

Major Advances in Soil Geochemical Exploration Methods for Areas of Thick Glacial Drift Cover

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ABSTRACT

In the last decade, soil geochemical techniques have been used for mineral exploration in areas of thick glacial drift with truly mixed results. Some organizations are now using them routinely and successfully to discriminate buried targets. Others have experienced high cost failures and have abandoned them as exploration tools. Upon examination of both the anecdotal and published successes and failures, it is evident that deep penetrating geochemical (DPG) techniques work well, only if: (1) the objective is sound, i.e., they are used in target identification and prioritization, not target generation; (2) proper field sampling protocols are followed; and (3) data interpretation is carried out by personnel with a basic understanding of surficial geochemical processes. From 1994 to 2005, the OGS and our industrial, government and academic partners carried out eight major projects investigating soil geochemical techniques. The studies determined, with a high degree of confidence, that detectable signals related to mineralization can occur in surface soils through more than 50 m of glacial overburden cover. Four of the eight projects were supported by CAMIRO including perhaps the most important study of its kind to date: Deep Penetrating Geochemistry, Phase 2. The discovery, during that study, of 'reduced chimneys', 'acidic caps' and a shallow metal accretion zone support an integrated geochemical model that argues metals move upward in reduced form, oxidize near the water table, producing acid, and depositing commodity elements over the deposit and secondary geochemical responses that often occur in a halo surrounding the deposit. A 3-component soil geochemical methodology is recommended that includes analysis by (1) a selective leach method; (2) a soil hydrocarbon technique; and (3) soil slurry pH. Using all three methods at once will improve the likelihood of success as they each detect a different aspect the large-scale geochemical process described by the integrated model. Selective leaches target the primary (i.e., originating from ore) and secondary (i.e., resulting from pH/Eh changes) elemental responses. Soil hydrocarbon techniques target the reduced chimney indirectly by measuring the products of autotrophic organisms that thrive at soil redox boundaries. Soil slurry pH targets the acidic cap but may also detect a 'basic chimney' below the water table or alkaline groundwaters from kimberlites or ultramafics that may have reached the soil zone. An optimized sampling protocol is presented and methods of data interpretation outlined. Interpretation must always consider the possibility of 'false anomalies', which occur commonly due to changes in surficial conditions but are less common with hydrocarbon techniques (specifically SGH[®]). Variable moisture content is a major source of false anomalies in mineral soils, whereas variable clastic input is the dominant source of false anomalies in peatlands.

INTRODUCTION

A number of agencies including the Ontario Geological Survey (OGS) have been investigating soil geochemical techniques that are suitable for mineral exploration in areas of thick glacial overburden. In the last decade, in addition to smaller projects and individual case studies, there have been 8 major projects, all of which have had OGS involvement, that have significantly increased our understanding of soil geochemical responses over deeply buried mineralization in glacial terrain. Table 1 lists these and describes the major contributions of each. At the outset of the studies, there was no consensus among geochemists that soil geochemical responses had ever been definitively demonstrated to occur over mineralization in areas of thick glacial clays. Many

scientists, including some of the principal researchers (e.g., the author), believed it theoretically impossible that elements should migrate through more than about 10 m of glacial clays in the ~ 10 Ka since glaciation. That opinion was one of the earlier theoretical casualties of the studies, which resulted in important new theories and the discovery of demonstrable geochemical processes occurring in such environments. Later the studies demonstrated the importance of maintaining a consistently shallow sampling depth and uniform soil type, which has led to the development of field sampling protocols for both 'dry' boreal forest and peat terrains.

As research projects, these studies have been very successful, but this has not yet resulted in unequivocal success in the use of these techniques in mineral exploration, particularly in the glaciated terrain that our studies have focused on. Selective leach techniques, for example, are now used routinely by some

Table 1: Summary of major geochemical studies in glaciated terrain.

