium. The Gibellini manganese ore also contains, on average, 3.2% zinc, 1.7% nickel, 0.49% vanadium, 0.3% cobalt, 0.12% copper, and 0.11% molybdenum. This enrichment in most of the first row transition elements is lacking also in the other manganese ores.

The occurrence of sub-economic platinum mineralization associated with manganese ore has not previously been reported in the literature and does not appear to be a common feature of Nevada manganese deposits. The hydrothermal platinum mineralization at Gibellini appears to be only coincidentally associated with manganese but bears a resemblance, in certain respecta, to other hydrothermal PGE deposits.

The Gibellini platinum occurrence is similar to PGE mineralization at the Boss Mine in the Goodsprings district, Clark County, Nevada. Both deposits are hosted by late Paleozoic carbonate rocks wherein fault breccias have controlled hydrothermal fluid flow and ore deposition. However, the Boss Mine planitoids are associated mainly with copper mineralization.

Hydrothermal platinum occurrences around the world have in common the fact that they occur proximally to logical source rocks, generally mafic to ultramafic intrusives. In fact, they are usually hosted by these intrusives where structural zones have provided for the circulation of hydrothermal fluids and mobilization of platinoids. These intrusives may be especially favorable source rocks not only because of their high background PGE contents but also because of the lability of the sulfide mineral hosts from which the platinoids can be leached by cartain solutions. The resulting hydrothermal PGE deposits typically are associated with Cu, Cu-Ni, or Cu-Ni-Co mineralization, reflecting the geochemistry of the labile hosts from which they were remobilized and fingerprinting the source rocks as mafic of ultramafic.

Within 0.2km of the Gibellini PGE mineralization is an allochthonous block of Devonian Woodruff Formation black shale, thrust from the west during Mississipian tectonism. This shale is not only kerogenous to the extent of being an oil shale but is also extremely metalliferous. Horizons in the shale contain hundreds to thousands of ppm of most of the first row transition elements. Metalliferous black shales commonly contain 50 to 100ppb platinum, which, in order of magnitude is higher than the background platinum contents of most crustal rocks. Furthermore, transition metals contained within black shales generally occur as sulfides or organo-metallic compounds from which these metals are readily mobilized. Certain black shales are, therefore, attractive PGE source rocks.

No mafic rocks are known to occur in the region and the Mn-V-Ni(Zn-Mo-Co-Cu) geochemical signature of the Gibellini mineralization points to a black shale source for metallization of the limestone. The Woodruff Formation is the logical, proximal source rock for the Gibellini PGE mineralization.

GEOCHEMICAL EXPLORATION IN THE CENTRAL ASIAN MOUNTAINS

C.J. Moon, Abdul Khaliq, Wang Chang Lin
Geochemical Exploration in the Central Asian Mountains

Although the mountain belt is larger than Western Europe very little is known of its mineral deposits and still less of its exploration geochemistry. This reflects the climatic and cultural diversity in an area that includes the world's highest mountains. Recent geological studies suggest that the uplift started around 15 Ma in response to the collision 30 Ma earlier of the Indo-Pak plate with an Asian plate, which had already collided with marginal island arc terranes, such as Khoistan and Ladakh. The Asian plate, north of the collision zone, has a complex geological history and consists of accreted terranes as well as Precambrian nuclei.

Our efforts have concentrated on the geochemistry of the more arid parts of the area in northern Pakistan and the Xinjiang Autonomous Region of China.

In northern Pakistan, we have devised a scheme for regional exploration, which must, for safety and logistical reasons, rely on ground-based transport and on relatively wide-spaced sampling. As part of orientation studies we have invetigated the dispersion processes in areas of rapid uplift, >3 mm/yr for the Nanga Parbat peak and on some of the world's steepest slopes.

Any exploitation is likely to involve the extraction of high value comodities so we have concentrated our efforts on gold. This occurs in three previously known settings, as placers and small porphyry diorites on the northern contact of the Khoistan arc with the Asian plate, and as epithermal (As- Sb- Hg- Ag) deposits associated with major faults on the Asian plate.

The association of gold, uraninite and pyrite in modern placer deposits in the Indus River and its major tributaries, near Gilgit, at the northern margin of khoistan, is of particular significance both for studies of modern dispersion and of the generation of Witwatersrand style paleo-placer deposits. We investigated this problem by sampling tributaries which have only gold and pyrite. In one drainage, at Bagrot, we located a bedrock source for the gold and pyrite within volcanic-hosted quartz veins and skarns associated with granitoids. Gold and pyrite are rapidly eroded in terraces and glaciers and, later, remobilised into incised braided rivers. the excessive dilution, which we will try to quantify, is caused by rapid movement of material and results in a far superior anomaly/background ratio for panned concentrate samples relative to grab or wet-sieved samples. Part of the reason for the effectiveness of panned samples is that auriferous pyrite is preserved for long distances downtream (up to 15km). On a regional scale gold and pyrite-rich rivers are associated with the probable suture between khoistan and the Asian plate. Road sections indicate that this mineralization has a polyphase history with protores pre-dating dyke intrusion at 70 Ma.

Uraninite seems mainly to be associated with gold and pyrite in the major rivers and probably has a different source in the leuco-granites and pegmatites of the Asian plate. Thus the gold-uraninite-pyrite association seems to be the result of erosion at high levels in the mountain belt, and occurrence in the rivers seems empirically to be associated with cold, glacial rivers. We will present the results of laboratory experiment on mineral solubility at various temperatures to test this observation.

In sharp contrast, the previously known epithermal gold deposit in Chitral has no placer signature. High grade gold is concentrated in sulphosalt mineralization along a major scarp fauting Cretaceous limestone against Paleozoic sediments. A few hundred metres north of this scarp, jasperoidal gossanous limestones give encouraging surface gold assays, which decline with depth. SEM and chemical evidence suggest that this is in part due to movement of sulphosalt scree into pockets in the carbonates. Traverses down alluvial fans indicate that the movement of scree is responsible for severe dilution and dry-sieved samples show a short downslope dispersion for the sulphosalt mineralization. A sediment orientation study showed that panned concentrate sampling was most effective for base metals, arsenic and antimony, but failed to define gold. Grab samples in this area show, in spite of the excessive dilution, gold anomalies reflecting the dissemination of gold in a low density matrix. More regional panned concentrate sampling, at the head of accessible valleys, defined major metal anomalies which can be correlated with differing host rocks.

The northern part of Central Asia presents different problems, as wind blow dispersion becomes very important. We will present a case study around the producing Hatu mine in the Junggar Basin. Chinese geochemists have used concretional shallow soil sampling techniques, developed in Eastern China, to define anomalous areas. However the multi-element anomalies associated with the Hatu deposit and the Qiqu 1 and Qiqu 2 prospects are excessively large (up to 4 km long) and elongated in a SE direction. Unfortunately, this is both the direction of the prevailing wind and one of the major structural trends. We will present the results of a programme that attempts to solve this problem by comparing the shallow soil sampling with near surface coarse material (lag samples).

We will also attempt to place the geochemical studies in the wider context of Central Asia and compare them with previously published material on the wetter areas of Nepal.

GEOCHEMICAL ORIENTATION SURVEY OF GOLD-COPPER MINERALIZATION AT PHU THONG DAENG AND PHU THAM PHRA, NORTHEAST THAILAND*

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Results are described in this summary report covering one component of a comprehensive investigation into the nature of geochemical dispersion patterns associated with gold-copper mineralization near Phu Thong Daeng in northeastern Thailand. The aim of the overall study is to identify appropriate geochemical exploration technique for similar deposits in comparable environments in Thailand. Results from the first year of research drew attention to anomalous gold contents in soils associated with known copper mineralization at Phu Thong Daeng, and confirmed anomalous gold concentration in soils

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(*)Sumary of Progress Report 2 covering the period June 1987 - May 1988 northeast of the copper mineralization. In addition, regular zoning patterns were recognized, indicative of a large hydrothermal system. Gold concentrations in stream sediment samples draining the anomalous areas were erratic, a feature which was provisionally attributed to variations in depositional environment at different sample locations.

The results described in this report relate to element distribututions in soil samples collected over the entire study area. Samples were collected at 25 m intervals along lines separated by 200 m. Four adjacent field samples were composited and analyzed for 32 elements. Distribution patterns of anomalous concenctration of many elements exhibit groupings associated with one or more of five distinctive anomalous sub-areas within the study area. Each sub-area exhibits unique element associations; 1) Cu, Mo, W, Sb at Phu Thong Daeng; 2) Cu, W (Mo) at Phu Baw Lek; 3) Au, Co, As at Phu Tham Phra; 4) As, Au (Co) at Phu Yai; and 5) Lu, Sc, Sm, Yb, Ce, Eu and La in the southeast portion of the stydy area. The patterns found in the first four sub-areas are interpreted as reflecting an extensive gold-associated porphyry copper system. The economic significance of mineralization reflected by these patterns requires further assessment, but the results indicate the important role that multi-element soil geochemistry can play in exploration.

The results of this survey, combined with results of work carried out in the first year of research, allow specific recommendations to be made regarding the efficient application of soil geochemistry to gold exploration in similar areas. In addition, results allow recommendations to be made regarding continued exploration within the study area itself.

Future work will involve examination of samples collected from deeper in the weathering profile and consideration of the distribution of gold in stream sediments. Research will be aimed at examining the relationship between gold in soil and that in weathered rock and, to the degree possible, in underlying fresh bedrock. Information of this nature should be helpful in determining the significance of anomalous concentrations in soil with respect to primary mineralization. Attention will also be focussed on the examination of the distribution of gold in drainage sediments in the hope of arriving at more reliable techniques for stream sediment reconnaissance surveys in the area.

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GEOCHEMICAL PROSPECTING FOR VANADIUM AND CHROME IN THE IRAMAIA SHEET, BAHIA STATE, BRAZIL

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Results originated from geochemical prospecting of Vanadium and Chrome in granulite and volcanic-sedimentary terranes in the central-south portion of Bahia state, Brazil are presented. The region has a semi-arid climate with annual precipitation less than 1,000 mm and rivers that flow intermittently. The vegetation is type "caatinga" containing caducifolia trees, cacti, and spiny bushes.

Stream sediment samples and pan concentrates were collected during the regional (1:50,000) and semi-detailed (1:10,000) exploration phases. Rock lithologies present were characterized and samples taken along cut lines. Based on the results obtained, a detailed (1:1,000) exploration program was elaborated in the favorable areas. This consisted basically of soil sampling through open pits and hand auger drilling.

Composite sampling manually from the center of the drainage was undertaken during stream sediment sampling. Vanadium values were determined fot the less than 80 mesh fraction by optical spectrography. Duplicate samples were used to evaluate the precision of the analytical results.

The concentrate of heavy minerals was obtained by panning 20 l of material in a wooden pan, also by composite sampling. Chrome and Vanadium were analyzed by optical spectrography. Standards and duplicate sample were also utilized as controls to the analytical results.

At this stage of exploration program two target areas were deliminated: one for Chrome, the "Morro do Lírio" target; and a second for Vanadium, the "Capivara" target.

The "Morro do Lírio" target was chosen from analytical results of the heavy mineral concentrates, where values up to 7% of Chorome were obtained from one of the drainages sampled.

For the soil sampling program an exploration grid was delineated with a base line parallel to the elevation of interest. One of the transverse lines was located near the drainage with anomalous values and the other lines had regular spacing.

Inicialy, exploration was undertaken through the openning of pits with the objective of obtaining information about: 1) the soil profile as well as the determination of the granulometry and; 2) the method of analyses best suited for the delimination of the anomaly. The location of the pits was chosen by the manner that areas were to be sampled in the areas of possible mineralization as well as in adjacent areas not mineralized. In this manner three pits were opened in the transverse grid line near the refered to drainage and othen three in a more distant transverse grid line. The pits were dug according to the local topography; i e. base, mid-slope and top (or near this).

The soil profiles encountered are mainly colluvial, thick, without horizontal development and with the constant presence of gravel and blocks immersed in a sandy-clay matrix. Only one pit, situated near the drainage divide revealed an in-situ developed profile with depths of 92cm and horizons A, B, and C well characterized. This pit contained the highest values of Chrome obtained in this target (4,400 ppm).

Apart from being an area with predominantely a transported cover, where sampling near the berdrock is ideal, the interpretation of the analytical results together with the question of practical order and speed, resulted in the first 50cm depth to be chosen for the sampling of the next phase. The granulometric fraction less than 20 and greater than 60 mesh offered the best contrasts. The determinations were made by optical spectrography.

The map of the values, shows clearly a NW-SE trend, oblique to the direction of elevation, apparently without topographic control. Through the use of probability graphs the threshold value for the area was estimated at 900ppm.

The Capivara target is situated at the apex and on the east flank of a plunging antiform composed of amphibolites and gneisses resulting from the metamorphism of a compositionaly mafic sequence. In this area the values of Vanadium obtained from the panned concentrates was greater than the stream sediment samples, however, the spacial distribution revealed more defined patterns that led to the discovery of decimeter size blocks of titaniferous - vanadiferous - magnetite outcropping mid-slope of a small elevation. Values of up to 1% V_2O_5 were encountered after analyses of blocks.

After the discovery of this occurrence a systematic mineral exploration program was begun in an area of approximately 10km extending in a N-S direction, by 5km in an E-W direction coinciding with the area of the antiformal structure.

This systematic program consisted of: opening of lines, magnetometry, geological mapping at a scale 1:10,000, excavation of trenches, petrography, geologic drilling, and drill core sampling for chemical analyses.

The magnetometry identifield two large anomalies; one in the east of the structure, and another in the north part of the fold (nose). A third smaller anomaly was also identifield on the west flank.

These three anomalies were tested by rotary drilling and from this the presence of massive and disseminated titaniferous - vanadiferous - magnetite was identifield in the eastern part of three drill holes.

The results of this study identified a mineralized body elongated in a lensoid form striking N20E, approximately 400m long, and associated with a differentiated mafic sequence of rocks. The principal associated lithologies present in the sequence are:

pyroxenites → pyroxenites + magnetite →
magnetite + pyroxenites → magnetite →
magnetite + pyroxenites → pyroxenites

Results of chemical analyses from drill core yeld values up to 1.3% V_2O_5 with the average around 0.9% V_2O_5.

GEOCHEMICAL SIGNATURES OF GOLD MINERLIZATION IN SURFICIAL MATERIALS, EASTERN NOVA SCOTIA, CANADA

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Various geochemical sampling strategies have been applied recently to gold exploration in the Meguma Group (Cambro-Ordovician turbidites and slates) of eastern Nova Scotia. Detailed soil, till and biogeochemical studies were conducted over the Beawer Dam gold deposit and the Mill Shaft gold occurrence within the Meguma Group. Data from these surveys show a varied geochemical response to Au and related elements for each of the exploration media. This paper examines and compares these responses. •

Within the study area gold occurs in its native form in association with arsenopyrite and carbonate in quartz veins. These veins occur mainly in northeast-trending dome-like structures. Wide zones of silicic, carbonate and phyllic alteration around the deposits are related to large scale shear structures. Ice movements are recorded from the north, and later from the northwest. In the Beaver Dam area the latter have had the greater influence on sediment dispersal.

The Mill Shaft area is located about 1km west of the principal ore zone of the Beaver Dam deposit. Here quartzite of the Goldenville Formation is intercalated with zones of argillite. Two narrow auriferous zones occur near Mill Shaft. The principal structure, and overtuned fold known as the Beaver Dam Anticline, trends westward across the property. The area is cut by a series of northwesterly fault zones. A gravel- to sand-rich till is the main surficial unit present. Glaciofluvial gravels of variable thickness occur at depth, interfingered with this till. The drift is generally thin (<5m), although locally it is more than 25m thick.

The area is poorly drained and has a mixed boreal forest cover with local boggy areas. The biogeochemical survey extended into these boggy areas, which were impractical to sample for either till or soil, in an attempt to extend previously identified anomalous zones and thereby test this application of biochemical exploration.

Samples were collected at 50m intervals on a previously established exploratin sampling grid. Several hand-dug pits and backhoe excavations were made in the overburden across- and down-ice from the mineralization at Mill Shaft. Samples of B-horizon soil developed on till, and samples of fresh till from below the zone of surface weathering and leaching (2-3m) were collected from each site, where possible. Two 500g aplits of each 6-8kg till sample, and all of each soil sample (aplit into two), were dried and sieved to obtain five size fractions. Heavy mineral concentrates (HMC) were obtained from the remaining 5-7kg of each till sample, and analyzed for Au +25 elements by neutron activation (INAA). The five size fractions of the soils and tills were analyzed for Au, As, Sb, Cu, Zn, Co, Fe, Mn, Cr, Ba, Mo, W, Hg, Pb, Cd and As by various atomic absorption and inductively coupled plasma spectrometry techniques.

Each red spruce outer bark sample was obtained by scraping 30-50g of scales into a paper bag. Obvious contaminants, such as loose moss and sap globules, were excluded. The outer scales were selected because the inner bark is chemically different from the outer dead tissues. In addtiion, 200g of the most recent five years growth of balsam fir twigs and needles were collected. The samples were air-dried, the needles removed from the fir, and the bark and twigs were ashed at 470°C. The controlled ashing process results in little or no volatizatin of the elements of interest, yet serves to concentrate these metals. Encapsulated ash samples weighing from 0,5-1g were submitted for a similar suite of elements by INAA as those obtained for the HMC. No correction for the slight differences in ash yield has been made to the data reported here.

Gold is the element in the tills which is the best indicator of gold mineralization. A good response to the mineralization is shown also by As, and a weaker response by Sb, Cr, Co, Ni, W, Th, U, Mo, La and Hf. Similar elemental responses are evident for B-horizon soils. The HMC component of the tills contains strong enrichment of Sb and As over the same area as the Au anomalies. The soil and till anomalies extend as narrow ribbon-like dispersal trains about 100m wide and 300m long, trending southeast from the gold-bearing veins.

The elements in the spruce bark samples which are most strongly enriched above background levels are Au, As, Sb and La. There is moderate enrichment of Sc, Na and K. The distributin pattern of Au in the bark is broadly similar to the other media in outlining the disppersal train, with concentrations up to 40ppb Au in ash. In addition, there is a parallel dispersal train of both Au and As indicated about 100m to the north. This area is boggy and could not be adequately sampled for tills or soils.

Balsam fir twigs also indicate the presence of mineralization by elevated concentrations of Au, As and Cs, and to a lesser extent by Cr. Gold concentrations are up to 30ppb in ash, but the southeasterly dispersal of Au (and As) is less evident than in the other sample media. The parallel anomaly to the north is apparent from the twig analysis, but the response is more subdued than that shown by the spruce bark. Values of up to 70ppb Au outline an area worthy of further investigation.

The sampling at Mill Shaft provides an opportunity to compare data for several fractions of B-horizon soil and till with those for the vegetation cover along a traverse over the subcropping gold occurrence. The Au distribution pattern is similar in all size fractions of the B-horizon soil and the till (2-200ppb). There is a strong gold response in the coarse soil and till fractions with generally lower levels in the clay fraction (< 2 um). The highest Au concentrations occur, as would be expected, in the HMC (110-4800 ppb). In all fractions of both soils and tills, the Au concentrations are at background levels approximately 150m south of the Au mineralization, where the samples passes out of the southeast-trending dispersal train.

Both B-horizon soil and till respond well to gold mineralization at Mill Shaft, with the best response in the coarser fractions of both media in the HMC of the till. Spruce bark data indicate patterns of Au enrichment similar to the other media, but the higheast values are in closer proximity to the subcropping mineralization. Data derived from analysis of the balsam fir twigs show broad enrichment of mineralization-related elements in the area, but the twigs do not clearly define the location of the Au mineralization.

GOLD - HUMIC SUBSTANCE INTERACTIONS

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Humic substances have been postulated to influence gold mobility in surficial environments for many years. Mechanisms by which Au may interact with humic substances include dissolution and complexing of elemental Au and reduction of dissolved Au species, possibly followed by steric stabilization and transport of the resulting elemental Au colloid. In this presentation, results from a series of laboratory experiments designed to investigate the relative importance of these mechanisms will be discussed.

Peat was collected from a bog located 30km south of Rio de Janeiro, Brazil and humic and fulvic acids were extracted using 0.1N NaOH under a $N_2(g)$ atmosphere. These extracts were purified by a combination of filtration, washing with water, and passage through XAD^{-8} resin columns. Humic and fulvic acid solutions were then converted to the $H+$-satured form by passage through a cation exchange resin and freeze-dried. These humic and fulvic acids were then resolubilized and mixed with gold (III)-chloride solutions. Final concentrations of humic substances and dissolved gold ranged from 2 to 20mg/l. Reduction of gold (III)-chloride to elemental colloidal Au was followed spectrophotometrically as a function of time, pH, and metal cation concentrations. Reduction was completed in about a week, a low pH (< 4.5), and was lower at higher pH values. Furthermore, the newly formed colloidal gold persisted as a stable suspension at ionic strengths < 0.01 M.

The inclusion of Cu (II) at concentrations as low as 2.5 μM in gold (III)-chloride/humic substance solutions resulted in essentially instantaneous reduction and the elemental gold colloids formed rapidly settled from solution. Calcium (II), however, did not accelerate the reduction or settling rates as greatly as equimolar Cu(II) concentrations. It is hypothesized that both the pH and metal ion influence on the reduction process relate to the degree of metal ion-humic substance complexing and charge repulsion between the humic substance and gold (III)-chloride anions. Ultrafiltration (500 MW cut-off filters) revealed that dissolved Au concentrations remaining after reduction of 2mg/L gold (III)-chloride solutions with 20mg/L humic and fulvic acid solutions were < 1 and 1μg/L respectively, which indicates the reduction is essetially complete.

In another series of experiments, 2-5 micron elemental Au powder was added to 10mg/L humic and fulvic acid solutions which were slowly agitated for up to 120 days. Aliquots from these solutions were periodically removed and analysed for dissolved Au. In all cases, dissolved Au concentrations were < 1μg/L indicating negligible dissolution and complexing of Au by humic and fulvic ligands.

These two series of experiments suggest humic substances function primarily as one of the several geochemically important reductants (in addition to Fe (II), Mn (II) and FeS^2) of oxidized gold species and do not dissolve elemental gold to any appreciable extent. Thus, their role in the transport of gold may rest with the formation and stabilization of elemental gold colloids which, upon subsequent aggregation, can result in nugget formation.

LEAD ISOTOPES IN EXPLORATION FOR PRECIOUS METAL MINERALIZATION ASSOCIATED WITH PALEOZOIC VOLCANIC AND SUB-VOLCANIC SEQUENCES IN EASTERN AUSTRALIA.

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Lead isotopic fingerprinting techniques have been used for over a decade in Australia and other parts of the world in exploration programs for a variety of styles of mineralization. The technique is based on a comparison of the characteristic Pb isotopic composition of known mineralization in a particular region ("isotopic signature") with that of exploration samples, whether they be soils, stream sediments, surface rocks or drill core.

Over the past few years, the CSIRO Division of Exploration Geoscience has been gathering an extensive database on the Pb isotopic compositions of precious metal mineralization in the various tectonic domains of the Lachlan Fold Belt and the New England Orogen of Queensland and New South Wales. The regions is highly prospective and includes Kidstonm one of Australia's largest gold deposits.

Many styles of mineralization are present. They include polymetallic massive sulfide deposits with significant Au and Ag credits (e.g. Cobar, Highway), metamorphic vein mineralization (e.g. the Hodgkinson Province), mesothermal vein mineralization associated with granite emplacement (e.g. Charters Towers and Georgetwon Provinces), porphyre and breccia hosted deposits (e.g. Goonumbla, Kidston) and epithermal mineralization (e.g. Pajingo, Wirralie). This paper will concentrate on methods developed to discriminate these later groups, which have good bulk tonnage potential, from minor mineralization.

The results to date of this ongoing study are summarized below:

1 – In any tectonic domain, mineralization associated with a particular metallogenic event has a distinctive isotopic signature or range of isotopic compositions which distinguish it from mineralization associated with older or younger events. For example in the Charters Towers Region of N.E, Queensland, phorphyry and breccia style mineralization associated with Permian volcanism (e.g. the Mt Leyshon Deposit) has a $^{206}Pb/^{204}Pb$ ratio of 18.32, compared with generally uneconomic vein mineralization associated with older events which have $^{206}Pb/^{204}Pb$ ratio between 18.03 to 18.15.

2 – The isotopic systematics of the source rocks in a particular region dictate the isotopic signatures of mineralization. Thus it is important to understand the relationship of ores to their source rocks. For example, the Kidston deposit has a distinctively different signature to Mt Leyshon ($^{206}Pb/^{204}Pb$ of 17.81 vs 18.32) despite its relative proximity (about 200km), similar age (~310Ma vs 280Ma) and similar paragenesis. This difference is almost certainly due to the presence of Proterozoic granulite facies basement at Kidston and Lower Paleozoic greenschist facies basement at Mt Leyshon. As another example, Lower Paleozoic porphyry-to-epithermal mineralization in the Lachlan Fold Belt of NSW has a distinctive range of isotopic compositions, all strongly depleted in $^{207}Pb/^{204}Pb$ relative to other styles of mineralization in the region. This is a result of a major component of the Pb being derived from mantle rocks.

3 – Isotopic signatures may thus apply to a restricted tectonic domain if they are dependant on a unique source rock geochemistry (for example Kidston and the "mantle" porphyry signature of the Lachlan Fold Belt of NSW) of they may be present over very large areas, such as the Mt Leyshon signature which can be found in Permo-Carboniferous mineralization in S.E. New South Wales, over 2,000km away.

4 – Isotopic signatures can be recognized in soils or any surface material. Thus by using Pb isotopic fingerprinting techniques early in an exploration program, the most prospective ground can be targeted or drilling.

MAGMATIC OXIDATION AS AN INDICATOR OF GOLD MINERALIZATION, CASE STUDY: KIRKLAND LAKE, ONTARIO.

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Recent studies have shown that some major Archean lode-gold deposits were derived from oxidized hydrothermal fluids (E.M. Cameron and K. Hattori, Econ. Geol., 82, 1177-1191, 1987). These include the Au-Te deposits at Kirkland Lake, Ontario, which contain sulphate minerals, hematite and ^{34}S-depleted pyrite, all indicative of a high oxidation state for the hydrothermal fluids. The deposits at Kirkland Lake are mainly hosted by syenitic intrusion. Preliminary studies showed that these were likely derived from relatively oxidized magma, thus suggesting a relationship between the fluids and the syenitic magma.

The preliminary studies were carried out on hydrothermally altered syenite near the mines. However, a large area of relatively unaltered rock was identified in the Murdock Creek intrusion, immediately southwest of Kirland Lake. This permitted the much more comprehensive study of magmatic oxidation reported in this paper. The intrusion is a composite syenitic pluton composed of several cogenetic units: an early-crystallizing mafic consisting of clinopyroxenite, meladiorite, melamonzodiorite, and melasyenite that encloses an extensive felsic core of alkali-feldspar syenite. Chemical and petrographic data from these units indicate that fractional crystallization was the dominant process controlling magmatic evolution A coeval intrusive hornblendite unit, outcropping sporadically throughout the pluton, is believed to be genetically related to the same parental magma which produced the Murdock Creek intrusion.

The composition of primary igneous pyroxene and biotite indicate that the Murdock Creek intrusion crystallized from an intrinsically oxidized magma which maintained a high oxygen fugacity (fO^2 throughout its evolution. Pyroxene from all units is Ca-rich (Wo content 46-49 mole%) diopside with consistently low Fe/(Fe + Mg) ratios (0.10-0.32) and high $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios (0.20-0.85). Biotites are extremely Mg-rich with very low, uniform Fe/(Fe + Mg) ratios (average - 0.41) indicating an fO^2 pf approximately 10^{-12} log units. The atomic proportions of Fe^{3+}, Fe^{2+}, and Mg in biotites suggest equilibration with a magma having a very high and uniform fO^2 near the hematite-magnetite (HM) buffer. Consistent with the above data is the abundance of primary magnetite and titanite in all units.

Felsic magmas as oxidized as this are rare. The association of the Murdock Creek intrusion with strongly oxidized ore fluids, in the second largest gold camp of Archean age in North America, is not coincidental. These are two possible causes for this relationship. The firts is that the Au-bearing CO_2-H_2O fluids were derived directly from the magma. The second (E.M. Cameron, Geology, 17, 26-29, 1989) is that both the oxidized magma and the Au-bearing, CO_2-H_2O fluids were produced during the passage of CO_2 of mantle origin through pervasively permeable ductile shear zones in the lower crust or mantle, with both fluids and magma then rising independently in the shear zones to their present position.

Whatever the precise relationship between magma and fluids, the presence of felsic plutons derived from unusually oxidized magma in the vicinity of major transcursal shear zones is an indicator of possible gold mineralization. Because of the size of plutons and the uniformity of magmatic oxidation, this feature, may be recognized in areas of poor exposure or where only occasional boulders from a pluton occur in surficial materials.

PLATINUM-GROUP ELEMENTS IN OPHIOLITE COMPLEXES.

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Platinum-group elements (PGE) are traditionally not thought to be significantly concentrated in ophiolite complexes, with Os, Ir and Ru only present at ppb rather complex. are unusually high, with Pt and Pd values commonly of 20ppm each, but the tonnages are small. The discovery in this ophiolite suggests that other ophiolite complexes may potentially be sources of Pt and Pd.

Recent studies of the basic and ultrabasic complex in the Shetland Islands, the most northeastern islands in the United Kingdom, have shown that this complex forms the lower part of a typical Penrose-type ophiolite complex. The sequence consists of harzburgite, overlain by dunite, wehrlites, pyroxenites and gabbros intruded by a dyke sequence in their uppermost levels. Chromite-rich lithologies are associated with dunite lens in harzburgite and with the overlying dunite (Prichard 1985).

During a research project to examine the chromitites (Gass et al. 1981), platinum group minerals (PMG) were identified (Prichard et al., 1981). Further examination of the chromitites, using beta-autoradiography (Potts, 1984), revealed the presence of a large variety of platinum-group element-bearing minerals (Prichard et al. 1988). The greatest concentration of PGE occurs in association with chromite in a dunite lens in harzburgite.

All the PGE form major components of PGM and their textural positions show a crystallisation sequence for the PGE. Os-, Ir-bearing laurite is situated within chrome-spinel and pure laurite associated with irarsite, and native osmium is located in the altered chromite rims. Interstitial to the chromite grains, hollingworthite, sperrylite and stibiopalladinite are found. It is suggested that PGM sulphides form first, followed by antimonides and arsenides. Subsequently, PGE-bearing alloys are produced with the removal of arsenic and antimony (Prichard and Tarkian, 1988).

If the abundances of the PGE are normalised to chondrite values and plotted in order of melting point, i.e. Os, Ir, Ru, Rh, Pt and Pd, then analyses from layered complexes, such as, the Bushveld and Stillwater, give predominantly positive trends with the enrichment of Rh, Pt and Pd, and analyses from ophiolite complexes give negative trends with the enrichment of Os, Ir and Ru. Samples from the Shetland ophiolite complex give both types of slope suggesting that ophiolite complex give both types of slope, suggesting that ophiolite complexes may indeed be enriched in Pt and Pd. PGE concentrations in other ophiolite complexes will be discussed.

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POTENTIAL USE OF LEAD ISOTOPES IN EXPLORATION FOR ARCHEAN GREENSTONE DEPOSITS IN THE RED LAKE AREA, NORTH-WESTERN ONTARIO, CANADA.

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An evaluation of the lead isotope method in exploration for, and the source of gold in, Archean greenstone gold deposits has been undertaken in the Red Lake area of north-western Ontario, Canada. The Red Lake area chosen in preference to other camps in the Superior Province because of: (i) the detailed geological (including structural) basis provided by the Ontario Geological Survey, (ii) the excellent stratigraphic control provided by precise zircon U-Pb ages, (iii) the gold occurrences in rocks of different composition and different ages ranging from -3000 Ma-old mafic/ultramafic/felsic volcanics to ~2700Ma-old granitoids, (iv) the ~300 Ma time interval of stratigraphic development compared with the limited time span of less than 20 Ma in the Abitibi and most other gold-bearing greenstone belts in the Superior Province, and (v) a variation in the deposit size from the giant Campbell and A.W. White deposits to minor occurrences.

Over 300 samples of surface, underground and drill core material have been analysed and include whole rocks and feldspars from the various rock units to compare their isotopic patterns with sulfides (pyrite, pyrrhotite, arsenopyrite, sphalerite, rare galena) and gold from the diferent deposits and including minor occurrences.

Lead isotopic patterns of older (~300 Ma) mafic and felsic volvanics are similar and do not allow validation of the source question. These same units isotopic patterns that are distinguishable from the younger (-2700 - 2740 Ma) volcanics and granitoids but the latter may be ultimately derived from the same source as the older rocks.

Even though many sulfides do not reflect their inicial signature at the time of formation because of in situ radioactive decay of uranium and thorium to lead over a period of >2700 Ma, it is possible to distinguish a number of generations of sulfides, especially in those cases where galena or lead-rich samples occur. There are three major lead isotope groups, two conforming to the older and younger rock units and a third, often lead-rich group which has closer affinities with the older group. The lead in gold also appears to be derived from old source material although no gold bas been available so far for analysis from the younger group. The younger and older groups are those associated with major gold producers or post producers whereas the signature of the third group is that for the minor occurrences. On the basis of these significant isotopic differences it is suggested that lead isotopic analyses of sulfides from either surface, underground or drill core can provide a potential discriminatory tool in the Red Lake area.

RECONNAISSANCE AND FOLLOW-UP EXPLORATION FOR GOLD IN CENTRAL KALIMANTAN, INDONESIA

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Soesila, B.

Methodology and exploration philosophy for gold exploration in a remote, relatively inaccessible wet tropical area is described.

It is demosntrated that sampling of only one medium is not desirable. Large numbers of elements were not required for the follow-up phases.

Using a step-by-step approach, 4,000 Km^2 of ground was first reduced to 400 km^2 in some six months and then to about 50 km^2 of prime interest over a further four months. These time frames included analytical and intepretative work.

Total cost was of the order of US$100,000 for the year.

SEASONAL VARIATION IN TRANSPORT OF GOLD AND MAGNETITE IN HARRIS CREEK: IMPLICATIONS FOR EXPLORATION

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INTRODUCTION

Previous studies of the behaviour of gold in Harris Creek, a small gravel bed stream in the southern interior of British Columbia, have: (i) shown that gold and magnetite preferentially accumulate in bar head gravels (Day and Fletcher, 1986); and, (ii) indicated that concentrations of gold at such sites might be strongly dependent on (seasonal) discharge conditions in the stream (Fletcher and Day, 1988). Such variations of gold content of stream sediments would have important implications for geochemical exploration and heavy mineral surveys for gold. Detailed studies of transport of gold in Harris Creek were therefore initiated during 1988.

STUDY AREA

In this part of its longitudinal profile, Harris Creek consists of a series of meandering and braided reaches. Bars, armoured with cobbles, form riffles; sands are deposited in bar-tail pools. The study site is on one barpool sequence.

Stream flow is strongly seasonal with discharge increasing from less than 1 m^3/sec to a peak exceeding 10 m^3/sec (1988 peak: 19.57 m^3/sec on May 14) during the annual snowmelt flood in early summer. Transport of sand in Harris Creek is virtually restricted to the period of above normal discharge associated with this event.

METHODOLOGY

Pit-type sediment traps were installed at the head, midsection and tail of the bar. Each trap consisted of a length of 30 cm diameter concrete water pipe installed vertically in the bar with its upper rim level with the bar surface. A removable plastic pail (20L) was placed in each trap and covered with a 1 cm^2 screen lid. Sediment was removed from the traps, at irregular intervals as they filled, between April 18 and June 17. Stream discharge was measured continually over the same period.

In the laboratory sediments were wet sieved to give eight size fractions ranging <53u to >2mm. Each fraction was dried and weighed. A magnetic fraction was then separated from the five size fractions between 425u and 53u. In addition, a non-magnetic minus 100+270 mesh heavy mineral concentrate (SG >3.3) was prepared for sediment from one of the traps. This was analyzed for gold by fire assay-atomic absorption.

RESULTS

The capacity of Harris Creek to transport sediment is strongly influenced by discharge. For example, the increase in average discharge from 4.28 m^3/sec, prior to the flood peak, to a maximum of 19.57 m^3/sec on May 14, increased the rate of sediment accumulation in a bar-tail trap from less than 10 g to 1880 g per hour. Thereafter, rates of sediment accumulation decreased with minor pulses corresponding to fluctuations in discharge. Similar relationships were observed in the mid-bar and bar-head traps.

Magnetite concentrations in transported sediments are typically close to 10%. However, from May 12 to 14 concentrations increased to a maximum of nearly 20%, as discharge reached its peak, with the greatest increases in the -7+100 and -100+140 mesh fractions. Over the same interval gold concentrations in the non-magnetic heavy mineral concentrates increased abruptly from <15 ppb to 1115 ppb on May 13. Thereafter, concentrations of both gold and magnetite fell to their normal values.

DISCUSSION

Results clearly indicate that: (i) the annual snowmelt flood is responsible for a very large increase in the amount of sediment transported by Harris Creek, and (ii) gold and magnetite content of the transported sediments is also closely related to discharge. Anomalous concentrations of gold were only transported during the peak discharge of May 13-14.

Day and Fletcher (1986) have shown that gold and magnetite are preferentially stored in bar head gravels. The increased concentrations of magnetite and abrupt appearance of gold in the traps during peak discharge might therefore result from release of the heavy minerals from these sites when discharge becomes sufficient to disrupt the cobble armour and framework of the bars. This requires further study.

Whatever the reason, the increased concentrations of magnetite and gold in sediments transported during peak discharge have important implications for exploration geochemical surveys. These can be summarized as follows:

1 - Gold content of "active" sediments in gold-rich streams depends on discharge conditions and may not be anomalous at all times.

2 - Gold-rich sediments, deposited immediately after the flood peak, might be buried by gold-poor sediments as discharge falls. Once buried these anomalies will not reappear until a new flood releases the gold. Sampling soon after high discharge should give the best anomaly contrast.

3 - The extent to which gold-rich sediments are likely to be buried by post-flood sediments probably depends on the elevation of the site above the normal water level. Sampling at higher elevations on gravel bars or collection of overbank deposits should be investigated to see if these provide a more consistant record of the presence of gold in a catchment than do conventional sediments.

4 - The erratic appearance and disappearance of gold (and other heavy mineral) anomalies in streams can be explained by the processes described. If gold anomalies can be buried, it should not be assumed that the upstream cutoff of an anomaly is necessarily close to the source.

CONCLUSIONS

Transport of gold and magnetite in Harris Creek is closely related to seasonal variations in discharge. This has important implications for design and interpretation of geochemical and heavy mineral surveys.

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SOME ASPECTS OF GEOCHEMICAL EXPLORATION IN A NEW PRECIOUS METAL PROSPECT IN SARDINIA, ITALY

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The investigated area is situated in southern Sardinia, on the northeastern border of the NW-SE-trending Campidano rift, between the towns of Serrenti and Furtei. It consists of an elliptical outcrop, about 7 km x 5 km containing mainly andesitic volvanics, in both the subvolcanic facies and the extrusive, the latter mostly pyroclastic. These volcanics, belonging to an Oligo-Miocene calc-alkaline volcanic cycle, are bordered and partially covered by Miocene sediments along most of their perimeter; Quaternary alluvial terrains partially border the southwestern side and fill a few small valleys.

All the complex is affected by alteration, that appears arranged concentrically, with a core characterized by propylitic alteration and a rim of advanced argillic alteration.

In the core zone, sulphide manifestations, mostly pyrite and minor chalcopyrite, are present as dissemination and stockworks.

The rim zone width exceeds 1 km; it completely surrounds the core except on the northeastern side, where the Miocene cover reaches the core.

Apart from the commmon presence of abundant kaolin, the alteration in the rim commonly includes silicification, both pervasive and as stockworks or thin veinlets, and pyritization with the sulphide content often exceeding 10%.

Other important phenomena include zones of brecciation, occurrence of sulphates (mainly gypsum) and veins of quartz and/or carbonates.

Previous sampling in the southern and eastern parts of the area showed the presence of gold, in contents reaching a few p.p.m. in pyritized and silicified materials and in the veins; a detailed prospection is currently being perfomed by a mining Company in there parts of the area.

The northern and western parts of the area are characterized by low relief and alluvial and soil cover; thus, it was decided to ascertain the possibility of the occurrence of mineralization through geochemical sampling.

Given the smooth relief and poor drainage, a regular square grid was chosen.

A 2,000 m x 4,200 m rectangle was subdivided into 400 m x 400 m squares; in this way a total of 72 sampling sites were fixed; after discarding those situated on the Miocene or on the thick alluvium, 48 sites were retained for sampling.

Both soil and rock samples were collected wherever possible; but since, at a few sites, only soil was available, a few rock samples are missing.

The number of elements to be researched was been limited to eight so far the samples being retained for further analyses. The chosen elements, Pb, Zn, Cu, Ag, As, Sb, Bi and Te, represent both metals common in Sardinian metallogeny and elements which proved to be associated with the gold indications on the island, except for Te which is being studied for the first time.

Au was not systematically analyzed because of the well-known high variability in samples of small size and low content; therefore, Au analyses were restricted to macroscopically mineralized samples.

Further gold and silver analyses were performed on samples collected other than those from the regular sampling sites, on presumably interesting geological objects, such as quartz veins, areas of intense silicification and/or pyritization etc.

The treatment of the analytical results has provided information concerning both the exploration procedure and the possibility of occurrence of economic precious metal mineralization.

As expected, the collection and analysis both of rocks samples and of soil samples showed that the two sample sets are well correlated; in fact, soils are thin and poorly developed, given the semi-arid, temperate climate.

As far as the grid is concerned the original 400 m spacing has permited the definition broad anomalous areas, but, of course, this is too loose for relatively small targets, as is normal in mineralized outcrops of the expected type. Apart from the fact that the grid can easily be tightened over the whole area or locally, further information was obiously acquired by direct field prospecting and by studying samples collected other than from the regular sampling sites. An example of the efficacy of this mode of operation is given by the discovery of mineralized outcrops through the collection of the sample SFN9, outside the regular grid; the analysis of this sample gave 15 ppm Au and 194 ppm Ag. Concerning the possibility of economic mineralization, the study showed that precious metal indications exist also in this part of the Serrenti-Furtei area, in addition to those already found in the rest of the area. In particular, reflected light microscopy and SEMQ studies showed the presence of gold-silver tellurides in Te-rich samples.

SUPERGENE GEOCHEMISTRY AND CRYSTAL MORPHOLOGY OF GOLD IN A SEMIARID WEATHERING ENVIRONMENT: APPLICATION TO GOLD EXPLORATION

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Oxidation of sulfide- and carbonate-rich vein gold deposits under semi-arid conditions can be represented as a three-stage process, each creating supergene environments conductive to dissolution and reprecipitation of gold-silver alloys. Neoformed gold crystals in the weathering profile have distinct composition and morphologic characteristics from the hypogene gold crystals associated with the sulfide- and carbonate-rich ores. Secondary gold crystals are generally associated with iron and aluminum oxides/hydroxides, or with kaolinite; this association becomes useful in prospecting for gold deposits in weathered terrains.

A study of the weathering profile at the Fazenda Brasileiro deposit in northeast Brazil provide an example of gold behavior in a semiarid weathering environment. The features observed are believed to be generally representative of gold mobilization effects in similar worldwide climates. Hypogene gold mineralization at Fazenda Brasileiro is associated with zones of silicification, carbonation, albitization, and sulfide enrichment (Marimon et al, 1986). Primary gold crystals are hosted by quartz, arsenopyrite, pyrite, or occurs as vein-fillings in these minerals. The crystals range from submicroscopic up to 150μ and show irregular morphology (figure 1). One common characteristic is the three-dimensional crystal growth, and the smooth surface these crystals display. Primary gold varies in composition, but has an average of 7.2% Ag, traces amounts of iron and copper in the alloy (Vasconcelos, 1987). During weathering, both the crystal morphology and composition will change, as primary gold is dissolved and reprecipitated as secondary crystals.

The three-stage weathering process of sulfide-carbonate gold veins is depth dependent, and develops from the younger, lowermost weathering horizon at the water table, through an intermediate weathering horizon at the oxidation zone above the water table, culminating at the oxide-rich upper saprolite and oxisol.

The initial stage of weathering involves oxidation of sulfides, dissolution and leaching of carbonates, and precipitation of sulfates and arsenates. Sulfide oxidation releases a variety of sulfur species into solution, including $SO_4^{=}$, H_2S, HS^-, S°, $SO_3^{=}$ as well as metastable species such as $S_2O_3^{=}$ and $S_4O_6^{=}$. (Goleva, 1969; Goldhaber, 1983). Under these conditions gold-silver alloys enter solution as $Me(S_2O_3)^{-3}$ complexes, which can be readily destabilized by decrease in pH, by increased oxidition potential, by dilution, or by reaction with active surface sites (Goleva, 1969; Stoffregenm 1986; Webster, 1986). This secondary gold type is generally associated with sulfates and arsenates, and has a three dimensional morphology similar to primary gold, though the secondary gold is commonly silver enriched.

The second stage takes place within the oxidized zone above the water table. Sulfates and arsenates will dissolve in O_2- and Cl-rich meteoric waters. Dissolution of sulfates and arsenates and the oxidation of Fe^{+2} to Fe^{+3} creates the acid oxidizing conditions favorable to dissolution and transport of gold and silver as chloride complexes (Mann, 1984). $AgCl_2$, the silver complex formed under these conditions is more stable than $AuCl_4$, the gold complex. Consequently, upon reprecipitation of gold, silver will remain in solution. Thus, the fineness of this type of secundary gold increases. Secundary gold reprecipitated in this environment is generally associated with iron and aluminium oxides/hydroxides and with kaolinite, which led some researchers to postulate that gold reprecipitation is a surface controlled phenomenon (Nachayev, 1984; Nachayev and Nikolenko, 1986a, 1986b). This type of secundary gold shows a distinct composition from primary and Type-I secondary gold; the crystals are silver depleted (less than 1% Ag) and show enrichment in iron and silica. In addition to the fineness, this gold type also shows a distinct morphology. The gold grains are generally two-dimensional, indentated, show a very stippled surface, and seem to have grown as a surface painting on the substrate mineral (figure 2). The crystals show a common hexagonal cross-section, which could be the result of cube-octahedra crystals growing with the (111) o face or dodecahedral crystals growing with the faces (110) parallel to the substrate. Similar gold morphologies have been observed elsewhere (Machairas, 1967; Fujii et al., 1977; Lawrance, 1988).

The final stage of weathering involves dehydration of hydrous iron oxides formed during stage 2. During long periods of drought the hydrous iron oxides lose their boundwater, resulting in the formation of deciccation cracks. Sulfates persist from stage 2 in association with the iron phases. The H_2SO_4- bearing acid water generated will migrate through the desiccation cracks, and will carry along dissolved metal species, including gold as $AuCl_4^-$ complex. Further dehydration or input of fresh rain water will contribute to metal precipitation. Gold formed by this process is also silver depleted. This gold type is also two-dimensional, constrained by the limited space available on the desiccation cracks; crystals are easily differentiated from the primary gold found in hypogene quartz and sulfides (figure 3).

The soil profiles overlying the ore lithologies are genarally shallow. These soils vary from a thin (5-12cm), brown A horizon, into a thicker (10-30cm) intense reddish-brown B horizon, which grades into a yellowish-brown, fine-grained C horizon. Soil pH's vary from a neutral to alkaline A horizon (pH = 7.3), into a neutral to slightly acidic B and upper C horizon (pH = 6.9). The deep yellow lower C horizon (Ccs) can have pH's as low as 4.75. Gold crystals found in soils vary from equant, silver-rich coarse grains (up to 150μ), believed to be primary gold crystals that behaved as resistates (figure 4), to silver-depleted gold flakes, similar to Type II gold crystals (figure 5).

The distinct gold crystal morphologies and compositions observed in the primary and secondary ores are useful in geochemical exploration. The flattened, silver depleted secondary gold crystals have settling velocities three to six times smaller than equivalent lenght equant primary crystals (Tourtelot, 1968). Therefore, the secondary gold crystals are more likely to be transported by sheet wash than the primary crystals. Grain count in pan concentrates is widely used an exploration tool for gold (Teixeira, 1981). Gold and silver assaying of pan concentrates could add another parameter indicative of the proximity of primary gold deposits, because high silver to gold ratios would indicate less transport. Even though the increase in fineness of gold away from primary sources has been a long-known characteristic of gold distribution, most authors atribute this change in composition to partial leaching of silver from the gold crystals (Desborouh, 1970; Fisher, 1945, MacKay, 1944). The present work shows that in situ formation of flattened silver-depleted gold crystals, with subsequent transport of these crystals can also easily account for the increase in fineness away from primary source.

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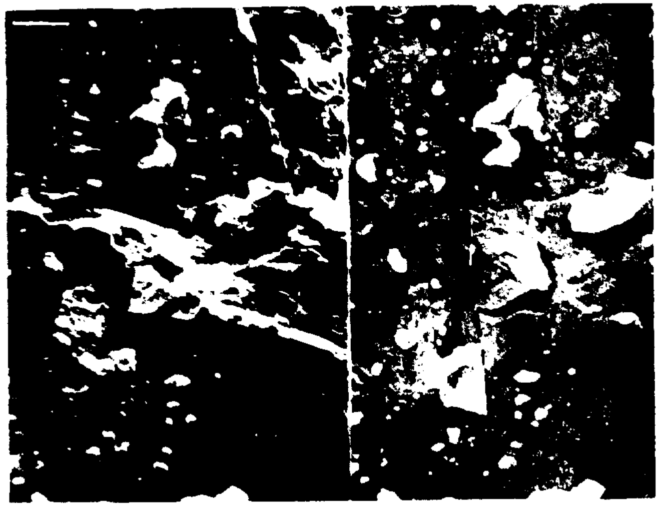

Fig. 1 – SEM photomicrographs of gold crystal (light gray, on arsenopyrite surfacer (dark gray).
Right field of view shows the image on the left under backcattered electron imaging. The figure shows the abundance of euhedral to anhedral gold crystal, varying from less than 1 μ up to more than 100 μ. Scale on the upper left hand corner = 10 μ.

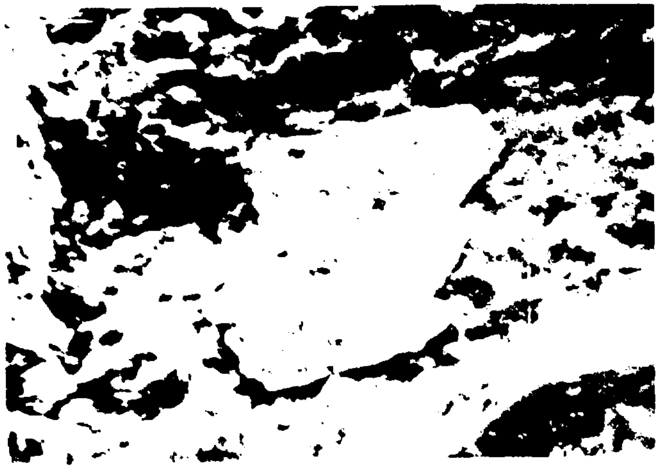

Fig. 2 – SEM photomicrograph of gold crystal grown on quartz/iron hydroxide surface.
Note the serrated aspect of this crystal. Scale on the upper left-hand corner = 7 μ.

Fig. 3 – Backscattered electron photomicrograph of gold-bearing desiccation cracks in iron oxide/hydroxide. Alternating light/dark bands in iron oxide/hydroxide is caused by variation in silica and manganese content.

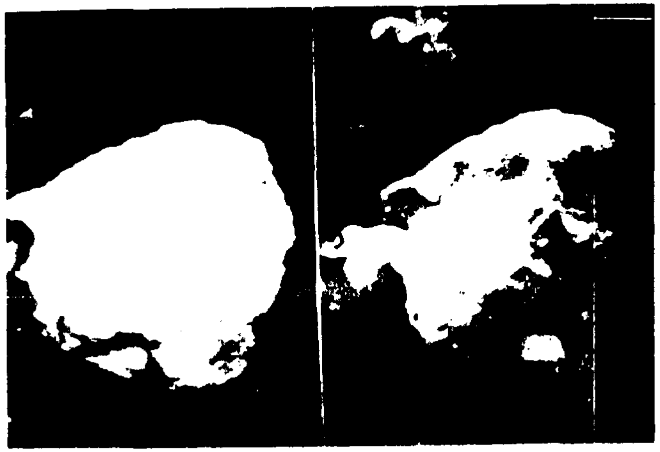

Fig. 4 – Irregular and angular-shaped gold crystal on soil concentrate.
This crystal is silver-rich, and the composition and grain morphology indicates that it is probably a resistate. Scale on upper right-hand corner = 15 μ.

Fig. 5 – Flat gold crystal in soil concentrate.
This crystal is silver-poor and is believed to represent Type-II supergene gold. Note the similarity between this crystal and the crystal in Fig.2. Scale on the upper left-hand corner = 15 μ.

THE BEHAVIOUR OF PLATINUM GROUP ELEMENTS IN THE SURFICIAL ENVIRONMENT IN CANADA.

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Over the past few years, a multidisciplinary study of the geochemistry of the platinum group elements (PGE) has been under way at the Geological Survey of Canada (GSC). The expertise involved includes surficial geochemists, biogeochimists, remote-sensing as applied to mineral exploration. This study includes examination of the distribution and dispersion, as well as the glacial dispersal, of the PGE's and associated elements within soils, tills, humus, vegetation and water, and the detection of related surface features by remote-sensing techniques. The objective is to develop an adaptable methodology that can be used to explore for PGE's under varied surficial conditions and degree of burial beneath glacial sediment cover.

The date, field areas include Ferguson Lake, N.W.t., Rottenstone Lake, Saskatchewan and Sudbury, Ontario. Conditions vary from continuous-discontinuous permafrost to no permafrost; and from arctic desert to boreal forest.

At these locations the PGEs occur as minor constituents of nickel-copper sulphide mineralization related to mafic-ultramafic intrusive bodies.

Results are presented for a variety of media. These include B-horizon soil (< 180μm, <63μm. <2μm); till and gossan (2-6mm (ground to <75μm, <180μm, <63 μm, <2μm and heavy mineral concentrate (HMC) S.G. >3.3); humus (ashed); and several plant species (ashed). Representative samples of the bedrock and mineralization (ground to <75 μm) from each study area were also collected. The sampled materials, after preparation into the components indicated above, were analyzed for Au, Pt, Pd and Rh by fire assay/inductively coupled plasma mass spectrometry (FA/ICP-MS) or by fire assay atomic absorption spectrometry (FA/AAS); for As, Sb, Bi, Ge, Se and Te by HCl/HNO_3 digestion hydride generation ICP; for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, and Pb by HCl/HNO_3 digestion AAS; for S by gravimetry; and, for Se by hydride generation AAS. The precision and accuracy of all analytical data were determined by the routine insertion and analysis of duplicate and reference control samples.

As the PGE's generally are present at low levels in surficial materials, development work on anaylitical techniques was an essential part of this study. There is a need to provide precise and accurate low level PGE analytical data, particularly in the case of waters and the organic media. A cost-efficient method has been developed at the GSC whereby Au, Pt, Pd, Pd and Rh can be determined in 1 to 2g samples of ash to detection limits of 0.5 to 2ppb. The potential advantage of the new method over a FA/ICP-MS determination is total absence of contamination from impure fire-assay "blanks". Therefore, more precise data can be obtained on smaller samples. The method involves ashing at 870°C, acid decomposition, tellurium coprecipitation of the elements, and analysis by graphite furnace -AAS or ICP-MS. Determinations on material ashed at different temperatures indicate that Pt, Pd and Au contained in vegetation tissues show no tendency to volatilize during ashing up to 870°C.

The results available to date are at a preliminary stage of interpretation. This interpretation will be refined as more data becomes available.

The surficial geology of the Ferguson Lake area is dominated by constructional glacial landforms, except on the uplands where thin drift and bare bedrock are common. The only indicated ice flow direction is to the southeast. This site is within the zone of continuous permafrost, where till-sampling is facilitated by the presence of frost boils, sites of periglacial churning that eject till at the surface.

At Ferguson Lake, a number of pits were hand-dug within the gossanous zone over the PGE-bearing nickel-copper mineralization, containing up to 70ppb Au, 590ppb Pt and 2,500ppb Pd. Gold (up to 280ppb), Pt (up to 1,300ppb) and Pd (up to 16,200ppb) occur at significant levels in the gossanous till (<63μm) and in fact show a marked degree of surface (supergene) enrichment. The spatial distribution patterns of Au, Pt and Pd in till clearly indicate the exposed gossan zones, as expected, but also indicate a possible extension of the zone beneath a peat bog till covered area. There appears to be only limited, one to two-hundred-metre, down-ice dispersal of Au, Pt and Pd in the <63μm component of the till samples collected from frost boils.

The concurrent biogeochemical study at Ferguson Lake indicates that glandular birch (Betula glandulosa) and Labrador tea (Ledum groenlandicum) accumulate high levels of PGE's: in ashed birch twigs Pd ranged from 6.4 to 3.071ppb; Pt from <2.0 to 135ppb; and Rh from < 1.0 to 104ppb. The highest values are associated with the gossan and the lower values with background areas. These data indicate that the PGE's remain at elevated levels for several hundred metres down-ice of the gossanus zones. In vegetation the PGE enrichment extends for several hundred metres down-ice and is best defined by Pd in birch twigs.

Detectable, although extremely low, levels of Pt (2.8ppt) and Pd (2.0ppt) are present in waters in the vicinity of the gossanus zones at Ferguson Lake.

The surficial geology of Rottenstone Lake area is characterized by a thin (generally less than a few metres thick), discontinuous cover of silty-sand till on bedrock ridges interfingered with graciofluvial and glaciolacustrine sediments in depressed areas. The main ice flow direction is to the south-southwest.

At Rottenstone Lake moderate to high concentrations of PGE's Au, base metals and pathfinder elements (Se, Bi and As) were found in ahed twigs of black spruce (Picea mariana) (Pt < 2 to 468ppb, Pd < 2 to 1.318ppb and Au < 1 to 265ppb) and the HMCs of the tills (Pt 32 to 4.504ppb and Au < 1 to 115ppb) for a distance of less than two hundred metres down-ice of the mineralization. Low Pd (< 2 to 8ppb) and Au (< 1 to 16ppb) centtrations were present in ashes spruce twigs about one kilometre down-ice of the mineralization, where only the HMC's of the tills yielded anomalous concentrations of Pt (1 to 878ppb) and Au (18 to 435ppb). At three sites up-ice of the mineralization, precious metal enrichment was found in the spruce twigs (Pt 19 to 26ppb, Pd 25 to 99ppb, and Au 15 to 23ppb) and HMC's (Pt 2 to 197ppb and Au 88 to 286ppb). This suggests that there may be an area of bedrock enrichment of three elements north of the mineralization.

There appears to be only limited dispersal of the PGE's and Au. These data indicate that only the HMC's and the spruce twigs are of value in detecting Pt and Au in this area. Palladium presents a different picture, being detectable in only some of the soils, absent in tills and HMC's, yet appreciably enriched in the twig ash. The inference is that Pd is moving in solution and is somewhat being adsorbed in the soil but is much more significantly being taken up by the plant roots.

Samples of the dominant plant species near the mineralization at Rottenstone Lake were collected, dissected into tissue types and analyzed for a wide vary of elements. The precious metals, base metals and Cr, As, Se, Te and Bi are preferentially concentrated in the twigs and outer bark of black spruce. In deciduous trees, the partitioning of most elements between plant tissues is far less pronounced than in the conifers.

The surficial geology of the two properties sampled in the Sudbury area is characterized by bedrock ridges covered by a thin, generally only a few metres thick, silty-sandy till interfingered with lenses of glaciofluvial outwash material which grades into glaciolacustrine sediments in depressed areas. The most recent ice flow directions were to the south and south-southwest.

Sample media in the Sudbury area were similiar to those of the other study areas, except to date no vegetation has been collected. The PGE's, hosted in the Ni-Cu mineralization, are best reflected by elevated levels in the ashed humus of almost all elements examined. There is only minimal response in PGE's and Au to the mineralization from any of the fractions of the soil; whereas, the < 2 μm fraction of the B-horizon soil reflects the mineralization by elevated levels of As, Sb, Se, Cr, Co, Ni, Cu, Pb and Zn. Only HMC's from the tills show enrichment in PGE's, Au and variable enrichment in As, Sb, Se and the base metals. The < 2 μm portion of the tills tends to be most enriched in As, Se, Cr and the base metals.

This ongoing study shows that surficial materials and vegetation are effective in identifying areas of concealed PGE mineralization. Various pathfinder elements (e.g. As, Se, Cr and the base metals, particularly in the < 2 μm B-horizon soils and tills) may be informative in a preliminary evaluation of the PGE potential of an area prior to undertaking the more expensive precious metals analyses. Both the humus and vegetation appear extremely effective, and most cost efficient, for identifying areas with PGE potential; whereas HMC's from tills appear most effective for zeroing in on the site of the PGE mineralization.

Technical Session
Laterite Exploration Geochemistry

ADSORPTION OF COLLOIDAL GOLD ONTO COLLOIDAL IRON OXIDES

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Secondary gold deposits associated with laterites, have been the object of interest in the last years. The mechanism of enrichment is not well understood, and some models are better accepted than others. We think that colloidal gold is one of the species that must be taken into account, because gold species in solution, such as $[AuCl_4]^-$ and $[Au(S_2O_3)_2]^{3-}$, are unstable, i.e., tend to the reduced form Au^0. If these atoms join together and the number of gold atoms is sufficient to form a particle of 1 nm in diameter, a colloidal particle will be obtained.

It is known that ferric oxides have a great affinity for gold. Goethite and hematite are the most cammon ferric oxides present in laterites. The objective of this work is to study the behaviour of colloidal gold in the presence of these oxides.

Colloidal gold was obtained by reduction of $HAuCl_4$ with sodium citrate in solution. Before the experiments, the colloidal gold dispersions were treated with mixed ion-exchange resin to diminish the ionic strength of the medium (Enüstün and Turkevich, 1963).

Goethite was prepared by precipitation from a ferric nitrate solution with potassium hydroxide and ageing at 60°C for 24 h (Atkinson et al., 1967).

Hematite was obtained by ageing ferric hydroxide in a teflon-lined pump for about 8 h (Breeuwsma and Lyklema, 1971 Before their use, the oxides were washed with distilled/deionized water. The crystallinity of the oxides was confirmed by x-ray diffraction using Fe-Ka radiation.

Prior to the adsorption isotherm experiments, we cheked the linearity between the amount of colloidal gold adsorbed and the mass of oxide (Nagy, 1988).

The adsorption isotherms of colloidal gold onto the ferric oxides were obtained by agitation of fixed amounts of the oxide, dispersed in water, with different amounts of colloidal gold. The gold concentration used in the experiments varied from 2μg/ml to 43μg/ml. The goethite and hematite masses used in the experiments were 3,4 x 10^{-2}mg and 4,1 x 10^{-1}mg respectively. The pH of the suspensions varied from 5.5 to 6.5, depending on the amount of colloidal gold added. All measures were duplicated. The flasks containing the mixtures were agitated in a bath at 25.0°C for times varying from 1 to 4 hours. After this time, the suspensions were centrifuged and the amount of gold in the supernatant was determined by atomic absorption spectroscopy using $\lambda =$ 242.8 nm. Low ionic strength was mantained throughout the experiments to avoid enhancement of heterocoagulation, which was observed after salt addition ($NaNO_3$ = 10^{-3}M up to 10^{-2}M).

All isotherms obtained are of the high affinity type (H) (Giles et al., 1960), beginning with a positive value for the "concentration in solid" axis. The amount of gold adsorbed per unit mass of oxide increased with the time of interaction. The isotherms obtained after 4 hours of interaction showed a maximum of adsorption for the initial gold concentration of 12μg/ml. At this concentration, the amount of adsorbed gold was 0,374 kg Au/kg α-FeOOH and 0.133 kg Au/Kg α -Fe_2O_3.

Literature values for B.E.T.(N_2) areas for oxide preparations similar to those used in this work are 70.9 $m^2.g^{-1}$ for goethite (Atkinson et al., 1967) and 30 $m^2.g^{-1}$ for hematite (Breeuwsma and Lyklema, 1971). Thus, the difference in the adsorption values obtained may be explained by the relative surface areas of the oxides.

The adsorption values obtained in this work agree in order of magnitute with those found in the literature for other mixed systems (Hansen and Matijevic, 1980).

However, if the results are viewed in terms of Clarke levels, or even in terms of the gold deposit concentrations, they are very high. This means that any gold present in soil solutions can easily be immobilized by the ferric oxides unless other species act as inhibitors.

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CONTROL OF THE DISTRIBUTION OF Mn, Co, Zn, Cr, Zr, Ti AND REE DURING THE EVOLUTION OF LATERITIC WEATHERING COVERS ABOVE ULTRAMAFIC ROCK COMPLEXES

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Lateritic weathering covers above ultramafic rock complexes can be subdivided into autochthonous and semiautochthonous weathering horizons. The latter are constituded of a mixture of (a) autochthonous, Fe-Cr-rich limonitic material derived from ultramafic rocks and (b) Al-Si-Ti-Zr-rich weathering material derived from spatialy associated sialic rocks (MARKER, 1988). Although generally neglected and often difficult to identify, such polygenetic weathering covers are abundant above ultramafic rocks worldwide, as recently reported by SCHELMMAN (1989). They can be expected above various types of bedrock and may be responsible for the occurrence of highly unusual element distribution patterns in the lateritic environment.

Serpentinized dunites and peridotites of Las Buenas and Olympic Mines in ophiolitic belts of the Philippines and serpentinized dunites of the Jacupiranga Alkaline Complex in Brazil are overlain by Fe-rich limonitic laterites of the latosol type, grading towards the bottom into a saprolite zone. Semiautochthonous laterite horizons, which constitute the top portion of these laterites, generally accumulate in morphological depressions, which in Brazil and the Philippines are related to the formation of peridotite karst.

Profile development and element distribuction are controlled by (a) autochthounous weathering processes, (b) formation parameters of the semiautochthonous laterite and its (c) podsolic or lateritic superimposition.

In the upper saprolite, Cr, Mn, Co and Zn are subject to mobilization and depletion (figure). The considerable depletion of silicate-bound Cr during initial weathering is of high importance, since this element is often used as an internal standard for mass balance calculations. In this study, mass balances have been calculated by using unweathered chrome-spinels as internal reference. While Cr remains depleted throughout the profile, Co and Zn are newly enriched in the zone of Ni-silicate formation in the upper saprolite. Mn and Co show distinct enrichment in the autochthonous lower limonitic zone, where they occur in the form of mon-stoichiometric manganese oxides like asbolite. These mineral phases act as sinks for Ce and other REES which may anomalously be concentrated in this zone. The enrichment of Mn, Zn and Co results from their mobilization in upper profile parts and subsequent downward migration. Since mass balance calculations indicate Mn and Co excess, lateral supply and mobilization from already eroded profile portions are likely (GOLIGHTLY, 1981).

In the semiautochthonous laterite horizon, the low contents of "ultramafic" elements like Cr, Mn, Co and Zn are not only caused by the above mentioned depletion. In the first place they result from dilution by "sialic" A-Si-Ti-Zr-REE-rich weathering material, which has been suplied by colluvial transport. In the semi-autochthonou laterite, Zr- and Ti-contents characteristically increase towards the profile top. Both elements show enrichment factors relative to the source rock of > > 10, indicating absolute mechanical supply from sialic lithologies rather than in-situ lateritization, as also confirmed by SCHELLMANN (1989). The upward increase of these elements coincides well with increasing contents of zircon, ilmenite, rutile and Ti-magnetite in the heavy mineral (HM) fraction and of Al and Si in the Bulk weathering material, while the chrome-spinel contents increase towards the bottom, thus controlling the distribution of Cr in the semiautochthonous laterite. This fact is explained by increasing supply of sialic material during later stages of the formation of the semiautochthonous laterite. Sialic material is derived from veins and dikes of gabbroic and leucocrate composition, wich are abundant in the ultramafic. Less intensive weathering and desintegration of sialic rocks in comparison to ultramafics results in later erosion and deposition of their weathering products in the semiautochthonous laterite (Marker, 1988). While Ti and Zr in the heavy minerals remain essentially immobile in this horizon, Ce and other REEs become mobilized during lateritic/podsolic superposition of the semiautochthonous laterite and migrate downward into the autochthonous laterite bound to Mn-colloids. Under rising pH-conditions, they precipitate together with Mn-oxides. The enrichment of Ce and other REEs is very significant in the area of the Jacupiranga Alkaline Complex, where secondary Mn-phases may contain more than 16 wt-% Ce. Besides Ce, the heavy REEs Yb and Lu are slightly enriched in relation to the intermediate REEs and thus show a distinct fractionation in relation to alkaline and peralkaline rocks, which constitute the source for the REE.

Drainage and geomorphology control the spatial distribution of the elements in the weathering cover. Due to higher mobility, Mn, Co and REE migrate along the topographical gradient within the basin structures and accumulate in the basin floors, where drainage is temporarily impeded and concentration of the solutions is high. In Jacupiranga, zones of restricted drainage above silcrete layers, which serve as geochemical barriers for downward migrationg solutions, result in enhanced formation of Mn-oxides which trap REE. Thus, as the example of the Jacupiranga Alkaline Complex shows, REE anomalies in laterites can be expected in geological settings, where Mn-rich ultramafic and REE-rich alkaline rocks are intimately associated and thick semi-autochthonous laterites with high allochthonous sialic proportions have developed. Furthermore, morphological traps like peridotite karst structures favour accumulation of REE, Mn and Co.

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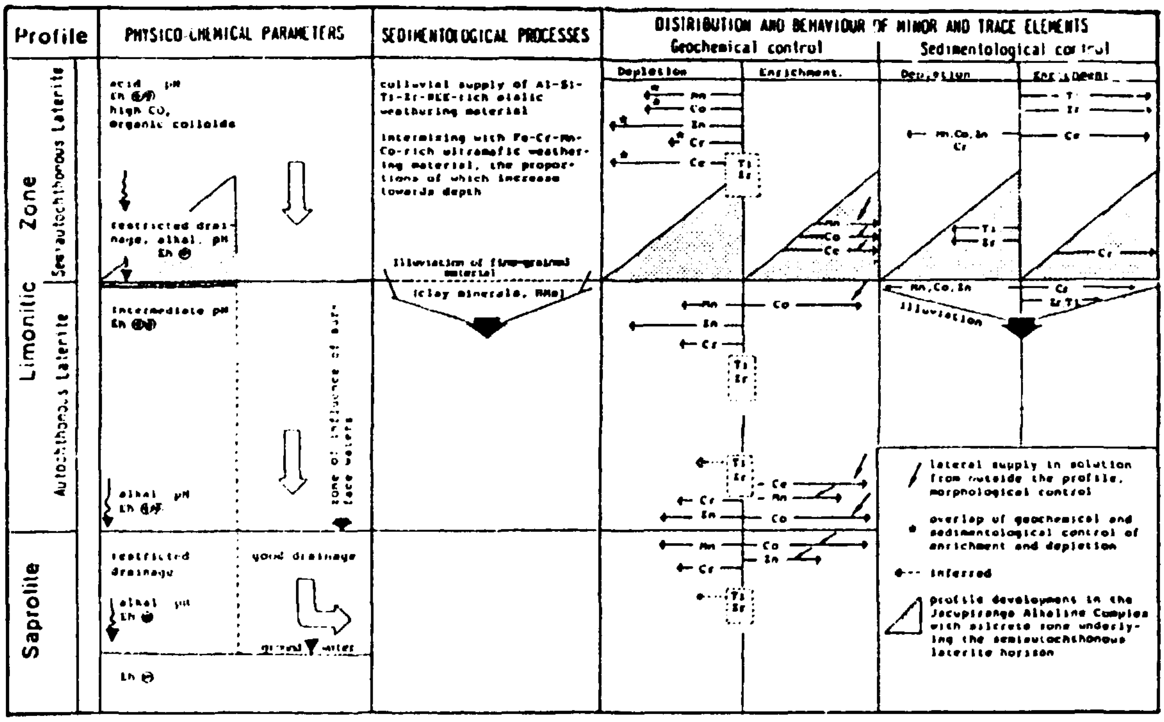

Distribution and behaviour of Mn, Co, Cr, Zn, Ti, Zr and Ce in lateritic weathering covers overlying ultramafic rock complexes in function of geochemical parameters and sedimentological processes; mass balance calculation base on chrome-spinel contents as internal reference; length of arrows approximately corresponds to degree of depletion/enrichment.

COPPER BEHAVIOUR IN LATERITIC WEATHERING OF CUPRIFEROUS ORE DEPOSITS IN BRAZIL

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Three copper deposits, located between the 5º and 24º South Latitude, were selected in Brazil to study copper behaviour during lateritic weathering. In each area, petrological and geochemical analyses with a geochemical and mineralogical balances were carried out.

