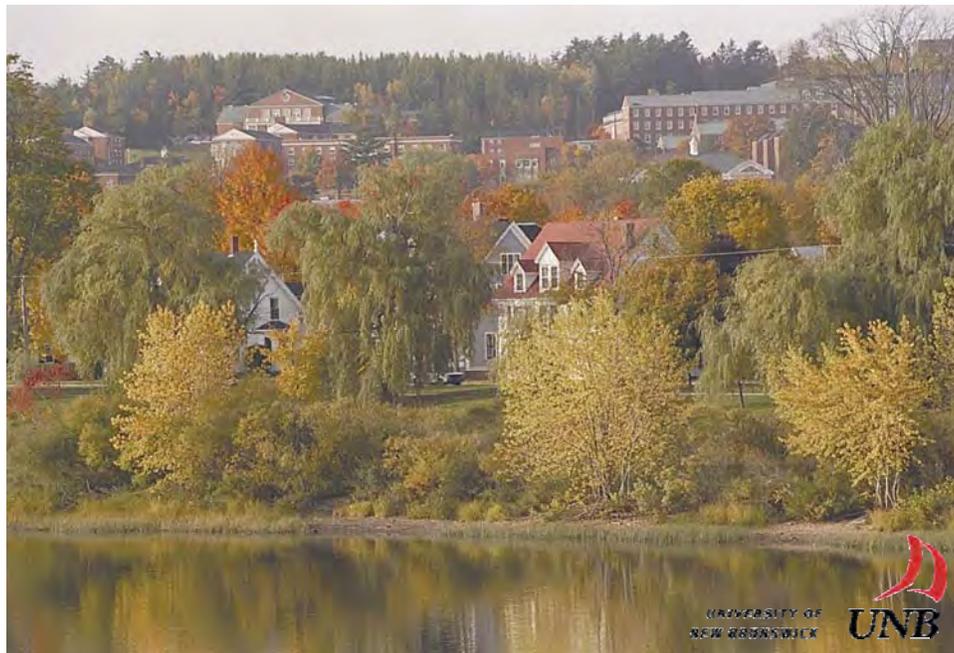




**PROCEEDINGS OF THE 24TH
INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM
FREDERICTON, NEW BRUNSWICK, CANADA**



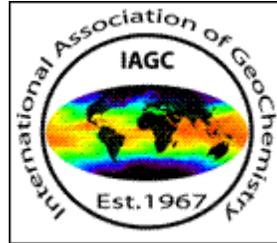
JUNE 1ST-4TH, 2009

EDITED BY

DAVID R. LENTZ, KATHLEEN G. THORNE, & KRISTY-LEE BEAL



VOLUME I



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VOLUME I

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DEEP SEARCH GEOCHEMICAL EXPLORATION METHODS

EDITED BY:

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Exploration for deeply buried gold deposits in the Bendigo region, Victoria, Australia: regolith geochemistry of the Lockington area

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ABSTRACT: Soil surveys and blind tests conducted over the Lockington East Au (\pm As, \pm Sb) deposit, which lies 60 km northeast of Bendigo in northern Victoria, have demonstrated that soil samples can reveal the presence of geochemically anomalous basement at depths of 40 to 60 m beneath transported Murray Basin cover. A soil sampling protocol for Au exploration in northern Victoria in covered areas using aqua regia analysis of the A-horizon >1 mm size fraction for Au and As is recommended, followed by sampling of A2-horizon soils, generally at a depth of 10 to 20 cm. A2-horizon samples should be subjected to several partial extractions in order to yield useful results. A digestion using 0.1 M Na-pyrophosphate and analysed for Au, As and Sb by inductively coupled plasma mass spectrometry (ICP-MS): Fe, Mn and Ca analysed by ICP-optical emission spectroscopy (OES): and organic C analysed spectroscopically in the Na-pyrophosphate digestion extract is recommended. The data should either be normalised to Fe, Mn, C or Ca, as appropriate, or residuals calculated from regression analysis. A2- and B-horizon samples should also be subjected to aqua regia digestion and analysed for Au, As and Sb by ICP-MS and for Fe and Ca by ICP-OES in order to provide verification of the Na-pyrophosphate results. Again, the data must either be normalised or subjected to regression analysis in order to identify anomalous areas. A weak alkaline digestion analysed for Fe, As and Sb may also yield useful results, as would the use of 4M HCL at room temperature followed by analysis for As, Sb and Au. The use of BLEG analyses for Au and Ag on small (100 g) samples has not been demonstrated to be statistically significant in this study, but larger (i.e. 2 kg) BLEG samples may be useful at a reconnaissance scale. A minimum follow-up sample spacing of 50 m is suggested in order to generate multi-sample anomalies. Sampling toward the end of summer or in autumn prior to significant winter rainfall is recommended in order to maximise metal concentrations measured relative to analytical background, and to enhance potential anomalies. Soil pH should be determined on all soil samples (5:1 de-ionised water to soil mixture) and can also be used to verify areas of anomalous soil response. The resolution and accuracy of the results are such that preliminary drill targets can be defined using surface soil sampling.

KEYWORDS: *soil, partial extractions, gold, geochemistry*

INTRODUCTION

The discovery of buried gold mineralisation at Lockington under between 40 and 100 m of Murray Basin sedimentary cover was made in mid-2004 by Gold Fields Australasia Pty Ltd as a result of combined geophysical targeting and regional soil sampling. Further buried gold mineralisation has subsequently been discovered on the Lockington East group of exploration licences, approximately 3 km east of the original Lockington discovery. By late 2007, over

100,000 m of aircore and nearly 11,500 m of diamond core had been drilled to define disseminated pyrite and arsenopyrite Au mineralisation in Ordovician basement 45 km north of the Fosterville gold deposit.

Detailed soil traverses were undertaken by CSIRO over the Lockington deposit following its discovery to determine the optimal grain size fraction for sampling. In 2006 Geoscience Victoria initiated the Developing Gold Undercover program with the intention of aiding mineral explorers in their search for buried gold

deposits in Victoria (Figure 1). The Lockington discovery provided a timely opportunity to study the soil anomalies associated with buried gold mineralisation in northern Victoria, and to further refine sampling and analytical protocols. The results of these investigations are summarised in Arne *et al.*, (2009).



Fig.1. Location of the Lockington deposit in northern Victoria. The locations of a number of major central Victorian gold deposits are also shown.

GEOLOGICAL SETTING

The Lockington area lies in the Riverina Plains region of northern Victoria, 60 km northeast of Bendigo. Palaeozoic basement in this region is overlain by Late Cretaceous to Quaternary marine to terrestrial sediments of variable thickness. Depth of cover in the study area ranges from 40 m to more than 100 m, and is characterised by a regolith profile through rocks ranging in age from Ordovician to Tertiary. This profile is typical of the Riverina Plain in the Murray Basin and includes several extended periods of erosion. The basement consists of metamorphosed Ordovician mudstones, siltstones and sandstones that are typically weathered to an average depth of 15 m. These rocks belong to the Bendigo Structural Zone, which is well endowed with orogenic Au deposits further south, and are inferred to have similar mineralisation potential beneath the Murray Basin.

GEOCHEMICAL INVESTIGATIONS

Shallow (<10 cm) soil samples for particle size analysis were collected from an area over the Lockington deposit for separation into seven grain size fractions at CSIRO. These, along with a bulk soil sample, were analysed for Au and a suite of 18 other elements by ICP-OES and ICP-MS following an aqua regia digestion. Soil samples to test a range of partial extractions were collected by Geoscience Victoria at depths of 0-20 cm (A-horizon), 20-40 cm (A-B transition) and 40-60 cm (B-horizon) over the Lockington East deposit. Top soil and leaf litter were removed prior to sampling the A-horizon. The soil samples were sieved to less than 2 mm in the field and tested for the presence of pedogenic carbonate with dilute HCl. These samples were analysed by aqua regia digestion, bulk leach extractable gold (BLEG), a weak alkaline digestion containing dilute cyanide, a 4M HCl digestion and a 0.1 M Na-pyrophosphate digestion.

As a regional observation, arsenic is concentrated in the >1 mm soil fraction, and defines broad-scale anomalies in areas of shallow bedrock or residual soil. It has probably been adsorbed onto amorphous secondary Fe oxides, some of which have formed pisoliths. By contrast, Au is generally concentrated in the clay-sized fraction of transported soils.

Gold is elevated over buried mineralisation at Lockington East in the aqua regia digestions, and the pathfinder elements As and Sb are elevated in the Na-pyrophosphate (Figure 2), weakly alkaline and 4 M HCl digestions above buried Au mineralisation. However, the metals also show strong positive correlations with either aqua regia Fe or partially extracted Fe from the weak alkaline digestion. In addition, As and Sb in the Na-pyrophosphate extraction show a strong positive correlation with the amount of organic C in humic acids.

Soil anomalies present in the raw element data from a variety of extractions are attributed to the effects of metal scavenging onto the surfaces of either Fe oxides or humic/fulvic acids. These metal

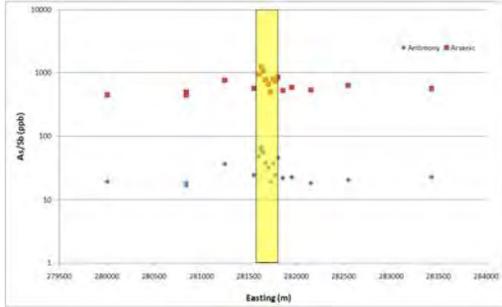


Fig. 2. As and Sb in Na-pyrophosphate digestion from A-horizon soil samples ~40 m above the Lockington East Au deposit. The position of the buried Au deposit is shown by the shaded rectangle.

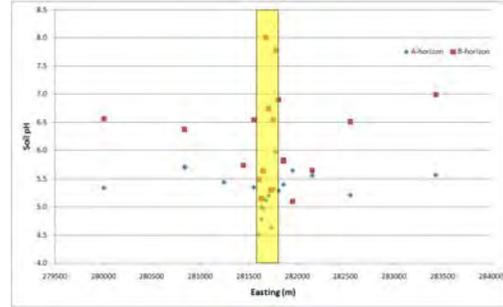


Fig. 3. Soil pH over the Lockington East Au deposit. The position of the buried Au deposit is shown by the shaded rectangle.

anomalies are associated with lower soil pH in the A-horizon and elevated pH in the B-horizon (Figure 3).

Soil anomalies over bedrock mineralisation are still apparent in some partial extraction data once corrected for the effects of scavenging, either by normalisation of metal data to Fe or organic C, or through the use of residuals from regressions through scatter plots of associated elements. The Au/Fe ratios from aqua regia digestion of A2-horizon samples, As/Fe ratios from aqua regia digestion of B-horizon samples, and Sb/C and As/C ratios from A2-horizon samples from the Na-pyrophosphate digestion all provided surface anomalies with hypergeometric probabilities less than 5%. The lowest hypergeometric probability (0.08%), and therefore the parameter least likely to be a random effect, is provided by Na-pyrophosphate Sb data normalised to both aqua regia Fe and spectroscopic organic C. A similar ratio from Na-pyrophosphate As data also provides a statistically acceptable hypergeometric probability if a slight degree of lateral dispersion is allowed (i.e. if a sample on either side of the vertical extension of bedrock Au mineralisation are included as “anomalous”).

The results of a blind test over a region with ~60 m of transported cover indicate that BLEG Au, and Na-pyrophosphate Sb/C and As/C provide a good indication of mineralised bedrock at depth.

Data from the Na-pyrophosphate partial extractions and estimates of organic C contained in humic and fulvic acids from spectroscopic determinations show poor reproducibility over time. Analysis of data from re-sampling in September 2007 show significantly lower results over bedrock mineralisation than the original orientation survey conducted in April 2007, although the general pattern appears to be preserved. Re-analysis of the duplicate field samples in the same batch indicates that this variation largely reflects seasonal variations in metal content of the soils, possibly related to rainfall patterns, but also includes a component of laboratory variation between batches.

CONCLUSION

Soil geochemistry using partial extractions has detected weakly mineralised basement below 40 to 60 m of transported cover in northern Victoria, Australia. Au, Sb and As are elevated in A-horizon soils following aqua regia, BLEG, weakly alkaline, 4 M HCl and Na-pyrophosphate digestions. These metals show a positive correlation with Fe and, in the case of the Na-pyrophosphate digestion, with organic C. Statistically valid anomalies remain for aqua regia Au, and Sb and As in Na-pyrophosphate following normalisation of the data for Fe and C content. They are also associated with lower pH in A-horizon soils and higher pH in B-horizon soils.

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REFERENCE

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Fingerprinting mineral deposit types using iron-oxide chemistry: Application to till from Thompson, Manitoba, Canada

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ABSTRACT: Magnetite and hematite are common in a range of deposit types. These minerals form a range of partial to complete solid-solutions and they are resistant to supergene weathering. The compositional differences are used to construct discriminant diagrams that separate different deposit types. A first diagram using Ni+Cr vs. Si+Mg allows isolation of Ni-Cu-PGE deposits and Cr deposits from other deposit types. Similarly, the Al/(Zn+Ca) vs. Cu/(Si+Ca) is used to isolate Cu-Zn-Pb VMS deposits. Samples plotting outside the Ni-Cu-PGE and Cu-Zn-Pb VMS fields are discriminated using the Ni/(Cr+Mn) vs. Ti+V diagram that efficiently separate IOCG, porphyry, BIF, skarn and Fe-Ti-V deposits. The method is applied to magnetite and hematite separated from three till samples collected near the Thompson Ni-Cu massive sulfide deposits, Manitoba, Canada. Tests for heterogeneity of the till magnetite chemical composition show that sub-samples provide similar compositional ranges. Iron oxides chemical composition from till samples collected down-ice from the Pipe and South pits of the Thompson mine plot in part within the field of Ni-Cu massive sulfide deposits, demonstrating the potential of the method in mineral exploration in regions overlain by glacial sediments.

KEYWORDS: magnetite, hematite, till, nickel, geochemistry, mineral

INTRODUCTION

Iron oxides (hematite and magnetite) are common minerals found in magmatic and metamorphic rocks and can be major to accessory minerals in a range of mineral deposit types. The range in chemical composition of the various deposit type environments likely controls the chemical composition of iron oxides in mineral deposits, such that this compositional variety can be used to fingerprint mineral deposit types (Carew 2004; Gosselin *et al.* 2006; Beaudoin & Dupuis 2009).

In addition to their ubiquity in mineral deposits, magnetite and hematite have potential to be used for mineral exploration from heavy mineral separates because they are resistant to chemical weathering and mechanical abrasion during transport, an important feature of indicator minerals (Belousova *et al.* 2002). Because of their resistance to weathering, the iron oxides can be a useful indicator mineral in highly weathered terrains. Magnetite is present in all shield-derived tills and because of its magnetic

properties it can be easily recovered from surficial sediments. The <2.0 mm ferromagnetic fraction of till is routinely recovered from exploration samples during heavy mineral processing at commercial laboratories and set aside for archiving. In the Thompson Nickel Belt (TNB), for example, till samples contain between 1 and 80 g of magnetite per 10 kg, on average 8 g. This translates into 1000s of grains per 10 kg.

ANALYTICAL METHODS AND SAMPLE PREPARATION

Polished thin sections or iron oxides grains polished in epoxy mounts were analyzed using Université Laval CAMECA SX-100 5-WDS electron microprobe under a beam of 15 kV at 100 nA, using a range of natural and synthetic standards. After counting over the peak for 20 to 30 sec, background is measured on both sides for 10 sec. These settings yield minimum detection limits (mdl) as low as 20 ppm for elements such as K, Ca, Al, Si, Ti and Mg, 50 ppm for Mn, Cr and V, 200 ppm for Cu,

Zn and Ni. The optimized analytical routine allows analysis of one spot in less than 5 min.

The ferromagnetic fraction of the till samples was separated by standard methods by Overburden Drilling Management Ltd (ODM). Subsamples containing 22 to 110 randomly selected grains were prepared by ODM. To test for heterogeneity, two sets of 5 subsamples, from 2 till samples, were prepared from the 0.5-1.0 mm size fraction using a plastic riffle at Université Laval.

IRON OXIDE SIGNATURE OF MINERAL DEPOSIT TYPES

We have developed a series of discriminant diagrams that empirically allow discrimination of a range of deposit types. Some diagrams are useful to uniquely discriminate samples from one deposit type from all other types of deposits, whereas others distinguish fields that are characteristic for several deposit types. Because of compositional variation between grains and samples from a deposit, we compute the average composition of a deposit using non-parametric distribution modelling methods to take into account less than detection limit data (Helsel 2005).

The Ni+Cr vs Si+Mg diagram is efficient in separating the average composition of Ni-Cu-PGE deposits from other deposit types (Fig. 1). A podiform chromite deposit plots at high Ni+Cr values, but the high Cr in magnetite from podiform chromite deposits allows unambiguous identification.

Volcanogenic massive sulfide deposits (VMS) plot with a high probability within a distinct field in the Al/(Zn+Ca) vs. Cu/(Si+Ca) diagram (Fig. 2). This diagram is based on the compositional characteristics of magnetite in VMS that typically has high Zn, Ca and Si, and low Al. Magnetite from the unusual massive magnetite alteration zone at the Ansil deposit plots outside the VMS field (Fig. 2).

The Ti and V content are related to the deposit type, such that the sum of Ti+V is useful to discriminate between deposit

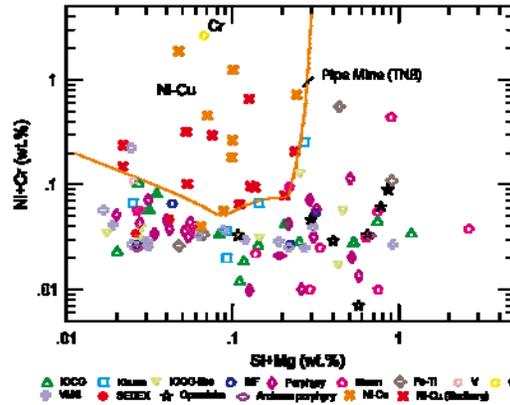


Fig. 1. Discriminant diagram to identify Ni-Cu massive sulfides and Cr deposits. The average composition for a deposit is shown.

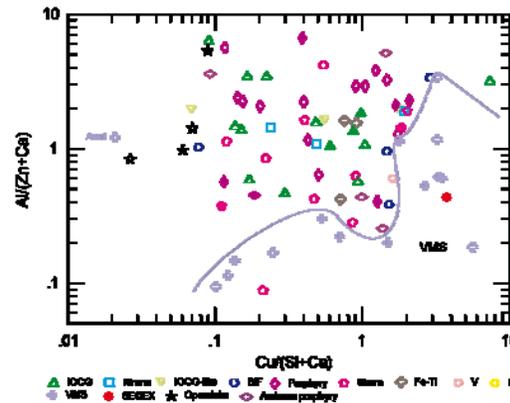


Fig. 2. Discriminant diagram to identify VMS deposits. The average composition for a deposit is shown. Ni-Cu massive sulfide deposits are not shown on this diagram.

types, in combination with Ni/(Cr+Mn) (Fig. 3). To avoid clutter, Ni-Cu-PGE deposits, identified using the Ni+Cr vs. Si+Mg diagram (Fig. 1) are not plotted because the Ni/(Cr+Mn) vs. Ti+V diagram does not discriminate for these deposits.

In the Ni/(Cr+Mn) vs. Ti+V diagram (Fig. 3), fields for IOCG, Kiruna, Cu-Mo-Au porphyry, V and Fe-Ti deposits are well defined. Hostrock magnetite from IOCG and porphyry deposits plot outside the respective fields for mineralization (Fig. 3). The Routivare deposit plots outside the field for Kiruna-type deposits. Several VMS deposits plot within the IOCG field, but VMS deposits are uniquely identified using the Al/(Zn+Ca) vs. Cu/(Si+Ca) diagram (Fig. 2). One Opemiska Cu-Au

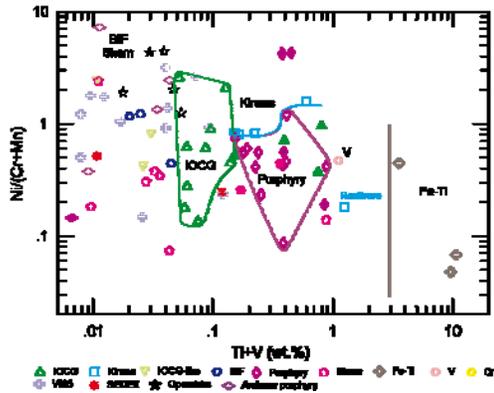


Fig. 3. Discriminant diagram to identify Fe-Ti, porphyry Cu-Mo-Au, Kiruna, and IOCG deposits. Filled symbols are for magnetite from hostrocks. The average composition for a deposit is shown. Ni-Cu massive sulfide deposits are not shown on this diagram.

vein plots within the IOCG field. Skarn display no characteristic compositional signature in the Ni/(Cr+Mn) vs. Ti+V diagram, but can be discriminated using a Ca vs. Ti+V diagram (not shown).

CASE STUDY: GLACIAL TILLS FROM THOMPSON

The Thompson Nickel Belt (TNB), Manitoba, Canada, is host to world class magmatic massive sulfide Ni-Cu-PGE deposits. The deposits subcrop beneath 2 to 30 m of glacial sediments and have been eroded by glaciers flowing SW and then W during the Wisconsin glaciation.

We report, here, results for three till samples from a large regional study (McClenaghan *et al.* 2009): 1) 05-MPB-08, from the south shoulder of the Thompson Mine South pit, contains abundant pentlandite and chalcopyrite; 2) 06-MPB-58, from a location 600 m west and down-ice (W) of the main ore zone at the Pipe Mine, contains sperrylite; 3) 06-MPB-61, from the west shoulder of the Pipe Mine open pit, 200 m W (down-ice) of the ore zone, contains sperrylite.

Magnetite and hematite grains from the ferromagnetic fraction of till samples 05-MPB-08, 06-MPB-58 and 06-MPB-61 were randomly selected by ODM. A total of 22 grains from sample 05-MPB-08, 69

grains from 06-MPB-58 and 110 grains from 06-MPB-61 were selected for analysis. To test the heterogeneity of the heavy mineral concentrates, five sub-samples of the 0.5-1.0 mm size fraction of till sample 06-MPB-58 and 06-MPB-61, labeled, each, A to E, were aliquoted using a plastic riffle and prepared for microprobe analysis (from 33 to 82 grains for each subsample).

The composition of magnetite and hematite selected by ODM from the three till samples is shown in Fig. 4. Although the composition of only one grain from sample 05-MPB-08 plots within the field of Ni-Cu deposits, the average composition of iron oxides from this sample plots within the field for Ni-Cu deposits. Four grains from sample 06-MBP-58 plot within the field for Ni-Cu deposits but the average composition for this sample plots outside the Ni-Cu deposits field (Fig. 4). Several grains and the average composition of sample 06-MPB-61 plot within the field of

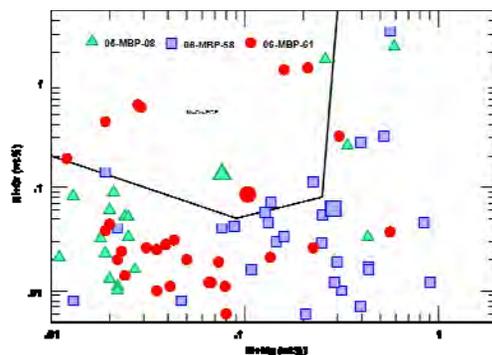


Fig. 4. Composition of magnetite and hematite grains from the till samples prepared by ODM. Larger symbol is the average composition for all analyses for each sample.

Ni-Cu deposits (Fig. 4).

These results are confirmed by comparison of five sub-samples from 06-MBP-58 and 06-MPB-61 (Fig. 5). A small proportion of each sub-sample of 06-MPB-58 plots within the Ni-Cu deposits field whereas the average of all sub-samples plots outside the Ni-Cu deposits field (Fig. 5A). Similarly, a number of grains and the average composition of each sub-samples from 06-MPB-61 plot within the field for Ni-Cu deposits (Fig. 5B).

DISCUSSION AND CONCLUSION

The chemical composition of iron oxides is useful to discriminate a range of mineral deposit types. Discriminant diagrams can be used to identify potential for specific mineral deposit types to occur in an area that has been glacially eroded using till. In this study, a small subset of the ferromagnetic fraction (50 grains, 0.5-1.0 mm size fraction) of a till has been shown to adequately display the compositional

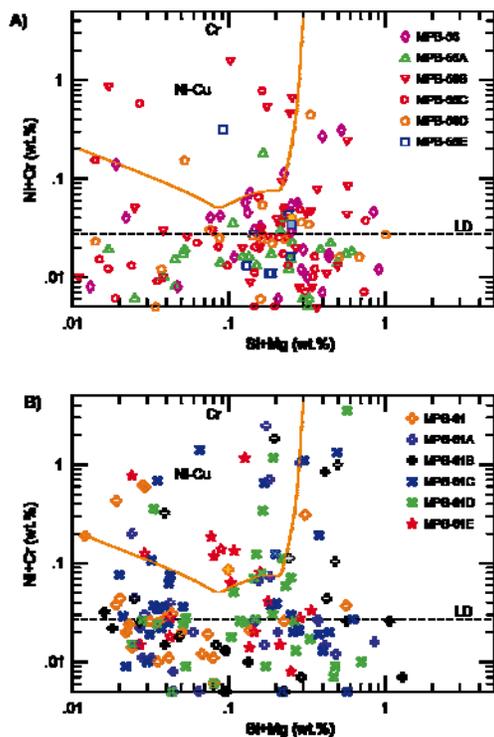


Fig. 5. Composition of 5 sub-samples from A) 06-MPB-58 and B) 06-MPB-61. Filled symbol is the average composition. The horizontal line LD shows the value for the combined detection limits of Ni+Cr, such that analyses that plot beneath this line are not significant.

range of iron oxides from that sample.

The TNB case study shows that iron oxides from till samples down-ice from Ni-Cu massive sulfides have a similar chemical signature to that in magmatic Ni-Cu deposits. Further testing of additional till samples from varying distances down-ice of the TNB would provide further insights into the TNB Ni-Cu deposit signatures and glacial transport distances.

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We thank the DIVEX research network and the Geological Survey of Canada for their continued support for this research.

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Indicator mineral signature of the Halfmile Lake Zn-Pb-Cu volcanogenic massive sulphide deposit, New Brunswick, Canada

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ABSTRACT: Till and bedrock were sampled around the Halfmile Lake Zn-Pb-Cu volcanogenic massive sulphide (VMS) deposit, Bathurst Mining Camp as part of the Geological Survey of Canada's Deep search Targeted Geoscience Initiative-3. The purpose of this study is to document the till indicator mineral and geochemical signature of a VMS deposit. The deposit is hosted by the volcano-sedimentary sequence of the Ordovician Tetagouche Group. Epiclastic rocks, felsic pyroclastic rocks, crystal-rich felsic tuffs, quartz-feldspar porphyritic intrusions, intermediate and basic dikes, sulphides, and gossan are the main rock types found surrounding the Halfmile Lake deposit. A thin (<2 m) layer of silty sand, locally derived subglacial till covers most of the deposit area. The till contains 20-40% pebble to cobble sized clasts that are angular-subangular in shape. A preliminary set of indicator minerals identified in mineralized bedrocks include: chalcopyrite, pyrite, galena, sphalerite, ferro- and nonferromagnetic pyrrhotite, ilmenite, goethite, and beudantite. Indicator minerals identified in till include: chalcopyrite, pyrite, native gold, goethite, jarosite, and beudantite.

KEYWORDS: *indicator minerals, till geochemistry, VMS deposit, mineralogy, heavy mineral concentrate*

INTRODUCTION

The recovery of indicator minerals from till has become an important exploration method in glaciated terrain in the past 30 years and now include suites for detecting a variety of ore deposit types including diamonds, gold, Ni-Cu-PGE, porphyry Cu, massive sulphide and tungsten deposits (McClenaghan 2007). Indicator minerals are important as an exploration tool because their dispersal in surficial sediments may provide an exploration target much larger than the mineralized zone.

Till geochemistry and boulder tracing are well established exploration methods in Canada for base metals (McClenaghan 2007) however, there has been limited research on minerals that are effective in exploring for VMS deposits in glaciated terrain. To address this knowledge gap, the Geological Survey of Canada (GSC) has undertaken a study to document the indicator mineral and till geochemical

signature of the Halfmile Lake Zn-Pb-Cu VMS deposit.

Till and bedrock were sampled in 2007 around the Halfmile Lake Zn-Pb-Cu volcanogenic massive sulphide (VMS) deposit, Bathurst Mining Camp, New Brunswick (Fig. 1) as part of the Geological Survey of Canada's Deep search project, Targeted Geoscience Initiative-3 (2005-2010). This project is a collaborative effort between the Geological Survey of Canada, the New Brunswick Department of Natural Resources and Queen's University.

GEOLOGICAL SETTING

Bedrock Geology

The Halfmile Lake deposit consists of massive, breccia, and stockwork Zn-Pb-Cu sulfide mineralization hosted by volcanic and sedimentary rocks of the Ordovician Tetagouche Group (Mireku & Stanley 2006; Adair 1992). The main sulphide minerals in the deposit are

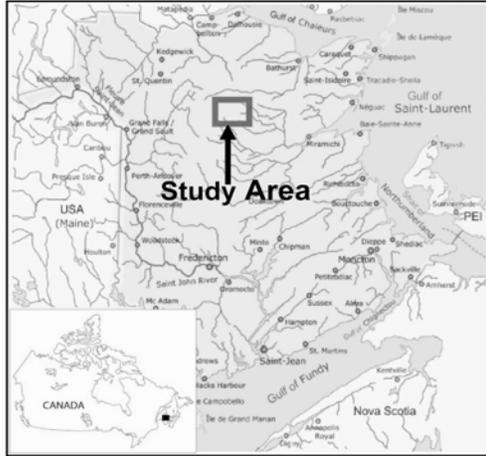


Fig. 1. Location of the study area in eastern Canada.

sphalerite, galena, chalcopyrite, pyrrhotite and pyrite (Adair 1992). Subcropping preglacial (Pliocene) gossan is preserved over parts of the deposit (Boyle 2003). Epiclastic rocks, interbedded fine-grained felsic pyroclastic rocks, crystal-rich felsic tuffs, quartz-feldspar porphyritic intrusions and intermediate and basic dikes are the main rock types hosting the Halfmile Lake deposit (McCutcheon & Walker 2001).

Surficial Geology

A thin (<2 m) layer of silty sand, grayish-yellow to yellowish-brown, locally derived subglacial till covers most of the deposit area. It is found on the lee sides of hills, usually in valleys, and may be Early Wisconsinan to pre-Late Wisconsinan in age (Parkhill & Doiron 2003). The till contains 20-40% pebble-cobble sized clasts that are angular-subangular in shape. Ice-flow indicators together with till fabric analyses, till clast provenance studies, till geochemistry, and the distribution of boulder erratics indicate that the dominant ice flow direction associated with this surface till was to the east (070°–110°) (Parkhill & Doiron 2003).

METHODS

Sampling

Forty eight bedrock (5 kg) samples were collected of ore and host rocks from surface outcrops and drill holes. Fifty six,

25 kg till samples were collected up-ice (west), overlying and up to 2 km down-ice (east) of the Halfmile Lake deposit from existing exploration trenches, hand dug holes and new backhoe trenches. Till samples were collected from the C-soil horizon or B-C-horizon.

Sample Preparation and Analysis

Bedrock and till samples were processed at Overburden Drilling Management Ltd. (ODM) in Ottawa to produce heavy mineral concentrates. Bedrock samples were milled to <2.0 mm and the <2.0 mm material was passed over a shaking table. The heavy mineral fraction was then further refined using heavy liquid separation in methylene iodide diluted to a specific gravity of 3.20. The resulting heavy mineral fraction was separated into a ferromagnetic and nonferromagnetic fraction. The non-ferromagnetic fraction was sieved into four size fractions: 0.18-0.25, 0.25-0.5, 0.5-1.0, 1.0-2.0 mm. The 0.25-0.5 mm fraction was further separated into <0.6, 0.6-0.8, 0.8-1.0, and >1.0 amps based on the paramagnetic properties of minerals to assist picking this very fine grained fraction. The 0.25-0.5, 0.5-1.0, 1.0-2.0 mm fractions were then examined for indicator minerals. Till samples underwent a similar sample processing procedure as the bedrock samples except that a larger weight was processed. Mineralized bedrock samples and all till heavy concentrates were micropanned to recover gold and sulphide minerals in the <0.25 mm fraction. Selected indicator mineral grains will be picked from bedrock and till samples to be photographed and analyzed by SEM, electron microprobe and laser ablation ICP-MS techniques.

Bedrock samples were analyzed at Actlabs using four acid digestion ICP-MS to determine major, minor and trace element concentrations.

The <0.063 mm fraction of till was analyzed by aqua regia and lithium metaborate fusion-nitric acid digestions ICP/ES and MS.