| Project | Duration | Properties | Principal Researchers | Research Affiliations | Funding Agencies | Important outcomes |
|--|-----------|--|---|-----------------------|-----------------------|--|
| Claybelt Geochemistry | 1994-1998 | Niunisco: Au, Ni, Cu, PGE Shoot Zone: Au Band Ore: Au Queenston (Willy): Au Hislop (Marsh Zone): Au Stimson (VMS) Holt-McDermott: Au | Jackson, Bajc, Hamilton | OGS | OGS | <ul style="list-style-type: none"> • Demonstrated that metal responses occur at 6 sites in soils over mineral deposits and other features covered by up to 50m of glacial clays • Studied possible mechanisms of vertical transport of elements through clay concluded electrochemical transport was only viable process in the time available (~10 kA) • Shoot Zone stratigraphic data and groundwater and till geochemical data by the OGS formed the basis of several subsequent studies at the site • Publications include an open file report (Jackson, 1995) and 2 journal articles (Bajc, 1998; Hamilton, 1998) |
| Victoria Creek / Shoot Zone Selective Leach, pH and SP | 1995-1998 | Victoria Ck.: Au Shoot Zone: Au | McClenaghan Hamilton Bajc Hall | GSC, OGS | GSC, OGS | <ul style="list-style-type: none"> • Showed excellent responses by a variety of selective leaches in peat and B-horizon that correlate with pH and SP responses • Results released in several minor publications, numerous oral presentations and posters • Final report and data release in preparation |
| Phase 2 Deep Penetrating Geochemistry | 1999-2002 | Cross Lake: VMS Half Moon Lk.: VMS Marsh Zone: Au | Cameron Hamilton Hall McClenaghan | ECG, OGS, GSC | CAMIRO, OTH, OGS, GSC | <ul style="list-style-type: none"> • Demonstrated definitive metallic responses above mineralization covered by thick (>40m), young glacial clays in Ontario and pediment gravels in Nevada and Chile • Demonstrated that the 'MMI protocol' of sampling very shallow (10-25 cm) in mineral soils is optimal but consistent soil media is also extremely important • Proved, among other things, the existence of the 'reduced chimneys' & 'acidic caps', predicted to occur as a result of 'redox-gradient' vertical transport of metals • Publications include 3 journal articles (Hamilton et al. 2004a&b; Cameron et al. 2004) and more than 20 reports contained in a final release CD (Cameron, 2002) |
| TGI Selective Leach Geochem over 3 Kimberlites | 2002-2005 | B-30, 95-2, A4 kimberlites | McClenaghan Hamilton | GSC, OGS | GSC, OGS | <ul style="list-style-type: none"> • Demonstrated significant responses over thick sand covered kimberlites, particularly in Ca, Mg & Sr, suggesting kimberlite – impacted fluids are reaching soil zone • Showed evidence of 'reduced chimneys' and <i>positive</i> pH & SP responses • Documented the strong bias that can occur due to variable organic matter and sample heterogeneity • Results were released in OFR (McClenaghan et al., 2006) and in numerous presentations |
| Comparison of selective leach signals over kimberlites and other targets | 2003-2004 | 11 Kimberlites 2 Carbonatites 2 proven non-kimberlitic mag targets | Burt Hamilton | OGS | OGS | <ul style="list-style-type: none"> • Demonstrated that measurable signals exist over kimberlites and are different from those generated by carbonatites and other buried features • Hampered by the 'cluster sampling' technique employed and thereby demonstrated that full transects are necessary to recognize selective leach signals from buried features • Results released in an OFR (Burt and Hamilton, 2004) |
| 3-D Geochemistry: Methods Development | 2002-2004 | Cross Lake: VMS Marsh Zone: Au | Hall, Hamilton McClenaghan Southam Cameron | GSC, OGS, UWO | OMET, OGS, GSC | <ul style="list-style-type: none"> • Characterized the 3-D nature of shallow (<1.5m) elemental anomalies over VMS and Au deposits in dry terrain and peatlands • Determined, using Pb-isotopes, that metals originate from ore • Demonstrated the co-relationship between redox, soil hydrocarbons (SGH) and bacteriological parameters in shallow soils over mineral deposits. Therefore soil hydrocarbons are excellent proxies for redox. • Developed sampling protocols for variable dry / peat terrain in glaciated areas • Showed graphite can be distinguished from sulphide using soil geochemistry • Recommended the methods be used for target identification and prioritization but not target generation because large-scale grid sampling generates numerous false responses due to variable moisture, organic and clastic content |

Table 1 continued: Summary of Major soil geochemical studies in glaciated terrain.