In the Chapada Grande area (central Brazil), under a wet savanna climate, a thick lateritic layer (40m), partially covered by an Fe-crust, was investigated. The chalcopyrite and pyrite mineralization, is poor (0,4% Cu) and disseminated into proterozoic metassediments.

The copper is leached in the whole profile. The leaching is less significant at the bottom and increases gradually toward the upper part. In the weathering products, (smectite at the base, goethite and kaolinite at the top) an association Fe-Cu appears. In the saprolite, the microprobe analysis of weathering products shows a significant linear correlation coefficient Fe-Cu which increases towards the upper part of the saprolite. In the surface horizons (Fe-crust and the underlying horizon) where the rock structure is destroyed the Fe-Cu correlation disappears. However, Kinetic selective extractions of Fe oxihydroxides, with Tamm U.V., indicates that the Fe-Cu association still exists, but only for 20 to 50% of the Cu of these horizons. The formation of a non-identified Cu phase, independent of goethite and, also, of the single Al mineral (kaolinite), is proposed. The mean Cu content in goethite is low (about 1%).

The disseminated and poor mineralization results in low Cu^{2+} in weathering solutions. Moreover, in the weathering profile (1) goethite is the main supergene mineral which fixes Cu, (2) the Cu content in goethite is low, and, (3) the goethite concentration is low (15% in the Fe-crust). Therefore, the Cu is leached.

In Salobo 3A (Carajás mineral province, North Brazil), under an equatorial climate, the weathering cover is thick (50m). The chalcopyrite and bornite mineralization (0.8% Cu) is associated with a proterozoic schist formation and located on the steep, slope of a hill.

In the saprolite, the Cu contents don't show significant variations with those of the fresh rock. The saprolite is a potential ore. Cu is strongly leached only in the upper part of the profile where the rock structure is destroyed. The Cu released by weathering of sulfides, which are concentrated in the magnetite rich facies, is redistributed in the weathering products of the different facies. The Cu is mainly trapped by an interstratified biotite/vermiculte (Ib/v) formed by weathering of biotite.

As a matter of fact, in the saprolite, 70 to 80% of the Cu is associated with Ib/v where 15 to 25% is associated with goethite and about 6% with smectite. Therefore, the Cu behaviour is essentially related with that of Ib/v. Indeed, (1) in the upper part of the profile, only the destruction of the IB/V allows the release and the leaching of the Cu (-89% as compared with fresh rock), (2) at the base the lower proportion of Ib/v, where sulfides are completly weathered, results in the leaching of 50% of the initial Cu. It can be noted that Ib/v is the main secondary mineral of the weathering of a biotite rich facies, which is considered as sterile in the fresh rock.

The special structure of the fresh rock, the foliation plains which are perpendicular to the slope direction, certainly results in a slow percolation of the weathering solutions, inducing the formation of Ib/v and the slight leaching of the Cu. Moreover, the ferruginous primary paragenesis favour the formation of an important quantity of goethite. In this special context, the initial stock of Cu is a globally held in saprolite horizons.

In Santa Blandina (Souther Brazil), the mineralization occurs as massive sulfides (chalcopyrite, bornite) pockets or veins in a skarn formed by 67% (in weight) of garnet (grossular, andradite). Under a sub-formation of a saprolite with a signicant porosity (70%). A karst is formed by the weathering of a marble lenses embedded in the skarn. The weathering of massive sulfide pockets leads to the formation of a gossan, and the Cu released accumulates at the base of the profile. In the first stage, on the quartz is dissolved; Cu^{2+} and H_4SiO_4 are high enough to precipitate chrysocolla. In the second stage, garnet is dissolved together with quartz, and the Si and Al released react with Cu to form clay like products. They are composed of a mixture of chrysocolla and clay minerals (smectite and interstratified smectite-kaolinite). Near the karst, the leaching increases, but the contribution of Cu coming from the upper horizons allows the stability of chrysocolla at the expense of the clay minerals.

The special mineralogical context of Santa Blandina induces higher Cu^{2+} and H_4SiO_4 in the solutions as compared to the other areas, and leads to the formation of chrisocolla. The Cu is accumulated.

In the weathering profiles of the three studied areas, four secondary minerals trap the Cu: (1) field and laboratory observations indicate that Cu is absorded on goethite. (2) smectites fix the Cu as an exchangeable form. (3) In the interstratified biotite/ vermiculite, Cu is not exchangeable, and located in interlayer positions in a bivalent form and is in 6-fold coordination (Ildefonse et al. 1986). (4) In a special mineralogical context (Santa Blandina) chrysocolla is precipitaded.

In the lateritic profiles developed in a special structural and mineralogical context, the Cu behaviour depends on:

- the nature and quantity of secondary products
- the capacity of these products to trap Cu
- Cu^{2+} and H_4SiO_4 in weathering solutions

This study shows that a particular structural and mineralogical context can lead to the formation of economic Cu concentration in a lateritic environment. In terms of geochemical exploration, in this environment goethite is the mineral which best maintains the memory of a possible Cu mineralization up to the surface.

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GEOCHEMICAL EVOLUTION OF LATERITES FROM TWO AREAS OF THE SEMI-ARID REGION IN BAHIA STATE, BRAZIL

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In the state of Bahia the occurrence of lateritic covers, in areas of different geologic terrains and climatic conditions, is a common feature.

Two of these areas, situated in regions of semi-arid climate, were selected for geochemical study and their potentiality for gold mineralization, and the results of these studies are presented in this paper. One of the researched areas is situated in the western portion of the Chapada Diamantina physiographic region. It is geologically characterized by a sequence of metasedimentary rocks (Espinhaço Supergroup), mostly metapelites-psammites, in the lower horizons of which the association of acidic-intermediate metavolcanic rocks is common. The occurence of sills of gabbros interlayered in this stratigraphy is reported. The contact, between the mostly metasedimentary sequence and these sills, is characterized by metasomatic zones where an intense ferruginization and silicification took place. In these contact zones, levels of quartz occur the thickness of which averages from a few centimeters to six meters, ferruginous metarenites, a hybrid type of metarenite and gabbro, thin iron oxide horizons, quartzites, a cornean iron-rich rock derived from clayey-metasiltite and a quartz-kaolinite material, which is the product of alteration of restricted anorthositic zones of the basic intrusion. Since these materials are the products of the metamorphic-metasomatic processes between the host rocks and the basic intrusive body, it is expected that they are not frequently observed in all the exposed zones except for the quartz levels and the ferruginous metassedimentary rocks. Native gold was economically deposited in the contact zone. The weathering affected the basic and the ferruginous metasomatized metasedimentary rocks and developed a lateritic cover which is typified by red latosols and cuirasses.

The Post-Pliocene climatic changes have caused the destabilization of the lateritic profile, which is marked by the evolution of the concretionary cuirasse into pisolitic nodules and red latosols. This latosol that is derived from decay of the cuirasse, is very similar to that red latosol derived from the gabbro and from the ferruginous metasomatized metasedimentary rocks. The primary gold participated in these weathering processes and it was remobilized and reconcentrated to economic and sub-economic levels in the lateritic products. This geochemical model is termed "Gentio do Ouro" after the most important Gold District of the region. The other researched area, Sento Sé, is situated farther north from that previously described and it is near the outer northwestern boundary of the Chapada Diamantina. It is characterized by a sequence of metasedimentary rocks (Colomi-Barreiro Complex) to include quartzites, metarenites, quartz-mica-schists, intermediate to acidic metavolcanic rocks and BIF-carbonates (volcanochemical metasedimentary rocks). There is no record of economic gold occurrence, though some analytical values, locally registered, may be of about X (up to 6) ppm. The weathering effects here were similar to those described in the "Gentio do Ouro" model. In the early stage (Pliocenic) of more humidit conditions, the action of the weathering on the volcanochemical metasedimentary rocks developed the lateritic cover that is mostly of red and ocher latosols and cuirasses. In the Post-Pliocene stage, when the climatic conditions changed to present day arid weather, the cuirasse began to disintegrate to form pisolitic nodules and pisolitic-bearing latosols The cuirasse in this area are thicker (up to six meters) than those reported in the "Gentio do Ouro Model". No significant gold content is recorded in both volcanochemical metasedimentary rocks and lateritic products. The content of aluminium is much lower in the original silicate and carbonate facies iron formation and associated banded magnesian carbonate than in the derived lateritic cover. The iron content is lower in the banded magnesian carbonate than in the lateritic products. Is is suggested that at least part of the aluminium was mobile and that gold remained in mobile during the stages of rock alteration and lateritic cover formation.

In terms of the latosol → cuirasse → pisolite evolution, the comparative study of chemical data from lateritic products of both areas characterizes four types of geochemical behaviour. Type A is so termed when there is an enrichment as follows: latosol → cuirasse → pisolite, that is, the behaviour of Ti. Type B occurs when the cuirasse is richer than the latosol and the pisolite, that is, latosol → cuirasse ← pisolite. P has this kind of behaviour. Type C is the situation in which there is an enrichment of the element in the way latosol ← cuirasse ← pisolite, Cr and V being included, and type D when the cuirasse is poorer in the element than the latosol and the pisolite, that is, latosol ← cuirasse ← pisolite and is recorded for Mg, LREE and HREE. In this paper, the geochemical behaviour of each analysed chemical element is also discussed in terms of its content in the original rock-type and its content in the different products of the weathering.

GEOCHEMICAL FEATURES OF THE Sn, Zr, Nb, Y AND REE BEARING LATERITIC PROFILE FROM "SERRA DO MADEIRA" - PITINGA (AM)

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The "Serra do Madeira", located in the Pitinga region (Amazonas State), was built over lateritic formations derived from alkaline-granitic rocks, with singular metalogenetical importance in Brazil. The mineralizations are as much in the laterites as in the parent rock, especially for the following ore minerals: cassiterite, zircon (Zr, REE), columbite, pyroclore, xenotime (Y, REE) and fluorite.

While the parent rock has deserved the attention of petrological research (Carvalho et al. 1983; Horbe et al. 1985; Daoud et al. 1985; Macambira et al. 1987; Daoud, 1988; Horbe et al., in this Symposium), the laterites began to be systematically studied with the present work. Here, we present the first of a larger project which as a whole, is intended to characterize the geological and geochemical evolution of the laterites and to attempt to define the controls, distributions and genesis of the mineralizations in their wider aspects. The work was favoured by the availability of detailed research data (boreholes, wells, trenches, and topographic maps) besides the total support of the Paranapanema Group.

This paper exhibits the partial results of two wells, including geological, mineralogical, chemical and granulometric aspects that give an idea of the complexity of the "Serra do Madeira".

Mineralogical studies were made by x-ray difraction and the chemical analyses for the major and trace elements (Sn, Nb, Ta, Zr, Y, REE, F, Ga, Rb, W, Pb, Hf) by x-ray fluorescence, induced coupled plasma (ICP) spectroscopy.

The laterites are mature, highly weathered and partially transported, giving rise to a Belterra Clay-like material, Relics from the crust and the bauxitic horizons are observed over the clayey horizons, which gradate to the saprolite and to the parent rock. The latter is represented by metasomatized alkaline-granite, composed of quartz (10-30%), albite (20-30%), microline (5-10%) and mafics, besides the following accessories: fluorite, zircon, cassiterite, titanite, sericite and opaques.

The lateritic profile is composed of kaolinite, quartz and gibbsite in the saprolite; kaolinite, quartz, goethite and gibbsite in the clayey horizon; gibbsite, hematite and quartz in the bauxitic horizon and in the crust. The Belterra Clay-like cover contains gibbsite, kaolinite, goethite and quartz. The ore minerals cassiterite, zircon, columbite and xenotime behave typically as resistates

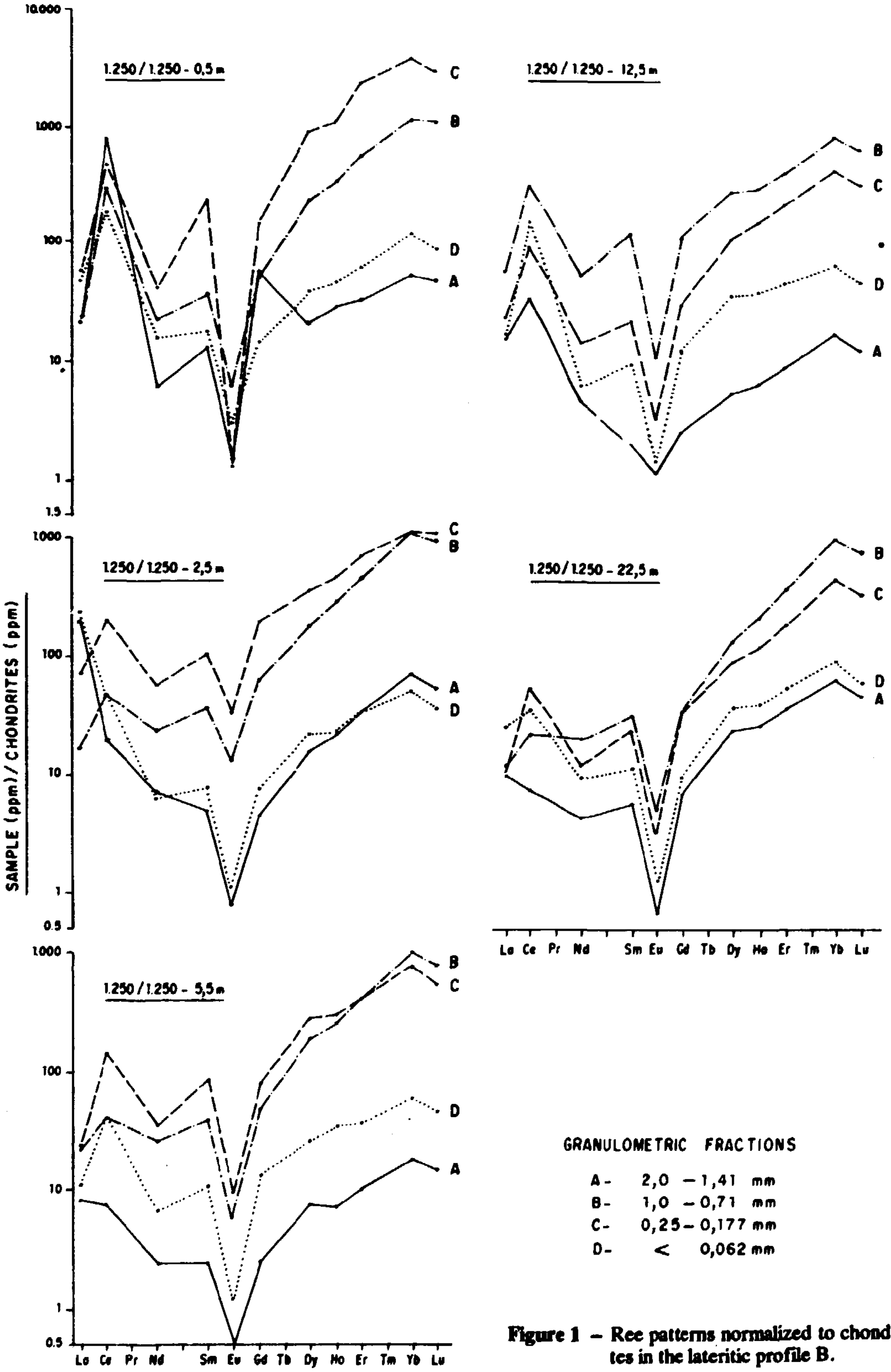

Figure 1 – Ree patterns normalized to chondrites in the lateritic profile B.

Table 1 Results of chemical analyses of the lateritic profile B.

Prof.		Si_2O_2 %	Al_2O_3 %	Fe_2O_3 %	FeO %	Na_2O %	K2 %	PF %	F %	Sn %	Zr %	Nb ppm	Y ppm	Pb ppm	Ga ppm	Hf ppm	Ta ppm	Rb ppm	P ppm	W ppm
A		82,40	7,30	4,40	1,30	0,04	0,01	3,28	0,070	0,13	0,14	400	142	80	35	*200	30	19	70	44
B		80,00	4,50	3,40	0,88	0,03	*0,01	2,22	0,077	0,84	5,00	280	340	124	39	1.620	110	26	190	180
C	0,5	61,50	6,30	7,90	1,90	0,03	0,01	3,30	0,066	4,50	6,30	18.200	1.200	2.360	78	3.000	–	–	870	–
D		24,60	44,90	11,30	0,44	0,04	*0,01	15,65	0,150	0,15	0,35	5.500	180	455	180	*200	300	*10	120	100
A		93,40	2,30	1,10	1,20	0,04	*0,01	0,90	0,035	0,04	0,28	240	23	150	28	220	15	12	*50	30
B		84,40	2,00	3,10	1,00	0,03	*0,01	0,93	0,040	1,10	4,50	410	160	560	26	2.200	120	17	110	140
C	2,5	62,00	4,70	10,00	2,60	0,02	*0,01	1,54	0,081	4,40	4,70	29.000	500	7.900	95	1.900	1.960	*10	260	250
D		36,40	38,90	7,40	0,44	0,02	*0,01	15,25	0,301	0,06	0,09	1.440	82	260	124	300	130	17	*50	38
T		52,20	25,80	6,40	0,37	0,06	*0,01	10,91	0,270	0,58	1,30	4.410	132	930	98	1.320	310	10	*50	48
A		97,80	0,35	0,22	0,88	0,08	0,02	0,12	0,029	0,02	0,05	82	*10	80	*5	*200	*15	48	*50	12
B		86,40	0,57	3,10	1,30	0,05	*0,01	0,29	0,037	0,61	4,80	300	148	290	18	2.000	93	27	130	120
C	5,5	64,60	1,00	11,20	2,40	0,06	*0,01	–	0,045	5,20	5,90	21.000	300	5.500	67	3.000	1.320	17	200	190
D		42,50	35,50	6,20	0,44	0,02	0,02	13,60	0,390	0,08	0,09	3.300	34	740	130	200	210	54	*50	33
T		62,40	20,10	5,10	0,29	0,04	*0,01	7,81	0,260	0,60	1,50	4.340	94	1.040	94	1.720	350	*10	*50	48
A		97,40	0,24	*0,10	1,30	0,06	0,02	0,01	0,015	0,12	0,03	68	*10	26	*5	200	15	55	*50	*3
B		93,50	*0,10	*0,10	1,00	0,04	0,01	0,14	0,019	0,47	2,80	144	54	124	*5	1.100	56	46	61	110
C	12,5	85,30	0,55	3,30	1,90	0,02	0,02	0,31	0,029	1,90	1,90	11.000	185	1.790	12	1.240	1.000	38	100	120
D		40,30	32,20	12,40	0,74	0,02	1,40	11,78	0,240	0,06	0,05	1.240	48	300	116	*200	64	1.800	*50	20
T		61,10	18,50	8,30	0,29	0,03	0,83	6,97	0,220	0,44	1,50	2.940	102	690	94	1.380	210	1.150	*50	55
A		95,90	0,97	1,50	0,52	0,12	0,15	0,57	0,081	0,013	0,07	166	16	56	29	*200	35	440	*50	1.400
B		90,70	0,72	0,46	1,30	0,06	0,12	0,37	0,110	0,75	3,40	210	72	92	18	1.300	47	490	120	120
C	22,5	90,10	1,40	0,13	1,50	0,02	0,60	0,63	0,430	1,30	1,80	1.180	118	1.060	14	340	550	3.100	92	120
D		44,70	32,80	2,90	0,59	0,03	3,15	9,91	0,790	0,05	0,07	3.200	90	540	92	*200	190	6.000	52	42
T		65,40	19,10	2,70	0,44	0,04	2,20	6,15	0,530	0,41	0,89	3.360	122	600	80	750	260	4.600	51	75

* Below the detection limit; – without analyses; T total sample
Granulometric strip A: 2,0 – 1,41mm B: 1,00 – 0,71mm C: 0,250 – 0,177mm D:<0,062mm

and are found thoughout the profile.

The granulometric studies show four large fraction populations:

2-1,41 (A), 1-0,71 (B), 0,25-0,177 (C), -0,062 (D) mm, domaining the fine fraction in the midle-lower part of the profile and the coarse fraction in the top. The fine fraction is formed by clay mineral in the clayey horizon and in the saprolite and by gibbsite, hematite and goethite in the bauxitic horizon; quartz forms the coarse fraction throughout the profile.

The distribution of the SiO_2, MgO, K_2O, Al_2O_3, Fe_2O_3 and TiO_2 contents, show the classical behaviour of lateritic profiles. The high SiO_2 contents attest the participation of the coarse quartz rich granite. The trace elements that form the resistate minerals show in a general sense, relative enrichment to the top of the profile (REE, Zr, Sn, Y, Nb, Ta, W) and its increasing contents in the finner fractions confirm the presence of its minerals. The resistates are formed in the fraction B and C (zircon and cassiterite) and C and D (xenotime and columbite).

Other trace elements with a distinct behaviour from the resistates are F, Rb and Ga, with contents relatively high at the base of the profile, being enriched in the finnest fraction.

While the Ga contents increase to the top of the profile, the Rb is completely leached and the F does not present significative variations on its contents.

The informations obtained by the correlation matrix allow to identify two great geochemical associations: 1) Al-Fe-K-F-Ga-Rb-PF with two sub-associations: Al-Fe-F-Ga-PF, representing the neoformed minerals like Al and Fe oxihydroxides: and Al-K-Rb-F-PF, representing the neoformed clay minerals. 2) Sn-Zr-Hf-Nb-Ta-Y-W-Pb-REE, related to the resistates where Sn-Zr-Hf, representing cassiterite and zircon: Nb-Ta-W, the columbite, Nb-Pb-Zr the pyroclore and Y-P-REE have more significance.

The REE show enrichment in the heavy rare earth elements (HREE), with high negative Eu anomaly. The Ce presents a positive anomaly, increasing to the top of the profile in the fraction B and C related to xenotime and zircon,

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GOLD DISTRIBUTION AND MOBILITY IN THE CARAJAS REGION, BRAZIL

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The existence of lateritic gold deposits, growth of placer nugget and other features in humid tropical terrains suggests gold may be mobile in these environments. However, little direct information is available on the distribution and mobility of gold in these regions. Consequently, field studies were conducted at the Salobo Cu-Au deposit and the Bahia Au deposit in the Carajas region with the cooperation and assistance of DOCEGEO in October, 1988, near the end of the dry season. Gold concentrations were determined in water, vegetation and sediment samples near these deposits.

The Solobo Cu-Au deposit is on a steep mountainside and primary magnetite-sulfide mineralization is covered by up to a 60 meter oxidized zone. Waters draining the deposit are characterized by near neutral pH values (6-7.4) and low conductivities (50-280 μS/cm). Dissolved Au concentrations were 11 and 13 ng/L in a stream and spring draining the deposit while background stream concentrations were 2-3 ng/L. Sediment samples from streams draining the deposit were also enriched with concentrations up to 2,400 μg Au/g sediment found. Waters from 2 drill holes and a test adit also contained elevated dissolved Au concentrations with values of 73, 18 and 11 ng/L, respectively. Elevated dissolved gold concentrations are tentatively attributed to complexing by thiosulfate or other sulfur species or to elemental colloidal gold.

The Bahia Au deposit is located at the edge of a plateau and has been subjected to deep (up to 100 meters) lateritic weathering. This plateau has been incised to depths of 250 meters in more recent times and several small tributaries now drain the plateau near the deposit. In the top 10 to 20 meters of the deposit, economic Au mineralization mushrooms out from the primary mineralization to occupy a zone of enrichment up to 150 meters wide, apparently formed by lateritic processes. Waters from the 5 small tributaries draining the plateau are slightly acidic (pH 4.9-6.5) and dilute (conductivites 20-45 μS/cm). Dissolved gold concentrations in these streams are at background levels (1-3 ng/L) which contrasts with Salobo and suggests a lack of significant gold transport below the water table or in streams near this deeply weathered deposit.

At both deposits, vegetation growing over the mineralized zones was enriched in gold with values ranging from 70-400 μg Au/g plant ash. It is hypothesized that vegetative uptake in rainforest areas, subject to intense weathering under stable physiographic conditions, contributes significantly to the formation of lateritic gold deposits. Gold species released from decaying vegetation could then migrate a short distance before being fixed in the soil by adsorption or similar processes or being assimilated again by vegetation.

NI-RICH CLAY MINERALS IN LATERITIC PROFILE AT NIQUELÂNDIA, GOIÁS, BRAZIL

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At Niquelandia, Goias, Brazil, lateritic weathering of ultramafic rocks leads to the formation of important nickeliferous reserves. The cumulated reserves of the deposits of Jacuba, Coriola, Angiquinho, Corrego da Fazenda, Vendinha and Ribeirão do Engenho deposits contain 33 million tons with 1.45% Ni. These ores are not only dunitic and peridotitic weathering products (oxidized ores), as are most of the lateritic nickeliferous lodes in the world, but also pyroxenitic (silicated ores).

Pyroxenites are interlayered with dunites and form suspended valleys between hills of dunite. At Jacuba, a selected profile developed on pyroxenite, was studied in order to establish the petrological relationship between the supergene NI-products and parental pyroxenes.

Oriented samples were collected after detailed field description, and were studies by optical microscopy, x-ray diffraction (XRD) scanning electron microscope (SEM). The most Ni-rich silicated ore (smectite) was studied by transmission electron microscopy (TEM), and by spectroscopic methods. Bulk chemical analyses were obtained by means of atomic absorption from samples of 3 kg. The chemical composition of minerals was obtained by extensive electron microprobe analysis.

From the base to the top of the profiles, pyroxenes are replaced by goethite and kaolinite through a series of transitional Ni-bearing phyllosilicates. Upward through the profile occur Fe-saponite, pimelite, Ni-saponite, Fe-Al-saponite, beidellite and hisingerite. Ni atoms are located in the octahedral sheet of the smectitic clay. Thus, Ni-saponites, with 70% of Ni in the octahedral sheet, are the most Ni-enriched smectites known to date in a lateritic weathering profile.

The lateritic weathering processes, the geological setting and the geomorphological situation of parent rocks, all combine to yield extremely high Ni contents.

PROTEROZOIC LATERITIC PROFILES: WEATHERING HERITAGES AND DIAGENETIC REEQUILIBRATION

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Paleoweathering horizons are potential indicators of conditions in the ancient terrestrial environment and therefore important from a metallogenic point of view. But in many places their original features have been modified by subsequent events such as diagenesis. Especially, if the ancient profile has been covered by a thick pile of sandstones, it could be profoundly affected by the new physico-chemical conditions. The most important unconformity-type uranium deposits, from Australia and Canada, are located in the immediate vicinity of a Proterozoic lateritic profile. It is, therefore, very important to discriminate the signatures of the different alteration processes.

We have studied the alteration profile which is located immediately below the Athabasca sandstones in the Carswell structure and near the Cigar LAke deposit in Saskatchewan (Canada). Four major zones have been distinguished which are from the botton to the top: (1) a green basal zone, (2) a red-green central zone, (3) a rede zone and (4) sometimes a thin bleached zone. The original rock texture is preserved in the first three zones whereas zone 4 is essentially argillaceous. The extent of the whole profile and of the different zones are influenced by the lithology. The green zone represents 40 to 65% of the whole profile, the red-green zone 20 to 40% and the red zone 15 to 20%.

This work includes petrographic and mineralogical aspects, especially of the clay minerals, distribution of uranium by induced fission tracks, major and trace element geochemistry, stable and radiogenic geochemistry $\delta^{18}O$, δD, $^{87}Sr/^{86}Sr$, Pb-Pb, Halter et al., 1988, Pagel et al., submitted).

Kaolinite and hematite hydrated muscovite and chlorite are the most abundant alteration minerals in the profile. Kaolinite (1T polytype) is present only in the red and bleached zones. The chlorite composition varies from brunsvigite in the green zone to sudoite in the upper part of the profile. The hydrated muscovite is more aluminious in the red zone than in the red-green and the green zones. Its crystallinity index (Kubler index) is generally between 2.5 and 5, however lower crystallinities have been found. Hydrated aluminious phosphates (crandallite-florencite-goyazite solid solutions) are present in the red-green and the red zones. Diaspore has also been observed.

Whole-rock Rb-Sr dating on two profiles indicates ages which are 1.56-0.02 Ga and 1.61-0.02 Ga. respectively and two whole-rock Pb-Pb ages which are 1.59-0.01 Ga and 1.29-0.01 Ga (Pagel et al, submitted). The significance of the 1.6 Ga ages is discussed in terms of mixing between two components. The 1.3 Ga age corresponds to the major episode of uranium deposition in the Athabasca basin.

The crystal-chemical data obtained on clays, the stable isitopes data and microthermometric data on fluid inclusions with the interpretation of Sr are used together to deduce the nature and the temperature of equilibration of chlorite and hydrated muscovite.

Cathelineau and Nieva (1985) and Cathelineau and Izquierdo (1989) have shown that some structural composition of chlorite and illite strongly depends on their crystallization temperature. The crystal-chemical composition of chlorite and muscovite in the Athabasca sandstones and in the alteration profile are quite comparable indicating that they have equilibrated under the same temperature conditions, between 200 and 270°C. These temperatures are in good agreement with those derived from a fluid inclusion study on quartz overgrowths in the Athabasca sandstones i.e. 220°C in the Carswell structure (Pagel, 1975). At 200°C, the stable isotopic composition of the fluid in equilibrium with hydrated muscovites in the alteration profile is -80 to -50% (dD) and +3 to +10% ($\delta^{18}O$). These compositions are comparable with those of the diagenetic brine in the Athabasca sandstones, -70 to -35% (dD) and +2 to +8% ($\delta^{18}O$).

The calculated 87Sr/86Sr ratio at 1.3 Ga is low in the upper part of the profile (0.7045 to 0.7069) and higher in the lower part (0.7177 up to 0.7698). These data could be interpreted as the existence of two sources: the basement for the radiogenic strontium and the Athabasca brine for the less radiogenic strontium.

In the alteration profile under the Athabasca sandstones, a lateritic horizon is recognized (kaolinite, hematite, florencite, diaspore) but a significant reorganization due to an intense diagenesis have occurred. It is important to note that it seems that the kaolinite has retained its original characteristics (1T polytype whereas dickite is present in the Athabasca sandstones).

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STUDY OF SUPERGENIC BEHAVIOR OF NICKEL AND SOME PRACTICAL CONSEQUENCES

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Brazilian nickel resources come essentially from supergenic deposite which occur scattered throughout the country, being rarer in the northeastern region and in the south, below 25° latitude. They are mainly associated with Archean mafic-ultramafic massifs of large dimensions such as, Niquelândia and Barro Alto, Cretaceous ultramafic-alkaline complexes, such as, Santa Fé and Jacupiranga and with small ultramafic Alpine-type Precambrian bodies, for instance, Morro do Níquel. Most of them occur in central Brazil, under a tropical climate with contrasting seasons.

The investigations carried out in many of these deposits (Trescases & Oliveira, 1978, 1981; Oliveira & Trescases, 1980, 1982; Oliveira et al., 1988) allowed the evaluation of the role of petrographic and morphogenetic conditions in their genesis and led to the following conclusions (Melfi et al., 1979; Oliveira et al., 1989):

- the deposits are mainly derived from lateritic alteration of dunites and peridotites, but can also be found associated to pyroxenites (Niquelândia);
- the degree of lateritisation was moderate, leadind to rather shallow profiles where the silicated ore prevails over the oxidised one;
- the most important ore minerals are Ni-serpentine and Ni-smectite; garnierites which, despite the very high Ni contents, are scarce;
- the deposits can be correlated to two erosional cycles, namely, Sul Americano (Lower Tertiary) and Velhas (Upper Tertiary); accordingly, they can be found either in highlands and in lowlands;
- highland deposits are covered by a silcrete layer; in lowland deposits, a higher degree of lateritisation is observed.

The nickel lateritic profiles are derived from rocks formed essentially of olivine, serpentine and pyroxene. In the earlier stages of the alteration process, olivine is gradually hydrolised, releasing Mg, Si and Ni, which are precipitated, either as amorphous products filling the void spaces between the fibers of serpentine or as neoformed garnierite in the cracks of the altered rocks. As the alteration proceeds, serpentine is destroyed, leaving behind a Ni-goethitic residue. The garnierite is no more stable and is dissolved as well. The pyroxenes change initially into Mg-Ni trioctahedral smectites, later transformed into Fe-Al dioctahedral varieties, and finally into kaolinite and Fe-hydroxites (Colin et al.,1989).

The release of nickel, due to the destabilisation of either the neoformed products (smectite and garnierite) or the inherited parent minerals (serpentine), leads to its redistribution in the phylossilicates at the bottom of peridotitic profiles and downslope in the topographic sequence.

Pyroxenitic profiles, due to their low original nickel content, are not mineralized, except when situated at footslope of peridotitic elevations. In this case, solutions released from the upper parts percolate the pyroxenitic profiles providing Ni for the formation of trioctahedral smectites.

The history of the weathering blankets developed on ultramafic rocks in Brazil began in the Lower Tertiary, on the lately-formed Sul Americana Planation Surface. At that time, two different alteration mechanisms were active:

- silicification at the bottom of the profiles, probably related to semi-arid climatic episodes;
- lateritisation of these profiles promoting nickel concentration.

In the Upper Tertiary, a new erosion cycle named Velhas was established, dismantling the Sul Americana surface and originating a new one at lower altitudes. The alteration profiles developed on the older surface were eroded down to the silicified horizon, which behaved as a protection against the general levelling. Products derived from these ancient profiles are found today mixed with the upper levels of the lateritic profiles developed on the Velhas surface.

The lateritic weathering has gone on up to the present day both in the highlands under the silicified layer and in the lowlands. This process has occurred together with a lateral migration of nickel. As a consequence, the more eroded the Sul Americana surface, the more intense have been the migration processes, being nearly absent where the Sul Americana surface has been well preserved.

The results achieved so far have some interesting consequences for the prospection of new deposits and give important information for planning mineral dressing techniques.

The first point to be taken into consideration is that lateritic nickel deposits must be prospected preferentially in tropical regions where the Sul Americana surface is at least partially preserved, as in central Brazil, in Amazonia and in some points of the Brazilian eastern region. The silcrete layer impregnated by garnierite on the top of the elevations can be a good hint for the discovery of new deposits.

The following point to be considered refers to the fact that the Brazilian nickel lateritic ore is quite special as compared with those from other deposits in the world. Being predominantly of the silicated type, with Ni generally occupying the octahedral position in the phyllosilicates lattice, the well established mineral dressing techniques designed for more oxidised ore are no longer apllicable. New techniques must take into account the rather great difficulty in extracting nickel.

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SUPERGENE DISSOLUTION AND DISPERSION OF GOLD PARTICLES IN LATERITIC PROFILES UNDER EQUATORIAL RAIN FOREST CONDITIONS

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In Gabon, under equatorial rain forest conditions, gold haloes have been found in lateritic profiles, overlying gold mineralizations.

The weathered mantle ranges from the fresh rock to the surface of three main layers: a saprolite, a nodular layer and a sandy-clayey layer. The gold haloes especially develop within the two upper layers.

The present study was undertaken to explain the gold dispersion halo found at Ovala, Dando Mobi, Mebaga and what the possibilities are of relating gold particles within the weathering profiles to those of an underlying gold deposit. In these three areas, detailed study was performed from petrological, geochemical and mineralogical points of view.

In this paper we give the results of the morphological and chemical studies carried out on about 6,000 gold particles, extracted from the fresh rocks and the weathering layers within the haloes. The morphology of gold particles was examined by optical microscopy, scanning electron microscopy (S.E.M.) and was studied by means of mathematical treatments. The chemical composition of particles was effectuated by extensive microprobe analyses, mapping and image-processing.

The results obtained show that the gold particles are residual and are subjected to increasing in situ weathering, upward through the profiles from the fresh auriferous parent rock to the surface and then laterally at the surface toward the rims of the dispersion halo. Gold parcicles gradually become smaller, their edges more rounded, both the number and size of dissolution pit increase and their Ag content decreases.

As the lateritization digests an increasing amount of mineralized bedrock, gold parcicles are chemical weathered and physically dispersed. This vertical and lateral evolution of gold particles must have taken place during the collapse of weathered rock and may be promoted by short-distance creeping.

THE DEVELOPMENT OF PLATINUM-GROUP ELEMENTS IN LATERITES

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Consideration of the solution chemistry of the platinum-group elements has shown that they can enter into solution at low temperatures under acid conditions with a high Eh. Studies of lateritic soil profiles indicate that they provide the required conditions of acidity and Eh and that, within these soils, the platinum-group elements may be taken into solution. Under these conditions, the platinum-group elements may be dissolved, transported and redeposited to form large nuggets or small crystals with well-defined crystal faces. These processes have become accepted in our understanding of the development of secondary gold. The conditions required for the same processes to act upon the platinum-group elements are shown to be less extreme than those required for gold, and it is concluded that solutions similar to those which can transport gold can equaly act upon the platinum-group metals. Examples of platinum-group minerals considered to have formed in this way will be discussed.

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WEATHERING AND ITS EFFECT UPON GEOCHEMICAL DISPERSION AT THE POLYMETALLIC WAGGA TANK DEPOSIT, NEW SOUTH WALES, AUSTRALIA

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Base metal mineralization with subordinate gold occurs at the Wagga Tank deposit 540 kilometres west-northwest of Sydney in western New South Wales. The deposit is hosted by clastic sediments assigned to the Lower Devonian Mount Kennan Volcanics, a formation within the Mount Hope Group and part of the Cobar Supergroup. The mineralisation is structurally controlled and lies within a curvilinear zone of strong tectonic breciation and hydrothermal alteration at the contact between a volcaniclastic unit and a thin-bedded turbiditic unit. The volcaniclastic unit consists of interbedded slate, siltstone, sandstone, conglomerate and intermediate to acid tuff. Yonger turbiditic rocks comprising slate and siltstone contain minor framboidal pyrite and abundant sedimentary structures consistent with the D and E divisions of the Bouma turbidite model. Turbidites do not crop out within the prospect area but drilling suggests a conformable and gradational contact with the volcaniclastic unit. In many instances, the lithologic contact is obscured within the broad zone of strong tectonic brecciation and hydrothermal alteration.

Base metals are concentrated within numerous sub-parallel, slightly arcuate zones of strong sulfide mineralization within a low grade mineralized envelope. Four distinct, steelpy-dipping lodes can be recognised, but only three are significant. The lodes have a strike lenght of less than 100 metres but a vertical persistence of at least 40 metres below the surface. Primary zone mineralisation occurs a vuggy massive sulfide, colloform banded sulfide, quartz-sulfide veins and disseminated sulfide in silicified and sericitised host rock and kaolinised fault gouge. Primary sulfide minerals are pyrite, sphalerite, galena and chalcopyrite. Secondary minerals include goethite, hematite, jarosite, malachite, azurite, digenite, chalconite, pyromorphite and hidalgoite.

The deposit has been subjected to weathering since Palaeozoic time with lateritic weathering occurring during the Early Tertiary. Subsequent climatic changes during Late Tertiary to Quartenary times have led to the reworking of the lateritic material and development of a veneer of residual soil and transported overburden over the contact between the two major rock units. The climate is now semi-arid with a mean annual rainfall of 500mm and average daily temperature ranging from 4 to 10°C during winter and 20 to 35°C during summer. Weathering persists to a depth of 100m with feldspars, chlorite, carbonates and sulfides being destroyed and clays (especially kaolinite) and Fe oxides being formed.

Geochemical and mineralogical study of profiles through the regolith across the prospect indicates that the distributions of the base metals can be used to understand the weathering processes at Wagga Tank.

Copper occurs as supergene sulfides and carbonates at the current water table whereas Pb and Au occur above it, sub-parallel to the upper surface of weathered rock which is defined by the occurrence of maghemite. Zinc is completely leached from the weathered rocks.

Because the individual lenses at Wagga Tank are than 7.5m thick in fresh rock and the distribution of the ore-related elements may be greater than 100m wide in weathered rocks, lateral dispersion appears to have occurred during weathering. Lead and gold appear to have formed in a zone sub-parallel to the original Tertiary lateritic surface and remained in such a position despite subsequent climatic change. Copper, however, has been affected by the more arid conditions and has concentrated at the new (lowered) water table with perched anomalous concentrations sometimes retained.

Soils overlying the deposit contain a large component of transported material. However, they also contain ferruginous pisoliths formed during the Tertiary weathering. Redistribution of these pisoliths through the soil profile may account for the anomalous Pb and other ore-related elements present in the near surface soils over the deposit.

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DISTRIBUTION OF FLUORINE IN GRANITIC ROCKS ASSOCIATED WITH FLUORINE MINERALIZATION IN KOREA AND ITS POTENTIAL AS A PATHFINDER ELEMENT IN LITHOGEOCHEMISTRY

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The Wolagsan granite mass of the late Cretaceous age is exposed, about 360 km^2 in area, in the center of the South Korean peninsula. The mass belongs to a magnetite series with a magnetic susceptibility of more than 0.1 x 10^{-3} SI unit. and is geologicaly assumed to be associated with the copper-lead-zinc, tungsten-molybdenum and fluorine mineralization nearby. Most of the fluorite deposits occur as vein and/or replacement type in limestone around the northern and western parts of the mass. The differentiation trend could be earlier in the southern part than the northern part of the mass.

Fluorine content of the mass ranges from 172 to 1,932 ppm with an average of 701 ppm. Abnormal distribution of fluorine is particulary characteristic in the northern part of the mass where fluorine mineralizations are predominant. Abnormal content of fluorite in the mass is partially due to the occurrence of fluorite, and fluorine content in the mass is not definitely proportional to the abundance of biotite. Fluorine shows close geochemical association with tungsten, rubidium, beryllium, lithium, lead and potassium.

Abundance of fluorine in Precambrian granitoids in Korea is relatively high-ranging from 704ppm (Naedeogri granite) to 3,280ppm (Wangpiri tin granite), whereas fluorine content in the Cretaceous granitoids in Gyeongsang basin, in which no economic fluorine mineralizations have been found so far, is relatively low-ranging from 340 to 503ppm. Enrichment of fluorine is particularly characteristic in Korean granitoids genetically associated with fluorine-and tin-mineralizations (Refer to Table1).

Granitoids	Mean	Range	Coefficient of variation (%)
Cretaceous Wolagsan granite mass (39)	701	172-1931	64
Cretaceous Opyeong stock (9)	696	511-1,031	23
Cretaceous Bulgugsa granitoids (23)	503	150-1,249	48
Cretaceous Bulgugsa granitoids* (172)	340	35-944	95
Jurassic Daebo granitoids (26)	621	240-1,451	44
Precambrian Buncheon granite gneiss (46)	913	550-1,410	31
Precambrian Wangpiri granite (14)	3,280	2,130-4,660	29
Precambrian Naedeogri granite (13)	704	650-780	6
Precambrian Nonggeori Granite (22)	956	830-1,070	5
average**	850		
Low-Ca granite***	850		
high-Ca granite***	520		

Tabela 1 – Abundance of fluorine in some major Mesozoic and Precambrian granitoids in Korea. Number of analyzed specimens in parenthesis and unit in ppm.

* Source : Jin (1981)
** Source : Taylor (1964)
*** Source : Turekian & Wedepohl (1961)

FLUID INCLUSION STUDIES AS TOOLS IN MINERAL EXPLORATION OF TIN AND TUNGSTEN DEPOSITS ASSOCIATED WITH THE HERCYNIAN GRANITES OF WESTERN SPAIN.

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The Sn-W metallogenic province of the Iberian Peninsula is one of the most important in Europe. The deposits extend from Galicia through the north of Portugal to the southwest of Spain. They are located exclusively in the Hesperic Massif and a large number of them are in the central-Iberian Zone (CIZ). The predominant CIZ rocks consist of Hercynian granites and a monotonous flyschoid marine sequence–the Schist-Graywacke Complex–, pre-Ordovician in age; minor amounts of late Precambrian, Ordovician and Silurian rocks are also present. The most important feature of these Iberian Sn-W deposits is the relationship between the ores and the group of granites-metasedimentary rocks of marine origin. Although there are stratabound deposits, some of them related to volcanism, the most important deposits are related to the syn to late tectonic Hercynian granites.

Despite the importance of the Spanish deposits, there have been very few studies of fluid inclusions (Little, 1960; Sider, 1979; Mangas, 1981 and 1987; Mangas y Abbirbas, 1984, 1987, 1988 a, b and c, 1989; Guijarro et al., 1984; Durán et al., 1989; Gumiel et al., 1989; Quilez et al., 1989 and Saez et al., 1989). Thus, these studies carried out in quartz, cassiterite, scheelite, beryl, fluorite and calcite crystals of veins and greisenized rocks, have been made by different methods–microthermometry, Raman spectroscopy and crushing test–in the following types of deposits: a) disseminated mineralizations in granites (Sn)–Golpejas (Salamanca) and Penouta (Orense)–, b) the pegmatitic ore deposits (Sn)–Feli and Perena (Salamanca)–, and c) the quartz veins (Sn, Sn-W, W)–Bajo Corumbel (Huelva), Garganta de los Montes (Madrid), La Parrilla y Teba (Cáceres), San Finx (La Coruna), San Nicolás (Badajoz) and Virgen de La Encina (León).

Taking into occount their chemical composition, the fluid inclusions belong to the following types: I) Complex CO_2-arqueous inclusions (H_2O-NaCl-CO_2-CH_4-N_2-H_2S), II) Complex CO_2 inclusions (CO_2-CH_4-N_2-H_2S), III) Low-salinity aqueous inclusions (H_2O-NaCl, and IV) Mixed-salt aqueous inclusions (H_2)-NaCl and other chlorides).

Assuming that the evolution of the deposits developed in response to decreasing temperatures and pressures, and taking into occount the paragenesis and the results of the fluid inclusions studies, three main episodes can be distinguished.

The first episode is characterized by the entrapment of fluids belonging to H_2O-NaCl-CO_2-CH_4-N_2-H_2S system with salinities below 15 eq. wt., % NaCl an densities varying from 0.55 to 0.8 g/cc, trapped at temperatures ranging between 200 and 700 C., although mainly at between 300 and 450 C and pressures below 3,250 bars. During this stage, the density of the aqueous solutions increases, the saliity and concentration of CO_2 and other volatiles decrease as the temperature drops.

These solutions are contemporaneous with deposition of Sn-W mineralizations (cassiterite, wolframite and scheelite) as well as early minerals and alteration processes.

The second episode is represented by low-salinity aqueous inclusions with salinities below 10 eq. wt., % NaCl and densities range between 0.7 and 0.95 g/cc, trapped at intermediate homogenization temperatures varying between 60 and 350 C, and pressures below 1000 bars. In general, it is seen that this is a dilution of aqueous fluids, with a concomitant decrease in temperature and salinity.

This stage can be correlated with the precipitation of polymetallic sulphides and related alteration.

The third episode is characterized by higher salinity aqueous fluid inclusions containing NaCl and other chlrorides, with salinities below 45 eq. wt., % NaCl and densities ranging between 0.9 and 1.3 g/cc, trapped at low homogenization temperatures ranging between 60 and 170 C and low homogenization pressures (below 100 bars).

The different compositions and the contrast of salinities found between the second stage and the third is probably due to a mixing of magmatic solutions with fluids of a different source, either meteoric, connate, or metamorphic waters.

It can be stated that tin-tungsten mineralization in western Sapin were caused by fluide belonging to the first episode. Therefore, the tin and tungsten were most likely transported in the form of aqueous, chloride and carbonate complexes. Consequently, any change in the physical-chemical factors–temperature, pressure, density, composition and concentration–is enough to cause destabilization of the tin and tungsten complexes and give rise to the precipitation of cassiterite, wolframite and scheelite. These changes occur when the mineralizing fluids react with the host rocks or with other fluids of a different nature. They are common in vein systems associated with granites, where hydrothermal convective cells are produced. In addition, the results here roughtly agree with experimental studies on the solubility, transport and deposition of tin and tungsten.

The study of fluid inclusions can be used in the search for new ore deposits or to extend those which have already been discovered. Given the frequency with which these types of tin-tungsten mineralizations occur in Spain, the data obtained from the study of fluid inclusions may be helpful in distinguishing the mineralized ore bodies from the barren ones, and as a guide in the exploration of new Sn and W deposits in the Hercynian province of the western Spain. However, these analyses are not a unique and miraculous answer, but in fact must be used alongside detailed geological and paragenetic studies.

The evolution of the mnineralizing fluids in different types of tin and tungsten deposits of western Spain is similar to that which has been described in other Sn-W ore bodies associated with Hercynian granites of Europe and northern Africa.

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GEOCHEMICAL CHARACTERISTICS OF THE CRYOLITE-TIN-EARING GRANITES FROM THE PITINGA MINE, NORTHWESTERN BRAZIL - A REVIEW

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The Proterozoic cryolite, tin and rare elements (F, Zr, Nb, Ta, Y, REE, Rb) bearing granites from Pitinga (Amazonas State, Brazil) have been object of many studies in differents fields of geology. Several papers have been published in the last year in Brazil about their petrological and petrochemical natures, geochronology and economic potential (Fig. 1).

The aim of this work is to present a compilation of these papers, added to the new data obtained from recent analyses (major oxides, trace elements and rare earth elements), in order to characterize as fully as possible the geochemical behaviour of these granites, particularly the geochemical behaviour of the apogranitic facies associated with them.

The mineralization of the Pitinga Mine are related to two granitic bodies called Madeira Granite (MDG) and Água Boa Granite (ABG), with Rb/Sr age of 1,689 ± 19m.a. These granites are intruded into acid to intermediate volcanic rocks of the Iricoumé Group and clastic sedimentary rocks of Urupi Formation. The refered country rocks are related to Middle Proterozoic. These two bodies are intrepreted as being cogenetic due to the great similarity with respect to petrological, petrochemical and isotopic characteristics.

The MDG shows an outcroup surface of 60km^2. Exposed area of the pluton shows an elongated structure in a northeastern direction.

Thisi body is composed by an outer zone of rapakivitic granite facies, intruded by a biotite granite facies essentially equigranular and by an apogranite facies in the central part, that promoted the development of a metassomatic aureole affecting on the early facies. The contacts between the first and second facies are evident, since enclaves of rapakivi granite, embodied by the biotite granite, are found. The contacts among the apogranite and the magmatic phases are abrupt, often marked by narrow fractured subvertical bands and by the absence of chilled margins and enclaves within the apogranite.

The Água Boa granite has an exposed area of some 350 km^2 and it is constituted by a rapakivitic facies cut by fine porphyritic granite. These two earlier phases are cut by an equigranular biotite granite. Another later phase recorded is represented by dikes and veins of microgranites.

The petrographic characteristics are commom to both plutons, being the apogranite an exception within this igneous association. Thus, the commom petrographic features of these two bodies will be described together.

The rapakivi granites are predominantly equigranular in ABG and porphyritic in MDG. The mineralogy of these granites is consituted by feldspar (ranging from 55 to 80%, where Σfeldspar + quartz = 100%), quartz (15-30%) and sodic oligoclase (until 10%). In the porphyritic types, the groundmass is normally micrographic, enveloping K-feldspar phenocrysts which exhibit surrounding plagioclase mantles.

The accessory phases are Fe-bearing biotite and amphiboles, identified as Fe-hastingsite, which frequently show symplectite intergrowths. Accessory zircon, fluorite, tourmaline, opaques and topaz are commonly recorded.

The biotite granite is equigranular, formed essentially by perthitic K-feldspar (50-60%), quartz (30-35%) and biotite, defining a hipersolvus behaviour for this facies, in spite of some samples of the biotite granite of ABG present until 10% of sodic oligoclase.

Microscopically, these granites show hypidiomorfic granular texture or, seldom, a porphyritic tendency. The biotite is an iron-rich term (annite) whose pleochroism ranges from reddish brown to yellow, occurring as moderate to highly chloritized tabular crystals. The commonest accessory phases are the opaques, zircon and fluorite. The fine porphyritic granite shows a panxenomorphic groundmass, highly affected by late hydrotermal processes, that envelops K-feldspar phenocrystals (40-50%), quartz (25-30%) and sodic oligoclase (10-25%), with little percentage of accessory biotite ($\leq$5%).

The apogranite is restricted to MDG and the majority of the works attributes a residual hydrothermal origin to this body. They consist in alkali-feldspar granites and granites with variable grades of microclinization (potassic metassomatism) and albitization (sodic metassomatism), that culminate in albitites. In a general description, they may be characterized as equigranular rocks, with medium granulation and whitish, greyish or reddish colors. The mineralogy is composed essentially of K-feldspar, albite and quartz with the respective proportion ranging in accordance to the depth within the body, defining a sucession stages of metassomatism that fit perfectly in the models described in the literature.

The texture is equigranular pan-xenomorphic, but the porphyritic terms are commom. The albite is the typical mineral of the apogranite, occurring as high temperature albite and as low temperature albite, but the An contents are always equal to zero. The accessory phases are fluorite, cryolite zircon (malacon), lepidolite, arfvedsonite, columbite, cassiterite, monazite, xenotime, etc.. Variable proportions of biotite (maximum of 2%) also occur and is intepreted as being inherited from the biotite granite.

The geochemical behaviour of the granites from Pitinga was studied through analyses of about 140 rock samples from the two bodies, submitted to the determination of major oxides and trace elements, besides 20 analyses for rare earth elements. (Tables 1, 2).

The main characteristics of magmatic rocks are the high contents of SiO_2 and Al_2O_3, moderate to high content of Na_2O and K_2O and very low contents of CaO and MgO, defining their alkaline character as slightly peraluminous. The differentiation trends go from the rapakivitic granite (less evolved) to the biotite granite (more evolved). These trends are well-marked by the increase of SiO_2, F, Rb, Be, Li and Sn contents and by the decrease of TiO_2, FeO, MgO, CaO, P_2O_5 Ba and Sr contents. The apogranite, in a general way, follows these trends, except for the SiO_2 contents, that decrease, and for CaO contents that increase promoting the formation of mesonormative fluorite and cryolite. The facies constitutes the most differentiated term of the association. The Na_2O and K_2O present a uniform behaviour in all facies, except in apogranite where Na_2O is more abundant. On the other hand, K_2O is depleted in the apogranite, while remaining constant in the other facies.

The Zr, Rb and F contents are very high in all facies and, in the apogranite, they can be considered as major elements. The REE show a similar fractionated pattern in the magmatic facies of these two granites, with pronounced Eu anomalies, while the heavy REE are moderatly fractionated in relation to the light REE. The rocks of the apogranite show the REE contents within the abundance intervals of the magmatic series, but completely distinct variation patterns, including samples from the same borehole presenting marked discrepancy among REE contents and fractionation petterns. These rocks show strong Eu anomalies, positive and negative anomalies of Ce, seldom observed in granitic rocks reflecting different fluid oxidation stages, and generally high HREE/LREE ratios, indicating the enrichment of HREE by zircon and xenotime. The whole represents a chemically heterogeneous liquid, where the volatiles had an important role in the determination of their final characteristics, which only with difficulty could be explained by crystallization from primary magmatic phases, indicating, through the petrological and geochemical evidence, a metassomatic origin for the apogranite.

The mineralization of cassiterite occurs as alluvial deposits in the vicinity of these two granitic bodies,

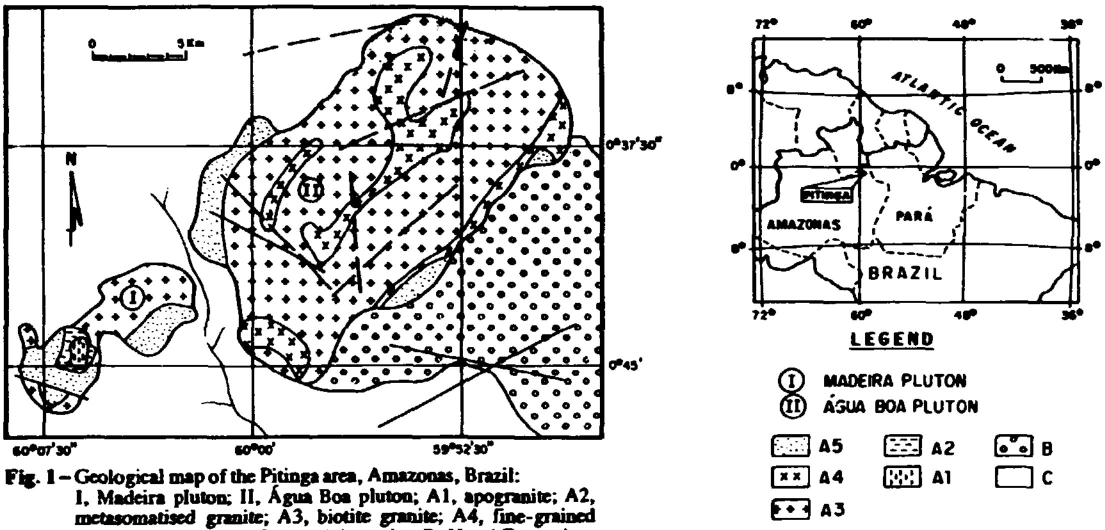

Fig. 1 – Geological map of the Pitinga area, Amazonas, Brazil: I, Madeira pluton; II, Água Boa pluton; A1, apogranite; A2, metasomatised granite; A3, biotite granite; A4, fine-grained porphyritic granite; A5, rapakivi granite; B, Urupi Formation; C, Iricoumé Group.

Table 1 - Major element analyses of the Madeira and Água Boa Granites.
Range of concentrations in parenthesis.

	MADEIRA GRANITE				ÁGUA BOA GRANITE		
GRANITE TYPE	RAPAKIVI GRANITE	BIOTITE GRANITE	METASOMATISED GRANITE	APOGRANITE	RAPAKIVI GRANITE	FINE PORPHYRITIC GRANITE	BIOTITE GRANITE
Nº SAMPLES	40	26	14	20	5	11	19
SiO_2	70,96 (68,00-76,30)	75,37 (71,00-77,80)	73,78 (70,00-77,40)	69,07 (63,90-75,50)	73,03 (72,50-73,80)	74,97 (73,40-76,30)	74,41 (72,00-75,90)
Al_2O_3	13,36 (11,20-15,30)	12,32 (10,80-14,40)	12,56 (10,90-14,60)	12,66 (11,10-16,10)	13,30 (12,70-13,70)	12,87 (12,00-13,40)	13,40 (11,90-13,60)
TiO_2	0,43 (0,10-0,80)	0,13 (0,05-0,42)	0,30 (<0,05-0,52)	0,02 (0,01-0,11)	0,26 (0,22-0,33)	0,13 (0,07-0,33)	0,18 (0,07-0,33)
Fe_2O_3	1,64 (0,20-3,50)	0,73 (0,21-1,60)	1,66 (0,40-2,30)	1,50 (0,10-3,50)	1,28 (0,27-2,40)	0,70 (0,10-1,90)	0,76 (0,09-2,10)
FeO	2,04 (0,67-3,80)	0,97 (0,38-2,45)	1,12 (0,30-1,90)	1,66 (0,58-3,20)	1,20 (0,24-2,10)	0,63 (0,24-1,30)	1,13 (0,28-2,00)
MnO	0,05 (0,05-0,10)	0,05 (0,05-0,06)	0,05 (<0,05-0,08)	0,04 (0,02-0,06)	0,05 (<0,05-0,08)	0,05 (<0,05-0,05)	0,05 (<0,05-0,05)
MgO	0,28 (0,02-0,66)	0,12 (0,03-0,40)	0,17 (0,01-0,33)	0,10 (0,01-0,17)	0,13 (0,06-0,17)	0,06 (0,01-0,17)	0,08 (0,02-0,25)
CaO	0,94 (0,34-1,70)	0,49 (0,02-1,10)	0,64 (0,06-1,00)	1,35 (<0,05-3,90)	0,74 (0,49-0,95)	0,34 (0,00-0,64)	0,64 (0,00-1,10)
Na_2O	3,55 (3,10-4,40)	3,35 (1,50-3,80)	3,67 (2,50-4,10)	4,95 (2,50-8,00)	3,30 (3,00-3,60)	3,54 (2,40-4,60)	3,75 (2,90-4,00)
K_2O	5,35 (3,50-6,50)	5,45 (4,70-7,00)	5,15 (2,90-6,00)	4,11 (0,85-5,20)	5,44 (5,00-5,90)	5,26 (4,60-5,90)	5,55 (4,20-5,90)
P_2O_5	0,12 (<0,05-0,60)	0,06 (<0,05-0,30)	0,05 (<0,05-0,17)	0,08 (<0,05-0,15)	0,05 (<0,05-0,11)	0,05 (<0,05-0,09)	0,05 (<0,05-0,09)
F	0,15 (0,02-0,34)	0,32 (0,03-0,50)	0,22 (0,05-0,50)	2,16 (0,01-3,30)	0,29 (0,10-0,49)	0,44 (0,15-0,71)	0,53 (0,09-0,72)

Table 2 - Trace element contents (ppm) of the Madeira and Água Boa Granites.
Range of concentrations in parenthesis.

	MADEIRA GRANITE				ÁGUA BOA GRANITE		
GRANITE TYPE	RAPAKIVI GRANITE	BIOTITE GRANITE	METASOMATISED GRANITE	APOGRANITE	RAPAKIVI GRANITE	FINE PORPHYRITIC GRANITE	BIOTITE GRANITE
Ba	538 (140-1040)	231 (81-980)	363 (67-560)	34 (<20-66)	387 (330-440)	160 (20-310)	182 (110-310)
Be	10 (4-18)	30 (6-192)	78 (8-350)	25 (12-56)	6 (3-9)	29 (8-80)	18 (6-58)
Ce	-	-	-	381 (1,20-2047,00)	-	-	-
Ga	21 • (11-30)	21 (17-27)	24 (17-46)	67 (59-86)	28 (22-31)	33 (17-54)	30 (22-40)
Li	31 (20-60)	99 (22-197)	58 (10-181)	-	36 (21-50)	167 (63-295)	130 (26-200)
Nb	56 (<20-215)	49 (<20-116)	288 (12-1480)	1264 (800-2200)	38 (30-44)	57 (34-88)	45 (30-68)
Pb	41 (22-74)	54 (16-143)	121 (32-370)	704 (174-1460)	63 (44-88)	74 (24-196)	60 (29-118)
Rb	436 (250-790)	782 (290-1120)	1183 (360-3200)	5080 (1590-8400)	507 (400-680)	851 (580-1080)	684 (570-920)
Sn	70 (5-570)	39 (5-172)	370 (12-1840)	1074 (400-1920)	10 (7-17)	15 (5-26)	13 (5-20)
Sr	87 (17-130)	33 (<10-92)	47 (<10-78)	36 -	92 (39-140)	52 (10-140)	47 (10-130)
Ta	<15	<15	<15	112 (52-210)	<15	<15	<15
Y	107 (23-190)	146 (60-440)	155 (62-270)	319 (54-1080)	196 (122-280)	156 (38-340)	111 (36-380)
Zr	449 (172-1555)	254 (132-820)	1162 (210-5150)	7097 (4110-17000)	427 (280-520)	230 (168-350)	327 (176-660)

constituting the biggest Brazilian reserves, and also as primary mineralization in the apogranite. The apogranite also presents primary mineralizations of fluorite, columbite, zircon (malacon), xenotime, pyrochlore and minor concentrations of thorite, samarskite, bastnaesite and Y-pyrochlore.

GEOCHEMISTRY OF ELEMENTS OF THE IRON FAMILY (Fe, Mn, Ti, Cr, Ni, V) IN THE JURASSIC DEPOSITS OF THE AFGHANO-TADJIK DEPRESSION

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The distribution regularities of elements in the iron family (Fe, Mn, Ti, Cr, Ni, V) in the deposits of the Jurassic terrigene-coalbearing formation, generated under the humid and arid climate conditions in the Afghano-Tadjik depression, were considered.

It was established that the distribution regularities of these elements in the Jurassic polyfacial sedimentary rocks, studied by a detailed lithologo-facial method, depended on a number of factors: the tectonic regime of the region, climatic conditions, source rocks, lithologo-facial environments of sedimentantion.

In continental - alluvial and lacustrine-boggy facies the total content of elements of the iron family has the mixed type of distribution in the different lithological groups of rocks. The maximal contents of the elements are found in coarse-grained rocks - gravelites and sandstones, the minimal ones - in aleurolites and argillites. Such a distribution picture in continental facies is connected with the element migrations the form of coarse, suspended material and their accumulation at a short distance from the source rocks, and apparently the inheriting one.

Along with transition from continental facies to marine ones the element differentiation took place. For the all marine facies deposits it was established the well regulated type of elements distribution - that is, the increasing of the element contents from sandy rocks to argillites. This is especially clearly displayed for Fe and Mn. Such distribution of elements is evidently due to intensification of hydrolytic decomposition of fragmentary material and an increase in the solution role in the migration of elements and their accumulation in fine-grained sediments as a result of adsorption processes when being removed from the source rocks region.

The data on the element distribution in the various granulometric fractions of the rocks show that certain elements - Fe, Mn- are accumulated in fine-pelitic fractions (≤ 0.001 mm), and others - Ti, Cr, Ni, V - in aleuritic and coarse-pelitic fractions. It was established that the distinct trend of the increase in Fe and Mn contents in fine-pelitic fraction of sediments from alluvial facies to the marine ones, and then to the deeper parts of the sea basin. The distribution of Ti, Cr, Ni and V shows the opposite trend - their maximal contents are characterized for continental facies.

The migration rows of the elements were calculated, based on the concentration coefficient - K, determined as a ratio of the element content in pelitic fraction of considered facies to the element content in pelitic fraction of alluvial sediments, which, being the last is considered as inheriting from the source rocks.

For continental lacustrine facies:
Fe > Mn >Ti > V > Cr> Ni
K: 1.3 1.2 1.1 0.9 0.8 0.7

For marine humid facies:
Mn > Fe > Cr > Ti > Ni > V
K: 2.2 1.6 1.3 0.8 0.5 0.4

For marine arid facies:
Mn > Fe > Cr > Ni > V > Ti
K: 3.5 3.0 1.5 1.2 0.8 0.6

The regular increase in Fe, and especially Mn content, in pelitic fraction of sedimentary rocks from continental facies to marine ones and the decrease in Ti, V and Ni contents in the same direction was the ground for using content ratios Mn/Ti (from 0.014 to 0.078), Mn/V (from 2.25 to 18.46) and Mn/Ni (from 3.23 to 15.0) as geochemical indicators of facial environments of sedimentation at the paleogeographic reconstructions.

Taking into account the source rocks provinces and genesis of sediments, the geochemical background of elements of the iron family for the different lithological types of sedimentary rocks of the Afghano-Tadjik depression and surrounding regions were calculated. It is established that the average contents of elements of the iron family in all the types of rocks considered are less than the clarkes of these elements in sedimentary rocks, that ore evidently due to peculiarities of the source rocks provinces. The formation of the Jurassic deposits in the Afghano-Tadjik depression had been proceeding in general at the expense of destruction products of middle and acid igneous rocks, characterized by low contents of the elements considered.

GEOCHEMISTRY OF PRECAMBRIAN GRANITOIDS IN RELATION TO MINERALIZATION IN KOREA

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Precambrian granitoids have been established by K/Ar and Rb/Sr isotope dating in the central eastern part of the southern Korean peninsula, i.e. in the Sangdong and the Ulchin areas.

Pegmatites of similar age and with low-grade cassiterite mineralizations are only located in these two areas and show a close genetic relation to the granitoids. A total of 95 samples were collected from the four plutons of granitoids which are spatially close to tin occurrences: Naedeogri and Nonggeori granitoids in Sangdong area, and Buncheon and Wangpiri granitoids in the Ulchin area. Lithogeochemical studies to determine the chemical variation of K, Na, Ca, Mg, Fe, Mn, Al, Ti, P, Li, Rb, Be, Sr, Ba, La, V, Cr, Co, Ni, Zr, Cu, Pb, Zn, F and Sn (total and cassiterite tin) have been undertaken in order to discriminate tin- associated granitoids from a geochemical viewpoint. Correlated groups of elements for each pluton are not similar to the cluster analysis of multielement data, which probably indicates differences in their petrogenesis. Wangpiri granitoids in Ulchin area display distinctive features of tin-granitite in their contents of specific elements such as Li, Rb and Sn, and element ratios such as Ba/Rb, Li/K, K/Rb, Mg/Li, and Rb/Sr. Enrichement of Li, Rb, Be and Sn, and depletion of Ca, Mg, Fe, Ti, Sr, Ba, La, V, CO, Ni, Zr are particularly characteristic in comparison with element concentrations in the Buncheon granite gneiss.

Average total tin content in Bucheon granitoids is about 3 ppm, and total tin content in Wangpiri granitoids ranges from 38 to 208 ppm with as average of 97 ppm. Cassiterite tin content in Wangpiri granitoids averages 30 ppm. Nonggeori two mica granites in Sangdong area show quite different geochemical features compared with those of Naedeogri granitoids.

The total tin content of both Nonggeori and Naedeogri granitoids averages about 14 ppm, but the geochemical characteristics of the Nonggeori granites are indicative of a productive pluton associated with tin mineralization in terms of the ratios of selected elements such as Ba/Rb, Li/K, Rb/Sr and Mg/Li.

With geochemical evidence such as, high $(La/Yb)_N$, an incompatible element, strong negative Eu anomalies (0.24-0.32) and a low compatible element, the alkaline Buncheon granite gneiss (I-type) is probably derived from a "low degree" of partial melting under the high oxygen fugacity condition of rather geochemically evolved igneous rocks (e.g. granitic to granodioritic compositions) in which the plagioclases has already been depleted. High Rb/Sr ratios and geochemical characteristics in the Buncheon granite gneiss are difficult to reconcile with an origin by partial melting of mafic materials, and a relatively siliceous source can more easily be explained by its higher number of incompatible elements.

The small variations of chemical composition, low CaO content (0.58-0.68), high normative corundum and primary muscovite in the Nonggeori and Naedeogri granitoids suggest that they may be generated by partial melting of relatively homogeneous and less hydrous sialic crust (S-type).

RARE-METAL ACCUMULATIONS – PRODUCTS OF GEOCHEMICAL AND GEOTECTONIC SPECIALIZATION

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Rare-metal mineralization in general, and tin mineralization in particular, display a time-related development during geological evolution: from high-temperature ore phases (oxides only) in pegmatites during the Precambrian to low-temperature ore associations (oxides + sulphides) in greisens and vein complexes of Phanerozoic ages. Typically, Ta-dominated pegmatites occur in Proterozoic amphibolite-grade metamorphic terrain of mixed volcanic-sedimentary sequences, which may include partly reworked greenstone-type rock associations; mining is mostly from eluvial placers and/or from deeply-weathered primary deposits. In contrast, Nb-dominated mineralizations are mainly found in carbonatites and felsic ring complexes, i.e. indicators of anorogenic magmatism related to deep-seated fracture systems.

One type of area, where both types of rare-metal mineralization are combined, is the tin-province of Nigeria: Outstanding in their tin-minning potential, the Jurassic ring complex province of Nigeria is unique among the widespread occurrences of petrologically similar anorogenic ring complexes elsewhere in Africa (Hoggar/Mali; Air/Niger; Nuba Montains/Sudan; Bayuda Desert/Sudan). These "Younger Tinfields" of Nigeria are preceded by the "older Tinfields", rare-metal pegmatites of Pan-African age, which are confined to a SW-Ne trending belt of about 400km length, extending from southwestern to central Nigeria. Rb/Sr dating comfirmed the Pan-African ages of the rare-metal bearing pegmatites in the range of 560-520 Ma. In spite of being emplaced in the same time span, mineralogy, geochemistry and mineralization of these pegmatites differ according to their host-rock lithology. Occurrences from SW Nigeria, which are emplaced into Proterozoic metasedimentary-metavolcanic sequences, are enriched in tantalum relative to niobium. In contrast, pegmatites of central Nigeria, which are mainly emplaced in granitoid gneisses, are very low in tantalum.

From geophysical evidence, tha emplacement of the Jurassic ring complexes was strongly controlled by WSW-ENE trending fracture zones within the basement, suggesting the reactivation of major Precambrian tectonic lineaments. Similarly, all of the productive rare-metal pegmatites of Nigeria are located along a major SW-NE trending tectonic lineament, which has been active at various stages in the evolution of this crustal segment, and which seems to be part of a continental tectonic network. This SW-NE trending lineation of crustal weakness is considered to have acted as pathways for both a higher heat-flux and the introduction of fluid phases to higher crustal levels. The host-rock lithology has contributed significantly to the individual characteristics of each occurrence. Obviously, rare-metal mineralization at the earlier stage of geological evolution had a distinct affinity to mantle-derived mafic volcanic sequences rather than to acidic intrusive complexes, which are dominant in the late Phanerozoic. Typically, rare-metal potentials of economic importance are dominated by specific lithological patterns, overprinted by multiple crustal reactivation and shearing, which provided energy and fluid phases to accumulate the regionally available rare-metals to ore-grade.