RESULTS

Mineral Identification in PTS

Several minerals have been identified in polished thin sections of various rock types including massive sulphide, gossan, intermediate crystal-lapilli tuff, and felsic ash tuff (Fig. 2). These minerals include: apatite, monazite, zircon, allanite, titanite, xenotime, magnetite, cassiterite, cobaltite-gersdorffite, rutile, ilmenite, goethite, sphalerite, galena, arsenopyrite, chalcopyrite, pyrite, and pyrrhotite. These minerals range in size from 20 µm to 250 µm and represent potential indicator minerals.

Bedrock Indicator Minerals

Sulphide minerals were recovered only in the 0.25-0.5 mm fraction because of their fine-grained nature in the bedrock. A preliminary set of indicator minerals include:

- 1) unweathered ore:
chalcopyrite, pyrite, galena, sphalerite, ferromagnetic and nonferromagnetic pyrrhotite, magnetite, ilmenite, goethite and beudantite;
- 2) gossan:
pyrite, galena, sphalerite, goethite, and beudantite; and
- 3) altered and mineralized host rocks:
chalcopyrite, pyrite, sphalerite, ferromagnetic and nonferromagnetic pyrrhotite, ilmenite, and goethite.

Till Indicator Minerals

A preliminary set of indicators identified in till immediately down-ice of the deposit and gossan include: chalcopyrite, pyrite, gold, goethite, jarosite and beudantite. Heavy mineral grain abundances

decrease down-ice (east) of the Halfmile Lake deposit (Fig. 3).

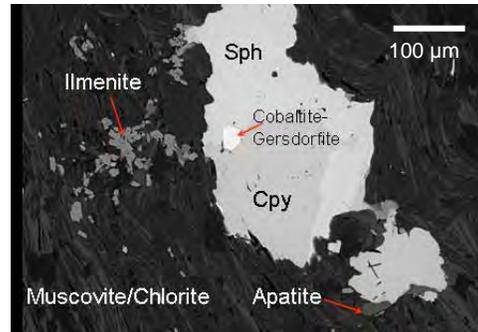


Fig. 2. SEM image of several minerals identified in PTS in a felsic volcanic rock.

IMPLICATIONS FOR EXPLORATION

The outcomes of this study are:

- a set of indicator minerals of a VMS deposit,
- till contains indicator minerals up to 750 m down-ice, and
- heavy mineral sampling methods are suitable in the Bathurst Mining Camp, especially areas covered by thick till.

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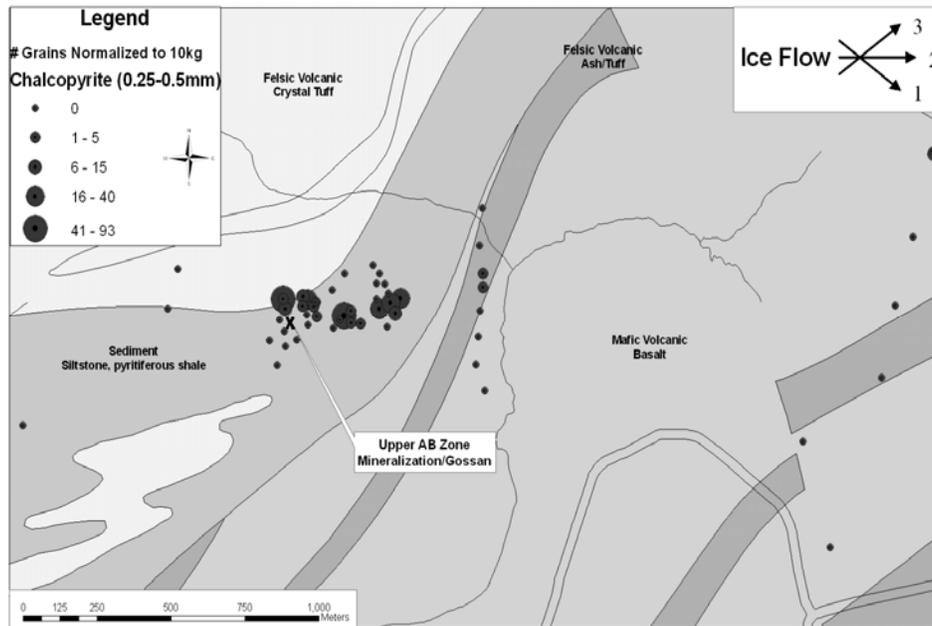


Fig. 3. Distribution of chalcopyrite grains in 0.25-0.50 mm fraction of till samples normalized to 10 kg sample weight. Bedrock geology from van Staal et al. 2003.

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Surface geochemical anomalies in northern Chile: product of the extended metallogenesis of buried copper deposits

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ABSTRACT: Work starting in 1999 showed saline-metal anomalies at the surface above copper deposits buried deeply beneath piedmont gravels. These were identified as a product of saline basement waters rising along fracture zones during earthquakes. A visit to the Radomiro Tomic copper mine, also in 1999, suggested that anomalies were a surface expression of a larger process where pulses of fluid expelled by dewatering of the forearc basin moved through deposits replacing some primary supergene minerals with atacamite, a copper oxychloride. This proposal proved controversial, since atacamite was considered a primary oxide. Recent work, mainly at the University of Chile, has shown: (a) salinities of fluid inclusions in atacamite are the same as local saline groundwater; (b) ³⁶Cl data indicate that atacamite could not have formed earlier than 1.5 Ma, contrasting with alunite dates showing primary supergene oxidation extended over the period 44 to 9 Ma; (c) U-Th dating of gypsum-atacamite intergrowths give Pleistocene ages of 237 ka for Chuquicamata, 127 ka for Spence and as low as 75 ka for other deposits. These recent ages for saline metasomatism of deposits and, by inference, for surface anomalies, show why anomalies can be readily recognized by soil surveys, rather than having been removed over time by erosion.

KEYWORDS: Chile, copper, atacamite, anomalies, Pleistocene

INTRODUCTION

Studies beginning in 1999 in the Atacama Desert identified saline-metal anomalies above copper deposits buried beneath thick piedmont gravel cover (Cameron *et al.* 2002, 2005). Anomalies formed as a result of basement fluids rising along fracture zones that cut the deposits and gravels. From the beginning it was apparent that more was involved in the process than simply the formation of anomalies. A visit to the Radomiro Tomic mine in 1999 suggested that the same saline fluids that had created the surface anomalies had substantially modified the initial supergene assemblage, including the formation of atacamite, a mineral that accounts for a substantial amount of the copper production of northern Chile.

THE ATACAMITE STORY

Supergene enrichment played a critical role in making northern Chile the world's prime copper-producing province. For copper porphyry deposits in the central

Atacama Desert supergene enrichment extended from 44 to 9 Ma, reaching a maximum at 21 to 14 Ma (Arancibia *et al.* 2006). Supergene oxidation required significant rainfall, and was terminated by the onset of hyper-aridity. The visit to the Radomiro Tomic open pit in 1999 showed a basement hill of supergene ore covered by piedmont gravels. The principal ore mineral at Radomiro Tomic is atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$, found in many of the deposits of the region (Fig. 1). Both specifically for this deposit and for the region, atacamite was considered a primary product of supergene oxidation. But this was not possible given the geological relationships displayed in the pit. Atacamite is readily soluble in meteoric water (Woods & Garrels 1986) and would have been removed by the rainfall that accompanies supergene alteration and/or by stream waters that carried the gravels that bury the hill of ore. At this deposit, atacamite could not have formed prior to the

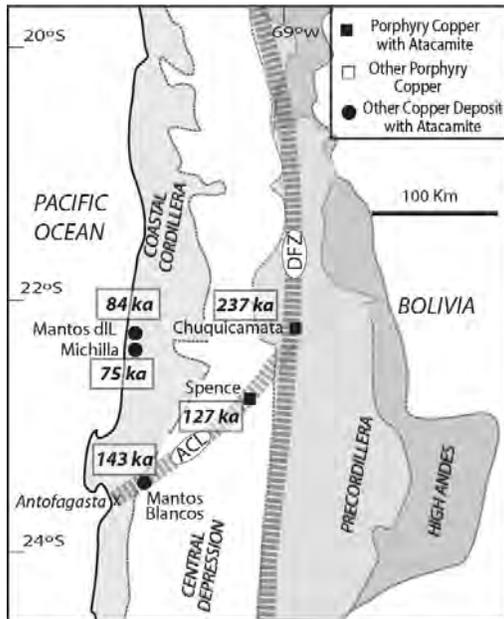


Fig. 1. Distribution of copper deposits in northern Chile including those containing atacamite in the oxide zone. DFZ is the Domeyko Fault Zone and ACL is Antofagasta–Calama Lineament. The land between the High Andes and the coast is the hyper-arid central Atacama Desert.

deposition of the gravels at c. 10 Ma. Further, atacamite-bearing upper and lower oxide zones are separated, immediately below the water table, by a zone lacking atacamite. When water dripping from the pit wall was tested with a conductivity meter, it proved to be meteoric. Later analyses showed the water to be rich in copper. A slow flow of this layer of meteoric water, 'floating' on deeper saline water, has removed atacamite from this zone.

Hydrogeochemical studies at the Spence deposit, also a hill of atacamite-bearing ore covered by gravel, showed that rising saline waters have caused primary supergene minerals, such as brochantite, to be replaced by atacamite. Episodic pumping caused by earthquakes forced the waters to the surface to create the saline-metal anomalies at Spence, at Radomiro Tomic, and elsewhere.

SALINITIES OF FLUID INCLUSIONS IN ATACAMITE

If atacamite has formed in recent times by rising saline groundwater, then fluid inclusion salinities should match that of saline groundwater at the sites. For the Mantos Blancos and Spence deposits salinities of inclusions in atacamite are the same as those measured in saline groundwater sampled from drill holes (Reich *et al.* 2008). The correspondence between groundwater and inclusion salinities is made more significant by the substantial difference in salinities between the two deposits: average values in NaCl_{eq} for Mantos Blancos water is 7.6 (n = 32), inclusions 8.4 (n = 49); Spence water 2.3 (n = 13), inclusions 2.7 (n = 43). Salinities of fluid inclusions in atacamite are coincident with that for gypsum supersaturation. TEM observations show an intimate association between atacamite and gypsum at the macro to nanometer scale.

Isotopic data for $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ for the saline waters at Spence established that these are formation waters of deep origin (Cameron & Leybourne 2005; Leybourne & Cameron 2006). The deep origin of these waters is also revealed by their high iodine content. Also, soil anomalies are linked to the waters by their high iodine content; up to 1.6% water-soluble iodine above the West Fault that cuts the Mansa Mina deposit, south of Chuquicamata. Concentrations of iodine are low in seawater and freshwater, because iodine is fixed by organisms, but reaches high levels in forearc fluids. Forearc sediments are rich in organic material, from which iodine is released during deep diagenesis. The Atacama Desert is the world's largest producer of iodine from surface deposits. These were thought to be atmospheric precipitates from marine aerosols. Feyn *et al.* (2007) have shown that the radiogenic isotope ^{129}I in this iodine is too low to be of seawater origin, but is consistent with 'old' iodine derived from Jurassic and Cretaceous sediments of the forearc that underlie the Atacama Desert.

DATING ATACAMITE

Reich *et al.* (2008) measured ^{36}Cl in atacamite from Mantos Blancos, Spence and three other deposits. These show low ^{36}Cl -to-Cl ratios (11×10^{-15} to 28×10^{-15}), comparable to previously reported ratios of deep formation waters. Further, ^{36}Cl -to-Cl ratios in atacamite correlate with U and Th concentrations in host rocks. This suggests that subsurface production of fissiogenic ^{36}Cl was in secular equilibrium with waters involved in atacamite formation. Because atacamite does not contain U or Th, production of ^{36}Cl is not continued once chlorine has entered the crystal structure; from that time the ^{36}Cl -to-Cl ratio decreases with age. The fact that measurable ^{36}Cl is present indicates that atacamite formation occurred less than 1.5 Ma ago (five times half-life of ^{36}Cl).

The intimate association between gypsum and anhydrite permitted a further refinement in dating. The U-series disequilibrium method is based on the natural fractionation of U and Th isotopes that lead to the preferential precipitation in authigenic minerals of parent nuclides over insoluble daughter products. The method has been successfully applied to obtain absolute ages of minerals that precipitate from aqueous solutions (e.g., gypsum, anhydrite, and halite), in a range between <10 and 350 ka. Only primary gypsum associated with atacamite in veins and veinlets, with no evidence of recrystallization or dissolution, was measured using the isochron approach of Luo & Ku (1991) that corrects for initial ^{230}Th contamination. Samples from five deposits all show Pleistocene ages, with Chuquicamata being the oldest, 237 ± 8 ka. Younger ages are obtained for Mantos Blancos, 143 ± 29 ka; Spence, 127 ± 29 ka; Mantos de la Luna; 84 ± 11 ka; and Michilla, 75 ± 0.4 ka. Chuquicamata and Spence are copper porphyry deposits, the others are stratiform copper deposits of the Coastal Cordillera (Fig. 1).

CONCLUSIONS

The metallogenic evolution of the copper porphyry deposits of the Atacama Desert included a long phase of supergene

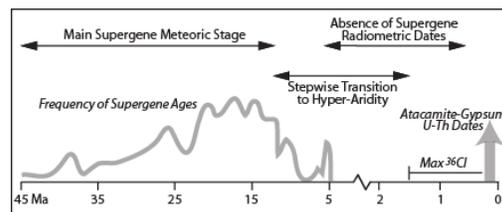


Fig. 2. Geochronology of supergene processes for copper deposits in northern Chile (modified from Reich *et al.* 2009).

enrichment extending from Eocene to Miocene time (Fig. 2). After several million years, many of these deposits experienced a second stage, during the Pleistocene, where saline forearc waters converted part of the initial oxide assemblage to atacamite, an important ore mineral. The second stage also involved stratiform copper deposits in the Coastal Cordillera. We infer that the formation of the saline-metal anomalies at the gravel surfaces above the deposits was synchronous with the rise of saline forearc fluids through the deposits, modifying the original supergene oxide assemblage to one containing atacamite. Near Mantos Blancos, Palacios *et al.* (2005) found a link between atacamite formation and surface anomalies. Green coloured salt efflorescence containing atacamite and chalcantite occur along the surface trace of major faults that cut deeply buried copper mineralization. A Pleistocene age helps explain why the anomalies can be readily recognized during soil surveys. Anomalies formed at an earlier time might have been removed or redistributed by surface erosion or rainfall. Indeed, climate played a critical role in the evolution of the deposits, the anomalies being part of their metallogeny. Rainfall in an arid to semi-arid climate during the first stage made possible supergene enrichment. Hyper-aridity during the second stage ensured the preservation of saline-metal anomalies and atacamite; with rainfall sufficient to cause recharge of meteoric water through gravels to the oxide zones, atacamite would have been dissolved. The Pleistocene age for the northern Chile anomalies provides a link with anomalies

above the Mike gold-copper deposit, Nevada. This deposit is covered by a thick sequence of Carlin Formation. Metal anomalies are located on the surface trace of a Pleistocene age fault that cuts both the deposit and the cover rocks (Cameron *et al.* 2005).

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Geochemistry of Archean sulfidic black shale horizons: combining data at multiple scales for improved targeting in VMS exploration

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ABSTRACT: Metalliferous black shales are a common but minor component of many subaqueous volcanic successions. These shales are commonly drilled during volcanogenic massive sulfide (VMS) deposit exploration programs. Although ore metal enrichment can be determined by conventional assay methods, matrix dilution and post-burial hydrothermal and metamorphic processes may obscure information on the type and mechanism of metal addition to the shale. We used a combination of geochemical methods at a variety of scales to discriminate between VMS-prospective and VMS-barren horizons. In addition, element signatures associated with hydrothermal plume fallout were identified and used to determine relative direction to the palaeo-venting centre. Portable x-ray fluorescence (pXRF) analysers were used to identify and correlate prospective mineralized horizons within exploration drill cores. pXRF is a rapid and relatively inexpensive method of analysis that can deliver quantitative geochemical information at a cm-scale and help to identify intervals meriting further, more costly and time-consuming analyses. Subsequently, laser-ablation ICP-MS analysis of metal sulfides was used to constrain hydrothermal, hydrogenous and diagenetic end-member compositions, and to quantify element remobilization during post-burial alteration. These data were then used to refine the pXRF survey methodology and develop primary vectors toward potential concealed VMS deposits.

KEYWORDS: *black shale, VMS, exploration vectoring, LA-ICP-MS, portable XRF*

INTRODUCTION

Metalliferous sediments are a common component of modern ocean-floor sedimentary sequences, recording halos of metal dispersion from seafloor hydrothermal vent systems (Gurvich, 2006). Sulfidic black shales are also commonly present as intercalations in ancient subaqueous volcanic sequences, where each likely represents a significant hiatus in volcanic activity and deposition. These shale horizons form geophysical anomalies (conductors) that are routinely drilled during exploration for volcanogenic massive sulfide (VMS) base metal deposits.

Some horizons are enriched in ore metals and associated elements (e.g. Zn, Cu, Ag, Cd, Sn), whereas others are barren. However, element distributions in such rocks are commonly extremely

heterogeneous and identification of enriched horizons is therefore largely dependent on the assay interval selected. Identification of structurally repeated horizons and correlation of individual shale horizons between drill holes is commonly problematic. Even where horizons can be correlated, the variable dilution of hydrothermal signatures by terrigenous and hydrogenous shale matrix minerals hinders interpretation of metal sources, especially where drilling coverage is limited or element-enrichment is subtle. In addition, later hydrothermal and metamorphic redistribution may have modified any primary exhalative enrichment patterns.

The objectives of our study are to provide an accurate, precise, robust and cost effective framework within which sedimentary horizons can be assessed to

provide evidence of: a) the presence or absence of hydrothermal metal input; b) the type of hydrothermal activity recorded within, and prospectivity of, any one horizon; and c) the direction, along strike and down dip extent, and relative distance to the coeval venting centre (where a single horizon has been intersected more than once). This was achieved by the combination of geochemical analytical methods including: conventional whole-rock analysis, laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and portable x-ray fluorescence (pXRF) analysers; each optimised for different spatial resolution, and with varying cost and sensitivity characteristics.

GEOLOGY AND MINERALOGY

Metalliferous sedimentary rock horizons occur as intercalated units between volcanic rocks of the 2.7 Ga Kidd-Munro assemblage (KMA) of the Abitibi sub-province, Canada (Hannington *et al.*, 1999). The shale horizons are widely distributed within the KMA and commonly occur as carbonaceous (graphitic) and/or sulfidic argillaceous shale units. Multiple horizons may be present in any one drillcore, representing both primary depositional stratigraphy and subsequent fold repetition.

Pyrite and pyrrhotite are the dominant sulfides in the shale horizons, with minor sphalerite, galena and chalcopyrite. Iron sulfides occur in six distinct textural habits: *Py1*, pyrite-rich laminae and framboids (sub-mm to 1 cm; primary chemical sedimentary); *Py2*, recrystallized and remobilized laminae and disseminations (early diagenetic); *Py3*, crustiform bands displaying growth textures and banding, commonly much disrupted (0.3 to 2 cm; early to late diagenetic); *Py4*, nodules displaying no internal fabric, and concretions displaying concentric zonation (0.5 to 4 cm; early to late diagenetic); *Py5*, metamorphic porphyroblasts, overgrowths and pressure shadows (0.2 to 3 cm; peak to post-peak metamorphic). Finally, *Py1* to *Py4* have been subject to variable late-stage alteration and replacement by secondary pyrrhotite.

GEOCHEMICAL ANALYSIS METHODS

Whole-rock geochemistry

The metal budget of any individual shale horizon reflects a variable admixture of materials with a number of end member compositions. Even where the sulfide component of a sample is >10%, conventional discrimination plots used to identify and quantify hydrothermal input such as Co/Ni ratio (e.g., Meyer *et al.*, 1990) or rare earth element plots (e.g., Johannesson *et al.*, 2006) are hindered in their application due to dilution by the non-sulfide silicate detrital minerals.

Principal component analysis (PCA) of bulk sample geochemical data has been used to identify element associations that reflect major source contributions. Plotting first and second principal components of whole rock geochemical data has identified three dominant element groupings: 1) hydrothermal – Ag, As, Bi, Cd, Cu, Hg, In, Mo, Ni, Pb, Sn, Te, Zn; 2) hydrogenous – Au, Ca, Cr, Mn, Pt, Sb, Sc, Ti, V; and 3) terrigenous – Al, Ba, Be, Ce, Cs, Dy, Er, Eu, F, Ga, Gd, Hf, Ho, La, Lu, Mg, Nb, Nd, Pr, Rb, Sm, Sr, Ta, Tb, Th, Tm, U, Y, Yb, Zr. Iron and S do not have eigenvalues consistent with the major PCA groupings, and their eigenvalues in the second principal component suggest that their abundance may in fact be due to water column, rather than hydrothermal, processes. Hence, absolute pyrite and pyrrhotite abundance are poor indicators of hydrothermal input to black shales.

Laser-ablation ICP-MS

In-situ LA-ICP-MS trace element analysis of Fe-sulfides of various textural types was used to investigate inter-element correlations and sulfide end-member compositions. Trace elements of putative hydrothermal origin showing significant enrichment in pyrite include Ag, Au, As, Bi, Cu, Pb, Sb, Sn, Ti and Zn, whereas Co, Ni, Mo, Se, Pt and Te enrichments are presumed to have a hydrogenous origin. Comparison of these element groupings with those determined from bulk chemical analyses highlights further the complex nature of element distributions and associations within the sulfide component

of the KMA black shale horizons. In general, the early, visibly included pyrite forms (Py1 to Py3) have the greatest trace element contents, and later, inclusion-free metamorphic pyrite (Py5 and pseudomorph pyrrhotite) contains the lowest trace element abundances.

A complication of the LA-ICP-MS technique is that few elements substitute stoichiometrically into the pyrite crystal lattice. Arsenic, Co and Ni demonstrate stoichiometric lattice substitutions, but many others are more commonly incorporated as non-stoichiometric substitutions, and as microinclusions of other sulfide minerals within pyrite (Deer *et al.*, 1992). Recrystallization, annealing and metamorphism will further exclude these trace elements from the pyrite structure (Large *et al.*, 2007). This is clearly seen in the variable transient signals of different elements during the laser ablation process. In a single ablation, elements such as As, Co, Ni and Sb commonly show distinct covariance with Fe, indicative of substitution within the pyrite lattice; however, elements such as Zn, Cd and Ag display sharp spikes in the transient LA-ICP-MS profile, indicative of their presence within sulfide microinclusions or as non-stoichiometric substitution within the pyrite. Other elements such as Cu, Pb and Bi show a mixed transient signal, most likely reflecting zonation within the pyrite grains. At present, it is not known if these elements are hosted within the pyrite, or whether minerals that host these elements form extremely fine dispersions that are not resolvable by the laser technique (~30 microns).

Portable XRF

Although not yet routine, the use of pXRF analysers both for rock outcrop and core elemental determinations is already showing much promise. Their analysis window is approximately 1 cm in diameter, such that pXRF instruments offer a compromise between the spatial resolution offered by micro-analytical techniques such as LA-ICP-MS, and the

bulk sample integration of traditional chemical analysis methods.

It is apparent from our pXRF analyses that at the scale of the analytical window, there are regular, reproducible, variations in element enrichments between sulfide accumulations (nodules, concretions, crusts) and shale matrix. Some of the largest base metal and associated element contents measured in the field (e.g. Zn ≈ 1.4 wt%; Cu ≈ 600 ppm; Mn ≈ 1 wt%; Cd ≈ 90 ppm; Hg ≈ 50 ppm) are in apparently (to the naked eye) sulfide-free shale. The majority of such enrichments appear to be due to the incorporation of disseminated, very fine-grained, Fe-rich sphalerite. In many instances this is not evident even when using a hand lens, and care must be taken not to overlook these cryptic enrichments.

Pyrite commonly displays distinctly different trace element abundances than the host shale matrix. Figure 1 demonstrates that elemental abundances can vary significantly even between adjacent sulfide masses. Element exclusion is greatest where the associated pyrite is strongly recrystallized or is of metamorphic origin, with “dirty” concretions and crustiform material showing the least deviation from matrix abundances.

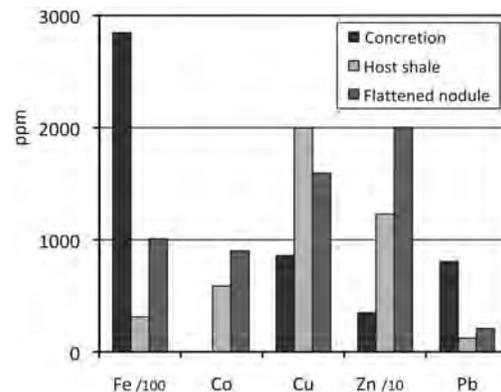


Fig. 1. Selected portable XRF element analyses for two pyrite masses and their shale host. The two masses, both ~2 cm in diameter, are within 5 cm of one another but display different trace element contents, both from one another and from their silicate host. The shale matrix analysis is taken between the two.

CONCLUSIONS

Hydrothermal geochemical signatures are recognized by the use of traditional whole-rock geochemical analyses. However, their intensity can vary greatly over narrow intervals; furthermore, they are difficult to quantify and are subject to significant sampling bias. These signatures are a result of elements being hosted in multiple mineral phases within a single horizon. In order to more effectively and efficiently rank areas meriting additional work in VMS exploration, it is essential to understand the sources, distribution, and mineralogical and paragenetic association of geochemical signatures observed in shale horizons.

Various analytical methodologies have been assessed with respect to better constraining geochemical anomalies. Traditional whole-rock methods can integrate signals from a wide core interval, but are relatively expensive (\$50+ per sample) and time-consuming. Laser-ablation ICP-MS analysis is a powerful tool for deconvolving sulfide chemistry and paragenesis, however, sample size is limited (making the technique prone to sampling bias), analysis costs are high, and lag times on data feedback are long. Portable XRF analysis is non-destructive and provides cost-effective and essentially instantaneous information on sample composition and can be performed on site, during a drill program, and so used to refine exploration targeting on the fly. Combination of the three approaches provides a comprehensive and powerful investigative methodology for elucidating element signatures in shale horizons, and opens the way for potential development of exploration vectoring protocols for application during routine core analysis.

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An investigation of partial extractions designed to solubilize Pb and Zn from soils using a complexation desorption mechanism

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Abstract: Soil samples collected across the till-covered Northeast Zone of the Gay's River carbonate-hosted massive sulfide Zn-Pb deposit, Stewiacke, Nova Scotia, were analysed for metal concentrations using several partial leaches. This experiment was designed to determine the optimal reagent that solubilizes metals via a 'complexation desorption' mechanism, whereby ligands producing strong complexes 'encourage' desorption of metals from mineral(oid) surfaces. Several salinities of K-halide solutions were tested. Exploration accuracy and geochemical contrast were determined for each digestion using minimum hypergeometric probability and Student's t-test probability procedures. Pre- and post-digestion pH-pE conditions of soil samples illustrate that ambient pore water pH and pE conditions are strongly controlled by an Fe⁺²-Fe(OH)₃ buffer, and indicate that this buffer remains important even during digestion. Overall, partial digestion results were unsuccessful and did not accurately produce anomalous samples over 'anomalous sites', with high geochemical contrast. Nevertheless, the relative performances of the digestions can be related to the reagent behaviours and Pb- and Zn-complex stability constants. As a result, it is likely that the distribution of adsorbed Zn and Pb in soils at Gay's River does not have a geometry that conforms to an ideal vertical or up-dip element dispersion model.

Keywords: *partial digestion, complexation, desorption, geochemical exploration, MHP, MTP, pH, pE, digestion monitoring.*

INTRODUCTION

In many places on earth, mining companies have already discovered (mostly in the last 50 years) the majority of mineral deposits exposed at the surface. As a result, mineral deposits that have not been discovered are typically buried by some form of surficial material, such as gravel, till or volcanic ash. This exotic cover makes exploration for most buried mineral deposits expensive and difficult, because the chemistry of this overlying material is different from that in the mineral deposits or its host rocks.

Fortunately, ground waters dissolve and transport metals from mineral deposits at depth to the surface, where the metals adsorb onto the surfaces of organic matter and Fe- and Mn-oxy-hydroxide particles in the soil. Unfortunately, the adsorption of these ions contributes only a small amount of additional metal to the soil, resulting in marginally anomalous

concentrations of elements above mineralized zones.

Partial digestions can be used to specifically extract the labile component of an element concentration in a soil. Loosely bound metals can be solubilized using a leach that is not strong enough to dissolve mineral(oid) substrates or to solubilize background elements hosted within soil particles. Because the background element components are not digested by these extractions, high geochemical contrast between anomalous and background samples commonly exists.

Thus, one approach to the liberation of electrostatically-bound ions from soil particle surfaces involves the use of partial leaches containing complexing ligands (such as halide salt solutions). These liberate the adsorbed metals by forming complexes, thereby out-competing the adsorption surfaces for these metals.

METHOD

Thirty-two soil samples on a N-S traverse were collected from the brunisolic B-horizon (20 cm average depth) in May, 2008 over the drill-defined Northeast Zone of the Gay's River carbonate hosted massive sulfide (CHMS) Zn-Pb deposit, Stewiacke, Nova Scotia. This mineral target is buried by up to 10 m of exotic till and c. 10 m of gypsum, and so represents an ideal location to evaluate the exploration performance levels of partial digestions designed to extract labile elements from soil particle surfaces.

Potassium halide salt solutions were used to test a soil particle desorption mechanism involving preferential metal-ligand complexation. Samples of 0.5 g were immersed in 40 ml of reagent at STP and periodically agitated for 4 hours, filtered through a 0.45- μ m filter, and then analysed by ICP-MS. Results from a range of ligands of different ionic radii (F⁻, Cl⁻, Br⁻, I⁻) and concentrations (0.01 M, 0.1 M, 1 M) were obtained. A de-ionized water leach control and a commercial aqua regia digest were used for comparative purposes.

In addition, because all of these soils contain Fe(OH)_{3(am)} [the mineraloid ferrihydroxide], both before and after digestion (based on colour), the pH of each soil and the resulting solution after digestion were measured, along with the soluble iron concentration (Fe⁺²). Using these data and the equilibrium:

$\text{Fe}^{+2}_{(aq)} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_{3(am)} + 3 \text{H}^+ + \text{e}^-$, which defines a corresponding mass action equation, the pE of the sample can be calculated:

$$\text{pE} = -3\text{pH} - \log \alpha_{\text{Fe}^{+2}} - \log K.$$

This equation allows determination of how the partial digestion affected the pH and pE of each soil sample, and determines which component, soil or reagent, most acted as a buffer during digestion.

RESULTS

A hypergeometric probability (HP) can be used to quantitatively measure the accuracy of a soil geochemistry program tested over a mineral deposit target with

known location (*i.e.* an orientation survey). This statistic, when applied to exploration samples using a specific threshold, yields the probability that the same number of anomalous samples, randomly located in space, will occur over the known anomalous sites with the same frequency as that observed in the orientation survey. The lower the HP (*e.g.* the minimum HP for any threshold; MHP), the less random the result, and the more likely that the observed anomalies are a result of non-random processes (*i.e.* the anomalous samples are not likely due to random noise, but are rather due to a true anomalous character in the soils).

The Student's t-test probability (TP) measures the geochemical contrast (essentially equivalent to precision) of an exploration method. This probability identifies the likelihood that anomalous and background concentrations, defined by a specific threshold, are derived from the same population by measuring the difference between the mean anomalous and background concentrations. The lower the TP (*e.g.* the minimum TP for any threshold; MTP), the more geochemical contrast and the more likely that random variations will not influence or change the results.

Because accuracy and geochemical contrast are both desirable traits for an exploration method, a combination of the MHP and the associated TP at the MHP-defined threshold defines the quality of the exploration method, in this case, the best ligand type and concentration of partial digestion for soils over the target CHMS deposit (Figs. 1, 2). Two different extractions for Zn and Pb have the best exploration accuracy scores (lowest MHPs) and associated acceptable geochemical contrast (TPs) at the MHP threshold.

For Zn, the most successful digestion appears to be 0.1 M KF. Unfortunately, all but two of the analyses for this digestion were at or below detection, and one above detection analysis occurs directly over the mineralized zone, resulting in an artificially low MHP. As a result, the best partial digestion for Zn is 1.0 M KF (Fig. 3),

because it has a low MHP and results are mostly sufficiently above the detection limit. In contrast, the most accurate partial digestion for Pb is 0.01 M KBr (Fig. 4).

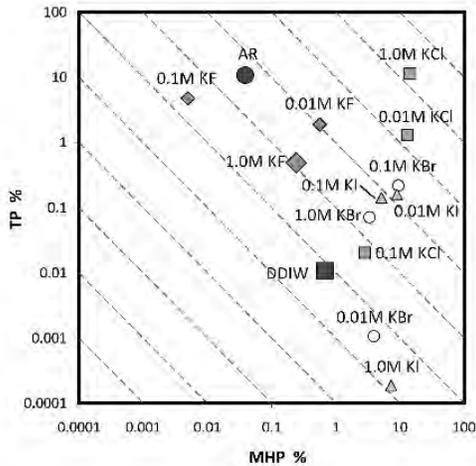


Fig. 1. Logarithmic scatterplot of MHP versus TP at the MHP threshold for Zn to identify the best partial digestion for detecting mineralization at the Gay's River CHMS Zn-Pb deposit, Nova Scotia. AR = Aqua regia; DDIW = distilled, de-ionized water.