| Project | Duration | Properties | Principal Researchers | Research Affiliations | Funding Agencies | Important outcomes |
|------------------------------------|-----------|---|---|------------------------------------|------------------|---|
| 3-D Geochemistry: Case Studies | 2002-2004 | Cross Lake: VMS 180 E: Au Crossroads: Au Gemini: VMS Shoot Zone: Au Perseverance: VMS Prosser: graphite | Bloom, Jackson, Closs, Southern | Analytical Solutions CSM UWO | OMET, CAMIRO | <ul style="list-style-type: none"> This project involved methods development and case studies at a number of deeply buried mineral deposits using a variety of geochemical techniques Bacteriological studies showed higher anaerobe : aerobe in shallow soils over sulphides at 3 sites with very different terrain - strongest responses are in dry terrain; weakest responses are in peat A continuous leach orientation study on soils over a Au deposit and 2 VMS deposits showed anomalous mobile commodity elements over mineralization OFR contains a compilation report (Jackson, 2005b) of selective leach results over Au deposits in glaciated and arid terrains OFR contains a report on peat sampling of the Gemini VMS (Jackson 2005a) that is the first study in peatlands that shows definitive pH and selective leach responses over polymetallic sulphide deposits A study on a barren graphitic unit (Prosser) was carried out and, significantly, no response was noted over the conductor. Unfortunately, the report to accompany data from this study was omitted from the final OFR Data and reports were released in an OGS OFR (Bloom, 2005) |
| Soil Gas Hydrocarbons Camiro 01E02 | 2002-2004 | Over 20 case study areas: U, Au, VMS, Ni-Cu-PGE, Ni-Cu, Ni, kimberlites, plus non-economic targets | Sutherland, Southern, Leventhal, Sherwood-Lollar Klussman Hamilton | Actabs, UWO | CAMIRO | <ul style="list-style-type: none"> Includes methods development studies and an impressive number of case studies using SGH over known deposits Many sites show very good results and many of the others show some indication of a response, even if the orebody cannot be outlined Usefulness of final report CD is hampered by poor and inconsistent data presentation. Extremely variable presentation styles/formats and different levels of detail combined with a restrictive HTML / Flash format that prevents copying (and in some cases even printing) makes site to site comparison very difficult. Reformatting and augmenting of site data for some of the case studies could make this an important resource for interpretation of SGH signals |

OGS = Ontario Geological Society; GSC = Geological Survey of Canada; CAMIRO = Canadian Association of Mining Industry Research Organizations; ECG = Eion Cameron Geochemical Inc.; UWO = University of Western Ontario; Actlabs = Activation Laboratories Ltd.; CSM = Colorado School of Mines; SGH = Soil Gas Hydrocarbon®; SDP = Soil Desorption Prolysis™; OFR = open file report; OTH = Operation Treasure Hunt (Ontario Provincial Government fund); OMET = Ontario Mineral Exploration Technologies program; TGI = Targeted Geoscience Initiative (Canadian Federal Government fund).

exploration companies to successfully discriminate buried targets. However, others have experimented with the methods and have experienced high cost failures before abandoning them as potential exploration tools. Upon examination of the successes and failures, it is evident that deep penetrating geochemical (DPG) techniques work well, only if: (1) the objective is sound, i.e. they are used in target discrimination and prioritization, not target generation; (2) proper field sampling protocols are followed; and, (3) data interpretation is carried out by personnel with a basic understanding of surficial geochemical processes.

Three classes of soil geochemical methods are described here that have been found to detect signals related to underlying mineralization. The most commonly used are selective leaches, which seek to measure a previously mobile component of metals in a soil sample, perhaps originating from buried mineralization. The second technique measures hydrocarbons in soils and is a recently developed tool that shows much promise. Soil hydrocarbon techniques have shown responses over buried sulphide deposits and particularly strong responses over kimberlites. The third technique described here is soil-slurry pH, which is both simple and inexpensive and can add value to soil geochemical surveys, especially in areas with uniform moisture content.

The purpose of this document is to summarize some of the salient findings of the above-noted studies as a guide for the use and implementation of soil geochemical techniques for mineral exploration in glacial sedimentary environments, but also to give an indication of their limitations. Readers interested in the supporting science or who require more detailed examples from case studies are invited to obtain some of the publications and reports cited herein.

UPWARD TRANSPORT OF ELEMENTS IN THICK GLACIAL DRIFT

Soil geochemical techniques in areas of exotic (i.e., transported) glacial drift are predicated on the dispersion of elements upward from mineralization and rock followed by their attenuation in shallow soils. Elements disperse from mineralization by many processes including mechanical transport by ice, water and wind; and hydromorphic dispersion by diffusion, advection, convection, capillary action and electro-migration. In the unsaturated zone, transport of metals in gaseous form has also been suggested as a possible mechanism. Demonstrated elemental anomalies in soils over mineralization in areas of thick drift almost invariably take the form of either a single peak response directly over the deposit or twin-peak responses immediately flanking it. As mechanical transport mechanisms in areas of glacial sediments would result in lateral displacement, it is likely that some form of vertical hydromorphic dispersion is responsible for these observed anomalies.