RECONNAISSANCE AND DETAILED LITHOGEOCHEMICAL EXPLORATION FOR PRECIOUS METAL MINERALIZATION DUGWAY MINING DISTRICT, UTAH, USA

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Reconnaissance and detailed lithogeochemical surveys were carried out in conjunction with geologic and alteration kmapping of the Dugway Mining District, Utah to aid in the evaluation of its gold potential. The area consists of Lower Paleozoic sedimentary rocks intruded by rhyodacitic igneous rocks of Tertiary age. Complex, high-angle normal faulting resulted in uplift of a northwest-trending horst in the central part of the district.

Mineralization consists of small, high-grade pods of precious and base-metal mineralization localized along faults in the sedimentary and volcanic rocks. Four types of alteration of carbonate rocks were distinguished; (1) silicification; (2) bleaching; (3) recrystallization; (4) argillization. Igneous rocks were propylitically altered. The distribution of altered rocks was controlled by high-angle structures and favorable lithologies.

One hundred and eighty-five mineralized, altered and unaltered rock samples were collected throughout the district to characterize, on a reconnaissance scale, geochemical dispersion of trace elements in mineralized rocks. Samples were analysed for 30 elements by a semi-quantitative, direct-current arc emission spectrographic method (Fe, Mg, Ca, Ti, Mn, Ag, B, Ba, Be, Co, Cr, Cu, La, Mo, Nb, Ni, Pb, Sc, Sn, Sr, V, W, Y, Zn, Zr, As, Bi, Cd, Sb, and Au). Lower detection limits were obtained for five elements (Au, As, Cd, Bi, and Sb) by more sensitive atomic absorption methods. R-mode factor analysis was employed to distinguish between two types of precious-metal mineralization in the area: (1) a quartzite-hosted type characterized by a Bi-Au-Cu-Fe-Ba association and concentrated in the northwest part of the district; and (2) a carbonate-hosted type characterized by a Sb-Mo-As-Ag-Pb-Au association located in the South Horst zone.

A follow-up lithogeochemical survey was conducted in the South Horst zone. One hundred and ninety-six rock chip and composite dump samples were analyzed for 15 elements. Gold was determined by a graphite furnace atomic absorption procedure; silver was determined by AAS; and As, Cu, Hg, Mo, Pb, Sb, Ti, Zn, Bi, Cd, Ga, Se, and Te were determined by ICPES. R-mode factor analysis was again employed to assist in identification of mineralization. Three associations were recognized: (1) Cd-Zn-Cu-Pb carbonate-hosted base-metal mineralization, and (3) Ag-Au-Mo carbonate-hosted base and precious-metal mineralization, and (3) Ag-Au-Mo carbonate-hosted precious-metal mineralization.

Anomalous gold was detected along a zone extending for 7,000 feet in lenght. Distinct geochemical zonation exists with base and precious-metal enrichment in the northwest part and precious-metal mineralization in the southeast. Application of a sedimentary rock-hosted precious-metal deposit model may be applicable in the southeast geochemical associations characteristic of mineralization and provided additional insight into geological interpretation of the data.

ROCK CHEMISTRY, FLUID INCLUSION AND REMOTE SENSING STUDIES AS EXPLORATION TOOLS FOR ORE DEPOSITS IN GRANITIC BATHOLITHS OF CALABRIA, SOUTHERN ITALY.

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Hercynian granitic rocks found within the Sila, Stilo, Polia Copanello, and Aspromonte Alpine tectonic units in the Calabria-Peloritani arc have a potential as hosts of base- and rare-metal deposits. The granitoids feature a late Hercynian plutonic activity developed probably in an external portion of the Variscan belt.

The calck-alkaline Sila batholith (600 sq.km) (Peacock index = 57) is the best studied example of the Hercynian granites in the region. The batholith consists of shallowly emplaced, coalescing, nested, contamporaneous intrusives ranging from leucogabbro to peraluminous, cordierite-, andalusite-, sillimanite-, and muscovite-bearing leucomonzogranite, although tonalite and granodiorite predominate (Messina et al., in press). 40Ar/39Ar age spectra from various plutons within the Sila complex document a single Hercynian emplacement and cooling history (about 300 - 270 Ma) with no evidence of later thermal effects (Sutter et al., 1988). Calck-alkaline modal variations include a tonalitic low-K trend in the sphene + magnetite + allanite-bearing rocks, and a medium-K trend in the granodiorites. Distinct modal variations distinguish the foliated (e.g., syntectonic tonalite) intrusions from the massive (e.g., peraluminous) plutons. Smooth and progressive chemical changes in major- (e.g., range in SiO_2 = 55-77 wt.%, K_2O/NA_2O = 1.4) and trace- elements from least to most evolved, however, are consistent with a chemically related region for the batholith as a whole. Trace element variations in tonalites and granodiorites generally resemble those of plutons formed in orogenic margins (e.g., RB = 100-150ppm, Y + NB = 30-45ppm). Peraluminous granites overlap chemical fields of plutons generated at orogenic and collisional setting (RB >150ppm, Y + NB = 25-40ppm). REE contents range widely in the batholith resulting in a diversity of light-REE enriched, chondrite-normalized pattern (LAcn = 20-250, YBcn = 1-20) with moderate to large negative EU anomalies (EUcn ≈ 1-30), and a relative depletion in heavy REE (LUcn ≈ 2-5) that are characteristic of granitic rocks intruding a thick continental basement. Many granites having the highest contents of heavy REE (LUcn = 5-30 have relatively flat slopes for heavy REE (TBcn/YBcn = 1-1.2), large negative EU anomalies, and are found in the northern part of the batholith hosting many of the mineralized veins.

The resource potential of the Calabria batholiths was first recognized by a regional multielemental geochemical survey of the whole of Calabria (De Vivo et al., 1984). Numerous sulfide occurrences (sphalerite, galena, pyrite, chalcopyrite, molybdenite, and flourite) hosted by granitic rocks have been described both in the Sila and Le Serre areas; a few were mined in ancient times (De Vivo 1982). Field relations indicate that mineralized are as found near corundum normative, peraluminous, unfoliated plutons. Results of the regional geochemical stream sediment survey also identified previously unknown areas containing anomalous base- and rare-metal contents. Assessment of granite specialization was made on the degree of magma evolution and R-mode factor analysis of rock samples. Many of the siliceous, peraluminous rocks are relatively enriched in RB (>250ppm), NB (>29ppm), TA (>1.5ppm), and U (5ppm), and are depleted in ferromagnesian elements and SR; these plutons characteristically host sulfide-bearing veins. Granite-specialization indices including K/RB(<50), BA/RB(<50), and RB/SR(>7) are also typical of granitic rocks hosting sulfide-rich veins. Regional hydrothermal alteration in the batholith suggests that porphyry-MO-CU systems may are be present, most likely in the Le Serre granitic rocks (Stilo Unit) which contain numerous molybdenite occurrences. In the Sila unit, scheelite is found near the contact between medium to fine grained granodiorite and phyllitic country rocks, and secondary epigenetic U concentrations are found in lacustrine sediments. Galena in sphalerite veins has relatively radiogenic lead isotopic compositions:

206PB/204PB:18.357,
207PB/204PB:15.637,
208PB/204PB:38.746.

These PB values are more evolved than average crustal rocks, suggesting that the most important reservoir of PB is it the upper crust.

A reconnaissance fluid inclusion study has been conducted on samples from the Sila and Stilo tectonic units. Secondary monophase, two-phase (vapor + liquid), and three-phase (V + L + halite daughter crystal) aqueous inclusions occur in healed fractures in quartz. Microthermometric heating and freezing experiments reveal a wide range of vapour/liquid homogenization (80 to 420 C, uncorrected for pressure) and salinity (0 to >26 wt % NaCl equivalent) data for both the Sila and Stilo units. Data on first melting of frozen inclusions indicates the presence of additional cations (e.g., Ca^{2+}, Mg^{2+}) in the inclusion fluids. The range of temperature and salinity in the same sample suggest that the quartz has recorded the passage of various fluids, either during a single hydrothermal event or during events at different times. The salinity and temperature data found in some inclusions are similar to known mineralized caverinoments in other granitic terranes.

A Landsat image analysis was attempted in order to map the hydrithermal alteration haloes around the magmatic bodies. The initial results revealed the Le Serre pluton as the most suitable area for remote sensig studies because it has a poor vegetation cover and a higher degree of alteration around the intrusive bodies. In contrast, the Sila plutons have a dense vegetation cover, which masks the spectral features of the rocks. Digitally processed color-composite and color-ratio composite (CRC) images have, therefore, been used to locate hydrothermally altered areas, by enhancing the spectral differences due to the OH absorption bands of clay minerals and chlorite (2.2 and 2.3 um respectively) in the spectral region of tm band 7.

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ROCK GEOCHEMISTRY OF AN IRON ORE FIELD IN THE DIVRIGI REGION, OF CENTRAL ANATOLIA, TURKEY. A NEW EXPLORATION MODEL FOR IRON ORES IN TURKEY.

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Rock samples of iron deposits and their host rocks were analysed for 10 major elements and 31 trace elements on 160 samples. In addition, thirty samples were analysed for Rare Earth Elements. Geostatistical analyses were carried out on the 160 rock samples for 24 elements from the Divrigi iron ore region.

The results of the analyses yield a division into different rock types (Discriminant analyses) and several element associations (Cluster- and Factor analyses), which reflect the different rock types. The individual rock types were geostatistically treated as well resulting in different element associations. These groups helped with the interpretation of the genetic relationship between the ore and the host rock enabling a more subtle intepretation of the possible geological environment. The geochemistry of the REE indicated also the genetic relationship between ore and host rock. The rock geochemistry gave not only a geochemical characteristic of the ore and their host rock, but also an indication of the origin of the iron ore and later mobilization caused by serpentinization and intrusion of granitic rocks. The intepretation of the element association suggests that the iron ores are closely associated with mafic to ultramafic rocks, their serpentinization and also later hydrotermal events.

These results have been utilized in a geochemical exploration model for iron ore in Central Anatolia, Turkey. The results have led to new magnetic field measurements, and discoveries of potential iron ore have already been established.

THE 2 Ga. PERALUMINOUS MAGMATISM OF THE JACOBINA - CONTENDAS MIRANTE BELT (BAHIA-BRAZIL): GEOCHEMISTRY AND METALLOGENIC POTENTIAL

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The Jacobina - Contendas Mirante belt represents a Transamazonian (2 Ga) orogenic domain elongated N-S, about 500 km in the central part of Bahia State. Numerous peraluminous leucogranitos have been recognized: the Campo Formoso, Carnaiba and jaguarari granitics to the North and the Gameleira, Riachos das Pedras, Lagoinha, Lagoa Grande and Caetano granites to the South. Their mineralogical and geochemical, and some of their metallogenetic characteristics, closely resemble their Hercynian and Himalayan equivalents. Biotite is, however, on average, slightly more magnesian and less aluminous in the Jacobina - Contendas Mirante leucogranites. The peraluminous magmatism of the Jacobina - Contendas Mirante belt probably represents a signature of a continental collision at 2 Ga.

Trace element geochemistry implies variable source compositions and/or melting conditions between the different granitic plutons and some different facies within the same plutonic unit. The scarcity of illmenite and the general occurence of magnetite, their peraluminous index, suggest a restricted implication of graphite-bearing sediments in the source. Archean acid meta-igneous material, such, as the Sete Voltas TTG suite, represent a suitable source for some of the granites.

Sn, W, Li, F and Be enrichment of these granites are much weeker than in their mineralized Variscan equivalents. Beryl, molybdenite and scheelite mineralizations are related to the most specialized bodies, the Campo Formoso and the Carnaiba granites. In many of these granites uranium contents are comparable to the values measured in mineralized Hercynian leucogranites. The occurrence of hexavalent uranium minerals and episyenitic alteration are favorable criteria for the presence of Variscan type uranium mineralizations.

THE ITU, GRACIOSA AND SERRA DO CARAMBEÍ GRANITOIDS (STATES OF SÃO PAULO AND PARANÁ, BRAZIL): LITHOCHEMICAL AND ZIRCON TYPOLOGY DATA*

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Data concerning general chemistry, REE and zircon typology of the Itu (State of São Paulo), Graciosa and Serra do Carambeí (State of Paraná) complexes are presented and compared. The Itu complex is a rapakivi intrusion with typical alumina rich composition and a moderately alkaline tendency expressed by the presence of Fe-Hastingsite.

The Graciosa complex is less aluminous and more alkaline, caused by the occurrence of aegirine, and the Serra do Carambeí is the most alkaline of the three intrusions considered. This gradual change in the petrographic/lithochemical aspects from the Itu, via Graciosa to the Serra do Carambeí complex is clearly displayed in the m.p. CaO - (K_2O + Na_2O)- Al_2O_3 diagram, as well as in the Rb: Ba: Sr diagram in which the Serra do Carambeí complex is the most envolved (i.e. enriched in Rb and depleted in Sr and Ba). This agrees with the REE - pattern of the two extreme compositional cases, the Itu and the Serra do Carambeí complexes in which the latter show an about 10 - times higher Eu - depression.

The chemical differences between the three complexes considered is very well expressed by the location of their zircon morphology data in the zircon typology board. Thus, the data concerning the Itu complex lay consistently on the subalkaline-alkaline field, whereas those from the Graciosa complex occupy mainly the alkaline field and the data concerning the Serra do Carambeí fall entirely in the alkaline field.

The comparison between the zircon morphology and geochemistry data show that zircon typology methcd is a sensitive tool for the discrimination of different granitoid series, even if their chemical compositions are quite similar.

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Technical Session
Geochemistry of Carbonatites and Rare Earth Metals

GEOCHEMICAL AND MINERALOGICAL FEATURES OF A RE-ENRICHED ZONE WITHIN THE GOUDINI CARBONATITE COMPLEX, TRANSVAAL, SOUTH AFRICA

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The Goudini carbonatite complex intrudes basic igneous rocks of the western lobe of the Bushveld Igneous Complex. The complex, approximately 5.5 x 5.4km in size, forms a caldera with an outer breccia ring and an inner, basin-shaped structure in which sovite, metabeforsite, other carbonatitic rocks and bedded, carbonatized tuffs outcrop (Verwoerd, 1967). Petrographic study of drill core identified pseudomorphs after olivine, pyroxene, nepheline, and possibly melilite, suggesting that primary magmatic/volcanic material was of olivine melilitite or alnoitic affinity. U-Pb data (Nelson et alii, 1988) suggest an age of about 1,250Ma which is within the age bracket of 1,200 1,400Ma for the pilansberd suite of alkaline intrusives found in the Transvaal (Hunter, 1981). Investigation has centred on an area in the central-western part of the caldera in which a silicified, carbonatized, iron-rich zone of hydrothermally altered tuffs bears highly anomalous yttrium and heavy, rare earth values.

The area of interest was outlined by mapping, a ground radiometric survey, and grid soil geochemical sampling an 50m centres, with analysis for yttrium and other trace elements by XRF. Follow-up by trenching, shallow percussion and diamond drilling, with systematic XRF analysis, and checks on yttrium values using I.C.P. techniques. A total of 25 samples, most of which were composited from relatively high yttrium zones, were analysed by sequential I.C.P. for the rare earth element (R.E.E.) suite plus yttrium, lanthanum, scandium and thorium. Petrological studies involving microscopic analysis, XRD, SEM, and SEM-EDS were undertaken in conjunction with field studies.

Soil sampling outlined a near circular zone of anomalous yttrium (plus 250ppm, against a background of 50 to 120ppm Y_2O_3). The anomaly overlies an apparently pipe-like zone of intense hydrothermal alteration within bedded, carbonitized and silicified tuffs, marked by sporadic outcrop or dark-coloured iron-rich silicified carbonatite. Satellite imagery utilizing a clay-iron prediction shows the alteration zone clearly. Detailed ground magnetometry does not define the alteration zone, the northern margin of which is marked by a linear resistivity low. Only a small part of the zone shows strong radiometric activity, but the area of interest is broadly defined by slightly anomalous radiometrics.

Two trenches across the northern rim of the anomaly, in the vicinity of the resistivity low and the area of greastet radiometric activity, expose altered tuffs. Iron-rich zones are highly radioactive. Channel samples were analysed by XRF for Th and Y, and a package of 34 other major and trace elements including Fe, F, Ca, Ba, Sr, Nb, Zn, Mo and As. Five angled percussion holes (total 400m drilling) were sunk in the vicinity of the trenches, and 2m composite samples were analysed for the same suite of elements. Selected samples were subsequently composited and analysed for the rare earths. The flank of the anomaly, intersected 363m of carbonatized tuffs, agglomerates and probable flows, which exhibit a near-pervasive ankerite-albite-aegirine assemblage. Multiple phases of veining and alteration are evident. A metadolerite which intrudes the succession was intersected, and proved to be affected by the main hydrothermal event. Alteration is more marked, and yttrium grades are higher, on the northern side of the dyke. The dyke appears to belong to a post-carbonatite event, thus Y-REE mineralization has taken place some time after emplacement of the caldera.

Yttrium grades in the trenches are high, ranging up to 0.45% Y_2O_3 over 22m in one trench, with a peak of 0.97% Y_2O_3 over 2m. Here, and in two adjacent percussion holes, there is a strong positive correlation between yttrium and thorium, contained largely in yttrian thorianite, but this does not hold true elsewhere. The percussion holes returned values of 0.22 to 0.,25% Y_2O_3 over interected widths of 30 to 50m, while the diamond drill hole returned an average grade of 0.19% over 150m, below the dolerite dyke: i.e. at least large parts of the hydrothermally altered zone have an yttrium oxide grade of c.O.2%, or more.

The heavy rare earths (Sm to Lu) show a strong positive correlation with yttrium, but correlation with the L.R.E.E. is poor and substantial decoupling is indicated (ref. Tabela 1, which also details La, Sc and Th values). Chondrite normalization emphasises the extreme H.R.E.E. enrichment (from samarium) at Goudini, in relation to "normal" carbonatite values. Negative cerium and neodymium anomalies are also evident. Typical values of interest for other elements are: Nb500-1500ppm, Mo 80-400ppm, Pb 100-500ppm, Zn 300-2000ppm, As 50-300ppm, Ba 0.1-400ppm, Pb 100-

Tabela 1 – Rare earth, yttrium, lanthanum, scandium and thorium values in samples from the goudini complex.

Sample	L.R.E.E Ce – Nd	H.R.E.E Sm – Lu	Y_2O_3	La_2O_3	Sc_2O_3	ThO_2
DDHI (No.I)	5210	2940	4170	1840	24	1070
DDHI (No.2)	70	2770	4300	90	27	130
PHD1 (Highest total REE)	5440	2300	3120	760	91	560
PHD1 (Lowest total REE)	1910	880	990	500	71	590
PHD2 (Av. 6 samples)	2350	1810	2150	700	88	440
PHD3 (Highest total REE)	5640	2870	3870	1770	102	780
PHD23 (Av. total REE) 4 samples)	4330	1970	2470	1460	95	620

All values in p.p.m.
PHD = Percussion drill hole sample
DDH = Diamond drill hole sample
Av = Arithmetic mean
R.E.E. values are as oxides.

500ppm, Zn 300-2000ppm, As 50-300ppm, Ba 0.1 to 6.0%, Sr 0.1 to 3.0%.

Mineral phases positively identified in the ore samples, based on XRD and SEM-EDS techniques, are thorianite, monazite and ancylite. Yttrium thorianite was identified in samples from one of the percussion holes. A common Sr, Ca, Y, Ba carbonate occurring as inclusions in dolomite, ferroan calcite or barite, was identified as either burbankite or donnayite. A Ca-Ca-La-rich phase is probably synchisite. Monazite, though present, is rare. A Ca/Y carbonate + fluoride was tentatively identified as doverite. Thus, the R.E.E. minerals occur essentially as carbonates, and to a lesser extent as phosphate. Yttrium occurs mainly as a carbonate and to a lesser extent as oxide. High acid consumption and poor recoveries are obstacles to possible economic recovery.

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GEOCHEMICAL EXPLORATION ON THE MAICURU ALKALINE-ULTRAMAFIC-CARBONATITIC COMPLEX

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The Maicuru Hill is located in the northwestern part of the Pará state, 210km far from northeast of Santarém city, in a straight line (figure 1). It was studied by the "Companhia Meridional de Mineração" in the beginning of the 70's and by the RADAMBRASIL project at the same decade. In 1984, Maicuru began to be studied by Docegeo, who discovered phosphate and titanium ores. In these researches the company was advised by the Universidade Federal do Pará's professors whose results are presented in this paper.

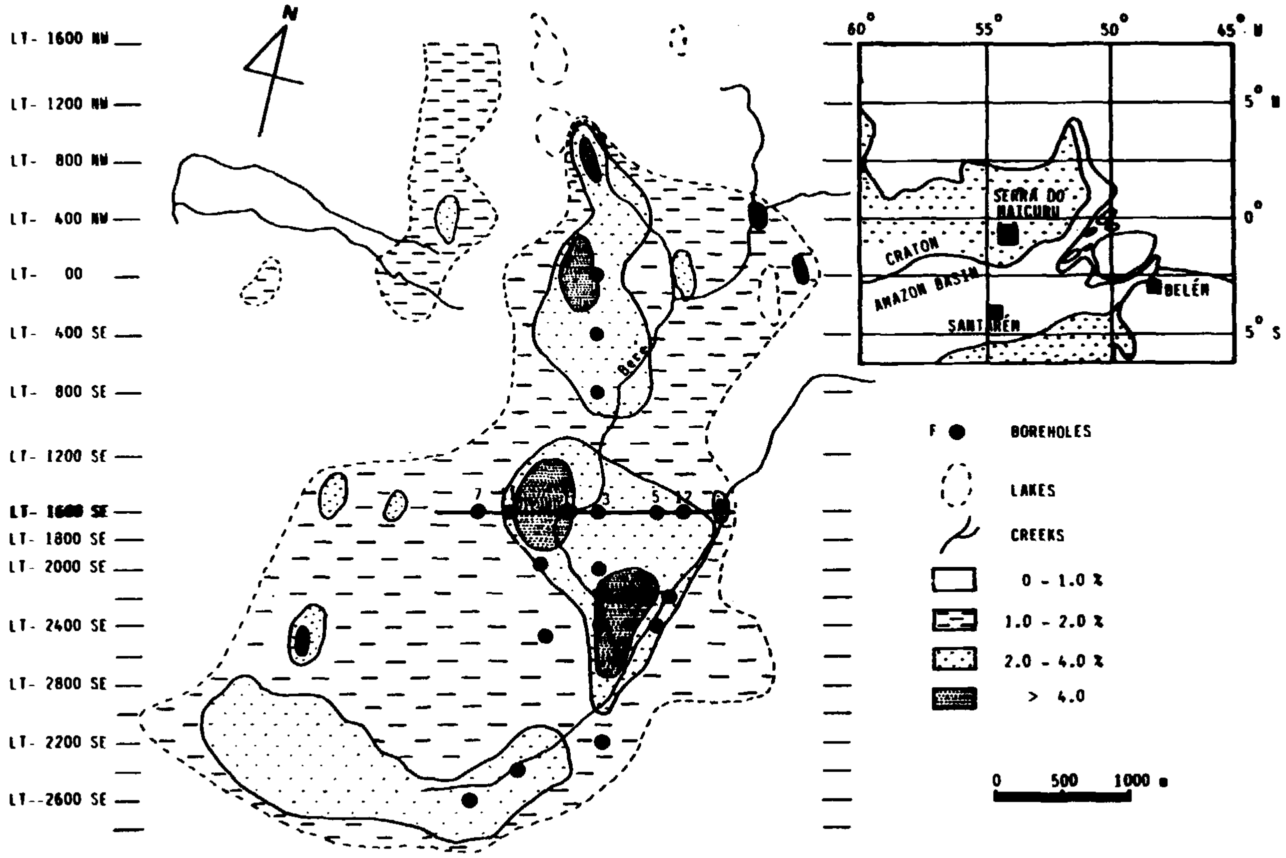

Figure 1 - Geochemical map for P_2O_5 in laterites and soils in the Maicuru Complex.

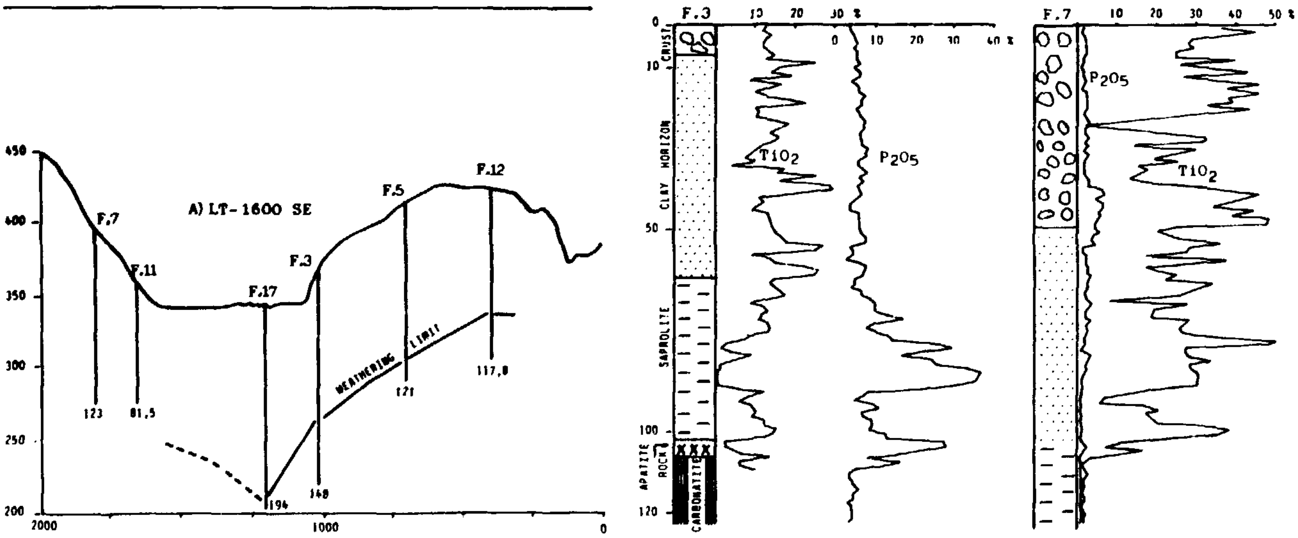

Figure 2 - A) Geological Section along the LT 1600 SE Traverse in Maicuru.
B) Distribution of the P_2O_5 and TiO_2 contents from the Boreholes F. 3 and 7 in the Maicuru Complex.

The Docegeo company performed in Maicuru a great and systematic work, involving fotointerpretation, topographic survey, geological maping in a 1:5.000 scale and stream sediments, soil and lateritic rocks sampling in a 100 x 200m grid. After the evidence of phosphate and titanium in soils and laterites the company implemented a program of 18 rotative boreholes and 38 deep wells. Therefore, about 1452 samples of surficial materials (soils and laterites) and 2850 meters of drill cores were colected.

The soil samples (fraction smaller than 80 mesh), and the laterites that were pulverized at the same fraction, were analyzed for Mn, Ni, Co, Cr, Cu, Pb and Zn (Atomic Absorption), P_2O_5 and TiO_2 (Colorimetry) and Fe_2O_3 (Volumetry). These data, together with those achieved by UFPA amount to more than 16,000 analyses, which were treated with statistical softwares for IBM-PC/XT compatible microcomputers.

In surface, the Maicuru Hill shows an oval form, with 9km lenght in the greater axe and 6km in the smaller one. Its top is located about 280 meters over the surrounding topography. The hill correspond to an alkaline-ultramafic-carbonatitic Complex, intruded in the Guianas Craton. Over these rocks, a thick lateritic profile was developed, which is represented in the surface by: magnetic ferruginous lateritic crust; aluminous (phosphatic and/or bauxitic) laterites, concretionary lateritic soils and clayey soil. Under the soils and laterites, the bedrock is composed by: apatite-perowskite-titanite and titanomagnetite rick-priroxenites, which are crossed by apatite veins and apatite bearing sovitic-carbonatites and syenites.

In terms of tectonics, the complex was enclosed in the great NE-SW and NW-SE thrusts that cross over the Guianas Craton.

The analytical results obtained in lateritic and soil samples showed anomalous values for P_2O_5 (as aluminous phosphates) in an elongated zone in the central N-S part of the Complex (figure 1) and also economic concentrations of TiO_2 (as anatase and ilmenite) in two areas: in the southwestern and in the northeastern parts of the Maicuru Complex. The zone delimited by the isocontent contour line greater than 2.0% P_2O_5 over laterites and soils was submimted for drilling, reaching apatite mineralized rocks. Some holes also show that the high titanium contents extend to hundreds of meters deep and are inversely related to the P_2O_5 contents (figure 2).

In the titanium domain area, the thickness of the laterites can exceed 200 meters.

Besides these elements, significative anomalies were detected for rare earth elements (REE) and niobium, where the REE contents are directly related to the crandallite group. In these, the REE_2O_3 contents reach 20% as crandallite-goyazite-florencite solid-solution. The contents of niobium reach about 3000 ppm in the laterites. The research of laterites from Maicuru shows to be very important for geochemical study, allowing the identification of anomalies, ore and increase knowledge about its evolution.

The authors would like to thank the Docegeo Company and Brazilian FINEP for the finantial suport of this research.

GEOLOGIC, PETROGRAPHIC AND PETROCHEMICAL ASPECTS OF ANGOLAN CARBONATITES

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Based on a study of 164 rock samples icnluding 54 carbonatites, and complemented with specialized literature data, we present some geological, petrographic and petrochemical aspects of the Angolan carbonatites. The samples are from the following massifs: Bonga (16), Bailundo (16), Virulundo (9), Lupongola (6), Monte Verde (4), Longonjo (2) and Coola (1).

The carbonatite massifs are intrusive in granites and gneissic and migamititic rocks, with the exception of Lupongola, which intrudes anorthosites. No mafic or ultramafic rocks are associated with the carbonatites.

The distribution of some minor and trace elements in the different minerals was studied at the CBMM laboratory in São Paulo, using SEM-EDS and backscattering equipment. Cathodoluminescence and XRD were also used.

Bonga massif is a large plug mainly constituted of apatite-calcite carbonatite, with fluidal textures. Accessory minerals are strontianite, parisite/synchysite and pyrochlore (the whole-rock average Nb content of 1,992ppm). Other associated rocks are: apatite-dolomite-carbonatite in which ankerite presents microscopic strontianite inclusions; ferrocarbonatite shows ankerite transformation into calcite/dolomite and Fe oxides; polimictic carbonatite pipe breccia has a more differentiated matrix with late interstitial quartz associated with barite and REE Ca-carbonate of the parisite-synshysite group a mineralogical feature common in ferrocarbonatites and apatite-dolomite carbonatites too; rocks possibily formed by interaction of country rocks carbonatite, such as, potassic fenites and nepheline syenites; silexites present relict textures and minerals of replaced carbonatites.

Bailundo massif shows a ring structure with carbonatites in its central elevated portion, surrounded by colluvial and leached alluvial material and barite-goethite gangue. An outer marginal ring presents mainly fenites and silexites. Apatite-calcite carbonatites predominant in the analyzed rocks, present interstitial quartz and fibrous REE Ca-carbonate, aggregated or not. Dolomite carbonatites (magnesiocarbonatites) and apatite-calcite-dolomite carbonatites rich in iron oxides (ferrocarbonatites) are subordinated. Nb-rich silexites (with Ba pyrochlore) were derived from carbonatites; they also show REE phosphates.

The Virulundo massif is similar to the Bonga occurrence. Apatite and pyrochlore are common accessory minerals, especially in calcite carbonatites. These rocks, as well as dolomite carbonatites when chemically classified in ferrocarbonatites, show transformation of primary ankerite. Late minerals of the parisite/synchysite series, and barite and strontianite, interstitial or in veins, are also found in these rocks. Hybrid rocks were also investigated, presenting feldspathic fenite fragments in carbonatite matrix.

Lupongola occurrence is a ring dike of elliptical shape, with calcite carbonatite and hybrid silicate-carbonatite rocks. These calcite carbonatites show the highest CaO/MgO and La/Y ratios of all analyzed sovites, as well as the most Sr, and they are also impoverished in Nb and P_2O_5. The rocks are mainly protoclastic, with enclaves of feldspathic fenites and anorthosites on the outside of the ring feature, smaller dikes cut anorthosites. Carbonate-feldspar interaction may form epidote/allanite reaction rims. A dike-like fluorite-calcite carbonatite is also observed at Lupongola.

At Monte Verde, feldspathic carbonatite and undersaturated alkaline rocks are found in association with calcite carbonatites. The main accessory minerals in the carbonatites are parisite/synchysite, strontianite and barite, with some pyrochlore and apatite. Only sovites are found in Monte Verde and Lupongola. La/Y ratios in the Lupongola and Monte Verde carbonatites are the highest found in all the sovites analyzed.

A few carbonatites, feldspathic-carbonatite breccias and feldspathic rocks were studied from the Longonjo occurrence. Dolomite-carbonatites are rich in iron and erratically distributed; they also show late quartz, REE Ca-carbonate, barite and REE-phosphates. Commonly weathered samples present barite and hollandite; MnO contents vary from 0.48 to 2.7%.

The small alkaline-carbonatitic complex of Coola, presents Ba and F in abnormally high concentration. Besides carbonatites, undersaturated and feldspathic rocks occur.

Among the studied samples, sovites (59%) predominate over ferrocarbonatites (24%), and these over magnesiocarbonatites (17%). These three carbonatites are found in Bonga, Virulundo and Bailundo and the passage from sovites into ferrocarbonatite is marked by an increase in the La/Y ratio.

In general, carbonatites are characterized by a high Fe_2O_3/FeO ratio, and low TiO_2 contents. Mafic minerals are subordinated. The main apatite in sovite is fluorapatite, as suggested by a P_2O_5/F ratio of about 10. U, Th and Ta, which, when in anomalous values, is positively correlated with Nb contents and concentrated in pyrochlore - type minerals. The main Ba-minerals or minerals with Ba are found in carbonatites (barites), fenites (Ba-rich K-feldspar) and silexites (Ba-pyrochlore). REE are presented mainly in REE Ca-carbonate of carbonatites and REE-phosphates of silexites.

Whole-rock chemical analysis show that Bonga and Bailundi present the highest P_2O_5 contents, whereas BaO is highest in the Coola and Longonjo rocks. Sr concentration occurs predominantly in the Lupongola carbonatites.

Chondrite-normalized REE diagrams are presented (ICP analysis), for the various carbonatite phases.

Brecciated potash fenites are found in Bailundo. The Virilundo fenites, predominantly constituted of K-feldspar, subordinated albite and sodic mafic minerals, are sodic-potassic rocks. Fe_2O_3/FeO ratios are high in both occurrences. The observed feldspars are cloudy, showing a red luminescence as a result of Fe^{3+} activation.

HIGH-TECHNOLOGY METALS IN ALKALINE AND CARBONATITIC ROCKS IN GREENLAND: RECOGNITION AND EXPLORATION.

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High-technology metals such as Zr, Y, Nb, Ta, REE and Ga are generally associated with alkaline and carbonatitic rocks, where ore grade concentrations of the metals may be found in rock units produced by extreme magmatic differentiation, or in zones of intense late to post magmatic hydrothermal alteration. For this reason, the recognition of alkaline magmatic provinces or carbonatitic complexes is an obvious first step in the exploration for high-technology metals.

Low density exploration data, including airborne gamma-spectrometry and stream sediment surveys, have been obtained by the Geological Survey of Greenland over large parts of south and west Greenland. These data have clearly outlined a major Proterozoic alkaline igneous province and, within the Archaen basement outside this province, two Cenozoic carbonatite complexes. The best single indicator on a reconnaissance scale appears to be Nb in stream sediment, which gave distinct anomaly patterns over all of the alkaline and carbonatitic intrusive complexes. The anomaly patterns for other elements Y, Zr, Ga, Mn, Sr, Zn, U, and Th are also indicative of the alkaline/carbonatite intrusions, but they are less regular and consistent. This illustrates the geochemical differences between the individual intrusive complexes and helps to identify prospective areas for individual metals.

Four prospects within the alkaline and carbonatitic rock complexes have been further explored with respect to Zr, Y, Nb, Ta and REE. The prospects contrast geologically and geochemically, hence, different exploration approaches were made to locate the ore zones.

In the alkaline Gardar igneous province, in southern Greenland, two prospects in the Ilimaussaq intrusion concern rock units rich in eudialyte (Zr, Y, REE). In one case the eudialyte-bearing rock is medium to coarse grained, and geological mapping and visual recognition of concentrations of the conspicuous red mineral was enough to locate the ore zones. In the other case, the eudialyte-rich rock is fine-grained, and geological mapping, combined with analyses of chip sample, were used.

The third prospect in the Motsfeldt intrusion, in the Gardar province, concerns zones of intense hydrothermal alteration. The zones, rich in Nb, Ta, Zr, REE, U and Th, were located by helicopterborne gamma-spectrometry and, subsequently, grid-sampled to assess Nb and Ta contents.

The fourth prospect is situated in the Sarfartoq carbonatite complex, where alteration zones with solid pyrochlore (Nb) were located by airborne and ground radiometry, combined with detailed stream sediment sampling.

Based on the experience from Greenland, it is concluded that alkaline and carbonatitic complexes are easily recognised in low density geochemical data, and most efficiently by anomaly patterns for Nb, U and Th. Further elements help to differentiate the intrusive complexes and distinguish rock units or alteration zones with potential for high-technology metals. Ore zones may then be located using radiometric methods, combined with geological mapping and datailed geochemical surveying.

RARE EARTH ELEMENTS (REE) ACCUMULATIONS IN THE CURITIBA BASIN (BRAZIL)

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The Guabirotuba Formation in the Curitiba basin (South Brazil) is mainly composed of grey clays and minor arkosic sands of Pleistocene age. In this formation, lanthanite crystals have beem accumulated within an interval of about 30cm. Lanthanite is a REE hydrated carbonate: $(REE)_2\ (CO_3)_3.8H_2O$. The mineral from Curitiba has the following REE composition: $La_2O_3 = 20.55\%$; $Ce_2O_3 = 0.06\%$; $Pr_2O_3 = 5.39\%$; $Nd_2O_3 = 24.44\%$; $Sm_2O_3 = 4.10\%$; $Eu_2O_3 = 0.83\%$; $Gd_2O_3 = 1.71\%$; $Tb_2O_3 = 0.16\%$; $Dy_2O_3 = 0.40\%$;

$Er_2O_3 = 0.05\%$. This lanthanite accumulation is located near the topographic surface, inside the weathering profile developed on sediments, which shows from the bottom to the top:

- fresh sediments composed of prevailling smectite, illite, irregular illite-smectite, minor kaolinite, quartz, and K and Na feldspars:
- calcrete and/or dolocrete (3-5m) formed of soft and hard nodules, veinlets and discontinuous hardpans in a clayey sedimentary matrix;
- lanthanite horizon (0,3m) in which REE carbonate crystals appear as millimetric to centimetric concretions and rosettes, or as a millimetric pellicule of platy crystals lying on the upper face of the calcrete or dolocrete; lanthanite is authigenic, developed by epigenesis of the host sediment;
- brownish-grey horizon (6m) composed of smectite, illite, irregular illite-smectite, kaolinite, quartz, K and Na feldspars;
- reddish-grey horizon (2m) composed of kaolinite, illite, minor smectite, quartz, K feldspar and hematite;
- red horizon (0.5m) composed of kaolinite, illite, quartz, hematite and gibbsite.

So, the weathering profile is characterized by i) basal carbonate accumulation horizons and ii) surficial leached horizons.

The REE distribution has been investigated along the weathering profile in order to determine the mechanism responsible for their accumulation. Compared to fresh sediments, the REE contents of each horizon show that:

- the red horizon is depleted in all REE's, excluding cerium;
- the reddish-grey horizon is also depleted in all REE's, excluding lanthanum and cerium;
- the brownish-grey horizon, above the lanthanite horizon, is enriched in all REE (2 to 3 times);
- tha lanthanite horizon is strongly enriched in all REE's apart from cerium, and the enrichment is more important in light REE (50 to 60 times) than in heavy REE (5 to 10 times);
- the top of the calcrete or dolocrete is enriched in all REE's, except for cerium, and the enrichment is more important in heavy REE (3 to 5 times) than in light REE (1.5 to 2 times);
- lower down in the calcrete or dolocrete, the more clayey matrix is weakly enriched in all REE's, excluding cerium, whereas the carbonate are depleted.

Considering that the surficial horizons are depleted in REE's and the basal horizons are enriched in REE's, relative to the sediments, this REE distribution is assumed to be the result of the sediment leaching (Fortin, 1989). During kaolinization, REE's, except cerium, have been released from weathered minerals and have been partly accumulated lower down in the profile. Different REE accumulation horizons are distinguished: cerium in leached horizons, light REE in the lanthanite horizon and heavy REE at the top of the calcrete or dolocrete. So, the behaviour of REE can be followed from their release to their accumulation through the study of REE-bearing minerals. In the fresh sediment, all granulometric fractions have comparable REE contents and two main REE bearing phases have been recognized:

- the manganese oxihydroxides by barium psilomelanes, mainly containing cerium;

- the clay minerals in which 9% of ΣREE can be released in a barium chloride solution according to an ion exchange process.

Cerium accumulation in leached horizons can be related to the behaviour of manganese during kaolinization. In the uppermost horizons, psilomelanes are slightly leached and manganese reprecipitates nearby or lower in the profile as lithiophorite. On the other hand, cerium is less easily leached and forms residual phases in which the Ce_2O_3 content can reach 60%. Hence, cerium has a residual behaviour which is explained in terms of its oxidation ($Ce^{3+} \rightarrow Ce^{4+}$). Indeed, under the acidic and oxidizing conditions which prevail during leaching, the stable cerium compounds are insoluble tetravalent oxides or oxihydroxides.

Accumulation of the other REE's can be explained by the mineralogy of horizons through which solutions percolate. The small enrichment observed in the brownish-grey horizon, above the lanthanite horizon, concerns the clay fraction. This fraction, still smectitic, acts as a first trap of REE's during their transport in solution towards the base of the profile. The contact between the percolating solutions and the carbonates of the calcrete or dolocrete has induced a pH increase, and resulted in the main precipitation of REE (and especially light REE) as lanthanite. The enrichment in heavy REE which is lastly observed at the top of the calcrete or dolocrete concerns the clay fraction, which has acted as a final trap. Fractionation between light and heavy REE is interpreted as a consequence of the greater stability of heavy REE ions relative to light REE ions in basic solution.

The different REE accumulation horizons, observed along this weathering profile, give evidence of the relative mobility of REE's during laterization conditions. Cerium is almost immobile and has a residual character. The other REE's are mobile but light REE's are less mobile than heavy REE's.

Calculation of mass balance indicates that at least 35 meters of sediments must have been weathered in order to achieve the total amount of REE's accumulated in the profile. This value has been obtained with lanthanum and, considering that the total amount of this REE has been entirely accumulated in the profile, it appears that a small part of the total amount of the other light REE's and half of the total amount of the heavy REE's have been evacuated out of the profile. These results are in agreement with the relative mobility of REE's.

Although this REE accumulation does not form a deposit, it shows that REE's can be mobile under supergene conditions and accumulate to a great extent under conditions other than those prevailing in placer depoits. Moreover, the Guabirotuba Formation shows higher REE contents than the average comparable sedimentary rocks. According to isotopic data obtained on the surrounding basement rocks, the sediments and the pure lanthanite, the primary sources of the REE's are assumed to be alkaline intrusions which are regionally known. Thus, this REE accumulation occurs in a peculiar environment which requires unusual conditions. Nevertheless, other lanthanite accumulations are known to exist in the Taubaté and Resende basins (Brazil) (Coimbra et alii, in press), which seem to have similar origins, sedimentary characteristics and evolution to the Curitiba basin.

THE MAIN GEOCHEMICAL FEATURES OF CARBONATITES

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Carbonatites are the main source of a number of useful minerals that make these endogenic rare-metal rocks very significant, so it is reasonable to develop criteria to distinguish them amongst all endogenic carbonate rocks. The mineralogical characteristics may be used to classify carbonatites, so geochemical invetigations should be considered as very important in this respect. It was found that along with the close relation to alkaline petrogenesis and mantle nature (i.e. isotopic features) the rocks of the carbonate set have geochemical features, in particular, constant simultaneous enrichment with TR, Sr, Ba and V, which makes them stand out from other dominantly carbonate rocks, i.e. endogenic, metamorphic and sedimentary.

On the background of common geochemical features characteristic of carbonatites there are significant variations in their composition due to carbonatite heterogeneity, formation of these rocks in different geological and physico-chemical conditions. Thus, it is possible to recognize formational and facial types of carbonatites and to perform geochemical classification considering their diverse ore productivity. From the apllied aspect, of particular interest is classification of different formation types* (formation is intepreted as rock paragenesis in a suitable geologo-tectonic setting). Carbonatites are formed in oceanic and continental environments, with the abundant continental carbonatites having considerably higher ore productivity. They are formed under different geologo-tectonic conditions in paragenesis with various associations of alkaline rocks and belong to the following formations:

1 – Sodic alkaline ultrabaisc rocks in rift zones on protoplatforms, i.e. Precambriam continental crust (provinces of Brazil, East /Africa, Canada, Scandinavia, USSR, USA). Niobium, tantalum-niobium, phosphate ore deposits.

2 – Potassic alkaline ultrabasic rocks in rift zones on the protoplatform (East Africa). Deposits are unknown.

3 – Potassic, highly alkaline syenites in rift zones on the Precambrian and Phanerozoic continental crust (Afghanistan, West Africa, India, Mongolia, the USSR). TR, Sr and Ba deposits.

4 – Potassic subalkaline syenites in rift zones on the Phanerozoic continental crust (Mongolia, the USA). TR, Sr and Ba deposits.

5 – Calc-alkaline syenite (potassium type) in rift zones on the Phanerozoic continental crust (Mongolia). Deposits are not known.

6 – Near-fault alkaline metasomatites in zones of deep faults on the Precambrian Continental crust (the USSR, China). Tr and Nb deposits.

Tabela 1 – Average contents of some elements (ppm) in the carbonatites.

Elements	1	2	3	4	5	6	7
Sr	6300	5000	7500	8000	5200	6900	5100
Ba	2800	3680	6900	16300	2000	760	4600
TR	2560	1657	6990	8140	1410	1490	1480
V	110	170	82	73	120	84	219
Nb	290	348	58	8	2.5	690	118
Ta	13	18	0.2	0.1	0.1	11	6
Pb	52	29	320	390	66	76	92
Zn	270	120	190	130	58	100	148
P	12600	110000	2900	1700	2600	5700	6900
Sr/Ba	2.3	1.4	1.1	0.5	2.6	9.1	1.1
Zn/Pb	5.2	4.1	0.6	0.3	0.9	1.3	1.6
Ce/Y	11.6	10.6	34.5	47.5	18.0	9.2	15.7
La/Yb	117	77	428	632	165	82	64
Ba/Nb	9.7	10.6	119	2040	800	1.1	39
Pb/Nb	0.18	0.08	5.5	49	26	0.11	0.08
TR/Nb	9	5	121	1017	564	2.2	21
$P\left(\frac{Nb}{Ba + TR}\right)$	682	717	12	1.3	1.9	1753	115
n	927	36	74	125	34	62	28

1-6 – continental carbonatites (a number in acordarce whit the text),
7 – oceanic carbonatites.

Formation of 1-5-type carbonatites is related to fractionation of mantle alkaline magmas of type 6 with interaction of mantle cabonate-alkaline fluids with the crustal substratum. Cosiderable differences are recognized in carbonatite compositions of the above formation types (table 1). This allows their chemical classification from levels of total concentration of P, Nb, Sr, Ba, Pb, Zn, TR and relative Sr/Ba, Zr/Pb, $\Sigma Ce/\Sigma Y$, La/Yb. These differences are due to geochemical relations to initial, alkaline magma composition, in particular, expressed in enrichment of carbonatites with P, Nb, Ta, Zn, and depletion in Ba, Pb and TR with increasing Na content in these magmas. In this connection, the important characteristics of magmagene carbonatites are Ba/Nb, TR/Nb values, as well as (Nb/Ba + TR). The differences in carbonatite chemistry are found in comparing their formation types formed under the same facial conditions with respect to temperature and depth as a whole and at the level of individual carbonatite complexes.

Considering various ore productivity of carbonatites in different formation types, their geochemical classification is important both for geochemical prospecting and for developing geochemical methods of ore-bearing carbonatite prospecting.

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THE USE OF RARE EARTH ELEMENT GEOCHEMISTRY TO DISCRIMINATE THE LATERITE DERIVATION IN THE GURUPI REGION (EASTERN AMAZONIA)

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The Gurupi Region, located in eastern Amazonia, represents a classical region covered by mature, complete and fossil laterites. They are outstanding for their chemical and mineralogical variation in the upper parts of the profiles, extending from the bauxitic to the phosphatic composition, involving all of the possible intermediate phases (table 1). their mineralogical richness is notable, involving, besides the classic iron and aluminium oxi-hydroxides and the clay minerals, many kinds of aluminium phosphates, specially those of the isomorphic series of the crandallite group. The presence of the minerals from this group in diferent rates incite instigating anomalous geochemical behaviour of some trace elements that are not common in laterites, such as the rare earth elements (REE), Sr, Pb, Ba, Y, Rb, etc.

Among these, heavy and light rare earth elements (HREE and LREE) deserve a great distinction, being enriched in the crandallite-bearing phosphate laterites, while in the bauxitic they are leached, with contents under the crustal levels. Therefore, in the phosphate lateritic profiles, the absolute contents of these elements increase towards the top of the profile (figure 1), while in the bauxitic, they decrease. It is clear that crandallite is the main carrier of these elements, along with the Sr, Ba and Rb under the way of the crandallite-goyazite-florencite solid-solution, where the members, crandallite and goyazite, are the most common, according to the Ca and Sr contents, always in percent units.

The absolute concentrations are classically controlled by their pre-existing contents in the parent rock and by the kind of mineral structure that absorbs them.

In the Gurupi Region, lateritic occurrences and deposits are found with great contrasts among them, in terms of their rare earth element concentrations (table 1). Itacupim, with its phosphatic laterites derived from ultramafic-alcaline rocks, presents about 1,033 ppm (La + Ce + Nd), while those derived from sediments and metasediments reach up to 288 ppm (La + Ce + Nd) individually. Therefore, the two occurrences of phosphatic laterites derived from sediments contrats, indicating different compositions for their parent rocks.

The absolute concentrations of the rare-earth elements are excelent to classify the laterites according to their parent rock because their absolute contents between different deposits are not directly correlated with the O_2O_5 contents.

The presence of anomalous concentrations of REE in laterites is a strong indicator of the phosphates as much in laterites as in the parent rock and, less common, as an indicator of resistates.

This work depended upon the long term financial support from Brasilian CNPq and FINEP.

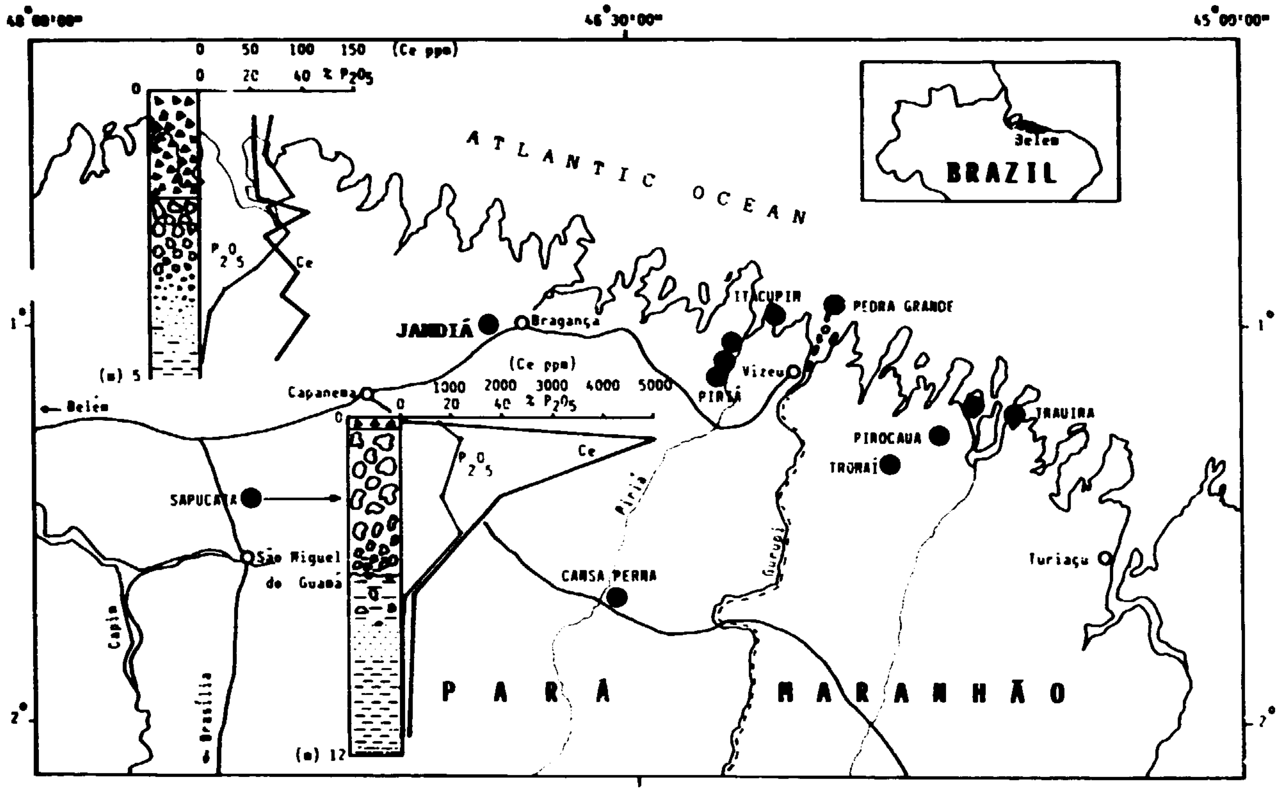

Fig. 1 – Phosphate occurrences on the Gurupi Region and the distribuition of P_2O_5 and Ce in the lateritic profile of Jandiá and Sapucaia.

Tabela 1 – P_2O_5, and Y average concentrations of the laterites from the Gurupi region.

Ocorrences	P_2O_5 Wt. %	La	Ce pp	Nd m	Y	Parent rocks
Phosphatic Laterites:						
Itacupim	11,2	377	495	161	197	Alkaline ultramafic rocks
Trauira	20,7	<56	<78	<42	37	Basic rocks
Sapucaia	13,0	282	782	451	268	Sediments
Jandiá	18,7	42	93	50	21	Sediments
Cansa Perna	16,4	60	109	84	119	Metasediments
Phosphatic/bauxitic Laterites:						
Pirocaua	15,6	33	109	84	79	Metasediments
Peito de Moça	7,5	37	98	63	35	Metasediments
Bauxitic Laterites:						
Piriá	0,5	<37	<50	<34	38	Metasediments
Jacaré	0,5	20	<50	47	16	Basic rocks

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Technical Session
Analytical Techniques:
New Developments in Exploration Geochemistry

A COMBINATION OF CHEMICAL, PHYSICO-CHEMICAL AND DXRD METHODS FOR THE RECOGNITION OF METAL-BEARING PHASES ASSOCIATED WITH IRON OXIDES/HYDROXIDES IN LATERITES

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The main goal of the experimental procedure presented here is to break up, very selectively, the iron oxides and hydroxides of natural samples in order to localize and determine the quantities of included trace-elements.

It combines the results of (1) chemical extrations by citrate-bicarbonate (CB) and dithionite-citrate-bicarbonate reagents associated with a kinetic control of the reactions, (2) X-ray diffraction (DXR) and differential X-ray diffraction (DXRD) which enable the determination of the substituted ratios in hematites and goethites, and (3) physico-chemical analysis which enable characterization of the textures as well as the solid-reagent contacts.

The deferrification obtained with this new procedure is as efficient as the classical hot DCB and is more specific, especially in the presence of aluminous oxides/hydroxides. Furthermore, because of the longer reaction time, the kinetic study can be achieved more easily.

Samples were obtained from a lateritic core, which had been extracted for evaluating the potential of a Burundian nickeliferous deposit. They belong to the following units: yellow laterite, red saprolite, dismantled duricrust and red soil.

In this way, differential behaviour of some iron oxides/hydroxides has been shown by measuring together the evolution of the residue and the associated amounts of other elements such as aluminum, chromium, manganese... all throughout the reduction. The existence of chromium substitution ratios in goethites, which perverts significantly the DXR interpretation, the preferencial association of titane phases with hematites, and the non-correlative relationships between extracted iron with copper and manganese have been pointed out. The absence of correlation in the case of copper can be explained by inclusions of this element in a residual mineral having a spinel structure. In the case of manganese, which can be partially reduced by dithionite, no clear conclusion can be yelded. This shows one limit of the methodology presented in this communication.

Based on these few examples, it may be concluded that despite the complex nature os lateritic environments it is possible to carry out metal-bearing phase identification in the case of ferruginous minerals.

DETERMINATION OF RARE EARTH ELEMENTS IN GEOLOGICAL SAMPLES BY ISOTOPE DILUTION MASS SPECTROMETRY

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Among the many raw materials that are being used in modern industry, rare earth elements are playing an increasingly important role. Since their early commercial exploration, great changes have taken place in the type of deposits explored, as well as their industrial application. New advances in the development of analytical techniques, established by geochemists, are helping in the characterization and quality control in the fields of rare earth element application, permitting the precise and accurate determination of these elements, even at very low concentrations.

Considering the importance of precision (and accuracy) in the analytical data, the objective of the present study was to establish the mass spectrometric isotope dilution technique for the analysis of the rare earth elements, as this technique possesses high sensitivity, precision (and accuracy). Within this general objective, chemical separation methods involving ion exchange chromatography were established for the group and individual separation of the rare earth elements.

The method was established for the international rock standards AGV-1, GSP-1, G-2 and PCC-1 and the results obtained compared with the literature values. The analytical procedure established involved the preparation and calibration of the tracers by isotope dilution mass spectrometry, sample digestion, chemical separation and isotope analyses using a fully automated thermoionic mass spectrometer micromass VG isotope model 354. The sample dissolution was carried out in a teflon vessel under pressure. The material (samples + tracer) was digested using a mixture of concentrated HNO_3 and 40% HF in the pressure vessel at 160°C for a period of 18 hours. The sample solution was evaporated and, later, a mixture of concentrated $HClO_4$ and HNO_3 was added and evaporated again. Finally, the residue was dissolved in 2N HCl and taken for chemical separation. The elaborate dissolution procedure was necessary as the rare earth elements are generally present in the accessory, resistant minerals.

The chemical separation was carried out in two steps in cationic resin columns. In the first column, the total rare earth elements were separated from other elements using 2N HCl and 8N HNO_3 as eluiting agents. In the second column, using 0,25N α-HIBA (pH = 4.6) as an eluiting agent, rare earth elements were separated into individual fractions (La, Ce and Nd) and sub groups (Sm-Eu-Gd and Yb-Er-Dy). Nine elements (La, Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb), with concentrations in the range 0.5ppm to 400ppm, were determined with a total precision of 1 to 2% and an accuracy of 5%. The rare earth element concentrations, determined in the rock standard PCC-1, demonstrated the low blank levels in our analysis.

The results obtained in the present study have shown that the analytical procedures developed and employed are satisfactory, as indicated by the high precision and accuracy obtained for the elemental concentrations values. Further, the great advantage of the technique, as shown by the present study, is the non-dependence of the precision and accuracy on the concentration levels of the elements in the samples. The study has also shown that α-HIBA is an efficient eluiting agent for the separation of individual rare earth elements.

DETERMINATION OF URANIUM AT THE PPT LEVEL BY TIME-RESOLVED LASER-INDUCED SPECTROFLUOROMETRY: APPLICATIONS IN THE ENVIRONMENT AND IN GEOLOGICAL SURVEY

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Analytical control of uranium at a very low level required in several fields, such as, nuclear geology medicine and prospection. Due to its high sensitivity and selectivity, time-Resolved Laser-Induced Spectrofluorometry (TRLIS) is the method chosen for such applications. The principle of TRLIS is based on the fact that uranium is known to exhibit visible fluorescence in solution when excited by a UV pulsed source. In phosphoric medium, the uranium fluorescence is characterized by a long lifetime (> 100 us). Measurement of the fluorescence a few microseconds after the laser pulse permits the elimination of the short lifetime fluorescence (< 1 us) of organic matter, This temporal resolution leads to very selective and sensitive measurements.

Besides a nitrogen laser used as the excitation source, the new apparatus "FLUO 2001", specially designed for such applications, consists of a cell-holder for receiving the solution to be analysed, a monochromator, a multichannel detection (intensified photodiodes array), a control unit that assures both the pulsed funcioning of the intensifier and the photodiodes array and, finally, an IBM-AT computer that plots the whole system with specially adapted hardware. Analytical software is used for both concentration determinations and lifetime measurements. For the moment, the most interesting results have been obtained for uranium, with a limit of detection of 1 ppt 5×10^{-12}M) in a phosphoric medium. Some lanthanides and actinides have also been determined by TRLIS with good sensitivity (ppb level and lower). Furthermore, remote sensing measurements can be carried out with fiber optics and optrodes. This adaptation has the advantage of allowing measurements in

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*Author to whom correspondence should be sent difficult access environments at several tens of meters, at several locations, with only one central monitor.

TRLIS was used for uranium determination in alkaline water with high chloride and sulfide contents in order to have a better understanding of uranium mobilization in natural reducing conditions. Results obtained on several waters from different areas in France (Corsica, Pyrenees), at different chloride concentrations, are presented. These data seem to confirm that, even at very low uranium concentrations (<50 ppt), thermodynamical control by a mineral phase, takes place. Results obtained on the analysis of uranium in soils at several locations show that TRLIS is a fast and reliable method for such determinations.

NOVEL PROCEDURES FOR DECOMPOSING SELECTED REFRACTORY ORES FROM GHANA

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Conventional methods for sample decomposition could not be successfully applied to completely decomposed chromite and certain sulfur-bearing ores. However, in a series of experiments, details of which are the subject matter of this paper, acid-salt mixtures of different acid/salt ratios were tried and their efficiency of decomposition (EOD) values have been tabulated. Analysis of principal constituent elements following solubilization was made by atomic absorption spectrophotometry and standard colorimetric procedures. 100 samples of chromite, gypsum, analcite from field prospecting teams were treated and evaluated.

PROGRESS IN DESIGN AND APPLICATION OF EDXRF-FIELDLABORATORIES

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Minimum delay between sampling and receiving results is often essential in geochemical exploration (e.g. in anomaly follow-up or overburden drilling programes). In this case, field laboratories are able to save time and costs. Field laboratories also avoid the need to disrupt normal laboratory operations in central laboratories with requests for HIGH PRIORITY - RUSH analyses (Fletcher, 1981).

Radionuclede-excited, as well as low-power, air-cooled tube excited EDXRF systems have been used by our research group in mobile laboratories for several years in multi-element prospecting (Kramar & Puchelt, 1981; Kramar, 1982; Kramar & Puchet, 1983; Kramar, 1984).

The fast development in electronics and computer technology now enables a more compact desing of the EDXRF field-laboratories including sophisticated interpretation aids as an integrated part of the analytical system.

Until now, the interpretaion aids include basic statistics (frequency-distributions, cumulative frequencies, 5 number sumary, and scatter - plots) as well as colour and black and white mapping facilities. For the mapping facilities, moving averages (point Kriging) using different filter functions is available. Multivariate-techniques (cluster and factorial analysis) are in preparation).

A radionuclide-excited systems has been installed at the Mineralogical Department of the Universidad Autonoma de Nuevo Leon (U.A.N.L.) in Linares/ Mexico. A tube-excited system is used by the Institute of Petrography & Geochemistry of the University Karlsruhe in Germany.

Two case histories of stream and soil surveys demonstrate the possibilities of these integrated systems.

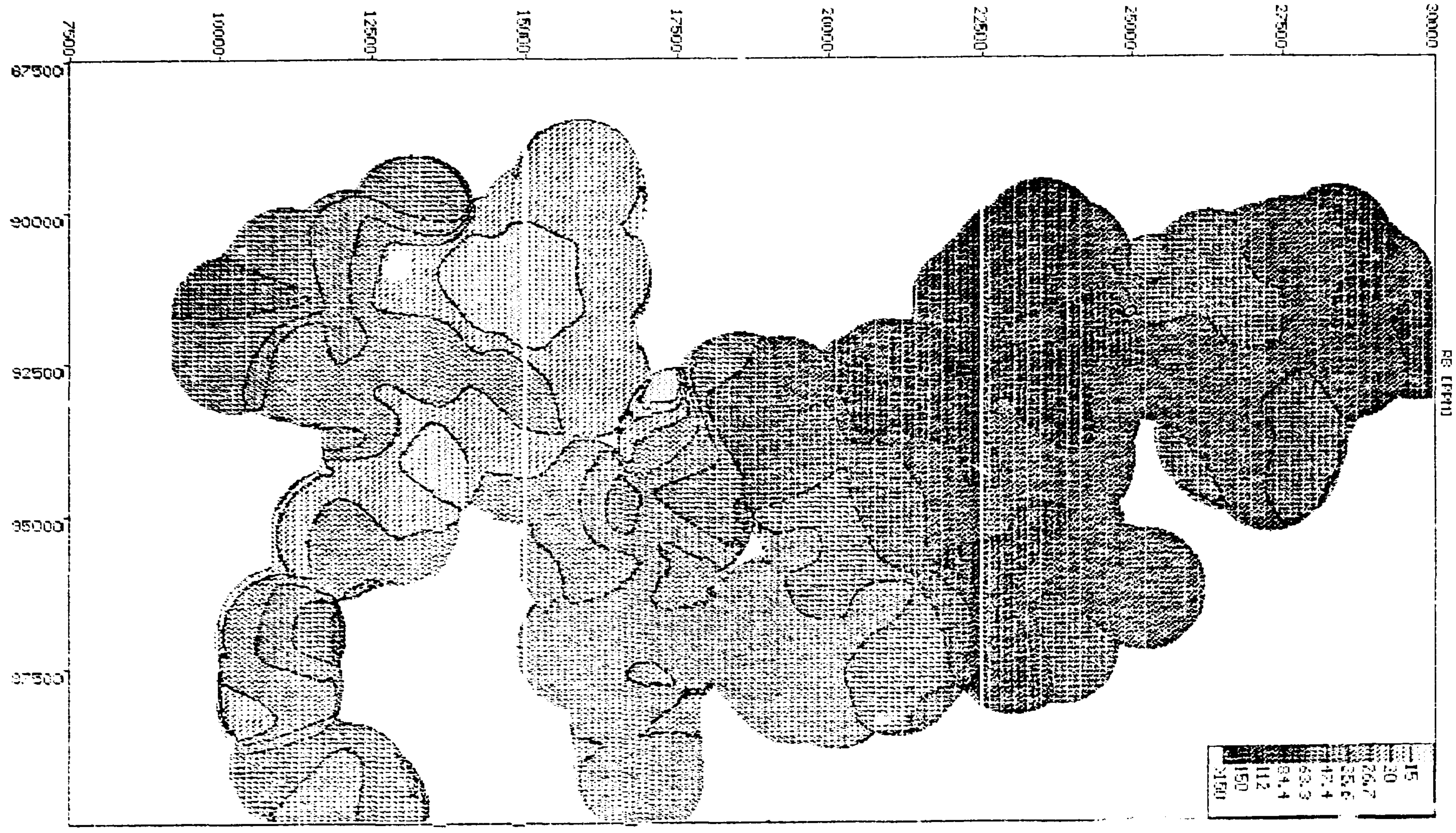
In co-operation with Sachtleben Bergbau A.G. and Cominco a geochemical soil survey has been carried out in the vicinity of the Meggen pyrite - sphalerite - barite deposit.

The survey area is located in the Sauerland - mountains about 100km east of Cologne/West Germany. From an area of 10 km^2, about 700 soil samples have been taken from the A/B Horizon along 9 traverses with a sampling distance of 25 m.

The underlying rocks in this area are middle and lower Devonian schists.

The middle Devonian schists consist of pelites with calcitic and bituminous components. The lower Devonian schists are represented by pelites with more silty and sandy intercalations.

From the -80 mesh ($-177\mu s$) fraction of the soil samples 10 elements (Ti, Fe, Cu, Zn, As, Rb, Sr, Y, Zr, Mo, Ba and Pb) have been determined simultaneously in



Map. 1 – 1: Rb - concentrations of stream sediments in Sierra San Carlos. - Rock types can be outlined from different concentration ranges. Rock types from north to south: diorites syenites, gabbros end sedimentary rocks.

the EDXRF field laboratory.

Only six days from the beginning of the campaign, the first geochemical maps were available. These maps could be used in the interpretation and further planing of the campaign. The element distributions reflected clearly the chemistry of the underlying rocks and indicated smaller hydrothermal Pb-, Zn, -Ba mineralizations.

The second case history is located in the San Carlos Mountains/Tamaulipas/northeast Mexico.

The San Carlos mountains are part of the alkaline belt in eastern Mexico. The origin of the mountain is intrusions of alkaline magmas into the calcitic detritical series of the lower Cretaceous. Due to the intrusions, metasomatic alteration of the Cretaceous rocks occurred and marbles, garnet scarns and metasomatic copper deposits were formed. These metasomatic copper mineralizations, located in the part of the research area were mined at the beginning of this century. The intrusive rocks in the "sierra" are diorites with small intercalations of gabbros in the northern part, alkaline and nepheline syenites in the middle and a series of gabbro intrusions in the southern part.

More then 700 stream sediment samples have been taken and analysed by the both EDXRF - systems. A part of the samples has been analysed directly in the field for anomaly follow-up works using the radionuclide-excited system of the U.A.N.L.

The intrusive rocks can be easily outlined from the concentration maps of the trace elements. An example is given in map 1. The ancient mining district is characterised by extremely high Cu-anomalies. An additional Cu-anomaly is located in the southern gabbro area. The central syenites are characterised by the high Nb an Th concentrations. In this area, indications for hydrothermal activity were also observed.

The new concept to integrate statistical methods and mapping facilities into the analytical system is able to speed up the data interpretation in field laboratories and enables the use of the full advantages of multi-element analyses in geochemical exploration, even in remote areas.

The invetigations in Sierra San Carlos and the EDXRF - system of the U.A.N.L. have been granted by the Stiftung Volkswagenwerk.

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SEQUENTIAL ANALYSES FOR GOLD IN SOILS, SERRA DOS CARAJÁS, PARÁ

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The area of Salobo 3A, serra dos Carajás. Pará, belongs to the WNW elongated zone of a metamorphosed sequence of the amphibolite grade, composed of gneisses, quartzite, banded iron formation, metabasites, garnet, grunerite-magnetite schist. This archaean sequence is mineralised with copper sulphides.

The gold occurs principally as metallic inclusions in sulphides at depth, while, in surface soils, it is associated with goethite, limonite and organic matter.

In this paper, we studied the gold concentrations from the known subareas of anomalous values.

The -120 mesh fraction was submitted to sequential analyses, complemented by organic extraction with MIBK and the gold concentration determined by AAS. The samples analysed were collected from the depths 0-10cm and at 50cm from the surface, and also from the pits of 9m and 21m depths. These soil samples belong to the areas of banded iron formation and garnet-mica schists.

By means of an initial decomposition with distilled water, Au was detected only at the 50cm depth, in concentrations of 2 and 11ppb. This indicates the presence of salts, whose precipitation could be related with percolation and evaporation of rain water.

The decomposition of the samples with ammonium acetate and acetic acid produced maximal results of 12ppm, not correlated with the total-Au content.

The digestion with hydroxylamine hydrochloride that liberates metals associated with oxides-hydroxides of iron (amorphous) and manganese carbonates and sulphides, produced results between 30 and 50ppb, but also were not correlated with the similar ones of other fractions or the total-Au.

The decomposition with H_2O_2 that frees Au-complexed or adsorbed on organic matter, produced values compatible with total-Au. The greatest concentrations of Au occur in samples rich in organic matter, consequently, in surface samples, or in those localities where total-Au shows higher concentrations.

The hydrazine chloride digestion produced lower results than expected. This may be a consequence of analytical problems or of the low concentration of crystallized oxides and hydroxides of iron in the soils.

The decomposition with $HF + HClO_4$ shows that most of the Au in soils is fixed in the silicates (clay minerals and quartz) in a non-metallic form. Similar results were obtained by the applications of $HF + HClO_4$ + aqua regia.

The sum of the results of the sequential analyses is comparable with those acquired through the digestion $HF + HClO_4$ + aqua regia or by neutron activation.

Therefore, for gold prospection in soils of Salobo 3A, both the aqua regia digestion alone as well as the H_2O_2 are suitable to indicate concentrations of the metal.