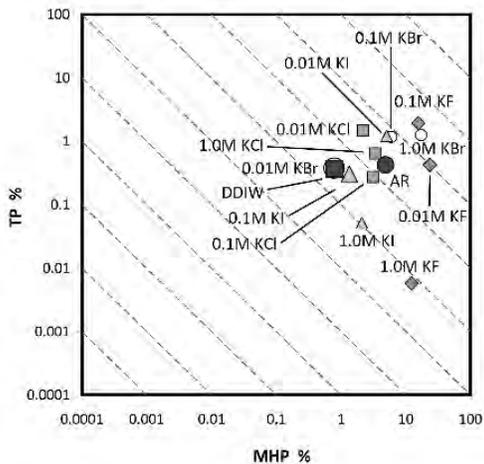


Fig. 2. Logarithmic scatterplot of MHP versus TP at the MHP threshold for Pb, analogous to Figure 1.

In the following graphs, the two best extractions for Zn and Pb are presented in traverses across the Northeast Zone at Gay's River. In these graphs, the dashed line represents the threshold that produces the lowest (most accurate) MHP for each element and digestion.

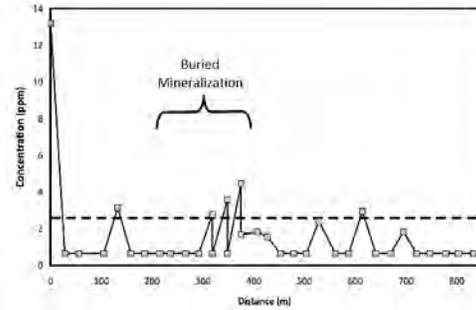


Fig. 3. A N-S soil traverse of Zn concentrations obtained using a 1.0 M KF salt solution partial extraction.

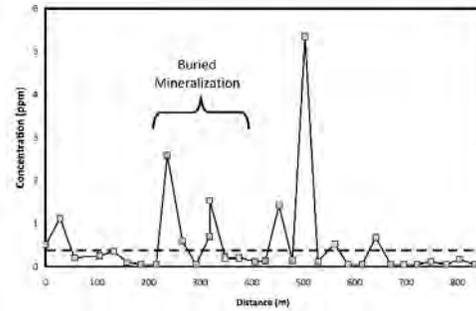


Fig. 4. A N-S soil traverse of Pb concentrations obtained via partial extraction using a 0.01M KBr salt solution.

DISCUSSION

Overall, the best geochemical accuracies for the partial extraction of Zn were obtained with KF salt solutions (MHPs = 0.56 %, 0.005 %, and 0.24 % for 0.01 M, 0.1 M, and 1.0 M KF, respectively; Fig. 1). The effectiveness of KF, over KCl, KBr, and KI, can be attributed to the higher stability constant of ZnF^+ ($\log K_{ZnF^+} = 1.15$) in comparison to the stability constants of the other Zn halides ($\log K_{ZnCl_3^-} = 0.50$, $\log K_{ZnCl^+} = -0.58$, and $\log K_{ZnI_2^0} = -1.69$).

Similarly, the best geochemical accuracies for the partial extraction of Pb were obtained with 0.01 M KBr, 0.1 M KI, and 1 M KI salt solutions (MHPs = 0.79 %, 1.3 %, and 2.1 %, respectively). The effectiveness of KI and KBr can be attributed to the relatively high stabilities of PbI_4^{-2} and $PbBr_3^-$ ($\log K_{PbI_4^{-2}} = 4.40$ and $\log K_{PbBr_3^-} = 3.00$). Although the stability of PbF_3^- ($\log K_{PbF_3^-} = 3.42$) is also relatively high, the extraction efficiency is probably affected by fluoride, which is a weak base,

resulting in a high pH that triggers formation of insoluble lead hydroxide.

A pH-pE diagram illustrating the stability fields of $\text{Fe}^{+2}_{(aq)}$, $\text{Fe}^{+3}_{(aq)}$ and $\text{Fe}(\text{OH})_{3(am)}$ is presented for the 0.01 M KF extraction in Figure 5. This describes the change in ambient pH and pE during digestion.

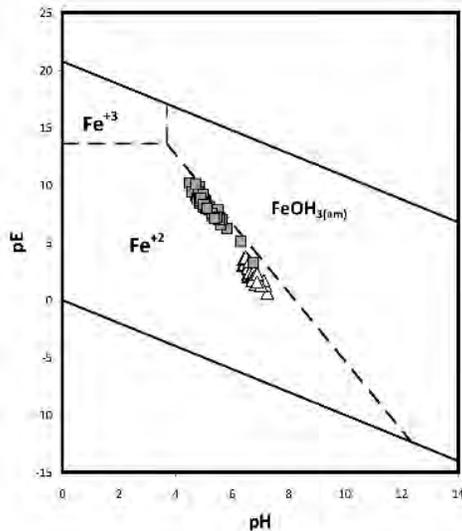


Fig. 5. A pH-pE diagram for the 0.01 M KF extraction. Grey squares represent the soil pH-pE conditions in equilibrium with distilled, de-ionized water (the ambient soil pH-pE conditions), whereas the open triangles represent the pH-pE conditions of the soil-reagent slurries after digestion.

Because most of these soils have similar soluble Fe concentrations, ambient soil sample pore water conditions plot close to a single line with slope of -3, corresponding to the Fe^{+2} - $\text{Fe}(\text{OH})_3$ stability boundary, and confirming the presence of $\text{Fe}(\text{OH})_3$ in the samples (Fig. 5). Because fluoride is a weak base, digestion with KF caused an increase in pH. In contrast, fluoride should not cause a change in pE. Nevertheless, the pE decreased during digestion, precisely because the Fe^{+2} - $\text{Fe}(\text{OH})_3$ buffer responded to the pH change imposed by the KF salt solution. As a result, both pH and pE changed significantly during digestion, pH because of the reagent, and pE because of a redox buffer in the soils.

These changes have significant effects on the solubility of metals in the KF solution. Firstly, the reduction in pE caused some reduction of $\text{Fe}(\text{OH})_3$ to Fe^{+2} , increasing the Fe concentration in the digestion and lowering the stability boundary between Fe^{+2} and $\text{Fe}(\text{OH})_3$. Secondly, the higher pHs resulted in less adsorption of Pb and Zn, and possibly the precipitation of Pb and Zn hydroxides, resulting in less Pb and Zn in solution and more concentrations below detection.

Clearly, knowledge of the redox changes and controls operating during digestion is critical in the interpretation of partial digestion results.

CONCLUSIONS

Partial extractions of KF, KCl, KBr, and KI solutions were tested over a buried CHMS Zn-Pb mineral deposit. Results indicate that these reagents were not very successful in detecting the location of mineralization, as MHPs were not low, indicating relatively random behaviour. Nevertheless, results do appear to behave in ways that suggest that these partial digestions did effectively solubilize adsorbed Pb and Zn from soil particle surfaces. This may suggest that transported ions adsorbed to soil particles above the Northeast Zone are irregularly distributed, and assumptions involving an ideal accumulation zone above or up-dip from this mineralization may not be valid for data interpretation.

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3D GIS as a support for ore vectoring

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ABSTRACT: Exploration for deep-seated mineral deposits in mature mining camps requires integration of large and heterogeneous data sets. Traditionally, geological, geochemical, and geophysical observations have typically been acquired independently and only within a restricted spatial context. Although methodological developments are still in progress, new 3D GIS technologies already provide powerful tools that can be used to integrate such heterogeneous data sets and to visualize, compare, and characterize geological relationships in a realistic environment. The present paper provides examples from the Noranda mining camp demonstrating the applicability of 3D GIS as a new tool in mineral exploration.

KEYWORDS: 3D GIS, Noranda, Horne Mine, Blake River Group, Mineral Exploration

INTRODUCTION

Mineral exploration in maturing mining camps is challenging as the likelihood of discovering new ore bodies at or close to surface diminishes over time (Fig. 1). Exploration for deep resources is accompanied by an increase in risk and exploration costs as deep targeting relies on limited data. Traditionally, exploration is conducted using one or two methods for near surface mineral detection, with a strong focus on testing geochemical or geophysical anomalies. A more sophisticated exploration strategy is required to locate hidden ore bodies, typically involving interdisciplinary data comparison and interpretation, with a strong focus on a team-based approach.

3D GIS provides a particularly useful method to address the challenges of deep mineral exploration as it permits spatial data analysis in a rigorous fashion (de Kemp 2007). Based on examples from the Noranda camp, one of Canada's most mature and economically important mining camps, the present paper highlights innovative approaches that can be

employed for deep exploration using 3D GIS.

GEOLOGICAL ENVIRONMENT

Massive sulfide exploration in the Noranda camp has traditionally focused on the delineation of intersections between favourable horizons and hydrothermal up-flow zones. In almost all cases, these up-flow zones coincide with synvolcanic structures that crosscut the local volcanic stratigraphy at high angle (Gibson & Galley 2007). Recognition of hydrothermal up-flow zones associated with massive sulfide ore bodies relies on detailed field investigations, supplemented by extensive geochemical surveys and structural, stratigraphic and volcanological analysis (Setterfield *et al.* 1995).

Recalculation of whole-rock geochemical data to normative corundum represents a particularly useful geochemical tool that can point to hydrothermal alteration zones. Normative corundum represents alkali imbalance in sub-alkaline rocks which is generally an indicator of Na depletion and K

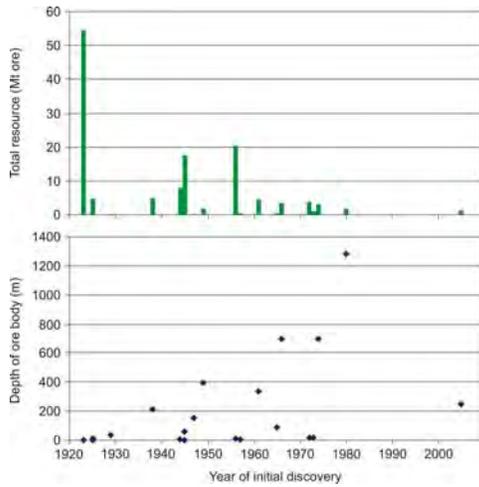


Fig. 1. Tonnage and depth diagram of historic massive sulphide discoveries in the Noranda camp (data from Gibson & Galley 2007).

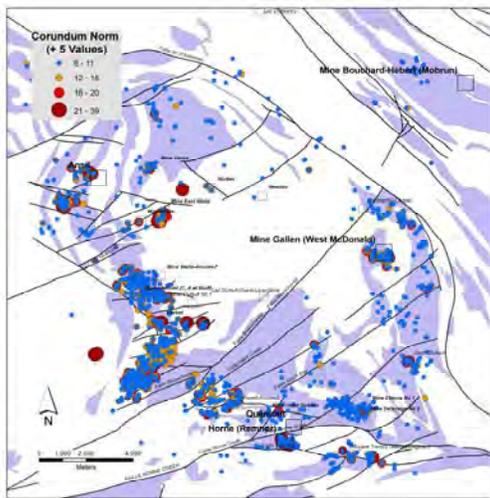


Fig. 2. Distribution of samples in the Noranda camp that are typified by >5 normative corundum values. Felsic volcanic rocks are given as shaded polygons.

enrichment (Grunsky 2007). A simple abundance and map distribution plot highlights the importance of high corundum values as a vector to mineralization (Fig. 2). However, 3D interpretation of the geological relationships has to be performed when data derived from drill holes are included in the analysis (Fig. 3). This is particularly important in the Noranda camp as there is a 40-60° easterly regional fold plunge

which can dramatically offset geochemical plots that are simply projected to surface.

3D GIS also provides the framework for placing geochemical data, lithological information, structural data, and interpreted geologic elements into one common environment (Fig. 3). Analysis of the data shows, for example, that corridors of high normative corundum values coincide with zones of dyke emplacement along early structures. Important hydrothermal up-flow zones such as the McDougall-Despina fault set (Setterfield *et al.* 1995) can be readily identified this way.

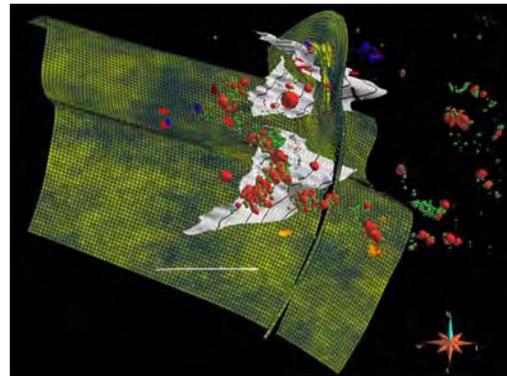


Fig. 3. 3D representation of the Noranda camp looking down plunge. The figure shows the distribution of ore bodies (orange) and a lithological simulation (green-yellow grid). The favourable horizon (white surface) is contoured at 1 km depth intervals. Variably sized spheres with >5 normative corundum values mark the location of alteration zones. Horizontal scale is 5 km at ground elevation (data from E-Sigeom, RNFQ, and Xstrata Copper).

At the scale of an individual deposit, 3D GIS can be used to visualize metal zonation patterns and their relationship to geological elements such as syn-volcanic intrusions (Fig. 4). 3D GIS also represents the tool of choice to examine the geometry of an ore body and to target drilling in areas of possible extensions.

MULTI-DATA INTERPRETATION

Visual correlation between geological, geochemical and geophysical data is

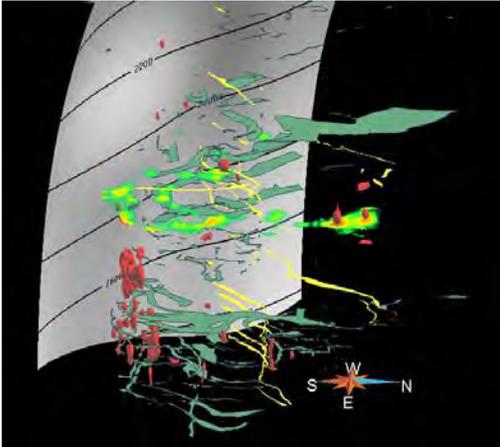


Fig. 4. Lower part of the Horne deposit depicting relationships between synvolcanic mafic dykes (green), late syenite dykes (yellow) and high grade Cu mineralization (red bodies). Structural contours are 200 feet.

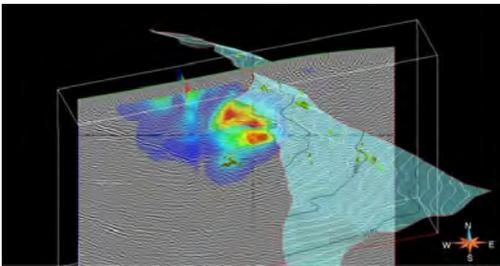


Fig. 5. Locations of massive sulfide ore bodies (green) at marker horizon (C-Horizon) along the Amulet high-resolution seismic line of Bellefleur *et al.* (2007). Intensity of chlorite alteration is superimposed (data from Xstrata Copper).

dramatically enhanced in a 3D GIS environment (Fig. 5). Particularly useful are high-resolution seismic surveys as these data increase the ability to interpret the degree of spatial continuity and the anisotropy directions of geological features observed in drill core and in surface outcrops. Based on geophysical surveys, a single key observation can be upscaled for at least several hundreds of metres.

GEOSTATISTICS

Kriging-based estimation techniques also represent an important toolset allowing the recognition of spatial distribution patterns

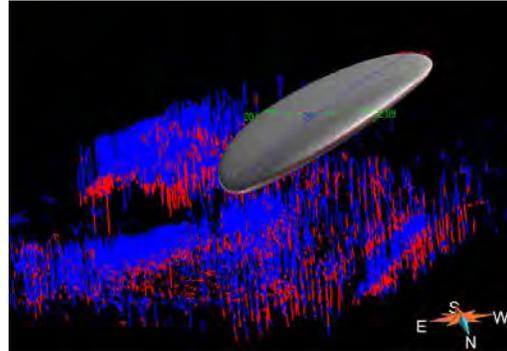


Fig. 6. 3D visualization of a UVW spheriogram in relation to a control drill hole data set. Red and blue intersections indicate the presence and absence of felsic volcanic rocks, respectively (data from Xstrata Copper).

(Figs. 6). Although these techniques have traditionally been used mostly by ore reserve engineers, the mineral exploration community can now take advantage of these powerful geospatial tools in the 3D GIS environment.

DEPOSIT ANALYSIS

The advantages of using 3D GIS technology at the deposit scale can be illustrated using the Horne deposit as an example. Integration of geologic and geochemical data reveals that zones of high Cu content are spatially related to syn-volcanic dykes that are interpreted to mark the locations of early structures (Fig. 7). In an exploration scenario, structural and stratigraphic interpretation combined with a simple visual inspection of the geological relationships could be employed to identify areas of high mineral potential.

INDUSTRY APPLICATION

3D GIS provides new and exciting opportunities for the mineral exploration community. Successful application of this technology, however, requires a change in exploration culture. To take advantage of this technology in the search for deep resources, a number of strategic decisions need to be made by exploration companies. These include:

- (1) Investing in 3D data management

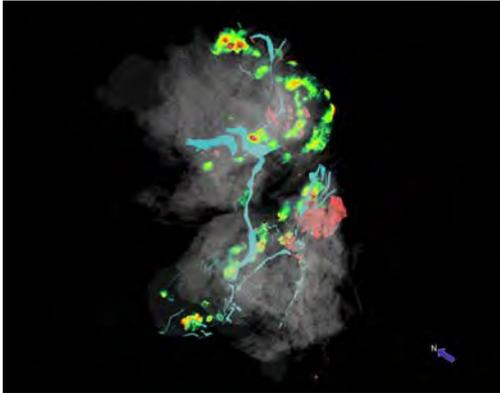


Fig. 7. Top view of the Horne deposit showing massive sulphides (transparent white), synvolcanic mafic dykes and sills (blue), and areas of high Cu grades (red).

through hiring and training of personnel as well as the acquisition of software and hardware.

(2) Development of a corporate 3D IT strategy to built multi-disciplinary 3D exploration teams.

(3) Establishing 3D training sets to define critical geological elements and geometrical relationships at the camp scale through integration of surface and subsurface lithological, geochemical, and geophysical data.

(4) Advancing geological knowledge through 3D cross domain data reconciliation and team-based data interpretation.

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Element Distribution Patterns and Mineral Discoveries using Biogeochemical Methods

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ABSTRACT: Studies over the past half century have greatly advanced the understanding of biogeochemical processes. Uranium biogeochemical anomalies identified 30 years ago are now known to contain multiple zones of rich U deposits. Mapping of multi-element patterns in southern British Columbia suggests that, among other elements, Tl and Hg may be biogeochemical pathfinder elements for Broken Hill-type Sedex deposits. The halogens in plants, too, may provide additional vectors toward base metal-mineralized areas. Opportunistic sampling during field mapping projects can add important focus for detailed exploration, and help trace the source of till anomalies. Molybdenum in cedar foliage has outlined the MAX Moly mine area and generated additional targets of similar magnitude of unknown origin. Investigation of one of these in southern BC has resulted in the discovery of low-grade mineralization in rocks exhibiting similar characteristics to the MAX Moly deposit. Moving forward, more emphasis on the distribution of volatile elements (e.g., Hg; halogens associated with fluid inclusions) as well as commodity elements, and an improved understanding of the role of bacteria in mobilizing metals should further entrench the role of biogeochemical methods for assisting in the exploration for mineral deposits.

KEYWORDS: *Biogeochemistry, Exploration, Uranium, Base Metals, Molybdenum*

INTRODUCTION

Over the past half century there have been significant developments in the understanding and application of biogeochemical methods to the search for buried mineral deposits – both deep and shallow. It is now apparent that depth of root penetration and relationship of plant chemistry to soil composition are not critical to obtaining subtle biogeochemical responses to deeply buried mineralization. Various processes invoked for explaining partial leach soil anomalies are equally relevant for explaining signatures of elemental anomalies in plant tissues. These include movement by diffusion, electrochemical cells, seismic pumping, artesian flow, and particularly bacterial movements. These processes are, however, somewhat modified and controlled by plant requirements and tolerances, so that the ‘barrier mechanisms’ identified by Kovalevsky (1979) come into play and need to be

considered when interpreting data from biogeochemical surveys.

Information from surveys conducted decades ago can now be viewed in light of subsequent exploration activities, and the value of biogeochemical surveys (when and where to use the techniques) can be more accurately assessed and applied using the rapidly-advancing analytical methodologies (e.g. ICP-MS) that are now widely available.

URANIUM

More than 30 years ago it became apparent that sandstones of the Athabasca Basin in Saskatchewan are host to significant deposits of uranium. Previous work elsewhere, primarily in the Colorado Plateau (Cannon 1964) and the former Soviet Union (Kovalevsky 1972), had shown that plants are capable of accumulating high concentrations of U. Surveys near the eastern margin of the Athabasca Group revealed an area of

about 10,000 km² within which U in spruce twigs consistently contained more than 10 times the normal background level of U in plant tissues (10 ppb U in dry tissue, Markert 1994; Dunn 2007), with far higher concentrations extending over several thousand km². This 'Wollaston Uranium Biogeochemical Anomaly' (Dunn 1982) is underlain by the Wollaston Domain that hosts 25% of global U production. Within this anomaly, where depth to the U-hosting Athabasca unconformity with the Wollaston Domain ranges from 0-300 m, detailed surveys over known mineralization showed a strong response in the vegetation. Over the McClean Lake deposit, at a depth of 150 m, U in spruce trees showed the classic Rabbit's Ears-type of response that has been attributed to electrochemical cells (Govett 1976). Over the 30 years since that discovery, within the Wollaston anomaly more than 16 U deposits have been discovered that contain more than 1 million lbs U₃O₈. The most recent of these is the Roughrider zone of Hathor Exploration Ltd. discovered in 2008, where drilling has intersected up to 23 m grading >11 % U₃O₈ at a depth of 300 m (<http://www.hathor.ca>). Currently, the CAMIRO Athabasca project is testing the surface signatures of many geochemical techniques, including vegetation, to known mineralization more than 400 m deep.

BASE METALS

The Geological Survey of Canada has a 'Targeted Geoscience Initiative' (TGI-3) program, which in south and south-central British Columbia helps stimulate base metal exploration activities. The terrain in much of this area is rugged, has variable thickness of till cover and is heavily forested, yet in light of past discoveries it remains highly prospective for various types of metal deposit. Of five known groups of Zn/Pb deposits within a cover sequence that mantles Palaeoproterozoic core gneiss, mineralization at Kingfisher and adjacent deposits comprises the only group below the tree-line. The widespread regional distribution of thin calcareous units that host these deposits lends

credence to the concept that similar mineralization may lie beneath the extensive area that is covered by a veneer of glacial deposits and dense forest.

As part of the TGI-3 program several biogeochemical surveys have been undertaken. A helicopter-supported survey was conducted over 700 km² that included the stratigraphic setting of the Kingfisher deposit and similar stratigraphic units that border Tsuius Creek, to collect 562 Douglas-fir tree tops at 1 km spacing.

Analysis of dry twigs revealed areas of Zn enrichment with associated elements (Cd, Tl and Mn) that show a spatial relationship to areas of Pb enrichment (with Fe, Hg, REE, Al, and Ti), especially south of Tsuius Creek. A strong Pb/Zn zonation is typical of Broken Hill-type Sedex mineralization. Of particular note were localized high Tl values.

Subsequent analysis of the ashed needles from these twigs confirmed the patterns established from the dry twigs. It served to enhance some signatures (notably Ag) and added a layer of data for the halogens, demonstrating a F association. Also from these additional analyses a pattern of Cd and B enrichments at Kingfisher was evident.

Follow-up ground studies involved the analysis of outer bark from western hemlock collected at 100 m sample spacing over the Tl anomaly south of Tsuius Creek. This permitted more clearly defining the extent of the Tl anomaly (600 m x 600 m) and its relationship to other trace elements. Figure 1 shows the Tl anomaly and the spatial relationship of Hg which appears to define a conjugate set of lineaments interpreted as leakage from structural weakness. The multi-element association at this locality suggests that Tl and Hg may be pathfinder elements to concealed base-metal mineralization.

In the Bonaparte Lake area of south-central BC, samples of outer bark from Engelmann spruce and lodgepole pine were collected on an opportunistic basis during the course of field mapping. Consequently, the sample distribution was uneven, but expedient and sufficient to

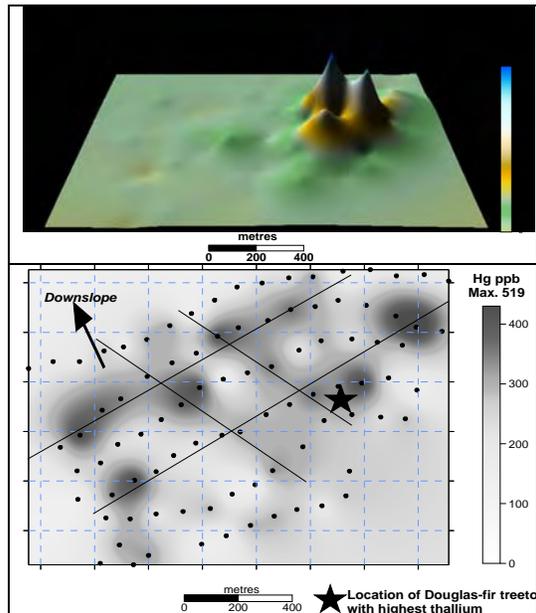


Fig. 1. Thallium (3D plot, viewed from south) and Hg in dry western hemlock bark – Tsuius Creek, BC (Dunn & Thompson 2009a).

provide indications of areas with potential concealed mineralization.

Five hundred samples were collected. The analytical data provided a basis for comparing and contrasting the geochemical signatures of the two types of bark and defining those elements that generated the same or similar signatures while establishing other elements that generated different distribution patterns because of tolerances to, or requirements for, those elements. Most elements generated similar distribution patterns attesting to the robustness of the biogeochemical method and reinforcing the significance of the signatures (Dunn & Anderson 2009). Elements that tended to show different patterns (e.g., Ba, Sr) were those that were significantly more concentrated in a particular sample medium. The pine bark was more enriched than the spruce in Ag, Al, Cd, La, Pb and Sb. Conversely, spruce was more enriched in Ba, Ca, Mn, Rb, Sr, and Zn.

Results from a recent till survey (Plouffe *et al.*, 2009) revealed unusually high concentrations of thorianite in the heavy mineral concentrates. Plots of thorianite-

related elements – Th, U, and REE – in the conifer bark samples indicate an area of subtle enrichment that is located up-ice from the proven direction of ice movement. This may help to more closely focus on the source of the thorianite. Multi-element signatures in the bark assisted, too in identifying known Cu mineral occurrences, delineating areas of Au enrichment and possibly PGE, as well as defining signatures characteristic of the principal plutonic and volcanic units. For example, there are significant increases in Ni, Cr and Co over known and concealed mafic to ultramafic units.

MOLYBDENUM

The MAX property lies near the north end of the Kootenay Arc in tightly folded, strongly sheared Palaeozoic metasedimentary rocks. The reported commodities are Mo, W, Pb, Zn and Cu. The area is heavily forested rugged terrain with outcrop largely obscured by a cover of till. Cedar foliage was collected along several traverses up the steep hillside toward known mineralization.

The location of the discovery outcrop was clearly outlined by Mo in cedar, and two additional Mo anomalies of unknown source and similar intensity were identified (Fig. 2). In mid-2008, Roca Mines drilled two drill holes, 100 m apart that targeted the northern biogeochemical anomaly. They reported “*Intense silicification, hornfelsing, locally strong quartz veining, and pervasive sericite alteration with trace molybdenite throughout...reminiscent of the MAX resource itself where the extent of a relatively minor molybdenite mineralized zone on surface lies atop a large-scale mineralized deposit currently being mined.*” Roca Mines press release, 12th August 2008 (www.rocamines.com).

CONCLUSIONS

(1) Examination of data from past biogeochemical surveys in context of subsequent discoveries has established their relationship to mineralization.

(2) Pathfinder and commodity element distribution patterns from recent surveys have delineated new targets for base

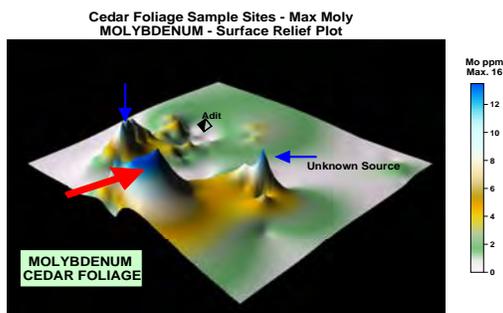


Fig. 2. 3D plot of Mo in cedar foliage. MAX Moly mine (Dunn & Thompson 2009b).

metals and other commodities, and resulted in new discoveries.

(3) It is anticipated that focus on volatile elements (especially halogens and Hg) and improved understanding of processes (notably bacteria) in mobilizing metals from depth will provide further successes for biogeochemical surveys.

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ESS Contribution No. 20080669

Spatio-temporal geochemical dynamics of an acid rock drainage stream in the Yukon Territory: implications for mineral exploration

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ABSTRACT: Acid rock drainage (ARD) is a natural phenomenon known to occur via water-rock interactions at or near base-metal deposits. As part of the Geological Survey of Canada (GSC) TGI3 (Targeted Geoscience Initiative) Deep Search Project, this research aims to enhance our understanding of the surficial geochemical and biogeochemical processes that influence the mobility and dispersion of elements, and to evaluate their importance when using ARD stream geochemistry to detect subsurface mineralization. A sampling campaign was conducted at an ARD stream at the XY-deposit (Pb-Zn SEDEX (sedimentary exhalative) deposit), Howard's Pass area, Yukon Territory, during the summer of 2008. The watercourse was sampled across the spring-summer seasonal cycle for aqueous geochemistry, authigenic mineral precipitate geochemistry and mineralogy, and detrital components. Our results indicate that seasonal changes may lead to spatio-temporal variations in surficial processes that effect element dispersion, and thus these processes require further investigation to determine their importance when using ARD geochemistry to detect subsurface mineralization.

KEYWORDS: SEDEX deposit, Yukon Territory, acid rock drainage, mineral exploration vectors, groundwater.

INTRODUCTION

Acid rock drainage (ARD) is a natural phenomenon generated through the interaction of groundwaters and base-metal deposits, primarily, the oxidation and dissolution of Fe-sulphide minerals. The acid generated from these reactions is a strong agent of rock dissolution, and consequently ARD groundwaters carry with them a record of the rocks encountered along their flow path. Stream waters such as these may carry anomalous loads of dissolved base metals, which could potentially be used by the exploration industry to detect subsurface mineralization. Surficial geochemical and biogeochemical processes strongly influence element mobility and dispersion in ARD streams, especially in cold climates where extreme seasonal changes can lead to spatio-temporal variation in these processes. As such, this project aims to investigate the degree to which these processes are important when using ARD to detect subsurface mineralization. It is doing so by investigating a single stream with ARD

emanating off the "XY" SEDEX deposit, Howard's Pass, Yukon Territory.

GEOLOGICAL SETTING

The XY-deposit at Howard's Pass is a stratabound Pb-Zn deposit formed during the lower Silurian, hosted by a succession of carbonates, cherts and carbonaceous pyritic shales in a syncline structure that underlies Sugar Mountain and Yara Peak (Fig. 1; Morganti, 1979). The deposit is comprised of finely laminated sphalerite, galena, chalcopyrite, and pyrite. Tectonic deformation has left the bedrock highly fractured, which is inferred to control the flowpath of groundwaters emanating from the deposit (Jonasson and Goodfellow, 1986). During the spring, stream drainage from the deposit is fed mainly by snowmelt, while in the summer meteoric and groundwaters are important sources of runoff. A detailed description of the Howard's Pass XY-deposit can be found in Morganti (1979) and Goodfellow *et al.* (1983).

SAMPLING AND METHODOLOGY

The sampling campaign on the ARD stream was conducted between June and August, 2008. Samples of surface water and associated authigenic mineral precipitates and detrital sediment were collected on a daily basis. Samples were taken along the entire length of the ARD stream, ranging from an altitude of 1690 m.a.s.l. to approximately 1400 m.a.s.l. The temperature, pH, Eh, and DO were measured *in situ* using a pre-calibrated field multimeter (Eureka Manta multiprobe). Dissolved ferrous iron was measured colourimetrically on-site by the 1,10-phenanthroline method. The surface waters were filtered (0.45 µm pore size) and acidified with ultra-pure HNO₃ to a final concentration of 1% (v/v) for major and trace element analysis. Filtered, unacidified samples were also collected for major inorganic anions analysis. Sediments were collected daily. All samples were securely stored at 4 °C for up to four weeks prior to shipment to the GSC laboratories in Ottawa.

Major and trace element concentrations in the acidified samples were determined via ICP-MS (inductively coupled plasma mass spectrometry) and ICP-OES (inductively coupled plasma optical emission spectroscopy) at the GSC's Geochemistry Research Laboratory. Dissolved anion concentrations were measured by IC (ion chromatography) on the unacidified samples, also at the GSC's Geochemistry Research Laboratory. Characterization of the sediment mineralogy and texture by XRD (X-ray diffraction), SEM (scanning electron microscopy) and TEM (transmission electron microscopy) is ongoing.