This paper considers two types of hydromorphic transport that are considered to dominate in fine-grained and coarse-grained saturated glacial sediments respectively: redox-gradient (electrochemical) and flow-related (advective and convective) groundwater transport. From a practical perspective, the mechanism of vertical migration is important because it can result in a characteristic surface geochemical signal in soils. Other possible mechanisms are not thought to be significant in glacial sedimentary environments either because they are too slow to account for responses in soils in thick overburden in the 10,000 years or so since glaciation, or because they operate only in unsaturated environments (e.g., root uptake, capillary transport).

Redox gradient transport (Hamilton, 1998, 2000) is now a popular explanation for vertical mass transport in glacial sedimentary environments because it unifies many commonly observed phenomena that occur over ore deposits into a related set of processes and therefore simplifies the interpretation of geochemical results. The model argues that reduced 'columns' or 'chimneys' should form in saturated glacial sediments over mineral deposits and kimberlites, and one of the more important outcomes of the Camiro Phase 2 fieldwork was to demonstrate the existence of these features (Hamilton et al., 2004a,b). The model relates the formation of 'acidic caps' to the oxidation of reduced metals where the reduced chimney meets the water table (Figure 1). The profound pH anomaly thus produced, changes the solubility of many elements and minerals, resulting in depletions, accompanied by enrichments on the flanks of the deposit that give rise to elemental 'rabbit-ear' responses. Chief among these are depletions / enrichments in carbonate. Other elements that commonly show rabbit-ear responses, possibly due to this process, are rare earth elements and halogens such as Cl, Br and I. Hydrocarbon responses in shallow soils are now understood to be related to an increase in the numbers of autotrophic (formerly known as chemotrophic: 'chemical eating') bacteria that occur over mineralization in response to the strong redox gradients associated with the reduced chimney.

Advective groundwater transport may be an important mechanism in coarser-grained materials including glaciofluvial sands and gravels and would also result in the development of a reduced chimney if reduced groundwater is transport upward. In these materials, upward hydraulic gradients at discharge zones and convection resulting from a bedrock heat-source (Mann et al., 2005) could cause upward migration of fluids from depth. Heat sources that might drive convection include exothermic oxidation reactions and, in cold climates, higher thermal conduction from depth in massive sulphides relative to country rock. Horizontal groundwater transport can also occur, potentially resulting in displaced elemental anomalies in surface soils or peat near areas of groundwater upwelling or discharge. This is particularly likely near the edge of fens, bogs or water bodies. Groundwater transport may result in the whole fluid reaching the soil sampling horizon, unlike electrochemical transport, wherein only certain redox-active solutes are expected to migrate.

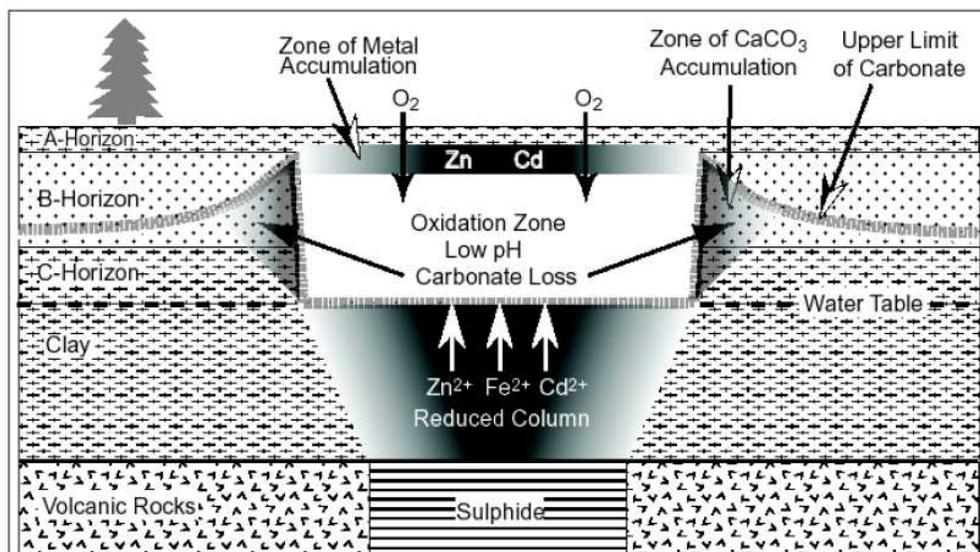


Figure 1: Model (Hamilton 2000) for development of anomalies through glacial clays. A reduced chimney is generated above the sulphide body. Reduced metal ions are oxidized at and above the water table by infiltrating oxygen and thereby generate H^+ ions which in turn dissolve carbonate (from C-horizon clay soils) that reprecipitates on the flanks of the zone of low pH (from Cameron et al., 2004).