The application of the complete sequential analysis method is very time consuming, hence, it should be used only for orientation studies, resulting in selecting the appropriate analysing steps to obtain optimum results.

USE OF ELECTROCHEMICAL METHODS IN ANALYSIS OF GEOCHEMICAL OBJECTS (GOLD, SILVER AND OSMIUM)

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The Clark geochemistry of gold and silver in sedimentary rocks is still not studied enough, and osmium geochemistry is the "white spot" of the present day.

The possibility of application of an inverse current-voltage curve method for the analysis of gold and silver contents in sedimentary rocks of the Tadjik depression, and also the kinetic determination of osmium with current-voltage registration of reaction rate, were under study.

We used the polographe LP-7 for gold and silver determination. The coal-paste electrode served as indicator one, and for osmium determination, the platinum rotating microelectrode was used. The 1 M solution of HCl for gold and 5% solution and H_2PO_4 for silver served as indifferent electrolites.

The conditions of preliminary concentration of microgram quantities of gold and silver, the character of the electrode process, the dependencies of electrolytic oxidation current on a changing rate of electrode potential, time and electro-accumulation potential, concentration of background solution and the depolarizator, have been studied.

The effect of interdependence of gold and platinum, silver and mercury on the surface of coal-paste electrode was found. This effect was used to increasing the sensitivity of the analysis.

The analysis of sandy and clay rocks of the Tadjik depression showed that the polarograph method with accumulation, combined with preliminary gold concentration by isoamil alcohol extraction, and silver in the form of ditizonate allows the determination of gold with a low limit of determination $-5.10^{-8}\%$ from 10gr sample, silver $-1.10^{-6}\%$ from 0.5gr sample with a relative standard deviation of 0.17.

The determination of osmium by kinetic method based on indicator arsenite-periodate reaction may be achieved only by distilling it in the form of OsO_4 from a reaction mixture under a controlled temperature. The low limit of osmium determination is $5.10^{-8}\%$ from a 1gr sample with a relative standard deviation of 0.30.

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Technical Session
Computer and Statistical Applications in Exploration Geochemistry

ALKEMIA —A DATABASE AND PROGRAM PACKAGE FOR GEOCHEMICAL EXPLORATION

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ALKEMIA is an ADP system which combines information of geochemical exploration projects with analytical data. The ALKEMIA program is designed to be used by explorers for supervising projects, retrieving geochemical assay data, for statistical and graphical applications.

The ALKEMIA system stores the data in well-normalized relational data-bases, which are built using the flexible Rdb/VMS relational data-base management system. It is possible to store field and assay data from various sampling materials in the same system. In the Geological Survey of Finland, stream sediment, lake sediment, till and lithogeochemical materials will be stored in ALKEMIA databases.

The information about projects includes general data as schedules, invetigation status, project manegement, study area definitions and notes about publications and produced maps. The sampling and analytical status is continuously updated with data about ordered services and exact data about completed sample preparation and geochemical analyses.

The user interface is a menu-driven interactive program. The project information can be checked on the screen or printed as a report. Retrieving assay data is based on sampling area, sampling material and methods, sample preparation, analysis methods and analyzed elements. The retrieved data can be presented as symbol maps or color surface maps, and the data can be analyzed with a statitical program package.

APPLICATION OF SOME PERSONAL COMPUTER-BASED TECHNIQUES TO WEATHERED ROCK GEOCHEMICAL DATA FROM THE BROKEN HILL AREA, NEW SOUTH WALES, AUSTRALIA

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The objective of the work described here has been to evaluate the extent to which personal computer-based techniques could be used more effectively and accurately to interpret weathered rock geochemical data from the Broken Hill area of New South Wales, Australia. This is done at two levels: 1) evaluation of the simplistic data management and plotting techniques, and 2) evaluation of multivariate statistical techniques; both with a view to improving exploration methodology.

The lead-zinc-silver deposit at Broken Hill is one of the largest and richest in the world, spurning continued exploration in the surrouding area. Numerous base metal occurrences in the prospective horizon are known, but these are often difficult to evaluate due to deep weathering, which has left little or no outcrop. For this reason, weathered rock geochemistry has become a standard method of prospect evaluation. Although weathered rock geochemistry appears to work well using relatively simplistic display and processing techniques, it may be possible to extract more information from the data, both quantitative and qualitative, through the use of computer-based techniques which could take advantage of multi-element anomalies and characteristic element associations.

The data-base considered consists of results from aproximately 7,000 samples distributed over 13 different survey areas, all within a 30 km radius of Broken Hill. The surveys include a series of samples taken from a line directly over the Broken Hill lode, as well as 12 others with varying relationships to mineralization. Samples were collected with the aid of a power auger, at depths ranging from 2 to 20 m, depending on overburden characteristics. Samples were normally collected at 15 m intervals from lines separated by 300 m. The samples were analyzed by atomic absorption for Pb, Zn, Cu, Ag, Mn, Co, Cr, and Ni.

The single element distributions of both Pb and Zn appear to reflect, in a general sense and in most areas, both the location and significance of mineralization at surface. Neither Pb nor Zn consistently display larger or more distinctive anomalous zones than other. In some cases, zones of anomalous concentrations of these two elements are offset from one another. The distributions of Cu, Ag and Mn are much more erratic and less distinctive, although each is variably associated with anomalous concentrations of Pb and Zn in the different survey areas. The concentrations of Co, Cr and Ni typically show less variation, and are more sporadicaly distributed.

The polymetallic nature of mineralization at Broken Hill and the zones of anomalous weathered rock indicate that additional information may be gained from the application of multivariate statistical procedures. For this reason, both R-mode factor analysis and discriminant analysis were applied to these data in an effort to: 1) draw attention to and quantify metal association in each of the survey areas, perhaps typing them and 2) develop multi-element composite scores which could provide a more consistent and reliable measure of mineralization potential than any individual element concentration.

The application of factor analysis to data from each of the survey areas consistently yields factors composed of Pb, Zn ± Cu, Mn and Ag, although the amount of variation explained by this factor varies from area to area. The most important control over these factors, referred to as "mineralization factors", appears to be the percentage of samples from a given survey area that are influenced by the effects of mineralization. Although the prominence of the mineralization factor varies widely from area to area, its character does not. With the exception of one survey area, the metal associations identified by factor analysis are very similar, implying a single type of mineral occurrence. Typically, either Pb or Zn is the most highly weighted element in the factor, with the other close behind. Factor scores, which are weighted combinations of the concentration values, have similar distribution patterns to the concentration pattern of the most highly weighted variable in the factor, although the factor score distributons typically show more consistency and less contrast.

Discriminant analysis was also apllied by using samples directly over the Broken Hill lode horizon as one end member training group (anomalous), and data from an area which only minor mineralization as the other member training group (background). Metal associations identified by discriminant analysis and resultant discriminant scores are very similar to the mineralization factors identified in factor analysis, as might be expected, given that the discriminant score and factor score equations are weighted highly in the same variables.

Factor analysis and discriminant analysis results have drawn attention to common mental associations in the area; however, the incremental advantage of the composite scores, when compared with unprocessed concentration values, is not as clear. Simply plotting the composite scores, such as, factor scores or discriminant scores, against the concentration values of the most important variable in the score equation typically yields a strong linear relationship, implying little difference between the two, other than scale.

In summary, results of multivariate statistical techniques have provided some additional information and insight; however, the incremental advantage of the composite scores does not appear to be particularly significant in this case. Perhaps in cases where the original single element anomalies are more subtle and not as easily recognizable, this would not be the case. In addition to the multivariate statistical techniques, the less glamorous, but equally important, data management and plotting techniques proved critical to the examination of these data. Using strictly manual methods, the most rudimentary processing for these 7,000 samples from 13 different areas and analyzed for eight elements would have proven onerous to the point of being impossible. As it was, with the aid of a microcomputer-based system, each element in each area was quickly processed and plotted. This has ensured that sufficient attention was devoted to each element/survey combination to recognize and evaluate the important features, something that would not have been possible using only manual methods.

INTERPRETATION OF EXPLORATION GEOCHEMICAL DATA: BACKGROUND AND THRESHOLD

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The concept of a threshold value, separating anomalous and background metal concentrations, is familiar and widely applied to interpretation of data from exploration geochemical surveys. However, discussions on procedures for determination of the threshold are often confined to the pros and cons of one or more statistical procedures for data evaluation and classification. Properly applied, these procedures are extremely powerful in revealing hidden relationships and trends. They should not be used, however, as a substitute for an understanding of geochemical relationships in the design and interpretation of exploration geochemical surveys. Some of the many factors that influence background variations of metal concentrations in soil and stream sediments will therefore be considered with respect to:

(i) what should be sampled, (ii) the field observations required, and (iii) use of this information in classification of samples prior to estimation of threshold concentrations.

MINERAL EXPLORATION FOR HIDDEN ORE BODIES IN GUANGXI PROVINCE, CHINA, USING DATA ANALYSIS AND MICROCOMPUTER SYSTEMS

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Duan Lihua
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Wei Wenzhuo
Guangxi Research Institute of Geology, CNNC, Nanning, China
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This paper describes mineral exploration in an established wolfram-tin ore field in the Pinggui region, in the southern part of China. Here, mining activities have been operated for more than 30 years and two major industrial mines are in operation today. Most known deposits and prospects are found in the Devonian strata system where bedded ore association of stratiform cassiterite-sulphides are controlled by the contact zone of the Yujiang and the Donggangling group. Large scale quartz-vein systems with wolframite and alluvial cassiterite deposits are also important. As a district of tin production, the valuable ore elements also include Au, Ag, Cu, Pb, Zn and rare-earth metals.

The projects main objective is to locate new hidden ore deposits of tin minerals in a selected area, 40 by 70 km. the second objective is to develop and introduce methods for data analysis and data administration based on microcomputer technology and software. The computer systems used are IBM PC and Apple MacIntosh connected to a digitizer, a plotter and a laserprinter. The software used are SIMCA for multivariate data analysis, TerraBase for digitize, data storage and map production and a kriging program for geostatistics.

A geochemical soil sampling was established in 1985 by the 272 Geological Team of Guangxi, CNNC. In lines 500 m apart, 50,000 samples were collected and later analysed for 14 trace elements. In 1988, data for 15,000 samples, in lines 250m apart, were stored in the project data base. This co-ordinate database holds sample identity and the topographical map co-ordinates, together with element values for W, Sn, Cu, Pb, Zn, As, Sb, Ag, F. Using the TerraBase software in an Apple MacIntosh, different kinds of statistics and maps can be produced in color on the computer screen or directed to a laserprinter or a color penplotter.

After evaluation of single element maps, three training areas near different types of mineralizations were defined as model subsets. The multivariate structures of each geochemical dataset, 300-600 samples, were calculated in terms of principal component analysis (SIMCA) and compared to geological models. After polishing the subsets, final models with two for three components where used in classification of all samples for the research area, and the resulting score and distance to class values for each sample were added to the database.

The multivariate fingerprints in the geochemical data have a good correlation with geochemical zoning patterns around mineraliztions, associated to intrusive bodies, such, as biotite granite in sedimentary strata from the Devonian to the Permian period. The feature models indicating mineral associations, now relates the geochemical anomalies to skarn mineralization, alluvial deposits. quartz vein and sulphide assemblages.

In a grid co-ordinate data-base composed of 10,000 pixels, selected variables have been introduced. The X,Y coordinates for all data are transformed into a common grid co-ordinate system according to a north-south orientation. The affinity of each sample to the three mineralization models were transformed with a universal kriging technique from sample point to pixel format. Data from an aeromagnetic survey, made by the Geophysycal Exploration Company, MMI, were included together with gravity measurements produced by the Bureau of Geology and Minerals of Guangxi. A binary coding of the geological map completed the database.

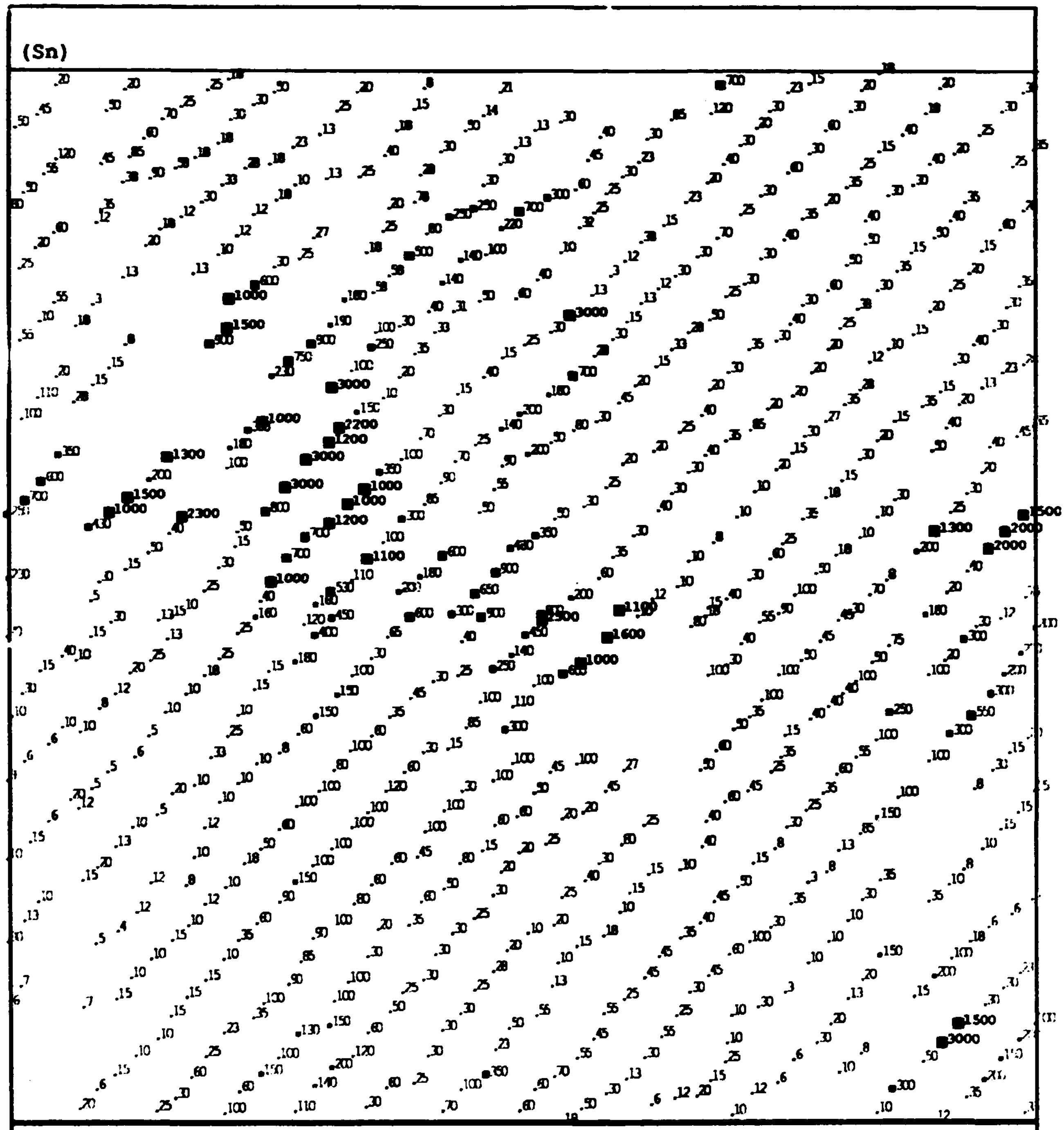
To increase the prediction power of the models, an integration of the geochemical and the geophysical data was made with a Partial Least Square regression method, implemented in SIMCA. The variable relation and prediction power has been calculated.

Based on the results in the project, new areas for further prospecting activites has been selected and follow-up work initiated.

(dT)

.49,42	.47,7	.43,7	.40,7	.42,21	.41,42	.21,9	.16,94	.17,65	.20,9	.27,69	.30,59	.28,82	.26,5	.29,65	.33,53	.27,9	.36,14	▪51,59	■61,
▪56,34	▪54,23	▪50	.44,33	.44,98	▪56,5	.25,89	.18,26	.20,9	.24,94	.31,37	.36,52	.36,1	.31,97	.34,91	.39,6	.42,12	.48,34	▪57,26	.35,
■63,51	■62	▪57,36	▪51,49	.45,9	.46,29	.18,12	.5,22	.28,6	.29,48	.35,8	.39,7	.39,74	.37,72	.38,9	.44,9	.47,66	▪50,88	▪54,4	.45,
■67,3	■65,23	■61,21	▪53,3	.49,92	▪59,37	.35,4	.35,6	.31,62	.31,03	.33,5	.38,21	.37,76	.36,02	.41,46	.47,71	.49,1	.41,7	.42,77	.40,
■67,16	■65,83	▪59,9	▪55,97	.48,03	▪53,4	▪50,3	.42,37	.36,19	.32,66	.33,84	.35,64	.34,4	.36,51	.42,18	.46,2	.39,3	.36,42	.35,77	.36
■67,20	■70,4	■65,96	■62,15	▪59,6	■60,62	▪54,95	.46,36	.37,9	.33,22	.34,11	.35,1	.33,42	.35,06	.39,1	.42,68	.36,65	.31,8	.30,3	.27,
■62,2	■64,26	■64,72	■63,8	■67,95	■66,84	▪55,89	.45,6	.40,46	.38,31	.38,7	.37,93	.33,18	.32,59	.44,6	.41,78	.34,41	.30,7	.30,41	.34,
■65,72	■63,05	■62,3	▪59	■64,69	■70,93	■64,6	.47,71	.43,33	.44,6	.47,82	.46,99	.42,39	.34,5	.40,48	.43,02	.37,5	.33,51	[illegible]	[illegible]
■66,53	■63,35	▪59,2	▪59,97	■63,3	■69,4	■70,45	▪58,18	▪50,8	▪56,63	■60,45	■61,09	▪55,8	.49,03	.47,36	.48,6	.36,12	.30,51	.23,59	.29,
■65,5	■62,1	▪59,75	▪58,92	■61,6	■70,21	■70,82	▪52,1	▪58,9	■67,56	■72,9	■74,6	■65,24	▪57,31	▪55,75	■62,73	▪51,9	.35,9	.34,1	.35,
■60,8	■60,25	▪57,58	▪57,13	▪59,32	■65,39	■74	■62,57	■63,09	■70,7	■76,32	■74,96	■68,1	▪58,4	▪58,48	▪56,55	▪52,1	.41,5	.38,1	.39,
■60,96	▪59,66	▪56,4	▪55,23	▪56,87	■62,7	■61,79	▪55,16	▪52,5	■63,27	■71,67	■74,91	■69	▪52,97	.48,48	.45,8	.42,08	.37,63	.34,66	.30,
■60,75	▪58,5	▪54,23	▪53,05	▪53,9	▪54,48	▪54,74	.49,91	▪54,6	▪56,17	■69,06	■74,8	■74,22	■64,53	▪51,3	.48,76	.41,48	.36,46	.36,2	.35,
▪57,7	▪56,49	▪53,48	▪52,9	▪51,26	.48,44	.45,51	.36,7	.42,83	.45,35	▪53,8	■70,32	■69,05	■69	■65,6	■63,34	▪56,23	.44,9	.42,2	[illegible]
▪57,65	▪55,53	▪52,58	▪52,61	▪50,38	.46,64	.39,9	.37,67	.39,26	.42	▪51,14	▪57,28	▪58,16	■62,9	■69,90	■69,13	▪58	.49,5	.48,44	.48,
▪54,36	▪51,8	▪51,53	▪52,89	▪51,4	.46,5	.40,09	.35,07	.35,94	.36,69	.44,9	▪50,1	▪53,8	▪58,88	■63,53	■65,5	▪59,11	▪50,3	.49,1	[illegible]
▪56,3	▪52,91	▪50,02	▪50,2	.47,63	.44,8	.38,71	.34,5	.37,31	.38,49	.47,8	▪50,42	▪52,62	▪55,85	■60,3	■60,35	▪58,41	▪52,8	▪52,49	▪55,
▪52,54	▪51,47	.49	▪50,11	.47,7	.44,89	.39,4	.34,65	.35,59	.34,3	.41,89	.46,7	.48,22	▪50,9	▪54,67	▪56,68	▪55,3	▪51,73	▪52,96	▪56,
▪51,85	▪50,15	.42,3	.46,34	.45,6	.42,5	.36,79	.35,12	.36,3	.36,87	.41,87	.45,9	.45,1	.49,01	▪52,92	▪55,4	▪53,91	▪52,45	▪54,5	▪58,
.49,8	.45,5	.45,2	.46,93	.46,4	.41,07	.37,28	.36,34	.34,9	.35,61	.41,23	.45,8	.45,11	.47,5	▪50,9	▪56,55	▪55,57	▪52,46	▪54	▪55,

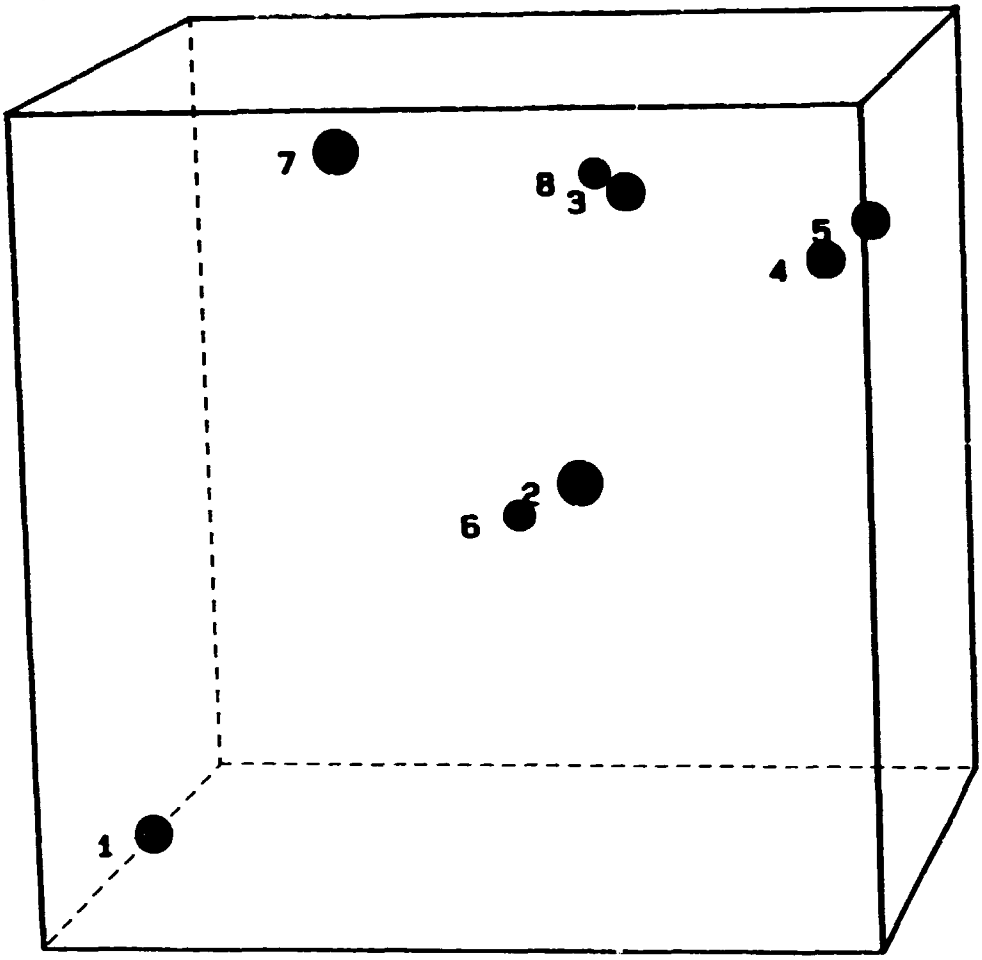
Ymax:	271600	95%:	63.00	Antal:	400
Ymin:	270600	90%:	60.00	Skala:	1: 17568
Xmin:	1955000	85%:	56.00		
Xmax:	1956000	80%:	50.00		



Ymax: 271600
Ymin: 270600
Xmin: 1955000
Xmax: 1956000

95%: 1000.00
90%: 500.00
85%: 250.00
80%: 125.00

Antal: 732
Skala: 1: 17568

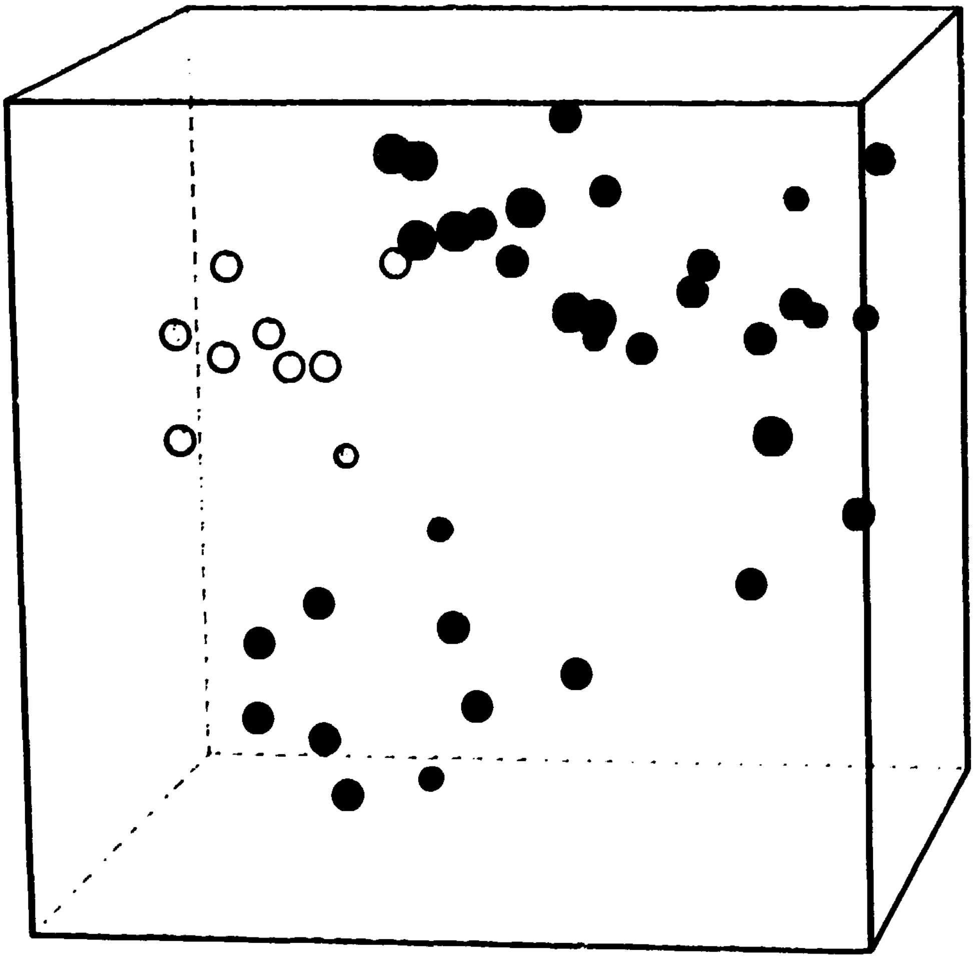


sueyentr. t14
X = Variable 1
Y = Variable 2
Z = Variable 3

Y–ax torsion = 350 °
X–ax torsion = 10 °

VARIABLE PLOT

1. W
2. Sn
3. Pb
4. Zn
5. Cu
6. As
7. Ag
8. Sb



sueyentr. t4
X = Variable 1
Y = Variable 2
Z = Variable 3

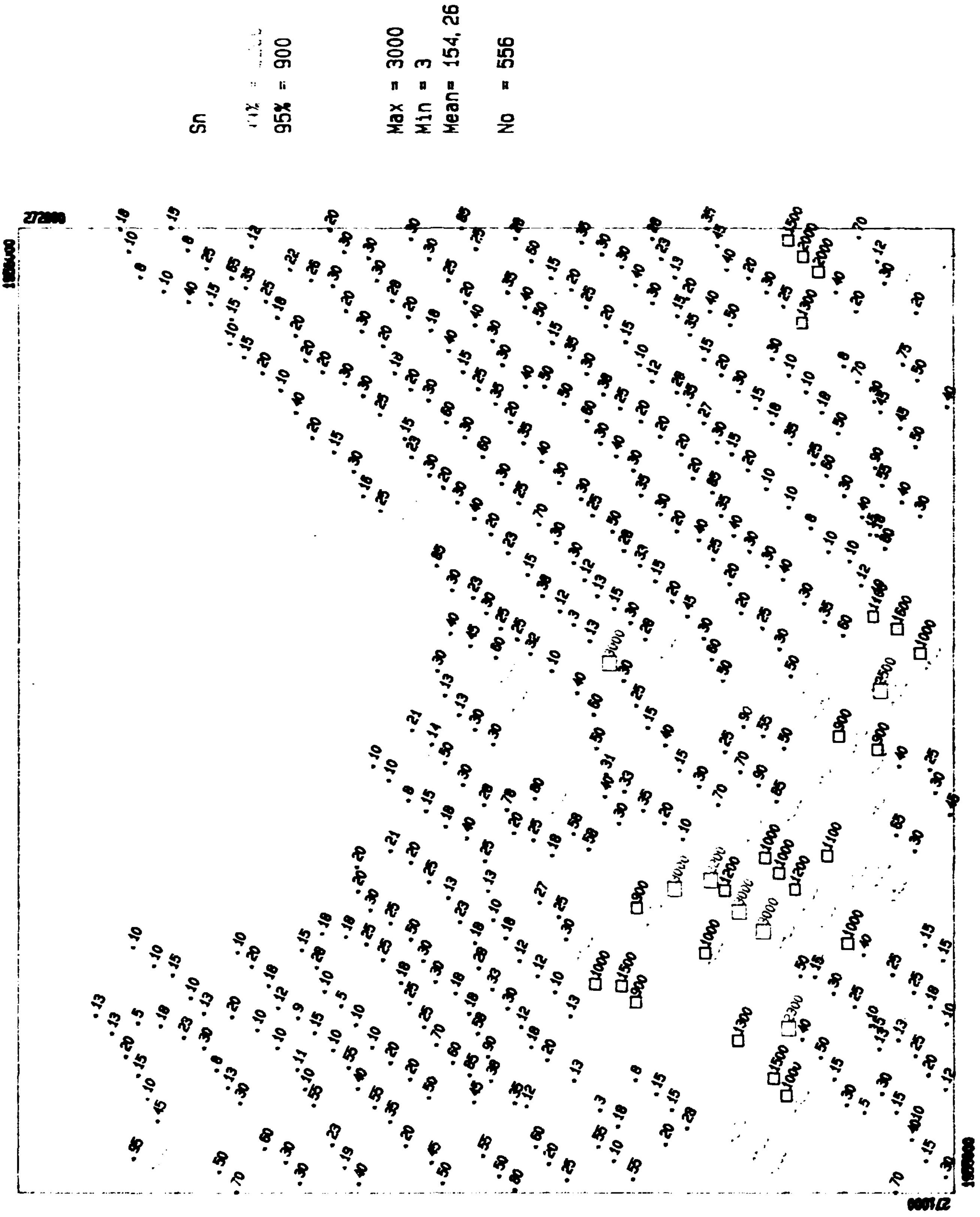
Y–ax torsion = 350 °
X–ax torsion = 10 °

SAMPLE PLOT – 3 comp.

Red – Samples high in Pb, Zn, Cu, Ag

Blue – Samples high in W

Green Background


Sn
95% = 900
Max = 3000
Min = 3
Mean= 154,26
No = 556

MULTIVARIATE GEOCHEMICAL DATA PROCESSING: THEORY AND APPLICATIONS

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Determination of the Beginning Anomalies Grade (BAG) and of the Significant Anomalous Grade (SAG) is a classical problem in exploration geochemistry. In this paper, the theory of fuzzy indicators is used to generalize the classical univariate elementary methods to the multivariate case.

In the univariate case, several techniques including zero-crossing, gradient, maximum likelihood and the dynamic cluster methods are used to dissect the histograms or cumulative functions into a mixture of finite distributions. The separate components are then identified as being either the background or else geochemical anomalies. The programming techniques, the limitations and the advantages of these methods are discussed.

The dynamic-cluster method is then generalized to the definition of multivariate anomalies: the grades of each sample are coeded by a set of fuzzy characteristic functions, related to the background or to the anomalous values. The results are then reported on elementary or multicomponent probability maps of occurrences.

The advantages of these fuzzy indicators are: (i) the generalization of Sinclair's method to the multivariate mixture distributions; (ii) the processing of truncated data; (ii) the production of probability maps of occurrences.

These methods are applied to several different case studies related to geochemical mineral surveys and to the exploration for a mercury-bearing sedimentary formation.

TECHNICAL SESSION 7
Petroleum and Coal Exploration Geochemistry

APLICATION OF COAL PETROGRAPHY AND ORGANIC GEOCHEMISTRY IN THE EVALUATION OF HYDROCARBON SOURCE ROCKS IN THE MIDDLE MAGDALENA BASIN COLOMBIA.

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A series of bituminous coals with high content in volatiles, belonging to the Upper and Middle Umir formation (located in the jurisdiction of Yarima, San Vicente de Chururi and Vanegas). Samples, cores and cuttings taken from the Lisama, Umir, La Luna and Tablazo formations (jurisdiction of Yarima) and oil samples from the Lisama, Colorado and San Luis fields in the Middle Magdalena basin were analyzed to determine the genetic relationship that exists between them. This was done employing petrographic, geochemical and technological parameters.

The coals present a high content of volatile matter, calorific power, exinitic macerals (fluorinite, esxudatinite, sporinite and resinite), fluorescence, bitumen extract, hydrocarbon in ppm a low-swelling index. Likewise the coals are within the window of liquid hydrocarbon generation. All these characteristics catalogue them as source rock for liquid hydrocarbons. Even though the rock samples are within the window of liquid hydrocarbon generation, they have lower bitumen extract content and hydrocarbons (in ppm) lower than those found in the coals.

On the other hand, after correlating the chromatographs obtained from oil samples, rocks and coals in the fraction of saturated ramified and cyclic hidrocarbons, it was found that the oils which came from the Lisama, Colorado and San Luis fields all come from the same family and are all similar to the coals found in the middle Umir formation, thus, indicating the genetic relationship that exists between the coals and oils found in these fields in the Middle Magdalena Basin.

ASPECTS OF CARBOHYDRATE GEOCHEMISTRY IN PETROLEUM EXPLORATION

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Moderns sedimentary environments vary widely in amount, variety, and preservation of sedimentary carbohydrate residues. Such residues as are preserved in sedimentary rocks, as determined by chemical, chromatographic and enzymatic analyses, offer possibilities for recognition and evaluation of petroleum source beds.

Deep sea environments are typified by sediments that contain only a few monosaccharides (ie. glucose, galactose), sugar degradation products (ie., furfurals), and low total carbohydrates (TC). Deep Gulf of California sediments contain glu, gal, xylose, mannose, furfurals, and moderate to high TC. Continental shelf sediments of eastern North America have glu, xyl, gal, furfurals and high TC. In oligotrophic lakes of Minnesota the sediments contain furfurals, few monoaccharides, and low TC. On the other hand, eutrophic lake sediments of Minnesota yield glu, xyl, arabinose, gal, rhamnose, man, ribose, furfurals, glucuronic acid and high TC. Temperate peat bogs in Minnesota contain glu, ara, xyl, gal, man, rib, and very high TC.

Evidence from drill cores in ancient sedimentary rocks indicates that carbohydrate residues may be preserved in some proportion to their original content, although degradation of the primary polymeric components to smaller fragments may take place fairly rapidly after deposition. In the case of B 1-4-linked polymers (ie., cellulose), fragments of greater than 7 such units have not been demonstrated in sediments prior to the Pleistocene Epoch, although older examples have been reported from fossil specimens.

Examples can be cited from Ordovician throug Carboniferous rocks of the Appalachian region, and from the Jurassic of the Gulf Coast and western United States to show the potential value of carbohydrate residues in source bed analysis.

Although methane can be derived from many classes of organic compounds, carbohydrates are potentially the most important source of biogenic,and perhaps indirecty also, of thermogenic methane. Methane derived from aquatic and terrestrial vegetaion is high in yield in fresh water marshes and in eutrophic lake sediments, moderate in yield in salt water marshes and estuaries and low in offshore marine sediments. In many samples studied, xylans appear to predominate over plant polysaccharides as methane sources. Some examples of the apparent relationship of carbohydrate contents to natural gas occurrences in the Devonian of the eastern United States are cited.

DIFFUSE REFLECTANCE FOURIER-TRANSFORMED INFRARED SPECTROSCOPY AND MULTIVARIATE DATA ANALYSIS IN PETROLEUM EXPLORATION: NEW PARAMETERS FOR BASIN-MODELLING

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Modern techniques of petroleum exploration, such as, basin modelling require quantitative geological data. Quantitative data can be obtained by using instrumental measurement techniques. Thus, chemical techniques, such as, GC-MS are today commonly used in the characterization and quantification of geological samples. The huge amounts of data produced by computerized instruments, typically thousands of data points per sample, require sophisticated data-analytical procedures if loss of information is to be avoided. Procedures for reducing the spectral profiles to peak heights of peak areas are time-consuming and operator-intensive oven for spectra or chromalograms of samples of moderate complexity. Furthermore, procedures for peak processing has been shown to be subjective and software dependent even for well resolved and simple multicomponent samples (1). Thus, more direct and automated methods are necessary to adequately represent the digital profiles provided by computerized instrumentation. The reduced digital representation of instrumental data can then be used directly as an input to multivariate data-analytical techniques.

The present contribution focuses on three aspects of the generation, presentation and use of instrumental data for type and maturity determination of organic matter: i) the use for diffuse reflectance Fourier-transformed infrared analysis to characterize geological samples, ii) automated and direct reduction of profiles obtained by instrumental analysis by means of a procedure related to maximum-entropy criteria, and, iii) the use of multivariate regression techniques, suitable for modelling data matrices consisting of more variables than the number of samples.

Mineral composition (2) and petrophysical properties, such as, permeability and porosity (3) have been shown to be predictable from X-ray diffraction data and wire-line logs, respectively, by use of a multivariate calibration technique. The same multivariate technique has been used to obtain quantitative estimates of thermal indicators, such as, vitrinite reflectance from diffuse reflectance Fourier-transformed infrared spectra, thus providing a rapid solid-phase technique for determination of coal rank (4). Results presented in this contribution imply that this technique is also useful for kerogen concentrates and asphaltenes from kerogens and oils (5,6). Thus, the present work indicates that the combination of diffuse reflectance Fourier-transformed infrared spectroscopy and proper multivariate data-analytical software (7) can improve basin simulation by providing quantitative estimates of such important parameters as type and maturity of the organic matter. Results from sample sets of natural and artificially matured kerogen concentrates and asphaltenes clearly show the potential of the present approach for adding new and complementary input parameters to programs for basin-modelling.

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ON THE DISTRIBUTION OF TRACE ELEMENTS IN COAL

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Trace elements are usually present in variable concentration in the organic and inorganic components of coal. The concept of "afinity" of an element for the organic or inorganic fraction of coal was first introduced by Goldschmidt (1) and it is relevant not only to coal geochemists but also to scientists and engineers involved in coal science and technology.

Although qualitative (2) and empirical (3) methods have been proposed to describe the distribution of trace elements in coal, it has been only recently that a quantitative method has been devised that allows for calculation of the concentration of trace elements in coal (4). The model is based on knowledge of the weight distribution of the inorganic and organic components of coal, and on analyzed elemental concentrations in coal fractions of varying mineral matter content. In this more general form, the model allows for calculation of the trace element concentration in each component of coal whose weight fraction is known. From the calculated values, elemental concentrations in the raw coal can be predicted and compared with analyzed values.

In its simplest form, the model cnsiders that coal is composed of two components (organic and inorganic) and that the elements are homogeneously distributed throughout each component. This assumption was used to verify the model and calculate elemental concentrations in a coal sample from Candiota, Brazil. Coal fractions of varying ash content were obtained through separation in liquids of varying specific gravity ("float-sink" tests) and were analyzed for 14 elements by various analytical techniques. The simplest version of the model was also tested with other Brazilian and American coals whose analyses were available in the literature.

The results indicated that the model gives good correlation for those trace elements that follow the basic assumption of homogeneous distribution in the organic and inorganic fraction of coal, even though the distribution itself may be quite uneven. For instance, vanadium was found to analyze 105.0 and 4.7ppm by wt in the organic and inorganic fractions of Candiota coal, whereas niobium gave 3.4 and 21.7 respectively. On the other hand, vanadium in Colchester nº 2 coal analyzed 4.7 and 93.4pp in the organic and inorganic fractions indicating that, contrary to Candiota coal, this element is primarily concentrated in the mineral matter. When these calcaulated concentrations were used to predict concentrations in the raw coal, was good agreement with the analyzed values.

However, the results also indicated that elements with strong affinity for the inorganic matter of coal could not be modelled on the basis of this simple version of the model. Thi means that for some elements the assumption of homogeneous distribution in the organic matter is not valid and they tend to concentrate in specific minerals. In order to model the distribution of these elements, the inorganic fraction of coal was divided into two fractions, sulphide and non-sulphide, whose weight fractions in the mineral matter of the coal could be determined with relative ease. The three-fractions version of the model was tested with data available from Gluskoter et al (3) for American coals. The results confirmed the forecasts of other authors that some elements (As, Cu, Zn, Pb) tend to concentrate in the sulphide fraction of the mineral matter.

Finally, the values obtained for the concentration of trace elements in the organic (Co), inorganic (Cl), sulphide (Cs) and non-sulphide (Co) fractions of Brazilian and American coals are compared and discussed with reference to the properties and origins of each coal. It is hoped that the method and the results will be helful to exploration geochemists.

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PRELIMINARY GEOCHEMICAL CHARACTERIZATION OF THE CRETACEOUS POTENTIAL HYDROCARBON SOURCE ROCKS OF THE PETEN BASIN, GUATEMALA

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The Cretaceous sequence of the Peten Basin covers the northern part of Guatemala. This study presents a preliminary geochemical characterization of the Cretaceous potential hydrocarbon source rocks, the Coban Formation, based on the available Total Organic Carbon, pyrolysis, kerogen coloration (TAI), vitrinite reflectance, chromatography and burial history data. Although there are some restrictions in the assessment of geochemical data regarding quality and quantity of results certian regional features from such data are evident and give a preliminary indication of source rocks potential. Source rocks are not widely distributed stratigraphically but are concentrated in the middle section of the Coban Formation (Cobon,H. C. Members) where maturity is sufficient to generate liquid and gaseous hydrocarbons, Guatemala crudes are very variable in gravity and gas-oil ratio. From previous work to distinct groups of oils can be recognized. The first comprises the Coban B Oils, which differ from Coban C Ooils of south peten bay the absence of a prominent C23 marker in the N-alkane chromatograms. Oil-source rock correlations have showed similar organic characteristics. Maturity modelling also took into account maturity levels from geothermal gradients, timing of oil generation and timing of oil migration. However, this thermal history has some uncertainties regaring the variations in present day geothermal gradients and amount of Tertiary uplift and erosion.

SURFACE GEOCHEMICAL PATTERN OVER PETROLEUM ACCUMULATION IN OVERTHRUST BELT OF YUMAN OIL FIELD, CHINA

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The study area is located in northwestern China, near Yuman Oil Field, the oldest oil producer in China. Structurally, it is characterized by a series of NW imbricate faults. The main source rock is Cretaceous mudstone and the Tertiary sandstone layers serve as a reservoir. The surface is covered by thick (n100-1,000m) semi-consolidated conglomerate, which is virtually the pediment of the Qiliang Range, lying south of the study area. 250 sites have been studied with an average density of one site per km^2. At each site, the following measurements were made: light hydrocarbon flux (C_1-C_5), hydrogen stripped hydrocarbon, delta carbonate, thermal evolved Hg, cold-extracted Hg, Fe, Mn, Sr, Ba, V, Ni, and Po-210. Thus, 20 parameters were obtained for each site, and they were contoured accordingly. Anomalies of those components which tend to migrate in gaseous state under the surface conditions such as light hydrocarbons, Hg, Po-210 show stripes parallel to the subsurface fault lines under the pediment. There are no oil accumulations under these anomalies, rather, they most probably occur between the anomaly stripes. Cold extractable Fe, Mn anomalies over known trap are explained by the existance of a reduction column, in which no additional Fe, Mn is added, but the low valence part has increased, hence the enhanced solubility. Sr, Ba anomalies, which are likely from oil field brine, have large lateral displacement which could be explained by the northward movement of groundwater. The spatial relationship between different parameters is a reliable indicator of the underground accumulations. Multi-parameter surface geochemical surveying can provide more information about the petroleum geology of the area. It is further demostrated that anomaly patterns are more important than their absolute values in exploration practice.

Technical Session
Uranium Exploration Geochemistry

COMPARISON BETWEEN ISOTOPIC (LEAD ISOTOPES AND ^{234}U/^{238}U DISEQUILIBRIUM) AND GEOCHEMICAL APPROACHES (MINERAL SATURATION INDICES) IN THE HYDROGEOCHEMICAL EXPLORATION FOR CONCEALED URANIUM DEPOSITS

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On different sites where the presence of underlying uranium mineralizations was known–West Morvan test area and Lodeve basin (France), Cigar Lake (Saskatchewan, Canada)–, we have tried to apply both isotopic and conventional geochemical methods based on major and trace element concentrations for the prospection of concealed uranium deposits. Isotopic methods comprise: 1) the analysis of lead isotopes in groundwaters, in order to find any contribution of radiogenic lead from the supposed sur[illegible]ng or overlying mineralizations; 2) the measurement of ^{234}U/^{238}U activity ratios, whose variations have been proved to be correlated to the presence of uranium accumulation. The conventional geochemical methods consist simply of looking for uranium or accompanying elements in groundwaters. A more elaborate method uses the notion of saturation indices of uranium-bearing minerals, thus requiring accurate and complete determinations of major ions and parameters of groundwaters.

We have proved that the analysis of lead isotopes was efficient in many contexts, and gives results that are rethar independent on the geochemical characteristics (i.e. reducing or oxidizing) of the waters. The information is global and expresses the presence of uranium accumulations in the vicinty of the sampling point. No information about grades and distance to the mineralization can be obtained. The information can be transported either in solution or on particles, as lead is readily adsorbed on many substrates, such as, clays or oxides. In some cases, when the conditions of the analysis are good, an information about the source of the mineralizations can be obtained when considering ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb ratios. Primary (i.e. magmatic sources) are generally richer in thorogenic lead because Th/U ratios are higher in such occurrences; on the contrary, Th/U ratios are generally low in secondary uranium deposits, resulting in low and uniform ^{208}Pb/^{204}Pb ratios compared to scattered and possibly very high ^{206}Pb/^{204}Pb ratios. The analysis of ^{234}U/^{238}U activity ratios in groundwaters provides information which is more difficult to decipher. In general, oxidized waters encountering uranium accumulations will show high uranium concentrations and low ^{234}U/^{238}U activity ratios, but groundwaters which are more reducing or close to uraninite saturation will produce either high ^{234}U/^{238}U activity ratios if the exhcange surface between uranium-bearing phase and groundwater is large enough to promote preferencial ^{234}U enrichment in the fluid phase (selective leaching or alpha recoil) or low ^{234}U/^{238}U activity ratios if the exchange surface is smaller. High ^{234}U/^{238}U are observed above dispersed uranium accumulations, frequently situated in the vicinity of massive uranium deposits. This is observed in all studies sites, where contrasting signatures between massive ore zones and surrounding secondary mineralizations are found. In this case, the ^{234}U/^{238}U activity ratio may give information on the succession of the relative ore-grades.

The use of uranium concentration anomalies has often been questioned, because: 1) non-significant anomalies may appear in oxidizing waters, 2) reduced waters may not be able to record significant U anomalies. The concept of saturation indices of uranium minerals generally allows a more accurate detection of the minera[illegible], but it requires a careful determination of redox potentials, in some cases by in situ measurements, but, more generally, by calculating the redox potential from dissolved iron, assuming equilibrium with iron oxides. Waters flowing through mineralized areas are generally saturated with respect to uranium minerals, without any clear U concentration anomaly (this is the case around the Cigar Lake U deposit). If they are generally strongly oxidized and thus show very high anomalies in terms of uranium concentrations (this is the case of the Nord-Tréviels part of the Lodeve uraniferous basin). If no uranium accumulation is present, saturation indices are generally strongly negative, but in strongly reducing waters, even far from any uranium deposit, one can obtain uraninite saturation. This is the case in the Lodeve sulphide-bearing waters, or in the alkaline geothermal waters from the Pyrénées. If we analyse both the U concentration and the U saturation index, we can seen that waters flowing through mineralized zones have either high U concentrations or are very close to U saturation. One can say that, with little doubt, any water that does not possess one of these two characteristics is of no interest for uranium prospection.

In conclusion, lead isotopes offer good indications of the proximity of mineralized areas, though no quantitaive information is likely to be obtained. However, the applicability of this method can be hindered by the necessity of a complex processing of samples and by the poor availability of mass spectrometric facilities. The determination of $^{234}U/^{238}U$ activity ratios is the only method among all those we have studied that allows a comparative estimation of the grade of the mineralization, although it is only qualitative. Uranium mineral indices may give useful information, and help in the selection of target areas.

HYDROMORPHIC DISPERSION OF URANIUM IN A SURFICIAL ENVIRONMENT IN NORTHERN FINLAND.

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The study area, in the commune of Sodankyla, stood out as a peak in radioactivity measurements made fron the air. The area lies south of the former ice divide in the Fennoscandian ice sheet. Tha last phase of ice movement was from the northwest. The radiation anomaly is situated in a mine on one bank of the River Ylijoki. The absolute heights vary between 205 and 280 metres a.s.1.

In order to investigate the origin of this anomaly, samples were taken from the weathering crust, till, sand, peat and groundwater. The total uranium content in the fine fractions of the mineral soil and in ash from the peat samples was analyzed by delayed neutron counting. Th, Si, Al, Ca, Mg, K, Fe, Ti, V, Mn, P, Zr, S, Sr and Nb were analyzed by X-ray fluorescence analysis. The weakly bound fraction of the uranium in the samples was studied by leaching the samples with 0.1 M citric acid and analyzing the uranium by colorimetry. The petrography of the till was studied by means of stone counts from the coarse fraction of the samples.

Since the bedrock surface is weathered, only a few samples of the unweathered bedrock were available for analysis. The site lies on a Precambrian granite bedrock which has a somewhat higher uranium content than the surrounding rocks. The uranium content of fresh granite samples varied between 3 and 29ppm, averaging 8ppm, and the thorium content between 10 and 350ppm, averaging 50ppm. The Ylikoji granite can be likened to the U-rich granites in Sweden in terms of its chemical composition.

The weathering crust is low in silicon and potassium and rich in aluminium and iron as compared with the fresh bedrock. The till in the area is composed, for the most part, of granitic rock material and contains more silicon, calcium, magnesium and titanium and less aluminium and potassium than does the weathering crust. The chemical composition of the sorted sand is much like that of the till.

The weathering crust, till and sand contain relatively high uranium concentrations (maximum values 99ppm in the weathering crust, 420ppm in the till and 497ppm in the sand.

Although thorium also has anomalus values (maximum 180ppm in the weathering crust and 100ppm in the till), the correlation between uranium and thorium is poor.

Cold-extractability tests showed that most of the uranium is weakly bound, indicating that the dispersion mechanism involved is hydromorphic. The high uranium content of the groundwater (maximum 520ppb) shows that the dispersion process is still active. Uranium is more firmly bound in the weathering crust than in the till or sand. The most coherent anomaly occurs in the groundwater discharge area, where the peat is also enriched with uranium.

During infiltration the water evidently leached uranium from the weathered surficial parts of the granite and possible mineralizations, so that, when the groundwater discharged to the surface in the seepage zone, uranium was fixed in the weathering crust via scavenging by the clay minerals and Fe oxides. The uranium was fixed via adsorption to the surfaces of the mineral grains in the till and sand and via complexation with organic matter in the peat. The measured uranium content of the groundwater is so high that it is very probable that there is a uranium concentration in the bedrock somewhere in the catchment area. From the prospecting point of view, the direction of flow of the groundwater should be determined carefully, while, from the environmental point of view, it is important to map and study areas of this kind, particularly if the soil is being used for housing, the groundwater for drinking water or the peat for fuel.

RADIATION-INDUCED DEFECTS IN KAOLINITE AS A POTENTIAL GUIDE FOR URANIUM PROSPECTION IN LATERITE-COVERED AREAS

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INTRODUCTION

Kaolinites are known to incorporate defects of various types, either extended or localized. Among them, stable paramagnetic defect centers have been recognized in all the Electron Paramagnetic Resonance (EPR) studies of natural kaolinites since the pioneering extensive study by Meads and Malden (1975). These defects result from an external irradiaton of kaolinite (Muller and Calas, 1989). We have tested the possibility of using these defect centers (i) to trace radionuclides migration in weathered materials and consequently, (ii) as a guide for uranium prospection in laterite-covered areas.

EVIDENCE OF RADIATION-INDUCED DEFECTS IN NATURAL KAOLINITES

Paramagnetic defect centers in natural kaolinites

EPR spectra of natural kaolinites exhibit two distinct signals visible at ambient temperature. The former, centered near $g=4.3$, is a complex signal characteristic of substitutional trivalent Fe in various kinds of sites. The latter, centered at values just above $g=2$, is due to an anisotropic center (A-center). It is interpreted as arising from a trapped hole near a silicon atom, favoured by the presence of impurities or vacancies located in the vicinity of the silicon atom. This center is stable up to 400°C.

Natural irradiation of kaolinites: study of a hydrothermal alteration associated with a uranium deposit

A uranium deposit, resulting from a hydrothermal alteration of volcanic rocks (ignimbritic tuff) in Sierra Pena Blanca, Chihuahua, Mexico, has been studied in detail. Several kaolinite parageneses have been defined according to their origin (fissure fillings and feldspars pseudomorphs), their location relative to an U-rich breccia pipe (core and rim of the pipe, surrounding welded rhyolitic tuffs), particle morphology, crystalline order and substitutional Fe-content (Ildefonse et alii, 1988). Paramagnetic defect centers in these kaolinites have been systematically investigated. The concentration of A-centers is always more important by order of magnitude than in supergene kaolinites. The variations are only correlated to the location of the kaolinites: the highest values are found in the breccia pipe. Moreover, other defect centers (B centers) are detected depending on the intimate misture with U-bearing minerals. It is concluded that the defect centers might allow an efficient fingerprint of two successive irradiations of kaolinites: the first one occurring during the crystallization of kaolinites from the radioactive hydrothermal solutions and the second one being due to permanent irradiation from the secondary U-silicates.

Experimental irradiations

A better understanding of radiation efficiency, as well as an accurate dose-rate estimation, are needed for a quantitative tracing of radioactive elements migration. Various kaolinites have been experimentally irradiated (α and γ-rays, Pb^{2+} and He^{+} ion beams) (Clozel et alii, 1989). These experimental irradiations induce an enhancement of the original signal, related to the "decoration" of the structural defect responsible, and/or reproduce the defect centers (A and B-centers) observed in the previously studied radioactive environment.

USE OF RADIATION-INDUCED DEFECTS IN KAOLINITES TO TRACE RADIONUCLIDES MIGRATION IN LATERITES

The previous data allow use of paramagnetic defect centers to detec natural irradiations of the kaolinite from laterites, during and after growth of this clay mineral.

A-centers as memory of radionuclides transit in a laterite from Cameroon

The variation of A-centers concentration S(A) has been systematically investigated along seven lateritic weathering profiles developed at the expense of a non-mineralized orthogneiss from Cameroon. Petrological and geochemical data have been obtained on the same samples. There is no relation between S(A) and the textural changes, the Fe-content of the kaolinite lattice and the crystalline order of this mineral. On the contrary, there exists a relationship between the integrated intensity of the ERP signal, on the one hand, and the Fe and the U-Th content of the bulk samples on the other.

A possible radiation source has to be sought in radioactive elements disseminated through the weathered materials and mainly accumulated in ferruginous materials. However, the present day U-Th contents is too low to explain the measured S(A) values. By taking into account the efficient chemisorption of radioactive elements on poorly crystallized iron oxides, the A-defects are attributed to an inherited irradiation of the kaolinites during the first stages of rock weathering and their subsequent crystallization. The major implication of the proposed model is that iron oxide gels precipitate at the weathering front, and absorb the radionuclides released by primary minerals. The evolution of iron oxides towards a more crystalline structure leads to a release of the radioactive elements, and the A-centers are thus the memory of their transit.

Application to uranium prospection in laterite covered areas: Laterites developed on mineralized zones (Brazil)

Kaolinites have been sampled in lateritic weathering profiles developed at the expense of both U-mineralization and barren host rocks from Brazil: U-mineralized albitite and barren host orthogneiss from the Lagoa Real subalkaline granitic complex, South Bahia; U-mineralized and barren arkose from Amorinopolis, South Goiás. The preliminarly results obtained on defect centers in kaolinite are the following: (i) kaolinites give a very intense signal corresponding to A centers when they are located in laterite developed over the uranium deposits, but a signal of significantly small intensity (down to twenty times) when found in petrographically similar laterite differentiated on nearby non-mineralized rocks; (ii) B-centers are detected in the most radioactive materials (field radioactivity measured with a SPP2 detector). These data confirm the results obtained both by experimental irradiations and on kaolinites from the Mexican uranium deposit. Moreover, it seems, by comparison between the variations of A-centers concentrations and the radioactive along weathering profiles, that these centers might be the memory of past radioactive elements transit.

CONCLUSION

Defect centers in kaolinites are due to irradiation from radionuclides. Kaolinite traces the cumulative radiation dose. The stable A-centers in laterite may remain as a trace of past irradiations, while B-centers are the most sensitive to present day irradiations. Radiation-induced defects in kaolinite could be then a potential guide for uranium prospection in laterite-covered areas.

Acknowledgments

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THE GEOCHEMISTRY OF ALBITIZATION AND RELATED U-MINERALIZATION, ESPINHARAS, PB, BRAZIL.

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The radioactive uraniferous deposit of Espinharas is situated in the northeast Brazilian shield. The U-mineralization is related to sodium metasomatism and episyenitization of amphibolite facies, gneisses and intrusive microgranites.

Two major well-defined groups of gneisses occur: granitic leucocratic gneisses and mesocratic, biotite-amphibolite gneisses. The former ones are considered orthogneisses and the latter, paragenic in origin. The gneisses are of old Precambrian, lower Proterozoic or, even more probably, of Archean age. Granitic and mesocratic gneisses are associated with sub-concordant structural relationships. The intrusive microgranites cut the gneisses as dikes of metric to decametric width and very variable extension (metric to kilometric). The microgranites are hololeucocratic and their age is most probably upper Proterozoic, though age determinations are inexistent for that specific area.

The uraniferous mineralizations are included in albitized and episyenitized rock portions that occur in a zone discordant of the high grade metamorphic regional foliation. This zone resulted from shearing stresses and fraturing that controlled first the intrusions of microgranites and, later, the percolation of the metasomatic mineralizing fluids along widened grain boundaries and microfractures. All the three major rock types: granitic gneisses mesocratic gneisses and intrusive micrograntes were affected. Dimensions and forms of the resulting metasomatized rock portions and the occurrence of higher grade uraniferous mineralizations depended additionally on the primary rock compositions (general mineralogical and chemical controls) and of the pre-existing regional foliations (structural/textural anisotropies only in gneisses).

The particular local geological situation forwarded undoubtedly correlate rock pairs and complete transition series of the above mentioned three major lithologies, including non-metasomatic and mineralized equivalents.

The qualitative and quantitative mineralogical and major chemical and trace element data are shown in tabs. 1 and 2.

Mineralogically, the main metasomatic processes resulted always in: (I) complete dissolution of quartz; (II) albitization of both: plagioclase and microcline; (III) chloritization and partial dissolution of biotite; (IV) precipitation of: coffinite, pyrite, chlorite, albite and carbonates frequently associated with minerals of Y and REE (xenotyme), partially filling the voids resulting from quartz dissolution. In the special case of the mesocratic biotite-amphibole gneisses there occurred, in addition, the precipitation of blue riebeckitic amphiboles epitactically overgrown on the primary ones (tab. 1).

Table 1 – Qualitative and quantitative mineralogical composition of non-metasomatic rocks. (1) granitic gneisses, (2) microgranite and (3) mesocratic, biotite-amphibole gneisses, from Espinharas.

Minerals vol %	**(1)**	**(2)**	**(3)**
Microcline	48	43	–
Plagioclase	20	22	38
Quartz	21	28	22
Biotite	8	3	17
Amphibole	–	–	17
Titanite	1	<1	2
Apatite	<1	<1	<1
Opaque ore minerals	<1	<1	<1
Muscovite	<1	<1	2
Chlorite	<1	<1	–
Epidote	<1	<1	<1
Clinozoisite	<1	<1	<1
Leucoxenite	<1	<1	–
Calcite	–	<1	<1
Sericite	<1	<1	5
	–	–	

The chemistry of major and trace elements further sustains the above mentioned processes and shows, in addition, important migrations in the trace element spectra (tab. 2).

For the purposes of geochemical exploration and ore genesis, it was important to identify elements that could safely correlate mineralized and non-mineralized parent rocks and characterize the mineralizing fluids. However, with the aid of the common main trace elements this was not always possible beyond doubt (tab. 2). Therefore, REE's were included in the studies. Fig. 1 shows mean REE distribution patterns (chondrite normalized) of non-metasomatical and mineralized equivalents of the three major rock types. It becomes evident that the light and intermediate REE precisely define the relationships of parent and mineralized rocks. U-mineralization goes along with a very characteristic enrichment of heavy REE's, Dy to Lu.

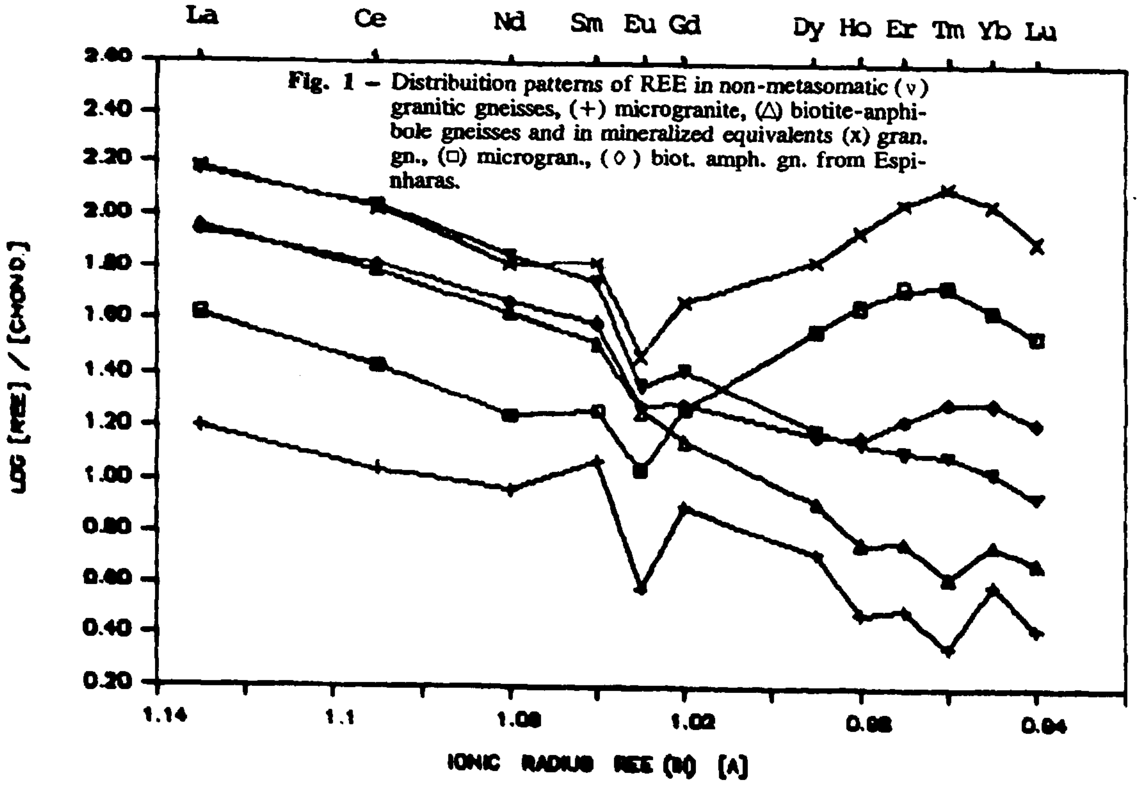

Fig. 1 – Distribuition patterns of REE in non-metasomatic (v) granitic gneisses, (+) microgranite, (Δ) biotite-anphibole gneisses and in mineralized equivalents (x) gran. gn., (□) microgran., (◊) biot. amph. gn. from Espinharas.

Table 2 –Major and trace element characteristcs of. (1) granitic gneises, (2) microgranit and (3) mesocratic, biotite amphibole gneisses; (A) non-metasomatic and (B) metasomatic and mineralized equivalents rocks from Espinharas (XRF and ICP-AES analyses).

wt. %	1		2		3	
Elements	**A**	**B**	**A**	**B**	**A**	**B**
SiO_2	71.10	62.20	75.10	62.90	65.31	59.43
TiO_2	0.43	0.54	0.07	0.08	0.62	0.91
Al_2O_3	13.70	14.90	13.50	17.20	14.54	15.84
Fe_2O_3	1.38	3.43	0.39	1.12	2.22	5.[illegible]4
FeO	1.89	1.47	0.44	0.70	4.27	1.97
MnO	0.02	0.09	0.01	0.02	0.15	0.07
MgO	0.54	0.54	0.10	0.40	2.34	2.71
CaO	1.75	3.37	1.09	3.50	4.56	1.73
Na_2O	3.36	8.54	4.30	9.94	3.31	8.76
K_2O	4.64	0.15	4.27	0.25	2.01	1.15
P_2O_5	0.07	0.24	0.01	0.16	0.15	0.22
LOI	0.39	2.69	0.24	2.86	1.18	1.80
Trace elements (ppm)						
Ba	349	167	219	124	357	367
Rb	177	79	165	21	83	51
Sr	108	114	186	114	313	148
Pb	39	83	28	55	12	27
Th	5	2376	7	407	<5	9
U	<10	4877	<10	279	<10	478
Nb	6	105	5	31	7	23
Y	10	271	11	141	21	46
Zr	96	87	79	92	119	194
V	<10	18	<10	15	91	135
Cr	<6	<6	<6	<6	91	89
Ni	5	21	5	7	52	58
Co	5	<4	<4	<4	21	23
Cu	4	4	6	10	4	77
Zn	19	28	17	9	75	83
Ga	15	22	17	20	14	17
Sc	<2	7	<2	<2	15	20
S	<50	3847	<50	87	<50	271

U VERSUS TH - CONCENTRATION PROCESSES ASSOCIATED TO NA - METASOMATISM IN GRANITES: THE LAGOA REAL DISTRICT (S BAHIA, BRAZIL).

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The Lagoa Real uranium ± Th deposits (1.4 Ga) in the central zone of the São Francisco craton (S. Bahia, Brazil) are associated with regional scale Na-metasomatism of Precambrian granites (1.7 Ga) metamorphosed to amphibolite facies (450 Ma) (Turpin et alii, 1988).

Granitoids locally preserved from deformation present 2 feldspars, strongly perthitic orthoclase and oligoclase ≥albite, quartz and Fe-rich amphibole-biotite ± clinopyroxene assemblages with ilmenite ≥magnetite, zircon, apatite, allanite and Nb-Y-U-Th ± oxides. Orthogneisses, which are the main rock-type, show non-perthitic microcline, albite ≥ oligoclase, Fe-rich hornblende and biotite (figure 1) with magnetite ≥ilmenite, sphene, zircon, allanite and Nb-Y-U-Th ± Ti oxides (Maruéjol, 1989). Major and trace elements geochemistry indicate a subalkaline association with alkaline characteristics (high Zr, Nb and Fe contents and increasing LREE during differentiation, but the agpaicity index (Na/(Al-K) remains always below 1 (Maruéjol et alii, 1987).

These subalkaline and alkaline orthogneiss enclose respectively U or Th mineralizations related to different types of post-magmatic Na-alteration.

Th-mineralization (200 < Th < 500ppm, U = 25ppm) occurs in quartz-bearing albitites where the main alteration is albitization of K-feldspar (figure 1). Mass balance calculations evidence a slight gain in volume (0 to 10%) with K loss, Na, Si, ± Ca, Fe, Th, Nb, U gain and constant Al, Ti ± Ca contents.

U-mineralizations occur in quartz-free albitites from the subalkaline granites. The alteration processes comprise (1) albitization as K-Na exchanges in feldspars with a low water-rock ratio (quartz-albitite), (2) leaching of quartz and albite ± calc-silicates new-formations with high water-rock ratio (quartz-free U-rich albitite) (Figure 1). Mass balance calculations of granite - quartz-free U-rich albitites pairs evidence as systematic loss of volume (10 to 18%) with Si, K, Ba, Rb, Fe^{+2} loss, Na, Fe^{3+}, U, V, Zr, ± Ca, ± Sr gain, and constant Al, Ti, Th and REE contents (Lobato, 1985, Maruéjol, 1989). This type of alteration may lead to economic uranium deposits (U ≥ 1.500ppm, Th = 20ppm).

It appears that the quartz-free and U-rich albitites are related to large fluid circulations of meteoric origin ($\delta^{18}O$ = -2.6%, Lobato et alii, 1983) during a high-temperature and post-magmatic (1.4 Ga, Turpin et alii, 1988) hydrothermal event. The Th-rich albitites are the result of two alterations processes: (1) a late-magmatic alteration related to F-rich fluid oversaturation of the alkaline granite and (2) a post-magmatic alteration related to the circulation of meteoric water at 1.4 Ha ($\delta^{18}O$ = +5.4%.

U-rich Nb-Y-Th ± Ti oxides (1.5 to 5.1 UO_2wt%) in the Lagoa Real granites represent the most likely uranium source for the uranium mineralization enclosed in the quartz-free U-rich albitites. They were sufficently metamict at the time of the hydrothermal circulations (300 Ma later than granite emplacement) to allow uranium leaching.

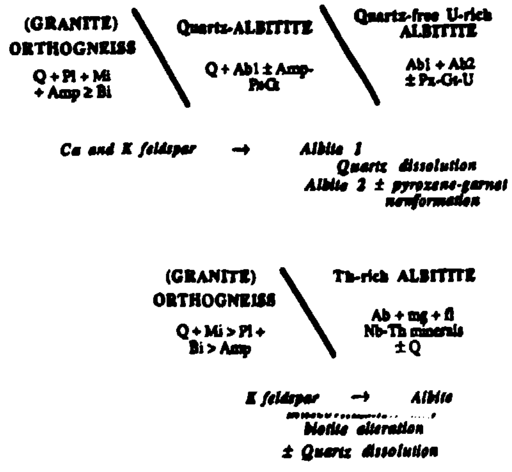

Fig. 1 – Lithological and mineralogical evolution from subalkaline orthogneiss to quartz-free U-rich albitite and from alkaline orthogneiss to Th-rich albitite. Q: quartz, Pl: plagioclase, Mi: microcline, Amp: amphibole, Bi: biotite, Ab: albite, Px: pyroxene, Gt: garnet, U: garnet, U: uraninite, mg: magnetite, fl: fluorite.

Technical Session
Geochemical Applications in Base Metal Exploration

BASE METAL EXPLORATION IN THE BENAMBRA AREA OF NORTH-EAST VICTORIA, AUSTRALIA, USING LEAD ISOTOPES IN SOILS

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The lead isotope method has been applied to an ongoing exploration program for volcanogenic massive sulfide deposits in north-east Victoria. The exploration licence is located in a sequence of lower Paleozoic volcanics, volcanoclastics and sedimentary rocks. Two deposits, Wilga and Currawong, had been outlined and exploration was for additional occurrences of base metals. Owing to the rugged terrane, exploration costs are high.

Following a pilot study which established that there were measurable lead isotopic differences between the target massive sulfide and a minor style of mineralization, a program was established to evaluate 22 geochemical and/or geophysical anomalies. This program was executed on a "blind" basis insofar as no information, besides lead contents and sample grouping was known. Analyses were performed mainly on B-horizon soils, rarer gossanous material and a comparison was made between the results for the soils and vegetation.

The anomalies can be classified into five groups on the basis of their lead isotopic signatures: (i) massive sulfide type characteristic of the Wilga and Currawong deposits, (ii) a disseminated type of massive sulfide, (iii) a minor vein style of mineralization, (iv) a variation of (iii), and (v) a type possibly related to nearby granites.

A comparison of the lead isotope assessment with that from five geologists familiar with the exploration program and based on geology, proximity to existing deposits, alteration, geochemistry and geophysics shows the lead isotope method to be superior.