RESULTS AND DISCUSSION

Interpretation of our hydrogeochemical results is complicated by the paucity of baseline data for ARD streams about the XY-deposit, which would allow us to identify "anomalous" metal concentrations. Baseline datasets for streams in the Selwyn Basin were compiled by Goodfellow (1983), however, these relate to alkaline to circumneutral streams,

precluding their use in our low pH system given the enhanced dispersion and mobility of base metals under acidic conditions.

Water samples collected during June have lower (4 to 44-fold lower) dissolved base metal concentrations (Table 1) relative to samples taken in August (Table 1), reflecting base flow dilution from the spring freshet. The spatial variation in authigenic mineral precipitates in ARD streams at the XY-deposit becomes increasingly visually apparent as the summer season progresses. Their bulk mineralogy and elemental composition is currently being analyzed, as well as their relationship with the stream microbial community. Such seasonal variation is likely a result of the temporal evolution of the stream hydrochemistry. These changes may be governed by the local hydrological conditions (fluctuations in groundwater flow and volume) and the underlying geology, both of which can contribute to base-flow dilution and acid-neutralization processes. The distribution of indigenous microorganisms can also influence the spatial evolution of ARD waters; for example, algal mats growing in ARD waters at MacMillan Pass, Yukon Territory, have been observed to concentrate Zn and Pb by one and five orders of magnitude, respectively, reflecting the ability of microorganisms to influence their local environment (Lawrence *et al.*, 1998). Together, the aforementioned surficial processes result in the spatial attenuation of dissolved base metals, through adsorption/coprecipitation reactions with authigenic mineral precipitates. Similar spatial variation has been reported for other ARD streams (Lee *et al.* 2002; Espana *et al.* 2006; Eppinger *et al.* 2007).

For mineral exploration purposes, spatio-temporal variations in ARD hydrochemistry may provide indicators to the location of an orebody; e.g., anomalous concentrations of dissolved base metals may suggest that the orebody is proximal to this anomaly. At XY, the highest concentrations of dissolved base

Table 1. Temporal variation in dissolved Zn (ppm) and Pb (ppb) concentrations for sites proximal to near-surface mineralization. Sampling locations distal to the near-surface mineralization were not accessible in June. See Figure 1 for reference to sampling location.

Sampling location	Zn (ppm)			Pb (ppb)		
	XY 5	XY 6	XY 7	XY 5	XY 6	XY 7
June 21/08	13.50	11.10	9.50	0.33	0.06	0.03
August 3/08	50.80	44.30	42.60	1.87	1.80	1.33
Concentration factor	4	4	4	6	30	44

Table 2. Spatial variation observed for select elements, moving from upper (1690 m.a.s.l.) to lower (1497 m.a.s.l.) reaches of the ARD stream. Concentrations are given in ppm for all elements, except Pb, which is in ppb.

Sampling location	pH	S	Mg	Al	Zn	Fe	Si	Ni	K	Na	Pb
S1	3.3	3503.7	996.4	847.5	475.3	303.1	29.1	15.3	4.3	1.9	10.7
XY2	3.4	1092.9	314.5	187.6	134.4	84.4	13.1	4.4	2.2	1.4	8.7
XY3	3.5	930.9	261.9	148.6	109.9	55.5	11.9	3.7	2.1	1.2	7.5
XY4	4.3	667.5	194.4	103.1	76.8	25.6	9.7	2.5	1.9	1.0	3.8
XY4.5	4.7	551.2	186.9	45.8	56.4	16.9	7.6	2.0	2.0	1.0	2.2
XY5	5.0	503.9	169.2	22.3	50.6	14.6	6.5	1.8	1.8	0.9	1.5

metals (Table 2) are found at the sampling location where the ARD waters first emanate from the skree (elevation 1690 m, sampling location “S1” in Fig. 1). However, this site is distal (>100 m vertically) to the orebody in comparison to other sites such-as “XY 4.5” (Fig. 1). These more proximal sites carry a dissolved metal load that is approximately 10-fold lower (Table 2). The lower dissolved Zn concentrations proximal to the near-surface mineralization are likely the result of preferential partitioning of Zn to biofilms, biominerals, and sediments under the local geochemical conditions along the flow path. Determining how one could identify the proximal sites as those closest to the orebody is part of ongoing research. This research includes analyzing biominerals and sediments to determine the extent to which temporal changes in the local hydrology and microbiology influence (or potentially mask) spatial changes in element mobility within the ARD stream.

CONCLUSIONS

The spatio-temporal variations observed at an ARD stream about the XY-deposit,

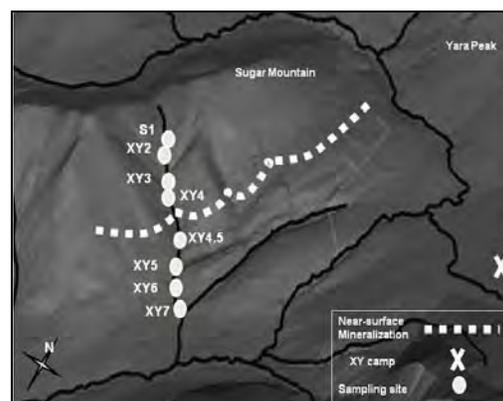


Fig. 1. Surface projection of the XY-deposit, Yukon Territory.

and other sites, suggest that a systematic understanding of these environments is required to maximize their use for mineral exploration. Static, single snap-shot measurements are insufficient for the establishment of baseline data from which anomalies related to potential subsurface mineralization can be detected, as these will generally not characterize the inherently dynamic nature of ARD systems. Without an intimate understanding of the surficial geochemical and biogeochemical processes influencing

the base metal concentrations in ARD systems, near-surface mineralization may go undetected by geochemical reconnaissance studies.

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Soil mineralogy and geochemistry of surficial materials around the XY base-metal massive sulfide deposit, Selwyn Basin, Yukon

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ABSTRACT: Selwyn Resources' Howard's Pass deposits in eastern Yukon, Canada, contains 386 Mt of massive sulfide mineralization distributed across 13 individual deposits. As part of the Geological Survey of Canada's (GSC) TGI3 Deep Search Project, soil samples were collected across the 'XY' deposit with the aim of developing new exploration strategies that can discriminate such mineralisation from the high local background values. Earlier research demonstrated that Pb is an effective discriminator of the XY deposit. In this research, Pb and Zn from a hydroxylamine partial leach analysis of 'B' horizon soils discriminate the XY deposit. However, in contrast to many surveys that focus on the uppermost B horizon, this survey demonstrates that the least weathered portions of the B horizon soils are those that effectively discriminate the orebody location. This is likely due to the geochemical signature having a detrital and not hydrochemical origin. It seems likely that the dominant pyritic black shale clasts within the XY soils provide a substrate that is readily destabilised by pedogenesis, and which are then consequently soluble via this partial leach protocol. It is likely that the soil matrix strongly influenced the results of this partial leach experiment.

KEYWORDS: *soil sampling; mineral exploration, partial, leach, base metals, Yukon*

INTRODUCTION

The Selwyn Basin in the Yukon Territory of Canada hosts major SEDEX Zn-Pb sulphide deposits, the biggest being the relatively large (~90.4 Mt) deposits at Howard's Pass (XY), owned by Selwyn Resources (Morganti 1979; Goodfellow 2004). This research focuses on the surficial geochemical expression of the 'XY' deposit, one of the 13 known orebodies within the Howards Pass district.

Soil geochemistry is a common method in many mineral exploration programs. Generally the aim of soil sampling programs is to determine a surficial geochemical expression of the rocks underlying the soil and overburden. Any potential buried mineralization is then interpreted from geochemical departures from background values. In the Selwyn Basin the problem is the background values, which on the whole are very high due to an abundance of sulfidic black shales (Morganti 1979; Goodfellow 2004). The research question addressed herein

is: "what is the best soil sampling protocol for high background geological settings such as the Selwyn Basin?" We addressed this question using a suite of 'partial leach' geochemical protocols on soil sample transects across the XY deposit. We only report the results of a hydroxylamine partial leach here, which is designed to dissolve amorphous iron oxides within the sample.

GEOLOGICAL SETTING

The XY deposit is a stratiform Zn-Pb-dominated massive sulfide 'SEDEX' orebody (Goodfellow 2004). It is situated near the base of the Duo Lake Formation within the Road River Group (Morganti 1979). The Duo Lake Formation is comprised predominantly of carbonaceous, sulfidic shales, with subsidiary cherty and phosphatic components in the strata immediately surrounding the ore horizon (Goodfellow *et al.* 1983). The Duo Lake Formation is underlain by carbonates of the Rabbitkettle Formation, which outcrop in parts of the valley in

figure 1. This sedimentary package underwent multiphase deformation during the Laramide Orogeny.



Fig. 1. Photograph across the alpine terrain at XY, with a hummocky till plain in the foreground backed by the orebody-hosting 'Sugar Mountain'. The soil sample transect follows the black line, stopping at the end of soils and start of the scree slope. The XY orebody's surface projection is at the base of the mountain.

Surficial deposits at XY are dominated by tills and colluvium, which have been locally reworked by alluvial and glacio-fluvial processes (Figs. 1 & 2a). On the transect reported herein, the depth of overburden varies from negligible on mountain sides to at least 5 m thick in central parts of the till plain in central valley areas (unknown maximum thickness). In the section of the traverse the XY ore zone is c. 10 m thick, and occurs below c. 3 m of colluvial overburden (Fig. 2). Pedogenesis is generally restricted to minor to moderate horization that has produced predominantly brunisols (Canadian Soil Classification System, Agri-Canada 1998).

METHODS

One hundred metre-spaced soil samples on two traverse lines were collected in the summer of 2007 (here we report one of those lines, Fig. 1). At each site the B horizon was sampled in 15-cm thick intervals; dependent on the thickness of the B horizon, between one and three samples per site were collected. B

horizons at XY were generally pervasively red at the top transitioning to mottled red-brown in lower samples, indicating lower degrees of oxidation and weathering with increasing depth.

The partial leach protocol used a 2-h leach, using 40 ml of 0.25 M hydroxylamine hydrochloride in 0.1 M HCl at 60°C, on 1 g of the <63- μ m fraction (Cameron *et al.* 2004). This hydroxylamine leach is designed to dissolve secondary iron and manganese oxides. This relatively aggressive leach protocol will also dissolve phosphatic, calcareous and amorphous clay components, and will likely desorb any ions weakly bonded to other components.

RESULTS AND DISCUSSION

The partial leach results indicate that there was considerable dissolution of multiple phases, including iron oxides (Fe, Fig. 2D), clays (Al, Fig 2F), carbonates (Fig. 2E), and phosphates (Fig. 2H).

Phosphatic shales and carbonates are at the surface only in the lowest portion of the valley. This is reflected in peak Ca and P values being at alluvial sites 10 and 11, indicating that the phosphates and carbonates are likely sourced from local erosion. Furthermore, the Ca and P values are highest in the lowest, least-weathered portions of B horizons, suggesting that weathering has leached these relatively soluble components from the upper portions of the soil.

Overall, the Fe and Al values by this partial leach are high, suggesting that this partial leach aggressively dissolved these soils, irrespective of the soil facies. Despite the changes in red colouration, and SEM petrography indicating mineral authigenesis was predominantly in the uppermost B horizon sample, with minimal secondary mineral authigenesis in the lower B horizon samples, the partial leach extracted more Fe from samples lower in the B horizon. Aluminium dissolved by this partial leach was consistently high across all B horizon samples. This distribution of high Al and Fe dissolution suggests that the partial leach did not only dissolve

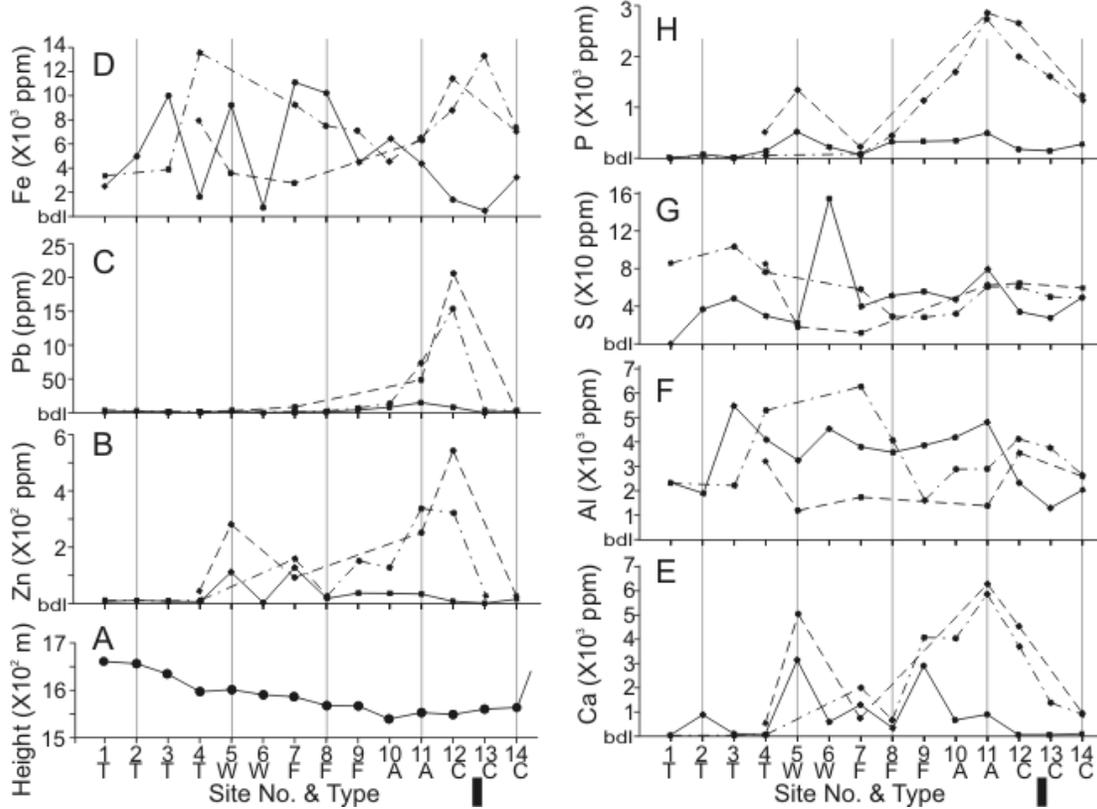


Fig. 2. Elevation (A) and chemical (B-H) crossplots against soil sample site number. Transect is south (left) to north (right). The different B horizon soil depths are given by different line characteristics: solid line = uppermost 15 cm of the B horizon; dashed-dotted line = 15-30 cm of the B horizon; dashed line = 30-45 cm of the B horizon. The XY orebody's surface projection is at the black bar. Gray lines in the background are to aid site projection across crossplots. The depositional characteristics of each soil site are: T – till; W – seasonally waterlogged till; F – fluvoglacial till; A – alluvium; C – colluvium.

secondary B horizon clays and oxyhydroxides, but also some other Fe- and Al-bearing components of the soil. SEM, XRD, and heavy mineral analysis all failed to report sulfides in any B horizon sample. Hydrolytic oxidation of pyrite forms sulphuric acid, which would likely destabilise the metamorphic clay components of the shale clasts. This would likely make them, plus the ex-pyrite Fe, susceptible to dissolution during this partial leach, which may be the reason for the relatively high Al and Fe values reported for this leach. Thus the Al, Fe, and S geochemical signatures found in this partial leach procedure are likely a modified detrital signature rather than a secondary pedogenic signature.

Petrographic research is investigating the weathering paragenesis of these samples.

Previous research had demonstrated that Pb was a good pathfinder element for the XY orebody (Goodfellow *et al.* 1983). However, the processes by which the soil materials around the XY orebody had obtained their geochemical signature were previously unclear. In this partial leach experiment, a number of pathfinder elements (e.g. Zn and particularly Pb; Figs. 2B, 2C) clearly discriminate the orebody, but only in the lower B horizon samples. Pathfinder elements in the upper B horizon samples do not discriminate the orebody horizon. This again suggests that the geochemical signal is not derived from weathering-induced B-horizon mineral precipitation, but more likely from detrital

components leached by the hydroxylamine protocol. This contrasts with the many soil sampling protocols that emphasize the uppermost B horizon as the preferred sample medium. These soil sampling protocols are primarily attempting to access a hydrogeochemical record of the underlying rocks that may be contained within secondary soil minerals (e.g. Mann *et al.* 1998; Cameron *et al.* 2004). Essentially this hydroxylamine leach experiment has detected a detrital record of the underlying orebody, and not the hydrochemical record generally sought in a soil sample partial leach experiment. The detrital record was likely made soluble via this partial leach protocol through pedogenic weathering processes.

CONCLUSIONS

This research investigated the soil geochemistry over the XY deposit, Howard's Pass, Yukon Territory, using a hydroxylamine partial leach protocol. In this case study:

- (1) The XY deposit location was clearly discriminated using Pb and Zn from the high background values in lower B horizon soils, but not in upper B horizon soils. This finding contrasts the many protocols that emphasize the upper B horizon as the most appropriate for soil sampling.
- (2) The geochemical signature of the XY orebody within these soils is likely derived from detrital sources, not hydrochemical sources. A hydrochemical signature of the XY orebody was not isolated in these soils by this protocol. Perhaps a less aggressive partial leach protocol may be more suitable given the substrate type.
- (3) Substrate types and the pedogenic processes they prompt can influence the results in partial leach experiments.

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Application of 'metals-in-soil-gas' techniques to mineral exploration in exotic overburden

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ABSTRACT: The use of ICP-MS combined with liquid collectors greatly improved the reliability of the 'Metals-in-soil-gas' (MSG) technique in the late 1990s. To date, the MSG technique has been successfully applied in various locations varying in: commodity type (e.g. gold, base metals and nickel), depth of burial, and climatic regimes (e.g. from semi-arid through to wet temperate). In this paper, three case studies are reported to illustrate the effectiveness of the technique. The results show that in MSG, a suite of chalcophile elements, similar to the association of commodity and pathfinder elements in the deposits, exhibit sharp anomalies above the known sulphide mineralization. Copper and Zn peaks can reach tens of thousands of ppb over a background of <100 ppb for Cu and <200 ppb for Zn. The authors suggest that the MSG technique can be used as a powerful tool for mineral exploration both in residual and exotic overburdens.

KEYWORDS: *Metals-in-soil-gas, gold, base metals, nickel, copper, mineral exploration*

INTRODUCTION

The 'metals-in-soil-gas' (MSG) technique, and advances therein, have been summarised by Wang *et al.* (2008). In the past few years, MSG geochemistry has been studied extensively with the support of the Chinese Geological Survey, Nature Science Foundation Committee (NSFC), and Program 863, Ministry of Science and Technology, China. The MSG technique was used to detect concealed mineralization including gold, base metals and nickel in China, although the process by which the metals migrate from deeply buried ore deposits to near-surface soil in gaseous form is controversial. Here, we report three case studies on base metal, nickel and copper mineralization buried beneath exotic overburden.

METHODS

A modified active method was used for collect 'gaseous' metals from soil air (Wang *et al.* 2008). The sampling device consists of a cone-shaped sampler, a special Millipore filter (0.45 µm), a liquid collector, and a battery-operated pump. The liquid collector comprises a high

density polyethylene bottle containing 15 ml of 3% HNO₃ prepared in a clean room with ultra-pure HNO₃ and deionized water. When sampling, the cone-shaped sampler is pushed 30-40 cm into the soil, and the 'Earth gas' is pumped through a silica gel tube and the Millipore filter to prevent coarse particles entering the liquid collector. The pumping lasts 2-3 minutes with a total of 3 litres of gas pumped through at each hole. At each sampling site, a composite of samples is collected from three holes at an interval of 2-3 meters to improve the sampling reproducibility.

All MSG samples, including blanks, were analysed by the IGGE (Institute of Geophysics and Geochemistry) Central Lab and the National Geological Lab using ICP-MS for 40 elements including Pb, Zn, Cu, Ag, Ni, Bi, Cd, Au, Mo, & W.

RESULTS

Jiaolongzhang base metal deposit, Gansu

Aeolian loess covers over 600,000 km² in China. Conventional surface geochemical techniques have not been successfully

employed in these areas. The Jiaolongzhang base metal deposit in western China is located in a loess-covered area. The 3600-m long by 200-m wide mineralized zones are covered by both loess (50-80 m) and tertiary red sandstone (20-50 m) (Ren *et al.* 1995; Wang *et al.* 2008). The blind ore bodies contain mainly Zn, Pb, Zn, and pyrite. The host rock is chlorite-quartz sandstone and limestone, and the main ore minerals are pyrite, sphalerite, galena and chalcopyrite. The bedrock comprises mainly intermediate and acidic marine volcanic rocks. Lead, Zn, Cu, Ag, Cd, Ag, Bi are highly enriched in the ore bodies, which are good indicators for an MSG survey.

Earlier research showed that a conventional soil (total decomposition) survey provided no anomaly and a 1M NH₄Cl partial leach for Pb and Zn produced only a one-point anomaly over the mineralization along Line 48 over Jiaolongzhang deposit. However, Cu, Pb, Sb, Bi in the MSG or geogas technique show sharp anomalies with double peaks over mineralization and the highest Cu, Pb, Zn concentrations can reach to over 1000 ng/L (Wang *et al.* 2008).

To understand the characteristics of the MSG response over the known mineralization zone, Lines 20, 28, 32, 40 and 48 were sampled in 2007. MSG signatures vary greatly with time, climate, devices and sampling team. Response ratios are calculated by dividing each sample value by the predetermined background value for that element under the same sampling conditions to reduce these errors.

Figure 1 shows MSG ratios for Cu, Pb, Zn, Ag, Cd, Ag and Bi along each profile: strong anomalies are evident over the ore bodies and Cu and Pb anomalies along different lines seem to be spatially associated with the known mineralized zone covered by thick transported overburden (Fig.1). The strong base metal MSG responses south of the mineralized zone along Lines 40 and 32 are as yet not

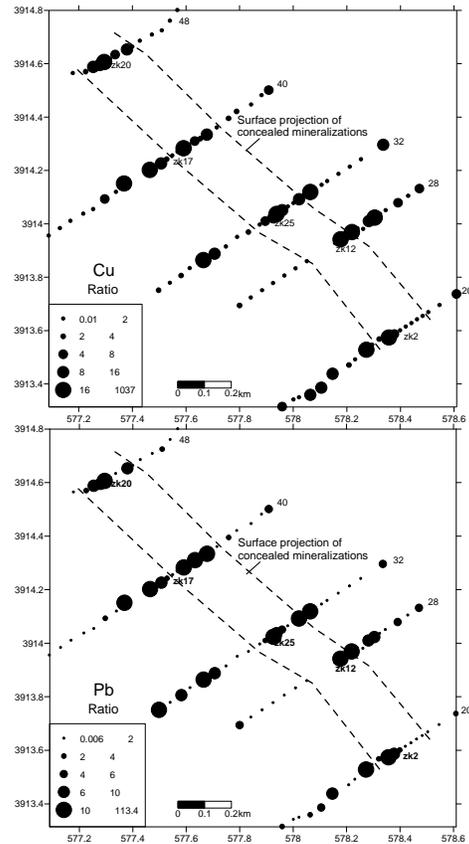


Fig. 1. MSG Cu and Pb signatures at the Jiaolongzhang base metal deposit, Gansu, China.

fully understood because the target area has not been defined by drilling.

Lashuixia Cu-Ni deposit, Qinghai

The Lashuixia Cu-Ni deposit in Qinghai has been mined for over 20 years and most of the known ore has now been excavated. Brownfields exploration using conventional geochemistry is not successful in locating concealed mineralization because most of the area is covered by quaternary sediments and a tertiary red layer. Moreover, the application of electrical geophysical techniques is difficult because of the highly conductive nature of clay cover. MSG techniques were used to test effectiveness of the method in this terrain and to define new targets for drilling.

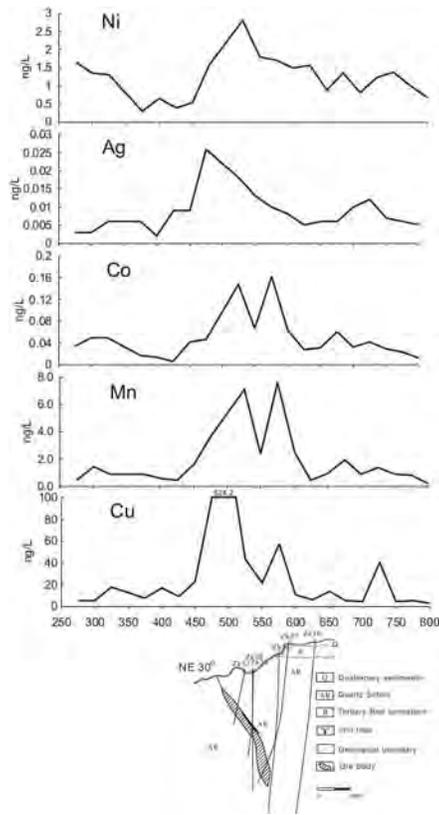


Fig. 2. MSG signatures of Cu, Mn, Co, Ag, & Ni along Line 204 of the Cu-Ni Lashuixia deposit, Qinghai.

Magmatic Cu-Ni ore bodies are hosted in quartz schist and partially in gneiss. The ore averages 4.2% Ni, 3.0% Cu, and 0.01-0.2% Co and contains a small amount of platinum group elements. The main minerals comprise violarite, pyrite, marcasite, chalcopyrite, quartz and plagioclase.

The MSG responses for Cu, Ag, and Ni along Line 204 are similar but that for Cu is particularly strong over mineralization (Fig. 2). Responses for Mn and Co are similar but their peaks occur to the north of the known ore bodies (Fig. 2). The results indicate the MSG technique can be useful in locating buried Cu-Ni mineralization.

An MSG grid survey was conducted to define potential targets; over 1500 samples were collected on a 50-m by 50-m grid. The MSG Cu and Ni responses

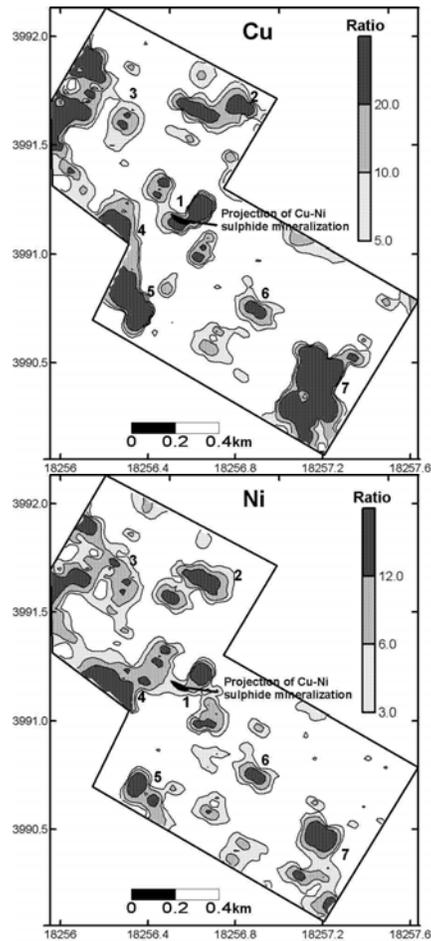


Fig. 3. MSG Cu and Ni contour maps at the Lashuixia case study area, Qinghai, China.

show only weak anomalies over the known Cu-Ni mineralization (Fig.3). The causes of this weak response likely are that (1) bedrock outcrops around known mineralization and (2) the soil cover is very thin, making it difficult to preserve the soil gas itself. However, several strong anomalies were delineated in an unknown area. Among these, Anomaly 4 is spatially adjacent to the known deposit and has the highest MSG response ratios, indicating potential for Cu-Ni mineralization.

Wangjiazhuang Cu deposit, Shangdong

The Wangjiazhuang Cu deposit is situated in Zouping County, Shangdong, China. The ore bodies are hosted in quartz diorite covered by 80 m of alluvium. The ore

averages 6.9% in Cu and consists of massive to disseminated sulphides including chalcopyrite and pyrite (Zhang *et al.* 2008). Thick quaternary cover prevents use of conventional geochemical methods although geophysical techniques played an important role in discovering the deposit.

A pilot MSG study along Line 15 was carried out to detect buried deposits in the area. Soils were also sampled to test the effectiveness of conventional geochemical techniques at several MSG sites. Elements in soil were determined by ICP-MS following the strong 4-acid (near total) digestion.

Strong, apical MSG anomalies were observed above the centre of the concealed main Cu ore bodies for Bi, Copper, Pb and Zn produced both apical and rabbit-ear anomalies over the known buried Cu mineralization. Silver yielded weak rabbit-ear anomalies at either side of the Cu orebodies (Fig. 4). However, in soil only the total concentrations of Ag, Cu, Pb, and Bi increase slightly.

CONCLUSION

These three case studies indicate that the MSG technique is indeed successful in showing strong responses over background in areas of base metal, Cu-Ni and porphyry Cu mineralization. All data support the contention that 'gaseous metals' do exist in soil gas and can be used as a practical tool for mineral exploration in areas covered both with residual and exotic overburden.

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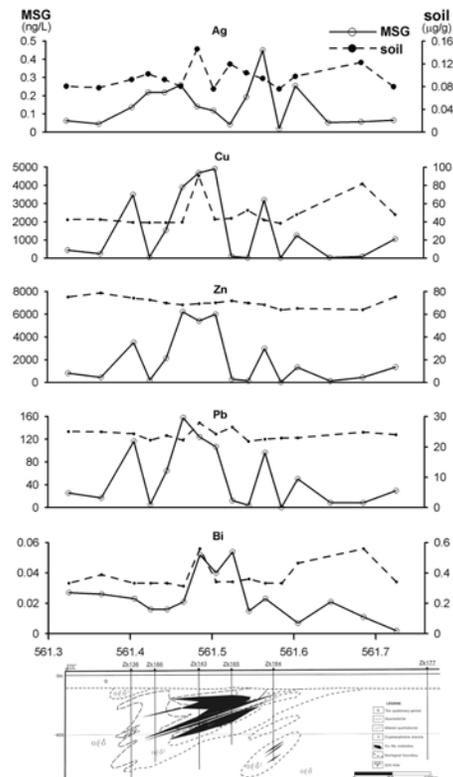


Fig. 4. MSG and soil signatures of Bi, Cu, Pb, Zn, Ag along Line 15 at the Wangjiazhuang porphyry Cu deposit, Shandong, China.

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In the beginning A personal retrospective of exploration geochemistry in the 1960s-1980s

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ABSTRACT: The discovery in the 1960s to early 1970s that rock geochemistry could be used to detect mineral deposits under 50-100 metres of post-mineralization rocks was probably one of the first indications that that geochemistry could be used for deep exploration. Some case histories from Cyprus and Canada are presented to illustrate this. The second important impetus to considering deep exploration was research into the mechanisms involved in the formation of anomalies. This led to the proposal of electrochemical models and the measurement of unconventional parameters such as pH, conductivity in water slurries of samples as well as measurement of elements in dilute leaches including water. These developments are illustrated by case histories from Canada and Australia.

KEYWORDS: *deep exploration, anomaly formation, halos, electrochemistry, sulfides*

INTRODUCTION

In an article in the Northern Miner in March 1973 I wrote, in part, that ".....geochemistry has been largely restricted to the search for near-surface deposits. Recent work at the University of New Brunswick suggests that this restriction is not necessarily valid – geochemical techniques can be developed to prospect for deeply buried deposits." (Govett 1973a). This is no longer a new idea as demonstrated by the Canadian CAMIRO project (Cameron *et al.* 2004) and Australian Cooperative Research Centres based at CSIRO (e.g., Butt *et al.* 2005; Anand 2009) that are developing geochemical methods for the problem of the thick cover.

Although much research at both UNB (University of New Brunswick) and UNSW (University of New South Wales) was on drainage and soils geochemistry, this paper will deal mostly with rock geochemistry and anomaly formation.

ROCK GEOCHEMISTRY IN CYPRUS

The sparse literature on element distribution in rocks around mineral deposits in the 1960s reported measurable concentrations for only a few metres from mineralization unless there was a

leakage halo. It was incomprehensible to me that large concentrations of metals in ore bodies would not leave an imprint on the enclosing rocks.

Research on the cupriferous massive sulfide deposits of Cyprus while working for the United Nations Development Program in 1967-68 resulted in one of the first regional rock geochemistry surveys published outside the USSR (Govett & Pantazis 1971). The sulfide deposits occur in a pillow lava and dyke sequence peripheral to the plutonic basic and ultrabasic rocks of the Troodos Massif. An outcrop length of about 550 km was sampled along 20 traverses at right angles to the strike over a total traverse length of 93 km.

There is a significant regional variation in trace elements: Cu decreases away from the Troodos Massif and Zn increases. Most of the known deposits lie in low Cu (<65ppm) zones with high Zn (>65ppm) and generally enhanced Co contents.

The difference in the element concentration in the vicinity of mineralization relative to background is small and single element anomalous patterns extend a maximum of several tens of metres from mineralization. Significant differences in

populations, however, can be detected as much as 135m stratigraphically above mineralization. LDF (linear discriminant functions) were calculated for a variety of combinations of Cu, Zn, Co and Ni and a program was developed to calculate discriminant scores for individual samples (Govett 1972).