SELECTIVE LEACHES

Soil geochemistry in mineral exploration seeks higher concentrations of key elements and groups of elements that are indicative of specific types of rock or mineralization. Selective leach geochemistry seeks to extract only the mobile portion of metals from a soil sample. Typical soils contain high concentrations of 'endogenic' metals (i.e., that are an intrinsic component of the soil) and as most soil parent materials in Ontario have been transported by glaciers, the endogenic metal signal has no chemical relationship to that of the underlying mineralization. Selective leach techniques are very weak extractions that attempt to selectively dissolve the 'exogenic', or mobile component of metals that stick to the outside of the mineral grain. Since metals originating from mineralization buried by exotic (i.e., transported) glacial overburden are most likely to be part of the mobile component, selective leaches are more successful at detecting a signal from mineralization than are conventional strong acid digestions that dissolve most of the soil sample.

Choosing a selective leach method

Most of the selective leaches commonly used in mineral exploration are designed to extract metals from particular phases. For example, Enzyme Leach[®] targets manganese oxides; hydroxylamine-hydrochloride targets iron oxides; and sodium pyrophosphate targets organics. None of these methods are completely selective to their target phase. The term selective leach is currently in common usage and therefore is used here to describe selective and non-selective extractions.

The two most popular selective leaches used for mineral exploration are Enzyme Leach[®], a patented method marketed

by Activation Laboratories (www.actlabs.com); and MMI (Mobile Metal Ion[™]), which is a proprietary leach owned by MMI Technology and marketed by SGS Minerals in Toronto and ALS Chemex in Australia (www.mmigeochem.com). Both leaches were tested as part of the Phase 2 CAMIRO investigation (Cameron, 2002) and found to be effective in detecting VMS mineralization through as much as 50 m of fine-grained glacial sediments. In addition, to being the most common commercial leaches, they are also among the weakest. Paradoxically, a weaker leach is desirable because it is less likely to extract part of the endogenic component of metals in soils and will, therefore, have a higher signal to noise ratio. Figure 2 shows the ranges of Cu extracted by several of the leaches tested as part of the CAMIRO work. Enzyme Leach is the weakest of all, sometimes showing ranges that are lower than distilled water. MMI is next, followed by ammonium acetate and then hydroxylamine. Sodium pyrophosphate is not shown but like hydroxylamine, is a relatively strong leach.

The Camiro Phase 2 study (Cameron, 2002) compared analytical extractions against one another. The very weak leaches were found to best detect a mineralization-related signal through thick cover. The successful leaches included: distilled water, weak HCl, ammonium acetate, Enzyme Leach and MMI. The water leach and weak HCl showed more variability and poorer precision than the other leaches. In contrast to either the MMI or Enzyme Leach, the ammonium acetate suppressed the response in some elements over the centre of mineralization relative to the response on either side. This may be because the leach solution is buffered to pH 5 or 7. Otherwise, ammonium acetate showed good performance and may be better suited to higher-pH environments in carbonate-rich terrain. However, regardless of the reason, MMI and Enzyme Leach appear to show the most favourable results in glacial environments and their analytical methods are briefly described below.