For such an exploration program, the soils are a more satisfactory media for lead isotope analysis than vegetation because of easier collection, less laboratory contamination, simpler analytical procedures and better anomaly enhancement.

FOLLOW-UP STUDIES OF ANOMALOUS ZINC - AND BARIUM AREAS IN CENTRAL AND WESTERN NORTH GREENLAND

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In central and western North Greenland, reconnaissance geochemical surveys, based on stream sediment collected at a density of one sample per 20-30km^2, were carried out by the Geological Survey of Greenland. The geological environment comprises a shelf sequence to the south where Proterozoic and Palaeozoic sediments overlie a crystalline basement, and a folded, deep-water sequence (the North Greenland fold zone) to the north, consisting of Phanerozoic sediments. The data from the reconnaissance survey showed that within the shelf sequence a Cambro-Ordovician platform margin is anomalous with respect to Zn and Ba (Steenfelt, 1987). Small-scale overburden sampling delineated a vein-type mineralization and indicated a stratabound mineralization in a Cambro-Silurian shelf and slope sedimentary sequence (Jakobsen, 1989).

The aim of the follow-up was to determine the general geochemical character of the main lithologies, to locate the stratabound mineralization and determine its type by the element association. The detailed follow-up studies were carried out by rock sampling in profiles. The detailed rock sampling programme was concentrated on the Cambro-Ordovician margin sequence (in the southern part) and the Cambro-Silurian shelf and slope sequence, respectivelt. A comparison was made between geochemical data from stream sediments and rock samples for the elements Ba, Cu, Pb and Zn. In general, there are great chemical similarities between the primary and the secondary environment. However, a close correlation between Ba and Zn observed in the secondary environment does not exist in the primary environment. The detailed rock sampling programme enables the localization of minralized horizons, which the stream sediments did not.

Rock geochemistry shows the enhanced or anomalous lithological units with a high content of the respective elements. Furthermore, thin mineralized horizons can be determined and the element association indicates the type of mineralization. It is a logical step in the strategy of a follow-up survey to include detailed rock geochemistry.

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LITHOGEOCHEMICAL EXPLORATION OF MASSIVE SULFIDES AT PERAU BASE METAL MINE, PARANÁ, BRAZIL

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The Perau deposit is located in the Adrianópolis township, 30km south of the São Paulo-Paraná State limits, southern Brazil. The deposit is formed by two distinct orebodies. In the first one, the ore is mainly composed of galena, pyrite, chalcopyrite and sphalerite, and has an inferred reserve of 1.8 million metric tons, with 4% Pb, 2% Zn and 85g/t Ag, and the second is a copper deposit with 830,000 metric tons of ore with 2% Cu, locate below the first one. The main orebody has a stratabound structure, with dimensions of 800 x 700m, up to 6m thick striking 10°N and dipping 35°NW. The ore is underlain by a graphitic phyllite and overlain by a barite layer and a banded iron formation. All this suite is intercalated with calc-silicatic rocks. These are underlain by quartzites and overlain by mica-schists with intercalations of amphibolites. The whole sequence forms the Perau Formation of the Setuva Group, which is underlain by the pre-Setuva schists and gneisses. In the main orebody, zoning is recognized by its mineralogical distribution and revealed by trend surface analysis applied to 69 ore samples, with Zn increasing to the NW, Pb and Au to the SE and Cu to the NE. Tha statistical results from 84 rock samples, analysed by optical spectrography and atomic absorption, for 30 elements in the study of the geochemical halo were as follows: concentration-distance diagrams indicated progressive enrichment of Pb, B, Mg, Mn, Ba and K in the direction of the ore: whereas Be, V, Y, Cr, Ni, Sr, and Zn indicated depletion. Simple correlations with distance-to-ore indicated enrichment of Mn, Pb and Mg and depletion of Rb, Be, Sr and Sn. Cluster analysis was not able to separate samples taken near to the ore from those taken far from it. Multiple regression of distances-to-ore gave better results, with B and Cu for foot-wall rocks and Sr, Pb, Mn, La, B and SiO_2 for hanging-wall rocks showing enrichment and Ni, Zn, Be, Co, Cr and Ba showing depletion. Discriminant analysis was able to separate samples taken up to 200m from the ore from those taken at greater distances. The results obtained with concentrations corrected for lithological variation were little better than those for uncorrected ones. More weathered samples gave greater residuals in regressions and more misclassifications in discriminant analyses. Combining the results of all methods used, an enrichment is observed near the ore for La, B and Cu in foot-wall rocks and for Pb, B, Mg, Cu and K in hanging-wall rocks, with depletion for Sn, Zn, Be, Ni and Cr in hanging-wall rocks. The geochemical halo in rocks can be detected up to 200m from the ore. The behaviour of chemical elements and the stratigraphical and structural controls of the deposit are in accordance with an exhalative hypothesis for the ore genesis. The secondary halo in soils is expressed by Cu, Pb and Zn concentrations, as revealed by a 126-sample orientation study and a detailed 600-sample prospective survey. In this survey, the cost for detection of the halo in rocks and soils has proved to be nearly the same. The sampling of rocks in traverses perpendicular to the main geological survey and analysis for Cu, Pb, Zn, B, Mg, K, Fe, Mn and Ca, are recommended for prospecting deposits similar to Perau in this province.

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MULTIDISCIPLINARY EXPLORATION OF THE BOG VMS PROSPECT BATHURST, NEW BRUNSWICK, CANADA

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The BOG volcanogenic massive sulphide occurrence lies within 3 km of the now mined out wedge deposit, in the Bathurst Camp of New Brunswick, Canada. Proper application of soil sampling first identified anomalous conditions, an initial routine survey conforming to normal industry standards failing. The prospect area is relatively flat. The BOG occurrence lies in a residual or residual-like (i.e., very local till) environment comprising 1 to 2 m of inorganic and upto 1 m of organic unconsolidated material. The prospect was found by drill testing a base metal anomaly defined by a Marlow deep overburden survey of 73 holes. The first drill intersection over 3.9 m averaged 18% Pb + Zn, 0.8% Cu, 70 gm/T Ag and 1.3 gm/T Au.

Conventional geophysical exploration and diamond drill testing of geophysical anomalies was unsuccessful. Moreover, orientation geophysical surveys have failed to locate the known massive sulphide occurrence, leading to the conclusion that the occurrence is too small to be geophysically responsive Lithogeochemistry of ore, pathfinder and alteration element anomalies defined by analysis of drill core were catalogued and metal zonation patterns amongst deep overburden samples mirror metal patterns in drill core. The B horizon soil survey provides a larger target displaced up to 50 m from its roots in bedrock. The case history illustrates the utility of a deep overburden survey preliminary to diamond drilling to test geophysical or other targets as a routine procedure. The BOG prospect evaluation has not resulted in a commercial discovery.

PRELIMINARY STREAM SEDIMENT ORIENTATION SURVEY FOR COPPER MINERALIZATION UNDER SEMI-ARID CONDITIONS, NORTH-EAST BRAZIL

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An orientation stream sediment survey was undertaken near Cu mineralization under semi-arid conditions in Paraiba State, NE Brazil. Mineralization in the study area consists of malachite and azurite disseminations in amphibolites intercalated with biotite schists and gneisses. The purpose of the study was to evaluate the effectiveness of different sediment size fractions and partial extraction techniques to delineate mineralization under semi-arid climatic conditions.

The firts phase of the program involved isolation of the minus 32 plus 80 mesh and the minus 80 mesh fractions of sediment material, metal extraction using (1) cold 1 M Na acetate, (2) hot 0.25 M hydroxylamine hydrochloride and (3) hot 4:1 concentrated HNO_3:$HClO_4$, and metal concentration estimation of Cu, Mn and Fe by AAS. All combinations detected mineralization. Hydroxylamine hydrochloride-extracted Cu in the minus 80 mesh fraction provided the optimum response, revealing a 6.3 X contrast and a 1.8km dispersion train. Na acetate-extracted Cu in the minus 32 plus 80 mesh fraction gave the lowest contrast (1.2 X) and negligible dispersion train. Iron data provide information to prioritize anomalies influenced by coprecipitation. Manganese concentrations in the area sediments were low and did not affect anomaly identification.

The second phase of the project assessed variations in response of Cu extracted by 0.25 hydroxylamine hydrochloride from the minus 9 plus 16 mesh and the minus 16 plus 32 mesh sediment fractions. Contrasts were 5X and 4.4X, respectively, whereas dispersion trains were 1.7km for both fractions. These values are comparable to those from the minus 80 mesh fraction and indicate that coarser fractions can be used. Considering the scarcity of minus 80 mesh material in active stream sediments of semi-arid environments, these results are highly significant for improved geochemical exploration under these conditions.

Technical Session
International Regional Geochemical Mapping

A CLASSIFICATION OF ORE DEPOSITS FOR REGIONAL GEOCHEMISTRY

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There have been many attempts to group ore deposit types ranging from purely descriptive classifications, such as, Smirnov (1968), to genetic classifications such as Lindgren (1933), and classifications based on associated host rocks (Staton 1972). I was the demonstration that Late Proterozoic to Phanerozoic mineral deposits could be related to their tectonic setting, as pioneered by Bilibin (1900) and later developed for plate tectonic analysis by Mitchell and Garson (1981) and Streng (1972), which provides the basis for modern classifications of ore deposits. This information, together with isotopic, fluid inclusion and petrological data, can be used to formulate mineral deposit models such as those which have been published, along with systematic compilations of their attributes, by the U.S. Geological Survey, the Geological Association of Canada and the Geological Survey of Canada (Eckstrand 1984). In general such models and compilations lack imput from systematic regional geochemical, geophysical and remotely sensed data sets, however, and exploration criteria have hitherto not been formulated explicitly for screening large spatially related datasets.

In this paper, a new classification of ore deposits is proposed, based on earlier compilations of deposit types, especially those of Eckstrtand and others. The classification is designed for the interactive analysis and integration of multi-element geochemical detasets in relation to geophysical and remotely sensed data using Image Analysis Systerms (IAS) and Geographical Information Systems (GIS). Two main groups of ore deposits can be distinguished. The first group consists of deposits with a sedimentary or sedimentary basin association. These include placers, paleoplacers and laterites as well as several types of U and base metal (Sedex and Mississippi Valley Pb-Zn and Kufterschiefer Cu) deposits, the genesis of which can be related to the tectonic and thermal evolution of sedimentary basins. Regional geochemistry can be used for the direct detection of such deposits but ore metals are generally concentrated from large volumes of rock by geological processes with only a slight decrease in the regional metal conentration. The main role of regional geochemistry in exploration and resource analysis for this type of deposit is thus the identification of favourable source provenances for deposits formed by descending groundwaters; or favourable sedimentary sequences where basinal fluids are the main source of metal. Lode gold deposits in Archean greestone belts are also considered to be related to basin evolution, whereby new crustal segments were formed following extensional orogenic basin development, and geochemical methods for identifying favourable settings for such deposits are described.

The second main group of deposits are those of volcanic and plutonic association. This group is subdivided into deposits formed by hydrothermal activity around volcanic or plutonic rocks emplaced at a high level in the continental crust and those formed by essentially magmatic processes in which any contamination pre-dates significant magmatic differentiation. Primordial mantle normalised trace element plots are presented to demonstrate variations in the primary geochemistry of igneous rocks associated with ore deposits of both associations and changes associeted with water-rock interaction to produce hydrotermal ore deposits are described.

EXTRACTABILITIES OF ELEMENTS - A NEW APPROACH TO INTERPRETATION OF REGIONAL GEOCHEMICAL DATA

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Regional geochemical mapping has been regarded as a useful method for studies and exploration and, more recently, for environmental studies, too. Increasing attention is being given to very low density sampling of different geomedia over extensive areas in the production of atlases. With a sparse sampling grid, it is possible to depict large-scale phenomena such as favourable regimes for ore-forming processes or areas sensitive to acid rain effects. Direct location of ore deposits or other small-escale features is rarely possible.

The first Geochemical Atlas of Finland is bsed on C-horizon till, sampled at a density of 1 smaple per 300km^2. Since the till is relatively local in origin, the data are considered to reflect well the distributions of elements in the underlying bedrock. First the -0.06mm fraction is screened for analysis, after which many of the 42 elements are determined by ICP-AES polychromator on two leachates: not concentrated aqua regia ("AR") and cold hydrofluoric acid, boric acid and nitric aqua regia ("HF"). The leachates generally give partial concentrations and the rate of extraction of an element depends on: a) chemical efficiency of the leaching agent(s); b) grain size distribution; c) mineral composition; d) distribution of the element among its minerals.

Carbonates, phosphates, sulphides and some oxides dissolve well in AR. However, silicates are partially decomposed and, thus, the leaching of elements incorporated in silicates depends on factores, such as, the ionic character of the Si-O bond, the silicate structure, the isomorphic composition and surface phenomena. It is noteworthy that the solubility of the secondary minerals, associated with alteration due to mineralization, is often fair.

The HF method is less selective and gives essentialy total concentrations for elements from most of the rock-forming silicates, carbonates, oxides, pphosphates and sulphides. Simple Al silicates and oxides, muscovite, garnets and spinels are poorly soluble.

At the regional scale of the Atlas, most of the element lost are expected to be carried by silicates and to a lesser extent by "mineralized" phases. Hence, characteristic solubility properties of different silicates must be a source of interesting information which can be exploited with the aid of concentration ratios such as M_{AR}/M_{HF} (extractability), trace M_{AR}/major M_{AR} or more complex analyses of data. Examples of observed extractabilities of some elements from the Atlas and solubilities of their host minerals are given in the following:

Element	**Estracta-bility Mar/Mhr**	**Host minerais**	**agua régia**	**Solu-bility hydrofluoric acid**
		biotite	fair	total
Barium	5 - 15 %	k–feldspar	poor	total
		plagioclase	poor-fair	total
		Ca-ric plagioclase	poor-fair	total
Calcium	5 - 15%	Ca-poor	fair	total
		carbonates	total	total
		amph./pyrox.	poor-moder.	total
		biotite	fair	total
Chromium	20 - 50%	chronmite	insaol.	poor
		pyroxenes	moder.	total
		caly minerals	poor	moder.

With the use of total concentrations (HF), the extractabilities and known solubilities of host minerals, many anomalies of the Atltas are easily interpreted by the mineral compositions of the source bedrock. Some extractability anomalies may be attributed to extensive alteration of the bedrock (e.g. the main sulphides ore belt of Finland). Acid rain mobilizes Al and other harmful elements in the soil, which may be reflected in or caused by anomalously hight ratio of Al_{AR}/Al_{HF} in other areas.

Many of the recently employed analytical techniques (AAS, ICP-AES, ICP-MS) for trace elements require insertion of sample solutions and thus permit analysis of leachates. Analyses of two or more carefully chosen leachates enables a more comprehensive interpretation and more applications than conventional total analyses (XRF, INAA) only. Analytical data on selectively leached samples can be particulary useful for modelling of formations and mineral deposits.

GEOCHEMICAL ANOMALIES MAP OF THE REPUBLIC OF CUBA AT A SCALE OF 1:500,000

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Toropchanina, S.
Brito, G.
Altarriba, I
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The map of complex geochemical anomalies at a scale of 1:500,000, was elaborated on the basis of the generalization of geochemical studies at the scales 1:100,000 and 1:50,000.

This map reflects the structure of the geochemical fields of some ore-bearing regions and characterizes the overlay of the monoelemental represetations of some geochemical fields. The anomaly contours of the indicative elements delimit the fields of development of metallogenic processes, and give information on the spatial distribution regularities of the chemical element associations for the solution of the prognostics metallogeny problem.

This map reveals 118 anomalies, obtained by different methods. The composition of these anomalies are denoted along the anomaly contour by chemical element symbols in descending order of their conventional productivities.

An adjoining catalogue, containing all the needed information for every revealed anomaly is attached. The evaluation of the anomalies are related to the analysis of the geological conditions, composition complexity, intensity and row of rank, such evaluation, together with geological and geophysical data, creates the basis for the quantitative approach to the mineralization forecast.

Also, this map allows precise determination of some elements, the geological constitution of mineral fields, metalliferous horizons, position of faults, etc.

PEDOGEOCHEMICAL MAP OF BAHIA STATE, BRAZIL: SECOND VERSION

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The project "regional geochemical orientative studies", undertaken by the SGM-SME-BA, showed the possibility of defining, from a pedogeochemical point of view, a limited number of homogeneous domains distributed throughout the State. The Pedogeochemical Map at a 1:1,000,000 scale (Nascimento & Teixeira, 1986) divided the soils of the State into domains on the basis of the degree of base saturation DS, and attempted to determine the influence of clay minerals, organic matter and secondary oxides of iron and manganese, as well as the granulometric distribution of the soil components, on the secondary retention of some chemical elements. At this point, so many questions remained open that a follow-up study was started and is still in progress. It is already clear that some modifications of and corrections to the Map are necessary, and a second version is being prepared.

Within the State, there are ample variations of geological substrate, present climatic conditions, natural vegetation, geomorphological situations and land use. Other factors of interest, such as local soil drainage and erosion rates, are practically unknown from a quantitative point of view.

Three main geological assemblages occupy roughly equal areas. Older Precambrian assemblages of various ages include low- to medium-grade, deformed metavolcano-sedimentary sequences together with their basement and associated granitoid intrusives. Some high-grade equivalents have been recognized. Subduction (island arc, continental margin, rear-arc basin), continent-continent collision and intracontinental anorogenic assemblages have been identified. The metavolcano-sedimentary sequences are, traditionally, priority prospection targets, and a number of mines are sited within them. Large extensions of medium- to high-grade terrains are, however, still inadequately studied.

Late Precambrian assemblages include an extensive platform sedimentary cover in the centre of the State. Brasiliano-age orogenic assemblages are restricted to small areas at the extreme N and S of the State. Phanerozoic assemblages include rift-related sediments in the E, internal basin sediments in the W, and widespread but thin sedimentary covers of diverse origins, deposited during the Tertiary and Quaternary.

Present climatic conditions are tropical, varying from humid within a narrow belt, parallel to the Atlantic coast, to semi-arid over much of the interior. Some ill-defined pockets of wetter micro-climate are present within the semi-arid. In the extreme W, where the Central Brazilian Plateau begins, the climate becomes sub-arid/sub-humid. Transitions between climate zones are usually quite abrupt.

The main geomorphological zones include a narrow coastal plain, with an usually smooth transition to the neighbouring zone. Highly dissected terrains are typical of the Atlantic coast granulite belt, and are also found as transition zones in other areas. Smoothly undulating country typifies the sedimentary areas, as well as large areas over crystalline basement. Mountain ranges and isolated blocks compose the last main terrain type. Transitions may be smooth or abrupt.

About 620 published soil profile descripptions include basic soil textural and structural details, together with routine soil size fraction and pedo-chemical results. Some profiles have accompanying qualitative microscopic descriptions of coarser size fractions and X-ray diffractometric analyses of finer fractions. This data base was complemented, during the first part of the study by about 90 samples collected on a regional scale, mainly over unmineralized rocks. During the follow-up, about 75 samples were collected on a detailed scale, divided between two areas of contrasting geological substrates, climatic conditions and regional geomorphological situation. In both areas, mineralizations are present.

After calculation of total cation exchange capacityu (TCEC), exchangeable bases (EB) and degree of saturation (DS = EB x 100/DS), statistical and linear correlation analyses were performed on data referring to the upper part of the B soil horizon or, where this horizon is absent or ill-defined, the C horizont was used. In the first version of the Map, with the small population of XRD results then available, a clear relationship was found between (Ca^{2+} + Mg^{2+} + Na^{+}) and the spectrum of clay minerals present. This, together with DS values, allowed the separation of soils with defined pedological evolution into three domains, each with two subdomains. A fourth category of soils, those with undefined evolution (regosoils, soils developing over alluvium, etc.) were not studied further.

In domain I (0 < DS < 30), latosoils and podzolics predominate. This domain type is widespread, and has the largest areal extension in the State. Kaolinite is the main clay mineral. In domain IA, gibbsite and chlorite are the accessory secondary minerals of greatest importance, and they are joined in domain IB by illite and vermiculite. In domain II (30 < DS < 70), kaolinite is still a major clay mineral, but it is joined by smectite in domain IIB. Gibbsite is absent, but the accessory clay minerals are the same as in domain IB. In domain III (70 < DS) , kaolinite remains important in IIIA, but is present only as an accessory mineral in IIIB. Illite appears in both sub-domains, while vermiculite is limited to IIIA. Domain III include neutral to alkaline soils.

In the follow-up study of a typical domain I within a zone of climatic transtion between humid and semi-arid, proportions of accessory clay minerals are reduced to traces. In any case, with the possible exception of vermiculite, these minerals are unlikely to have a significant influence on TCEC. In a second area over calcareous rocks under semi-arid conditions, smectite/kaolinite ratios may vary with position in the local relief.

Organic matter has a clear influence on TCEC. Strong or very strong correlations between TCEC and C_{org} are found in all domains. Over rocks of the crystalline basement under semi-arid conditions, undisturbed soils are suprinsigly rich in humic acid-rich material, but worked soils show rapid degradation. Over sedimentary, rocks in the semi-arid, and over all types under humid conditions, organic material is usually less abundant, and fulvic acid-rich.

Secondary oxides of iron and manganese have only been investigated in a qualitative fashion. Iron oxihydroxides are frequently important components of the cement which bins mineral aggregates, and also occur as thin films coatting and penetrating larger mineral grains. So far, pisoliths are un uncommon feature. Goethite is identified in many soils and is a major component of the clay mineral fraction in some cases. In red-toned soils, hematite becomes important.

A preliminarly study of site retention of Fe, Mn, Cu and Zn was attempted using sequential, selective chemical attacks; (i) acetic acid/sodium acetate, cold; (ii) hydroxylamine hydrochloride 1% cold; (iii) 100 vol. hydrogen peroxide; (iv) hydroxylamine hydrochloric 10% hot; (v) 1:1 agua regia hot. Part of the iron is always retained in less reactive secondary iron oxides, there being little difference between domains. Most copper is retained in resistanty minerals, although organic material and less reactive secondary oxides are also important. Inter-domain variation may be significant. Both manganese and zinc show more complex, domain-dependent behaviour. Manganese may be retained in easily leached sites, in very reactive secondary oxides, by organic material, in more resistant secondary oxihydroxides, and by resistant minerals, and the case of zinc is similar. The follow-up study includes these elements and Al, Ca, Ni and Co.

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THE FEASIBILITY FOR WIDE-AND ULTRA-WIDE-SPACED SAMPLING FOR GEOCHEMICAL MAPPING IN AUSTRALIA – INITIAL COMMENTS

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Interest in low density sampling for geochemistry stems from four prime perspectives:

- mineral exploration with regards to defining mineralized provinces;
- environmental geochemistry with regards to natural provinces and culturogenic impact on the environment;
- the desire for a national overview with regards to the above, that would be used by government agencies as well as private enterprise;
- as part of an international overview of Earth's land masses, which would have an obvious impact upon understanding the fundamentals of global geology, mineral exploration, enviromental health, and pollution studies.

Comments are made on aspects which would govern the feasibility of a national geochemical mapping endeavour for Australia, the paper being prepared in response to the launching of the IGCP Project 259, International Geochemical Mapping (Project Leader, Arthur G. Darnley, Geological Survey of Canada). The purpose of the paper is to initiate discussion both of the Australian environment, and regions or countries elsewhere that have similar regolith/landform characteristics. Another purpose is to facilitate identification of Australian researchers interested in the topic.

Australia has been divided into eight regolith/landform regions (CSIRO: Soils, an Australian Perspective, 1983). Existing knowledge of the applicability of specific sampling approaches is reviewed in terms of some of these regions, and provinces within them. The prime sampling methods considered include stream sediment approaches, soils, and laterite geochemistry. Hierachical choices to provide optimum information are discussed.

For such an excerise on a national scale, each region needs to be reviewed in terms of specific approaches that are operational, making comparisons of the characteristics of each approach. The need for research into additional possible sampling media would be highlighted.

Several examples of operational procedures of low density sampling will be presented, the characterintics of the methods compared and discussed.

THE INTERNATIONAL GEOCHEMICAL MAPPING PROJECT

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A world geological atlas was completed in 1984, having been in preparation for several decades. Tectonic, metallogenic and metamorphic maps have been published for many parts of the world. There are geophysical maps which display aeromagnetic and gravity data for large regions, for example North America. Unfortunately, until recently, very little consideration has been given to the desirability of having a world geochemical atlas to provide a systematic overview of relative geochemical abundance levels, regional trends and anomalous patterns.

Surficial geochemical data are relevant to a wide variety of mineral resource, agricultural, forestry, environmental and health quaetions, as well as fundamental geological investigations. Systematic maps created from a suitable data base can provide ans index and a strarting point for detailed studies relating to the many apllications of geochemistry.

Technical Session
Environmental Geochemistry

GEOCHEMICAL BACKGROUND: IMPLICATIONS FOR ENVIRONMENTAL GEOCHEMISTRY IN NOVA SCOTIA, CANADA

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Since the early 1950s, exploration geochemical surveys have been carried out on a variety of surficial materials in Nova Scotia. To date most of this effort has been directed exclusively at resource potential applications with the intention of stimulating development in the mineral sector of the economy. During this exploration phase an extensive geochemical database has been collected. A traditional mineral producer, Nova Scotia has a high population density sharing a relatively small area. This demographic reality exacerbates a land use issue often represented as a conflict between the desire for a clean environment versus the need to generate wealth from the abundant mineral resources of the province. The impact of mineral development on the landscape and quality of life is an important environmental issue in North America and especially Maritime Canada.

Most geochemical exploration activity has concentrated on stream or lake drainage systems by sampling sediments and/or surface waters. Lake and stream catchment basins are important repositories of geochemical information concerning the composition and characteristics of their drainage areas. Modern drainage systems can be considered as mass storage devices (Ogden et al., 1988) which contain the 'geochemical genetic code' for each catchment. The extension of the catchment basin concept to exploration geochemistry (Bonham-Carter et al., 1987) forms a bridge to environmental geochemistry. This paper will consider studies of a number of catchment basins in Nova Scotia.

One of the principal aims of exploration geochemistry is the estimation of geochemical background to define threshold levels and indicate anomalies. Recognition of 'natural' background levels in surface materials of various elements is needed to define baseline element levels and principal controls + and to monitor changes in the ecosystem. Widely different element levels can be found in stream and lake systems. It is possible to define various natural and imposed geochemical controls present in stream and lake drainage systems. Principal geochemical factors governing background levels include catchment lithology, chemical mobility, and dispersion and dilution of metals during transport. pH is one of the most active geochemical factors and also the one most readily affected by imposed external loading, such as, from acidified rainfall. To estimate the pH effect on heavy metal mobilities, background levels and vector properties of these metals in natural systems must be elucidated.

Catchment basin analysis (CBA) has been used to characterize background for 1,500 stream sediment and water samples from the Cobequid Highlands. Background is modelled for element concentrations in stream sediment as a function of the areal proportion of map units occuring within each catchment basin. Step-wise regression uses areal proportions of mapped units as independent variables to model geochemical background for Cu, Pb, Zn, Ag, Fe, Mn, Ni, Co, As, Hg, U and Mo in sediment and U, F and pH in water for each of 65 mapped lithologic units. Calculated background levels for each map unit are given as weighted means for each element. The model thereby determines a measure of the association between the geology and surficial geochemistry. Volcanic and granitic units of the central upland core have much higher background levels for most elements when compared to other units. After subtraction of background, the residual variance of catchment basins reveals areas of anomalies, which, as elevated concentrations, could be seen as potential hazards in terms of heavy metal content. The CBA model also distinguishes variance due to scavenging by Fe and Mn and pH effects on the mobility of elements, such as, U, Mo and As. Catchment basin plots for these elements clearly outline the pH response in terms of the underlying geology.

We call attention to, and illustrate, two important properties of limnic systems:

a) Catchments with definable sub-watersheds can show distinctive biostratigraphic and geochemical signatures throughout the lake basin. We describe Soldier Lake, Halifax County, Nova Scotia (Ogden and Rogers, 1988) which has a hydrogen ion $[H^+]$ gradient from distinct sub-watershed units ranging from 0.7 μeq L^{-1} (pH 6.2) to 102.3 μeq L^{-1} (pH 2.99). Mass balance studies (Ogden and Machell, 1985) indicate retention (presumably by deposition) of 33% of Al, 63% of organic C, and 85% of Fe entering the lake. Outlet pH values of 4.6 (25.1 μeq L^{-1}) imply neutralization of 38% of the $[H^+]$ entering the lake. We show the presence of distinct geochemical and biostratigraphic (diatom) domains related to water chemistry, independent of regional (allocthonous) pollen deposition.

b) Sediment cores from three connected lake basins in the St. Margaret's Bay area, Halifax County, Nova Scotia, which have shown substantial acidification, with pH values from 6.0 to 6.3 in 1979 and from 4.8 to 5.6 in 1987, reveal four goechemically (and biostratigraphically) distinct horizons or zones:

1) Initial (ca. 12,500 RYBP (Radiocarbon Years Before Present)) high energy meltwater deposition of coarse (sand and gravel) sediment including a large proportion of extra-catchment materials, with little or no organic matter.

2) A silt to clay transition horizon (ca. 11,500 RYBP) with very little organic carbon and very low hydraulic permeability (Ogden, 1986), which effectively seals an initial catchment geochemical signature unaffected by biological modification.

3) A mid-postglacial period of warm/dry conditions (3500-5500 RYBP) of reduced hydraulic throughput, increased organic production, and longer water residence times, which provided increased opportunity for organic/inorganic geochemical interaction.

4) A post-colonization period of increasing anthropogenic influence, land disturbance, and changing atmospheric geochemistry.

In the St. Margaret's Bay area, development and construction activities have been primarily limited to the Five Island Lake catchment area, and are mostly residential and seasonal cottage developments. A number of new residential developments are currently under way in this watershed, and may be expected to change both runoff and water quality as development pressures continue to affect many of the present hydrogeochemical parameters. With increasing acidification, we infer the development of geochemical deposition domains in these lakes in future, similar to those described for Soldier Lake.

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GEOCHEMICAL ENGINEERING AND THE ENVIRONMENT

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Geochemical engineering is defined here as the dsicipline that uses (geo-)chemical means to modify the enviroment. Goechemical engineering is related to environmental geochemistry in a similar way to that in which biotechnology is related to biology.

There are five fundamentally different options to solve environmental problems, namely:

- decay, breakdown or neutralisation
- concentration
- dilution
- immobilization
- isolation

Each of these options has counterparts in nature. The study of natural processes can help us to develop new environmental technologies, but most natural geochemical processes proceed at too slow a rate to be technologically feasible. We must therefore optimize these processes to achieve acceptable rates, which can be done by raising the temperature, and increasing the reactant surface and the concentrations of the reactants.

Some of the examples that have recently been developed by our group, and that find their inspiration in geochemical processes include:

- the neutralization of industrial waste acids with olivine, mimicking the process of chemical weathering.
- the removal of fluoride from high fluorine drinking waters by passing them over beds of gypsum grains; by thus increasing their calcium concentration, the solubility of fluorite is exceeded, and fluorite precipitates.
- the removal of phosphate from organic waste streams by the addition of magnesia. As most organic waste streams contain an excess of ammonia and/or potassium, the mineral struvite, an ammonium- or potassium magnesium phosphate is formed, which is a valuable fertilizer.

Local high levels of toxic trace elements are a normal feature of nature, and ore deposits are the most dramatic example. By studying the ways in which nature minimizes the impact of such "pollutions" on the environment, it is often possibel to design cheaper, more effective and environmentally soud sanitation technologies.

GEOLOGY OF ACID RAIN IN CANADA

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An ongoing problem in evaluating the effects of acid rain is distinguishing natural (spatial) variations of the geochemical environment from anthropogenic (temporal) variations. In other words, it is important to determine whether a lake is naturally acid because of it's geological setting, or whether it has been acidified as a result of dry and wet acid deposition. To provide a model that might aid in answering these questions, the Geological Survey of Canada has carried out a series of sampling programs on the south central part of the geologically complex Canadian Shield. With these programmes we have tried to link the easily observable lithological variations of bedrock with the chemical composition of overlying glacial deposits with the geochemical compositions of lake sediments and lake waters. Presumably, once these linkages are understood, variations in life systems that inhabit terrestrial and aquatic environments in the areas sampled will be easier to evaluate.

The ultimate goal is to provide a base against which observed variations in life systems can be judged as natural or anthropogenic. In addition, sound geological data can be used to refine estimates of SOx and NOx target loadings and to determine areas where acid deposition may mobilize potentially noxious trace metals into the hydrologic cycle.

The importance of establishing geological and geochemical linkages is illustrated by the fact that significant parts of the Canadian Shield, while formed of granitoid rock, are overlain by calcareous unconsolidated sediments that have been glacially transported long distances from limestone sources. For instance, in areas north of Lake Superior and in Eastern Ontario, high concentrations of carbonate minerals in glacial sediments overlying carbonate-poor bedrock result from glacial transport of carbonate minerals tens to hundreds of kilometres from limestones on their up-ice sides. In these same areas, high concentrations of As, Hg, and other trace elements in sediment and water can be related to glacial dispersal from bedrock, known to host mineralized occurrences, or high background concentrations of these elements.

Awareness of bedrock composition and of glacial distortion of the chemical signature of bedrock is essential for insuring that a complete and credible database is provided to the legislators and regulatory agencies charged with establishing realistic target loadings for acid deposition.

THE OCCURRENCE AND GEOCHEMISTRY OF FLUORIDES IN NATURAL WATERS WITH REFERENCE TO THEIR GEOMEDICAL IMPLICATIONS

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General geochemistry

Elemental fluorine, the most electronegative and reactive of all elements, is a common component in lithosphere, although its concentrations are low. In surficial exogenic and hidrological cycle F is predominantly of geogene origin and is derived only to a minor extent from oceans as airborne sea water spray and from anthoprogenic sources. It occurs as a fluoride ion in mineral lattices and is released in weathering into aqueous solutions as a relatively mobile anion.

The average F content in magmatic rocks is only 0.03%, but there are large variations depending on the rock type. Unorogenic rapakivi granites exhibit by far the highest F concentrations among all granites: 0.2-0.4% and 0.05-0.1%, respectively (Sahama 1945, Vorma 1976). Concentrations diminish towards more subsilicic varieties of plutonic rock types, such as, gabbros and peridotites (down to 0.05-0.002%, Allman and Koritning 1978). The granite veins in migmatites may locally increase F contents.

The most important F-bearing minerals are fluorite and fluor-apatite, wich are common accessory minerals in rapakivi granites and to a lesser extent in ordinary granites. Topaz and turmaline play a minor role. Among the main F sources in rapakivi and ordinary granites are OH-bearing minerals, such as, micas and amphiboles and, sometimes, pyroxenes and chlorites, where F concentrations may range from 0.2 to 1.1% (Simonen and Vorma 1969).

The common regional metamorphic rocks are impoverished in fluorides (generally 0.01-0.05%), which mainly occur in micas, amphiboles and chlorites. Also, sedimentary rocks show generally only low F concentrations.

In some young alkaline volcanic rocks, there are exceptionally high F concentrations. The Neogene nephelitinites and phonolites of Mount Meru volcano, in Arusha, Tanzania, the average F concentrations are 0.15 to 0.32% (Gerasimovsky and Savinova 1969). High weatherability of porous volcanics and highly soluble secondary F-rich precipitations (trona, villiaumite) in soil, together with profuse seasonal rainfall, mobilizes abundances of F into surface and groundwaters.

Fluoride concentrations in natural waters

In a hydrogeochemical mapping project in Finland about 5,900 water samples were collected from springs and from wells dug into overburden and drilled into bedrock and analyzed for main cationic and anionic components including fluorides. The Wiborg rapakivi granite batholith with its satellitic Suomenniemi and Mantyharju intrusions in southeasterns Finland and Laitila, Vehmaa and Aland rapakivi granite plutons in southwestern Finland emerge strikingly as anomalous province from the rest of the country, wich depicts less than one order of magnitude lower F concentrations (figure 1).

The average F concentrations in groundwater representing rapakivi granite areas are 1.0-2.0 mg/l, while in the rest of the country concentrations are generally less than 0.1 = 0.2 mg/l. The same conditios prevail is stream waters draining catchments composed of rapakivi granites. Elevated F concentrations are independent from the chemical type of water and total amounts of dissolved componentes.

In many parts of the world natural waters contains high abundances of fluorides. The tropical and subtropical climate with seasonal rains favour weathering processes of rock and soils, releasing fluorides into waters, while high evapotranspiration strongly enriches F concentrations in solution. Although the highest F concentrations are found in the areas composed of young alkaline volcanics, the elevated concentrations in waters of granitoid areas are, from the regional point of view, more important in Africa and particularly in India and China.

The F concentrations may reach the values of 10-50 mg/l in groundwaters, while in running surface waters, they are generally lower (Bugaisa 1969, Nanyaro et al. 1984). In some ponds and lakes, functioning as evaporation basins in the easterns African rift valley, F concentrations may reach the level of several hundreds of mg/l (Kilham and Hecky 1973).

The low Ca concentrations are replaced by sodium in F-rich natural waters, which are generally of Na (HCO_3) type. The low Ca contents allow high F contents to be mobilized. In semi-arid environments, salts are concentrated in topsoil to be flushed away during the rainy season. $Na_2(CO_3)$, $Na(HCO_3)$ and $2H_2O$ salts or magadi (trona), encountered commonly in eastern African rift valley, are sometimes very-F-rich. With the onset of the rainy season, they contribute to F concentrations in surface waters and shallow groundwater.

Health implications caused by fluorides

Fluorides are among a few elements which are ingested by man and higher animals, mainly through drinking water. In Filand, this is, however, true only in the rapakivi granite areas, where the average F concentrations in drinking water are well within the recommended range of 1 to 1.5 mg/l. consequently, the F intake through water may be several milligrammes per day, while the estimated intake through Finnish food is about 0.5 mg only (Varo and Koivistoinen 1980). The elevated F concentrations have been found to reduce the incidence rate of dental caries in Finland (Parviainen et al. 1977). Only in exceptional cases do F concentrations exceed the upper permissible limit of 3.0 mg/l and no F toxic effects were recorded in this country.

The overwhelming part at this country's waters contain too low concentrations generally below 0.1-0.2 mg/l. In spite of this fact there is only one town (Kuopio), which has resorted to the fluoridation of water distributed to the public. This is mainly because the beneficial F range is quite marrow and must be carefully monitored. Furthermore, only a small fraction of distributed water is used for drinking, wich makes tis expensive process doubtful.

The tendency of mobile fluorides to be enriched in water under strong evapotranspiration in tropical and subtropical conditions and, on the other hand, the large amount of drinking water consumed particularly by outdoor labourers enhance the health problems caused by excess fluorides. Tens of millions of people, particularly in eastern Africa (Tanzania, Kenya and Ethiopia) and in vast areas of India and China, are affected. The dental fluorosis, causing mostly aesthetic problems by staining the teeth, is quite cammon in F-inflicted areas. The most deleterious is, however, skeletal fluorosis, which is also encountered in eastern Africa (e.g. Nanyaro et al. 1985, Lahermo 1987), India (e.g. Teotia 1981) and China (e.g. Minggao et al. 1986).

In tropical and subtropical regions of Brazil, there are large granitoid areas, which are potentially hazardous areas in terms of fluorous groundwater. Surface waters do not, however, generally cause concern in this sense.

Other geochemical applications of fluorides

Fluorides, being quite mobile elements, are among the most suitable hydrogeochemical pathfinders in mineral and ore exploration. It can be used in the prospecting of copperpyrite type deposits, but is most

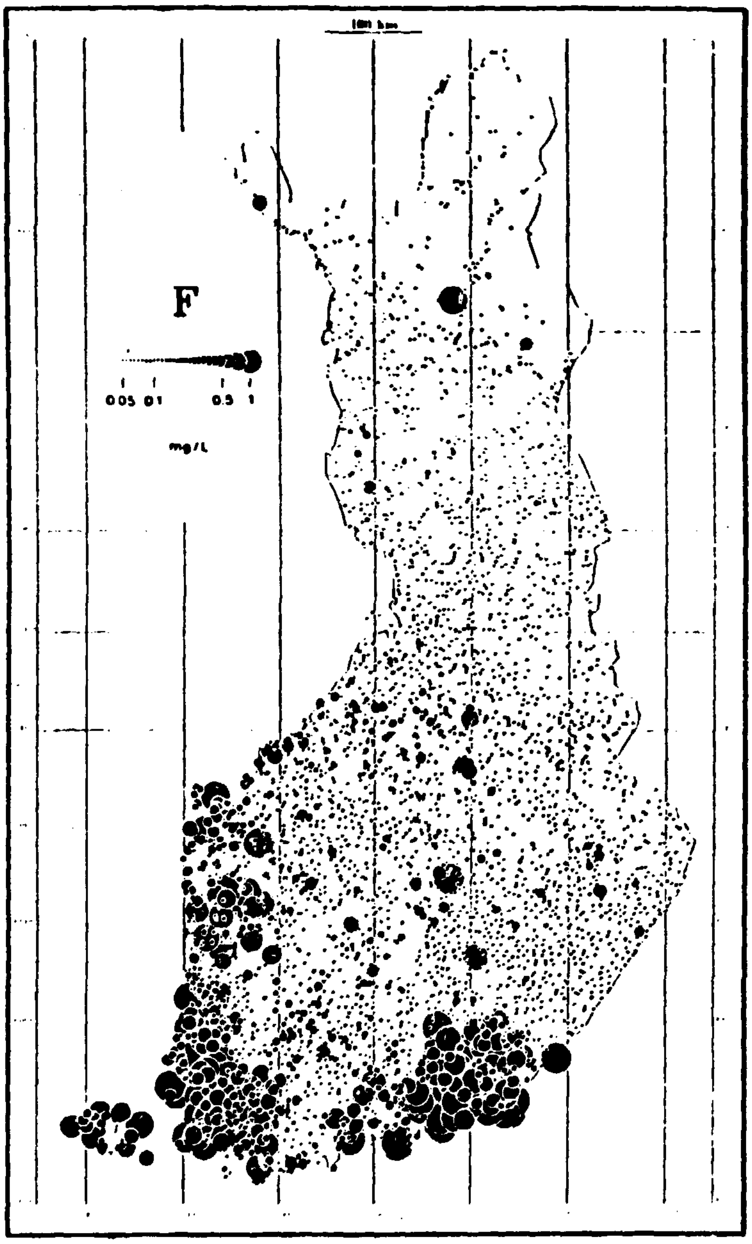

Figure 1 – F concentrations in groundwater from wells dug into overburden in Finland. The consistently anomalous provinces in the southeast and southwest of the country are composed of rapakivi granites.

suitable in granitoid areas in searching for Mo and Sn ores and beryllium-fluorite deposits (of. Miller 1979). Also it offers a potential method for delineating the occurrence of carbonatite massives.

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SAMPLING VARIABILITY OF RADON IN SOIL GASES

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Little information is available on the long-term reproducibility of radon in soil gases, or on the vertical distribution of radon concentrations in soil gas. For five sites in central Pennsylvania, the radon activity in soil gas at depths exceeding about 70 cm varies by factors of 3 to 10 during the year. Values are low in winter and high in summer, apparently because radon diffusion into air-filled pores is inhibited in the wet soils of the winter season, possibly accentuated by temperature effects. Values at depths, shallower than about 70 cm, at one site studied in detail, appear to average slightly higher in winter than summer, but with erratic highs and lows defining a 3-fold annual range.

Vertical profiles show reversals and other features differing from previous models for simple diffusive transport. The limited literature on long-term variations indicates that 3- to 10-fold seasonal variations are common. Most other studies show high radon in winter or in wet or frozen soils, attributed to capping by saturated or frozen soil, but clay-rich soils in Sweden have their highest radon in summer and fall. Soils that crack in dry weather can have low radon.

These phenomena must be considered in comparing surveys performed during different seasons and interpreting surveys of soils with laterally differing texture or moisture content.

THE EFFECT OF SCALE ON THE INTERPRETATION OF GEOCHEMICAL ANOMALIES

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The purpose of geochemical surveys changes with scale. Regional surveys at scales of 1:100,000 or smaller identify areas where mineral deposits are most likely to occur, whereas intermediate surveys at scales of 1:10,000 to 1:50,000 identify and prioritize specific targets. It is usually only at detailed scales, larger than 1:10,000, that specific deposit models may be applied and deposits delineated.

The interpretation of regional geochemical surveys must take into account scale-dependent differences in the nature and objectives of this type of survey. Overinterpretation of regional data should be resisted, as should recommendations to restrict intermediate or detailed follow-up surveys in the search for specific deposit types or in a too-limited suite of elements. Regional surveys identify metallogenic provinces, within which a variety of deposit types and metals are most likely to be found. At intermediate scale, these regional provinces often dissipate into discrete clusters of anomalous areas related perhaps by a common structural setting or tectono-stratigraphic terrane. At detailed scale, individual anomalous areas reflect local conditions of mineralization and may seem unrelated to each other. Four examples from arid environments illustrate the dramatic change in patterns of anomalies between regional and more detailed surveys.

On the Arabian Shield, a broad regional anomaly reflects the distribution of highly differentiated anorogenic granites. A particularly prominent part of the regional anomaly includes, in addition to the usual elements related to the granites, the assemblage of Mo, W, and Sn. Initial interpretation suggested potential for granite-related, stockwork Mo deposits. Detailed work within the prominent anomaly led to three separate sources for the anomaly: a metal-rich granite, a silicified and stockwork-veined area with scheelite and molybdenite, and scheelite/powellite concentrations in skarn deposits adjacent to a ring-dike complex.

Regional-scale geochemical, geophysical, and remote-sensing data in the Sonoran Desert, Mexico, define a series of linear features interpreted to reflect fundamental, northeast-trending fractures in the crust that served as the prime conduits for mineralizing fluids. At a larger scale, the linear, northeast-trending anomalies can be shown to result from a series of discrete mineralized systems with different ages and mineral assemblages. The linear pattern of anomalies disintegrates. In the case of porphyry deposits, concentric anomalies for the base metals are zoned around a common center.

A regional-scale geochemical survey in the Sonoran Desert in southwestern Arizona displays a cluster of samples anomalous in Pb, Mo, Bi, and W. In detailed areas, additional anomalous elements correlate spatially with this initial element suite, and the original regional anomaly separates into four discrete anomalous areas, each with its own distinctive suite of elements, geographic distribution, and age of mineralization. These four anomalous areas are evidently juxtaposed fortuitously in a complex structural mosaic.

A prominent regional gold anomaly in the Gobi Desert, Xinjiang, Peoples Republic of China, extends southeastward for 30 km from known lode gold deposits. Because the anomaly cuts both lithologic units and the structural grain, and because it parallels the prevailing direction of high-velocity winds, it was originally attributed to aeolian dispersion. At a detailed scale, the regional anomaly consists of several east-west-trending anomalies, parallel to local lithology and structure. These most likely reflect independent sources of lode gold. The regional anomaly results from smoothing, which is inherent to regional surveys, of an en-echelon set of local anomalies.

These examples emphasize that interpretation of regional anomalies must be tempered to consider regional-sized geologic features. Attempts to overinterpret anomalies by assigning deposit-scale attributes to regional anomalies can lead to confusion and incorrect interpretations, and can cause the overlooking of potential targets that can be readily echieved only at intermediate or detailed scales of study.

THE EFFECT OF TILL ACIDIFICATION

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The acid neutralizing capacity of till, as well as some weathering reactions promoted by increasing acidity, were studied in a number of tills in northern Finland. Different types of morainic landforms were considered, including drumlins, rogen-moraine, disintegration moraine and end moraine.

pH-profiles were measured in the field. In the laboratory the samples were sieved into three fractions: 0.06, 0.06 - 0.25, 0.25 - 0.6 mm. From each fraction the acid neutralization capacity (ANC nmol/100 g sample) was measured as a function of the varying acidity of solution. Further, the concentrations of Al, Ca, Mg, Fe, K, Mn, Zn, Cu, Pb and Sr were analyzed. The results are presented as graphs of ANC versus final pH of solution and as graphs of element concentration versus final pH.

The results clearly suggest that the acid neutralizing capacity of till correlates well with grain-size and also with sample depth. The solubility of each of the elements is bound to a certain pH-range: these were measured.

The pH measured in the test pits was lowest just below the ground surface (minimum 4), rises fairly rapidly to about 6 at a depth of about 1 m and then remains more or lesse constant with additional depth. The increasing acidity caused by acid rain, together with the natural soil forming processes, can lower the pH in the surficial part of till so much that toxic Al^{3+} dissolves, but precipitates again deeper down, where the pH is higher.

Technical Session
Unconventional Methods in Exploration Geochemistry and other Papers

A MICROBIAL METHOD OF MINERAL EXPLORATION: A CASE HISTORY AT THE MESQUITE DEPOSIT, SOUTHERN CALIFORNIA

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A new method of gold exploration, using a particular soil bacterium, *Bacillus cereus*, has been successfully tested over a variewty of mineral deposits in terrains ranging from desert shrub vegetation to boreal forest. Survey results from a study conducted in an arid environment over the Mesquite disseminated gold deposit, southern California, are presented in this report, Mineralized bedrock is exposed at the surface and extends up to 300 feet beneath alluvium. Soils and creosote samples were collected and analyzed for gold to determine if gold concentrations could be used as an exploration guide. Results show increases in *Bacillus cereus* spore populations coincident with the known location of buried disseminated ore. Gold concentrations in creosote vegetation, on the other hand, define only surface outcrops of mineralized bedrock. Soil gold concentrations, when collected at the basde of creosote vegetation, delineate the trend of the ore body at the surface nd at deapth.

An effective exploration program for buried ore deposits in extremely arid terrains of this region would involve sampling soils at the base of vegetation and analysis of soils for gold and Bacillus cereus concentrations.

ABUNDANCE OF TELLURIUM IN TILL AND ITS USEFULNESS AS A PATHFINDER FOR GEOCHEMICAL PROSPECTING

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The distribution of tellurium (Te) in the Earth's crust and especially in soils is scarcely known. This is due to its minor economic significanceand the lack of applicable analytical methods. Te is the most abundant element, with a atomic number above 40 in the solar system (Anders and Ebihara, 1982), but according to most estimates (1-5 ppb) it is one of the least abundant of all elements in the Earth's crust (Rosler and Lange, 1979). However, Te is among the most abundant trace elements in the human body (Schroder et al, 1967) being exceed only by Fe, Zn, and Rb (ICRP, 1975), all of which are many orders of magnitude more abundant in bedrocks than in the human body. Te is also rather abundant in food (Schroder et al, 1967). In the light of this inconsistency, Cohen (1984) has presented the question as to the real abundance of Te in soil, which is the major source of "minerals" for the human diet and body.

Independent tellurides of Au and Ag are common minerals in gold deposits (Boyle, 1979) and therefore could be a useful pathfinder in geochemical prospecting for gold. Furthermore, Watterson et al. (1977) assume that Te may indicate other kinds of mineral deposit (Pb-Zn-Ag and Cu-Pb-Zn veins, porphyry Cu and Mo deposits, Au-Ag deposits) and recomend inclusion of Te in geochemical exploration programmes.

In northern Finland, the determination of Te has been included in the geochemical mapping programme of till for some years and a few thousand Te values are now available. This was made possible by the development of a rapid and simple analytical method for Te at ultra-trace levels (Niskavaara and Kontas, 1989). The digestion and preconcentration methods are the same as those used for precious metals (Kontas et al., 1986). The method is based on aqua regia digestion and reductive coprecipitation of Te with stannous chloride as a reducing agent and mercury as a coprecipitant. The measurement is carried out by graphite furnace AA8, equipped with a Zeeman background corrector. The detection limit of the method is 3 ppb of Te in the sample.

Till samples are taken from the upper part of the overburden (unaltered C horizon) with a sampling density of one sample/4 km^2 (regional) and 16 samples/km^2 (local). After rying, the samples are screened and Te is determined from the -0.06mm fraction.

The Te contents of till have been shown to delineate clearly areal features of bedrock as well as some minor features. The abundances of Te in the fine fraction of till are rather high compared with estimates of its abundances in the Earth's crust. The median contents in various bedrock areas are as follows: granite 9 ppb, metasediments and meta-basalts 20 ppb and granulite 40 ppb.

On a regional scale, Te and Au anomalies do not generally coincide with each other. It seems that some bedrock units (potentially mineralized) produce most of the Te anomalies observed. However, on a local scale, high concentrations of Te in till can indicate mineralized zones of Au better than Au itself (A. Hartikaimen, prs commun., 1989). To date, we have no experience of the usefulness of Te as a pathfinder for other kinds of mineralization; more studies are required for them.

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AMMONIUM AS A CRITERION IN GEOCHEMICAL PROSPECTING FOR GOLD DEPOSITS

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The improvment of the already known and the development of new geochemical prospecting make it necessary to identify and employ the criteria which characterize the effect of the major ore deposition factors. Our experimental studies and the thermodynamic analysis of equilibria in the Au-Cl-S-Na-H_2O system allow elucidation of the main features of the behaviour of gold in the hydrothermal process and quantitative evaluation of the role of redox geochemical barriers in the gold concentration and scattering processes.

It was demonstrated that the decisive part in the behaviour of gold in natural hydrothermal systems is defined by process controlling the variation of the acidity and redox potential of minralizing media. A quantitative estimate of the participation of different forms of the fluid's volatile components (C, H, S, N) in gold mineralization was made; the estimate attested to the crucial role of various forms of carbon and sulphur in hydrothermal process (Figure 1).

Examination of the chemical composition of the organic matter and the isotopic composition of carbon in ore body carbonates points to an extensive participation of organogenous carbon in the hydrothermal process.

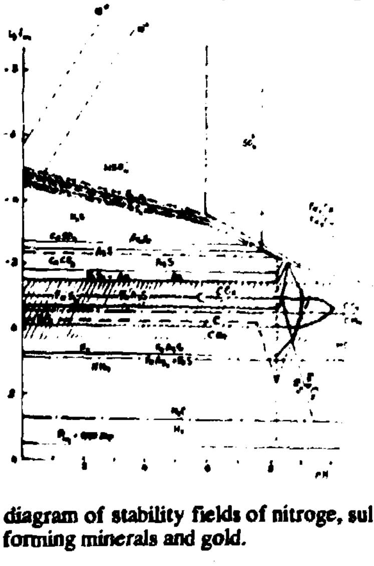

Fig. 1 – The diagram of stability fields of nitroge, sulfur, some ore-forming minerals and gold.

Bitumouids from ore associations, in contrast to preproductive and postproductive ones, are distinguished by oxygen concentration, lower hydrocarbon content, and the disappearance of nitrogen from the organic matter. Simultaneously, an analysis of gas liquid inclusions in vein quartzs of productive mineral association indicated the emergence of noticeable amounts of NH_4 ion in solution (Figure 2). Since the organic matter is an active reducing agent in the pH range determined by the potash feldspars-mica buffer system, a proportion of potassium in the newly formed hydromicas and potash feldspars should be substitute by NH_4 ion. Therefore, the presence of NH_4 disclosed in walk-rock metasomatites (micas, feldspars, pelites, montmorillonites) can be a sufficienily reliable criterion for deep-seated intense oxidation of the organic matter occurring in the redox potential range, providing for the reduction and precipitation of gold, silver, and a number of ore elements.

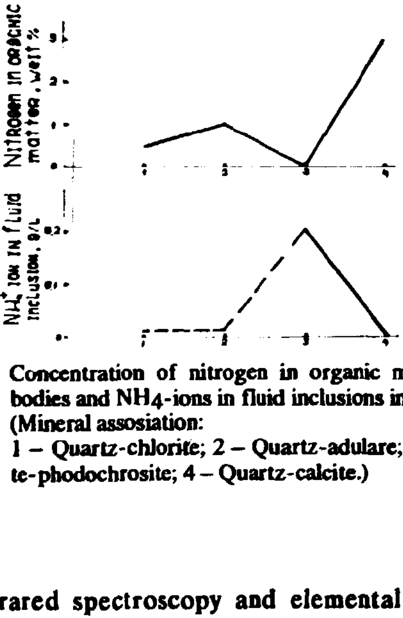

Fig. 2 – Concentration of nitrogen in organic matter of ore bodies and NH_4-ions in fluid inclusions in quartz. (Mineral assosiation:
1 – Quartz-chlorite; 2 – Quartz-adulare; 3 – Rodonite-phodochrosite; 4 – Quartz-calcite.)

Infrared spectroscopy and elemental chemical analysis (inluding our method of quantitative determination of NH_4 ion in micas, featuring the $1*10^{-2}$ wt.% detection limit, and the + 10% error) were employed in studying the state and concentration of nitrogen in micas of wall-rock metasomatites of a number of gold sulphide deposits (Fig. 3). It was found that the concentration of NH_4 ion in icas varies in the $1*10^{-2}$ - $6*10^{-1}$ wt.% range and can be used in evaluating the productivity of mineralization zones. The maximum ammonium concentration were noticed in walk-rock metasomatites of upper horizons of ore bodies with sulphide and gold mineralization.

The estimation of concentration of paramagnetic nitrogen-bearing centers in potassium feldsapars of ore bodies and alteration zones was made by EPR technique (figure 4). A regular distribution of NH_4-bearing feldspard around the zones with gold mineralization was established.

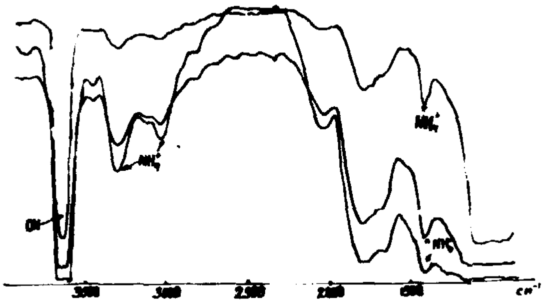

Fig. 3 – Infrared spectra of NH_4-bearing micas.

Fig. 4 – EPR-spetra of NH_3 ion radical in K-feldspars.

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AMMONIUM GEOCHEMISTRY OF SOME MEXICAN SILVER DEPOSITS

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Lithogeochemical sampling in the Guanajuato, Pachuca and Tayoltita silver mining districts of Mexico has revealed the presence of significant ammonium anomalies related to minerealised veins. The anomalies can be recognised in surface as well as mine crosscut and drill core samples and persist over depths of seveal hundreds of metres. Ammonium halos are best developed in the hanging-walls of major veins bu anoalous concentrations are also found in footwall regions.

The most detailed sampling has been carried out in the Guanajuato region at La Peregrina ans El Cubo mines. At the surface, pronounced ammonium anomalies extend for over 200m in the hanging wall to the Veta Villalpando. Similar anomalies occur in association with other veins in the area, but commonly used lithogeochemical indicator elements generally show no systematic relationship to the mineralisation. Data on surface, drillcore and mine samples allow the three-dimensional shape of the anomalies to be examined.

At Pachuca sampling was limited to underground traverses and, although hangingwall ammonium halos to the major veins were discovered, the results in relation to minor veins are not as clearcut as in the Guanajuato region. Surface and mine sampling at Tayoltita has also yielded anomalously high ammonium concentrations in association with major mineraised veins. In both areas ammonium compares very favourably with other geocheical indicators as a guide to proximity to mineralisation.

The results of this study suggest that ammonium geocemistry has considerable potential as an exploration tool for precious metal vein deposits.

CURATELLA AMERICANA LIN. AS A BIOCHEMICAL SAMPLE IN THE TILARÁN-MONTES DEL AGUACATE GOLD BELT, COSTA RICA.

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The Tilarán-Montes del Aguacate gold belt, Miramar Quadrangle, Costa Rica is a one in active exploration for and exploitation of epithermal gold deposits (Astorga & Campos, 1989; Ludington, Bagley & Bolivar,1987; Bolivar et alii, 1987).Biogeochemistry has not been used asan integrated part of geochemical exploration projects in Latin America. The possibility that the tree, *Curatella americana* Lin. (common name "raspa"), is a gold accumulator and can, therefore, be used in prospecting some districts of the gold belt,was suggested by Siegel & Segura P. (1989). The targests for exploration in the gold belt are high grade, low tonnage gold-bearing epithermal quart veins and low grade gold mineralized zones surrouding many of the higher grade vein systems.

Ten samples of *Curatella americana* Lin. were collected in a traverse across Cerro Conchal which is located near two active open-pit gold operations. Cerro Conchal has not been exploited presumably because any exploration there did not give indications of economic mineraliation. The traverse crossed a north-trending quart vein. Subsamples of twigs and closed pods from the vegetation were dried (not ashed) and analysed by neutron activation analyses for Au, its associates As and Sb, andother trace components (e.g., Co, Zn, Fe, Br). The analysis showed that Auin the dry plant matter is more concentraded inthe twigs (average of 2.9ppb) than in closed pods (average of 1.2ppb). In general, Sb acts similarly with 80ppb in twigs versus 50ppb in closed pods. However, As is more concentrated in closed pods (130ppb) than intwigs (90ppb). Spatially, Au, As and Sb in both twigs and closed pods of *Curatella americana* Lin. define the position of the quart vein, with the best definition shownby the twig geochemical data (figure 1). A soil samples with the highest Au concentration (1,000ppb - in the < 0.5mm sie fraction) ins closest to the quart vein and corresponds tothe tree with the highest concentration of Au in the twigs (7.2ppb) and in theclosed pods (2.4ppb).

The ten-sample traverse provides a satisfactory estimate of background values for Au, As and Sb in *Curatella americana* Lin. twigs and closed pods in this gold belt mini-district. Systematic sampling of this tree species and neutron activation analysis of dried (not ashed) selected organs for Au,As and Sb can be an efficient and cost effective way to find hidden quartz vein systems, associated with epithermal Au deposits in areas of Costa Rica and other Central American countries, where theplant ranges and has good spatial distribution.

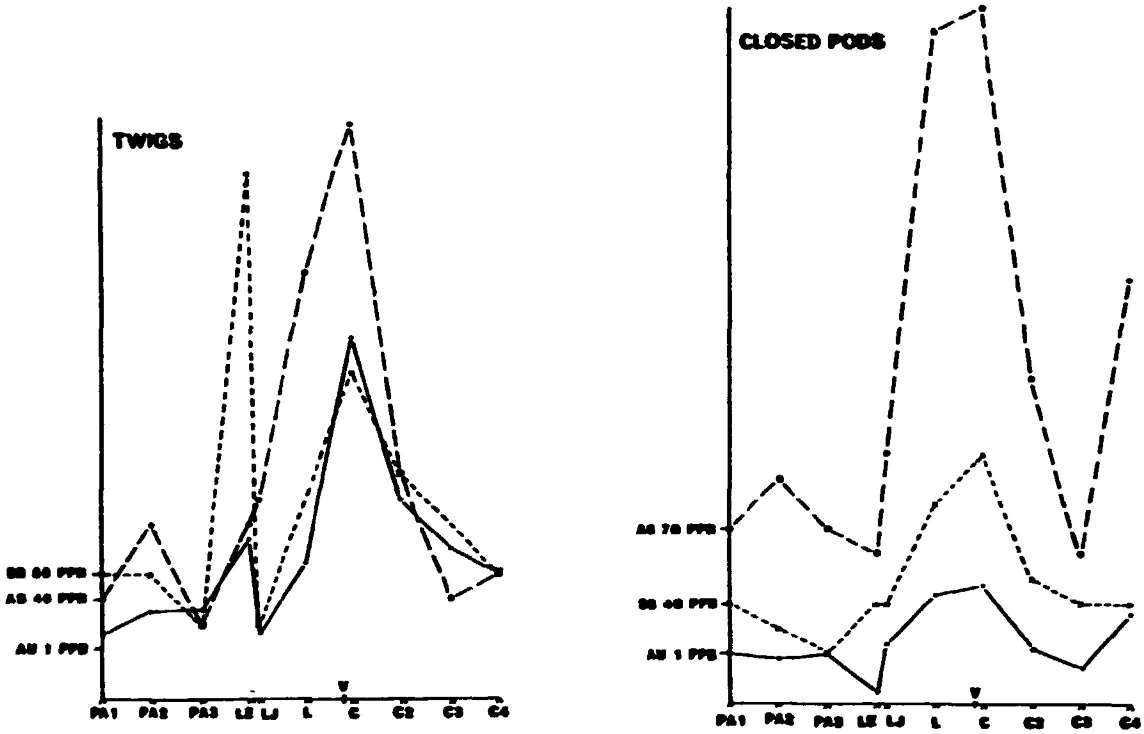

Fig. 1 – The distribution of Au,As and Sb in twigs and pods from Curatella americana Lin. in a traverse across Cerro Conchal. V marks the position of a quartz vein. Sample spacing is about 75m (exept for LE and I.J).

GEOCHEMICAL PROSPECTING BY MEANS OF WELL-SEDIMENT SAMPLING

S.P. Vriend
M. Jansen
J.A.M. Commandeur
M.J. Dekkers

On the northern exo-endo contact zone of the Nisa/Castelo de Vide granite complex, in Central Portugal, vein-type U, Ba, Pb, Zn and W mineralizations occur. The drainage pattern in the arid region is poorly developed leading to an ambiguous provenance of its stream sediments. The more conventional stream sediment sampling is therefore less suited for mineral exploration. However, a high density of water wells is found in the effective prospecting medium (Dekkers et alii, 1989). For the less soluble elements, well sediments were thought to provide an appropriate alternative.

Wells are excavated into the bedrock for domestic and agricultural purposes. The well walls are constructed with the excavated rock without the use of other building materials. Bottom sediments consist mainly of bedrock debris, organic material, gravel, sand and clay; all phases that may host ore-related elements.

Hundred and twenty well sediment samples were collected over an area of sixty km^2 in the granite-schist contact zone. The -63μm fraction was analyzed by XRF and ICPES for Fe, Mg, P, Ca, K, Ti, Rb, V, Nb, Be, Ba, Cu, Li, Y, U, W, Zn, Ni, Pb, Co, Mn, Sr and Zr. In addition, the organic content of the sediment was determined by colorimetry. In the field, the electro-condutivity and pH of the week waters were measured.

The interpretation leads to the following conclusions:

- Well sediment can be unambiguously assigned to granite and schist terrains on the basis of the chemical composition. Especially Rb, V, Y, Cr, U, Ni and Co reflect lithological differences best.
- Geochemical processes affecting the sediment composition were traced through factor analysis on the separate data sets of granite and schist. In the granite area, relations appear to be independent of the distance to the contact withthe schist. Scaveging of trace elements by iron phosphates, iron and manganese (hidr)oxides is most important. Oxidation-reduction is evident from an organic matter sulphur association. A third affiliationis formed by major and trace constituents of micas. Similar trends are observed in the schists area. However the proximity of the granite is clearly noticeable, especially for elements such as U and Y.
- No anthropogenic contamination efects were observed.
- Mos of the known mineraliations cause anomalies in the well sediments concurs with that of the ore composition. Additional anomalies, not related to known mineraliation, are of interest for furhter study.
- Well sediments are in close contact with deeper ground-water flows and thus have potential for the discovery of hidden ore deposits.

This study indicates that, in semi-arid terrains, well-sediment sampling is an attractive means for the detection of sub-outcropping ore-bodies, due to its interaction with passing-through groundwater.

THE MODE OF OCCURRENCE OF METALS IN TILL AS AN ORE GUIDE IN SOME AREAS IN FINLAND

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The mode of occurrence of metals in till is a very important thing to study when interpreting the anomaly type and locating the source of the anomaly. This study delas with base metals (Cu, Zn, Co) in one target area (Vahajoki) in northern Finland and in two target areas (Katumajarvi and Saajanmaki) in southern Finland. A copper- and cobalt-bearing iron ore, which has been considered as skarn type, occurs in the Vahajoki area. Magnesia metasomatic volcanic rocks in Katumajarvi contain sulphide dissemination. Saajanmaki is an area of basic volcanic rocks. There has been found a small Cu-Zn mineralization. The overburden consists of basal till in all three areas.

The till sampling has been done with a light-weight percussion drill. The samples were dried and sieved into three grain size fractions: < 0.06mm, 0.06-0.25mm and >0.25mm. The finest fraction was analyzed chemically by AAS. First, the total metal contents were determined by dissoling the samples in a mixture of perchloric, hydrochloric, nitric and hydrofluoric acids. Two weaker solvents were also used. One was citric acid, which dissolves the weakly bound metals, the so-called hydromorphic component. The other was a mixture of ascorbic aci and hydrogen peroxide. This solvent mixture dissolves the metals bound in sulphides but not the metals included in the lattices of silicate and oxide minerals.

The sand fractions of the samples were separated in tetrabromoethane. The heavy fractions were studied mineralogically by using a polarizing microscope, ascanning electron microscope, an electron microprobe and X-ray diffraction. The results show that the most important mode of occurrence of the metals studied is as sulphides. This shows at the same time the predominance of the mechanical dispersion. Only in some samples is the amount of the weakly bound metal significant.

Interesting features can be seen in the weathering of the sulphide minerals. Pyrite, pyrrhotite and chalcopyrite have, to variable extents, been altere into goethite. Chalcopyrite and bornite have been altered in places into covellite. As weathering products of sulphide minerals, two rare iron sulphates, szomolnokite ($FeSO_4 . H_2O$) and mlanterite (Fe, Zn, Cu, Co, Mg) $SO_4 . 7 H_2O$) were found.

It is important to investigate if the anomalous samples contain such secondary minerals as covellite or native copper, which are more copper-rich than chalcopyrite. If such minerals occur abundantly in samples, the geochemical anomaly may be too high as compared to the mineralization in fresh bedrock.

THE USE OF CESIUM AS A GUIDE TO MINERAL DEPOSITS

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Geochemistry Laboratory, Department of Geology, Eastern Washington University

Since 1982 we have carried out extensive studies on the use of yhallium as a guide to mineral deposits. These studies suggest that hydrothermally altered rocks are generally enriched in Tl as compared to unaltered rocks. In addition, the highly mineralized rocks and veins contain significantly low K/Tl and/or Ba/Tl ratios. Thallium is volatile at higher temperature (≥ 400°C). Because of its volatility, the mineral deposits formed at high temperatures do not show an enrichment of this element. Thallium is also immobile under oxidizing conditions at a pH ≥ 2, thereby restricting its use in reconnaissance surveys, especially hydrogeochemical surveys. In order to fill these gaps a study on the abundance and behavious of Cs, an element geochemically similar to Tl in several aspects, has been undertaken. The rocks selected for this project are associated with gold, silver, copper, molybdenum, and uranium deposits. The main purpose of this study is to explore the possibility of utilizing Cs as a guide to mineral deposits. Very little data exist on the concentration of Cs in hydrothermal altered rocks.

Cesium was analyzed in about 500 rock samples by a newly developed precise and accurate method by Zeeman graphite furnece atomic absorption spectrometry. In addition to Cs, a large number of major and trace elements were also analyzed; analyses of 200 - 300 rocks, soil, and water samples are in progress. The mineral deposits studied include: gold-silver deposits of the Republic mining district (Washington), Como mining district (Nevada), and Howard mining district (Oregon); gold deposits of North and South Moccasin (Montana), Craker Creek district (Oregon), and Criple Creek (Colorado); Carlin-type gold deposits of Carlin, Alligator Ridge, and Jerrit Canyon (Nevada) and Mercur (Utah); copper-molybdenum deposit of Mount Tolman (Washington); Uranium deposit of Midnite mine (Washington).

In all of the mineralized areas there is more Cs in hydrothermally altered rocks than in unaltered rocks. The enrichment factors for Cs differ from deposit to deposit. Hydrothermally altered rocks are enriched by a factor of 2 t0 100 or more, even the quartz and quartz-carbonate veins occasionally show high content of Cs. The highly mineralized rocks and veins contain extremely low K/Cs ratios. The ternary relationship between K, Rb, and Cs separate mineralized and unmineralized rocks into distinct populations, regardless of rock types, highly mineralized rocks and veins falling near the Cs apex. Although Cs+ has the same size and electronegativity as K+ and Rb+, it is concentrated more in hydrothermal fluids than K and Rb because it is a large cation and is admitted into the lattice position of K+ with some difficulty. The preliminary study suggests that Cs and K/Cs ratio can prove to be useful guides in delineating mineral deposits of hydrothermal origin formed at various temperatures. Since Cs is relatively more mobile than Tl, it can form broader dispersion halos and may prove to be a better pathfinder element than Tl in reconnaissance types of surveys.

Author's Index

SPECIAL TECHNICAL ADVERTISING GEOLOGICAL SURVEY OF NIGERIA

The Geological Survey Department was established in 1919 as a successor to the former Colonial Mineral Surveys of Northern Nigeria and Southern Nigeria which were disbanded in 1909 and 1913 respectively. The Department is one of the five professional Departments in the country's Ministry of Mines, Power and Steel. The other Departments are Mines, Steel, Electrical Inspectorate and Power.