THE UNIVERSITY OF NEW BRUNSWICK Rock Geochemistry

Following my appointment to the Department of Geology in September 1968 rock geochemical studies were undertaken on five Palaeozoic Zn-Pb (Cu) massive sulfide deposits in northern New Brunswick. A total of 115,000 analyses were performed on 13,000 rock samples from the environs of the Heath Steele B and ACD zones, BMS (Brunswick Mining and Smelting) No. 12, Caribou and Key Anacon sulfide deposits. In all cases significant anomalies were defined.

The variation in Pb and Zn contents in relation to the 50% probability line between anomalous and background conditions (calculated by LDF with Pb and Zn as variables) was essentially the same at BMS No. 12, Heath Steele ACD zone and the Caribou deposit, but at Heath Steele B zone the corresponding 50% probability line was at right angles to that at the other three deposits. Wahl (1978) concluded from these and other data that the Heath Steele B zone was a distal deposit whereas the others were proximal deposits. The major elements also define halos related to proximity to mineralization.

Goodfellow & Wahl (1976) investigated water-soluble Na, K, Ca, Mg, F, and Cl as well as pH and conductance at BMS No.12 and Heath Steele B zone. They found halos comparable to total Pb and Zn halos at both deposits.

On a regional scale (one sample per 5 km² over an area of 2,000 km²) in the Bathurst region of New Brunswick, the ore elements give the best patterns relating to mineralization (Govett & Pwa 1981). This is different from the mine scale where the major elements give the clearest anomalies.

Formation of Anomalies

An underlying theme in the majority of research projects was the problem of formation of anomalies. Sato & Mooney (1960) showed that the generation of self-potential patterns around sulfide bodies was due to Eh differences in solutions in contact with the orebody. Accordingly, some simple tank experiments were carried out that clearly indicated the possibility of an electrochemical mechanism for metal dispersion (Govett 1973b).

More sophisticated tank experiments led to electrochemical hypotheses on metal zoning in sulfides (Govett & Whitehead 1974) and a proposed model for the surface expression of ionic species that have migrated under the influence of electrical currents around a sulfide body (Govett 1976; Govett *et al.* 1976). The greatest concentrations were predicted to occur where the current density is greatest (at the margin of a conductor) with relatively low values over the conductor where the current density is least. The characteristic double peak was termed a "rabbit-ear anomaly" (Govett 1976).

Whitehead (1973) identified Mn halos in the iron formation overlying the Heath Steele B zone and showed that there were both vertical and lateral variations in Mn:Fe ratios. This was one of the first demonstrations of redox controlled dispersion that extended laterally on the paleo-seafloor for several km from the sulfide deposit.

At the White Lake Cu-Zn sulfide deposit (near Flin Flon, Manitoba) no geochemical signature had been obtained from conventional soil geochemistry. Where the deposit is overlain by 23m of barren rock and 8m of glacial overburden including an upper 1m of impermeable varved clay, a strong characteristic rabbit-ear H⁺ anomaly clearly indicates the location of the orebody, as predicted by the electrochemical model (Govett 1976).

THE UNIVERSITY OF NEW SOUTH WALES

In Australia a number of studies demonstrated extensive rock geochemical

halos similar to those of massive sulfides in Canada (e.g., Fedikow & Govett 1985).

The very thick and electrically highly conductive weathering residuum in Australia limited the use of conventional geochemical techniques. Nevertheless, the Elura Zn-Pb-Ag massive sulfide body in New South Wales showed trace element, H⁺ and conductance patterns in the A and B horizon soils over more than 100m of overburden similar to those found in Canada (Govett *et al.* 1984).

The last Govett PhD student from the UNB proposed a modification of the Govett electrochemical model (Smee 1983). This was adopted to interpret the results at Elura whereby the current density will be greatest at the base of the most conductive zone (which is at the base of the totally weathered zone at Elura). The current flow will be essentially horizontal before plunging vertically to the top of the margins of the sulfide body. Therefore, the greatest movement and concentration of cations will be at the base of the most conductive zone and at the margins of the sulfide body.

Cambro-Ordovician altered meta-rhyolitic pyroclastics are host to the Thalanga Zn, Pb and Cu massive sulfide deposit in Queensland (Govett & Atherden 1987). Beyond the sub-outcrop gossan zone mineralization is covered by up to 70 m of Tertiary horizontal terrestrial sandstones, conglomerates and siltstones (Campaspe beds).

Soil samples taken at a depth of 2-5 cm showed that where there is only one metre of Campaspe beds the anomalies are as expected: very strong Pb and Zn, distinct but low Cu, rabbit-ear conductance, and a triple peak H⁺. This pattern gradually changes with increasing thickness of Campaspe beds and where there is 50 m of Campaspe beds the Zn anomaly remains strong, there is no Pb anomaly, the Cu anomaly is distinct but low, and there is a well defined rabbit-ear H⁺ anomaly. EDTA-soluble Zn has exactly the same pattern as total Zn.

The interpretive dilemma at Thalanga is the same as at Elura and elsewhere, i.e., how to account for the surface anomaly.

The greatest movement and concentration of cations will be at the margins of the sulfide body along the base of the Tertiary Campaspe beds that are more conductive than the host rocks by virtue of their saline pore water. The presumption of upward diffusion of ions over great thicknesses of overburden to form surface anomalies that has been relied upon for so long is probably fatally flawed. It seems to be singularly unlikely that ions would move by diffusion in a straight vertical line to give surface anomalies immediately above an ore zone. Moreover, whatever the process, it has to be dynamic and continuing to give a precise anomaly in the top 2-5cm of soil overlying 50 m of Tertiary sediments that overlie the Thalanga sulfide deposit.

Long after the above work on electrochemical element migration described above was published, Hamilton (1998) pointed out that Govett (1976) and Bølviken & Løgn (1975) had described an electrolytic cell (which would not work as described) rather than a voltaic cell that should work. Hamilton was, of course, correct. I have passed over to him some unpublished data on Thalanga and I look forward to his interpretation of the dispersion patterns there.

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Firstly, I must thank Dr W.D. Goodfellow for suggesting that I write this up. I wish to thank UNB Emeritus Professor A.L. McAllister for my appointment to the department of geology and for supporting my unconventional approach to academic research. I must also extend my gratitude to dozens of research students at UNB and UNSW whose own research underpinned anything that I may have achieved.

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Controls on silver distribution in the Main Zone of the 2.68 Ga Hackett River Zn-Pb-Cu-Ag volcanogenic massive sulfide deposit, Nunavut, Canada

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ABSTRACT: The Main Zone of the Hackett River volcanogenic massive sulfide (VMS) deposit, within the Hackett River Greenstone Belt of the Slave Craton, is highly enriched in Ag. Of the total Ag, 79.4% is contained within Ag-rich freibergite (the Sb-bearing end-member), whereas chalcopyrite hosts 6.3% and galena 1.8%. Trace Ag-bearing minerals such as electrum, stephanite, acanthite and Bi-bearing sulfides host the remainder of the Ag and have a limited spatial distribution within the deposit. As constrained by the mineral assemblages, low-temperature and relatively oxidizing conditions favour partitioning of Ag into freibergite, whereas more reducing conditions favour partitioning of Ag into galena. At high temperatures (>250°C) and highly reducing conditions, Ag is enriched in Ag-Bi-Se-rich galena and other Bi-bearing sulfides whereas under less reducing conditions, Ag is concentrated in chalcopyrite. The principal controls on silver residence in the Hackett River Main Zone therefore are temperature, fluid redox conditions and the Bi and Sb content of the hydrothermal fluid available for coupled substitution with silver. The mineralization likely formed during sub-seafloor replacement of the host volcanic and volcanoclastic rocks with subsequent pervasive recrystallization of mineralization during amphibolite grade metamorphism. Deposit-scale zone refining resulting from dissolution of previously precipitated sulfides and subsequent re-precipitation due to interaction with circulating hydrothermal fluid is the most important control on the distribution of Ag.

KEYWORDS: *silver, VMS, freibergite, zone refining, redox*

INTRODUCTION

Volcanogenic massive sulfide (VMS) deposits are an important global resource for Ag. In Canada, VMS deposits are the principal source of Ag accounting for 52% of total production and 56% of measured and indicated reserves to 2006 (Lydon 2007). The Hackett River Zn-Pb-Cu-Ag VMS deposit is located within the Hackett River Greenstone Belt of the Slave Craton (Fig. 1) and is enriched in Ag (up to 3000 g/t). The Hackett River deposits rank at the 90th to 95th percentile for Ag grade in the global inventory of VMS deposits (Franklin et al., 2005). The Hackett River Main Zone (HRMZ) grades 127 g/t Ag, 0.30 wt. % Cu, 4.67 wt. % Zn, 0.75 wt. % Pb and 0.50 g/t Au for the stratigraphically higher massive sulfide lens and 65 g/t Ag, 0.91 wt.% Cu, 0.87 wt.% Zn, 0.11 wt.% Pb and 0.38 g/t Au for the stringer sulfides stratigraphically beneath the sulfide lens

(Wardrop 2006).

In this study, field, petrographic, bulk geochemical and mineral chemical data are presented with the aim of elucidating the mineralogical residence and spatial distribution of Ag within the HRMZ. A mass balance was calculated for Ag from electron microprobe analyses of sulfide minerals relative to bulk assays for the Main Zone deposit previously published by Wardrop (2006) for Sabina Silver Corporation.

GEOLOGICAL SETTING

The Hackett River VMS deposits are hosted within the Ignerit Formation and are part Yellowknife Supergroup within the Slave Craton. The Ignerit Formation consists of highly silicified felsic volcanic rocks of calc-alkaline affinity that are intercalated with discontinuous lenses of calc-silicate that are interpreted to be tuffs

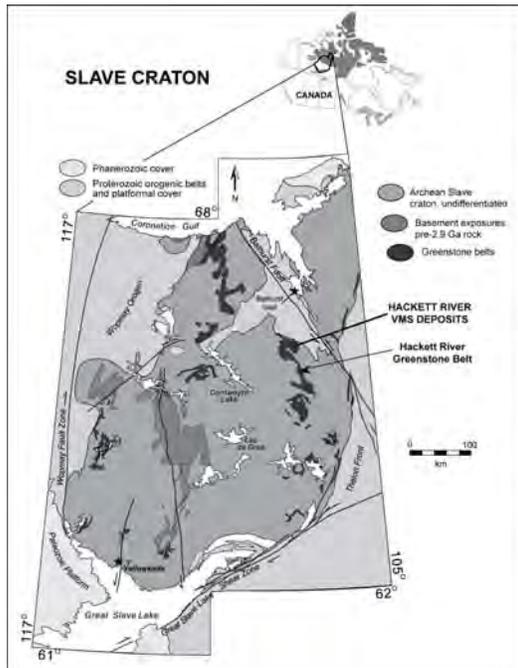


Fig. 1. Simplified geology of the Slave Craton and location of the Hackett River VMS deposits within the Hackett River Greenstone Belt (modified after Bleeker *et al.* 2007).

that have been carbonate altered and subsequently metamorphosed to amphibolite grade.

MINERALIZATION

The HRMZ consists of a semi-massive to massive sulfide lens with underlying copper-rich sulfide stringer mineralization. The deposit has been folded into an upright, relatively open south-plunging synform with a central barren massive pyrite and pyrrhotite core coincident with the NW-SE synformal axis through the approximate centre of the deposit. Our work indicates five different mineralization types within the HRMZ: 1) disseminated footwall sulfides of chalcopyrite, pyrrhotite and pyrite, 2) stringer mineralization containing chalcopyrite, Bi-Ag-Pb-bearing sulfides, pyrite, and pyrrhotite with trace galena and sphalerite, 3) pyrite-poor mineralization of sphalerite – pyrrhotite – chalcopyrite and freibergite [(Ag,Cu)₁₀(Fe,Zn)₂Sb₄S₁₃] located at the top of the stringer zone, 4) calc-silicate hosted sphalerite, pyrite, chalcopyrite, freibergite,

pyrrhotite, and galena, and 5) sphalerite-pyrite-galena and freibergite mineralization within the semi-massive to massive sulfide lens.

SILVER DISTRIBUTION

Compared to the bulk Ag content, 32% of the Ag in the HRMZ resides in type 5 mineralization with 31% of the Ag in type 4 and 29% within type 3 mineralization. The remainder of the Ag (8%) is hosted within type 2 stringer mineralization. Type 2 was split into subtypes 2a and 2b to differentiate between Cu and Cu-Bi enrichment, respectively.

Freibergite is the dominant host for Ag in the HRMZ, wherein Ag concentrations increase stratigraphically upwards with 99% of Ag hosted by type 5 mineralization (Table 1). Silver-bearing chalcopyrite contains 40% of the Ag in type 2a mineralization and 13% in type 3 where chalcopyrite contains up to 7.29 wt.%. Within both freibergite and chalcopyrite, Ag directly substitutes for Cu in the mineral lattice. Freibergite within the HRMZ is also consistently enriched in Ag (21.9 to 38.5%) compared to many other VMS deposits (e.g. Kidd Creek; Hannington *et al.* 1999, Heath Steele; Chen & Petruk 1980, Rosebery; Huston *et al.* 1996).

Silver occurs within galena by coupled substitution with Bi and to a lesser extent with Sb. Minor Ag-bearing minerals contribute significantly to the overall mass balance: matildite (AgBiS₂) and Bi-Ag-Pb sulfides of the lillianite-gustavite homologous series (Pb₃Bi₂S₆- PbAgBi₃S₆) are important Ag hosts within type 2b mineralization, whereas stephanite (Ag₅SbS₄) is an important host for Ag within types 2a and 3. Electrum was only documented in calc-silicate type 4 mineralization, where it has a high Ag:Au ratio of ~1.94:1.

DISCUSSION

The distribution of Ag within the HRMZ is a product of large-scale zone refining involving the redistribution by dissolution of lower temperature (<250°C) Pb-Zn-Ag

MINERAL	AG BUDGET (%)
Freibergite	79.4
Chalcopyrite	6.3
Galena	1.8
Electrum	3.4
Stephanite	3.6
Matildite	2.9
Bi-Ag-Pb sulfides	1.3
Other	1.3

Table 1. Mass balance of silver in minerals from the Hackett River Main Zone relative to the Ag bulk assays from Wardrop (2006).

minerals and reprecipitation of minerals by higher temperature (>300°C) hydrothermal fluids containing elements such as Cu, Se and Bi (Eldridge *et al.*, 1983). Minerals precipitated under the more reduced and higher temperature conditions (mainly chalcopyrite) were introduced into the HRMZ footwall stringer zone at the base of paragenetically earlier, lower temperature mineralization. A distinct high-temperature suite of Cu, Bi, Te, and Se is concentrated in the lower portion of the deposit and is particularly associated with the fluid upflow conduit (mineralization type 2b) where maximum temperatures and most reducing conditions occurred. Trace galena from mineralization type 2b contains up to 5 wt. % Se, 2.1 wt.% and 1.2 wt.% Ag. Incorporation of Se into galena is indicative of highly reduced conditions and is the only expression of elevated Se within the HRMZ. The mutual occurrence of Bi-Ag-Pb sulfides with the Se-Bi-Ag enriched galena also indicates precipitation from reduced, high-temperature (>300°C) fluids (e.g. Marcoux *et al.* 1996). Chalcopyrite is an important host for Ag only at higher temperatures, under more reducing conditions and in the lower portion of the HRMZ deposit.

The hydrothermal fluid migrated outwards and upwards from the higher-temperature stringer zone replacing an earlier low-temperature sulfide assemblage composed primarily of sphalerite and galena. The leading edge of this replacement is marked by a chalcopyrite mineralization front within mineralization type 3 at the base of the sulfide lens. Mineralization type 3 is a thin, <1 m reaction front separating mineral

assemblages that record a change in mineral precipitation conditions from high-temperature and more reduced to less reduced and cooler hydrothermal fluids stratigraphically up-wards. In addition to elements with a mutual lower temperature affinity (Pb, Zn, Sb, Cd and Hg), Ag released by the dissolution of earlier, lower temperature mineral assemblages was transported by evolving fluids upward during zone refining and reprecipitated in the upper and lateral parts of the HRMZ system.

An increase in oxidation state stratigraphically above mineralization type 3 is indicated by the presence of lesser amounts of pyrrhotite and chalcopyrite and increasing replacement of pyrrhotite by pyrite. Precipitation temperatures also decreased as shown by increasing amounts of sulfides stable only at lower temperatures (<250°C). The Ag content of galena decreases as the amount of Ag within freibergite increases. This is due to higher amounts of Bi within the hydrothermal fluid under more reduced conditions that increase the content of Ag in galena by coupled substitution with Pb (Amcoff 1984). Under more oxidizing conditions (and lower temperatures), the amount of Sb relative to Bi increases and Ag is preferentially incorporated into Sb-rich freibergite. This is also a reflection of increasingly more oxidized conditions stratigraphically higher in the HRMZ.

CONCLUSIONS

The major minerals that host Ag within the Main Zone deposit are freibergite, chalcopyrite and galena with trace Ag-bearing minerals such as electrum, stephanite, acanthite and Bi-bearing sulfides hosting the remainder of the Ag. Bulk Ag contents increase upwards and laterally within the HRMZ above mineralization type 3, and this is likely an artefact of zone refining and transport of Ag by increasingly oxidized and cooler fluids distally from the high temperature upflow zone. Low temperature and more oxidizing conditions favoured partitioning of Ag into freibergite in the upper portion of the HRMZ, and less oxidizing

conditions favoured galena as a host. At higher temperature, the most reducing conditions favoured Ag incorporation into Ag-Bi-rich galena (plus Se) and Bi-bearing sulfides or Ag-rich chalcopyrite under slightly less reducing conditions below the base of the massive sulfide lens.

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3-D element patterns above deeply buried mineralization: new evidence and insights into electrical dispersion

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ABSTRACT: Subsurface geochemical data from the Thalanga Pb-Cu-Zn prospect in Australia demonstrate that 'rabbit-ear' geochemical anomalies in areas of thick cover can have a distinct 3-D character extending from mineralization to ground surface. The pattern suggests dispersal in cover materials by 'redox-induced spontaneous polarization' at the edge of an inferred reduced chimney. Redox gradients at the margins of reduced chimneys are horizontal. Grains of semiconductive minerals in overburden will electrically polarize in these gradients developing negative poles in the positive redox direction, i.e. outward from the chimney. Voltages from multiple grain-dipoles configured end-on will be additive and a macroscopic, negative-outward electrical field will result. Current will move inward and in a donut-shaped current distribution will wrap downward toward ore and then outward from the reduced chimney in deeper areas where the redox gradient is weakest. Cations of ore-forming elements will be induced out of the reduced chimney and upward toward surface to complete the electrical circuit. Elements such as Pb and Cu will be partly attenuated as they move out of the reduced chimney. Zn, which has only one oxidation state will be attenuated least and will have the largest dispersion halo.

KEYWORDS: *Dipole, reduced chimney, SP, soil geochemistry, redox, Thalanga*

INTRODUCTION

In the 1960s and 1970s the use of soil geochemistry in mineral exploration led to the discovery of the now commonly observed twin-peak or 'rabbit-ear' geochemical anomaly (Govett 1976). From the time rabbit-ear anomalies were first described they were attributed to electrochemical processes but the theory proposed at that time could only adequately account for these features where deposits were buried under just a few metres of cover. However, subsequent case studies continue to demonstrate that such patterns and other evidence of electrochemical processes in soils persist as overburden thickens, even as the responses diminish in magnitude.

One of the early case studies with convincing evidence of electrochemical processes over deeply buried mineralization was carried out on the Thalanga Pb-Zn-Cu prospect in Queensland, Australia (Govett & Atherden 1987). That study showed strong rabbit-ear responses in surface soils in commodity elements and elevated H⁺ in

the same soils, despite the deposit being buried by up to 50 m of exotic cover. Previously unpublished subsurface geochemical data for one of the lines at Thalanga have become available that demonstrates the surface anomalies have a 3-dimensional character. This paper describes some of these data and interprets them in the context of recent ideas on electrochemical dispersion above ore deposits.

ELECTRICAL DIPOLES AND CURRENT DEVELOPMENT AROUND CONDUCTIVE ORE-BODIES

It was known for most of the last century that metallic ore bodies electrically polarize when in contact with country rock with non-uniform oxidative properties (Schlumberger 1920), and that this often results in measurable spontaneous electrical potentials (SP) on surface. Sato & Mooney (1960) argued that universally more oxidizing conditions above the water table result in the development of a cathodic pole to the upper portion of any metallic ore body that crosses it. The

upper ore becomes negatively charged due to the upward movement of electrons from reducing agents (electron donors) in groundwater at depth, toward oxidizing agents (electron acceptors) in the shallow environment. In order to maintain electrical neutrality a return current occurs in the groundwater electrolyte around the ore body. Current in the ore body occurs as electron movement and thus can only occur in ores that are electronic conductors or semi-conductors, such as pyrite or graphite. Current in the country rock is due to ionic conduction. This involves the movement of mass and charge with cations moving upward toward the cathodic part of the ore and anions toward the anodic part at depth (Fig. 1).

Sato & Mooney (1960) pointed out that the oxidation of the conductor itself cannot be responsible for the SP phenomenon because it would oxidize locally in the upper part of the ore-body where oxidizing agents are in direct contact with the ore and there would be no separation of charge and therefore no SP phenomenon. The redox reactions that produce SP therefore occur between reactants in the groundwater environment at the top and bottom of the ore body. This cathodically protects the upper part of the ore body from direct oxidation. Oxidation of the ore body can still occur (hence gossans) but results from local 'detached' oxidation which cannot produce SP.

LIMITATIONS OF THE DIPOLE MODEL

Natural electrical dipole development around electronic conductors in the earth is theoretically sound, supported by experimentation and well documented through 100 years of field observation. However the problem with it is that it only describes a subset of cases where SP occurs over ore deposits. It cannot account for cases where voltages exceed c. 500 mV (Sato & Mooney 1960) and these are not rare. There should also be no response at all over disseminated sulfides yet large porphyry deposits and other disseminated systems produce the largest SP responses so far documented

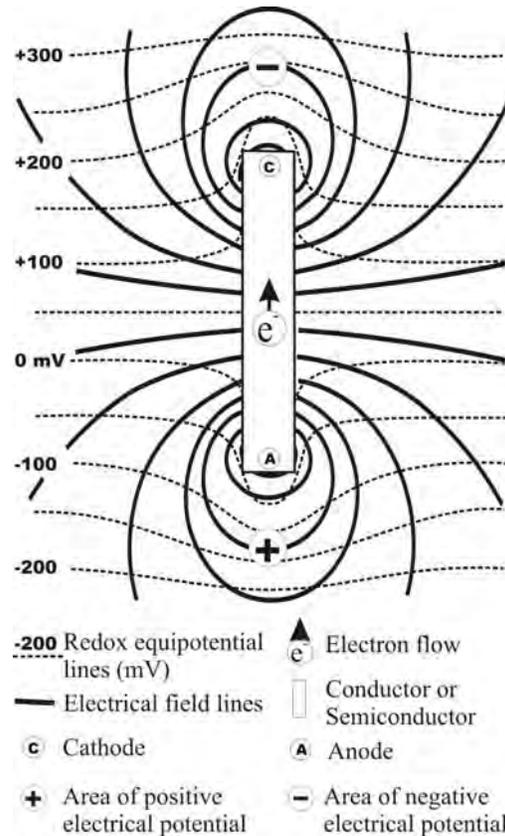


Fig. 1. Electrical dipole development around a conductor crossing redox equipotential lines. Positive current in the country rock (not shown) travels perpendicular to electrical field lines from the anode to the cathode (modified after Govett 1976 and Hamilton 1998).

with magnitudes commonly exceeding 500 mV (Corry 1985) and sometimes as high as several volts.

GEOCHEMICAL ANOMALIES WITH ELECTROCHEMICAL CHARACTER

In the 1970s, the dipole model was further developed to account for soil geochemical anomalies on surface above buried ore deposits (Govett 1976; Bolviken & Logn 1975). For the first time the current line and redox-equipotential distribution was illustrated (Govett 1976) and a modified version of that model is shown in Figure 1. This configuration was used to account for the existence of rabbit-ear geochemical anomalies in shallow soils. It was argued that the higher current densities at the top of the ore body would result in higher

concentrations of cations in soils on either side. In cases where thicker overburden cover was encountered, the vertical movement of cations to surface was explained by upward diffusion from these higher current areas. However, many subsequent studies have shown that this anomaly morphology is also characteristic of soil over deeply buried mineral deposits where it often exhibits discreet, high contrast anomalies that would not be expected to occur if diffusion were the vertical transport mechanism.

Govett & Atherden (1987) show Pb and Zn shallow soil geochemical data collected over the Thalanga Pb-Zn-Cu deposit. Four lines were sampled that represent burial depths of 0, 1, 30 and 50 m. The anomalies display a rabbit-ear pattern centred on the deposit regardless of overburden thickness. The magnitude of the anomalies diminishes with increasing cover and Pb diminishes more rapidly than Zn.

The Zn and Pb soil profiles for the Thalanga sample line with 50 m of cover are reproduced in Figures 2 and 3. The lower half of each figure, respectively, are previously unpublished data showing the subsurface Zn & Pb distribution in the Tertiary clastic sedimentary rocks (the Campaspe Beds) covering the deposit. Samples were collected in the early 1980s by rotary-air-blast (RAB) drilling and analysed by near-total digestion according to methods reported in Govett & Atherden (1987). The subsurface data were not published at that time for reasons of company confidentiality. They confirm what the surface transects had suggested, i.e. that the rabbit-ear morphology has a 3-dimensional character. This explains why the surface soil anomaly morphology remains largely intact, albeit of a lower magnitude, as overburden thickens.

REDOX-INDUCED SPONTANEOUS POLARIZATION

The 3-D results at Thalanga suggest that electrochemical processes are not only occurring in bedrock and basal overburden, but also throughout the entire sequence of cover materials to surface.

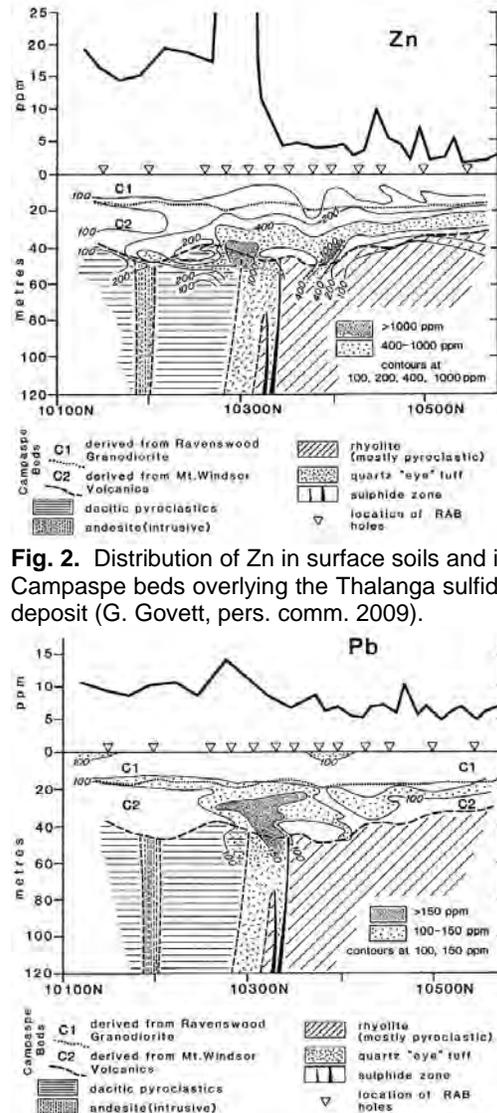


Fig. 2. Distribution of Zn in surface soils and in Campaspe beds overlying the Thalanga sulfide deposit (G. Govett, pers. comm. 2009).

Fig. 3. Distribution of Pb in surface soils and in Campaspe beds overlying the Thalanga sulfide deposit (G. Govett, pers. comm. 2009).

Dipole development around a conductor immersed in an electrolyte with uneven oxidative properties is scale independent. Even tiny conductive or semi-conductive mineral grains in overburden will develop dipoles if there are redox differences across them. Almost all solids have some semi-conductive properties and therefore the nature of the conductive minerals is of less importance than the existence of a redox gradient. Large redox gradients in overburden contain polarisable minerals,

each of which will develop a tiny dipole with a negative electrical pole pointed toward the oxidizing end of the redox gradient. Since the dipoles are all pointed in the same direction and many are aligned end-to-end their voltages are additive in series resulting in a macroscopic electrical field with a negative (cathodic) end aligned toward the more oxidizing conditions. This has been referred to as redox-induced spontaneous polarization (Hamilton & Hattori 2008)

Reduced chimneys' have been documented over mineral deposits (e.g. Hamilton *et al.* 2004) and are inferred to occur almost everywhere. At Thalanga, the gossans and deep oxidative profile are evidence that oxidizing agents are being preferentially consumed over the ore, thereby forming a reduced chimney. At the margins of the chimney, redox-induced dipoles will be mostly sideways and negative-outward (Fig. 4), inducing cations to move inward and downward. Since the redox gradient at the edge of a reduced chimney is strongest on surface and diminishes with depth, the magnitude of the resultant horizontal dipoles also decreases. These weaker dipoles contribute to the inward current and further direct it downward. Farther down, near the oxidizing ore body, the redox contrast between the reduced chimney and the surrounding groundwater environment is low enough that no major dipoles form and the return current wraps upward to complete the electrical circuit.

As the return current moves outward

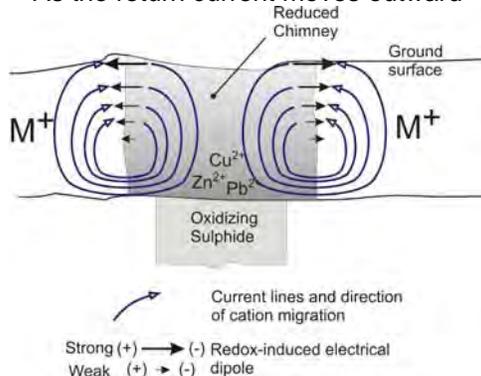


Fig. 4. Current distribution due to redox-induced spontaneous polarization at the margins of a reduced chimney.

and upward, the ore-related cations encounter increasingly oxidized conditions, which limit their mobility. Pb, the least mobile in oxidized environments, will attenuate first, followed by Cu. Zn, which has only one oxidation state, is not affected by the changing redox conditions and therefore travels the farthest and produces the largest dispersion halo.

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Lithogeochemical halos and vectors for ores in volcanic arcs and sedimentary basins

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ABSTRACT: Lithogeochemical halos and exploration vectors for a variety of volcanic- and sediment-hosted ore types are reviewed; including VHMS, SEDEX, BHT and orogenic gold deposits. Many deposits show two component halos; a regionally extensive distal halo which follows the favourable stratigraphy, and a more proximal cross-cutting texturally destructive halo immediately surrounding the deposit. For base metal ores the distal halos are defined by muscovite or carbonate alteration with Mn and Tl as the best pathfinder elements. For gold ores in sediments the distal halo is defined by pyrite and organic matter enrichment in the sediments and anomalous V, As, Mo, Se, Ni, Ag and Zn termed the VAMSNZ suite.

KEYWORDS: alteration, gold, VMS, sedex, VAMSNZ

VOLCANIC HOSTED MASSIVE SULFIDES

Volcanic-hosted massive sulfides (VHMS or VMS) have intense localised alteration zones and related halos that cut across the volcanic stratigraphy and provide obvious exploration targets. Mineralogical changes in both felsic and mafic volcanics involve proximal zoned alteration assemblages dominated by albite → sericite → carbonate → chlorite → quartz, and provide a clear vector to ores. Systematic compositional changes in key minerals, particularly sericite, chlorite and carbonate provide additional vectors. Use of the alteration box plot (Ishikawa AI versus CCPI) assists to discriminate diagenetic alteration from subtle to intense hydrothermal alteration, related to VHMS 1 (Gifkins *et al.* 2005; Fig. 1, Large *et al.* 2001a, b). Thallium and antimony are the best distal halo trace elements for the hanging wall of Zn-Pb-rich VHMS (Fig. 2), where they extend well beyond other halo indicators including Zn, Pb, S/Na₂O, Ba/Sr and Ishikawa AI.

SEDEX ZN-PB-AG DEPOSITS

Alteration halos may be regionally widespread, extending along the favourable stratigraphy for up to 15 km (Fig. 3). In the dolomite siltstone-hosted vent distal

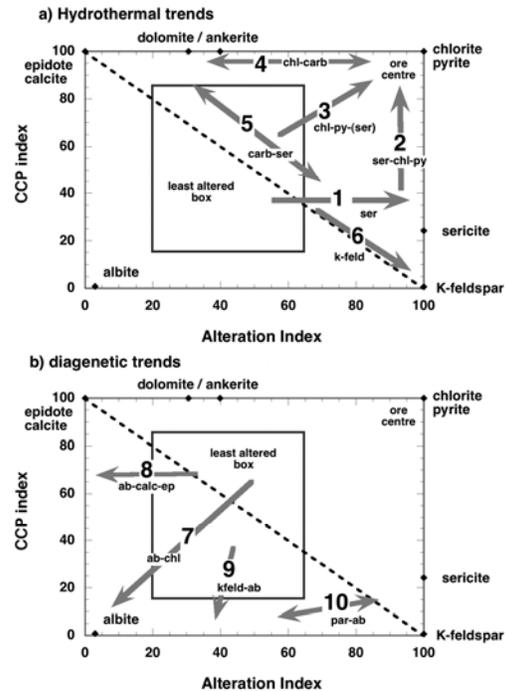


Fig. 1. Trends on the VHMS alteration box plot showing alteration related to (a) hydrothermal activity and (b) diagenesis.