FUNCTIONS

The principal functions of the Geological Survey Department are as follows:

i) Geological, geophysical and geochemical mapping of the country.

ii) Mineral Exploration and evaluation.

iii) Underground water resources survey.

iv) Geotecnical studies of foundation stability.

v) Statutory responsabilities such as the receipt and custody of borehole samples and reports from oil, mining and water borehole drilling companies.

vi) Provision of geological and mineral resources information and advice to government and private agencies.

vii) Acquisition and dissemination of geoscientific information by means of maps, reports and publications.

viii) Collaboration with mining parastatals and companies in mineral exploration.

ix) Liaison and collaboration with and membership of local and international geoscientific organisations.

ORGANISATIONAL STRUCTURE

In order of effectively discharge its onerous responsabilities, the Department has an organisational structure based on a combination of functional specialist sections at the Main Officies (or Field Headquarters) in Kaduna and even distribution of its field activities through its Zonal (or Branch) Offices which are located on the basis of geographical, logistic and workload considerations.

The Sections consist of:

i) Regional Geology (or Mapping).

ii) Economic Geology.

iii) Geophysics.

iv) Publications and Training.

v) Laboratory.

A modern central laboratory, a reference library containing over 44,000 publications and a geological museum are situated in Kaduna.

The total staff strength of the Department is 800, of which 220 are geoscientists. The others consist of administrative and support staff. About 140 vehicles are in the Department's fleet. Two motorised drilling rigs are also available.

TRAINING

The Geological Survey Department pursues vigorously a policy of retraining its professional staff with the result that over one third of its geoscientists hold second degrees in various disciplines.

PUBLICATIONS

The Gelogical Map of the country on a scale of 1:2 million is produced every ten years and the last edition was produced in 1984. The 1986 edition of Mineral Map of Nigeria, 1:5 million has been published. Other maps that have been produced are Fracture Map of Nigeria, 1:2 million (1985) and Structural Map of Nigeria, 1:2 million (1986). Results of the field activities of the Department are also made available in the form of Bulletins, Records, Occasional Papers and Unpublished Reports. The latest of these include Records Vol. 9 (1986), Records Vol. 10 (1987), Occasional Paper No. 10 (1985) and numerous Unpublished Reports.

FIELD ACTIVITIES

i) Mapping

About 97% of the country has been geologically mapped on a scale 1:100,000. Less than 5% has been done on 1:50,000. Sufficient work has not yet been done towards producing a geochemical atlas of the country which is still at its conceptual stage.

ii) Mineral Exploration

The Department has over the years prospected for, discovered and appraised different economic minerals in all parts of the country, the results of which have given rise to various mining enterprises. Limestone, marble, iron ore, tin, columbite, gold, lead, zinc, salt, felspar are such examples.

Geochemical orientation surveys of parts the country have been done but the follow-up reconnaissance surveys are yet to be carried out.

iii) Geophysics

About 80% of the country has been covered by airborne radiometric and magnetic surveys and plans are on to cover the rest of the country. Ground follow-ups are in progress in parts of the 80% of the country already flown. Gravity and altimetric surveys of Kaduna State at 5km interval has been completed. The Bouguer (gravity anomaly) map of the State is being processed and compiled for publication.

Six earthquake monitoring (seismic) stations have recently been established in the country.

Technical Assistance

The Geological Survey Department welcomes Technical Assistance in the execution of its projects.

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II *Brazilian Geochemical Congress*

Theme
Geochemical Exploration

AN ALTERNATIVE METHOD FOR STREAM SEDIMENT SAMPLING

Tolentino Flávio de Oliveira
Vanio de Bessa
Cia. Mineira de Metais - Paracatu - MG

Wet-sieving of stream sediment samples at the very site of sampling with the use of an organic flocculant ("separan") in the process of filtration, presents some advantages, such as: a) easy sieving of a finer fraction; b) adequate dimensioning of the final sample; c) lighter weight to carry in areas of difficult access, and d) samples are easier to dry.

The fraction used (-200#) provided good geochemical contrast for the assayed elements - Pb, Zn, Cu, As.

APLICATION OF DUNCAN TEST IN THE INTERPRETATION OF GEOCHEMICAL RESULTS IN GEOCHEMICAL PROSPECTING

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To use the DUNCAN test we need the special table A-7 of multiple range and multiple test at a 1 or 5% probability level in order to facilitate the statistical calculations and to manipulate the data without the use of advanced statistics.

In this work, the DUNCAN test shows significant ways to choose the mean values of results obtained from chemical and granulometric fractions.

We can compare more than two means with this test and group them in accordance with their magnitude.

Two adjacents means are compared at $P=2$ and separated by another mean at $P=3$

CHEMICAL COMPOSITION OF SEDIMENTS FROM THE PATOS LAGOON, BRAZIL

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Rio Grande - RS
Jean-Marie Jounneau
Institut de Geologie du Bassin d'Arquitaine - Université de Bordeaux I - Talence - France
Haroldo Erwin Asmus
Departamento de Geociências - Fundação Universidade do Rio Grande
Rio Grande - RS

Analysis of major elements (Si, Al, Fe, Mg, Mn, Ca, Ti, K, Na), trace elements (Pb, Cu, Zn, Ni, Cr, Zr, Ba, Rb, Sr, Co, Ga) and organic matter (C-org.; N-org., S and P), and of bottom sediments from the Patos Lagoon, aim to define the regional geochemical variables of this lagoon.

The results identified three main groups of trace elements: 1) trace elements associated with argillo-mineral and with organic matter: Zn, Ni, Cr, Rb; 2) trace elements of detrital origin: Ti, Za, Ba; and 3) trace elements connected exclusively to organic matter: Mn, Cu, Co.

The results of this study also demonstrate the main regional variations of the major and trace elements, of the organic matter and of the sedimentary grain size along a north-south profile in the lagoon.

Organic matter is the most important factor for the distribution of trace elements. The Guaiba hydrographic system is the main source for the detrital and non-detrital trace elements in the lagoon.

Gradual sedimentation along the Patos Lagoon can be pointed to as the cause of higher concentrations of Pb, Cu and Cr (partial fraction) in the southern part of the lagoon.

GENESIS AND ENVIRONMENTAL SIGNIFICANCE OF RECENT PELLET-BEARING SEDIMENTS FROM THE ANGOLA BASIN

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Departamento de Geologia
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Pellets-bearing sediments are widely present within recent sediments of the Angola basin, in the area comprised between the mouths of the rivers Zaire (Congo Republic) and Cunene in southern Angola (6° - 17°30' lat. S). Material representative of the first 5cm of seafloor sediments was collected during an oceanic cruise of the ship, Meteor N.R.S., in the period February-March, 1987. Sediments were collected from three profiles located near the mouths of the Zaire and Cunene rivers and in an intermediate area (profiles A, C and B, respectively). The materials collected include beach sediments, plattform and deep sea sediments. Structural, mineralogical and chemical features of pellets from the various profiles have been investigated. Pellets from profile A appear to be well-selected with prevailing spheric-ovoidal shapes. Their polished surfaces result from the high energy of abrasive agents. Pellets from profile C are dark-green coloured, moderately selected and frequently present irregular ovoidal shapes. In addition, most of them are fractured, the fractures being filled by lgihter material. A 10-30cm thick horizon of profile C is almost totally (99%) composed of pellets (greensand). Sedimentary material of profile B presents intermediate characteristic with respect to those of profiles A and C. The pellets result is clearly a mixture of the main A and E types. Analysis of pellets from the various profiles by electron microscope reveals a wide variety of structures, varying from perfectly homogeneous to strongly heterogeneous. In most cases, there is evidence of a fecal origin, and part of the inclusions are interpretable aas rest of fitoplancton, nanofossils (coccolithes) and foraminiferas. X-ray diffraction analysis indicates that pellets of profile A consist of a mixture of Fe-Mn phosphates (phosphorite and kryzhanovskite) and goethite and/or clay minerals (illite, caolinite). Semiquantitative chemical analysis by X-ray fluorescence shows that phosphate-goethite pellets are higher in a series of trace elements (Mn, Ti, Zn, Cu, Ni, REE) with respect to the clayish pellets. The pellets of profile C consist of glauconite with very few contents of other minerals and are rather low in trace elements, except for Rb and Cr. Paleoenvironmental and morphological arguments are presented to explain the different nature of the sedimentological material from the various profiles. The presence of a large plattform in the area, near the mouth of the Zaire river, contrasting with its virtual absence in correspondence with the mouth of the Cunene river, is considered a critical factor.

GEOCHEMICAL DISPERSION STUDIES AROUND THE PUR-BANERA BASE METAL MINERALIZED ZONE, BHILWARA DISTRICT, RAJASTHAN, INDIA

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The middle Proterozoic Bhilwara belt, in Rajasthan State, NW, India comprises several linear zones of base metal mineralization. Some of them are in the process of explotation and some are in stages of exploration. The Pur-Banera mineralized zone (25°18'N to 25°30'N & 74°31'E to 74°41'E) is one such linear zone under exploration. Geologically, the region is covered mainly by amphibolite facies metasediments and metavolcanics. Banded Magnetite Quartzite (BMQ), within a metamorphosed Banded Iron Formation (BIF) occurs as a persistent horizon in the region and shows close spatial association with the base metal mineralization.

A geochemical survey, using mixed media i.e., soil, rock and stream sediment, was carried out in this zone, characterized by semi-arid climatic conditions. From south to north, the zone can be divided into several sectors: 1. Tiranga, 2. Samodi, 3. Dariba, 4. Jipia and 5. Banera. In total, 600 soil, 90 rock and 65 stream sediment samples were analysed for Cu, Pb, Zn, Mn, Fe, Ni, Co, Cr and Ag using AAS, to study the dispersion patterns throughout the 25km-long zone.

Anomalous concentrations for base metals are observed in samples of all the media. Rock sample data show the confinement of the base metals only to BIF in general and BMQ in particular. Stream sediment samples, showing anomalous concentrations for base metals, have significantly restricted dispersion lengths due to limited run-off. The spatial distribution and the magnitude of the soil anomalies for base metals can be related to the primary ore concentrations, as revealed in bore holes drilled by different agencies. The apparent width of the anomalies in different sectors is significantly influenced by the topography of the area. Tiranga, Jipia and Banera sectors, with moderate relief, show a relatively greater extent of lateral dispersion, indicating the predominance of a mechanical process of weathering, whereas Samodi and Dariba sectors, with low relief, show relatively restricted lateral dispersion. The locally developed gossans and high concentration of Pb in relation to Zn in soil, and the reverse relationship in the ore body in these sectors of low relief, indicate possible vertical dispersion, suggesting limited chemical weathering.

The relationships and association between base metals in different media, derived from correlation matrix and R-mode factor analysis, corroborates the picture of enrichment of base metals in different sectors. Significant associations are Pb, Zn, Mn, Fe in all sample media; Cu, Ag in soil and stream sediments and Cu, Fe in rock samples.

All the base metal anomalies are mostly confined to the mesoscopic structures, indicating structural control of mineralization by later remobilisation. Geologically, the base metal anomalies also indicate lateral zonation of the stratabound mineralization: Cu at Banera in the north to Pb - Zn at Samodi and Tiranga sectors in the south. The general mobility pattern established for base metals in this region: Zn > Cu > Pb.

The significant zones, demarcated as target areas for detailed exploration are: Banera and Dariba sectors for Cu; Samodi and Tiranga sectors for Pb; and Tiranga, Samodi and Ranikpura hill (Banera) sectors for Zn.

A geochemical model is developed on the basis of the data obtained and in the consideration of the controlling factors, like climate, relief, nature of the deposit etc., in the evolution of the secondary dispersion patterns.

GEOCHEMICAL EXPLORATION FOR GOLD MINERALIZATION IN THAILAND

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The nature of gold dispersion in soils and stream sediments,associated with copper-gold mineralization in northeastern Thailand, has been investigated as a basis for identifying the appropriate explóration geochemical techniques in the search for comparable deposits in similar environments.

The area examined consists of approximately 7 sq. km, underlain by steeply-dipping Carboniferous sedimentary and volcanic rocks, intruded by minor intrusives of probable Permo-Triassic age. Mineralization within the area consists of an elongated zone of copper mineralization (Phu Thong Daeng), associated with a minor quartz-latite porphyry and an apparently associated gold occurrence (Phu Tham Phra), peripheral to the copper mineralization. The copper deposit consists of potential reserves of twelve million tonnes of 1.0 percent copper, based on drilling to a depth of 100m, but the gold occurrence has never been sufficiently tested. Although no bedrock gold had been located, prior to this investigation, were reported to contain up to 8ppm Au, and local workers have recovered gold from associated drainage systems.

Weathering is intensive and extensive, with soils typically consisting of a hydrated clay matrix, surrounding a variable percentage of rock fragments. Topographic relief is moderate, but, on the higher ridges, soils can be thin, grading into weathered rock within the upper 50cm. On the hillslopes and in valleys, soil profiles probably exceed 10m. The climate is tropical with a distinct rainy season.

Soil and stream sediment samples were collected from all available environments at a range of sample densities. Most sampling was conducted near suspected mineralization, but sampling was continued in adjacent background areas as well as in other background areas, remote from mineralization. Selected samples were divided into a series of size and density fractions, and each was analysed for a wide range of elements to determine which fraction(s) and element(s) respond best to mineralization. All samples were analyzed for Au and a suite of base metals, as well as potential pathfinder elements, using a combination of analytical techniques, dominated by instrumental neutron activation analysis.

Initial tests indicated that the majority of gold in soil is contained in the finest fraction (<63 μm). All soil horizons yielded similar results, making a B horizon at a depth of 10 to 20cm, the most practical and consistently available. Further, it was recognized that composite samples, representing equal parts of four samples, collected 25m apart, could be used to accurately outline the location of anomalous ones and significantly reduce initial analytical costs.

Results from a soil-grid survey outlined a 1 square km zone of Au greater than 60ppb in the B horizon, roughly coincident with the suspected area of bedrock gold mineralization. Anomalous gold concentrations were also found over the copper mineralization, but with lower contrast. A previously unrecognized, but relatively small, area of anomalous gold concentration was also located approximately 1km east of the primary copper mineralization.

The distribution of other elements in the soil samples outlined a number of zones with distinctive element associations. The known copper mineralization is well-identified by Cu >500ppm, and the areas of highest Cu values are generally outlined by Mo >10ppm and W>5ppm. The anomalous Au zone corresponds to anomalous concentrations of Co and, to a lesser extent,As. The "new" zone of anomalous gold concentration is associated with an extensive zone of As >60ppm. Collectively, the patterns in soil appear to outline a system of polymetallic mineralization, probably centered on a porphyry copper system, with satellite gold mineralization in the peripheral zones.

In drainage sediments, the majority of gold occurs in the <63μm fraction, but the grain-size distribution of the sediment varies considerably, reflecting a variety of stream energy regimes over a relatively short distance. Increased gold concentrations can be obtained by digging through the most recent sediments and collecting samples from 0.5 to 1.0m deep. Based on limited data, it appears that gold in heavy mineral concentrates does not reflect mineralization significantly better than a routine fraction; however, field-panning is usually indicative of anomalous drainage sites and has the advantage of providing immediate results in areas where field mobilization may be difficult. The field-panning results must be considered semiquantitative and should not be relied upon exclusively, because this method will not effectively recover fine-grained gold, which appears to be the dominant mode of occurrence of gold in this area.

The distribution of anomalous concentrations of most elements, including gold, in drainage sediments reflects well the distribution in soils, despite the considerable variations in stream environment encountered. Directly over the anomalous zones, drainage sediments contain up to 350ppb Au and values of >20ppb persist for 1km down drainage.

The relatively large and consistent zones of soil with anomalous gold concentrations, combined with the distinctively zoned anomalies in other elements, and the consistent dispersion patterns in drainage sediments, make geochemistry particularly effective for exploration in this environment, provided appropriate procedures are adopted. Based on the data available, and assuming that the gold mineralization at Phu Tham Phra is significant, recommendation can be made for three stages of geochemical exploration: 1) reconnaissance, 2) initial follow-up and 3) detailed follow-up.

RECONNAISSANCE

Drainage sediment samples should be collected at 500m intervals along drainages and above the confluences of tributaries. One to two kg of active stream sediment material should be collected, sieved to a fine fraction and analysed initially for Au and Cu. Additional analysis for Pb, Zn, Co, As, Sb, Fe and Mn should help to identify potential mineralization type. Highest priority should be given to areas with anomalous concentrations of both Au and Cu. Where drainages contain water and a sufficiently deep sediment profile is available, samples should be collected from 0.5 to 1.0m depth for field-panning. A fixed volume (e.g. 20 l) could be panned and examined for gold for an immediate indication of gold potential.

INITIAL FOLLOW-UP

Anomalous reconnaissance samples should be followed up with "ridge and spur", or, alternatively, "break-in-slope" soil samples at approximately 100m intervals. A fine fraction should be sieved and analysed for Au and Cu. Other elements, including Co, As æ Pb, Zn, Mo, Sb, W, Ag, Fe, and Mn could help to outline potential multi-element zoning and, thus, allow identification of the position in a mineralized system. Greatest attention should be given to multi-element anomalies similar to those found in the study area.

DETAILED FOLLOW-UP

A grid should be cut over anomalous zones identified during the initial follow-up stage. Line separations should be no greater than 200m, and sample separations no greater than 100m. At this stage, samples could be collected at close intervals, such as 25m, and composited. Analysis of the individual component samples of the composite samples could be carried out in areas that were identified as anomalous, based on the initial results.

GEOCHEMICAL EXPLORATION FOR PHOSPHATE IN THE STATE OF ACRE

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The geochemical prospecting conducted for phosphates in Acre which could explain the good fertility of the region was charged to discover this material. The phosphates are strictly built of all the bone structures and coprolites of the several fragments of vertebrate fossils, which are widespread in the region. The phosphatic fossils are bedded in the Solimões Formation, especially in its basal to intermediary conglomeratic bed. The fossils are constituted of low crystallinity apatite, and their matrix sediments include quartz, feldspars, smectite, halloysite and calcite. The P_2O_5 content reaches up to 5% in the sediments and up to 32% in the fragments. The fossils are enriched in U_3O_8 and rare earth elements. There is no perspect of classic ore mineral deposits but the geological knowlwdge will permit the improvement of the use of the soils in Acre.

GEOCHEMICAL IMAGES - MAP SHEET SD.22-Z-D

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The main purpose of this paper is to present the geochemical data of the SD.22-Z-D (Goianésia) chart. The analytical results are summarised in probability graphs and spatially represented by Geochemical Images and Isoteor Maps. This study was carried out with 1649 samples which were analysed for Cu, Pb, Zn, Ni, Cr, Co, Fe, Mn, B, Bi, Be, Ti, Mo, Sn, V, Ag, Zr, Y, La, Sc, Sr, Nd and Ba.

GEOCHEMICAL PROSPECTION FOR Sn MINERALIZATION IN THE CAPIVARI PARDO REGION, PARANÁ STATE, BRAZIL

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From the analytical data of a regional geochemical project carried out by Minerais do Paraná S.A. from 1980 to 1988, named "Projeto Capivari - Pardo", some strong Sn, W (in pan concentrates) and Cu, Pb (in stream sediments) anomalies arose. This kind of elemental association, never found until that time in the Paraná Precambrian Shield showed some very interesting anomalies. Two of them, named "Alvo Paraiso" and "Alvo Cantagalo", were worked intensively by means of geological mapping, detailed stream sediments and pan concentrates sampling. The results obtained directed the work to the "Alvo Cantagalo", where intense Sn, W and Cu anomalies are associated to greisenized outcrops. Soil sampling, trenching, and wide volume sampling were also performed.

The work presents in a chronological sequence, most of the methodological aspects and the principal results obtained, from regional to detail scale.

GEOCHEMICAL PROSPECTION IN DESERT AREAS

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The deposit potential of desert areas, covering roughly one third of the land surface, is less explored than that in other parts of the world. At present, great attention has been given to the possibilities of effective exploitation of prospecting geochemical methods, which, in many cases, yielded excellent results.

The deserts, even thought seemingly monotonous, form heterogeneous geochemical environments with specific processes strongly affected by the degree of humidity. Their development is also significantly influenced by changes of climate, especially by the existence of more humid periods in the recent past. the climatic changes, manifested by changes in the content of dissolved substances and solids in water, speed of chemical alteration of minerals, changes of pH values, biological and sorption activities, geochemical migration barriers and mobility of individual elements. Elements with large ion radii and low energy parameters usually exhibit low mobility.

Climatic changes controlled the development of secondary geochemical fields and the origin of geochemical anomalies, which, as a rule, are less extensive but with sharper contrasts than those in other climatic zones.

The effectiveness of the methods of geochemical prospection is the result of a complex of various processes of formation and preservation of weathering products, and of geochemical migration of elements liberated during weathering. Under the present conditions of geochemical anomalies, old gossans and crusts, enriched with trace elements, play an important role in many deserts. During the present degradation and erosion of these relics, from the times of rather weathering in more humid periods, the weathering products are penetrated mainly by ferruginous coarser-grained particles, which can be separated from the finer-grained material, often strongly contamined by eolian deposits, by means of sieving of paramagnetic separation, or even panning.

The origin of hydromorphic geochemical anomalies is limited owing to little sorption capacity of desert sediments and weathering products, and due to saturation of this capacity, namely with alkaline metals and earths elements. Migration is also affected by the low stability of the colloid systems; formation of complex ions has a positive effect.

The amount and granularity of the eolian sediments is regulated both by the character of the weathering products as well as by the relief. In regions of plains, the wind transports more coarser-grained particles than in the regions with a dissected surface.

Methods of geochemical prospection are based on the character of the desert. In the hammadas, a combination of the primary geochemical field research with the geophysical methods and remote sensing is of great importance. Deserts covered with various thicknesses of debris and pebbles are suitable for combination of the primary and secondary geochemical field research methods. In the deserts with rather continuous weathering products cover, the character as well as the thickness and origin of this cover play an important role. Areas with thick allochthonous covers, such, as dunes and playas are usually unfit for geochemical prospecting because this method is insufficient at greater depths.

Prospecting for raw-material resources should also be focussed on specific desert types of deposits, e.g. uranium or zinc ore and others.

Methods of geochemical prospection and their effectiveness are also influenced by various types of desert crusts, which change the conditions of compound migration in weathering products.

During more extensive geochemical prospection works in the desert areas, classification of the territory according to conditions for application of individual prospection procedures and their combination, is advantageous. Specialists from other fields (e.g. Quaternary geology and geomorphology) should participate in evaluation of these conditions, too.

GEOCHEMICAL PROSPECTION IN THE FAZENDA BARRINHA SOBRAL ULTRAMAFIC BODY, CEARÁ STATE

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A small ultramafic intrusion was discovered by CEMINAS near Sobral, north of Ceará state, and was searched for sulphides and PGM. The main body is peridotitic, with steatite and amphibolite lenses south and north respectively. Wall rocks include biotite-gneisses, calc-silicate rocks and a thin quartzite bed.

Soils were sampled along a 25 x 50m grid, and 133 samples from a 50 x 100m pattern were selected and analyzed by aqua regia/Atomic Absorption for Cu, Co, Ni and Cr. Some 46 soils samples over the body were analyzed by fire assay/A.A. for Pt, Pd and Au. Aqua regia results were processed with a microcomputer and the PROBPLOT program, and Pt, Pd an Au results were evaluated visually.

High values of Cr, Ni and Co perfectly outline the peridotite, but Cu is seen as isolated spots around the body. Ni and Cu distributions and relations suggest the absence of sulphides. Chromite levels were not detected, and Pt values are dissociated from high chromium results. The single sample with anomalous Pt and Pd may be related to magnetite enrichment of the peridotite.

GEOCHEMICAL SOIL STUDY AS A COMPLEMENTARY TOOL FOR GEOLOGIC MAPPING IN SERRA DOS CARAJÁS, PARÁ

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The region of Serra dos Carajás, Pará, consists of Archaean volcano-sedimentary sequences, one of them metamorphosed on the amphibolite grade, cover sediments, mostly sandstones, and intrusive proterozoic granites. The surrounding basement is mostly composed of gneisses.

162 soil samples were collected during the geologic maping of an area of approximately 770km^2 in this region, with the objective of the application of soil geochemical data as a complementary tool for geologic mapping. The statistical distribution of the concentration of the elements Fe, Mn, Na, Mg, Cu, Zn, Ni, Rb, Sr, Nb, Y and Zr were investigated.

The sampling was carried out by 18 groups of 3 undergraduate students of geology of the UFPA. The samples were collected (1) from a depth of 30cm, (2) with a change of lithology and (3) at about 1km intervals between sample locations.

The concentrations of elements in soils present a great variance because several factors that affect them were not considered. They are, for example: (1) the relatively low number of samples for the great variety of lithology, and (2) the participation of 3 chemical analysts and different times of the analyses. This is the reason that only the very characteristic results for each type of soil, representing different rocks, were considered for the geochemical interpretation.

The predominant factors that control the element distribution in soils are the composition of the bedrock and the processes of weathering, leaching and concentration.

The topography, geomorphology, vegetation, plus sampling, their preparation and analytical errors are the main factors whose variance was not investigated.

For the geochemical data, the values for the mean, minimum, maximum and standard deviation were calculated, and histograms and scattergrams were drawn.

Considering all the samples, a negative correlation between Fe and the elements Rb and Zr is verified. $\left(\frac{Fe}{Rb.Sr}\right)$ This correlation expresses the Fe-enrichment in hydroxides and the relative depletion of Rb and Zr, both components of clay minerals and zircon, respectively, by the laterisation.

The positive correlations between Fe and the elements Cu and Ni reflect the adsorption of the latter on the Fe-hydroxides. The negative correlation with Mg indicates its leaching with the weathering and laterisation. This reasoning is also valid for the soils over gneisses of the Xingu Complex, where the expression $\frac{Fe.Mn.Ni,Cu}{Mg.Rb.Nb.Zr}$ was found. This expression indicates solely the positive correlation of the Fe with the other elements of the numerator, and the negative with those of the denominator.

The soils over sandstones of Formação Igarapé Azul show $\frac{Fe.Zn.Nb}{Mg.Rb.Zr}$ that is coherent. The positive correlation between Mn and Zn in this soil indicates a regular occurrence of these elements in the bedrock.

In the soils over basalts of the Grão Pará Group, the positive correlation between Fe and Na can not be explained as yet. The same applies to the soils of the banded iron formation of the Formação Bueno, Pojuca area.

For the discrimination of the soils occurring over different lithologies in the area, we used the mean values of concentrations of the investigated elements.

We represent the higher mean concentration in the numerator and the lower in the denominator of one fraction.

The following are the expression for soils of corresponding lithologies.

Basalts of the Grão Pará Group $\frac{Ni.Cu.Zn.Mn}{1}$

Intrusive mafic rocks of Pojuca area $\frac{Mn.Na}{1}$

Mafic dikes of the Pojuca area $\frac{Ca}{Sr.Y}$

(These geochemical soil signatures area coherent with the composition of mafic rocks)

Amphibolites of the Bueno Formation (Pojuca area) $\frac{\mathrm{Mn.Na.Mg}}{\mathrm{Sr}}$

Gneisses of the Xingu Complex (Pojuca Area) $\frac{\mathrm{Zr}}{\mathrm{Fe.Mn.Zn.Ni.Rb.Sr.Nb.Y}}$

(This signature indicates the enrichment of quartz in the soil. Unfortunately, we do not yet have the Si data available)

Gneisses of the Xingu Complex (area near Parauapebas) $\frac{\mathrm{Mn.Na.Zr}}{\mathrm{Sr.Y}}$

The signature $\frac{\mathrm{Zr}}{\mathrm{Sr.Y}}$ is common to both gneisses)

Itacaiunas Granite $\frac{\mathrm{Na.Rb.Nb.Zr}}{\mathrm{Fe.Mn.Cu.Ni.Sr}}$

Carajás Granite $\frac{\mathrm{Rb.Sr.Nb.Zr}}{\mathrm{Fe.Mn.Cu}}$

(The signature $\frac{\mathrm{Rb.Nb.Zr}}{\mathrm{Fe.Mn.Cu}}$ is common to both granites)

Igarapé Azul Formation sandstones $\frac{\mathrm{Mn.Rb.Sr.Zn}}{\mathrm{Fe.Cu.Na}}$

BIF of the Carajás Formation $\frac{\mathrm{Mn.Nb}}{\mathrm{Cu.Ni}}$

BIF of the Bueno Formation $\frac{\mathrm{Cu}}{\mathrm{Mn.Ni.Nb.Y.Zr}}$

BIF of Bueno Formation (area near Parauapebas) $\frac{\mathrm{Zr}}{\mathrm{Sr.Y.Cu.Ni.Nb}}$

HYDROGEOCHEMICAL PROSPECTING FOR FLUORITE IN THE SERRA DO MAR, BRAZIL

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This paper presents a review and evaluation of pratically all the published data available on hydrogeochemical prospecting for fluorite and compares these with the author's data. Results of a pilot stream water, survey undertaken in the Rio Bonito area of the State of Rio de Janeiro, Brazil, are presented, together with a summary of other Brazilian hydrogeochemical prospecting results. A theoretical estimate of hydrogeochemical anomaly magnitudes is presented. Concentrations in the Rio Bonito mineralized area, compared to those in an adjacent non mineralized area gave geometric means of 120 gF^-/l and 25 gF^-/l respectively. Anomalous values in the Rio Bonito area were frequently above the 200 gF^-/l and 360 gF^-/l thresholds defined in other Brazilian surveys. Although mass transfer theory for veins exposed in stream beds predicts no significant anomalies, the field data from Brazil reinforce the same conclusion drawn from other surveys, that hydrogeochemical prospecting for fluorite is generally more effective and economical than sediment surveying. Evidence from the Rio Bonito and other surveys also indicates the usefulness of spring water as a sampling medium.

MULTI-ELEMENT REGIONAL GEOCHEMICAL PROSPECTION IN THE STATE OF MINAS GERAIS

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Metais de Minas Gerais S/A - METAMIG, a state government owned company, developed a mineral prospecting programme, during March 85 - August 88, totally supported by its own financial resources.

The programme consisted of a regional multi-element geochemical exploration, carried out over eight selected regions, representative of the main geologic tracts of the Minas Gerais State. An area of about 50,000km^2 was covered by stream sediment (6,500) and pan concentrates (3,160) sampling. The first was routinely assayed for up to 15 elements, while the second was prepared and described in the Metamig petrographic and mineralogical laboratories.

The geochemical data was stored and processed in a IBM-PC compatible microcomputer, using the Geoquant 1.0 system, developed by the Cia. de Pesquisa de Recursos Minerais - CPRM. Simple descriptive statistics furnished the basis for data categorization into three intervals, namely:

1st .($xi > > \bar{x}+3s$),
2nd. ($\bar{x}+2s < xi < \bar{x}+3s$), and
3rd. ($\bar{x}+s < xi < \bar{x}+2s$).

Visual comparision between maps containing the qualified geochemical data, geology, geophysical data and the heavy mineral distribution patterns, proved to be efficient in showing generalized, good correlation between data and geology, including known mineral occurrences, supporting therefore, consistent interpretations, despite the lack of orientation surveys and systematic data quality controls.

Several mineral indications and significant anomalies, were as a result, selected for follow-up.

PRELIMINARY GEOCHEMICAL EXPLORATION IN SEMIARID CLIMATE: THE CASE OF A PORPHYRY-TYPE OCCURRENCE IN SARDINIA (ITALY)

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In the southwestern part of Sardinia some subvolcanic andesitic bodies occur, related to rift structures.

Weak alteration phenomena and the presence of pyrite disseminations led the authors to better investigate the area through petrographical studies and geochemical prospecting on rocks and soils.

The geochemical survey showed that, given the local morphological and climatic conditions, rock and soil sampling are well correlated; furthermore some functions relating Cu with Ba and Sr proved effective in defining the anomalous areas.

The main anomaly area found by means of these studies could represent a porphyry-copper body.

RE-EVALUATION OF PEDOGEOCHEMICAL DATA IN THE SANTA CATARINA FLUORITE DISTRICT

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This paper includes the data obtained from the "Fluorita no Sudeste de Santa Catarina", "Rio das Corujas", "Rio Garrafão" and "Rio Cubatão" Projects. The "Fluorita no Sudeste de Santa Catarina" Project was an orientation survey carried out on the venular mineralization of fluorite to determine which are the best geochemical parameters to apply in future exploration. The last three projects were carried out in selected areas to find fluorite veins.

Geological work confirmed the presence of proterozoic granitic rocks hosting fluoritic mineralization (Pedras Grandes and Guabiruba Intrusive Suites), described in earlier papers. The sedimentary sequence of the Itararé Group and basic rocks of the Serra Geral Formation are also found, together with less common acidic rocK dikes and siliceous veins. Fluoritic lodes have variable dimensions, showing up as lenses, thinning laterally or in depth.

The present study compares the prospective data, especially for soils, obtained in the orientative program, and its application to potentially economic areas.

REGIONAL GEOCHEMISTRY OF THE PILAR DO SUL MAP SHEET – SÃO PAULO STATE

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This paper presents the results of a reconnaissance stream sediments survey, carried ou in Pilar do Sul, São Paulo State, comprising an area of 756 km^2. The minus 80 mesh fraction pulverized to minus 200 mesh was analysed for 30 elements by emission spectrograpy. The interpretation of the data obtained was made by both percentiles and factor analysis methods. As a result, the latter method revealed itself to be more efficient than the first one in distinguishing three main types of granites in the area.

RIO GARRAFÃO (SC): VARIOGRAPHY APPLAIED TO FLUORITE IN SOIL PROSPECTING

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Semi-variogram is a geostatistical tool that can be used in geochemical prospection. It is useful as it makes it possible to optimize sampling grids. The variographic study of 345 analytical results of soil samples (fluorine) from Rio Garrafão (Santa Catarina) is presented and discussed.

SEDIMENT GEOCHEMISTRY IN THE SÃO LUIZ DO PARAITINGA PEGMATITIC REGION

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This paper aims to present the geochemical pattern of stream sediment anomalies in the São Luís do Paraitinga pegmatitic field, São Paulo State. Several pegmatites were intruded both in the Cubatão shear zone area and in the surrounding granite-gneiss terrain. Some of these pegmatites have shown rare minerals (e.q. beryl, columbite-tantalite, triploidite) and internal zoned structure, what suggests the possibility of complex composition occurring in that region. The stream sediments sampling was carried out at a density of one sample per sq. km and the analyses were made for 30 elements by optical spectrography emission. Simple statistical treatment allowed the definition of the 1st., 2nd., and 3rd. order anomalies, respectively at the 95, 80, and 70 percentiles. The pegmatitic field was delimited by conspicuous anomalies of B, Ba, Be, Li, Sn, and Sr. Other elements are more scattered throughout the area and do not discriminate the pegmatites. As the pegmatites are related to shear zones in the most important pegmatitic fields of São Paulo State, geochemical programs like this one can be used in order to select and to determine the limits of the most favourable areas for exploration. In this sense, Nb, Y, B, Be, Sr, and Ba by spectrography emission, Li and Sn by more sensitive methods, and F, P, As, U, Ta, and REE by appropriate methods, are recommended.

STATISTICAL TREATMENT OF GEOCHEMICAL DATA: JARAGUÁ AREA MINAS GERAIS - BRASIL

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Statistical Discriminant Analysis was employed in order to 1) to point out the necessity of homogenizing the sampling universe previous to the application of any method of population analysis; and 2) to test the geological-geochemical model due to former application of cluster analysis to geochemical data of stream sediment samples collected in the area of the Jaraguá Map Sheet (SE-22-Z-D-IV) (content of Cu, Pb, Zn, Ni, Co, Cr, Fe, Mn, B, Be, Ti, V, Zr, Y, La, Sc, Nb and Ba). Samples were classified according to the predominant lithology in the drainage basin: Granitoid-Gnaissic Complex, Granitoid-Gnaissic Complex with granulite enclosures, Vulcanic-Sedimentar Complex; and Folded Metassedimentar Covering (Canastra Group). In the data matrix only those samples found in the contact area of the Granitoid-Gnaissic Complex and the Canastra Group were considered.

The results of this Discriminant Analysis confirmed the former proposed geological-geochemical model.

STREAM SEDIMENT GEOCHEMISTRY PILOT STUDIES IN THE UBAÍRA/JEQUIRIÇÁ REGION

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An orientative geochemical study was carried out on two areas located in the central-eastern part of Bahia State, Brazil, rather to the south of Ubaíra and Jequiriçá towns, which are bounded by the geographical coordinates: 13°15' to 13°30'S and 39°30' to 39°45' W Gr.

The region under investigation predominantly displays rocks of granulite facies, such as charnockites, augen-charnockites and granulitized migmatites. They are situated under a dry sub-humid climatic strip with an undulated to strongly undulated relief. Thirty-three stream sediment samples were collected from Areia brook (area 1) and Muquiba rill (area 2), and, at the same points, pH measurements on running water were performed, making use of a pH-meter appliance. In the CEPED laboratory the samples were sieved and partitioned into three grain size fractions: (-30 +80 mesh) (-80 +150 mesh) and (-150 mesh); they underwent strong applications attacks of a mixture of hydrofluoric acid, aqua regia, and perchloric acid, aimed at defining the best contrast for copper, lead, zinc, cobalt, nickel, iron and manganese.

The (-150 mesh) fraction showed the highest contrast, and then it was submitted to five sequential selective geochemical attacks, as follows: 1- cold acetic acid 1M; 2- cold hydroxylamine hydrochlorate 0,1M; 3- hydrogen peroxide 30% at 80°C; 4- hydroxylamine hydrochlorate 0,25M at 70°C; 5- mixture of hydrofluoric acid, aqua regia and perchloric acid. Some conclusions can be drawn from these results: - the best detection range for all the studied elements, as a whole, was that one obtained from the 5th attack, whereas the sharpest geochemical contrasts can be achieved through the 2nd, 3rd, 4th and 5th attacks, depending on the element taken into consideration. Finally, it is supposed that every element studied is strongly associated to iron and manganese oxides in their moderately crystallized mode.

THE APPLICATION OF SELECTIVE EXTRACTION PROCEDURES IN THE EXPLORATION FOR BASE METAL SULPHIDES IN THE CHAPADA DO ARARIPE - CE

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Selective extraction was used to discriminate anomalies originating from lead and zinc sulphides in the Chapada do Araripe - Ceará. A new extraction sequence was developed for the area, adapting the classical methods of Gatehouse, Rose and Suhr, Chao and Theobald, and Olade and Fletcher. This technique was utilized after conventional methods had failed, due to high background values and large variations in the lead and zinc concentrations in the rocks hosting the mineralization.

THE MORPHOLOGY AND CHEMISTRY OF TRANSPORTED GOLD GRAINS AS AN EXPLORATION TOOL

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Although a large volume of published data exists documenting the chemical and morphological characteristics of transported gold grains, the integration of such studies has apparently received little attention as an exploration tool. Morphological examination and electron microprobe analyses of gold grains from placer samples in lateritic terrain and from glacial till samples were performed in order to determine the variability in morphology and chemistry (expressed as gold/silver ratios) of gold within such samples and the extent to which transported gold grains from inferred sources or from unknown sources can be differentiated. Samples of bedrock gold from occurrences updrainage or up-ice from the collection sites of some of the transported gold grains were also analyzed. Results from such studies are important if they can confirm or eliminate known gold occurrences as the source of transported gold, or indicate the presence of additional sources.

Over short distances of mechanical transport gold grains often retain primary delicate features. With increasing distance of mechanical transport morphology changes from delicate to irregular to abraded. Because chemically transported gold may be reprecipitated in delicate forms, such morphology, in itself, cannot be taken as evidence of short transport distance. Furthermore, although the size of gold grains diminishes with increased distance of mechanical transport, large nuggets may form in and be shed from the supergene zone of gold occurrences, hence the large size of gold grains is not, in itself, indicative of short transport distance.

The chemical purity of gold is usually described in terms of fineness (1000 X Au/(Au + Ag)). The cores of mechanically transported gold grains are considered to retain the fineness of the gold in the source, whereas grain rims, particularly in placer gold grains, often display silver depletion relative to the core. In supergene zones a dramatic increase in the fineness of chemically transported gold relative to that of primary gold occurs.

Placer gold grains from three Ivory Coast locations in lateritic terrain display morphological characteristics typical of abraded gold transported in a fluvial environment. The large size of the grains (up to 5 mm in maximum dimension) suggests that they originate from a zone of secondary, reprecipitated gold and are not mechanically transported grains of primary gold. The pitted nature of many of the grains is evidence for the removal of inclusions of soft, possibly soluble material encapsulated during the growth of the gold nuggets in the secondary environment. Gold grains collected from what was thought to be highly weathered bedrock within two of the areas were also examined. In one of these sample the abraded morphology and large size of the grains indicates a high degree of mechanical transport of secondary gold. In the second sample the gold grains, which are up to 500 microns in maximum dimension, retain delicate features unmodified by mechanical transport. The latter gold grains are likely to have been collected at or very close to the source.

Inferences based on the morphological examination of gold grains in the Ivory Coast samples are supported by electron microprobe analyses. In all cases the transported gold grains display silver depletion in grain rims which is typically reported for mechanically transported placer nuggets. The silver depletion is also observed in gold grains thought to have been collected from highly weathered bedrock but which display morphological features consistent with transportation in a fluvial environment. The bedrock gold grains which retain delicate features show no depletion of silver in the grain rims and are unlikely to have undergone significant mechanical transport. In combination with gold grain morphology and knowledge of the geomorphological environment, the high fineness of the cores of the mechanically transported gold grains (878 to 972) and of the delicate gold grains collected at source (925 to 966) probably reflects the gold/silver ratios of gold in the supergene zone, not in the primary source. Although the fineness of undiscovered primary gold cannot be determined from available samples, increases in fineness of up to 100% have been documented for supergene gold relative to primary gold in other lateritic environments. An upper limit of 880 for the fineness of primary gold is suggested from the analyses of the core of one placer grain. This upper limit may be extreme given the proposed supergene origin for the gold grains, and should not be inferred as representing the potential Au/Ag ratio of an undiscovered primary deposit. The differences in fineness displayed by the gold grains within individual locations are consistent with a single source, however, multiple sources cannot be ruled out.

Transported gold grains from three Canadian samples were extracted from glacial till. Two of the till samples were collected immediately down-ice from major gold producers in the Superior structural province of Ontario; the third sample is from the Churchill structural province of Saskatchewan and is less than 100 metres down-ice from significant, undeveloped gold occurrences. Gold samples from inferred up-ice bedrock sources were available from two of the three sample areas.

Gold grains from both Ontario samples comprise 90% delicate grains interpreted to have been derived from local sources. The majority of gold grains are less than 75 microns in maximum dimension. For one till sample a single source has probably contributed delicate, irregular and abraded gold grains of high fineness (912 to 967), although the possibility of multiple sources of similar fineness cannot be excluded. A second source is indicated for abraded gold grains displaying low fineness (654 to 691). In contrast to the inferences presented for the Ivory Coast gold grains, the high fineness is considered primary, with the possible exception of large abraded grains having fineness up to 967. No sample of bedrock gold from the inferred source was made available for comparison.

In the second Ontario till sample a single source is inferred for the delicate and irregular grains (fineness 893 to 933) while two sources may be argued for the abraded grains (fineness 898 to 910 and 858 to 868). These fineness ranges match very well the fineness populations defined by gold in the bedrock sample. Fine-grained gold within pyrite grains in the bedrock sample displays a fineness of 917 to 923, while the fineness of gold in fractures in quartz veins is in the range 855 to 867. In this case the source of the gold can be assumed with confidence to be the deposit currently being mined.

Despite the proximity of gold occurrences to the Saskatchewan till sample, the sample contains only 11% delicate gold grains, while 63% are described as irregular. Many grains classified as having irregular morphology are described as "approaching delicate", suggesting that the figure of 11% delicate grains may be low and that, in this case, destruction of delicate features has occurred over a relatively short transport distance. An alternative possibility is that the gold grains in the anomalous till have, at least in part, sources other than the known occurrences - a possibility that is supported by analytical data. Based on fineness, at least three populations of gold can be identified among the analyzed gold grains from the Saskatchewan sample, while two distinct populations are defined by the two bedrock gold occurrences. Only one of the populations of transported gold grains corresponds to one of the bedrock occurrences - the two remaining populations of transported gold are significantly lower in fineness than either of the bedrock occurrences and must have other sources. One bedrock occurrence is not represented by the transported gold grains analyzed. The relative significance of the different populations should be assessed using a statistically valid sample size since it appears that undetected gold occurrences are certainly contributing to the gold content of the till.

Combined morphological and electron microprobe examinations of transported gold grains may provide important information to gold exploration programs. Significant variation in fineness among transported gold grains collected at a single site is indicative of multiple sources for the gold grains. Such data may indicate whether known occurrences are likely sources for the transported gold or whether other sources should be sought. Morphology appears to be a less reliable indicator than fineness in determining the existence of multiple sources for transported gold grains, however, an increasing percentage of delicate grains within samples may be a reliable indicator of proximity to source. In lateritic environments where chemical mobility of gold is high, morphological and chemical studies may aid in determining whether gold grains are of primary or secondary origin and whether they have undergone significant mechanical transport. Given the marked increase in the fineness of supergene gold relative to primary gold in lateritic environments, the recognition of a supergene source has significant implications in determining the future course of exploration efforts and in assessing the economic potential of an undiscovered primary bedrock source.

Theme
Lithogeochemistry and Isotope Geochemistry

BISMUTH, INDIUM AND THALLIUM IN THE MESOZOIC DEPOSITS OF THE TADJIK DEPRESSION.

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The Clark geochemistry of bismuth, indium and thallium in sedimentaty process is still extremely little studied. The deficiency of information is due to low concentrations of these elements in sedimentary rocks and difficulties in their analytical determination.

In the laboratory of geochemistry and analytical chemistry of the Institute of Chemistry of the Academy of Science of the Tadjik SSR, the methodics of spectral determination was worked out of Bi, In and Tl in the large chamber electrodes with the use of halogenized additions. The limit of determination of these elements is 10^{-5} - 10^{-6}%, the relative error - 5-13%.

The object of our investigations was the Mesozoic deposits of the Tadjik depression, where the whole cycle of sedimentary process presented itself most completely, beginning from destruction products of source rocks and finishing with accumulation of sediments in the sea basin.

The regularities of considered elements distribution, depended on the main factors of the sedimentary process: the composition of source rocks of feeding provinces, lithological and facial peculiarities of sediments formation, climatic conditions of sedimentation - were under study.

The average contents of the elements in the Jurassic humid deposits were stimated:

in clays: Bi-0.33 ppm, In-0.10 ppm, Tl-2.3 ppm;
in sandstones: Bi-0.23 ppm, In-0.19 ppm, Tl-3,0 ppm;
in limestones: Bi-0.14 ppm, In-0.09 ppm, Tl-2.0 ppm.

In the Lower Cretaceous arid clays, the Bi, In and Tl contents are 0.48, 0.41 and 1.7 ppm, respectively: in sandstones - 0.31, 0.21 and 1.6 ppm. These values somewhat exceed these of Clark for Bi, In, Tl in sedimentary rocks of the earth's crust, that are evidently due to the geochemical specialization of source rocks from feeding provinces.

The investigations conducted, led us to conclusions concerning some peculiarities of Bi, In and Tl distribution in the Mesozoic deposits of the Tadjik depression: 1) the differences in Bi, In and Tl contents in rocks of the same lithological and facial type are evidently due to their variations in source rocks; 2) the maximal contents of these elements are noted mainly in deposits of littoral facies; 3) the clayish rocks are characterized by much higher concentrations of Bi, In and Tl compared with sandstones; 4) climate aridization promoted the accumulation of Bi and In in sediments, while Ti is more characteristic of humid deposits.

CAJU GRANITE – CHEMICAL/MINERALOGICAL ASPECTS IN THE AREA OF INFLUENCE FROM THE CARANGUEJO AND UBATIBA RIVER DRAINAGE BASIN AND MARICÁ AND GUARAPINA LAGOON, RESPECTIVELY, MARICÁ, RIO DE JANEIRO

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The Caju Granite is important because of its location, between the drainage basin of Ubatiba and Caranguejo rivers, that flow into the Maricá and Guarapina lagoon, respectively, in the region of Maricá, Rio de Janeiro. For this, chemical (major, minor and trace elements) and mineralogical (transmitted and reflected microscopy) analyses were made. Values determined are discussed in the light of field and laboratory work providing a background for further lithogeochemistry/environmental research.

CHEMICAL MINERALOGICAL TRANSFORMATIONS INDUCED BY BASIC INTRUSIONS IN THE PROTEROZOIC SEDIMENTS OF THE CHAPADA DIAMANTINA, BAHIA STATE

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On the western margin of Chapada Diamantina in the central part of the State of Bahia, Brazil, several bodies of basic rocks cut sedimenatry sequences of Middle Proterozoic age promoting effects of recrystallization and chemical exchanges. Near the town of Ipupiara a 50-meter wide tabular body of diabase is concordantly intruded amidst feldsphatic greywackes and pelites in rhythmically alternating beds. Metamorphic and metasomatic effects reach as far as 200 meters into the sedimentary country rocks. The recrystallization did not destroy the sedimentary structures but rather made them resistant against to erosion appearing the previous chiefly pelitic rocks as positive topographic expressions.

The clastic sand grains of quartz and feldspars undergo authigenic growth, while the matrix materials next the intrusion have beem recrystallized into epidote, garnet, and tremolite, and far from it was transformed into micas. The hydrothermal effects are represented by silicification and carbonatation of the country rocks also resulting in the formation of quartz veins, which cut both the intrusive and host rocks. The metamorphic mineral assemblages and the chemistry of these rocks show that the main transforming factor was the increase in temperature, although the metasomatic exchanges of calcium, water, silica and copper have been responsible for much of the recrystallization process. Metamorphic conditions have reached the albite-epidote amphibolite facies of contact metamorphism with maximum temperatures ranging from 400° to 500°C.

The interactive processes of igneous intrusions whithin hydrated sediments created high hydrothermal activity which beside the quartz veins was responsible for small asbestos deposits in the adjoining pelitic host rocks as well as the concentration of malachite in quartz veins. There are also perspectives for mineralization of opal, gold, baryte and other hydrothermal mineral deposits associated with similar contextures, in that region.

COMPOSITE DIKES AT ENSEADA DOS ZIMBOS, PORTO BELO REGION, SC

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Composite dikes have been recognized at Enseada dos Zimbos, in the region of Porto Belo, state of Santa Catarina. Preliminary data on their petrography and geochemistry are presented. These intrusions show basic margins of sharp contacts with the acid core, which may contain swarms of dioritic enclaves, similar in petrographical and geochemical composition to the borders. Enclaves and basic rocks are composed of plagioclase, amphiboles and clinopyroxene, with minor amounts of biotite, chlorite, epidote and calcite; accessory minerals are sphene and opaques. The acid rocks are porphyritic rhyolites and dacites with brown biotite and minor amphibole; sphene, allanite, zircon and apatite are the accessory minerals: Both types of rocks are affected by a northeast-striking ductile shear zone, with superimposed mylonitic features. Geochemical data for the basic parts suggest a continental tholeiitic affinity, with possible contamination of K and Rb from the acid liquids, while the granitic rocks are similar to calc- alkaline, late- to post-collision granites.

DIFFERENTIAL GEOCHEMICAL BEHAVIOUR OF NATURAL ISOTOPES OF U AND TH IN AN AQUIFER IN HUMID TROPICAL TERRAIN

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Uranium and thorium isotopic analyses were performed on spoil samples from the saturated zone of a borehole drilled in the main ore body of a high grade thorium/rare earth ore, and on groundwaters from a borehole drilled in the zone. The deposit is located at Morro do Fero, a hill near the centre of the Poços de Caldas Plateau (MG), where an aquifer system developed in the weathered mantle due to *in situ* intense alteration.

For extraction of uranium and thorium a long chemical process was applied to the samples; activities of Th-228 and Th-232 isotopes (4n series) and also of U-238, U-234 and Th-230 isotopes (4n+2 series) were determind by the alpha spectrometry method.

U-234/U-238 activity ratios in groundwaters were between 1 and 2 but Th-228/Th-232 activity ratios showed marked isotopic fractionation between these nuclides. The mechanism of mobilization of uranium by complexation with humic substances is considered.

U-234/U-238, Th-228/Th-232 and Th-230/U-234 activity ratios in soil samples allowed consider action of other possible mechanisms related to the mobilization of uranium, such as, ion-exchange reaction and adsorption by Fe and Mn oxides.

EPIDOTE-BEARING CALC-ALKALIC AND ULTRAPOTASSIC PERALKALIC GRANITOIDS IN NORTHEAST BRAZIL: SULFUR AND OXYGEN ISOTOPES GEOCHEMISTRY.

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Five different groups of granitoids intruded the phyllites and schists of the NE-trending Cachoeirinha-Salgueiro Fold Belt (CSF) or the adjacent migmatites of its basement, NE Brazil, during the Brasiliano (= Pan-African) cycle. Porphyritic K-calc-alkalic batholits intruded the basement rocks along the northern boundary of the CSF at a depth of about 15km, around 580 Ma. Calc-alkalic tonalites to granodiorites with four textural types of magmatic epidote intruded phyllites in the middle portion of the CSF, at a depth of about 18 to 27km. Leucocratic, epidote-bearing tonalites to granodiorites, with continental trondhjemitic affinities are restricted to the area of outcrop of higher grade metamorphics of the Salgueiro Group, in the cores of two ring-structures, with over-saturated peralkalic rocks towards the margins. Ultrapotassic syenites with subordinate associated pyroxenite form a syenitoid line, emplaced at about 580 Ma, following pull-apart opening of fractures, along 150km of the southern boundary of the CST. In its northern extension, peralkalic rocks are replaced by shoshonitic granitoids.

Three of these groups of granitoids display $\delta^{18}O$ values between 9 and 10 permil$_{SMOW}$. The epidote-bearing calc-alkalic group, however, exhibit all values above 11 permil$_{SMOW}$, mostly between 12 and 13 permil, while "pyroxene-corrected" whole-rock $\delta^{18}O$ values for rocks in the syenitoid line cluster around 8 permil. The high $\delta^{18}O$ values for the epidote-bearing calc-alkalic plutons were probably inherited from the source rocks and this isotope behaviour cannot be generalized for plutons of the same kind elsewhere. All groups exhibit positive $\delta^{34}S$, usually higher than +6 permil$_{CDT}$. Values for the ultrapotassic syenites and pyroxenite range from 6 to 12 permil. The Sr, O and S isotope signatures of this ultrapotassic province, coupled with their LILE-enrichment suggest an anomalous mantle source, which may have existed beneath NE Brazil and part of west Africa since Archaean times.

GEOCHEMICAL DATABASE MANAGEMENT

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The implementation of a geochemical database management system being developed at the University of Brasilia, according to the IGCP-239-IGBA models, is described.

In the proposed system, through the screen layouts presented, the user can search geochemical and petrological data of Brazilian igneous rocks, mainly those concerning bibliographical reference, major, minor and trace elements, modal composition, isotopic age, isotopic ratios and supplementary information.

GEOCHEMICAL INVESTIGATION OF HIT-SHITHATHA THERMAL SPRINGS, WESTERN IRAQ.

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Thermal springs are scattered in the hit and Shithatha area, western Euphrater River in Iraq. It is well-established that the distribution of these springs is controlled by the major tectonic event, of pre-Tertiary age, known as the Hit-Abu Jir faults.

The springs are clsssified as thermal, whose maximum temperature reaches, up to 32oC, and some of these springs (in Hit) discharge bituminous materials, while no bituminous springs exist in Shithatha area.

The prevailing climates in the two areas are arid, with average rain fall of about 100 mm/year.

The origin of these springs and their inter relationship with the geological setting of the region need further investigation, a contribution to which is the aim of which this paper Furthermore, the paper deals with the geochemical behaviours of selected elements in the spring water, and in the soil sourrounding spring sites, which is drained by these springs under the prevailing climatic conditions of a highly arid nature.

Soil samples collected from sites influenced by the discharge of the spring water were analysed for the following major and trace elements; SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, P_2O_5, and SO_3, Sr, Mn, Ni, V, Pb and L.O.I. for spring water, the Ph, dissolved oxygen, conductivity, turbity and temperature, were measured in situ. Samples were then analysed for the following major and trace elements; Na, K, Mg, Cl, SO_4, HCO_3, H_2S, TSS, Ni, Cu, and Mn.

Factor analysis of the soil data showed five factors. The first factor includes SiO_2, Al_2O_3 and TiO_2 with positive factor loading, and CaO, L. .I with a negative loading, this may reflect the effect of transported clay material on the distribution of these variables. The second factor includes, Fe_2O_3, Al_2O_3, TiO_2, MgO, K_2O, P_2O_5, Mi and Mn, all with positive loadings and, therefore, might be correlated with the clay material, suspended in the spring water passing though the marl of the Euphrates Formation, which belongs to the late lower Miocene cycle. The third factor, which includes Na_2O, Ni and V with a positive loading and a ph with a negative loading. This latter factor may reflect the effect of bituminous material, which is discharged with spring water in the Hit area, though it is mainly due to the vegetation litter in the Shithatha area. The fourth factor includes only two variables, SO_3 with a positive loading and L.O.I with a negative loading; and are most probably due to the precipitation of gypsum on the surface, hence reducing the amount of organic material in the soil. The fifth factor includes only two variables; Pb with a positive loading, and PH with a negative loading, which may reflect the effect of a high Ph in the immobilisation of Pb in soil.

Concerning the hidrogeochemistry of the spring water, the results obtained show an evidently contrasting nature of the spring water of the two areas represented by higher rNa/rCl and H_2S, Ni and TSS concentration in the Hit springs water compared with the Shithatha springs water.

The paper concludes that, in spite of the structural relationship between the springs of the two areas investigated, they evidently differ as to source and origin.

The recharged source of the Hit springs is rather deeply-rooted to the hidrocarbon accumulation reservoir, while the recharge of the, Shithatha springs is rather shallower, and it seems that the two recharge sources are not connected.

GEOCHEMICAL SIGNATURES OF LATE CRETACEOUS DEPOSITIONAL ENVIRONMENTS, SAN JUAN BASIN, NEW MEXICO

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Huntite, $Mg_3Ca(CO_3)_4$, a metastable, ordered, double carbonate, has been found in surface or near-surface, low temperature, Holocene environments. Its origin has been attributed to geochemical weathering and evaporitic processes. Huntite always occurs as micron-sized, platy crystals associated with other carbonates. It is now known from core samples from the Late Cretaceous (Campanian-Maastrichtian) Fruitland Formation, San Juan Basin, New Mexico. The core and outcrops are characterized by coals, mudstones, shales, and sandstones, deposited in association with the oscillations of the Late Cretaceous epeiric seaway. The sequence is punctuated by volcanic ash.

INTRODUCTION

Huntite, $Mg_3Ca(CO_3)_4$ is a naturally occurring, metastable, rhombohedral carbonate whose composition is intermediate between dolomite, $MgCa(CO_3)_4$, and magnesite, $MgCO_3$. The polyhedral connectivity, however, differs, from that of the latter carbonate. The atomic arrangment in space group R32 is a = 9.5027(6) angstroms, c = 7.8212(6) angstroms.

It is a fully ordered within the accuracy of the data and the bond lengths are not significantly different from those found in dolomite. In huntite, the Ca polyhedron is nearly a trigonal prism, which is unusual for VI-coordinated CA, but not unusual for rare-earth elements. A series of borates are isostructural with huntite. In the more common rhombohedral carbonates, the Ca polyhedron is a nearly regular octahedron. There are two crystallographically distinct carbonate groups.

Unlike the dolomite structure, where each alkaline earth layer contains either Mg or Ca, the layers in huntite contain both cations. Also, in the calcite and dolomite structures, each Ca or Mg polyhedron shares three of its six corners with the Ca or Mg polyhedron in the layer above, and the other three corners eith the layer below. Edges are not shared.

In huntite, however, the cation polyhedra share corners with the edges above and below in such a way that two edges, one in each neighbouring layer, are also shared. This edge sharing forms three-octahedron-repeat, infinite spiral chains running parallel to the c-axis. The shared octahedral edges (2.63 angstroms) are substantially shroter than the unshared edges (3.00 angstroms).

OCCURRENCES

Huntite was first described as a near surface weathering product at Currant Creek, Nevada, and Eureka, Utah. Since then is has been described at several other localities representing four distinct depositional environments:

1) as a near surface weathering product.

As originally described, it is thought to have precipitated from cool, magnesium-rich ground waters that had traversed various intrusives. Similar deposits have been reported from Gabb, Nevada.

In Victoria, Australia, at Deer Park, Geelong, and Tea Tree Gully, huntite again is associated with weathered basalts and carbonates. It occurs as sporadic, white nodules in magnesite-lined vesicles in clays and shales underlying weathered basalts. The occurrences are consistent with it having precipitated from cold descending solutions.

2) as a constituent of "moonmilk" in limestone caves.

In Carlsbad Caverns, huntite occurs as a "nearly white and pasty to powdery" irregular, nodular coating on bedrock or other spleothems. It has been suggested that "moonmilk" has a biosynthetic origin.

In the dolomitic la Clamouse grotto of l'Hérault, France, the "montmilch" consists of huntite with 4.5% silica and hydrated iron oxide.

3) as a secondary mineral in soil.

In a Vertisol near Katherine, Northern Territory, Australia, huntite occurs as highly localized 1-5cm white nodules in the most porous part of an alkaline, clay soil, suggesting that it may be associated with "lost springs".

4) as a early diagenetic evaporite in a recent, supratidal, evaporitic environment.

Along the Trucial Coast, Persian Gulf, sediments, which initially, were totally carbonate, are being extensively dolomitized, and a suite of early diagenetic minerals is being developed by precipitation from interstitial seawater-derived brines and by reactions between original carbonate sediments and brines.

The supratidal surface has an elevation of 1-1.5m above mean sea level, and, in some areas, is more than 15km wide. The area results from partial infilling of marine lagoons and an essentially constant sea level over the past 4,000-5,000 years. Rainfall averages less than 4cm per year. The water table lies ... The huntite occurs as wisps and blebs 15-40cm below the surface in a muddy sand matrix and is associated with anhydrite, gypsum, celestite and traces of dolomite. It post-dates marine carbonate sedimentation.

DEPOSITIONAL ENVIRONMENT OF LATE CRETACEOUS HUNTITE

During the Cretaceous, from mid-Albian to mid-Maastrichtian time, the Rocky Mountain region was inundated by a shallow epeiric sea that extended approximately 5,000km from the Gulf of Mexico to the Artic Ocean and was approximately 1,500km wide, stretching eastward to the prsent day Mississippi River.

Deposition of sediments into the New Mexico portion of the basin was associated with five major transgressive-regressive cycles resulting from periodic sea level shifts during the late Cretaceous. The oscillations were controlled by global sea-level changes and tectonic episodes in the Cordillera. The source of sediments deposited in the basin is thought to have been a low-relief area to the southwest. During the late Campanian, early Maastrichtian, following the fifth transgression (T-5), the San Juan Basin lay along the western margin of the seaway. The non-marine Fruitland Formation is the lower coastal plain deposited behind the Pictured Cliffs shoreline. It is a sequence of paluidal carbonaceous shale and coal interbedded with silstone and lacustrine, fluvial or distributary sandstones.

Throughout the Cretaceous Period, volcanic activity produced widespread ash falls. It has been suggested that transgressions correlate strongly with periods of intense vulcanism. The Campanian regression (T-5) is also associated with intense vulcanism. The changing shape of the Basin during this period suggeste sea level changes due to tectonism.

Paleoenvironmental conditions of formation

The occurrences of huntite have been confirmed by X-ray diffraction analyses at five and, possibly, seven sampling horizons from a 94m (303.4 ft) continuous core drilled in section 24, T. 23 N., R. 12 W. of the Fossil Forest Study Area, located south of Farmington and north of Chaco Canyon in the west-central portion of the San Juan Basin.

The core and outcrops are dominated by sequences of coals, mudstones, siltstones, medium-grained sandstone and clay pebble conglomerate. Sideritic concretions are common, vary in morphology and are laterally extensive. Two resinous coal beds with ash and clay partings outcrop in the study area.

In the core, between 33.9 and 34.7 feet, huntite is associated with quartz, feldspar and clay in a yellowish-grey (5 Y 7/2) fine-grained silty sandstone. The contact below the horizon is non-conformable and is intensely stained greyish-blue (5 PB 5/2).

Between 80.3.81 feet from the top of the core, huntite occurs in association with siderite and trace amounts quartz and clay. It is very fine-grained, pale to dark yellowish brown (10 YR 6/2-10 YR 4/2). Ita grades into an overlying medium dark grey, carbonaceous mudstone (N4) with bedded coalified leaves and wood. Between 132.6 and 142.6 feet, huntite occurs in a very clean, medium-grained sandstone punctuated with coaly beds and mud clasts (clay balls). The sandstone is cross-bedded in some intervals. The carbonaceous horizons are resiniferous.

CONDITIONS OF DEPOSITION

Recent huntite depositional environments are characterized as quiescent, subaerial, low temperature environments at atmospheric pressure. In all cases, the huntite occurs as micron-sized crystals.

Periodic Laramide tectonism associated with the Nacimiento Uplift most likely restricted the flow of warm currents from the sourteast into the region. This resulted in localized shallowing of the Seaway and evaporite dominated environments. This depositional model is analogous to that seen in the Trucial Coast today, and suggests alternating drier and humid climates.

An alternative to the evaporitic model is the formation of paleosols. Either case suggests climate cyclicity previously inferred for the Late Cretaceous on the basis of marine carbonate cycles. In addition, these huntite occurrences provide evidence for climate control of coal deposition rather than the preponderant facies models seen in the literature.

GEOCHEMISTRY AND MEANING OF THE GEO-TECTONIC OF PLUTONIC ROCKS IN THE REGION OF CHAPADA, STATE OF GOIÁS, BRAZIL

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In common with other orogenic belts, in which the presence of both, granitic and small basic-ultrabasic intrusions are characteristics of medium-high pressure metamorphic terranes, the geological and geochemical evidences indicate a close relationship between the granitoid, gabbroic and pyroxenitic plutons and the orogenic metabasaltic rocks from the Chapada volcano-sedimentary sequence.

The granitoids are tonalitic and, on discriminant diagrams, they plot in the volcanic arc and pre-collisional fields. They display geochemical characteristics similar to the Jamaican oceanic arc-related granites. They show low LIL and low HSF element abundances, low (Ta, Nb)/(K, La, etc.) ratios and very low concentrations of Th, Hf, K and Y, when compared to patterns of calc-alkaline, alkali-calcic and alkaline-peralkaline granitoids of magmatic arcs. These chemical features are characteristic of immature island arcs mantle-derived intrusives.

The Chapada olivine gabbro has a chondrite-normalized spidergram, closely resembling those of island-arc basaltic lavas, the compositions of its coexisting olivine and plagioclase being similar to those from arc-related cumulate gabbros, and, therefore, it could be the plutonic equivalent of the arc volcanics in the Chapada region.

It is suggested that the evolution of the granitoids and gabbro intrusives from Chapada are related to a process of subduction that occurred in central Brazil during the Brasiliano/Pan-African event.

GEOCHEMISTRY OF META-IGNEOUS ROCKS FROM CEARÁ, NORTHEAST BRAZIL: AN EARLY MIDDLE PROTEROZOIC FAILED RIFT?

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In S and E Ceará State, a belt of low- to medium-grade meta-volcano sedimentary rocks with accompanying intrusives forms a prominent, boomerang-shaped element of the regional geology. Previous studies of the N-S arm of the boomerang (Mendonça and Braga, 1987; Sá et al., 1988) led to the conclusion that the rocks were deposited in an ensialic rift at the beginning of the Middle Proterozoic (Macedo et al., 1988) and were deformed during the late Upper Proterozoic.

In this study, a reconnaissance petrographical and geochemical investigation of meta-igneous rocks from the E-W limb, and from the southern extremity of the N-S limb was undertaken. In these sectors the hydrothermal activity, which accompanied the latest transcurrent shear deformation, was locally very intense, and resulted in extensive mineralogical transformations of some of the rocks. As far as posible, these were avoided in the present discussion.

The volcanic suite is bimodal. Many basic members were probably porphyritic flows. Their geochemical patterns (Pearce's F_1-F_2–F_3: 1976; Meschedo's Zr-Y-Nb: 1986; etc) are consistent, and show affinities with modern continental tholeitic WPB or anomalous MORB. The closest modern analogy found is with early continental break-up basalts. The felsic rocks include tuffaceous, hypabyssal and plutonic types whose geochemical characteristics most closely resemble those of crustally-derived rocks. Highly differentiated, initially mantle-derived, and hybrid types may be present. The ultrabasic and some basic rocks are cumulates and other components of a sill, and are probably not komatiites, which Mendonça and Braga (op. cit.) believe to have found in the N-S limb.

It is difficult to evaluate how closely present chemical spectra reflect primary patterns. Although they may rettain primary igneous textures, even the most preserved rocks possess completely transformed, metamorphic mineral assemblages with important quantities of hydrothermal minerals of at least one generation. Therefore, no satisfactory internal comparison standard is available to check element gains and losses. Nevertheless, to transform original orogenic geochemical patterns into the present, apparently anorogenic patterns, would require high mobility of elements such as Ti, Zr, Nb and REE. According to the bulk of current literature, such high mobility of these elements is unlikely to occur.

The associated metasediments include psammitic and pelitic types. A parallel laminated, argillite-siltite rhythmite is well preserved, with graded bedding seen in the coarser-grained beds. Chemically derived metasediments include BIF and limesontes. while metasediments of mixed origin include banded cherty felsic tuffs, locally mineralized with pkyrite. Also present are fine-grained tourmalinites and banded tourmaliniferous felsic tuffs, structurally continuous with the cherty tuffs. The origin of these rocks is uncertain, but they may have been deposited from volcanic emanations. The BIF and banded cherty rocks occur in a sector where basic metavolcanics and basic/ultrabasic metaintrusive rocks are abundant. Magnesite-rich rocks here are probably derived from ultrabasic protoliths by hydrothermal activity. Thus, submarine volcanism and associated sedimentation was important during the deposition of the belt. On the other hand, the present chemical composition of a few samples of felsic metavolcanic rocks may have resulted during a subaerial weathering stage.

The opportunities for mineralization are multiple. Mafic- and felsic-related submarine volcano-exhalative deposits are possible, although the geochemistry of the volcanic rocks, including the banded cherty tuff, does not lead to high expectations for base metal concentrations. The presence of crustally-derived felsic rocks suggests that the area could have potential for deposits related to this type of magmatism. Finally, the late deformation-related hydrothermal activity provides a chance for the secondary concentration of the elements. The latter process was important in another area in Northeast Brazil with similar depositional and deformational histories, in which U-albitite deposits are attibuted to this phase.

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GEOCHEMISTRY OF PIRANHAS GRANITE

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Geochemical studies in granitic rocks from the Serra Negra region, Piranhas, Goiás State, were developed, including the determination of major (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, P_2O_5 and H_2O^+) and minor elements (Cu, Pb, Zn, Ni, Cr, Mo, Li, Rb and Cs).

Special emphasis was given to the Mo determination in considering the molybdenite occurrence in some areas. Petrographic description, normative and modal analyses indicated homogeneous characteristics of granites. Only one sample presented anomalous Mo content (286 ± 10ppm).

INTERPRETATION OF THE CHEMICAL COMPOSITIONS OF THE CUMULATES OF THE GABRO-ANORTHOSITIC MASSIF OF RIO PIAU - BAHIA STATE

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The Rio Piau gabbroic and anorthositic complex is an Archean layered body, intrusive in the charnokitic and enderbitic terrains of the Jequié nucleous (São Francisco Craton, Bahia State, Brazil).

The geochemical data of the Rio Piau massif consists of two magmatic series, better identified by REE, titanium, phosphorous, niobium and gallium contents. These two magmatic series show an evolution following the typical tholeiitic and several types of cumulatic rocks.

The evolution of each magmatic series is made up by differentiation and accumulation, from basic terms ($MgO = 10\%$) up to intermediate terms ($MgO = 2\%$) and shows an evolution similar to the Skaergaard trends.

ISOTOPE GEOCHEMISTRY OF BRASILIANO AGE, COARSELY PORPHYRITIC, K-CALC-ALKALIC GRANITOIDS AND ASSOCIATED K-DIORITES, NORTHEAST BRAZIL

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Several porphyritic, K-calc-alkalic granitoids were syntectonically intruded in NE Brazil during the Brasiliano orogeny. They show bi-(qz) diorite and coarsely porphyritic granodiorite to qz monzonite ("Itaporanga-type") in commingling zones on a scale of cm to m irrespective of whether plutons are at the margins of the NE-trending Cachoeirinha-Salgueiro Fold Belt (CSF) or intruded metasediments of the Seridó Fold Belt (SFB). The bi-(qz) diorites are found in (a) magmatic or (b) stromatic structures and (c) narrow dikes which intruded the felsic facies. Amphibole geobarometry suggests emplacements around 5 kb.

SiO_2 in the porphyritic facies ranges from 61 to 72% with K_2O usually $> Na_2O$. K-diorites exhibit SiO_2 from 50 to 58%, MgO from 2 to 10% and K_2O from 2 to 5%. Both facies are usually Ba and Sr-enriched, with similar, highly fractionated REE patterns, lacking free of Eu anomaly. Primordial mantle-normalized multi-elemental diagrams for the K-diorites show negative slope, discrete P and Nb negative anomalies. In the SFB the Nb anomaly is negligible, P is more profound and MgO much higher, suggesting K-diorites locally represent less evolved magmas.

Quartz 180 values are considered homogeneous on the scale of these intrusions in the CSF, (8 to 10 per milSMOW). Bi-(qz) diorites exhibit slightly higher 180 (9.5 to 10.5 per milSMOW). In the SFB both facies are lower than 180. The oxygen isotope data for the porphyritic facies are compatible with I-type source with some metasedimentary component of variable proportion. As bi-(qz) diorites were formed pre- to post-porphyritic facies intrusion, their high LREE, K and 180 reflect their source rather than the interaction with the potassic felsic magma. Preliminarly sulfur isotope values suggest that porphyritic facies of granitoids in the SBF are lower in 34S than those in the CSF. Rb and Sr isotopes reflect source heterogeneity, complicated by mixing relations. Ages span from 510 to 630 Ma suggesting that the Itaporanga-type association was formed during uplift and cooling of the Pan-African I and onset of the Pan-African II orogenies, recognized in West Africa.

LEAD-LEAD DATING OF MIGMATIC ROCKS FROM THE REGION OF SÃO JOSÉ DOS CAMPOS, SÃO PAULO STATE, BRAZIL

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Lead isotope analyses have been carried out on the migmatitic rocks belonging to the basement of the Embu Complex occurring in the region of São José dos Campos, São Paulo State. These migmatites feature predominantly stromatolitic structures, with the paleosome made up of biotite gneisses and biotite-hornblende gneisses of granitic to tonalitic composition. The neosome is light grey coloured, fine-to medium-grained with granitic composition.

Five neosome and ten paleosome samples have beem analysed by the Pb-Pb method in the present study. The samples were processed chemically in a clean laboratory of the type class 100, using reagents distilled by the sub-boiling technique. The samples were acid-digested and the lead was separated using the ion exchange method, with HBr as the eluting agent. Lead isotope ratios were measured with a Micromass VG Isotopes model 354 thermal ionization mass spectrometer, and the ratios were corrected for isotope fractionation using a factor of -0.072% a.m.u., determided on NBS 982 standard.

When the points were plotted in a Pb-Pb isochron diagram, seven out of the ten paleosome samples defined an age of 2,335 ± 85 Ma, with an μ_1 value of 8.33. The data could be interpreted as the age of metamorphism with the rocks being formed probably in the Archean. The neosome samples yielded a Pb-Pb isochron age of 1,388 ± 290 Ma, with $\mu 1 = 8.15$, which could be interpreted as the period of migmatization.

Rb-Sr isotope dating of these rocks showed a large scatter of the data points on the isochron diagram. The regression analysis of the data points sugest age and initial ratio values of 2,425 ± 47 Ma with $(^{87}Sr/^{86}Sr)_{initial} = 0.706$ for the paleosome and 1,434 ± 40 Ma with $(^{87}Sr/^{86}Sr)_{initial} = 0.738$ for the neosome samples. The scattering of data points in the Rb-Sr diagram imply that the system was not isotopically closed during its evolution, unlike the Pb-Pb isotope system. The study thus demonstrates the better applicability of the Pb-Pb dating method for migmatitic rocks.

MINERAL CHEMISTRY OF METAPELITIC ROCKS OF THE SERIDO FORMATION, NORTHEASTERN BRAZIL.

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A chemical study of minerals in Precambrian metapelitic rocks of the Serido Formation, northeastern Brazil, was undertaken in order to characterize the mineral phases co-existing in these rocks. Two populations of biotite, garnet, and muscovite were analysed. Chemical analyses of the minerals suggest total (biotite) to partial (garnet) chemical re-equilibrium of first generation minerals during the second deformational event.

Al^{iv} and Ti content in biotites increases with increasing temperature. The anorthite component in plagioclase varies from 20-40%, and there is no correlation between X_{an} and temperature. Staurolite and cordierite do not show chemical zoning.

MINERALOGY AND CRYSTAL-CHEMISTRY OF CUPRIFEROUS SILICATED PRODUCTS OF THE SANTA BLANDINA MINE (ITAPEVA, BRAZIL)

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The copper index of Itapeva (about 250km west of São Paulo, Brazil) is associated to a mineralized skarn (chalcopyrite, bornite) generated through a metasomatic process along the boundary between a limestone lens and a granitic batholith (600 MY old). In the Santa Blandina quarry, the skarn, containing variable amounts of garnets (andradite-grossular), quartz and minor pyroxenes, is highly weathered into a highly porous saprolite. At the base of the profiles, copper is concentrated in two distinct Cu-bearing products.

(1) Clay-like products with brownish to green macroscopic colours, reflecting various chemical compositions ranging from (weight %) 4 to 12% Al_2O_3; 1.5 to 6% Fe_2O_3; 19 to 32% CuO. Toward green products, the main chemical variation is a loss of Fe_2O_3 and Al_2O_3 and a gain of CuO, while SiO_2 remains quite invariant.

(2) Chrysocolla (about 40% CuO).

Petrological observations argue for the epigenetic replacement of skarn minerals (garnets and quartz, essentially) by clay-like products. Unweathered primary minerals of skarn contain no copper, suggesting that Cu was supplied in secondary products by weathering solutions released by sulfides alteration. In leached higher horizons of the profiles, chrysocolla crystalizes along the void rims and in more porous zones, at the expense of clay-like products. This in situ mineralogical evolution is initiated through a leaching process by circulating Cu-enriched solutions.

Various clay-like products and chrysocolla were studied by means of XRD, TEM, IR and a more recent spectroscopic tool: EXAFS (Extended X-ray Absorption of Fine Structure), which provides information on local surroundings of a chosen atom (Cu i this case). One of the aims of this work was to characterize the intracrystalline distribution of Cu in secondary accumulation products.

X-ray diffraction results show that clay-like products are composed of an intimate association of smectite and regular smectite/kaolinite mixed-layer clay (S/K). The (b) parameter calculated from the (06-33) spacing underlines the dominant dioctahedral type of this clay fraction. Moreover, on XRD spectra and especially for green clay-like products, some large modulations at 2.85-2.90 and 1.63 A, could suggest the presence of chrysocolla in clay-like products.

Transmission electron microscopic observations on clay-like products show, in close association with platy clay particles, the typical fibrillar morphology of chrysocolla. Ponctual chemical analyses (STEM) however do not permit separation of Si, Cu, Al and Fe among two distinct fractions: chrysocolla (Si, Cu) and an aluminous clay fraction (smectite and S/K) (Si, Al, Fe, ± Cu).

Infrared spectra, however, confirm the presence of chrysocolla in clay-like products and reveal a mineralogical evolution from brown to green clay-like products: a gradual increase in typical chrysocolla absorption bands, together with a progressive removal of aluminous phases (smectites and S/K) of spectral features.

From EXAFS spectroscopic results, finally, it appears that Cu atomic surroundings (first and second coordination shell) is identical in both clay-like products and chrysocolla (figure 1). The Cu^{-}(O-OH) distances obtained for the first coordination shell correspond to highly distorted octahedral sites, characteristic of chrysocolla.

So, whatever the secondary accumulation products at Santa Blandina,copper is segregated in a separate phase: chrysocolla, which increases from brown to green clay-like products with a copper content. Clay fraction (smectite and S/K) contain probably no copper or very small amounts.

Copper segregation in a specific cupriferous mineral emphasizes the particular geochemical behaviour of copper. Cu^{2+} electronic properties (Jahn-Teller effect) involve a strong octahedral site deformation. Copper reacting with silica in solution tends to precipitate chrysocolla rather than incorporate a regular clay lattice.

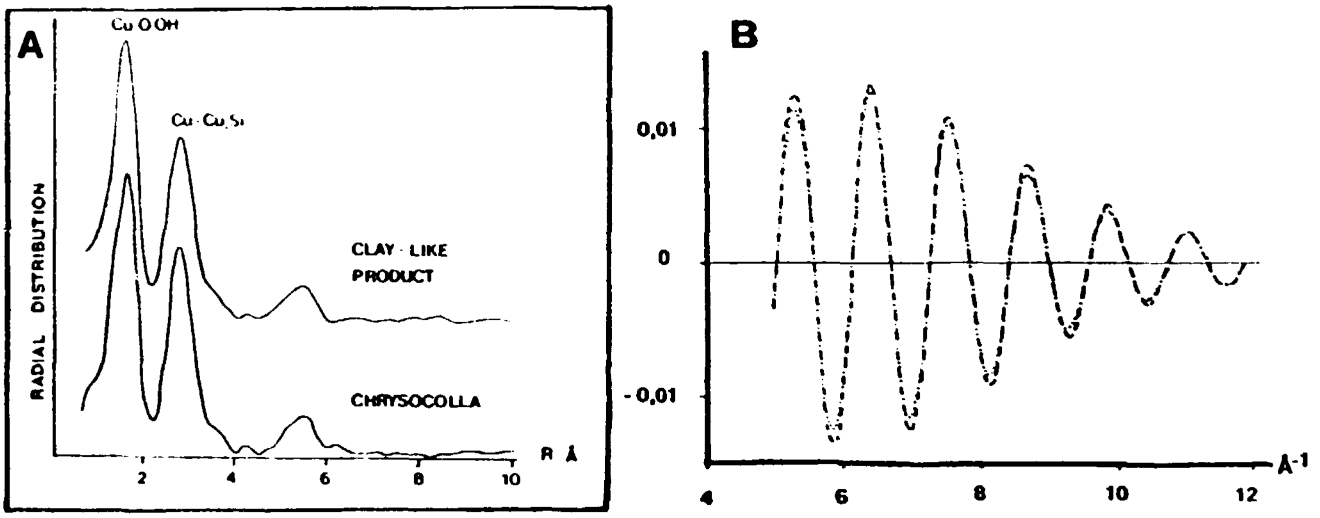

Figure 1 : EXAFS results. A : Radial distribution functions for clay-like product and chrysocolla (first and second coordination shells). B : Inverse Fourier transforms of radial distribution function for the second shell of clay-like product (dotted line) and chrysocolla (dashed line).

Mn^{2+} PARTITIONING BETWEEN MAGNESIUM AND CALCIUM SITES IN DOLOMITE STRUCTURE AS A GEOCHEMICAL INDICATOR OF CARBONATE FORMATION CONDITIONS

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The recent investigations of ESR spectra of dolomites have shown that Mn^{2+} ions occur in the two different positions in dolomite structure. It is known that the assymetric line of the ESR spectra of dolomites corresponds to substitution position of Mg^{2+} by Mn^{2+}, and the symmetric one - to Mn^{2+}, substituting Ca^{2+} site. The distinct recognition of manganese ions in Mg - and Ca-sites on the ESR spectra permits us to evaluate the Mn partitioning between these two structural positions.

We studied the powder samples of dolomite rocks of the Tadjik depression, formed at various facies environments in the Mesozoic shallow marine basin. For determination of relative contents of Mn^{2+} ions in the two structural positions, we usally used the high-field component of spectra, where these positions are distinctly visible. Taking into account that the area under each absorption peak is proportional to concentration of considered paramagnetic ions, the Mn^{2+} partitioning coefficient between magnesium and calcium sites in dolomite structure is estimated simply as the ratio of areas under corresponding absorption curves.

Our investigations show that Mn^{2+} partitioning between the two structural positions in dolomite is not dependent upon the concentration of element, but reflects the physico-chemical conditions of sedimentary rock formation. The partitioning coefficient increases regularly from the value 1.5 in dolomite rocks, formed in littoral and near-shore facies, to 4.0-5.0 in dolomites of the inner parts of sea basin, and reaches the maximal values (on average -8.6) in dolomite sediments, generated in bays and lagoons under arid climatic conditions.

The comparison of our data on Mn^{2+} partitioning in dolomite structure, obtained by the ESR method, with the results of paleohydrochemical investigations leads to the conclusion that the partitioning coefficient apparently reflects the initial Mg/Ca-ratio in the paleowaters of the sedimentation basin or in dolomitized solutions, that is, the increase in salinity and the Mg/Ca-ratio in paleowaters promoted the preferential entrance of Mn^{2+} ions into Mg-site in dolomite structure.

Thus, the Mn^{2+} partitioning between the two structural positions in dolomite is very interesting, not only from mineralogical aspect, but can subsequently serve as a geochemical indicator for the determination of facies conditions of dolomite formation.

PALEOHYDROCHEMISTRY OF THE JURASSIC HUMID AND CRETACEOUS ARID FORMATIONS OF THE TADJIK DEPRESSION

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The use of various geochemical data (the relative composition of ion-changing cations K, Na, Ca, Mg in the clayish rochs, the distribution of the different forms of B in them etc.) and the experimental investigations of sorption equilibria on the clayish particles and minerals permit the authors to characterize the paleohydrochemical formation conditions of the Jurassic humid and Cretaceous arid deposits of the Tadjik depression. The relative salt composition of sedimentational waters was calculated and their evolution traced in time.

Our investigations showed that, during the whole Mesozoic era, the sedimentation had proceeded, in principle, under conditions of perceptible freshing of sedimentational waters. This was the result of sedimentation peculiarities in the region considered: the epicontinental character of existing seas here, their shallowness, relative proximity of feeding provinces and the extensive influxes of river waters. The maximal freshing of sedimentational waters was established to be in the Jurassic humid climate.

The arid climate and frequent changes of transgressions and regressions of sea caused the essential instability of the hydrochemical regime during the Early Cretaceous. The connection of the Early Cretaceous sedimentation basin of the Tadjik Depression with the open sea was apparently insignificant. All these factors led to the wide spreading of sediments, formed in the lagoons and bays.

The Mesozoic basin occupied the maximal surface during the Late Cretaceous epoch, which was charactetized by the wide spreading of marine facies sediments. The high relative contents of Na in ion-changing cations composition in clayish rocks is supposed to testify to the close connection of the Late Cretaceous sedimentation basin with the open sea. In the south-western part of the region, the salinity of sedimentational waters was considered to be close to the "normal" marine one. The see regressions and arid climate resulted in sediments formation under the conditions of resting lagoons, with higher water salinity.

Thus, during the Mesozoic, the salinity of sedimentational waters gradually increased on average. This was connected as much with climate aridization as with the influence intensification of the open sea on the composition and salinity of the sedimentation basin waters of the Tadjik Depression, from the Early Jurassic to the Late Cretaceous.

PETROCHEMICAL CHARACTERISTICS OF SERRA DO MEIO ALKALINE GRANITE (CAMPO ALEGRE DE LOURDES-BAHIA STATE)

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The Serra do Meio granite outcrops near the town of Campo Alegre de Lourdes, north-northeast of Bahia State. The granite is intrusive into micachists, which are correlatives of the Salgueiro-Cachoeirinha Group (Early Proterozoic), during early to the syn-tectonic shear phase. The geological setting also comprises a phosphatic rock-bearing carbonatitic complex and gabbroid complexes with one of the main world resources of Fe-Ti-V. The granite mineralogical composition grades from Aegerine-augite alkali-feldspar granite/syenites to Leuco alcali-feldspar granite.

The geochemical analysis shows SiO_2-enrichment (67 to 76%), in alkalis ($Na_2 + K_2O$, 7,5 to 12,5%), Nb (up to 680ppm), Zr (up to 2,390ppm), Y (up to 250ppm) e REE (up to 796ppm). The geochemical behaviour is peculiar to alkaline series, denoting a silica-oversaturated, potassium-rich, magma.

The chondrite-normalized REE patterns display a first group with smooth slopes from the La to Lu, and a second one with negative slopes. Negative Eu anomalies are displayed in all the patterns. The first group is HREE-enriched, with low fractionation ratios. Samples with milonytic fabrics and higher fractionation ratios are related to the second group, suggesting the interaction of metassomatic fluids and the alkaline magma.

Discriminant diagrams for Nb, Y and Rb, coupled with geophysical data, point to an intrusive granite in an extensional within a plate tectonic setting of attenuated continental crust.

PROPOSAL FOR A GEOCHEMICAL AND GEOLOGICAL DATABASE AT THE UNIVERSITY OF BRASÍLIA

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Some attempts have been made in the world in order to standardise processes of storage and management of geochemical data from igneous rocks.

This work describes the principles and structure of an igneous rock data bank at the UnB - Universidade de Brasília (BRDI-UnB), associated to the IGCP Project 239 - IGBA.

The system was designed to run in PC-compatible microcomputers, as a contribution to the Brazilian Working Group of IGBA.

PYROXENE END-MEMBER PARAMETER RECALCULATION WITHOUT ALUMINA CONTRADICTION

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The calculation of pyroxene end-member parameters proposed by Cawthorn & Collerson (1974), which is widely-known and highly accepted, implies, however, an alumina contradiction problem in application to the pyroxenes of alkaline leucocratic rocks with high Na and relatively low Al_2O_3: After the calculation of the titanotschermak component, the rest of the Al_2O_3 becomes a negative value. The present paper shows a new method without alumina contradiction, based on cation balance equations.

The main pyroxene-forming elements are subdivided into 6 groups by their chemical behaviour: (Na, K); (Mg, Fe^{++}, Mn); Ca; (Al, Fe^{+++}); Ti; and Si, and the pyroxene end-members are classified into 5 clans:

Clinopyroxenes,	$Ca(Mg, Fe^{++}, Mn)Si_2O_6$
Orthopyroxenes,	$(Mg, Fe^{++}, Mn)_2Si_2O_6$
Alkaline pyroxenes,	$(Na, K)(Al, Fe^{++})Si_{26}$
Tschermak components,	$Ca(Al, Fe^{+++})$ $(Al, Fe^{+++})SiO_6$
Titanotschermak component,	$CaTi(Al, Fe^{+++})_2O_6$

Considering the latter 4 as variations of the first, they are attributed to the following 4 combined allo-valent substitutions:

$$Ca \rightarrow (Mg, Fe^{++}, Mn)$$
$$Ca(Mg, Fe^{++}, Mn) \rightarrow (Na, K)(Al, Fe^{+++})$$
$$(Mg, Fe^{+++}, Mn)Si \rightarrow (Al, Fe^{+++})(Al, Fe^{+++})$$
$$(Mg, Fe^{++}, Mn)Si_2 \rightarrow Ti(Al, Fe^{+++})_2$$

Each group of elements forms a cation balance equation related to these substitutions. Then there are 6 equations (6 group of elements) and 4 unknown parameters (4 substitutions). Theoretically, these equations have 15 solutions, but, in fact, 2 of them are nonsense. The solution for each clan is redistributed into the end-members. By means of comparison of these 9 solutions, reliability of the chemical data and recalculations can be checked.

In relation to the Cawthorn & Collerson method (1974), the new one provides relatively high acmite and Al-tschermak components, and low jadeite and Fe-tschermak components. The author presents a computer program for the new calculation in BASIC language of the MSX world standard, personal computers.

STEPS IN THE STRUCTURAL DISCRIMINATION OF GRANITOIDS USING DRAINAGE SEDIMENTS

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Drainage sediments collected over granitoids related to distinctive tectonic events, present meaningful geochemical differences and allow them to be used as an auxiliary tool in the chrono-structural positioning of these rocks.

About 288 sediments samples were grouped in 5 populations. Their statistical parameters were defined, and the larger differences among the average concentration for the 16 elements analysed by Emission Spectrography were calculated. The analytical data of some elements, that were selected on account of larger differences shown by their averages, were used in plottting binary and ternary diagrams applied for population discrimination. Results graphically plotted were confirmed and even overstressed the degree of differentiation established by Discriminant Analysis.

STRONTIUM ISOTOPIC CHRONOSTRATIGRAPHY IN PALEOZOIC SECTION OF SOLIMÕES BASIN

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Changes in strontium isotopic composition of sea water as a function of time is a promising tool for stratisgraphic correlation and dating. This possibility is related to the *insignificant* isotopic fractionation of strontium during mineral precipitation, so that the isotopic composition is an exclusive function of the $^{87}Sr/^{86}Sr$ ratio in the fluid from which it was precipitated.

Accurate measurements of this isotopic ratio in paleontologically well-dated sedimentary sequences, allowed the establishment of high resolution curves relating isotopic values with ages of the analysed intervals. Thus, it is possible in certain stratigraphic intervals, by using such curves, to obtain correlations and dating with an accuracy of around 1 million year.

As an application example, an evaporitic section of the Solimões Basin was selected, considered as Permo-Carboniferous in previous works in the area. The plotting of the isotopic results on the standard curves of Burke et alii (1986) demonstrates the lack of Permian sediments, allowing situating of the analysed sequences in the Pennsylvanian.

Theme
Environmental Geochemistry

ANALYSIS OF SOME OF THE CARRIERS OF COPPER IN A TOPOGRAPHIC SEQUENCE IN THE ITABORAÍ REGION, RIO DE JANEIRO STATE, BRAZIL

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The purpose of this study is to understand the general behaviour distribution of copper in solis elementary prisms, in a tropical climate region, localated in Itaboraí, Rio de Janeiro, Brazil. Such informations could be useful in basic Environmental Geochemistry studies.

The specific purpose was to understand the relations between landscape morphology in relation to copper mobility with concepts of supergenic fluxes and relations with principal copper ligands.

In elementary prisms were investigated, the positive occurrence or negative occurrence of (chemical, physical, textural and/or mineralogical) lateral variations, close to the concept of geochemical gradients.

22 samples were collected, composites, at different depths, in 6 elementary prisms, in a toposequence from hillside to lowland, from the drainage basin of the Gado River, Itaboraí, Rio de Janeiro.

In the laboratory the samples were separated into granulometric fractions, less than 2mm (TFSA) and less than 0,02mm and submitted to selective extractions (Speciation), to determine amounts of copper in the fractions; exchangeable, reducible, oxidizable and residual (silicates).

Total copper contents were included in ranges between 12 and 60ppm, considered inside normal limits of copper concentrations in soils.

The lowland sector the reducible fraction was more efficient with chiefly ligand for copper, while, at the hillside sector, the silicate (residual) fraction was more efficient; more important than other fractions, TFSA.

In this study, chiefly ligand translocations were the principal result for copper correlation, and were responsible to geochemical behaviour (distribution) of this metal, in the studied area.

To estimate the translocations in this study proposes the use of relations between copper content (in ppm), associated with each geochemical fraction (exchangeable, reducible, oxidizable and residual), with total content of copper for each elementary prism.

APPLICATION OF THE TECHNOLOGY OF "JACINTO D'ÁGUA" FOR PRE-TREATMENT OF EFFLUENTS FROM METALLURGICAL AND ORE-DRESSING PLANTS

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The water hyacinth (Eichornia crassipes) was studied as a pollution monitor for the accumulation of silver and subsequent recovery of the element from the plant tissues. After 24 hours in a silver solution containing 40mg/l, the plants were harvested, rinsed with tap water and dried at 100°C for 48 hours. The dried material was submitted to pyrolysis and chemical digestion, and the silver absorved by the plant was precipitated, calcinated and recovered in metal form. The average concentration of silver was found to be 9,000mg gr^{-1} of dried plant material. An atomic spectrophotometer was utilized for the analysis. The average concentration of silver recovered from the dried plant material, was 70% of the initial silver concentration in silver solution, and revealed a purity of 98%. The water hyacinth has the potential of producing 1 ton/ha/day of dried material and can be used for the production of biogas rich in methane (Wolverton B.C., Mcdonald R.C.).

After the waste water treatment, the harvested plants can be used for biogas production, and the residual sludge can be utilized for recovering and recycling of the valuable metal.

ATMOSPHERIC INPUT - FUNCTIONAL ANALYSIS BETWEEN PRECIPITATION AND CHEMICAL COMPOSITION

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Chemical analyses of Na, K, Ca and Mg in bulk deposition, using 230 events, showed that measured concentration is the variable which best explains variations in atmospheric input, rather than precipitation. Meanwhile, its relation to precipitation is an inverse potential function. These observations led us to an inverse Linear Model that makes it possible to calculate, from the measured concentrations, two components: the composition of the "cloudrain", a value supposed to be constant for the study area, and a quantity of material composed of particulates, aerosols and gases which are washed out from the atmosphere in the initial phases of the precipitation process. Applied to two years of the studied period, the model proved to differ by an average of only 7% from the calculated values. The initial component represents, on average, about 64% of the bulk deposition for the cations studied. Another conclusion which needs to be checked at other places in other to have general application is: the functions which explain the relations between atmospheric input and measured concentration are, within statistical limits, equal for the four cations.

CRITIQUE OF THE GEOCHEMICAL DISTRIBUTION CHARACTERIZATION METHODS OF HEAVY METALS IN SEDIMENTS: THE RIBEIRA BAY, RJ, BRAZIL CASE STUDY

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The methods for geochemical distribution characterization of heavy metals in sediments are based on statistics and graphical correlations between two single elements, a "mobile" element and an "inert" one, a "mobile" element and a geochemical potential support (organic matter for example) etc. To this aim are employed total and/or speciation concentration values of the metal in the argile size granular fraction of the sediments, generally.

Studies realized in the Ribeira Bay, Rio de Janeiro, Brazil, showed that these methods can lead to important gaps in the assessment of the distribution of heavy metals in sediments. An alternative mineralogical balanced method is proposed in this paper.

ENVIRONMENTAL GEOCHEMISTRY FOR INDIGENOUS LAND USE PLANNING IN ECUADORIAN AMAZONIA

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The ongoing conversion of forests in the humid tropics to agriculture, pasture, mines, urban areas, and other land uses is one of the most rapid transformations now occurring on the earth's surface. One way to stem forest convertion is to use the natural forest as indigenous peoples have done for millenia. However, to meet the demands of growing populations now exposed to a cash economy, as in the case reported here, has meant that traditional indigenous techniques need to be modified. One such modification is that indigenous

groups must develop land use plans that are acceptable to a central government. To do so requires developing western technical expertise among these groups. This paper reports on one such experience and the application of water conductivity as a means of rapid surveying of tropical rain forest lands for potential land use.

ENVIRONMENTAL MERCURY CONCENTRATIONS IN INLAND WATERS OF GOLD MINING AREAS IN RONDONIA, BRAZIL

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Total mercury concentrations in water, sediments and fish from gold mining areas with emphasis on the Amazon region are presented. Mercury concentrations were quite variable among rivers with the highest values found in samples from tributary forest rivers. Concentrations in water samples varied between 0,1 and 8,6 $\mu g.l^{-1}$, while, in bottom sediments the values reached 19,800 $\mu g.kg^{-1}$.

Concentrations in the edible parts of major locally consumed fish reached up to 2,700 $\mu g.kg^{-1}$w.w., surpassing almost 5 times the Brazilian standards for human consumption.

FACTORS CONTROLLING WATER BIOGEOCHEMISTRY IN THE MOGI-GUAÇU RIVER OXBOW LAKES AT THE JATAI ECOLOGICAL STATION (SÃO PAULO, BRAZIL)

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Water quality in oxbow lakes at the Jatai Ecological Station, in the floodplain of the Mogi-Guaçu River, is, during the dry season, strongly related with higly weathered sandy soils, existing in local watersheds, underlain by a sandstone/basalt intrusion bedrock (Botucatu Formation), as well as with the hydrologic characteristics of the floodplain (the relationships between the oxbows waters and surface - creeks and Mogi-Guaçu River - and ground waters).

This observation is achieved through major cation ratios obtained for the different water masses in association with soil and geologic matrix mineralogy. Lake classification as drainage and seepage lakes is made based on the hydrologic properties of the floodplain. In spite of the relatively small area of this floodplain site and the proximity of the lakes, these lacustrine systems are geochemically very distinct and possess relatively low ionic concentration at low water season.

At high water the multiple flood pulse event is the main mechanism promoting a significant enrichment and variation in the rather poor and stable chemical composition documented in the dry period by the relative mix of the Mogi-Guaçu River and local waters. Stable environmental isotope data are used in conjunction with biogeochemical data to verify field observations.

GEOCHEMICAL AVAILABILITY OF MICRONUTRIENTS (Fe, Mn and Zn) IN IRRIGATED SOILS, MAGÉ, RJ, BRAZIL

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In irrigated soils the micronutrients availability depends on the redox condition changes. A geochemical approach to these changes, using speciation chemical analyses, has been realized to evaluate the availability of Fe, Mn and Zn in irrigated soils from Magé Region, an agricultural country of Rio de Janeiro State, Brazil.

GEOCHEMICAL SPECIATION APPLIED TO MOBILITY STUDIES FOR HEAVY METALS IN ESTUARINE SEDIMENTS OF THE FRADE AND GUARDA RIVERS, RIO DE JANEIRO STATE

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Separation of metals (Cu, Cr, Pb, Zn, Cd, Fe and Mn) between fractions potentially available to biota and the chemically inert fraction (bound to crystalline lattice) is applied to superficial estuarine sediments of the Frade River (Ribeira Bay) and the Guarda River (Sepetiba Bay). The so-called "available" metal concentrations are compared to the respective "residual" ones, which are used as local tracers of the first, in order to determine sections along the estuaries, where metal removal from sediment to water is predominant, and those where metal deposition is greater. Chemical and physical processes that determine concentration variation in the estuaries are discussed. Besides great differences related to anthropogenic contamination between the Frade and Guarda rivers, variations in hydrodynamic factors seem to be contributing to differences between the two estuaries, observed in the geochemical behaviour of metals toward increasing salinities.

GEOCHEMICAL STUDIES OF THE VERTICAL DISTRIBUTION OF NUTRIENTS AT THE WATER-SEDIMENT INTERFACE OF MARICÁ LAGOON

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Nutrients (NH_3, $SO_4^{=}$) of intersticial waters and organic carbon, organic sulphur, total nitrogen in the sediments are analysed in two areas of Maricá Lagoon.The vertical distribution of analysed parameters shows a correlation with the depth. The values of nutrients of intersticial waters are dependent on time and space.

There is no regularity in vertical distribution due to the variation of the values. The two main processes, which this "anomalous" of vertical distribution are: enzimatic activity (bacterial activity in the redox process); molecular diffusion phenomenon through interface are influenced by grain size distribution and water circulation near the roots of the studied area. Organic material is originated from the dead plankton.

GEOCHEMICAL STUDIES ON THE NORTHEAST BRAZILIAN CONTINENTAL SHELF: NUTRIENT CYCLING AND TRACE METAL CHEMISTRY

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The distribution of nutrients (Si, N and P) and the abundance of certain trace metals (Fe and Mn) have been determined in continental shelf waters and sediment pore waters near the mouth of the Amazon River. These measurements were made during a period of low river discharge (October, 1979) and a period of a high river discharge (May/June, 1983). In the high turbidity waters near the river mouth, no uptake of nutrients was observed. When aggregation reduced the turbidity below 100 mg/l, biological activity commended with a significant decrease in nutrient abundance. Iron plays an important role in controlling the oxidation/reduction state in pore waters collected from the Brazilian shelf. In some sediment cores, the dissolved iron maximum extends over 50 cm in depth, with little evidence of sulfate reduction. These measurements are being compared with a more comprehensive data base collected recently during a cruise in August of 1989. On the August cruise, rates of C and Si uptake were measured as a function of turbidity in addition to the nutrient distributions. These analyses should reveal important information concerning nutrient cycling and its dependence on turbidity in estuarine waters.

In addition to Fe and Mn, the concentrations of several transition metals were determined in the recently collected Brazilian shelf samples to enhance the understanding of trace metal chemistry in this complex shelf environment. These data are being used to model the fate of particle-reactive species during the mixing of riverine and oceanic waters.

GEOCHEMISTRY OF HEAVY METALS IN THE RIVER SEDIMENTS OF THE MARICÁ-GUARAPIM LAGOONAR SYSTEM, RIO DE JANEIRO STATE

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Chemical and mineralogical analyses of stream sediments, were used to evaluate heavy metal geochemistry in drainage basins of Maricá-Guarapina lagoon, RJ.

Results show that primary minerals are the main geochemical supports of metals in the study area. Granites and diabase dikes are identified as important sources of Iron, Manganese, Copper and Chromium. Hillslopes and lowland environments, identified as principal basin domains by previous works, distinctly affect sediment mineralogy and heavy metals geochemical partitioning.

HEAVY METAL ACCUMULATION IN THE JACUIPE RIVER ESTUARY, CAMAÇARI - BAHIA.

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The Camaçari Petrochemical Complex was established in Bahia State in the early seventies and has since been worried about its waste effluents. In the late seventies, the Liquid Effluent Treatment Plant was established. The effluents from this plant are discharged into the Capivara Pequeno River, a tributary of the Jacuipe River, which discharges into the sea through an estuary dominated by mangroves.

Six sediment cores from the mangroves at the Jacuipe Estuary were collected to assess the environmental impact in the area.

Sedimentological results showed that the area is typically of low energy. Heavy metal concentrations are, in general, low, when compared to mean shale values. Highest metal concentrations were found close to the effluents releasing point, and decrease according to core depth. Correlationships between metals and organic matter and aluminium showed that Cu, Pn and Zn are associated with silicate minerals (clays) and with organic matter.

HEAVY METALS AND ORGANIC CARBON IN SEDIMENTS FROM THE TUY RIVER BASIN, VENEZUELA

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The Tuy river basin, located in north-central Venezuela, with an annual average temperature of 27°C and precipitation of 140 cm, was selected to conduct a geochemical study on botton sediment with the objetive of establishing the natural (lithology, precipitation and vegetation) and human influences on the abundance and distribution of Fe, Mn, Cr, Co, Cu, Cd, Ni, Pb, Zn and Organic Carbon (Corg.). According to the lithology the basin is divided in two sub-basins, North and South. The northern sub-basin drains a low-grade metasedimentary terrane, with a population density of 800 people/km^2 and 600 industries while the southern sub-basin in underlain by metavolcanic and ultramafic rocks, with a population density of less than 10 people/km^2.

Stream botton sediment samples (149) were collected during the years of 1981 to 1986 in 17 unpolluted sites and 15 polluted sites. The sediments were air-dried at room temperature and sieved through a 120 stainless steel mesh (125 μm). The grain size fraction smaller than 125 μm was the one analysed, being the heavy metals determined by atomic absorption spectometry and Corg by dry combustion.

The higher concentrations of heavy metals and Corg found in the pristine areas were in the south sub-basin, especially in those areas with higher annual precipitation and tropical forest. This indicated that the metavolcanic and ultramafic rocks yield a baseline containing higher concentrations of heavy metals than the meta-sedimentary rocks. It is also noted that the higher concentrations of Cr and Ni are associated with the ultramafic rocks. The results obtained from the sediment samples collected in the polluted sites show that the elements Pb, Zn and Corg are enriched up to 4 times as a product of all the human activities taking place in the basin. Corg is an excellent indicator of the domestic wastewater, Pb and Zn being good indicators of the automotive traffic and industrial effluents. The concentrations of each heavy metal did not show any significant correlations versus the grain size fractions; however, the concentration of Corg did show a negative correlation with grain size. The lithological, climatic and vegetation influence in the abundance of heavy metals and Corg in stream sediments clearly indicates the necessity of always establishing the baseline for the area under study when carrying out studies in environmental geochemistry. Besides, it is important to select a grain size fraction of the sediment which contains approximately constant distributions in grain size when using Corg as indicators of pollution.

HEAVY METALS INTERACTIONS WITH ORGANIC MATTER IN FRESHWATER SEDIMENTS

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Interactions involving some trace metals (Cd, Cu, Pb, Zn) and the organic matter present in freshwater sediments from the Paranoá Lake (Brasília), the Tiete River (São Paulo) and the Taquaral Lake (Campinas) were investigated.

Some kinetics aspects of the adsorption/desorption for cadmium of these sediments were also studied using both Ion Selective Eletrodes (ISE) and Anodic Stripping Voltametry (ASV) techniques.

FAPESP FUNDED RESEARCH.

HYDROGEOCHEMICAL STUDY OF THE NON-SATURATED AND SATURATED ZONE IN HUMID SUBTROPICAL TERRANES

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An Experimental Site was installed on the campus of the University of São Paulo in order to study the dynamics and the evolution of the chemical composition of water percolating the unsaturated zone as far as aquifer, in a region with a humid subtropical climate. It represents the first investigation of this kind carried out in Brazil.

The results of the chemical analyses of a weekly monitoring lasting 14 months (October 1985 - January 1987) were plotted on PIPER diagrams for classification. In accordance with these diagrams, the waters are classified as sodium-chlorated to mixed chlorated in the upper part of the unsaturated zone, passing to mixed-bicabornated, sodium-bicarbonated until sodium-chlorated with depth.

No significant variations were observed in the chemical composition with the seasons, reflecting the more-or-less homogeneous humid subtropical climate.

The results show that the climate influences the chemical composition of water in the upper part of the unsaturated zone, while the lithology controls in the lower.

Groundwater at the sampling point, PF, is sodium-bicarbonated, reflecting water from the unsaturated zone. At the other sampling points (piezometers), groundwater is classified as calcium-bicarbonated, being already mixed by the flows from all the other directions. This is typical for the upper part of groundwater, confirming results of studies on chemical zonality in groundwater, known from literature.

HYDROGEOCHEMISTRY OF ARTIFICIAL RESERVOIRS

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The forcing functions, regulating and controlling the hydrogeochemistry of artificial reservoirs are related mainly to the special characteristics of these complex ecosystems intermediates between rivers and lakes. Precipitation (intensity and periodicity) and runoff are fundamental processes in the input of macronutrients and trace elements. Water column circulation and thermal instability or stability (which depend on average depth, wind force and direction, morphometry and operational procedures) are basic factors in the vertical and horizontal distribution of chemical species and in the residence time of several elements.

Pulse function factors related to water level fluctuation, operation of discharge and periods of stability produce strong qualitative changes in the chemical composition of water, and sediment.

Equally important is the sediment water interface which can be highly dynamic depending on vertical circulation patterns and distribution of dissolved oxygen and Eh.

Cultural entrophication of reservoirs interface, mainly the N, P cycles and is related to watershed uses (agricultural activities, industrial and human population concentration), can be controlled and reduced by ecotechnological measures, such as, regulation of the residence time and watershed recovery.

Reservoirs located in the Amazon region, inundating a Tropical Rain Forest have a complex hydrogeochemical mechanism depending on decomposition of biomass, residence time and operational procedures at the dam.

The knowledge of the hydrogeochemical situation prior to the reservoir construction is fundamental to a prognosis of the main geochemical processes in the future reservoir.

Ecological evolution of the reservoirs, the establishment of processes and the dynamics of the hydrogeochemical cycle are interrelated processes.

LEACHING OF NATURAL MATERIALS: RAPID KINETIC METHODS

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Natural materials suffer modifications in stability determined by natural condition variations.

These modifications can be caused by: mineralogical transformations, decrease or increase in grain size, permeability, mass drop, volume variations, etc.

These processes are reflected by geochemical analysis and percolation/lixiviation water through these materials.

The purpose of this article is to provide a comprehensive methodology, based on fluxes interpretation and geochemical balances from controlled lixiviation experiments. The proposals: establishment of a Potential Reactivity Index (PRI), Critical Reactivity Index (CRI), and an analysis of the lixiviation curve forms.

MANGROVE ORGANIC CARBON: AN OVERVIEW

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Concerning mangroves and the carbon global biogeochemical cycle, this study shows that mangrove forests are important sinks for carbon in the land-sea interface. Results from an experimental forest studied for 4 years, and from literature, indicate that mangrove can accumulate, globally, up to 42 megatons of carbon yearly, contributing with circa 35% of total Carbon burial in coastal and deltaic sediments.

MERCURY POLLUTION IN GOLD MINING AREAS OF THE STATE OF RIO DE JANEIRO, BRAZIL

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Measured concentrations of mercury in water, sediments, fish and human hair samples from gold mining areas in the state of Rio de JaneiroBrazil, are presented. The biogeochemistry of Hg in such tropical ecosystem is almost unknown, therefore the fate of mercury in organic and inorganic compartments, must produce important information and might give a better understanding of the world wide Hg cycle.

In general all measured values for the analysed samples are in the same order of magnitude of natural levels. However, in some areas concentrations in sediments can reach values as high as 0.9 g/g of Hg and "traira", a carnivorous fish in the area, presents Hg concentrations, such as 0.6 ug/g, which is above the Brazilian Standard Value (0.5 μg/g) for human consumption.

NATURAL INDICATORS TO ESTABLISH THE HYDRODYNAMIC BEHAVIOUR AND SEDIMENT TRANSFERENCE IN RIBEIRA BAY, RIO DE JANEIRO, BRAZIL

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The purpose of this study is to provide an understanding of the hydrodynamic characteristics of Ribeira Bay, on the southeast coast of Brazil, based on natural indicators for environmental impact assessment. Chemical-mineralogical similarities between the continental and marine sectors indicate that the downstream portion of the river Bracuí is the main source of continental material for the marine environment. The behaviour suspended matter at surface and 1 m above the bottom leads to the conclusion that water turbulence is the major process acting during critical situations of cold front passages.

NUTRIENT REGENERATION AND DIFFUSION ACROSS THE SEDIMENT-WATER INTERFACE OF AN ORGANIC RICH SUB-TROPICAL BRAZILIAN LAGOON

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Transport rates of biogenic elements across the sediment-water interface were measured "in situ" and "in vitro" via the incubation of sediments with benthic chambers (0-60 cm, V. ~55 l) and cores (0-80 cm, V. ~1 L) in the organic rich (POC of sediments ~8-12%) lagoon of Guarapina, Brazil. The flux rates were calculated as the increment of loss of the element over incubation time, corrected for volume and area. In addition, sediment cores were taken in order to extract intersticial water, and estimate diffusive fluxes of the elements from the observed concentration gradients. Diffusive flux was estimated with Fick's 1st, law and empirical diffusion coefficients from the literature. The study was conducted over an annual cycle in 1987 and consisted of four intensive campaigns during the main seasons.

The mean annual Sediment Oxygen Consumption

(SOC), and release rates of ammonia and orthophosphate amounted to 520 gO$_2$ m^{-2}Yr^{-1}, 5.7 gNH$_4$-Nm^{-2}Yr^{-1} and 2 gPO$_4$-Pm-$^{-2}$Yr^{-1}. However, the theoretical expected flux estimated from the SOC rates and a RQ = 0,72 should have been 25mg^{-2}Yr^{-1} for ammonia and 3 mg^{-2}Yr^{-1} for orthophosphate. The high SOC rates, in contrast to the lower than expected release rates of ammonia and orthophosphate, indicate the presence of a substantial chemical oxygen demand in the sediments. Ammonia and orthophosphate fluxes predicted by diffusion amounted to 4.3gm^{-2}Yr^{-1} and 0.2 gm^{-2}Yr^{-1}, respectively. This shows that difusion is a main process with respect to ammonia release from the sediments in Guarapina lagoon.

In general, SOC and nutrient releases rates were subject to a marked relationship between pelagic primary production and SOC remained constant throughout the year with approximately 57%. This indicated that pelagic benthic coupling in Guarapina lagoon is intrinsic. The lagoon exhibited mesotropic conditions of the water column in winter and spring, and eutrophic conditions in summer and autumn.

ORGANOARSENIC COMPOUNDS IN NATURAL WATERS

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As a metalloid arsenic combines readily with carbon to form a variety of compounds containing As-C bound. Laboratory synthesis of organoarseic compounds goes back to 1760, when L. Cadet distilled a mixture of arsenic trioxide and potassium acetate in a glass resort looted to a glass receiver. Copper acetoarsenic soon after that became the first pesticide to be sold commercially, and from 1890 until the end of World War II, lead arsenate was by far the dominant agricultural pesticide. Large quantities of other organoarsenical were also manufactured and dispersed in the environment in the form of herbicide, defoliant, soil sterilant and wood preservative. Interest in the environmental chemistry of organoarsenic compounds has grown since 1942 when Challenger proved that arsenic can be biologically methylated. Since then, a lot of attention has been focused on the low molecular weihgt biogenic compounds, notably monomethylarsonic acid, trimethylarsine oxide, and their reduced analogues: mono-, di- and trimethylarsines.

The arsenic speciation in aquatic systems, however, is dominated by a number if structurally more complex orgonoarsenic compounds, only a few of which have so far been identified. The classes of compounds dissolved in water that may interact with arsenic include humic and fulvic substances, pigments, aminoacids, proteins, arsenolipids, and arsenosugars as well as hydrophilic acids. The humic and fulvic substances which constitute 40 to 60 percent of dissolved organic carbon, can play a dominant role in determining the final distribution of arsenic ions. Organic arsenicals either synthesized by organisms or formed by reaction with metabolites of the orgnisms can affect the distribution and form of arsenic in aquatic ecosystems.

To satisfy their phosphorus requirement, primary producers have to take up phosphate ion from their environment. This presents algae and other aquatic organisms with a serious problem, since chemically arsenate resembles phosphate rather closely. Once arsenate has entered the organism cell, it is rapidly transformed to a variety of organoarsenic compounds. In addition to methanoarsenate and dimethylarsenite, up to twelve soluble organoarsenic compounds have been observed in algae. Although the presence of several organoarsenic compounds like arsenobetaine and arsenocholine, have been reported in invertebrates and fish, little is still known about the fate and stability of these compounds once excreted or during the decomposition of deposited biological material.

We will present an overview of what is currently known about the formation, biogeochemical behavior and fate of organoarsenic compounds in aquatic ecosystems. We will also discuss new analytical methods for the isolation and determination of organoarsenic compounds, natural and synthetic, at very low levels.

POSSIBLE PRECIPITATION OF CERTAIN CARBONATES IN INTERSTICIAL WATER OF RECENT MARINE SEDIMENTS AT THE WATER-SEDIMENT INTERFACE

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To determine the equilibrium, many thermodynamic calculations are necessary, and each reaction gives complementary information.

The problem is the qualitative and quantitative determination of indispensable parameters of the system CO_2-H_2O-$CaCO^3$ to characterize the general equations:

$$CO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)} \rightleftharpoons HCO_{3(aq)} \rightleftharpoons 2HCO_3 + Ca^{2+}{}_{(aq)}$$

The intersticial water of sediments is extracted by "Peeper" (dialyses).

The alkalinity is determined by titration using HCl 0,0lN as titrant GRAN (1952). The results show precipitation of carbonates from 10cm below the surface, where CO_2 production is mediated by sulfate reduction.

Thermcdynamic calculations were applied to determine the saturation indices of different phases of carbonatic.

RIVER WATER COMPOSITION AND THE WEATHERING PROCESS, PADRECO RIVER BASIN, MARICÁ, RJ, BRAZIL.

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River water composition is conditioned by the weathering process.

With the purpose of characterizing the process of weathering operating in the drainage basin of the River Padreco, Rio de Janeiro, differents methods of estimation and characterization of this process were used. They are: climatology, chemistry composition of the landscape facies, mineralogical characteristic, estimation of the crystallochemical nature of the weathering mineralogical products, characterization of the hidrolysis process, estimation of the geochemistry migration intensity of the major elements analysis of the mass balance from the composition fluvial waters and thermodynamic plot diagrams.

Considering that these methods are essentially indirect and qualitative, the final estimation of the characterization of the weathering process was realized using convergence analysis of the information from the differents methods used.

Through of convergence analysis it was concluded that the area of this study is, in general, characterized by a tropical weathering of hydrolytic type, with a predominance of kaolinite as the weathering mineralogical product. But, the main geomorphological sectors of the area, upstream and downstream, showed partial hydrolysis with incomplete desilicification and disalkalinization.

On the other hand, the sectors showed differences in the intensity of the weathering process. The upstream are characterized as areas of lixiviation, and the downstream, as areas of accumulation and geochemical heredity.

SEPETIBA BAY: A SINK FOR HEAVY METAL POLLUTANTS

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Sepetiba Bay is a semi-closed water body with an area of approximately 450 sqm. Since two decades ago, this area has been considered very important for the implantation of various industries. North and northeast of the bay, particularly Ilha da Madeira, Santa Cruz and Itaguai districts have been industrialized, principally by metallurgical plants. Almost point source of emission of industrial effluents is taking place in these areas.

Almost sixty five surface sediment samples were collected at regular intervals to cover the whole Sepetiba bay for combined sedimentological and geochemical methods to try to understand the pattern of accumulation and dispersal of solid waste within the bay. A few sediment cores were also sampled to study complex historical record of industrial contamination and the use industrial of wastes as traces for sediment movement.

The oceanographic regime sets the energy conditions governing sedimentary processes in various longitudinal and latitudinal profiles of temperature, and salinity. Seston dry weight, particulate organic carbon and chlorophyll a were measured. The bay exhibited a highly dynamic behaviour in the distribution of water masses and suspended matter.

Comparative studies of bathimetry in time scale and sedimentological analyses revealed that various parts of the bay are suffering in sediment accumulation and in some other parts, erosion. Using FOLK's classification sediments were divided into mud sediment restricted to nearshore, north-northeast and south coast. Sand is often admited with mud covers in a specific area in front of Ilha Jaguanu. Silty sediments are sandwiched between them.

Generally high metal concentrations have been found near existing industries and organic rich sediments. Close to the point source, the established patterns of littoral transport, and the physical and chemical features of the depositional environment apparently control the distribution of heavy metals in sediments.

The heavy metal pollutants move out of the bay with the 63 m fraction. These findings suggest that this bay seems to be a leaky sink for wastes.

STUDY OF THE 210Pb METHOD APPLICABILITY TO GUANABARA BAY SEDIMENTATIONS RATE STUDIES

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In order to verify the applicability of the ^{210}Pb method to Guanabara Bay sedimentation rate studies, it was applied to sediment cores taken at two differents points of the Bay. Since a non-constant sedimentation rate was already reported, the so-called constant supply rate method was used to evaluate the results. The ^{210}Pb content in each layer was determined radiochemicaly through its descendent ^{210}Bi, and ^{226}Ra by the total alpha counting method after its separation as $BaSo_4$.

The results have shown that at the two sampling points a similar trend despite different sedimentation rates. It was observed at deeper layers that smalller rates change abruptly to bigger ones. This change was supposed to be correlated to an increase in the populational occupation surrounding Guanabara Bay, and a consequent creater/contributor to river erosion.

To validate the results, Hg and Cu concentrations in the different layers were determined and the results correlated with the layer age and the industrial history around the Bay.

THE BACKGROUND OF Hg IN THE MARANHÃO GULF REGION

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Analyses of mercury were carried out on samples of sediment, estuarine water and biological material drawn from the Bays of São Marcos, Arraial and stretches of the rivers Mearim and Itapecuru, with the objective of verifying the possible excess of this metal, announced by the Environmetal Monitoring Department of the Vale do Rio Doce Company in São Luís - Ma.

The results obtained did not confirm abnormal concentrations of mercury in any of the three categories of samples.

THE DISTRIBUTION OF Fe, Mn, Cu, Zn, Ni, Cr AND Hg IN THE DRAINAGE COURSES OF BELÉM, PARÁ STATE.

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Water and sediments of 15 km drainages of the city of Belém, Pará, have been investigated in terms of the distribution of the elements Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pn and Hg.

Just a Cr contamination has been clearly determined in the proximities of a tannery. High Hg values were determined in another drainage.

The water pH values of the drainage are in general slightly alkaline. This is related to the contamination by the organic matter of the sewerage system.

The analyses were carried out by spectrophotometry of atomic absorption.

THE EFFECT OF GEOGENIC FACTORS ON THE HYDROGEOCHEMISTRY AND ACID-NEUTRALIZING CAPACITY OF NATURAL STREAM WATERS IN CRYSTALLINE AREAS

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In the course of the Nordkalott Project set up in northern Fennoscandia by the Geological Survey of Finland, Norway and Sweden altogether 6,400 water samples were collected from streams draining the catchments of approximately $10 km^2$ in 1980-83 (Bolviken et al, 1989). The electrical conductance values (EC) were measured electrometrically, and Si, Ca, Mg, Sr, Na, K, Fe, Mn and Al were determined by ICAP spectroscopy. Because of the high detection limit the method was unsatisfactory for Ba, Ti, V, Li, Be, Zn, Ni, Cu, Co, Cd, Pb, and Mo.

The nordkalott project separated and analysed till, which is the most common soil type, minerogenic and organogenic stream sediments, stream moss, and heavy minerals from till and stream sediments (Bolviken et alii, 1986), thus providing an opportunity to consider the streams and their catchment as a composite unit.

Streams waters draining basement areas are very diluted, the average concentration of dissolved electrolytes being only 20 mg/l (median values of EC ate 25 mS/m, +25°C, 6336 samples). Water is of HCO_3 type, and anthropogenic sources generally have only a slight impact on water quality through regional airborne fallout (mainly SO_4, NO_3.

Particularly during dry spells of the year and in winter the stream waters are composed of shallow groundwater discharged into water courses (Lahermo, 1970). Hence, the general composition of stream water is ubiquitously controlled by the geochemical composition of bedrock and the overlying glaciogenic soils. The geogenically controlled parameters are Ca, Mg and Sr. Accordingly, elevated Ca, Mg and Sr (and EC values in stream waters) are encountered in the parts of the Karelian schist belt that are predominantly composed of subsilicic rocks.

Their gabbros, komatiites, metabasalts, amphibolites and greenstones contribute 2 to 5 times more dissolved electrolytes to stream waters than granitoids, which have the lowest average concentrations. The lowest abundances of dissolved load are found in streams draining the old basement complex of gneisses, which is often intermingled with granitic veins, granitic gneisses and granulites. Na, K and Si are not very clearly related to the lithological environment. Na is transported partly from the oceans as airborne aerosols. Along the coast of Norway, marine Na sources are responsible for Na concentrations of 3-4 mg/l in stream water, while, in Finnish Lapland the fraction of airborne marine Na is below 0.5 mg/l. Waters draining granite areas show somewhat higher Na concentrations than do those of mafic rock areas, although the correlation is not clearly geological. The highest Na concentrations are met in streams draining the southwestern corner of the study area partly owing to the presence of relict sea salts in this area, which was inundated by the Baltic Sea.

Despite the amplitude of the hydrogeochemical parameters in water quality, induced by fluctuating hydrometeorological conditions, the water quality and the acid-neutralizing capacity are controlled by the lithological and geochemical environment. Hence, the sensivity of stream waters to acidification is generally controlled by the lithological and geochemical properties of the catchments. This framework may occasionally be distorted by acid pulses of meltwaters into water courses. In terms of the Ca/Na ratio, the areas composed largely of mafic and ultramafic components show up better as well-buffered areas (figure 1).

The main inorganic buffering component is HCO_3 expressed in alkalinity. It correlates strongly with EC and Ca, as indicated by several studies of unpolluted stream and lake water and shallow groundwater (e.g. Lahermo, 1970; Kamari, 1984). This justifies the computing of bicarbonate alkalinity from EC values and Ca concentrations (or Ca + Mg). The computed areal distribution patterns are similar although the HCO_3 buffer capacity computed from Ca concentrations, gives a somewhat more coherent picture (figure 2).

The acid-neutralizing capacity of stream water is 2 to 5 times higher in geochemically reactive mafic and ultramafic bedrock areas than in more inert felsic environments. However, the mafic and ultramafic well-buffered areas, where alkalinity typically ranges from 0.4 to 1.2 mmol/l, comprises less than 20% of the studied area. In the extensive, more vulnerable areas, alkalinity ranges from 0.1 to 0.4 mmol/l.

Bicarbonate alkalinity is mainly due to the chemical weathering of silicate minerals; carbonates play only a local role. Since dissolved CO_2 produces equal amounts of HCO_3 in soil, irrespective of the lithological composition, the 2 to 5 times higher alkalinity values in femic environments are attributed to the high weathering rate of Fe-Mg-Ca-rich minerals. Biogenic CO_2 participates in the acid hydrolysis reactions by releasing mobile Ca, Mg, Na and HCO_3. Limestones and dolomites contribute regionally to the acid-neutralizing capacity only in the Perapohja schist area in the southwestern corner of the study area, where the stream waters richest in electrolytes are encountered.

It is assumed that the contributions of other naturally occurring bases, such as silica (H_3SiO_4-) and complex or colloidic Fe and Al to the acid-neutralizing capacity of stream water, is insignificant. However, the buffer capacity is undoubtedly largely due to dissolved or colloidic humic matter, as Finnish stream waters are among the most humus-rich anywhere in the world. The effects of humus compounds on the acid-neutralizing processes are not fully understood.

The capacity is greatest in the intensely paludified southern and southwestern parts of the study area, whereas the humus factor in the north is clearer and the humus-poor waters can be ignored.

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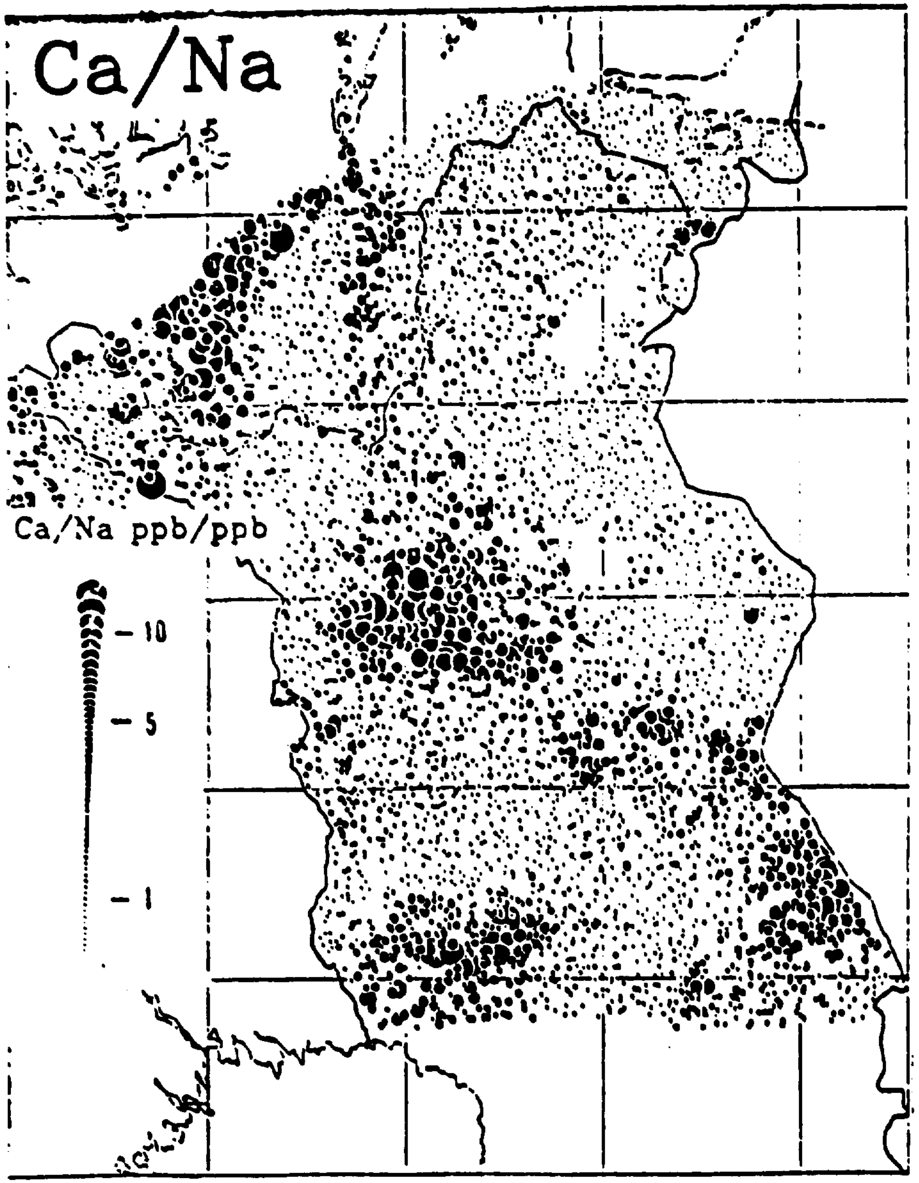

Figure 1 – The areas of elevated Ca/Na ratios depict highlybuffered stream waters that correlate with bicarbonate alkalinity.

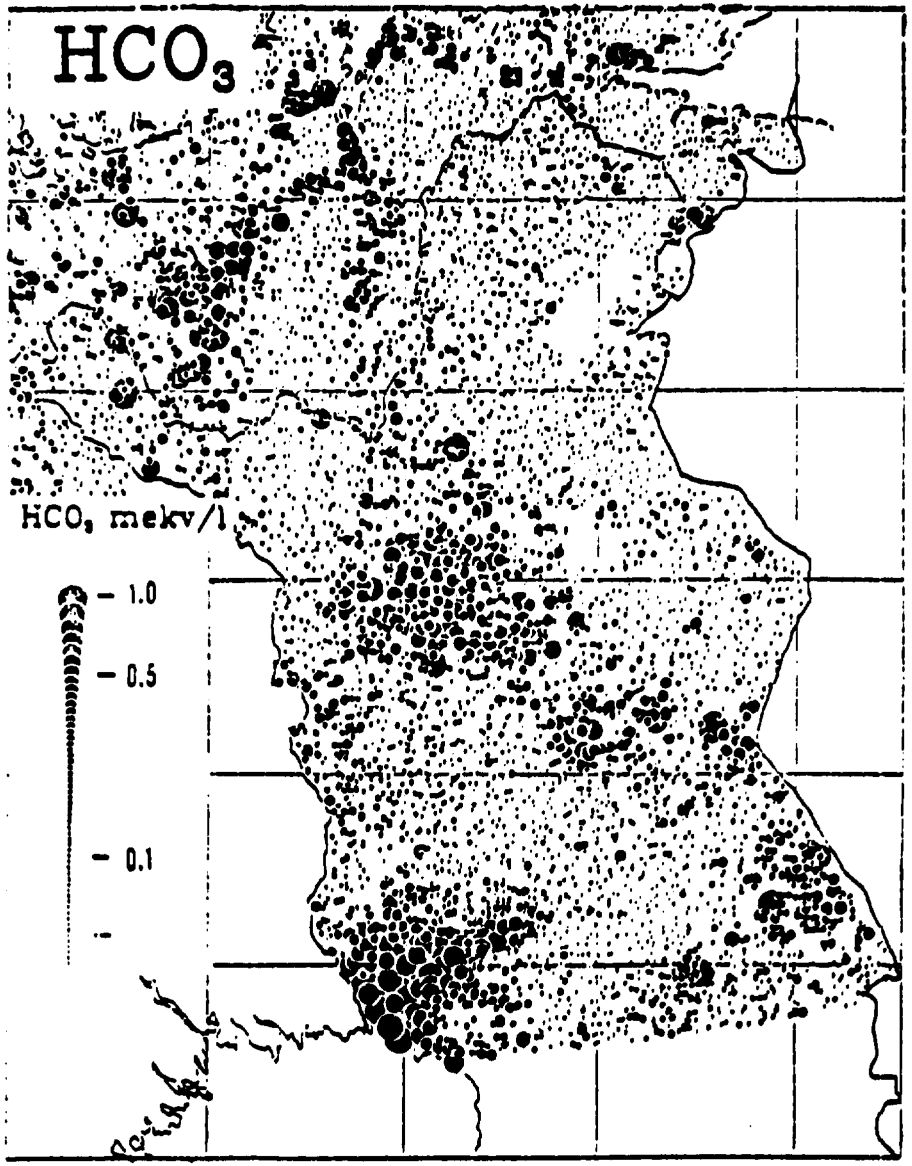

Figure 2 – The distribution of HCO_3 or alkalinity buffer capacity calculated from Ca concentrations.

THE METABOLISM OF SAQUAREMA LAGOON, RJ: RELATIONSHIPS WITH HYDROLOGICAL AND CLIMATOLOGICAL EVENTS DURING AN ANNUAL CYCLE

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Dominant metabolic characteristics (production and mineralization rates) of Saquarema Lagoon waters are presented through two annual cycles, and analysed in relation to bioclimatological and phytoplanktonic parameters.

Simultaneous measurements under "in situ" and "in vitro" conditions allowed evaluation of the role of sediments in biological activities in the water column.

As the study was carried out in two different compartiments of the lagoon, one of which was submitted to domectic waste discharges, the effect of such discharges upon the metabolism of the lagoon could be evaluated.

THE USE OF CONTROLLED LEACHING EXPERIMENTATION IN EIE STUDIES: THE SANTA AUGUSTA COAL MINE, CRICIÚMA, SC, BRAZIL.

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Natural materials suffer modifications in stability determined by natural condition variations.

These modifications can be caused by: mineralogical transformations, decrease or increase in grain size, permeability, mass drop, volume variations, etc.

These processes are reflected by geochemical analysis and percolation/leaching water through these materials.

These studies can be used in assessment, lixiviation diagnostics, mass drop and fragmentation of natural materials.

The purpose of this article is to apply a comprehensive method based on fluxes interpretation from controlled leaching experimentation in the Santa Augusta Coal Mine, Criciúma, SC, Brazil.

Theme

Geochemistry in the Secondary Environment

CHLORITIZATION AND SILCRETE FORMATION ABOVE SERPENTINIZED DUNITE AND ITS (PALEO-) CLIMATE IMPLICATION FOR LATERITEGENESIS IN THE JACUPIRANGA ALKALINE COMPLEX (SP), BRAZIL.

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Chloritization and silcrete formation is a common phenomenon in initial weathering stages of serpentinized dunite in the Jacupiranga Alkaline Complex. Both processes well reflect the moderately contrasting tropical climate (1,500-1,700mm/a) with presently restricted drainage conditions. Detailed mineralogical studies and field observations proved that the silcrete formed recently and does not necessarily require semi-arid conditions, as was postulated by former researchers.

Restricted drainage favours high element concentrations in solution, resulting in the formation and preservation of chlorite and irregular chlorite/vermiculite intergrades within the saprolite horizon. The structural characteristics of these phases were studied in detail by XRD, differencial scanning calorimetry (DSC) and thermogravimetry (TG). The compositional change during weathering was investigated by microprobe analysis on large crystals from different profile depths (Kanig, 1989).

Deeper zones of the saprolite contain higher proportions of vermiculite, as can be seen from the comparitively high intensities of the 14 angstroms basal reflection compared to reflections of a higher order (table 1).

Table 1 - Main XRD-reflection intensities (%) of chlorites and chlorite/vermiculite integrades from different depths of saprolite horizon of profile D 2-1W above serpentinized dunite, Jacupiranga Alkaline complex (SP). (N = untreated sample; G = glycerol treatment; 500° = heating temperature (°C)).

Depth (cm)	1250 – 1275			1050 – 1150			750 – 850		
Intensity (%) (001)	N	G	500°	N	G	500°	N	G	500°
(001)	100	95	30	60	50	25	75	65	40
(002)	40	45	5	40	45	5	45	40	5
(003)	45	50	5	50	50	5	55	50	5
(004)	60	75	10	100	80	10	100	100	15

The chlorite structure predominates towards the profile top, being manifested in more stable intensities after heating. Characteristic (201)-reflections clearly show Ia and Ib chlorite polytypes, corresponding to low temperature chlorites (Brown & Bailey, 1962). The average chemical and structural composition of chlorites (on the base of 14 oxygen atoms) is listed in table 2. The low average proportion of tetrahedral Al (< 1) is indicative for Ia and Ib chlorites (Brown & Bailey, 1962). The proportion of Si and the Fe/R^2-ratio classify the chlorites as clinochlore and penninite.

Towards the top of the saprolite, increasing Ni-substitution for Mg and Fe in octahedral position can be observed (up to 7.19 wt.% NiO). The loss of Mg and Fe is also compensated by increasing Al-substitution. As result, the total amount of cations per formula unit decreases. Most of the Al-substitution probably takes place in the brucite-like interlayer, forming gibbsite-like islands of Al-hydroxy polimers (Newman, 1987). This interlayer is incomplete, resulting from partial collapse when heating the sample at 500°C. High contents of interlayer water are also evident from TG measurements (up to 13.3 wt.% H_2O after grinding). Slightly acid pH-values in the saprolite (5.4 to 6.2) favour the predominance of hydroxy-Al as the principal interlayer material (Newman, 1987). The continuous Al-uptake in chlorite shifts the Si/Al-ratio more and more towards that of kaolinite, which is the only clay mineral in the overlying laterite horizon. The Al-incorporation in chlorite proves the supply of Al in solution, probalby under the participation of organic acids. This fact underlines the podsolic tendencies, which are evident in many soil profiles of the area (Kanig, 1989(. Most chlorites contain the top (table 2) since only little Ti can be substituted in 6-fold coordination (Albee, 1962), Ti-precipitation in the interlayer must be assumed. The highest chlorite concentrations are always found in the profile portions which have low goethite and quartz concentrations, and vice versa. The occurrence of either chlorite or goethite and quartz seem to reflect locally changing redox conditions. Freshly precipitated amorphous silica is associated with poorly crystallized Fe-hydroxide. Thus, chlorite and cloritized vermiculite tend to be stable under less oxidizing conditions. Fe^{2+} is readily oxidized and precipitated as hydroxide with increasing Eh. Fresh Fe-hydroxide precipitations are known to have an excellent adsorption capacity for Si, even from very undersatured solutions (Harder & Flehmig, 1970; Siever & Woodford, 1979). The adsorbed portion of SiO_2 increases rapidly until the solubility product of amorphous silica is reached. On ageing, the silica gel forms opal, chalcedony and quartz; all stages were found in the studied profiles. The formation of goethite, together with silcrete, is enhanced during the drier season, when Eh-values and Si-concentrations in soil solution tend to rise.

Table 2 – Chemical and structural composition of chlorites from different depths of saprolite horizon of profile D 2-1W above serpentinized dunite, Jacupiranga Alkali Complex (SP).

Depth (cm)	1250 – 1275	1050 – 1150	750 – 850
Oxide (wt.%)	$\bar{x}$	$\bar{x}$	$\bar{x}$
CaO	0.13	0.11	0.12
Al_2O_3	11.53	14.27	17.0
FeO	9.48	8.07	4.29
MnO	0.05	0.06	0.05
SiO_2	32.14	30.19	31.54
MgO	28.28	25.68	21.79
NiO	1.1	3.17	4.81
TiO_2	1.87	1.9	2.66
Cr_2O_3	0.5	0.43	0.37
Total	85.08	83.88	82.63
n	30	26	12
Si/Al	2.46	1.87	1.64
Si	3.223	3.092	3.207
Al (tet)	0.777	0.908	0.793
Al (oct)	0.585	0.811	1.243
Fe + Mn	0.814	0.706	0.370
Mg	4.256	3.941	3.302
Ca	0.014	0.012	0.013
Ni	0.087	0.258	0.395
Cr	0.040	0.020	0.030
Ti	0.139	0.146	0.203
Sum (oct)	5.935	5.894	5.556

The ferruginous silcrete horizon in the Jacupiranga area reaches thicknesses up to 30m (Oliveira & Trescases, 1985). Its composition includes all transitions between pure goethitic layers and massive quartz-rich zones. The silcrete zone does not form a continuous layer. In addition, it shows an orientation sub-parallel to the topography. Since the incision of the area by interfluves took place from E to W, the topography, as well as the silcrete zone, declines towards the E.

The sub-recent morphological development of the Alkaline Complex is characterized by retreat of the convex-shaped slopes due to solution processes, creating broad shallow valleys (Romer, 1988). Recent silcrete formation was observed on slopes and footslope areas, thus revealing a relationship to the development of the landscape. The thickness of the silcrete layer and its spatial orientation could well be explained by a continuous lowering of the weathering front over longer periods. Paleoclimatic records, on the basis of oxygen isotope data from marine sediments, give rise to the assumption that the seawater surface temperature did not show significant oscillations for the Jacupiranga latitude during longer periods of the Tertiary and Quaternary Age. Even during glaciation maxima, the average ocean surface temperature of the Southern Atlantic was about 20°C in August (Savin, 1977). The proximity of the Jacupiranga area to the Atlantic Ocean implies that the climate in the working area was always marine. Paleobotanic studies revealed that subtropical lowlands were less influenced by glacial/interglacial climatic changes. According to Wilhelmy (1951), the Jacupiranga area must have been affected rather by a pluvial climate during glaciation than by aridity.

Sub-recent chloritization and silcrete formation during serpentinite weathering express well the meridional location of the working area under a less pronounced contrasting tropical regime. Since paleoclimatic data imply only smaller climatic changes, we assume that both processes have been taking place for longer periods, and are still continuing in the present.

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GEOCHEMISTRY OF THE SUPERGENE ALTERATION OF THE ALKALINE ROCKS OF LAGES

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In the lateritic alteration (bauxites) of phonolites in Lages, S.C., shows, in general, the leaching of major and minor elements, including REE's, with exception of the Al, Fe, Ti, Ga, Nb, Th, Zr and V. Fluor is relatively enriched in bauxite, and zirconium presents a restricted mobility.