SEDEX deposits of northern Australia (e.g., McArthur River, Century, Lady Loretta), the lithogeochemical halos extend several hundred meters into the overlying stratigraphy and several kilo-

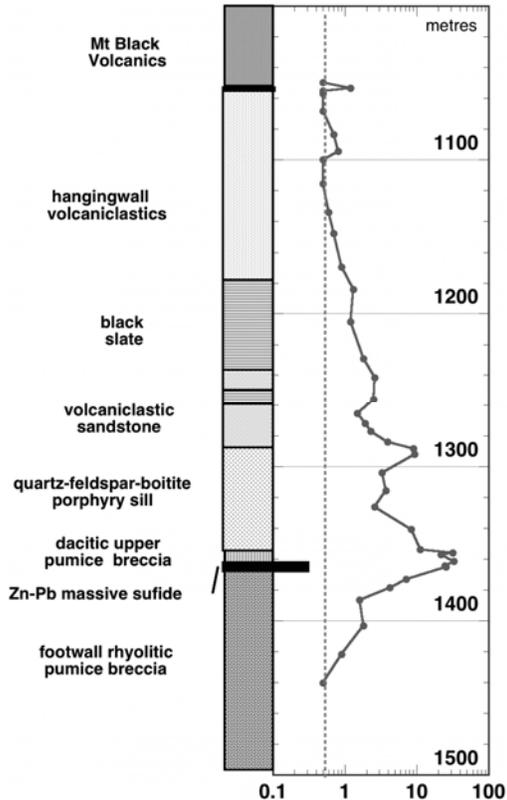


Fig. 2. Thallium halo to the Rosebery VHMS K-lens in drillhole 120R.

metres along the favourable stratigraphy away from the deposit (Broadbent *et al.* 2002; Large *et al.* 2001a, b; Large & McGoldrick 1998). The major mineralogical change in the alteration halo is the chemistry of the sedimentary and hydrothermal carbonate. Fe and Mn content of the carbonate commonly increases towards ore both across stratigraphy and along stratigraphy (Large *et al.* 2005). At Lady Loretta, the sedimentary carbonate zonation passing away from the deposits is, ore → Mn-siderite → Fe-Mn dolomite → dolomite. Century and McArthur river show similar patterns, although the siderite zone is absent at McArthur River. Turner (1990) and Goodfellow (2004) record similar zonation of carbonate minerals around the Tom and Jason deposits in the Selwyn Basin, Canada.

Chemical changes in sediments within the halo involve addition of FeO and MnO accompanied by depletion in MgO, CaO

and Na₂O. A SEDEX alteration index, based on these lithogeochemical changes, has been developed to assist mineral exploration (Large *et al.* 2000; Fig 4; Large & McGoldrick 1998). In sedimentary host rocks devoid of carbonate, the most common halo forming mineral is muscovite. Sullivan and the SEDEX deposits of the Anvil Camp in the Selwyn Basin all show widespread envelopes of muscovite alteration in the hangingwall sediments to ore (Carne & Cathro 1982; Lydon *et al.* 2000; Shanks *et al.* 1987). In addition to Mn, the other important lateral geochemical indicator that marks the favourable horizon, away from mineralisation is Tl. Thallium occurs at values of 100-1000 ppm through the Zn-Pb ores, and decreases systematically away from the deposit to values of less than 1ppm at distances of 1 to 20km along the favourable horizon (Large *et al.* 2000). Thallium is more useful as a geochemical vector than Zn and Pb because of its systematic spatial variations, compared with the erratic patterns shown by the latter. Other elements that may be enriched in the halo to SEDEX deposits are Ba, Hg, Sb, As, Ni, Bi and P (Leach *et al.* 2005). Carbon, oxygen and strontium isotopes of the calcareous sediments also hold potential as vectors to ore (e.g., Goodfellow 2000; Large *et al.* 2001a, b; Leach *et al.* 2005; Taylor *et al.* 2000).

BROKEN HILL TYPE (BHT) DEPOSITS

Walters *et al.* (2002) reports that alteration of meta-sediments and meta-volcanics surrounding BHT deposits is commonly defined by extensive zones of garnet spotting within the gneissic host rocks (e.g. Broken Hill, Cannington, Gamsberg). The ore lenses are commonly surrounded by quartz-Mn-garnet-rich zones that pass outwards into garnet spotted psammopelitic metasedimentary rocks. Rozendaal and Stumpfl (1984) record Mn-rich garnets over a distance of 1.5 km along strike from the Gamsberg deposit. The Mn content of garnet commonly increases towards the ore lenses. A characteristic package of altered metasediments and exhalites, including quartz gahnite rocks, thin

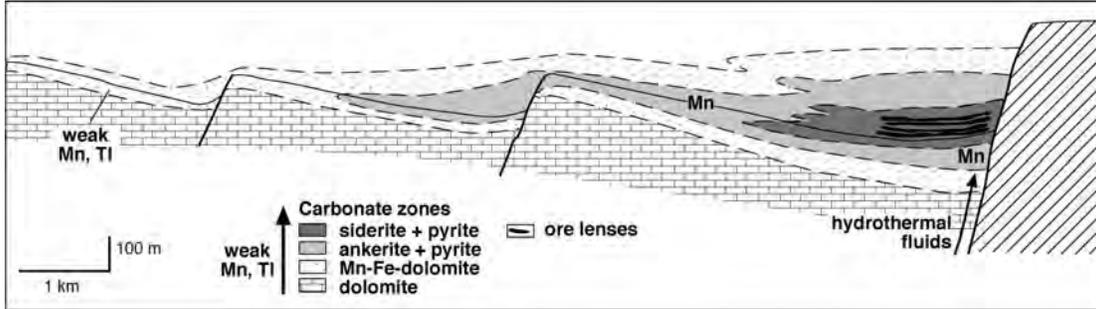


Fig 3. Regional stratiform alteration in dolomitic shales lateral to SEDEX Zn-Pb-Ag deposits.

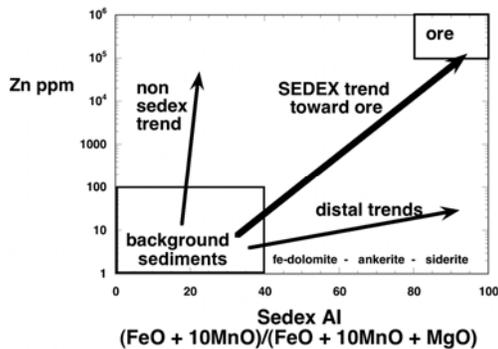


Fig. 4. Trends in sedex Al versus Zn.

banded iron formations and pegmatite with plumbian feldspar occurs along the favourable horizon away from the deposit (Walters *et al.* 2002). Geochemical studies show enrichment in Fe, Mn, K/Na ratio and Pb in the metasediments within the alteration halo, and depletion in Na, P, Ba and in some cases Ca, Mg and Al (Plimer 1979; Walters *et al.* 2002).

OROGENIC AU-AS DEPOSITS

Our recent research has defined two types of lithochemical halos related to sediment-hosted orogenic and Carlin type gold deposits. The first is a distal stratiform zone of regionally extensive carbonaceous sediments defined by anomalous V, As, Mo, Se, Ni, Ag and Zn, known as the VAMSNZ suite of elements. These define a lithochemical halo that may extend tens of kilometres along the favourable stratigraphy away from orogenic Au-As deposits. This suite of elements is concentrated, with gold, in organic matter and associated diagenetic pyrite, during sedimentation and diagenesis in anoxic to

euxinic environments (Large *et al.*, 2007). The second halo is more focussed around the gold deposit, and relates to fluid movement and gold up-grading associated with metamorphism and deformation. The inner zone is characterised by elevated As and Au, and the outer zone by carbonate spotting and muscovite alteration. This proximal halo varies from 50 to 200 m thick.

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Groundwaters in mineral exploration

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ABSTRACT: Groundwater is an important medium for geochemical exploration of many different styles of mineralization, including porphyry copper, volcanogenic massive sulfide (VMS), sandstone uranium, and gold. Groundwater recharges to depth, resulting in greater likelihood of interacting with buried mineralization than media used in surface geochemical methods, and thus providing a three-dimensional perspective. Advances in the understanding of ore formation processes, water-rock interaction and element transport/attenuation in the secondary environment are enhancing the efficacy of groundwater geochemical exploration. This paper describes key techniques and methodologies for sampling, analysis and interpretation of groundwater geochemical data, and provides two different approaches for use by industry: routine exploration and research approaches. New advances in analytical methods are providing new isotopic systems and improving the cost and speed of traditional isotopic techniques, which can greatly aid in interpretation of water sources, water-rock reactions and fingerprinting of ore sources. Case studies are presented for the use of groundwater geochemistry around a porphyry copper deposit in the hyperarid Atacama Desert of Chile, and VMS mineralization in a mature mining camp in Canada. This paper also summarizes key elemental associations for successful utilization of aqueous geochemistry in mineral exploration. The most successful aqueous-phase indicators of mineralization are those that are ore-associated and mobile in solution.

KEYWORDS: *groundwater, mineral exploration, deposit types, isotopes*

INTRODUCTION

Because many surface and near surface mineral deposits have been discovered, the challenge for mineral exploration is to find new, more deeply buried deposits, particularly in areas where thick cover exists and in mature mining camps (Cameron *et al.* 2004). Groundwater is proving to be a powerful mineral exploration medium because: 1) advances in analytical methods, in particular ICP-MS and, more recently MC-ICP-MS (multi-collector) have greatly lowered detection limits and have the potential to revolutionize the use of isotopes in geochemical exploration; 2) groundwaters recharge to depth so that there is potential to penetrate deeply into the earth's crust, so that unlike surficial geochemical methods, groundwater geochemistry offers the potential to explore into the third dimension and detect deeply buried mineralization; 3) groundwaters are chemically reactive with mineralization and host rocks, in particular where waters

are O₂-bearing; 4) groundwater flows away from the site of mineralization, providing a potentially broader exploration target than litho-geochemistry; 5) there is little sample preparation; and 6) for many species of interest in geochemical exploration, background concentrations are low, enhancing anomaly contrast.

Groundwater geochemistry is also proving to be a key tool in the interpretation of geochemical data from weak leaches of soils (Cameron *et al.* 2004). One of the difficulties of soil weak leaches is that interpretation of the results is hampered by poor understanding of metal-migration mechanisms (Goldberg 1998; Cameron *et al.* 2004). For example, recent work in the Atacama Desert of northern Chile has indicated that seismic pumping of groundwaters interacting with mineralization is a viable mechanism for producing significant anomalies in soils and gravels over porphyry copper mineralization (Cameron *et al.* 2002; Cameron *et al.* 2004) (Fig. 1).

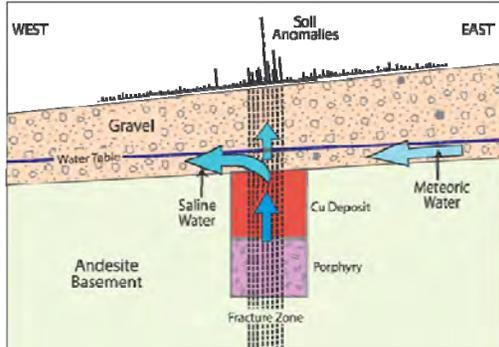


Fig. 1. Conceptual model for dispersion via groundwater flow after water-deposit interaction. This model also indicates the formation of soil geochemical anomalies from seismic pumping of groundwater.

Geochemical techniques for mineral exploration rely on the development of anomalies in the regional geochemical background. Critical to development of effective exploration strategies is an understanding of the mechanisms of anomaly development in different settings and for different sample media. In contrast to surface geochemical anomalies (dominated by mechanical dispersion), groundwater geochemical anomalies fundamentally develop by hydromorphic dispersion.

KEY CONSIDERATIONS

In some environments, such as northern Chile or parts of Australia, grid drilling is common, ideal for the purposes of groundwater geochemical exploration. Groundwater geochemistry is also practical in areas where domestic or agricultural wells already exist, and from springs and seeps that represent groundwater return to surface (indeed, stream waters generally represent shallow groundwater discharge). Groundwater from exploration drill holes provides additional data to litho-geochemistry; groundwater flow may provide geochemical vectors to mineralization even in an apparently barren hole. Sampling techniques range from simple down-hole bailers to complicated straddle-packer systems; the choice depends to a great extent on the objectives of the sampling program and the nature of the

hydrology.

A geochemical anomaly develops in groundwater by flow through mineralization; interpretation is greatly enhanced where there is information regarding the local and regional hydrology (Carey *et al.* 2003; Leybourne & Goodfellow 2003; Gilliss *et al.* 2004). Interpretation of hydrology is simplified in regions dominated by porous flow in unconfined aquifers, and significantly more complicated where flow is fracture-dominated, or where significant density contrasts between different groundwater flow systems exist (Carey *et al.* 2003).

A full understanding of groundwater geochemistry requires analysis and interpretation of the major ion composition. Major ions permit classification and interpretation of water type, mixing, evaporation, water-rock reaction and recharge. Although the major ion chemistry of waters in a hydrogeochemical survey should be interpreted and considered in conjunction with the trace metal data, owing to the complexities of water-rock reactions, cation exchange reactions and formation of secondary minerals, the major element chemistry of water should be used with great caution as an exploration guide in the absence of other (i.e., deposit-diagnostic) chemical data.

The degree to which a water sample will be anomalous with respect to proximal or distal mineralization depends on the solubility of the species that reflect that style of mineralization under the prevailing pH, Eh, and salinity conditions. Ideally, the geochemical explorationist would like any sample medium to have anomalies in all species that define the style of mineralization. In reality, this is rarely, if ever, the case. However, although waters and sediments will not necessarily have anomalies in all the relevant elements, it is important to understand why this is the case and avoid the temptation to include elements that are not diagnostic of the style of mineralization.

Traditionally, stable and radiogenic isotopes have not been used in routine mineral exploration programs. Use of

isotopes has been hampered by cost, additional requirements for sampling and perceived difficulties in data interpretation. Although this underutilization of isotopes in exploration is unlikely to change for large exploration programs, there are applications that warrant their incorporation. The light stable isotopes (e.g., O, H, S) can greatly assist in the interpretation of water sources, mixing and water sulfide interaction (Cameron & Leybourne 2005; Leybourne & Cameron 2006; Leybourne *et al.* 2006) (Fig. 2). In addition, advances in analytical methods in terms of detection limits, sample throughput and lower costs are such that some isotope systems may become as routine as ICP-MS elemental analyses are today. Isotopes of potential use in mineral exploration include the traditional stable isotopes (O, H, C, S), radiogenic isotopes (Pb, Sr), and non-traditional isotope systems, such as Fe, Se and Cu.

CONCLUSIONS

The following recommendations can be made with respect to the use of groundwater geochemistry in mineral exploration. There is a continued need for better integration of real aqueous geochemical data and thermodynamic modeling programs, in particular the incorporation of kinetic thermodynamics and adsorption to Mn and clay minerals. In addition, the thermodynamic databases for saline waters (greater than seawater) are limited with respect to most of the trace metals of interest to exploration. Accurate hydrological models are needed in a study area in order to connect surface aqueous geochemistry to groundwater flow and metal sources. In new areas or new styles of mineralization, orientation studies are important, in particular with a view to determining the elemental associations that are diagnostic of that style of mineralization. In these kinds of studies, emphasis should be placed on characterization of groundwaters (via wells, springs), surface waters and partial leaches of stream (and groundwater suspended) sediment. Determine the type of sampling apparatus to be used; routine

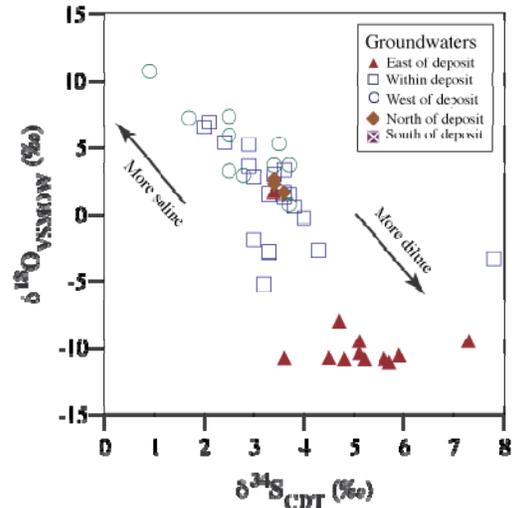


Fig. 2. Stable isotopes of S and O in groundwaters, Spence porphyry Cu deposit, Chile. These data are consistent with mixing between deep saline waters and regional dilute meteoric waters.

exploration may only require a flow-through bailer, whereas, more detailed studies will likely need some form of down-hole pump or straddle-packer system, particularly in fractured-rock media to provide optimal understanding of the redox state of the groundwater system. If resources permit, isotopic analyses can prove invaluable. In particular, Pb isotopes can be used to fingerprint metal sources and S isotopes (in both SO_4^{2-} and HS^- , as appropriate) can provide vectors to mineralization. Analytical methods are rapidly advancing in terms of technology and more rapid and cost-effective techniques. It is likely that isotopic analyses, such as Pb and S, will become cheap and routine in a small number of years. One of the great advantages of collecting groundwater samples during exploration is that the data is also critical in establishing local and regional geochemical baselines should the program be successful in finding mineralization and the decision made to initiate mining.

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Soluble ionic gold in soils

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ABSTRACT: Mobile Au in soil has been postulated for many years. It has been used by the mineral exploration industry in areas of transported overburden as a vector towards buried deposits. Until now, the nature of this mobile Au has not been known or investigated. Soil samples from a colluvial area above the Bounty Deposit (Yilgarn Craton, Western Australia) investigated by analytical techniques including laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and synchrotron x-ray fluorescence (SXRF) combined with X-ray absorption spectrometry (XAS) have allowed us to map the 'invisible' Au in these soils and suggests that at least some of it occurs in an ionic form.

KEYWORDS: *gold, synchrotron XRF, mineral exploration, ionic gold, Yilgarn Craton*

INTRODUCTION

For centuries Au was thought to be an inert (noble) metal dissolving only in highly aggressive solutions such as aqua regia or cyanide. However, over time it was postulated that metallic Au could also be dissolved in the natural environment by ligands such as thiosulphate, halogens and certain organic ions (Ong & Swanson 1969; Boyle 1979; Gray & Lintern 1998).

Recently, it has been shown that Au in soil can be dissolved using deionised water, the most benign of lixiviants (Gray *et al.* 1999). The reason for this is not clear: either (i) Au occurs in a soluble form within the soil, and/or (ii) deionised water is dissolving an adsorbed ligand in the soil such as cyanide that subsequently dissolves metallic Au. Notwithstanding these uncertainties, use has been made of this previously recognised soluble Au characteristic in soil by mineral exploration and analytical companies, to provide a possible vector towards mineral deposits.

The study of natural Au in soil has been hampered by low concentrations, typically in the ppb range. Investigating the presence of metallic ions has been made more difficult with very few traditional techniques that may be used (e.g. polarography, high voltage electrophoresis and ion chromatography). At the low concentrations of Au in soil, these

techniques may not have practical application at all. Here, we make use of SXRF to map Au in soil and demonstrate that some of the Au is ionic in form.

METHOD

Soil samples were collected systematically down a 2 m deep colluvial soil profile located over Au mineralisation at the Bounty Gold Deposit (Yilgarn Craton, Western Australia), prior to mining. Bulk samples were analysed by ICP-AES, ICP-MS and XRD and further sub-sampled and analysed to ensure that they contained detectable Au prior to detailed analysis by LA-ICP-MS, SXRF and x-ray adsorption near edge spectrometry (XANES).

Samples from the entire profile were analysed for 'soluble' Au using deionised water, iodide (0.1M KI) and cyanide (2000 ppm KCN) in a sequential digest using activated carbon to precipitate the Au (details of method found in Lintern & Butt (1992)).

Two samples from the soil profile were randomly separated into very small sub-samples (a few millimetres across) and analysed after *aqua regia* digestion to assess the heterogeneous nature of the Au distribution. Replicate sub-samples were analysed to assess the likelihood of finding Au in other soil particles using LA-

ICP-MS and SXRF. Based on low Au concentration variation for these sub-samples, further sub-samples of the remaining bulk material were mounted in epoxy resin to form discs (c. 2.5 cm in diameter) and polished for LA-ICP-MS, SXRF and XANES analyses

RESULTS

Water- (up to c. 20% of total Au), iodide- (c. 90%) and cyanide-soluble Au (100%) were recorded in all samples down the soil profile. Although the bulk sample Au-Ca correlation is strong down-profile, there is no correlation at the scale of soil particles. Soil particles with high Ca do not necessarily correspond with those high in Au. Critically, Au was present in all soil particles and the standard deviation in the results was acceptable with respect to the aims of the experiment. The results suggest that any soil particle of similar size from the two bulk samples may be investigated. We considered that Au concentrations were high enough (c. 600 ppb) and of sufficiently low variability (<20 % RSD) for the next stage of analysis by LA-ICP-MS and SXRF.

The Au and Ca LA-ICP-MS data for samples from the profile at Bounty indicate the following:

- (1) Au is highly variable but the samples containing the most bulk sample Au register the highest raw counts by LA-ICP-MS.
- (2) Sharp maxima suggest that some Au is particulate, and is not confined to one specific soil particle or location in the soil profile.
- (3) Ca concentrations are less variable and lack sharp maxima, suggesting that the distribution of calcite and/or dolomite is more uniform than Au.
- (4) Peaks in Ca and Au are uncorrelated.

SXRF maps reveal Au distributed throughout the specimen, with Au accumulations in certain areas. Gold is clearly associated with Br in some areas and potentially with other halides (which were not determined). XANES analysis suggests Au(I) speciation. Other areas of higher Au and Br show no correlation with each other.

The results confirm the hypothesis that some of the Au is ionic. This ionic Au appears to be associated with Br but other halogens or evaporites may also be present and play a role in complexing the Au. The results do not preclude the possibility that water is dissolving a ligand in the soil which in turn is dissolving and complexing other Au in the sample. Some Au in the soil appears to be metallic in form as nanoparticles.

Both inorganic and organic processes may be involved with Au mobilisation and precipitation. In laboratory studies, water and 0.1 M KI solutions are capable of dissolving substantial proportions of the Au in the profile at Bounty, although there are important differences in the Au dissolution response to the two lixiviants down-profile. Iodide-dissolved Au is closely correlated with total Au, whereas the proportion of water-soluble Au is greater (relative to iodide and total Au) near the top of the profile. This difference may reflect the relative ratios of ionic and non-ionic Au present in the sample. More water-soluble Au occurs near the surface and may be related to a greater mass of active plant roots, more micro-organisms or higher concentrations of organic compounds.

CONCLUSIONS

For many years, mineral explorers have been using soluble Au as vectors to mineralisation. The results described here may partly explain the nature of this soluble Au and increase our understanding of the processes that lead to its formation.

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Gold in pedogenic carbonate revealed

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ABSTRACT: Calcrete is an important sampling medium used for Au exploration in Australia and elsewhere. Until now, the form of the Au has not been identified *in situ* in calcrete even though concentrations have been in the hundreds of ppb. We present images generated using data derived from synchrotron X-ray fluorescence and X-ray adsorption near edge spectrometry that show the distribution of Au in pedogenic carbonate samples and demonstrate its correlation with Br. The images also show an association between Au and organic material in the carbonate sample that supports a previously proposed mechanism of Au accumulation in pedogenic carbonate that has been shown to occur through vegetation.

KEYWORDS: gold, vegetation, mineral exploration, Au-Br, calcrete

INTRODUCTION

Pedogenic carbonate of various forms (generically described as calcrete or caliche) has been sampled and analysed to locate Au mineralisation in Australia (Edgecombe 1997; Lintern *et al.* 1997; Lintern 2001; Drown 2003) and elsewhere. Trace amounts of Au are concentrated in calcrete occurring close to mineralisation and surficial regolith carbonates may even be anomalous for Au where mineralisation is buried beneath transported overburden (Bristow *et al.* 1996; Lintern 2007). The strong correlation of Au with alkaline earth metals (Ca, Mg, and Sr) in soil profiles is unexpected given the very different chemistries of Au to these elements and suggests that the processes leading to their co-location in the soil profile are similar. However, despite its importance to mineral exploration, various difficulties (e.g. the low concentrations) have hampered research on the detailed nature of the Au in calcrete.

METHOD

Samples were collected from a 2-m deep trench excavated prior to mining from the Bounty Gold Deposit in Western Australia. Bulk soil samples were analysed by ICP-

AES, ICP-MS and XRD, and further sub-sampled and analysed to ensure that they contained Au prior to detailed analysis by LA-ICP-MS, SXRF (synchrotron X-ray fluorescence) and μ XANES (X-ray adsorption near edge spectroscopy). Two samples from the trench were randomly divided into very small sub-samples (a few millimetres across) and analysed after *aqua regia* digestion to assess the heterogeneous nature of the Au distribution. Replicate sub-samples were analysed by ICP-MS to assess the probability of finding future Au in unanalysed soil particles using LA-ICP-MS and SXRF. Large sub-sample Au concentration variation would indicate a low probability of finding Au in other soil particles from the sample. As analytical variability for these sub-samples was low, further sub-samples of the remaining bulk material were mounted in epoxy resin to form polished discs (c. 2.5 cm in diameter) for LA-ICP-MS, SXRF and XANES analyses.

A LSX-200 Plus Laser Ablation System (CETAC Technologies, Omaha, Nebraska, USA), using a Nd:YAG laser with a wavelength of 266 nm, was used for the analyses. A spot size of 100 μ m was selected. Sufficient volume of ablated

material was required for Au to be detected. A 'trough' 100 μm wide and 2.5 cm long was left as the laser was tracked across the diameter of the discs.

SXRF imaging and XANES analysis were made at the PNC/XOR beamline at the Advanced Photon Source, Argonne National Laboratory (Heald. *et al* 2007) using photon energies of 17.0 and 12.5 keV for SXRF imaging and 11.8 to 12.1 keV for XANES analysis. XANES analysis across the Au L₃ edge used steps of 5 eV (from 11.82 – 11.89 keV), 0.5 eV (from 11.89-11.97 keV) and 0.07 k (from 11.97-12.1 keV) with a one second dwell per step.

SXRF imaging data were projected onto elemental images using the Dynamic Analysis method (Ryan 2000; Ryan & Jamieson 1993) in the GeoPIXE software package, which uses a standardless analysis approach (Ryan *et al.* 2005). The Dynamic Analysis method constructs a matrix transformation to deconvolute or 'un-mix' overlapping element lines and background to reconstruct separated elemental images with strong discrimination against interferences caused by overlapping lines and detector artefacts, such as tailing and escape peaks. In this work, it enabled the separation of Au L lines from interferences from W (L β , γ overlap with Au L α , β), Zn (K β overlap with Au L α), Yb (L γ overlap with Au L α), As (K α tails interfere with Au L α ; K β close to Au L β) and Br (K α tails interfere with Au L β). Spectra were extracted from selected regions of images and least squares fitted using GeoPIXE in order to verify in detail the accuracy of the deconvolution and the identification of important features such as the Au distribution.

RESULTS

The results show that Au is distributed throughout the specimens and ionic Au is partly associated with a root void and possibly filaments (rootlets) within the specimen. This is the first direct evidence for ionic Au in any regolith material and is consistent with Au mobilisation within the rhizosphere. Natural ionic Au species in

the weathered environment have only ever been reported before as dissolved Au in groundwaters or pore waters and as remnant Au-containing minerals. Ionic Au has been identified before in conjunction with so-called 'invisible' Au in arsenopyrites (e.g., Cabri *et al.* 2000; Xiaoqing & Zhonggang 2002).

XANES analyses show that ionic Au commonly occurs around cores of Au⁰ suggesting a dissolution-precipitation process, i.e. previously accumulated Au has been dissolved and is then dispersed into the surrounding soil; current observations are a snapshot of active processes. Gold is in part correlated with Br. However, the significance of the Br-Au association is unclear since other 'evaporites' such as chloride, sulphate or iodide that were not determined may be more significant. The Au-Br association may represent i) a simple Au bromide molecule, ii) a Au chloride molecule (with minor Br correlated with Cl), iii) a halogenated Au-organic complex or iv) a precipitation zone where saturation has been reached for a variety of salts that may include separate Au and Br ionic complexes. Any Au complex must be stable enough to survive the harsh and changing conditions in soil.

CONCLUSIONS

The results confirm the importance of biotic influences in the control of Au mobilisation in soil. Importantly, the results support the role that vegetation is playing in the formation of Au in calcrete anomalies by creating conditions in the rhizosphere that cause the precipitation of Au.

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Till indicator mineral and geochemical signatures of magmatic Ni-Cu deposits, Thompson Nickel Belt, central Canada

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ABSTRACT: The Geological Survey of Canada conducted a study around the ultramafic-associated Ni-Cu deposits in the northern Thompson Nickel Belt, Manitoba, Canada to document the indicator mineral and geochemical signatures of the deposits in till. Samples used in this study include archived till collected in 1996 and till and bedrock samples collected in 2005 and 2006. Ni-Cu mineralization indicator minerals identified in the study include pentlandite, pyrrhotite, sperrylite, chalcopyrite, pyrite, millerite and arsenopyrite. Indicators of potentially fertile ultramafic intrusions include chromite, Cr-diopside, forsterite, enstatite and Cr-corundum. Till geochemical pathfinder elements identified in this study include Ni, Cu, Pd, Pt, Co, As, Cd, Ag, Sb, Bi, Se, S, and Te. Six anomalous till samples from remote locations outside the Belt contain significant elevated concentrations of pathfinder elements and warrant further investigation. The Laurentide Ice Sheet flowed SW across the belt and subsequently W and exploration along the belt and in the surrounding terranes should consider both the older southwest and younger westward ice flow events when interpreting and following up till mineralogical and geochemical results.

KEYWORDS: *indicator minerals, till geochemistry, pathfinder elements, Ni-Cu exploration*

INTRODUCTION

Few case studies have been published for magmatic Ni-Cu-PGE deposits and even fewer that document the indicator mineral signatures of this deposit type. The Geological Survey of Canada (GSC) through its Targeted Geoscience Initiative 3, in collaboration with the Canadian Mining Industry Research Organization (CAMIRO) and the Manitoba Geological Survey (MGS) collected and analyzed a suite of bedrock and till samples from around the Thompson and Pipe ultramafic Ni sulfide deposits in the north part of the Thompson Nickel Belt (TNB), northern Manitoba, Canada (Fig. 1). The objective of the study was not to define the dispersal trains from each deposit. Instead sample sites were selected to characterize the geochemical and mineralogical signature of Ni-Cu mineralization at the deposit- and camp-scale at varying

distances down-ice and to define background.

GEOLOGICAL SETTING

The TNB is a 10 to 35 km wide belt of variably reworked Archean basement gneisses and Early Proterozoic cover rocks along the NW margin of the Superior Craton (Zwanzig *et al.* 2007). It hosts several world-class magmatic Ni-Cu deposits that have been strongly structurally and metamorphically modified. Nickel sulfide mineralization is associated almost exclusively with, or localized within, ultramafic bodies within the lower part of the Proterozoic rocks (Bleeker & Macek 1996). Primary (i.e., non-supergene) ores are dominated by pyrrhotite, pentlandite, pyrite, and millerite. Chalcopyrite, magnetite and ferro-chromite are ubiquitous minor phases (Layton-Matthews *et al.* 2007)

The most recent glaciation, during the Wisconsin, resulted in ice that flowed SW from an ice centre in Keewatin and then W from ice centred in Hudson Bay (Klassen 1986) (Fig. 1). Both ice flow events eroded and transported metal rich debris from the TNB deposits. In general, till across the region is thin (<3 m thick) and has a silty sand matrix. As the Laurentide Ice Sheet melted back 7800 years BP, the region was inundated by glacial Lake Agassiz for approximately 100 years, during which time rhythmically-bedded clay and silt were draped over bedrock and till, in places up to 40 m thick. As a result, the region is a flat lying clay plain comprising a relatively low relief, poorly drained landscape dominated by organic deposits with few bedrock outcrops. The TNB is the source of a well developed indicator mineral dispersal train best defined by Cr-diopside content in till that extends up to 300 km southwest of the Belt (Matile & Thorleifson 1997). The elevated Cr-diopside abundances in till overlying the TNB are accompanied by local occurrences of chalcopyrite, hercynite, chromite and loellingite in till proximal to the Ni deposits.