REE are mostly leached except cerium which is retained in manganese and iron minerals.

MICROMORPHOLOGICAL, CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF THE STRUCTURAL FACIES OF THE BAUXITE DEPOSIT OF MORRO DO FRAGA, IN THE MINAS GERAIS IRON QUADRANGLE

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The Morro do Fraga bauxite deposit comprises a slope type one whose profile presents the following facies sequence, from the bottom to the top: massive, friable, massive Al-Fe, nodular and soil.

Micromorphological, chemical and mineralogical analyses show the facies filiation (degradation toward the top of the profile) and that the friable facies represents an important internal degradation event in the profile.

Mineralogical transformations (hematite/goethite) and structural transformations occur at the same time. Fe_2O_3 and TiO_2 enrichment is observed toward the top. While secondary elements (Mn, Cr, Ni, K, Ca, Mg, Ba, Sr, Ga and V) show a little depletion.

Neverthless, distinct characteristics are observed at the down slope profile as a result of an important deferruginization process, which leads to a relative Al_2O_3 and TiO_2 enrichment.

MINERALOGICAL ASPECTS OF THE LATERITES OF MAICURU

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This paper presents the preliminary mineralogical data of the weathering materials derived from the alkaline-ultramafic-carbonatitic Maicuru complex, State of Pará. These material include several minerals species: iron, titanium and aluminium oxides/hydroxides as aluminous goethite, goethite, hematite, maghemite, lepidocrocite, anatase; and gibbsite; clay minerals of the smectite, chlorite, vermiculite and kaolinite groups and interstratified chlorite-smectite, mica-vermiculite, vermiculite-chlorite and kaolinite-smectite; and aluminous phosphates of the crandallite group, wardite, augelite, senegalite, wavelite and variscite. The principal characteristics of these minerals were obtained by x-ray diffraction, optical methods, electron probe microanalysis, energy dispersive scanning electron microscope, x-ray fluorescence, atomic absorption, inductively coupled plasma-ICP source spectrometry and colorimetric methods.

MORPHOLOGICAL, MINERALOGICAL AND CHEMICAL EVOLUTION OF THE BAUXITE DEPOSIT OF VARGEM DOS ÓCULOS, IN THE MINAS GERAIS IRON QUADRANGLE

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The study of the bauxite deposit indicates the existence of a type profile represented by three units, from base to top: lower clayey unit (represented by the transition facies), middle bauxitic unit (represented by the bauxitic, ferruginous nodular and degradation facies) and cover unit.

Morphological, mineralogical and chemical studies of such units have shown the existence of different organizations, which are suggested by distinct zones. These zones display a clear evolution in time and space due to the action of two deferruginization fronts, one topward and the other baseward.

These deferruginization fronts spread out at the middle bauxite unit, providing a relative gibbsite enrichment and thus an expressive bauxitic facies.

ON THE GENESIS OF A SURFACIAL URANIUM MINERALIZATION IN WEST CENTRAL SINAI, EGYPT.

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This paper represents a contribution to the genesis of the uranium mineralization in West Central Sinai on the basis of the geological, climatic, geochemical and mineralogical features, as well as on the factors controlling such a mineralization type.

1) Geologic Setting:

The Paleozoic sedimentary succession of West Central Sinai unconformably overlies the basement complex rock units of the Arabo-Nubian shield. These sediments are divided from base to top into: the lower unfossiliferous sandstone-shale facies (≈200m thick), middle dolomitic-limestone-clayey facies and a sandstone rock unit with marine fossils (max. 40m thick), and the upper shaly sandstone rock unit (≈150m thick). In fact, the middle dolomitic-limestone clayey and sandstone facies are assigned as lower Carboniferous in age. On the other hand, the West Central Sinai area is affected by two volcanic phases, the Permo-Triassic comprising basaltic sill, at the top of the Paleozoic sediments (Weissbroad, 1969), and a post Miocene magmatic activity, which produced abundant dolerite and basaltic dykes spread all over the area.

The West Central Sinai sedimentation model consists of the basement complex rocks, surrounded by the Paleozoic sediments from all directions, except the north. Thus, these basement complex rocks represent a part of the Paleozoic shore line (figure 1).

The lithologic facies gradually changed from the relatively deep sediments (dolomites) in the north and west to the shore sediments (sands) in the south and east. Inside the deposition basin, the Carboniferous succession is represented in W. Mureid by clayey-shale sediments (fairly radioactive) between two series of dolomites. However, in W. Alloga and W. Abu Thor, the Carboniferous succession is represented by a dolomitic facies, bedded in two clayey and silty facies (highly radioactive).

Concerning the structural features, it is clear that the Paleozoic rocks of West Central Sinai are very much affected by normal faults, which are seen everywhere and vary greatly in throw. The most common trends of these faults are N-S, NW-SE and NE-SW (figure 2). These normal faults bounded several grabens and horsts. It is remarkable that most of the mineralization anomalies do exist in the distinct graben (W. Kharig - W. Baba).

2) Uranium Mineralization:

The Paleozoic sediments of West Central Sinai are characterized by the presence of some economic deposits, namely; manganese, iron and cooper mineralizations. The radioactivity shows lateral and vertical variations according to variation in lithology. Thus, the radioactivity in the different rock types of lower and upper sandstone facies ranged around the background, with some exceptions of radioactive anomalies, especially in the lower sandstone. On the other hand, the middle dolomitic rock unit contains the main and important radioactive anomalies in the area studied. Dabbour and Mahdy (1988) studied the radioactive mineralization in this area and classified it into two types, namely, the secondary uranium minerals and the placer radioactive minerals. Besides these, other uraniferous minerals (jarosite and atacamite) have been also identified (table 1).

Table 1 – Identified uraniferous minerals in the West Central Sinai area.

Locality	**Facies**	**Minerals**
Ramlet Hemyir	Sandstone	Uvanite, Xenotime*
Abu Thor	Gravel	Uranophane, K-Zippeite Monazite*, Zircon*, Atacamite**
Alloga	Siltstone	Liebigite, K-Zippeite, Carnotite, Rb-Carnotite, Meta-Autonite, Hydrogen-Autonite, Meta-Torbernite, Meta-Zeunerite, Meta-Tyuyamunite, Jarostie** Atacamite**

* Detrital minerals ** Uraniferous minerals

3) Geochemistry:

The chemical features of West Central Sinai rock facies are given in table (2).

Table (2) – *Analytical results of some uraniferous sediments from West Central Sinai.*

Sample No.	Rock type	SO_4 % (1)	Sol.Cl^- % (1)	FeO % (1)	H_2O^- % (2)	O.M% % (3)	Fe_2O_3 % (4)	U (ppm) (5)	Th (ppm) (7)	Cu (ppm) (6)	MnU (ppm) (6)	pH
RR-1	S.S.	0.315	0.0000	0.10	0.21	0.27	0.80	165	170	40	50	8.6
RR-2	S.S.	0.482	0.0017	0.12	0.02	0.45	1.59	105	310	55	30	8.6
R-2	F.S.S.	0.352	0.0060	0.04	0.23	5.99	27.96	667	330	215	40	8.1
R-1	F.S.S.	0.278	0.0110	0.04	0.82	5.19	26.76	550	–	250	50	7.8
Alg-1-6-a	silt	7.307	0.0017	0.95	2.16	3.79	7.99	344	–	6500	3600	8.1
Alg-1-6-b	silt	12.547	0.0080	1.00	4.02	2.73	7.99	955	–	100	250	7.9
Alg-1-6-d	silt	7.053	0.0120	0.64	3.97	4.28	9.58	1000	–	2000	5140	7.7
Alg-1-6-e	silt	0.935	0.0020	0.32	2.90	4.31	14.37	833	–	5000	50	8.1
Alg-1-6-f	silt	0.466	0.0030	0.80	1.18	3.15	7.99	800	–	8500	2800	8.2
Alg-1-6-g	silt	1.036	0.0710	0.20	3.27	2.55	4.80	5083	–	1500	250	8.0
TH-1b	gravel	0.278	0.0120	–	2.83	4.87	7.98	1409	–	2286	1250	8.0
Th.4	shale	4.711	0.0240	0.16	2.92	7.87	12.78	212	55	400	750	8.0
TH-1a	shale	1.627	0.1430	–	6.43	8.05	13.92	585	80	1000	750	7.1
TH-3a	shale	0.993	0.1210	0.04	11.78	10.71	10.78	188	330	1571	1650	7.7

(1) wet chemistry.
(2) loss in weight at 110°C.
(3) ignition loss at 470°C.
(4) spectrophotometry.
(5) fluorimetry.
(6) atomic absorption.
(7) X-ray fluorescence.
S.S. = Sandstone.
F.S.S. = Ferruginous sandstone.

The data clarifies that there is marked enrichment in the concentration of U, Mn, Cu and Fe. Although Gindy (1971) proposed a simultaneous deposition of uranium with manganese, iron and copper ore deposits, due to hydrothermal solutions accompanying the Tertiary volcanic activity, careful investigation of the data obtained and previous literature indicate that is not the case. Hussein at al. (1971) stated that these is no consistent relationship between iron and/or manganese and radioactivity. Dabbour and Mahdy (1988) reported that the secondary copper mineral, atacamite, trapped the secondary uranium mineral K-rich zippeite in its laths network. In addition, the field observation revealed the presence of visual yellow secondary uranium minerals coating the green secondary copper mineral, atacamite.

The relationships between uraniun and each of the sulphate and soluble chloride reflect one medium of deposition. An evaporation process is the most acceptable explanation for this phenomenon, which is clearly observed in the field by the presence of gypsum, that may assay up to 5% of the host rocks mineralogical composition. The evaporation process is confirmed by the alkaline depositional environment, with pH values ranging from 7.5-8.5.

The ferrous/ferric ratio in the analysed samples ranges between nil and 0.125, which indicates an oxidation phenomenon. This confirms the result obtained by Dabbour and Mahdy (1988), that the uranium in West Central Sinai Carboniferous rocks does exist in the hexavalent state in the identified secondary uranium minerals. These mineral may represent the oxidation products of the pre-existing uranium minerals of the basement complex. The above interpretation explains the antipathetic relation between the uranium content and the organic matter that acts as a reducing factor in uranium deposition, which is not controlling the depositional environment in the area studied.

The oxidation process may be due to the action of the hydrothermal solutions or to the circulation of the ground water.

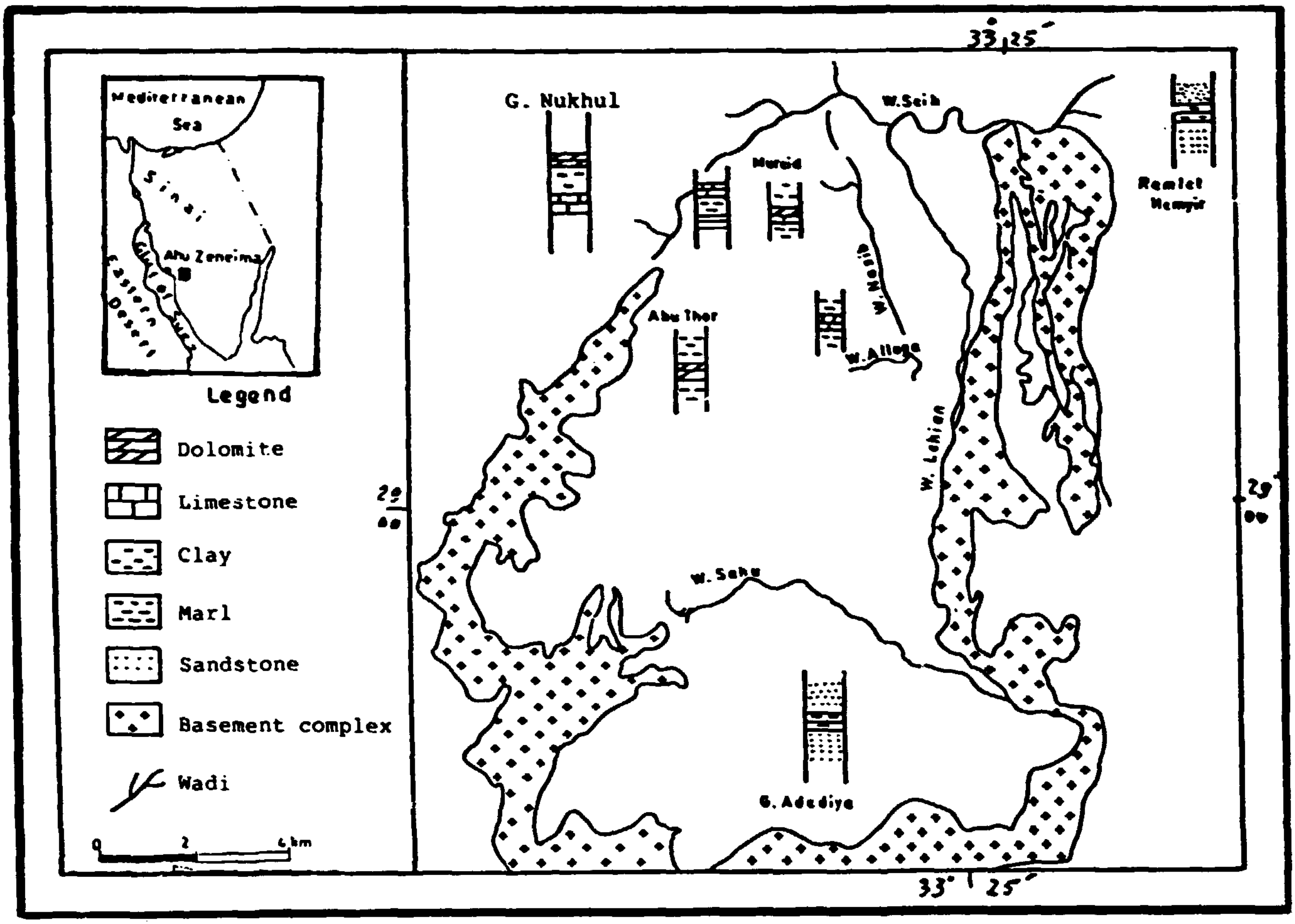

Figure 1 – West Central Sinai Deposition Model.

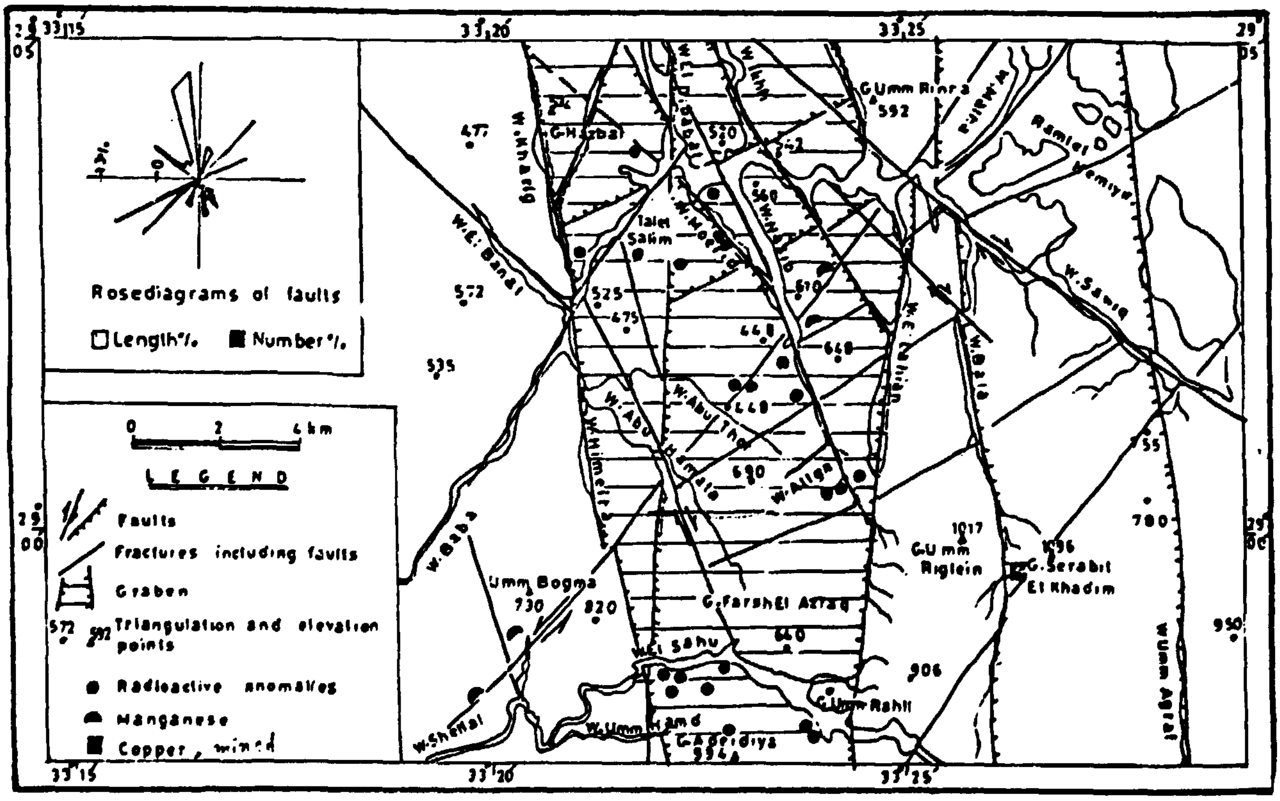

Figure 2 – Structural Map of the Studied Area West Central Sinai.

4 Genesis:

The formation of the West Central Sinai surfacial uranium mineralizations includes at least three geochemical processes which favour their deposition, namely:

a) The leaching of pre-existing uranium minerals present in the basement complexes, or elsewhere by oxidized circulating meteoric water.

b) Trapping of the uraniferous solutions at suitable geological, structural and lithological sites, which are represented, in our area, by clays, shales and dolimite associations.

c) Evaporation and redeposition processes of inland waters under arid climatic conditions, which involve low average rainfall, high average temperature and low average humidity. The same climatic conditions do exist in the calcrete area of Western Australia, where the carnotite mineral is predominant.

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THE USE OF RARE EARTH ELEMENTS GEOCHEMISTRY TO DISCRIMINATE THE LATERITE DERIVATION IN THE GURUPI REGION (EASTERN AMAZONIA)

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The Gurupi Region, located in eastern Amazonia, represents a classical region covered by mature, complete and fossil laterites They stand out by their chemical and mineralogical variation in the upper parts of the profiles, extending from the bauxitic to the phosphatic composition, involving all of the possible intermediate phases (table 1).

Their mineralogical richness is notable, involving besides the classic iron and aluminum phosphates, with distinction for those of the isomorphic series of the crandallite group. The presence of the minerals from this group at different rates incite instigating anomalous geochemical behaviors of some trace elements that are not common in laterites, such as, the rare earth elements (REE's), Sr, Pb, Ba, Y, Rb etc.

Among these, the heavy and light rare earth elements (HREE and LREE) deserve a great distinction, being enriched in the crandallite-bearing phosphate laterites, while, in the bauxitic, they are leached, with contents under the crustal levels. Therefore, in the phosphate lateritic profiles, the absolute contents of these elements increase to the top of the profile (figure 1), while, in the bauxitic, they decrease. It is clear that crandallite is the main carrier of these elements, and also the Sr, Ba and

Table 1 – P_2O_5, REE (La+Ce+Nd) and Y averange concentrations of the laterites from the Gurupi region.

Occurrences	**P_2O_5 (Wt.%)**	**La**	**Ce (ppm)**	**Nd**	**Y**	**Parent rocks**
Phosphatic Laterites:						
Itacupim	11,2	377	495	161	197	Alkaline ultramafic rocks
Trauira	20,7	<56	<78	<42	37	Basic rocks
Sapucaia	13,0	282	782	451	268	Sediments
Jandiá	18,7	42	93	50	21	Sediments
Cansa Perna	16,4	60	109	84	119	Metasediments
Phosphatic/bauxitic Laterites:						
Pirocaua	15,6	33	109	84	79	Metasediments
Peito de Moça	7,5	37	98	63	35	Metasediments
Bauxitic Laterites:						
Piriá	0,5	<37	<50	<34	38	Metasediments
Jacaré	0,5	20	<50	47	16	Basic rocks

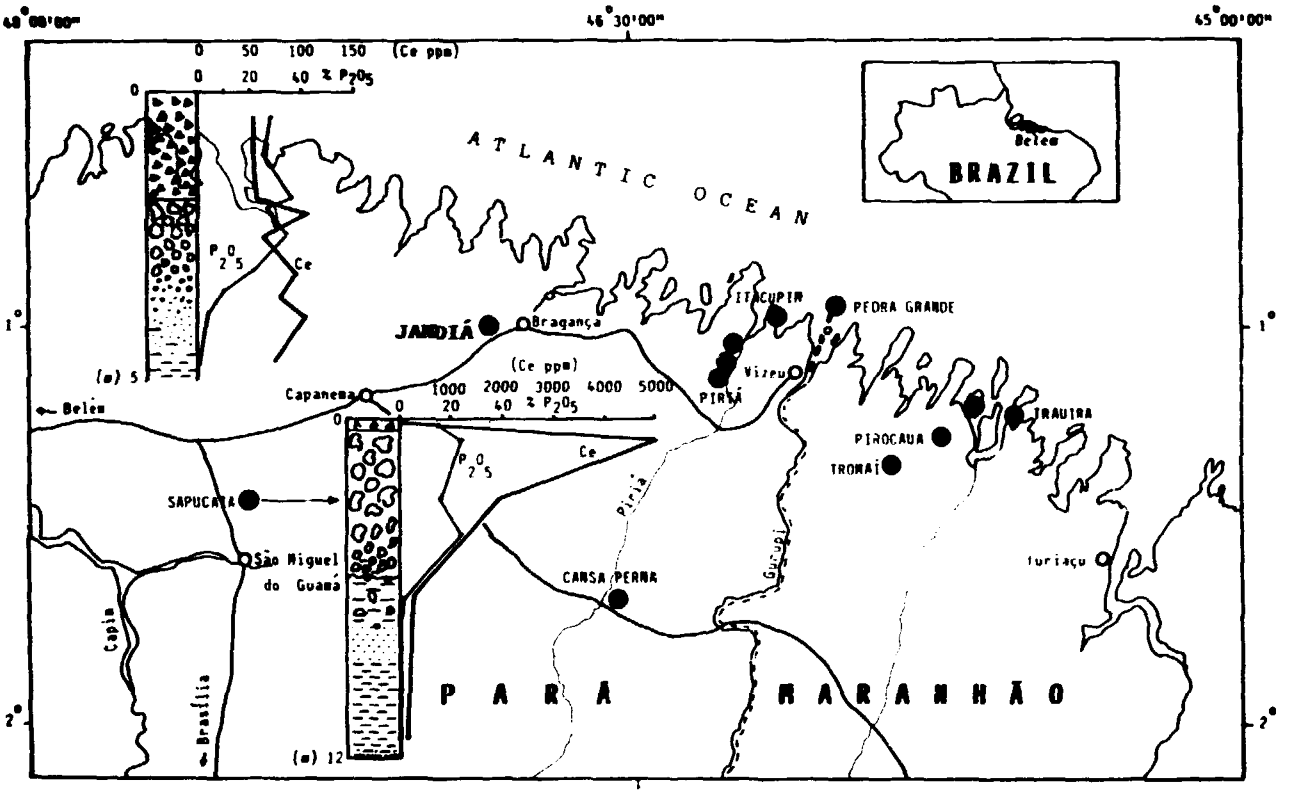
Rb via the crandallite-goyazite-florencite solid-solution, where the members crandallite and goyazite are the most common, as a function of the Ca and Sr contents, always in percent units.

The absolute concentrations are classically controlled by their pre-existing contents in the parent rock and by the kind of mineral structure that absorbs them.

In the Gurupi Region, lateritic occurrences and deposits are found to be greatly contrasting, in terms of their rare earth elements concentrations (table 1). Itacupim, with its phosphatic laterites, derived from ultramafic - alcaline rocks, present about 1,003ppm (La + Ce + Nd), while those derived from sediments and metasediments, reach up to 288ppm (La + Ce + Nd) individually. Therefore, the two occurrences of phosphatic laterites derived from sediments are contrasting between themselves, indicating different compositions for their parent rocks.

The absolute concentrations of the rare-earth elements are excelent to classify the laterites according to their parent rock because their absolute contents between different deposits are not directly correlated with the P_2O_5 contents. The presence of anomalous concentrations of REE in laterites is a strong indicator of the phosphates, as much in laterites as in the parent rock, and less commonly as an indicator of resistates.

This work depended upon long term financial support from Brazil's CNPq and FINEP.



ZIRCONIUM MOBILITY DURING THE LATERITIC WEATHERING OF ALKALINE ROCKS OF POÇOS DE CALDAS

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Some bauxitic profiles, developed from alkaline rocks in Poços de Caldas were studied. The preliminary results show that nearly 40% of the total zirconium existing in the rock is leached out of the profile during the bauxitization process.

On the other hand, it was evidentiated that only a small part of the bauxitic residual zirconium is present as zircon. The most of it is associated with the bauxite ferruginous phase (goethite and leucoxene) as colloidal hydroxides mixtures.

Theme
Analytical Geochemistry

BRAZILIAN LATERITE STANDARDS - I

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The Brazilian natural laterites are being prepared for use as reference materials at LAMIN - CPRM. The amount of material available places the two laterites in an intermediate position between a certified reference material and an analytical standard. This amount also limits the type of analyses and the number of laboratories involved in the study of the two laterite samples. The origin and collecting of the samples, the processing of these samples for chemical study and the way of assuring the homogeneity of the different bottles of the two laterite standards are fully described. The analytical scheme includes mineralogical identification and the chemical analysis of major and trace elements, rare earths and precious metals. The statistical data processing compares the analytical results for each bottle of laterite standard and provides a means for the analysis of variance among bottles. Two sets of tests are used for these specifical aims: Dixon's, k and h for the first one, and Cochran's and Bartlett's tests for the second one. The set of tests is available for usage in a microcomputer PC-type. Each laboratory participating in the present study will receive preliminary data of the two laterites and statistical tools, along with the samples to be submitted to analysis:

a) the mineralogical composition by X-ray diffraction; b) a scanning semiquantitative analysis by optical emission spectroscopy; c) the set of tests for usage in a microcomputer PC-type.

DETERMINATION OF MOLYBDENUM IN SILICATES THROUGH ATOMIC ABSORPTION SPECTROMETRY USING PRE-CONCENTRATION BY ACTIVED CARBON

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An analytical procedure for molybdenum determination in geological materials through Atomic Absorption Spectrometry, after pre-concentration of the Mo-APDC complex in activated carbon, has been developed, which is needed in order to reduce the dilution effect in the sample decomposition. During the development of this method the influence of pH, the amount of APDC for complexation of Mo and the interference of Fe, Ca, Mn, Al, K, Na, Mg and Ti were tested. It was shown that none of these causes any significant effect on the Mo determination proposed. The results of the analysis at the international geochemical reference samples JB-1 (basalt) and GH (granite) were very accurate and showed that the detection limit in rocks (1,00g) is 0,6 ppm, when using sample dilution of 1 ml and microinjection techniques.

DETERMINATION OF RARE EARTH ELEMENTS WITH GROUP SEPARATION IRRADIATION FOLLOWED BY NEUTRON ACTIVATION ANALYSIS. APPLICATION TO BRAZILIAN STANDARDS BB-1 AND GB-1

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In order to determine the rare earth elements (REE) in rocks, by neutron activation analysis, a group separation, before irradiation, was developed.

The Brazilian geological standards BB-1 and GB-1, provided by Instituto de Geociências da Universidade da Bahia, were analyzed.

The method was based on acid digestion of the samples, cation exchange separation with a Dowex 50WX8 column and coprecipitation of the REE with calcium oxalate. Interferents, like U, Th, Ta and Fe were eliminated.

The concentration values of ten REE's (La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Yb and Lu) were determined. The analysis of Pr made a contribution to the knowledge of the REE contents in these geological standards, since there are not yet results in the literature.

The other REE data obtained were compared with literature values and some discrepancies are discussed.

DETERMINATION OF TRACES OF COBALT IN ROCKS USING CONTINUOUS IN-LINE PRECIPITATION AND ATOMIC-ABSORPTION DETECTION

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A continuous preconcentration flame atomisation atomic absorption method for determining cobalt by precipitation with 1-nitroso-2-naphtol is described. The sample treatments, dissolution of cobalt-nitrosonaphtholate, optimization of analytical variables and measurable concentration levels where investigated. The sensivity, selectivity, rapidity and precision of the conventional batch method are significantly enhanced.

The proposed method has been successfully applied to the determination of cobalt at the $\mu g\ g^{-1}$ level in silicate rocks.

FLUORINE IN COALS FROM THE STATES OF RIO GRANDE DO SUL AND SANTA CATARINA

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Although the presence of fluorine compounds in coals deserves special attention, due to their hazardous effects during the combustion process, the content of fluorine in Brazilian coals remains unknown.

Fluorine is corrosive to steam generation systems and, even at low concentrations in the gas flow, is hazardous to human health.

Twenty eight samples of coal from Rio Grande do Sul and Santa Catarina were analysed, including some washed coals.

Fluorine was determined by alkaline fusion of the sample and further determination of fluorite with a selective electrode.

Coals from the coalfields of Guaíba, Santa Terezinha, Butiá-Leste, Candiota, Recreio, Iruí, Faxinal, Leão I and Charqueadas (Rio Grande do Sul), and from the mines of Verdinho - UM II, Santa Augusta and Sangão - mine A, (Santa Catarina) were analysed.

Fluorine content in ROM coals ranged between 85 and 257ppm, with an average value of 178ppm.

Washed coals showed lower fluorine contents ranging between 155 and 192ppm.

Densimetric tests were performed and the fluorine contents of the coals obtained in the various densimetric fractions were measured.

MODIFICATIONS IN TWO ANALYTICAL METHODS USED IN GEOCHEMICAL PROSPECTING: W AND SN

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This work describes little modifications to analytical methods used in geochemical exploration to determine tungsten and tin at ppm levels.

The composition of the colouring solution was changed to allow better dosage of W, and in both methods an organic solvent extraction step was introduced.

As a result of these modifications, the reliability and speed of analysis were improved.

SIMULTANEOUS DETERMINATION OF RARE EARTH ELEMENTS BY SPECTRO-FLAME ICP IN GEOLOGICAL MATERIALS.

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In science and technology there is an increasing demand for rare earth elements (REE). Consequently, analytical methods for the determination of REEs in the rocks and various REE minerals have to be developed. The REE contents in their minerals cover a wide range (e.g. 21.6% for La, 30% for Ce, and 440µg for Lu; values from Lister for IGS 41 bastnaesite). Most analytical methods are not suitable for determing all REE like neutron activation analysis which can only determine 6 REE's routinely without separation. For ICP-AES, the sample has to be brought into solution after preliminary digestion with hydrofluoric and perchloric acid or sodium carbonate and/or lithiumborate fusion techniques. The fusions cause a higher salt content and very often contaminations from the borate may occur. With the carbonate fusion, however, small amounts of the lighter REE together with scandium can be found in the filtrate of the alkaline and have to be recovered in this solution and added to the total amount of REE in the acid filtrate after the leaching.

Melting with lithiumtetraborate seems to be one of the most efficient procedures. Using ICP-AES Spectroflame nearly all natural REE can be determined for example in a 0.25g samples of the Canadian standard SY-3. There are some slight problems with Gd and Er, but these values can be predicted from the chondrite normalized plot of the the other REE.

The Spetroflame uses in its optical system 3,600 grooves/mm and sc in this optical system an optimum of fixed slits for different wavelenghts may be installed. The light tubes offer the possibility to add more optical systems to the same ICP unit. All units are controlled from one PC and the sophisticated software permits an optimal data treatment. If one compares the time factor for different techniques like AAS and INAA, the AES is a quick and reliable method for the determination of REE in their minerals, carbonatites and most rocks without separation and pre-concentration.

The analyses of bastnaesite IGS 41, monazites and carbonatite samples with high contents of light REE and strongly decreasing contents of Tb to Lu will be presented. These results will be checked against results of the Canadian standard SY-3.

REE minerals from granitic pegmatites, like synchysite and monazite, contain rather higher amounts of the heavier REE's and show a strong negative Euanomalie due to changes of Eu^{3+} to Eu^{2+}. Finally, the results obtained by Spectroflame will be compared to those results from Lister's data compilation of the bastnaesite IGS 41 from Great Britain.

SPECTROPHOTOMETRIC DETERMINATION OF TOTAL IRON CONTENT OF SILICATE ROCKS BY FLOW-INJECTION ANALYSIS

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In this work a method for total iron determination by flow -injection analysis (FIA) and spectrophotometry is described. The rock sample was decomposed by fusion with stochiometric mixture of boric acid and lithium carbonate, and the residue dissolved in diluted nitric acid.

The best manifold used as a reduction agent hydroxilamine hidrochroridrate, and, as a chromogenic reagent ortophenantroline was also used. The absorption peak is measured in 510 nm. The results obtained with international rock standards from USGS and GSJ were in good agreement with the certified values.

The analytical methodology developed is suitable for accurate total iron determination in silicate rocks, offering precision and quickness.

THE DETERMINATION OF FLUORINE CONCENTRATION IN APATITES BY RESONANT NUCLEAR REACTION ANALYSIS

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The fluorine concentration in apatites was determined by the Resonant Nuclear Reaction Analysis (RNRA). We reported results obtained through the $^{19}F(p,\alpha\gamma)^{16}O$ reaction, produced by a 340.5 KeV (resonance energy) proton beam interacting with the ^{19}F nuclei in the material being studied. The samples showed fluorine concentrations ranging from 0.85 to 2.02 wt.%. In the present conditions, the sensivity is about 0.06 wt.% of fluorine. The beam spot is 1mm in diameter, and work is being done to reduce to 50µm.

THE DETERMINATION OF PRECIOUS METALS IN GEOLOGICAL SAMPLES BY INDUCTIVELY COUPLED PLASMA MASS SPETROMETRY (ICP-MN)

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James Hager
SCIEX

ICP-mass spetrometry with laser sampling has been used to determine gold directly in solid fire assay beads. A small portion of the lead bead is vaporized by Nd:YAG laser, and the resulting particulate material is passed by a flow of argon into an ICP-mass spetrometer for quantitation of the gold content. Calibration with known geological materials gives linear calibration curves, and detection limits for gols are estimated to be 0.07 micrograms/gram in the original ore sample. The repeatability of the method is similar to that expected for traditional fire assay methods, and the analysis time for the solid lead bead is less than five minutes per sample.

X-RAY FLUORESCENCE SPECTROSCOPY, A RAPID ANALYTICAL METHOD IN MINERAL EXPLORATION

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In mineral exploration, it is quite normal that a huge number of geological samples be taken and need to be analysed as soon as possible. X-Ray Fluorescence Spectroscopy (XRF) is a non-destructive analytical method for qualitative and quantitative determination of a sample's element composition. It can be used to identify all elements from boron to the transuranic elements, and to determine concentrations of these elements in metals, pressed powder samples, glass beads and fluids (like water and oil). Depending on the specific application, concentrations from 1ppm up to 100% may be analysed. Applying special enrichment methods, trace element analysis in ppb are also possible.

Within the elements of the examined sample, the inner electrons will be activated by the X-ray beam in such a way that fluorescence X-rays of a defined wavelength characteristic for the activated element are emitted. Normal laboratory X-ray fluorescence equipments use a X-ray tube as the source of primary radiation.

Advantages of X-ray fluorescence analysis include multi-element capability, high precision, and short measuring times. For normal routine analysis of trace elements in Geological Samples (rocks, soils, etc), sample preparation is quite simple and rapid: crushing, grinding (minor than 60μ) and pressing of powdered material into tablets for XRF analysis. Using large number sample changers with fully automatic hard- and software control, facilitate continuous analysis during the night and weekend. Exploration statistical software packages allow rapid evaluation, interpretation and graphic documentation of the analytic data and prompt planning and action.

Inexpensive sample preparation and low costs per sample/element determination will compensate investment in the X-ray spectrometry equipment.

Theme

Geochemistry of Carbonatites and Rare Earth Elements

CLIMATIC CONTROL OF THE RARE EARTH ELEMENT DISTRIBUTION IN WEATHERING COVERS ABOVE ALKALINE ROCKS. SE-BAHIA STATE/BRAZIL

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The evolution of weathering covers above alkaline rocks in SE-Bahia, and the distribution of rare earth elements (REE) in the weathering products can be related to the climatic zonation.Considerably thick (> 4 m) fersiallitic weathering profiles have developed in the humid coastal region of the syenite massive of Itabuna. In the semi-humid areas inland, less mature hydromorphic soils predominate. The formation of Fe-Mn-duricrusts, occurring on hilltops and slopes is related to earlier weathering stages. Erosion and reworking of weathering profiles are common features of the semi-humid area between Itarantim and Palmeirão (CBPM, 1976).

Behaviour and fractionation of the REE is strongly related to the evolution of the weathering cover, which itself is controlled by climatic factors, drainage conditions and mechanical reworking. Fairly good drainage under humid tropical conditions, as represented in weathering profiles of Sta. Cruz da Vitória, led to the formation of fersiallitic weathering products above sodalite-aegirine-biotite syenites. Weathering is characterized by nearly total depletion of alkalis, while about 80% of the original SiO_2 remained in the profile, bound mainly in the form of kaolinite. Consequently, less mobile components, like weathering resistant heavy minerals have residually become enriched. This is manifested by a 2-fold increase of TiO_2, Nb, Zr and V, which are found in accessories like ilmenite, magnetite and zircon. Fe and Al show enrichment factors relative to the bedrock of max. 1,5. The more mobile minor and trace elements Mn, Zn, Ba and P are depleted throughout the profile. Ba is enriched by factor 1,5 in a 30 cm thick saprolitic zone above the bedrock. Almost all REE's are enriched throughout the profile by max factor 5 relative to the syenite. The highest values of 550 ppm REE were detected in the top-zone, and, at the profile bottom, shortly above the bedrock (figure A). Relative to the source rock, the fractionation pattern of the weathering material shows enrichment of Ce in the REE-rich topo and bottom zones, while enrichment of heavy rare earth elements (HREE) can only be observed in the top horizon. In the weathering products, the positive Eu-anomaly of the syenite has considerably decreased, indicating that the REE patterns are supergeneticaly controlled rather than exclusively inherited from the bedrock. This fact is also manifested by a considerable enrichment of Ce, which becomes immobilized after oxidation to Ce^{1+} in the wearthering environment. Together with HREE which have similar ionic radii, Ce may become fixed in interlayer sites of non-stoichimetric Mn-oxides (MARKER, 1988). In the bottom profile zone above the bedrock, the divergence of Ce and HREE may result from selective fixation of Ce^{4+} to mineral phases which also seem to bind Ba. The distribution of REE relative to the internal standard however shows, that the bulk of the REE have actually been depleted in the middle profile zone, whereas Ce, Yb and Lu are nearly constant (figure B). Only in the top and bottom zones of the profile, have REE actually become enriched. These zones may be related to two stages of formation, which favoured trapping and fixation of REE: REE enrichment in the top zone can be atribbuted to an earlier phase of Mn-oxide formation, the latter acting as sinker for Ce and HREE (MARKER, 1988). During a later stage of profile evolution, descendant dislocation of REE and fixation of predominantly Ce to Ba-Mn-oxides like hollandite as well as slight depletion of HREE took place. This stage reflects impeded drainage and rising pH conditions above the bedrock.

Weathering conditions in the more arid areas (Palmeirão) are characterized by restricted depletion of alkalis and Si and hydromorphic conditions. Indurated colluvial sediments, rich in quartz, silicates and heavy minerals overly the bedrock and indicate considerable reworking of weathering products. The REE patterns in the weathering profile of Palmeirão are mainly inherited from the syenitic bedrock as indicated by slightly negative Ce- and strong positive Eu-anomalies, reflecting the REE patterns of the bedrock (figure C). However, supergene REE-fractionation must have occurred, related to the formation of Mn-Fe pisolites, which are hosted in the top horizon. Relative to the bulk weathering material of the top zone, Mn-Fe pisolites show a slightly positive Ce-anomaly and distinctly lower concentrations of the remaining REE. The in-situ origin of the pisolites is disputed. They rather represent reworking products of Fe-Mn-duricrusts, which are abundant in the vicinity of the profile Microscopically, duricrusts and pisolites are constituted of a skeleton of brecciated silicates, quartz and heavy minerals, embedded in a matrix of Fe- and Mn-oxihydroxides, which occur in several generations. This may be indicative of supergene remobilization and reorganization of Mn and associated Ba and REE from formerly existing duricrust material. Seasonal hydromorphism, with dynamic reduction and oxidation conditions, is responsible for the relatively high concentration of REE's in the mottled zone of the profile (de OLIVEIRA, 1988).

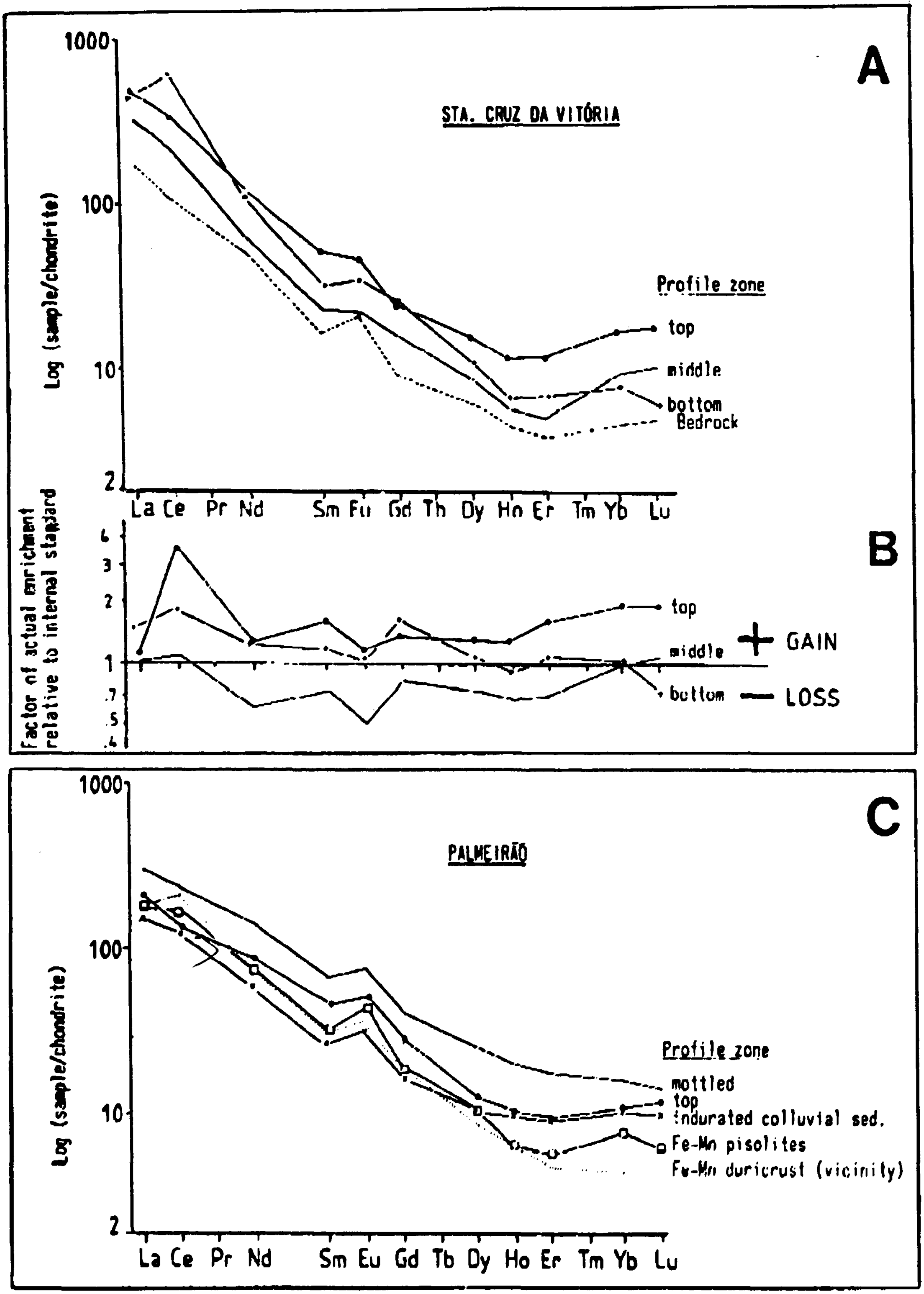

Figure - Rare earth element abundances and factors of actual enrichment in weathering profile above syenitic bedrock of SE–Bahia.

Concluding, Mn-oxides constitute the inicial trap for REEs, which are derived from the weathering of alkaline rocks. Fe, Mn, Ba and REE may have originally precipitated in autochthonous weathering material or as cement in colluvial deposits, forming duricrusts or pisolites. Here, Ce and HREE characteristically reveal positive anomalies in the secondary mineral phases while the positive Eu anomaly indicates heritage of high proportions of immaturely weathered feldspars, which constitute part of the skeleton. In the drier regions of Bahia, Mn oxides have essentially remained stable. Remobilization only took place on a small scale, Mn and REE reorganizing in secondary Mn minerals in the zone of hydromorphism and restricted drainage. In the more humid coastal regions of Bahia, however, the fersiallitic weathering environment may have resulted in major remobilization of REE's from Mn-phases and kaolinitic weathering material and subsequent fixation in zones of restricted drainage above the bedrock. Absolute supergene enrichment of REE can be observed, characterized by the nearly total disappearence of the Eu-anomaly and a distinct Ce- anomaly, indicating oxidizing conditions. HREE's are depleted in this environment. Further investigations beyond this initial stage of research will elucidate in detail the bonding of REE's and the morphological and bedrock control of profile development and REE-distribution over the whole area of SE-Bahia.

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Anais XXXV Cong. Bras. de Geol., Belém, Pará, 4, 1853-1860.

PRELIMINARY CHARACTERIZATION OF THE SUPERGENE EVOLUTION OF THE CARBONATITE ROCKS OF THE JUQUIÁ (SP). ALKALINE-CARBONATITE COMPLEX WITH PHOSPHATE ENRICHMENT

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Apatitic phosphate ores are often associated to alkaline carbonatitic intrusive bodies; in Brazil, several examples can be reported: Anitápolis, Araxá, Catalão, Tapira, Jacupiranga, Ipanema, Barra do Itapirapuã, Juquiá, Mutum, etc.

At Juquiá, the alkaline carbonatitic complex includes a beforsite containing dolomite, apatite and minor amounts of phlogopite, magnetite, baryte and other accessory minerals. The carbonatite body forms a continuous lithological unity at the present erosion level, being, in this sense different from other complexes, where carbonatites occur as veins or dykes.

Several analytical studies were carried out on samples from the weathering profile. The first results allowed a preliminaly recognition of some weathering facies and gave an outline of the phosphate behaviour. Chemical and mineralogical evolution during weathering, leading to the development of isalteritic facies in the lower and mediun levels, and alloteritic facies in the upper levels were established.

Two mechanisms of phosphate enrichment were recognized: relative accumulation, originated by dissolution of carbonates, and absolute accumulation, demonstrated by several generations of secondary phosphates.

The secondary phosphates are apatitic in the isalteritic facies, as due to the lithological context (only carbonatite). On the other hand, the upper alloteritic parts contain kaolinite and aluminium phosphates (crandallite group) showing a possible contribution from the surrounding alkaline silicatic rocks.

RARE-EARTH ELEMENT GEOCHEMISTRY IN THE LUANGA MAFIC-ULTRAMAFIC COMPLEX, PARÁ

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Six whole-rock samples (harzburgite, orthopyroxenic and norite) of the Luanga Mafic-Ultramafic Complex (Pará) were analysed for rare-earth elements (REE) through plasma spectrometry. The Luanga Complex is a deformed and metamorphosed layered mafic-ultramafic body of Archaean age.

The Complex underwent medium-grade metamorphism in three stages. The first stage (medium grade) involved local formation of tremolite and reduction of Ca content in plagioclase. The second stage (low grade) consisted of serpentinization of amphibole or ortopyroxene forming bastite and generation of albite + epidote + white mica + actinolite from plagioclase. The third stage involved renewed serpentinization and/or talcification of pre-existing minerals (including serpentine) along fracture and fault surfaces. The analysed rocks display light rare-earth element (LREE) enrichment up to sixty times the composition of the Leedly chondrite and La/Yb ratios from 6.2 to 20.0 They are low in medium rare-earth elements (MREE), displaying discrete to strong negative Eu anomaly even in plagioclase cumulates and are slightly enriched in heavy rare-earth elements (HREE), usually higher than chondrite values. The low MREE are related to the occurrence of orthopyroxene (bronzite) in a way similar to the pattern of alpine peridotites, while HREE enrichment is compatible with the presence of bronzite and Mg-olivine, probably an inherited igneous feature.

LREE enrichment in the meta-ultramafic rocks and the absence of positive Eu anomaly, or the occurrence of negative Eu anomaly in the plagioclase cumulates are interpreted as the result of aqueous-diffusion metasomatism in domaiN of stronger tectonism. The mineral that carries the high LREE values is an amphibole of the tremolite-actinolite series.

REE GEOCHEMISTRY IN RIVER SEDIMENTS OF THE GREENVILLE PROVINCE (WESTERN QUÉBEC)

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Since 1987, a regional program of exploration geochemistry was carried out by the Ministere de l'-Energie et des Ressources, in the western part of the Geenville Province, Québec, in the southeastern Canadian shield. This area, North of Ottawa, was already known for its REE potential. The program included stream sediments and heavy minerals sampling on the same site, with an average sampling of one per 10km^2.

Several anomalies were discovered; a careful interpretation is required, in relation to the specific behaviour of REE's in a sub-glacial environment. Former geochemical exploration programs failed because of a poor understanding of the behaviour of elements in this acidic environment. River waters of the Canadian shield are especially enriched in rare earth; their contribution exceeds more than 50% of the total input of REE's in the Atlantic Ocean (Goldstein et Jacobsen, 1987). This paper (1) presents the results of REE dispersion in the western part of the Grenville Province, (2) discusses the dispersion mechanisms and (3) proposes some new tools for their interpretation.

Methodology

Field operations were carried out during the summer of 1987, in an area of moderate relief. Two samples were taken at each site:

- 0.5 to 1kg of terrigenous material in order to extract the minus 177 μm fraction;

- 4 liters of sediment minus 850 μm in order to extract the heavy minerals, more than 2.8 g/cm^3. Magnetic fractions were removed with a magnet.

1,661 sites were sampled and analyzed for a surface of 17,700 km^2/ After weighting of the different fractions, both samples were analyzed for multi-elements, including La, Ce, Eu, Sm and Y by ICP methods after hot extraction with HNO_3-, and by NAA. Analytical data and maps for the heavy minerals have been published elsewhere (Choiniere, 1988). Multivariate data were processed with the MacSICAL (MERO) and the GDM (BRGM) softwares on microcomputers.

Geological setting and REE mineralizations

The study area is located in the Grenville Proterozoic Province. Two main units may be distinguished, the central gneiss belt to the northwest and the supracrustal formations of Mont-Laurier to the southeast.

The central gneiss belt belongs to the Allochtonous Polycycle belt (Rivers et al., 1989); it is composed of quartzofelsdpathic gneiss and migmatites with granitic rocks. Some charnockitic plutons and ultramafic units are known. Two superimposed metamorphic events of a higher order than in the adjacent terranes were demonstrated.

The supracrustal formations of Mont-Laurier belong to the Central Metasedimentary Belt (CMB). It includes marine platform and/or continental margin, possibly island arc deposits, locally overlain by continental and shallow marine sediments. Marbles are abundant. These formations are no older than circa 1300 Ma, and were metamorphosed during the Grenvillian orogenic cycle. It is considered as monocyclic.

Polyphase deformation is associated with a major Grenvillian metamorphic event reaching the granulite facies. It occurred between approximately 1,100 and 800 Ma. Potassic alkaline magmatism is closely related to the CMB (Corriveau and Gorton, 1989).

REE mineralizations are known in several districts; two main types may be distinguished: anatectic pegmatites, often located near the border of the CMB, display an U-Th-Cu-Mo-REE association; pyroxenic skarns in magnesian marbles are enriched in phosphates (apatite), uranium and LREE (Hogarth, 1988).

Interpretation of geochemical data

Geochemical prospecting in Canada is often much perturbed by the glacial cover. Distance of transport reaches several kilometers. However, in this study, due to the large scale sampling, effects of till dispersion are rather weak. Anomalies are generally displaced less than 5 kilometers, to the south, and relationships between the geochemical pattern and hard-rock geology may be preserved.

REE's are more abundant in the CMB than in the grey gneiss,. However, strong anomalies appear in the two geological units. Two main factors must be considered to understand the anomalies, the detrital and the chemical dispersion.

Mechanical dispersion concerns mainly heavy minerals. This fraction contains the highest concentration in U, Th, HREE. Principal component analysis displays a strong correlation between P, Ca, Sr, and Y, which is indicative of the presence of apatite; more than 85% of the samples indicate a P/Ca ratio characteristic of this mineral; apatite is, therefore, the main mineral controlling the dispersion of REE's. The correlation factor appears to be higher with LREE than with HREE, indicative of an enrichment of the apatite in LREE. Taking into account mixing with monazite, the La/Y ratio and total REE content of selected samples may be used to determine the type of apatite: sedimentary and magmatic apatites display specific composition in relation to their parent rock (Fleischer and Altschuler, 1982).

Using a regression of the REE against P, it became possible to characterize samples with and without apatite, REE oxides or carbonates are often associated with a high concentration of rare earth (EREE major 500ppm), and a high La/Y ratio; they may be related to alkaline magmatism, the best exploration target for rare earth.

Stream sediments fractions always contain some very fine grain heavy minerals; in order to obtain information which is more hydromorphic, a regression for every element in each pair of samples was performed, and the probable contribution of little heavy mineral was removed. New data represent, therefore, the "chemical component", composed of colloids, light minerals, chemical components adsorbed on oxy-hydroxydes. They are enriched in LREE, probabbly due to the presence of phyllite.

REE-P diagrams for stream sediments display a double correlation, a lower one identical to that observed with heavy minerals, and a higher one corresponding to REE hydrophosphates (rhabdophane), related to the dissolution of apatite (Banfield and Eggletton, 1989). Even with a high REE content, these samples do not display any clear relation with known mineralizations.

Conclusion and implications for exploration

REE dispersion in river sediments of the Grenville Province is mainly controlled by the apatite; the dissolution of this mineral in the weakly acid rivers is probably responsible for the high REE input of the rivers of the Canadian shield flowing to the Atlantic Ocean.

In exploration geochemistry, heavy minerals concentrate most of the HREE, Th, U content. The nature of minerals (apatite, monazite, xenotime) and dissolution of the REE phosphates may be followed using the PLAY (= Phosphore, Lanthanum, Yttrium) triangular diagram. Dissolution of the REE phosphates are characterized by an REE enrichment and increased fractionation. Using this diagram, it is easier to distinguish true anomalies, related to primary mineralogy, from secondary phenomena.

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RIFT ZONES IN RELATION TO INDIAN CARBONATITES

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The relationship between rift/fracture zones and carbonatite occurrences in India is described. A space-time-compositional typification of the magmatic activity has been attempted. Universalisation of the experience leads to a range or correlations between factors, such as: rift/fracture or fault zones, platforms, seismically active regions, regions with mantle heterogeneities and basement anisotropy, large negative Bouger anomalies, rejuvenation of older zones of tectonic weakness, platemovements, collision and transformation faults, thinned crust, asthenosphere swell, alkaline provinces, flood eruptions, diatremes, dyke swarms, ring complexes; lithotypes such as kimberlite, nephelinite, phonolite, layered gabbro-pyroxenites, lamprophyres, trachyte/trachyandesitem granophyre, ijolite, fenite, etc.; role of volatiles including Co_2, P, F, Cl, S, etc. besides H_2O and related processes such as fenitiation, theomorphism and enrichment in specific elements, such as, LILE, REE, F, P, Cl, S, Nb, etc. mineralizations such as fluorite, apatite, phlogopite, baryte, sulphides etc.

Detailed investigations in a number of carbonatite (and related) occurrences, such as, Ambadungar, Dugdha-Naswadi, Padwani, Badwani, Nisarpur, Mt. Girnar, Kala Dongar and other centers of eruption such as Pavagarh, Barda,Osham, Chogat-Chamardi, etc. in the alkaline sub-province related to the Narmada-Sone rift (older Vindhayan fault); Mundwara, Newania, Chandravati etc. related to Sabarmati graben, (older-Aravalli related), also of similar age to Deccan Traps, indicate that several of these factors are interdependent and resurgent, suggesting a cyclic nature of the activity. Carbonatite-nephelinite plugs (+veins, dikes & minor flows of Carbonatites) mark the closure of the cycle stemming from plate movement and updoming (due to plate collision?). Carbonatite - Kimberlite & Diamond and alkaline complexes related to Pre-Trap (Vindihyan and older) activities are known from the alkaline sub-province within Deccan Traps as well as the newly recognized alkaline province in Andhra Pradesh. Inthe former, the occurrences are directly correlatable with the Narmada-Son rift with a long drawn out history and the Sabarmati Graben (also related to Deccan Trap period). In the latter, they are related to NE-SW system left lateral strike slip faults (transform faults as per N.G.R.I. reports 1977-1978, Hyderabad).

A similar correlation may be rendered feasible for the Cuddapah rift (Chelima carbonatite), rifted troughs resulting from Precambrian "en echelon" faults (Sevattur, Samalpatti, etc.) and Nilgiri fracture ones (several complexes - the most important being at Sittampundi), typical of MC rift nature of the ENE-WSW.

The Armada-Son trough has been confirmed through several lines of evidence such as tectonic and geomorphological studies,flat linear nature and uniform with (controlled by faults and horst blocks) marked elongated negative gravity (i.e. lows) anomalies, of the order of up to 80 milligals, more than average heat flow and dyke

KEY WORDS: Carbonatite-Nephelinite Magamatism, Rift/fracture zones. Updoming, Plate movement and collision, Geochemistry, Mineralization.

swarms parallel to ENE-WSW a number of successive upwards, marked by a number of peneplanation surfaces. The most significant feature based on these erosional surfaces is the broad peninsular arching correlated to stages of Himalayan Orogeny. These major lineaments orlinear defiles have been noted through IRIS imagery and identified on LANDSAT images on 1:1,000,000.

Similarity of gravity picture elongated negative with sporadically spaced positive anomalies (marking intrusive masses) on the western coast south of Bombay prompts a search for Kimberlites (+ diamonds - known to occur with above referred two rifts/fracture ones) as well as for mobilised/mobile mineralization, such as, barytes, apatite, Pb-An sulphides, phlogopite, Nb-Ta (e.g. pyrochlore), and Zr etc. in this part.

STUDY OF RARE EARTH ELEMENTS FOR THE CHARACTERIZATION AND METALOGENETIC EVALUATION OF GRANITOIDS OF THE PARANAENSE SHIELD

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REE geochemistry combined with major and trace elements data, provided some diagnostic criteria regarding the origin, the geotectonic setting and the metallogenesis of granitoid intrusions in the Paraná Shield. The intrusions were grouped as mantle (Sintexis Series) and crustal (Transformation Series) origins.

The two lineages include six suites, with pre, syn, tardi-to-post and post-collisional emplacement. From the metallogenetic standpoint, the "Sintexis" granitoids can be labelled as "Mo-W-Cu-Au porphyry-granites" and the "Transformation" granitoids as "Sn-W greisen-granites".

Theme
Organic Geochemistry

AROMATIC BIOMARKERS DISTRIBUTION IN THE IRATI OIL-SHALE

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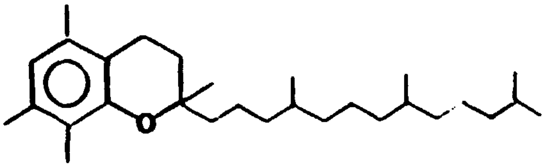
The distribution of aromatic structures in sediments and petroleums yields important informations on the origin and level of maturation of geological samples. In the present work, the geochemical significance of aromatic compounds characterized in Irati Formation (Permian), the largest reserve of oil-shales in Brazil, is discussed. An outcrop sample of the sediment was initially extracted with chloroform.

After precipitation of the asphaltenes, the hexane bitumen as submitted to a McCarthy & Duthie column (SiO_2, KOH) for removal of the acids. Thin-layer chromatography of the neutral lipids gave rise to a concentrate of aromatic which was analysed by high-resolution gas chromatography and mass spetrometry. Characteristic mass fragmentograms allowed identification, amongst others, of alkyl-derivatives of naphthalene (C_1-C_4), antracene/phenanthrene (C_2-C_4) and triaromatic steranes. Chromans (e.g., structure I), a recently recognized class of biomakers, were also detected in the fraction.



I

BEACH POLLUTION - ORIGIN IDENTIFICATION BY GC AND GC-MS

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Aiming at correlating an oil sample collected on the beach with oils from ships operating in the area during an oil spill, analyses were performed using capillary gas chromatography (GC), capillary gas chromatography-mass spectrometry (GC/MS).

The oils, in general, are very similar, but it was possible, through the pristane/phytane ratio and proportion among the steranes, to separate them into three groups, one of which included the oil collected on the beach and the cil from one of the ships.

BIOLOGICAL MARKERS APPLIED TO PALEOECOLOGY AND CHRONOSTRATIGRAPHY

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Petrobrás/CENPES

Biological markers or molecular fossils are organic compounds which occur as complex mixtures in sediments and petroleums, and whose molecular structures can be related to those of the precursor lipids biosynthetized by organisms originally present in the depositional environment.

During the last decade, the use of biological markers in petroleum exploration has increased in importance. The major applications of biological markers has been on oil-oil and oil-source rock correlations, migration, biodegradation and the assessment of thermal evolution of sediments and oils.

Recently the availability of a new breed of GC-MS instrumentation allowed the application of biological markers as paleoecological and chronostratigraphic tools. Furthermore, there is potential for ascertaining types of depositonal environment and age of the source rocks using only biological markers analysis of the derived oils.

CHROMATOGRAPHIC ASPECTS IN STERANE ANALYSIS

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The importance of biomarker analysis in petroleum geochemistry has grown in recent years. This places increasing emphasis on the optimization of gas chromatographic techniques.

The geochemical information obtained from sterane distributions depends on the degree of separation of their diastereoisomers.

Gas chromatographic parameters as well as apolar and polar capillary columns were optimized in order to achieve maximum resolution.

This improvement in resolution was performed without excessive increase in analysis time, by the use of SE-54 & OV-31-OH capillary columns coupled in series.

COMBINED APPLICATION OF MUD LOGGING, FORMATION EVALUATION, THE GAS RATIOS THEORY, AND PETROPHYSICS THROUGH PULSED NUCLEAR MAGNETIC RESONANCE IN THE IDENTIFICATION AND EVALUATION OF POTENTIAL OIL/GAS RESERVOIRS WHILE DRILLING

Jorge Horacio Poncetta
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Mud logging is well known as a useful direct method used in exploratory wells for early detection and evaluation of oil/gas shows.

Technological advances serve today's industry with accurate equipment has for detection and analysis of hydrocarbon gases. It also made it possible to obtain a deeper comprehension of the physico-chemical and mechanical processes taking place while drilling and influencing the release, transport to the surface and detection of formation hydrocarbons. Absolute magnitudes (ppm) were obtained when the parameters, influencing detection and chromatography analysis within the methane-pentane range, were normalized.

By having these data it was possible to develop a method for the mathematical treatment of it: the "Gas Ratios Theory". It is performed at the wellsite by using simple computing systems, thus providing an initial evaluation of the reservoir with respect to fluid type.

Traditionally, the petrophysical properties of reservoirs were derived from well-testing, wire line logs, and/or post-drilling lab tests. Wellsite use of a device, based on the principles of Pulsed Nuclear Magnetic Resonance, provides quick and continous data on porosity, permeability index, irreducible saturation, and free fluid.

The combination of both techniques (Gas Ratios and P-K), at the wellsite, allows for an early evaluation of the reservoir and, thus, makes, possible to adjust logging programs, well-testing, and completion.

In turn, conventional mud logging provides data on reservoir limits, lithology and shows.

The methodology of the Combined Analyses is presented with examples.

DETERMINATION, QUANTIFICATION AND ORIGIN OF HYDROCARBONS IN BOTTOM SEDIMENTS OF THE MANGUABA LAGOON SERGIPE-ALAGOAS BASIN

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Bottom sediments of the Manguaba Lagoon in Sergipe-Alagoas basin were sampled by the Vibracore system. Cores were collected in order to determine, by high resolution gas chromatography, gaseous hydrocarbons concentrations. The hydrocarbon distribution was mapped using a map generator program (GEOMAP) in PETROBRÁS IBM 3090 computer.

The origin of the methane, the main gaseous component, was ascertained by mass spectrometry. A special methodology developed by CENPES, which allows the handling of extremely small sample volume, was used.

The regional distribution of anomalous concentrations of hydrocarbons coincides with the alignment determined by two deep faults crossing the entire sedimentary sequence under the Manguaba Lagoon. These faults, acting as open ducts allowed the connection of source and/or reservoir rocks with the surface, thus making easier the migration of significant amounts of gaseous hydrocarbons. These gases are responsible for the drastic reduction in the speed of propagation of acoustic waves, up to 300 m/s in the subsurface portions of the Manguaba Lagoon.

Besides the methane of thermochemical origin, it was also observed the production of biochemical methane in bottom sediments. These two types, chemically identical, presented only the carbon isotope ratios markedly different. The gases, genetically distinct, are mixed in different proportions, with the predominance of thermochemical components only in areas where the deep faults subcrop.

GEOCHEMICAL CONTRAST BETWEEN THE FRASNIAN AND THE FAMENIAN - AMAZON BASIN - BRAZIL

René Rodrigues
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The biotic crisis worldwide, observed in the transition, Frasnian-Famenian, is well-documented paleontologically and geochemically in European and North American sedimentary sequences.

In Brazil, despite the occurrence of strata of the same age and well represented in the Amazon and Parnaiba basins, few studies were carried on and published in the literature.

Aiming at filling in part of that knowledge gap, the results of organic geochemistry analyses of the Upper Devonian of the Amazon basin are presented here.

In this basin, the transition Frasnian-Famenian, is characterized by a significant, decrease in total organic carbon, increase in the percentage of oxidized organic matter, bitumen carbon isotope values 1.0 to 2.0% less negative and by changes in composition of terpanes and steranes.

The origin of the phenomena reponsible for the biotic crises through geologic time, among them the transition Frasnian-Famenian, are still very controversial.

GEOMICROBIAL PROSPECTING IN THE DETECTION OF NON-HYDROCARBON-BEARING TRAPS

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The geomicrobial prospecting for petroleum is based in the ability of microorganisms to consume the gaseous hydrocarbons that commonly migrate to the soil surface from subsurface petroleum deposits. The developed methodology is quite simple having a low operational cost and high efficiency. It consists of the colection of soil samples at points previously selected. The microorganisms, that are able to consume exclusively the petroleum gases, are selected and statistically quantified by the most-probable number (M.P.N.) method. This developed methodology evidences the total absence of microorganisms, that utilize gaseous hydrocarbons as the only carbon source, in non-petroleum-bearing areas, while in petroleum producing areas the soil population reaches around 10^8 microorganisms from gramm of dry soil.

The methodology's efficiency was tested in 26 wells in Brazilian sedimentary basins and the predictions were made before drilling.

A correlation was obtained of about 33.3% for the hydrocarbon-bearing locations. Studies are being developed in order to increase this percentage.

Eleven locations with negative prognosis by the geomicrobial prospecting method were perfurated, and all of them were dry out, showing a 100% correlation.

LOW SALINITY WATERS IN THE PARÁ/MARANHÃO AND CASSIPORÉ BASINS – ORIGIN AND EXPLORATION IMPLICATIONS

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Chemical analyses of waters recovered from wells drilled offshore of the northern Brazilian coast, showed salinities much lower than those expected. This investigation demonstrates that the low salinities are due to the influx of meteoric waters, probably through reservoirs of the Rift Section. The hydrodynamic flow was responsible for chemical, physical and biochemical alteration of oils pooled in reservoirs less than 3000 meters deep. Oils in deeper reservoirs were not significantly altered. The porosity and permeability of the reservoirs, however, both in the rift and in the Marine Section, were severely affected.

MODERN SURFACE GEOCHEMICAL PROSPECTING AS A TOOL FOR PETROLEUM EXPLORATION

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Surface prospecting, based on the search for surface evidence of hydrocarbons, is the oldest method used for oil exploration and responsible for a large number of discoveries.

Surface geochemical prospecting has recently become important as an exploration tool. Presented in this paper are the basic concepts on which this method is supported, as well as some aspects relative to oil and gas migration towards the surface, and in particular, the dominant vertical component migration theory.

The sources for surface hydrocarbons are: organic matter in sedimentary rocks, biological processes, cultural contamination, and oil and gas deposits reservoir rocks. This paper deals with them and their relative significance. It shows how microseeps reach the surface. Processes and mechanisms, such as, diffusion, effusion, and flotability, are presented in some detail.

Surface geochemical prospecting methods are separated into direct and indirect, depending on whether they involve detection and quantification of hydrocarbons or not.

The methods most used by the industry are highlighted, particularly one of them, with its application in frontier exploration areas and in bordering areas.

Pilots studies are defined and characterized for their significance in the design, economy and validity of the geochemical method.

The economic feasibility of its use is as important as the technical feasibility, thus, it is also a matter of consideration, in this work.

PETROGRAPHY AND ORGANIC GEOCHEMISTRY OF COALS FROM THE STATE OF RIO GRANDE DO SUL, BRAZIL

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Petrobrás/CENPES

Geochemical and petrographic analyses were performed on coal samples from Faxinol, Leão, Capané and Candiota mines.

The analyses showed a wide predominance of woody-cellulosic organic matter, comprising macerals of the vitrinite and inertinite groups.

The higher plants composition of the organic matter, is also evidenced by the ratio pristane/phytane of greater than 5.0, predominance of normal paraffins of high molecular weight, high relative abundance of C19 and C20 tricyclic terpanes, tetracyclic terpanes, 17 α (H)-22,29,30 trisnorhopane (TM), 17 α (H), 21β (H)-30-norhopane, 17 β (H), 21 α (H) normoretane, 17 β (H), 21α (H)-moretane, 13β (H), 17 α (H)-24-etil-diacolestane, 5 α (H), 14 α (H), 17 α (H)-24-etil-colestane, 5 α (H), 14 β (H), 17 β (H)-24-etil-colestane.

SURFACE GEOCHEMICAL PROSPECTING IN PETROLEUM EXPLORATION - PARNAÍBA BASIN

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Surface geochemical prospecting is based on the assumption that hydrocarbons emanate to the surface from significant oil accumulations, contaminating the oil and causing physical, chemical and biological alterations

The emanations, when severe, grades into exsudations, easily observed through buddies in water bodies or characteristically stained soils. The emanations, however, in general, are not evident and its detection is only possible through specific analyses.

Besides the indication of subsurface oil accumulations, surface geochemistry also indicates the occurrences of important processes of generation and migration of hydrocarbons.

In the current exploratory process of the Parnaíba Basin, surface geochemical prospecting was applied on a regional scale to the northern portion of the basin, an area of approximately 86,000 square kilometers. Consistent anomalous concentrations of hydrocarbons were detected. The anomalies, when integrated with available geological data, indicated well-defined trends coincident with geo-structural features detected by other exploratory methods.

Through surface geochemistry the Vazante and Buriticupu trends (N30'E) and the Presidio Trend (N30'W) were characterized. No anomalies were detected to the west (Imperatriz-Gurupi region), where source rocks are absent.

THE DIABASE INTRUSION INFLUENCE OF THE IRATI OIL-SHALE AROMATIC BIOMARKERS DISTRIBUTION

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Temperature is the main parameter causing maturation of the sedimentary organic matter. Its importance is generally evaluated based on biomakers nature and content determined along, stratigraphic columns. Nevertheless, for long and deep columns maturation is related not only to the effect of temperature but also of pressure and time. An interesting way to study the temperature effect alone on the organic matter maturarion is to use a stratigraphic column which has been subjected to the effect of an igneous intrusion. This is the case of the Irati Formation (Permian). This paper describes stratigraphic distributions of aromatic hydrocarbons determined for the Irati column cut by a diabase sill. The samples were first extracted with dichloromethane. Then, the asphaltenes were precipitated and the resulting hexane solution of bitumen was submitted to McCarthy and Duthie's chromatography (SiO_2, KOH) to remove the acids. Thin layer chromatography (SiO_2), hexane) of the neutral lipids produced an aromatic fraction that was then analysed by high resolution gas chromatography - mass spectrometry. Mass fragmentograms allowed for the characterizition the distribution of benzenic, naphtalenic, phenantrenic/anthracenic and aromatic sterane hydrocarbons in the various samples. These results led to correlations between aromatization and temperature stratigraphic functions for this column.

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