METHODS

Bedrock (5 kg) and till samples (15 kg) were collected across the northern TNB in 2005 and 2006, most closely spaced around the Thompson and Pipe Ni-Cu deposits. Till samples collected in 1996 (Matile & Thorleifson 1997) were re-analyzed as part of this study. Bedrock samples were collected from various lithologies within or adjacent to the TNB, and mineralized and unmineralized ultramafic intrusions. Till samples included sites at varying distances down-ice (SW and W) of the Thompson and Pipe mines. The <0.063 mm fraction of till was analyzed using aqua regia and lithium borate fusion/nitric acid digestions and inductively coupled plasma emission and mass spectrometry (ICP-ES/MS) techniques. Gold, Pt, Pd were determined by fire assay/ICP-MS. Bulk till and crushed bedrock samples were processed using a combination of tabling and heavy

liquid separation to produce ferro- and non-ferromagnetic heavy mineral concentrates. Indicator minerals were examined and counted in the 0.25 to 2.0 mm portion of the concentrates. Electron microprobe analyses were completed for chromite and olivine from till and bedrock, in addition to Cr-diopside, olivine and Cr-corundum from till samples.

INDICATOR MINERAL RESULTS

A well developed indicator mineral signature (1000s to 10,000s of grains) occurs in till proximal (<1 km) to sulfide mineralization. Ni-Cu mineralization indicator minerals include pentlandite, pyrrhotite, sperrylite, chalcopyrite, pyrite, millerite, arsenopyrite and loellingite. Of these minerals, chalcopyrite and sperrylite are the most likely to survive glacial transport and subsequent surficial weathering (Averill 2007) and thus will be the most useful for regional exploration. Indicators of potentially fertile ultramafic intrusions include chromite, Cr-diopside, forsterite, enstatite, and Cr-corundum. Chromite and Cr-diopside (> ~1% wt.% Cr₂O₃) in till are most abundant in till samples proximal to mineralization. Mineral abundance patterns for chromite, Cr-diopside, forsterite, and enstatite also indicate that some of these grains are derived from ultramafic rocks east of the TNB, some of which may warrant further investigation for their potential to host Ni-Cu mineralization.

The composition of chromite in bedrock ranges from ferrochromite (FeCr₂O₄) with >60 wt.% Cr₂O₃ to Cr-rich magnetite (Fe(Fe,Cr)₂O₄) with >10 wt.% Cr₂O₃. A second trend ranges from magnesian chromite ((Fe,Mg)(Cr,Al)₂O₄) with >60 wt.% Cr₂O₃ to spinel *sensu stricto* (MgAl₂O₄). A striking feature of the magnetite trend chromites is their elevated Zn content (>2 to 18 wt.% ZnO) that is restricted in occurrence to mineralized bedrock at the Thompson, Birchtree and Pipe mines and proximal (<500 m) till samples. Zn-rich chromite was expected as other researchers have reported its presence in TNB deposits (e.g., Paktunc & Cabri 1995), as well as other magmatic Ni-Cu deposits around the world (e.g.,

Peltonen & Lamberg 1991). The cause of Zn enrichment in chromite in the TNB ores is likely related to the high grade of metamorphism that has affected the belt. The Thompson mine is at the highest metamorphic grade (granulite) of all the deposits in the belt and so the most Zn-rich chromites are expected here. Ongoing research is focusing on determining potential source(s) of the Zn in the chromites and identifying other trace elements that may fingerprint chromite associated with mineralization through laser ablation ICP-MS studies and on olivine chemistry.

The bedrock source of the 10s to 100s of Cr-diopside grains in till across the region has not yet been found. In spite of the predominance of pyroxenites and peridotites in the TNB, remnants of primary Cr-diopside are scarce because most rocks have been metamorphically and metasomatically altered such that serpentine has replaced olivine and orthopyroxene and amphibole, chlorite, talc and carbonate has replaced clinopyroxene. Because the Cr-diopside source is unknown, their compositional range and relationship to Ni-mineralization cannot be determined.

TILL GEOCHEMICAL RESULTS

Ni-Cu ores in the TNB are dominated by pentlandite, pyrrhotite, pyrite and millerite (Burnham *et al.* 2003; Layton-Matthews *et al.* 2007) and thus local metal-rich till is Ni-rich (up to 3760 ppm). Till samples that contain the highest Ni contents also contain up to 50,000 pentlandite grains/10 kg in the 0.25-0.5 mm fraction. Till with elevated Cu values (215 ppm) at the Thompson and Pipe mines contain up to 2500 chalcopyrite grains/10 kg. TNB ore also contains Te, As, Sb, Co, Cd, Se and Bi-bearing mineral species, which are likely the source of elevated concentrations of these elements in till proximal to the deposits. A variety of PGE minerals occur in the ores, thus, it is likely that PGE minerals are the source of the elevated Pd (up to 98 ppb) and Pt (up to 13 ppb) concentrations in till. Sperrylite grains were recovered from nine till

samples collected near the Thompson and Pipe mines. The full suite of till pathfinder elements for Ni-Cu deposits in the TNB include Ni, Cu, Pt, Pd, Co, As, Ag, Cd, Sb, Bi, S, Se, and Te (McClenaghan *et al.* 2009). Using these pathfinder elements, six anomalous till samples in remote locations collected as part of the 1996 regional survey were identified. These samples are new exploration targets as they may indicate the presence of previously unknown Ni-Cu mineralization.

IMPLICATIONS FOR EXPLORATION

- Till mineralogy and geochemistry are useful Ni-Cu exploration methods in the TNB. Exploration should consider both the older SW and younger W ice flow events when interpreting till data.
- Elevated chromite and Cr-diopside (> ~1% wt.% Cr₂O₃) abundances combined with the presence of Ni-Cu sulfide minerals are strong indicators of potential Ni-Cu mineralization. Elevated Zn content (>2 wt.% ZnO) in chromite is only found in strongly mineralized rocks and is the strongest indicator for mineralization other than the actual ore minerals. Zn content in chromite from Ni-deposits in regions with lower metamorphic grade might be considerably lower and this feature thus does not have universal application.
- Chalcopyrite and sperrylite are the most useful metallic indicator minerals identified as they are the most likely to survive glacial transport and surficial weathering.
- Till geochemistry of <0.063 mm fraction is a useful tool for Ni exploration in the TNB and surrounding region. Pathfinder elements include Ni, Cu, Pd, Pt, Co, As, Cd, Ag, Sb, Bi, Se, S, and Te.
- Several multi-element (Ni, Cu, Pt, Pd, Co, Cr, As) anomalies occur in till samples in remote locations SW and W of the TNB that suggest presence of mineralized bedrock and warrant further exploration.
- For Ni exploration in the TNB and surrounding areas, till samples in thin drift areas can be collected from the flanks of bedrock outcrops, and from till exposures in road cuts and along lake shorelines and river banks. In areas of thicker cover, backhoe trenching and overburden drilling

could be utilized to obtain till below the potentially thick clay cover.

- Indicator mineral techniques are one of the main exploration methods for gold and diamonds in glaciated terrain. This case study has documented indicator minerals for Ni-Cu deposits. These minerals can be used in tandem with gold and diamond indicators to assess the mineral potential of broad regions and at local scales.

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Lithogeochemical exploration vectors for Au-rich volcanogenic massive sulfide deposits: Examples from the world-class Doyon-Bousquet-LaRonde mining camp, Abitibi Greenstone Belt, Canada

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ABSTRACT: The Doyon-Bousquet-LaRonde mining camp contains some of the best examples of Au-rich VMS deposits worldwide in terms of size and grade. These deposits are associated with tholeiitic to transitional mafic to intermediate rocks and transitional to calc-alkaline felsic rocks of the Bousquet Formation that define a continuous rather than a bimodal trend. The ore lenses are associated with two principal types of alteration assemblages that locally coexist: 1) a neutral propylitic quartz, biotite, Mn-rich garnet and sericite assemblage represented by gradual gains in MnO and losses in Na₂O and, 2) an aluminous assemblage comprising mainly aluminosilicates and quartz marked by an intense leaching of all major oxides. The characterization of each unit using immobile element ratios helps define the stratigraphy and target the most fertile horizons, whereas the presence and intensity of one or the two alteration assemblages provide effective vectors to ore.

KEYWORDS: *gold-rich, volcanogenic massive sulfide, alteration, vectors, Abitibi*

INTRODUCTION

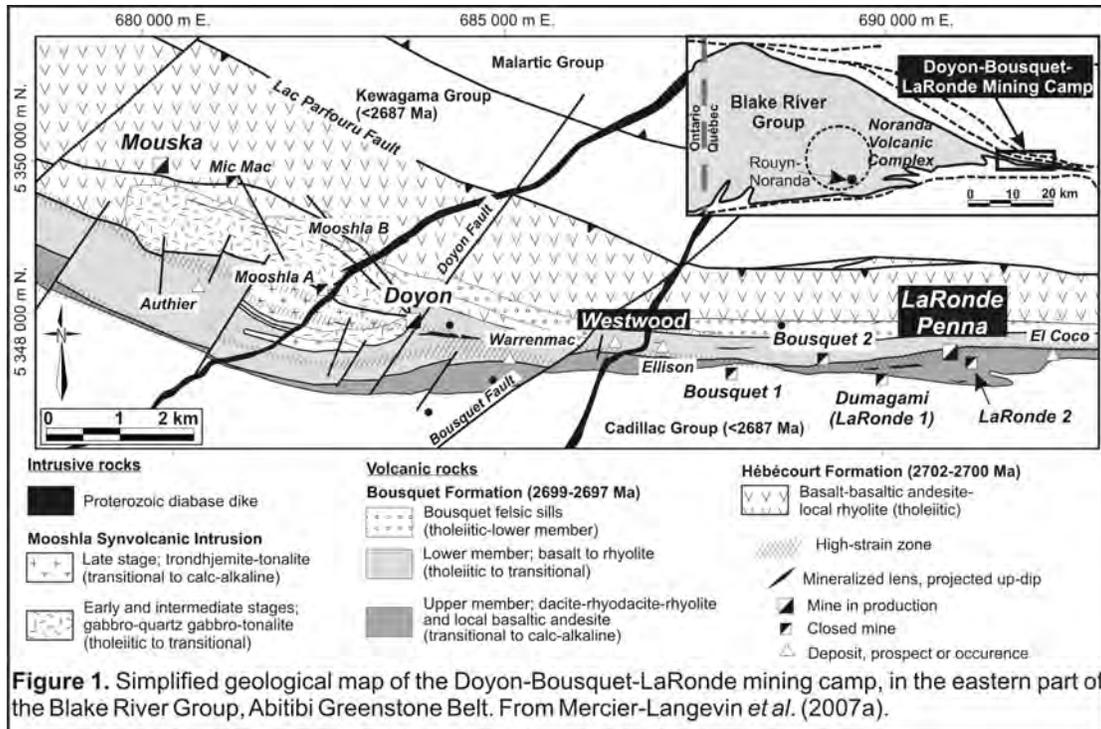
Gold-rich volcanogenic massive sulfide deposits (VMS) represent a prime exploration target as they commonly contain very large amounts of Au combined with significant quantities of base metals. Some of the world's best examples of Au-rich VMS deposits in terms of size and grade are located in the Doyon-Bousquet-LaRonde (DBL) mining camp in the Blake River Group of the Abitibi Subprovince (Fig. 1).

The VMS deposits of the DBL camp are associated with diverse styles of alteration assemblages that may coexist within the same deposit (Dubé *et al.* 2007). The variations in alteration style and intensity towards the numerous deposits and ore lenses of the DBL camp can be mapped using lithogeochemistry, which represents a powerful tool in characterizing prospective areas and stratigraphic horizons, and in vectoring towards mineralized zones, as discussed in the following sections.

GEOLOGICAL SETTING

The Doyon-Bousquet-LaRonde (DBL) mining camp deposits (~25 Moz Au) are hosted by the 2699-2697 Ma Bousquet Formation. The Bousquet Formation is part of the Blake River Group of the Southern Abitibi Greenstone Belt and comprises mainly intermediate to felsic, coherent and flow-brecciated volcanic rocks of transitional to calc-alkaline magmatic affinity cut by a synvolcanic tholeiitic to calc-alkaline polyphase intrusion (Mooshla pluton) and by mafic sills and dikes (Lafrance *et al.* 2003; Mercier-Langevin *et al.* 2007a). The Bousquet Formation now forms a steeply dipping, south-facing homoclinal sequence (Fig. 1). The main deformation event is responsible for some transposition and was accompanied by upper greenschist facies metamorphism that overprinted the primary hydrothermal assemblages (Dubé *et al.* 2007; Mercier-Langevin *et al.* 2007a).

The Au-rich polymetallic VMS deposits of the Doyon-Bousquet-LaRonde mining camp (Westwood, Ellison, Bousquet 1 and



2, Dumagami and LaRonde Penna; Fig. 1) consist of semimassive to massive sulfide ore lenses that formed on different stratigraphic horizons (stacking), in part by subsea-floor replacement of felsic flow breccia and mafic to intermediate sills and in part by exhalative activity during a single protracted synvolcanic hydrothermal event (Dubé *et al.* 2007; Mercier-Langevin *et al.*, 2007a).

The VMS mineralization of the DBL camp are associated with wide zones of discordant to semi-conformable neutral or propylitic, intermediate and advanced argillic style alteration that are thought to be the result of gradual mixing between seawater and magmatic fluids (Dubé *et al.* 2007; Mercier-Langevin *et al.* 2007a) generated in an intermediate setting between back-arc basin and volcanic arc environments (Mercier-Langevin *et al.* 2007b).

LITHOGEOCHEMISTRY

Host Rocks Signature

The mafic to intermediate and tholeiitic to transitional rocks of the Bousquet Formation are characterized by moderately enriched chondrite-normalized LREE and MREE patterns, flat HREE profiles and negative Nb, Ta, Zr, and Hf

anomalies. The felsic transitional to calc-alkaline rocks of the Bousquet Formation are characterized by high incompatible element contents, enriched LREE and flat HREE profiles, pronounced negative Nb, Ta, and Ti anomalies, and positive Zr and Hf anomalies (Fig. 2). These profiles can be compared to FI- and FII-type rhyolites of Leshner *et al.* (1986) (Fig. 2), highlighting the prospectivity of calc-alkaline felsic-bearing volcanic sequences for VMS, including those that are Au-rich. Contrary to many VMS-bearing sequences, the Bousquet Formation defines a continuous rather than a bimodal magmatic trend.

Each unit of the Bousquet Formation can be distinguished using ratios of hydrothermally immobile elements, helping define the stratigraphy in strongly altered, mineralized, and highly-strained areas of the DBL camp and target the most fertile stratigraphic horizons. The use of detailed lithogeochemistry helped demonstrate that the main polymetallic ore horizon of the Westwood deposit is at the contact between two distinct rhyolites and a basaltic-andesite unit, which is the lateral equivalent to the main ore horizon of the LaRonde Penna deposit (20 North lens, ~50 Mt) located about 5 km to the east, highlighting the potential for Au-rich

massive sulfide lenses in the western portion of the Bousquet Formation.

Alteration Zones and Vectors

The Au-rich VMS deposits of the DBL camp are associated with upper greenschist facies metamorphic assemblages that are derived from widespread synvolcanic hydrothermal alteration. There are two main styles of alterations developed in the vicinity of the ore lenses in the DBL camp: 1) a neutral or propylitic assemblage and, 2) an aluminous assemblage. These two assemblages can coexist within the same deposit as shown at the LaRonde Penna mine (Fig. 1). Along the 20 North lens, neutral alteration is associated with Au-Zn-Cu-Ag mineral-

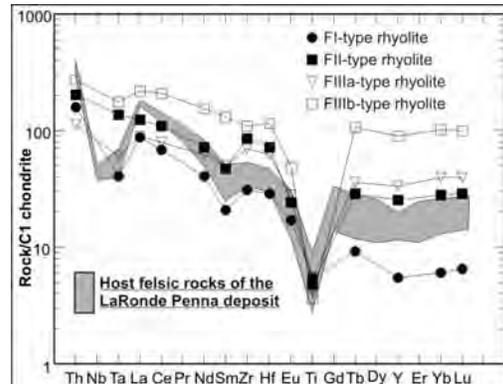


Figure 2. Chondrite-normalized REE-HFSE diagram of Archean F-type rhyolites against the pattern of the LaRonde host felsic rocks. From Mercier-Langevin *et al.*, 2007b).

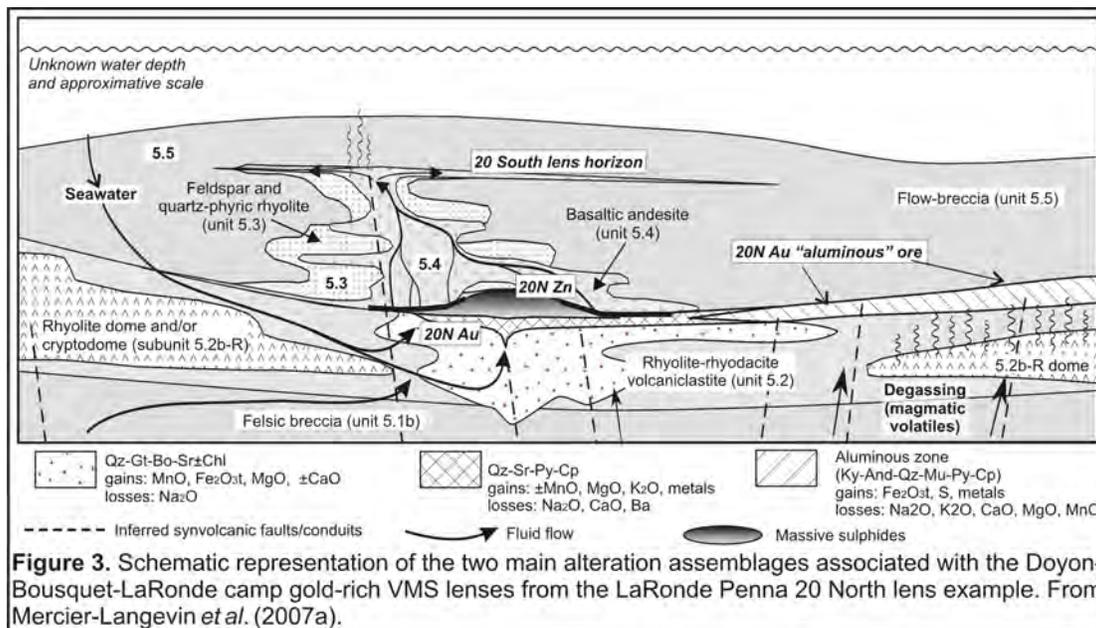


Figure 3. Schematic representation of the two main alteration assemblages associated with the Doyon-Bousquet-LaRonde camp gold-rich VMS lenses from the LaRonde Penna 20 North lens example. From Mercier-Langevin *et al.* (2007a).

ization that gradually (laterally) evolves toward an aluminous alteration and a Au- and Cu-rich zone (Fig. 3). In other areas, the neutral alteration can be distal and give way to aluminous alteration proximal to the ore, which is the case at Bousquet 1 and Bousquet 2 (Fig. 1).

The neutral alteration is mainly characterized by increasing enrichments in MnO, Fe₂O₃^(t), and MgO and losses of Na₂O (Fig. 3) towards the ore in association with the presence of a quartz,

biotite, Mn-rich garnet, sericite±chlorite, epidote and chloritoid (Dubé *et al.* 2007). In the transition zone, the Mn-rich garnet is gradually replaced by staurolite towards more aluminous alterations zones. The aluminous alteration zone is characterized by strong to total leaching of all oxides except Al₂O₃, Fe₂O₃^(t), and SiO₂ associated with the presence of aluminosilicates in a quartz-rich matrix that is the metamorphic equivalent of an advanced argillic alteration (Dubé *et al.* 2007).

CONCLUSIONS

Gold-rich polymetallic VMS deposits such as those hosted by the Bousquet Formation represent a very attractive exploration target. Lithogeochemistry is a key tool in mapping units and tracing hydrothermal vectors towards the ore in the DBL camp. Some key geochemical features are summarized here:

- (1) The Au-rich VMS deposits of the DBL camp are associated with felsic, transitional to calc-alkaline volcanic and volcanoclastic rocks of the FI- and FII-type;
- (2) Although ore zones are stacked in the stratigraphy, the main ore lenses are located along a key horizon at the contact between two distinct rhyolites and a basaltic-andesite unit;
- (3) The two main alteration assemblages of the DBL camp (neutral and aluminous) are characterized mostly by gains in MnO and losses in Na₂O, respectively, and by intense leaching of most oxides.

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Application of field-portable x-ray fluorescence spectrometers in mineral exploration, with examples from the Abitibi Greenstone Belt

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ABSTRACT: Field-portable x-ray fluorescence analyzers (PXRF) are being increasingly utilized in geological and geochemical applications. Benefits include: non-destructive, in situ or ex situ analysis, simultaneous multi-element (ca. 25) quantitative and/or semiquantitative determinations, portability, excellent detection limits for many elements, high sample throughput, and low cost per analysis. Their usability has been improved by technological developments (x-ray tubes, sensitive detectors, data reduction algorithms), that have increased the spectrum of elements that can be analyzed, the quality of the data, rate of data acquisition, convenience, and user experience. We have recently incorporated the use of hand-held and bench-top PXRF in our activities, and present here two case studies of their application in the Abitibi Greenstone Belt, one is chemostratigraphic mapping of volcanic units, and the other is discrimination between black shales that have a hydrothermal component and those that are barren.

KEYWORDS: *portable x-ray fluorescence spectrometry, portable xrf, geochemistry, chemostratigraphy, Abitibi*

INTRODUCTION

PXRF have been greatly improved over the last few decades such that they now can find far-reaching application in the fields of geology and geochemistry. Herein, we review features of currently available PXRF, discuss their benefits and limitations, and give practical suggestions and guidelines for their selection and use in mineral exploration. Finally, we present two case-studies from our recent work in the Abitibi Greenstone Belt in Ontario and Quebec, Canada.

THEORY & INSTRUMENTS

In energy dispersive x-ray fluorescence spectrometry, a sample is bombarded by x-rays that cause the atoms within the sample to fluoresce (i.e., give off their own characteristic x-rays) and this fluorescence is then measured, identified and quantified. The energy of the x-rays identify the elements present in the sample and, in general, the intensities of the x-ray lines are proportional to the concentration of the elements in the sample, allowing quantitative chemical

analysis. Details of the method can be found in Van Grieken and Markowicz (2002).

Recently, miniaturized, x-ray tubes have largely replaced previously used radioisotope sources for most applications as these provide higher x-ray fluxes, shorter count times, and better precision.

Silicon positive intrinsic negative (SiPIN) detectors are most commonly used today, and these convert incoming x-ray signals to voltage that is proportional to the energy of the incoming x-rays; these voltages are then sorted by a multichannel analyzer and fed to a miniature computer. Their energy resolution is too low to permit detection and quantification of many of the key light elements (LE; Mg, Al, Si). There are recent improvements that place the analytical path in a vacuum rather than air (most presently available PXRF). Because low energy x-rays generated by LE are attenuated in air, its removal maximizes the x-rays that are detected.

Silicon drift detectors (SDD) are now available in some PXRF; they have a higher energy resolution and count rates,

making them much more suitable for measurement of LE in an air path.

Hand-held PXRF are available in a lightweight pistol form. Bench-top PXRF are slightly larger and heavier, and have a more powerful tube than most hand-held PXRF, which provides better precisions and detection limits for many elements. There are numerous accessories available for PXRF. There are several manufacturers of PXRF models that are optimized for geological and geochemical applications.

ANALYTICAL ELEMENT SELECTION

Geological and geochemical applications of PXRF generally require multi-element analysis; however, the more elements that are included within an analytical test, the greater the likelihood of problems such as peak overlaps or interferences, and manufacturers typically will provide machine calibrations for 20-30 elements in a particular analytical mode (see below). Our instruments have been calibrated for a range of elements for characterization of lithological units, different mineralization types and associated hydrothermal alteration, and other geochemical exploration vectors.

CALIBRATIONS & ANALYTICAL MODES

Fundamental Parameters (FP) are universal standardless, factory built-in calibration programs that describe the physics of the detector's response to pure elements, correction factors for overlapping peaks, and a number of other parameters to estimate element concentration while theoretically correcting for matrix discrepancies (e.g., Figura 1987). FP should be used for accurately measuring samples of unknown chemical composition in which concentrations of light and heavy elements may vary from ppm to high percent levels.

Compton Normalization (CN) is an "internal" standard, in which spectra are normalized to the Compton peak, which is produced by incoherent backscattering of the source radiation and is present in every sample. The intensity of the incoherent radiation backscatter reflects

both the composition of LE in the sample matrix as well as the overall concentration of detectable elements (Nielson & Sanders 1983). LE-dominant matrices produce a larger Compton peak, so this method provides the best results for measurement of sub-percent concentration of heavy elements in samples composed mainly of LE.

Our instruments have 4 analytical modes, with the first two being most useful as they are relatively insensitive to sample matrix composition.

1) Process Analytical: employs FP and should be used for analysis of "ore grade or style" mineralization with some gangue; this provides "assay" level data and typical detection limits (DL) of 0.5 wt%.

2) "Soils": employs CN and should be used for analysis of soils, rocks, and other materials with a predominantly LE matrix; gives "geochem" level data at DL varying between 1 and 100 ppm.

3) Empirical Analysis: uses reference standards to establish an empirical calibration line (Piorek & Rhodes 1988) and can be useful for samples where all major elements present cannot be analyzed. The standards should be matrix-matched and contain a range of element concentrations bracketing the desired level of quantification.

4) "Analytical" or "Alloys": employs FP and should be used for native metals and provides typical DL of 0.1-0.5%.

POTENTIAL APPLICATIONS

PXRFs are well-suited to myriad applications within the entire exploration, mining, and remediation cycle. Among these are: 1) geological surface and underground mapping; 2) geochemical exploration (rock, soil and stream sediment surveys); 3) determination of metal contents of mineralized samples, mineral identification during prospecting and logging of drill core and cuttings; 4) mining and mineral processing grade control; and 5) environmental baseline and monitoring studies.

SELECTED EXAMPLES

PXRF analyses were used to assist in

distinguishing between different volcanic units of the Chibougamau area on the basis of high field strength elements (HFSE; Ti, Zr, Y), and to characterize the base metal contents of mineralization intersected in drillcore in the footwall of the Lemoine VMS deposit, Quebec (Fig. 1). Two major units can be recognized on the basis of HFSE contents: high Ti-low Zr, and high Zr-low Ti. PXRF Zr abundances are very similar to ICP-ES determinations of fewer selected samples, but an applied correction factor of 1.5 was necessary for PXRF Ti to match ICP values. However, data for both methods readily distinguished the units. The Cu-Zn-enriched nature of mineralization is correctly identified by both methods.

PXRF analyses of sulfidic black shales intercalated with volcanic rocks of the Kidd-Munro Assemblage were used to differentiate between sedimentary horizons that contain a hydrothermal component and those that do not; characterization of the element enrichment suite and metal abundance data of the former are being used to vector toward concealed hydrothermal vent sites and mineralization. Figure 2 depicts geochemical profiles for Cu and Zn in 3 drillcores situated stratigraphically along 2.3 km of strike length and located about 8 km north of the Kidd Creek Zn-Cu-Pb-Ag mine, Ontario, as determined by hand-held and bench-top PXRF. The figure shows that of the 3 broadly spaced

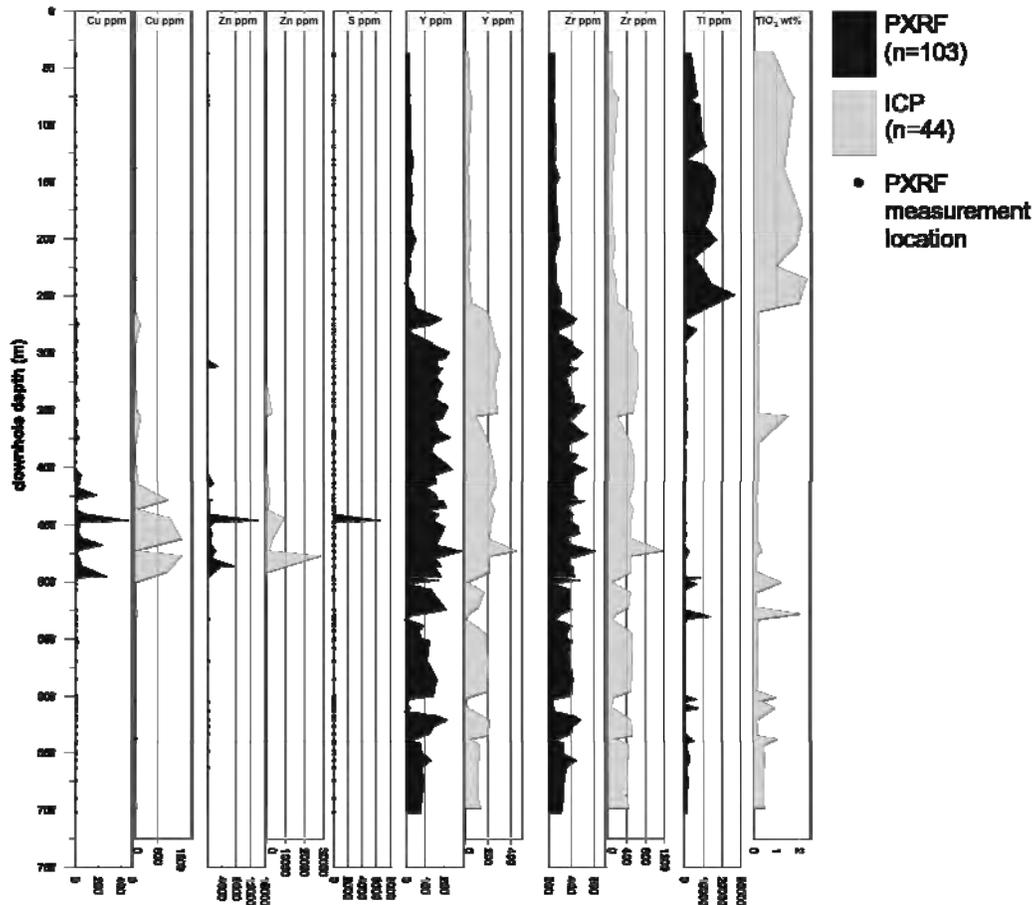


Fig. 1. Downhole log of selected element abundances in a part of drillcore LEM-40 from the footwall of the Lemoine VMS deposit, Chibougamau, Quebec as determined by conventional ICP and hand-held portable x-ray fluorescence spectrometer.

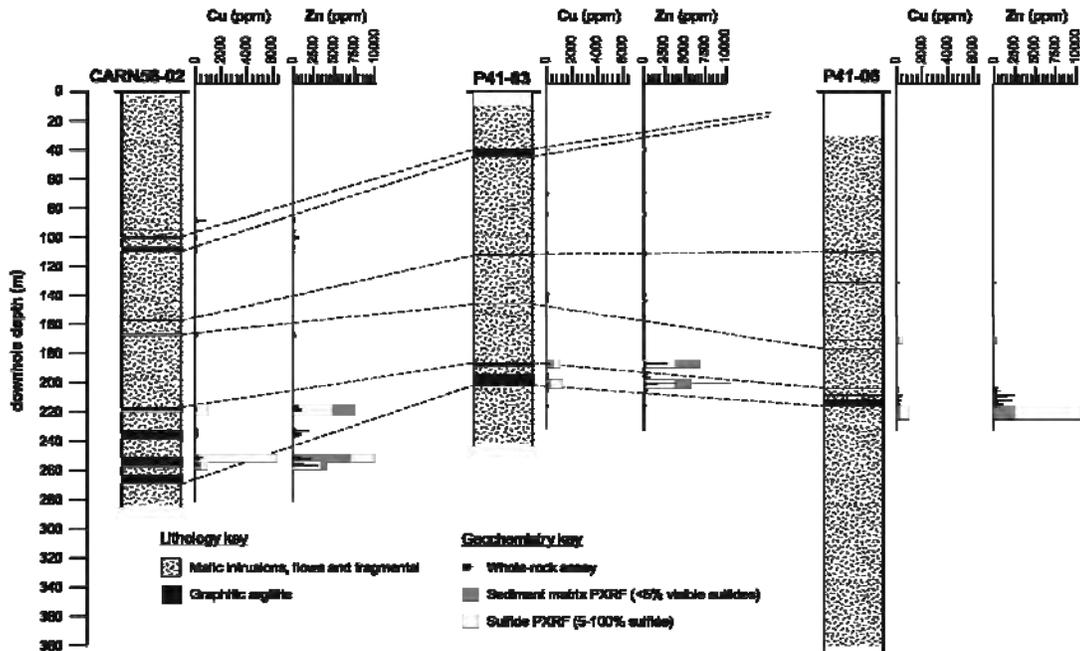


Fig. 2. Fence diagram of downhole Cu and Zn abundances in sulfide modules, concretions, crusts and laminae and matrix of graphitic argillite intersections in three drillcores 2.6 km apart and 8 km north of the Kidd Creek mine, as determined by bench-top and hand-held PXRF.

argillite-bearing intervals, only the stratigraphically lowermost contains a hydrothermal signature and the upper 2 are barren. Within this horizon, diagnostic decoupled distribution of Cu and Zn is not evident in conventional assay data but is clearly recognized in PXRF analyses. Vectoring along this lower horizon may guide further exploration.

CONCLUSIONS

PXRFs provide rapid, low cost, non-destructive, quantitative and/or qualitative multi-element analyses of many different sample media that require little or no sample preparation and instrument calibration for many applications. The two example presented here illustrate the use of PXRF in mapping rock units and mineralized zones, and this can empower the user to make on-the-fly decisions to optimize sampling strategy in order to

minimize analytical costs or maximize operational effectiveness.

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Exploration for Zn-rich mineralisation in semi-arid environments: an example from the Cobar region, NSW, Australia

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ABSTRACT: Detailed examination of soil fractions in the Endeavor Mine area in the Cobar region reveals that the coarse (>2 mm) and magnetic fractions are hematite- and maghemite- rich and consistently elevated in Ag, As, Fe, Pb and Sb and depleted in Al, Ca, Cd, Cu, K, Na and Zn relative to the fine (<63 µm) clay-goethite-rich fraction. Phosphorus and S are also generally elevated in the fine soil fraction. Recognition of this separation can be used to understand the significance of areas of Pb anomalism in pisoliths relative to partial leach Zn anomalies within the region. Despite the concentration of Zn into the fine soil fraction, the time involved in sample preparation would generally preclude its systematic use in regional exploration programs for Zn-rich mineralisation. However, other studies in the region suggest that the proportion of fine material in this semi arid region is generally 35-50% so that whole soil results may be used with caution.

KEYWORDS: *soil, geochemistry, mineralogy, Zn-Pb deposits, Cobar region.*

INTRODUCTION

Zinc-Pb-rich Cobar-style deposits occur in Palaeozoic metasediments of the Cobar region, NSW, Australia. Weathering has affected the region since at least the Tertiary. The Cainozoic weathering has extended to depths of about 60–80 m with residual soil generally <2 m thick. However 15–20 m sequences of colluvial cover commonly occur throughout the region with sequences locally >60 m thick in palaeovalleys (Chan *et al.* 2004). Lags in the region tend to be composed of quartz, lithic and ferruginous nodules/fragments (Dunlop *et al.* 1983), with maghemite a common component in the latter (Lorrigan 2000, 2005).

At the Endeavor (formerly Elura) Mine (43 km NNW of Cobar), the main lens of the Elura Zn-Pb-Ag orebodies is subcropping with a small patch of gossanous float present in an essentially flat landscape. There Pb in saprolite (>50 ppm in an area 1.4 x 1.0 km) and lag (>50 ppm in an area 2.5 x 1.6 km) define the underlying mineralisation. However Zn in soil is anomalous for >1 km to the southwest of the main lens (Lorrigan

2005). Similarly, at Wagga Tank (130 km south of Cobar), Pb >30 ppm in 1-2 mm soil material (in an area at least 200 x 200 m) readily defines subcropping mineralisation, whereas Zn anomalism in the same material is less coherent (Scott *et al.* 1991). The Hera Zn-Pb-Cu-Au-Ag deposit (80 km SE of Cobar), occurs under thin colluvial cover. Broad Pb anomalism occurs in surficial soils along traverses across the deposit, especially in the coarse and magnetic fractions (>100 ppm for 600 m; Scott 2006). Zinc anomalism (>40 ppm for 550 m) is also present in the coarse soil fraction but not in the magnetic fraction. Thus, how Zn occurs in soils in the semi-arid Cobar region needs to be understood.

This study documents the chemistry and mineralogy of soil fractions adjacent to the Endeavor Mine area to evaluate how best to use soils in regional exploration in western NSW.

SAMPLES AND METHODS

Approximately 3 kg of soil was collected from 0–15 cm at 4 sites in the Endeavor Mine area. Background residual soils

were collected at two sites located about 2 km north of the Endeavor headframe on Poon Boon Station. Soils developed on transported material that gives rise to the Bengacchah Zn anomaly (in bedrock 2.6 km SSW of the subcropping main lens) were also sampled at two locations.

Four surficial soils were collected from along a traverse across the projected position of the blind Northern Pods mineralisation (450 m below surface). This traverse was originally made to conduct a partial leach study over the Northern Pods, with samples 138538 and 138539 being soils with low mobile metal ion (MMI) response 250 m east of samples 138440 and 138441 which are directly over the mineralisation and show anomalous MMI response.

Soil samples were wet sieved into (a) 2–4 mm, (b) 1–2 mm, (c) 0.5–1 mm, (d) 250–500 μm , (e) 125–250 μm , (f) 63–125 μm and (g) <63 μm fractions. A ferruginous/magnetic fraction (m) was also prepared from the 2–4 mm fraction. Soil fractions were crushed, digested with $\text{HNO}_3/\text{HCl}/\text{HF}/\text{HClO}_4$ and then analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for Al, Ca, Cu, Fe, K, Mn, Na, P, S and Zn. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine Ag, As, Cd, Pb and Sb because of the lower detection limits by this method. The mineralogy of selected samples was determined by qualitative X-ray diffractometry.

RESULTS

Surficial soils developed upon transported material (Bengacchah) have <1% coarse material (>2 mm) and about 50% finer than 63 μm whereas the residual soils tend to have several percent coarse material and <40% fine material. Quartz in soils in transported material (Bengacchah) also tends to be more rounded than elsewhere.

Examination of soil fractions coarser than 250 μm indicates that they contain a substantial amount of magnetic material. The proportion of magnetic to non-magnetic (lithic) material generally

decreases with decreasing grain size. The mineralogy of the coarse and fine soil fractions suggests that coarser fractions contain hematite, goethite and maghemite. The <63 μm fraction is richer in clay minerals (muscovite/illite and kaolinite) and contains goethite as the only Fe oxide.

Chemical analysis shows that the coarse (>2 mm) and magnetic fractions are consistently richer in Ag, As, Fe, Pb and Sb than the fine (<63 μm) fraction which is richer in Al, Ca, Cd, Cu, K, Na and Zn. Phosphorus and S are also generally elevated in the fine soil fraction. However, high S (>600 ppm) occurs associated with elevated Ca in the coarse fraction in the Bengacchah area, reflecting the presence of gypsum. Iron contents are lowest in material sized between 63–250 μm but slightly more abundant in the fine fraction. This suggests that Fe is dominantly present in hematite and maghemite in the coarse soil material and present mainly as goethite in the finest material. The concentration of Pb in the coarse and magnetic fractions and Cu and Zn in the finest soil fraction should be noted.

Table 1 shows that in samples 138462 and 139464 (Bengacchah) and 138540 and 139541 (Northern Pods area), Zn and Cd are elevated in all soil fractions, with the values in the fine (<63 μm) fraction at least double those in corresponding samples from the Poon Boon area. (High Zn in the coarse fraction of 138462 is due to soil nodules composed of calcite and gypsum.) Sulfur also tends to be more abundant in all four Northern Pods samples than in the Poon Boon samples. Lead is slightly elevated in the coarse and magnetic fractions of the Northern Pods or Bengacchah samples relative to Poon Boon (background) samples.

DISCUSSION AND RECOMMENDATIONS FOR SOIL SAMPLING

As indicated above, Pb is preferentially concentrated in coarse and magnetic soil fractions, with Zn concentrated in the finer soil fraction. Dunlop *et al.* (1983) also observed this separation of Pb and Zn in

Table 1. Geochemistry of surficial soil fractions, Endeavor Mine area.

Location	Sample	Fraction	Ca ppm	Cd ppm	Cu ppm	Fe %	Pb ppm	S ppm	Zn ppm
Bengacchah (transported)	138462	>2 mm	5520	0.4	27	27.00	72	3400	220
		<63 µm	1760	0.3	47	3.95	37	260	220
		Magnetic	560	0.2	26	39.80	84	250	59
	138464	>2 mm	1270	0.1	21	29.60	71	690	43
		<63 µm	1330	0.2	41	4.10	39	260	150
		Magnetic	410	<0.1	27	41.70	91	200	39
Poon Boon (background)	138466	>2 mm	470	<0.1	25	23.20	50	100	42
		<63 µm	1890	<0.1	42	4.05	33	200	79
		Magnetic	540	<0.1	24	30.70	52	100	36
	138468	>2 mm	740	<0.1	18	36.20	61	140	23
		<63 µm	2140	<0.1	48	4.40	29	230	73
		Magnetic	640	0.1	22	43.70	72	110	36
Northern Pods- barren	138538	>2 mm	470	<0.1	17	46.00	84	310	13
		<63 µm	2660	<0.1	52	4.10	40	420	72
		Magnetic	450	<0.1	19	51.30	97	290	12
	138539	>2 mm	480	<0.1	16	38.90	86	280	12
		<63 µm	1790	<0.1	44	3.85	41	410	59
		Magnetic	410	<0.1	19	51.80	89	250	13
Northern Pods- mineralised	138540	>2 mm	500	0.2	20	36.80	68	200	66
		<63 µm	1610	0.8	43	4.40	36	390	460
		Magnetic	610	0.2	24	44.10	81	170	87
	138541	>2 mm	1370	0.1	25	35.20	62	230	69
		<63 µm	2970	0.3	48	4.40	36	330	200
		Magnetic	850	<0.1	21	38.80	68	150	77

drainage channel soils about the Endeavor Mine site. Furthermore, they found that Pb >50 ppm (with only low Zn) in 1-2 mm pisoliths from stream channels defined an anomaly for 5 km about the Elura orebody whereas the soil auger anomaly (Bengacchah) with Pb >50 ppm extends approximately 1.3 km SW of the Elura orebody in a palaeochannel. Such features of the Bengacchah anomaly are consistent with mechanical dispersion, probably from the wall alteration about the top of the Elura orebody (Govett *et al.* 1984; Lorrigan 2005) which formed a topographic high during the early Tertiary

(Gibson and Pain 1999). Ferruginous, coarse Pb-rich Bengacchah anomaly material would have been deposited over a relatively short interval in a palaeochannel and subsequently covered by later depositional material. However ferruginous material (commonly pisoliths) in the current stream channels reflects material transported and reworked over the period since the Tertiary. Thus the anomalous Pb in surficial coarse and magnetic soil fractions from the Bengacchah and Northern Pods area represents Tertiary to present mechanical dispersion.

Zinc is elevated in the fine (<63 µm) soil fractions relative to coarse and magnetic soil fractions but high values (>100 ppm) are found in the fine fraction of surficial soils in the Bengacchah area and immediately above the 450 m-deep Northern Pods mineralisation. Fine material from soils 250 m east of the latter are not so enriched. This suggests that the Zn is not particularly mobile, possibly reflecting derivation from a very local source, possibly siderite up dip from the Northern Pods and Bengacchah.

Although Zn contents are highest in the fine fraction of the soils, the time needed to prepare such a soil fraction makes its use impractical. However, because fine generally makes up 35-50 % of the whole soil in the Endeavor, Hera and Wagga Tank areas, it may be able to be used directly. For example, Zn ≥150 ppm occurs in the highly anomalous samples above Northern Pods mineralisation relative to <40 ppm in a sample 250 m away. However, one would need to determine details of the soil size distribution in other areas being explored.

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Soil micro-layer, airborne particles, and pH: the Govett connection

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ABSTRACT: Geochemical research in the 1960s and 1970s produced exploration methods that could be used to quickly explore large areas from the air using the Barringer-developed AIRTRACE collection and analytical system. Geochemical patterns seen from the analyses of dust from the soil-air interface, known as the soil micro-layer, were thought to be connected to the electrogeochemical model developed by Govett and his students in the early 1970s. This theory was closely linked to H⁺ release from oxidizing sulfide bodies. Additional studies from the '70s to the present by the author have shown that the measurement of pH and detection of pH-related patterns from the soil micro-layer may detect mineralization through appreciable cover and can be done in the field in real time at little expense. Two examples from this research are shown.

KEYWORDS: *Airtrace, pH, soils, micro-layer, electrogeochemistry, deep exploration.*

INTRODUCTION

The late 1960s and early 1970s saw the introduction of innovative research into geochemical processes that remain at the forefront of applied geochemical technology after nearly forty years. The leading research school at that time was Imperial College in London under the direction of John Webb. His students defined 'thinking outside the box' in applied geochemistry. The following retrospective connects a few of these ideas and offers a simple method for mineral exploration through cover that was ultimately distilled from this work.

AIRBORNE GEOCHEMISTRY

One of the more interesting aspects that appear to have been disfavored or at least lost in the last forty years was the work of W. Beauford and J. Barber at Imperial College, and G. Curtin at the USGS on the release of heavy metals to the atmosphere from plants. Much of this work was published later in the 1970s (Beauford *et al.* 1977; Curtin *et al.* 1974), but had caught the eye of Tony Barringer, one of the leading thinkers in mineral exploration technology in the late 1960s. Barringer had also been introduced to work done on the soil-air interface (the soil micro-layer) that had been shown to be a

zone of accumulation of ions. Some of this work was published in the later 1970s (Barringer 1977).

Barringer, ever on the lookout for methods to explore ground quickly (he was the inventor of the proton precession magnetometer, Input Airborne EM system, the Airborne mercury analyzer, the COSPEC airborne gas analyzer amongst many other technologies) thought that if one could collect airborne particles in an aircraft as it flew close to the ground and analyze them for many elements, one could then marry airborne geophysics and geochemistry in one aircraft. Barringer was granted patents on the method itself, which he called AIRTRACE, and on the particle collection method and the method of analyses of the particles (Barringer 1973a, b).

The AIRTRACE system was mounted on either a fixed wing or helicopter equipped with 'aerodynes' that ingested airborne particles and concentrated this dust on sticky tape that was inside the aircraft. The tape was advanced to a clean position for every five seconds of flight and a record number placed on the tape and the flight path camera film so that the location of the dust spot could be located on the ground.

This tape was analyzed in the Barringer laboratory in Toronto using the first ICP-

ES and the first laser ablation system on which Barringer held a patent for many years.

Microscopic examination of ablated particles showed that only the outer layer of dust particles was consistently being vaporized. Barringer knew that AIRTRACE was collecting the particles from the soil micro-layer: the location of ion accumulation in the soil.

This was recognized as being similar to a weak or selective extraction. Very often, the pattern of element responses over mineralization was 'double-peak' in form and restricted to the immediate vicinity of the deposits. A few published results illustrate these 'donut' (plan) or 'rabbit-ear' (profile) anomalies (Barringer 1977).

THE LINK TO ELECTROGEOCHEMISTRY

The reason for these patterns was not known. However the 1973 paper by Gerry Govett on electrogeochemical transport of ions was very timely. Govett proposed that ions might move through surface cover in response to a natural electrical force created by oxidizing sulfides. Further research both in the laboratory and the field confirmed that this was not only possible, but measurable, and produced in profile a 'rabbit-ear' pattern (Govett 1976). Govett & Chork, (1977) showed that this pattern was being controlled by hydrogen ion movement. This work was in part funded by Barringer Research who saw the 'potential' for explaining the AIRTRACE patterns. Govett showed that the techniques are applicable in an arid environment (Govett *et al.* 1984).

I studied the electrogeochemical phenomena in the laboratory and field while at the Geological Survey of Canada as part of my Ph.D. work under Govett. The field study area selected was in the varved clay belt of Northern Quebec over a VMS deposit covered by between 5 m and 30 m of till, varved clay and organic material. The varved clay was thought at the time to be a complete mask to geochemical movement.

Fortunately the Hudson Bay lowland-derived varved clay is alkaline and Ca-rich and provided an ideal substrate in which

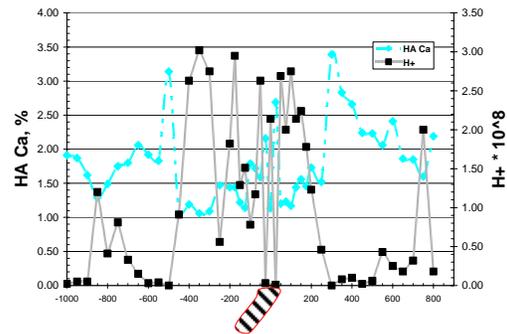


Fig. 1. Profile from the top of varved clay over a VMS deposit in Northern Quebec showing the relationship between H⁺ concentration and aqua regia soluble Ca. (adapted from Smee 1983).

to detect hydrogen ion anomalies. This work showed that not only did the surface soil produce a clear hydrogen ion response above and down dip from the VMS, but also moved the pH-sensitive elements (Ca and Fe) in response to changing pH conditions as shown in Figure 1 (Smee 1983). In the case of calcite, for a pH of <7 the Ca becomes mobile and may move in solution over time. Once the alkaline conditions are re-established, the Ca precipitates as calcite.

This movement of pH-sensitive elements, and Ca particularly has been used by me with success for the past 25 years as a routine exploration tool (Smee 1998, 1999, 2003) and has led to the discovery of several sulfide bodies. The use of a field pH meter and a bottle of water as a primary exploration method in alkaline terrain appears to be too easy to be true. However one can produce remarkable data with these simple tools and a drop of 10 % HCl.

USING PH TO HIGHLIGHT TARGETS THROUGH COVER IN ARID AREAS

Alkaline soil conditions exist in most semi-arid to arid conditions. Oxidizing sulfides should produce a change in pH in the surface soil as confirmed by Hamilton *et al.* (2004), and especially in the soil micro-layer where an upward moving front of H⁺ accumulates, as shown nearly 40 years ago. If this soil micro-layer is sampled



Fig. 2. Sampling the soil micro-layer in acid conditions. See text for analytical method.

(Fig. 2), slurried with distilled water and the pH measured, the response should be obvious.

However experience has shown that other factors such as a break-in-slope or a water-bearing structure can produce single-peak anomalies. These are somewhat confusing when attempting to interpret a soil survey.

The actual pattern in alkaline soils related directly to oxidizing sulfides should include two variables: positive H^+ surrounded by an increase in Ca concentration where the mobilized calcite re-precipitates. Both of these variables can be detected by initially measuring the soil slurry pH, then by adding a drop of 10 % HCl, stirring the solution for about 10 seconds and taking the pH again.

Soils of lower pH (high H^+ molar concentration) have mobilized the Ca and therefore the soil slurry will be relatively unbuffered. The addition of HCl to the solution will immediately drop the pH in these samples where calcite has been removed, but will have little effect where calcite been precipitated. These buffered soils should be on the edge of the low pH (high H^+). The pattern from an oxidizing sulfide should therefore be an H^+ high and surrounded by a small or no change in H^+ concentration when HCl has been added.

Plotting a variable that is significant when small is rather difficult. The method developed to clearly highlight the areas of calcite precipitation on a chart or plan map involves some manipulation. To do this, the acidified H^+ in moles (converted from pH) is subtracted from the non-acidified H^+ . The least differences are the areas of calcite precipitation. The inverse difference (1/difference) is calculated and plotted. This variable produces positive peaks which are far more pleasing to the eye. For ease these are called Inverse Difference Hydrogen (IDH) anomalies.

Two examples are shown: one from the porphyry copper-gold Hugo South Oyu Tolgoi area, Mongolia and one from a quartz reef hosted gold deposit south of the Bulyanhulu mine, Tanzania, Africa. Figures 3a-d over Line 475800 N at the

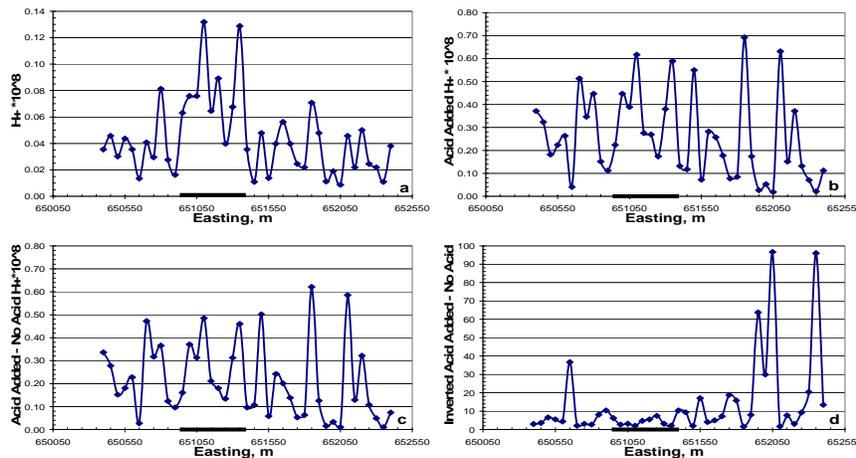


Fig. 3. Profiles of the step-wise handling of the pH data illustrated by Line 475800 N of the Hugo South Cu-Au deposit

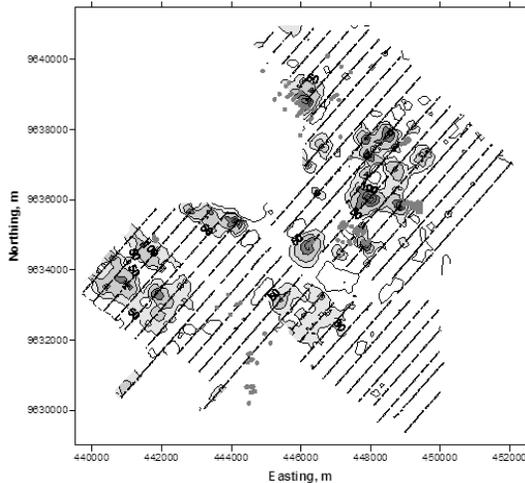


Fig. 4. Plan view of IDH in soils over extension of mineralized horizon from Bulyanhulu Tanzania. Dots are drill locations. The interpretation of soil pH was done after the drilling was completed.

south end of Hugo South shows the step-wise progression of data handling to produce both the H^+ and IDH patterns in profile. The acid peak surrounded by the calcite halo is easily seen. The thick black line at the bottom of each figure is the surface projection of the mineralization. Figure 3a is the H^+ moles $\times 10^8$ from the soil micro-layer. Figure 3b is the acidified soil slurry converted to H^+ moles $\times 10^8$. Figure 3c is acidified H^+ minus original H^+ . Figure 3d is the inverted difference from 3c. (IDH). Calcite is absent over the projection of mineralization and H^+ anomaly, but occurs outboard from the mineralization. Alluvium thickness c. 40 m.

The Tanzanian example in Figure 4 is a plan contour map of the IDH anomalies together with drill holes shown as dots. There is sparse to no outcrop with much of the area covered by fluvial and alluvial deposits. The drill holes were positioned using geological mapping and geophysics rather than the pH survey. The predominance of holes shows the location of gold mineralization. The soil IDH shows the areas of mineralization in many instances, and other areas which have yet to be tested by drilling.

This inexpensive technique was developed because of imaginative and

multi-disciplinary thinking nearly 40 years ago.

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I would like to thank Ivanhoe Mines and Mr. Dale Sketchley for assisting in the collection of the soil samples and allowing the data over Oyu Tolgoi to be released. Barrick Gold collected the information and allowed the data from Bulyanhulu South to be shown. Tony Barringer showed me that doing what other people have done will result in finding what other people have found. Gerry Govett inspired the initial research and has remained a mentor over the years.

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Robust 'organic' geochemistry identifies and vectors to deeply buried exploration targets

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ABSTRACT: Surficial soil surveys use pathfinder elements that have been shown to be useful as a predictive geochemistry in determining the location of exploration targets. Innovative analytics have been developed to similarly use organic compounds as a complementary exploration tool. Soil Gas Hydrocarbons (SGH) is based on a weak leach extraction of near-surface samples followed by an analysis having the sensitivity to detect the minute but unique organic hydrocarbons that bacteria have leached and metabolized from interaction with mineral deposits at depth. These compounds are not gaseous but migrate from depth with the electrochemically induced mass flow from the oxidation and reduction reactions in REDOX cells developed over buried targets. Surficial samples act as collectors of the over 160 specific heavier hydrocarbons that are grouped into chemically related 'pathfinder' classes that have dispersed to the surface. The expected order of dispersion or 'geochromatography' of these classes is able to vector to the location of buried exploration targets. Specific combinations of the classes identify the target type even at over 500 metres in depth. SGH is a dual purpose deep penetrating predictive geochemistry that can both locate and identify blind uranium, gold, SEDEX, VMS, nickel, and copper mineral targets, kimberlite pipes and petroleum sources.

KEYWORDS: SGH, hydrocarbons, partial extraction, deep penetrating organic geochemistry

INTRODUCTION

The use of 'organic' geochemical surveys for exploration has historically been confined to C1 to C4 compounds in the carbon series (methane, ethane, propane, butane) that are gases. However, the alteration of these signals by the biosphere and the effects of barometric pressure and precipitation on gas flux reduce their use in delineating buried targets. An alternative to these light compounds are relatively heavy hydrocarbon compounds that have been hypothesized to be present but at much lower concentrations. With customized lab instrumentation, a method has been developed to prove the existence and use of these heavier hydrocarbons in surficial samples for exploration. This relatively new geochemistry entitled 'Soil Gas Hydrocarbons' (SGH) represents a breakthrough in analytics as it has been able to obtain the higher level of sensitivity required to characterize the hydrocarbon signature related to mineral targets to a reporting limit of one part-per-trillion for

over 160 targeted compounds. The large suite of compounds is able to be subdivided into groups of chemically related organic compound classes. Each class has different solubilities, molecular weights, partition coefficients, etc., and thus they disperse through the overburden at different rates and can be observed at different distances from a buried target through the process of 'geochromatography' as measured by the analysis of near-surface samples. The observation of these dispersal patterns allows accurate vectoring to the location of blind deposits. The specific classes of compounds detected over a target have been associated with the organic signature developed from different mineral types and are thus 'pathfinder' classes that can identify the type of mineralization at depth.

METHOD

Originally only B-horizon surficial soil samples were collected for SGH surveys. Research by the Ontario Geological

Survey (OGS) and the Geological Survey of Canada (GSC) has indicated that the upper B-horizon soil resulted in a higher SGH signal and is thus probably the most ideal sample. In additional research it has been shown that other soil horizons, humus, peat, lake-bottom sediments and even snow are also collectors of the hydrocarbons targeted in this method. A fist-sized sample (c. 500 g) from a transect or grid design consisting of at least 50 regularly spaced sample locations that extend into background areas is best. Samples need no special preservation for shipping.

Samples are dried in temperature-controlled rooms kept at 40°C. The fraction that falls through a 60-mesh sieve (<250 µm) is collected and used for analysis.

A 0.5-g aliquot is analysed from the homogenized sample using an aqueous leach to target and extract weakly bound hydrocarbons from the surface of the sample particles or grains.

Samples are analysed using gas chromatography coupled with mass spectrometry (GC-MS). This instrument separates the organic hydrocarbons in the extract with a very high resolution fused silica capillary column prior to mass spectrometric detection. Acquisition parameters have been customized to detect the target list of 162 hydrocarbons with the sensitivity required to obtain 1 part-per-trillion reporting limits which represents an innovation in these analytics.

Specialized chromatographic deconvolution and integration software further isolates and accurately measures the mass ion responses for the specific hydrocarbons targeted. An external standard calibration method is used to compare the responses of these hydrocarbons to known response factors from a series of n-alkanes to obtain semiquantitative results. Concentrations are reported in an Excel spreadsheet without any statistical modifications.

DISCUSSION

In several research surveys samples have

been collected in duplicate from different soil horizons or of different sample types (e.g. peat and underlying wet soil). It has been found that the variation in results between different sample media including various soil types, glacial till, lake-bottom sediments, peat, and humus is minor to the extent that different sample types can be collected within the same sample survey. The variability of including different sample types is minor compared to the loss of data from missed locations as the hydrocarbon signature is independent of sample type.

The SGH compounds targeted are robust to general sampling, shipping and sample preparation procedures, largely due to the lower volatility of the higher molecular weight compounds. The technique is also robust to cultural activities, even to the extent that successful analysis and interpretation has been done from roadside right-of-way samples.

RESULTS

Several member mining companies of the Canadian Mineral Industry Research Organization (CAMIRO) sponsored a two-year research project in 1997 (CAMIRO 97E04). SGH organic signatures were tested and used to successfully locate nine of the ten targets that were blindly submitted to the lab from study areas known to be difficult for geochemical surveys. The targets studied included copper, gold, nickel, uranium and volcanic massive sulfide (VMS) deposits. SGH was also able to display a 'deep penetrating' nature as it located the McArthur River uranium deposit that was in excess of 500 m in depth.

In 2001, a second CAMIRO research project (01E02) was initiated. The objective of this project was to investigate the source of these hydrocarbons, and to further investigate the ability of this geochemical technique to discriminate between barren and ore-bearing conductors. This project was sponsored by additional mining companies and government agencies and extended into a third year. The project included other

target types of SEDEX, kimberlite and Olympic Dam type targets which were used to define new SGH geochemical signature templates. Microbiological lab experiments were independently conducted to investigate whether the hydrocarbons measured by SGH were related to bacterial activity. A consortia of bacteria were grown directly on various samples of ore, were extracted, and then analysed by SGH. It was discovered that the hydrocarbons were released in the death-phase of the bacteria presumably after eventual cell membrane rupture. A similar set of hydrocarbons were found in ore samples as well as surficial soil samples over the mineralization. Thus the SGH results from surficial samples were shown to be directly influenced by the bacterial activity on the ore at depth and reflected the type of mineralization. This confirmed earlier research where it was observed that the SGH signature from pulverized VMS shelf specimens representing modern black smoker and older Mattabi and Kidd Creek deposits matched exceptionally well in their SGH VMS signature and also to the signature detected in surficial soils over VMS deposits from geographically different locations.

During the CAMIRO 01E02 project, seven surveys were submitted from over kimberlite pipes. Research defined the SGH signature and studied the dispersion of the anomalous compound classes of hydrocarbons as shown in the following figures. With SGH, kimberlites are distinguished using higher molecular weight classes of compounds. In Figure 1, the heaviest pathfinder class of polyaromatic hydrocarbons moves through the overburden at the slowest rate and thus forms a halo anomaly that is dispersed to the greatest distance from the kimberlite as shown by the dotted oval. Figure 2 illustrates a slightly lighter kimberlite pathfinder class of alkylated-biphenyls that disperses less and forms the halo anomaly shown by the dashed oval. Figure 3 of branched-alkanes moves through the overburden more easily and forms the tight halo anomaly

that definitively shows the edge of the outer rim of the kimberlite pipe as the boundary of a REDOX cell. Together these classes accurately vector to the target location. The mix of classes found identifies the target as a kimberlite pipe.

From independent research, SGH appears to be an excellent tool for identifying reduced areas or REDOX cells in overburden (S. Hamilton, OGS, pers. comm. 2004).

CONCLUSIONS

The majority of the hydrocarbons detected by this geochemical technique have been proven to originate from bacteriological activity at depth. The heavier SGH compounds are robust and thus a wide variety of sample types may be used which is valuable in sampling in difficult Canadian environments. SGH is able to

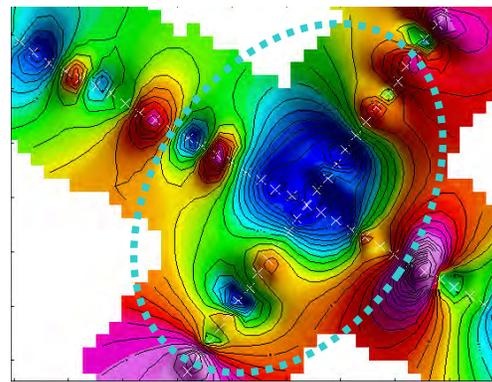


Fig. 1. Tertiary kimberlite pathfinder class.

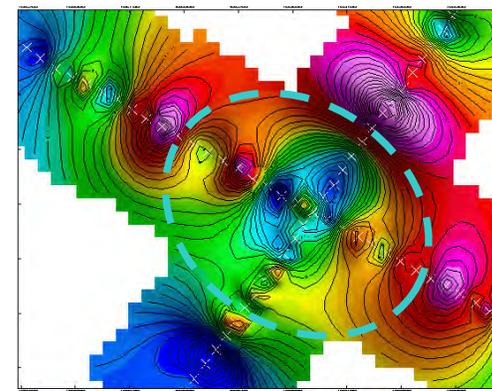


Fig. 2. Secondary pathfinder class.

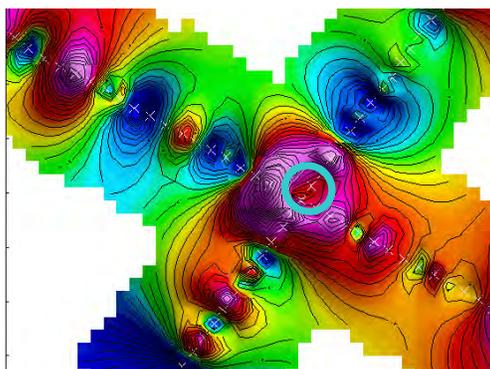


Fig. 3. Primary kimberlite pathfinder class.

locate the vertical projection of a target through geochromatographic vectoring of the various hydrocarbon pathfinder classes. The mix of the hydrocarbon classes detected is able to identify the type of mineralization at depth. It has been shown to be a deep penetrating geochemical technique that is able to discriminate between barren and ore-bearing conductors, and magnetic anomalies, prior to the planning of expensive drilling programs and thus reducing exploration costs. The SGH data from over 400 targets has been interpreted since 2004, thus thoroughly testing the various mineral templates used to confirm the identity of the buried target for a wide variety of commodities.

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