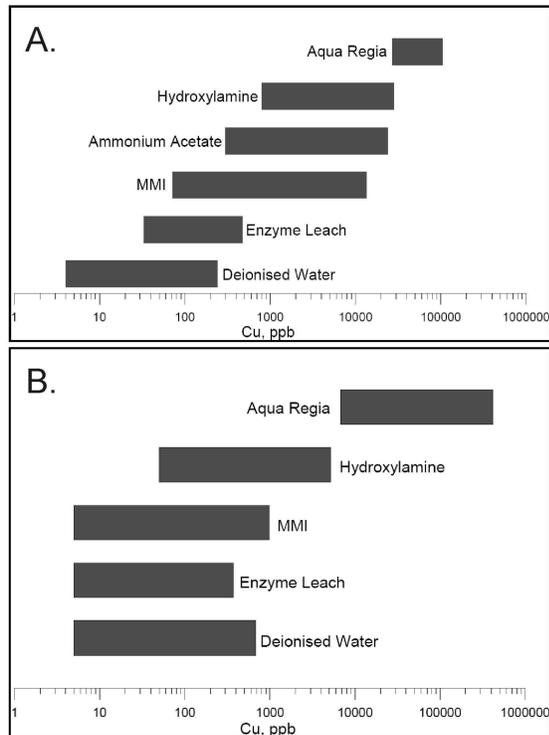


Figure 2: (A) Ranges for Cu extracted by 6 leaches for 61 soils collected over the Spence deposit in northern Chile. (B) Ranges for Cu extracted by 5 leaches for 121 B-horizon soils from the Cross Lake deposit in Ontario. (From Cameron 2002).

The Enzyme Leach analysis is performed on a 1 g sample dry soil pulp. The pulp is prepared by oven drying and sieving the soil to -60 mesh (-250 μm ; i.e., fine textured sand and finer) component of soil. The pulp is leached in a glucose oxidase solution which contains an enzyme. The enzyme reacts with amorphous MnO_2 and probably other phases, thereby releasing adsorbed metals. The metals are complexed with gluconic acid and the solutions are analyzed using an inductively coupled plasma mass spectrometer (ICP-MS). The analytical package consists of a suite of 60 elements at sub-part-per-billion to part-per-million levels. Selected anomalous samples are checked by repeating the process. Internal laboratory duplicate samples are run one for every 15 samples.

MMI analysis is performed by SGS Laboratories in Toronto, Ontario, Canada. A 50 g sample is subjected to weak extraction using a multi-component solution to release mobile ions. A high sensitivity ICP-MS analysis provides results at a parts-per-billion range for a specific but limited suite of elements that depends on the MMI leach solution being used. At the time of writing there were 8 MMI digestions listed on the MMI website and manual. We have tested 3 of these in glacial environments: the MMI-A, B and D digestions, which are respectively optimized for base metal, precious metal and diamond exploration. The MMI-A leach reports Cu, Pb, Zn and Cd; the MMI-B leach reports Au, Ag, Ni, Co and Pd; and the MMI-D leach reports Ni, Co, Pd, Nb, Cr, Mg, Rb and Y.

Selective leaches and soil type

Much of Ontario's boreal forests are underlain by relatively thick accumulations of fine-grained glacial clays and tills interspersed with coarser grained esker sands and glaciofluvial outwash. Flat lying fine-grained sediments are often water saturated and overlain by modern organic deposits of peat of varying thickness. Exploration geochemical programs in this terrain that target a specific, very shallow sample interval (<0.5 m, see below) are likely to encounter variable types of sample media. It has been recognized for many years that different soils have different background geochemical signals and that mixing sample media is a major source of geochemical 'noise'. This is particularly true for selective leaches.

Inorganic soil media

Figure 3a shows Enzyme Leach Zn concentrations for various soil types collected on transects in background areas near the Cross Lake VMS deposit in northeastern Ontario. The figure shows that Zn concentrations are strongly influenced by soil type. The median concentrations for a clay substrate for the B, Ae, A1 and humus horizons are 15, 22, 57 and 191 ppb respectively. In an area of sand substrate, the median concentrations for the B and Ae are below detection (5 ppb) but are much higher for the humus, which has a median of 1710 ppm. Figure 3b shows concentrations for the same horizons over mineralization. With the exception of humus over a sand substrate, the concentrations for each soil medium are higher over mineralization than in background areas. However, the signal due to mineralization in a given soil horizon is much smaller than the total variation in background concentrations for all media. This means that indiscriminate sampling of soils without regard to medium may result in a signal to noise ratio that is too low to detect mineralization. Figures 3a and b also show that consistently sampling an inorganic soil medium that consists of either or both the Ae or B horizons should show an acceptable background to anomaly contrast.

Organic soil media

Figure 4 shows background and anomalous Zn responses in organic soil media. It is apparent from the figure that drier organic media show much higher metal responses. The median concentration for peat is below the detection limit of 5 ppb whereas $\frac{3}{4}$ of the dry humus samples show concentrations over 300 ppb. Also apparent from the figure is that the median value and range for dry humus (sand substrate) over mineralization are very similar to those in background. The anomaly to background contrast is higher for moist humus (clay substrate) but not as high as for the underlying inorganic media (Figure 3a and b). This suggests that organic media in dry terrain is not an appropriate sample medium because the high baseline metals concentrations tend to obscure any metals signal due to mineralization.

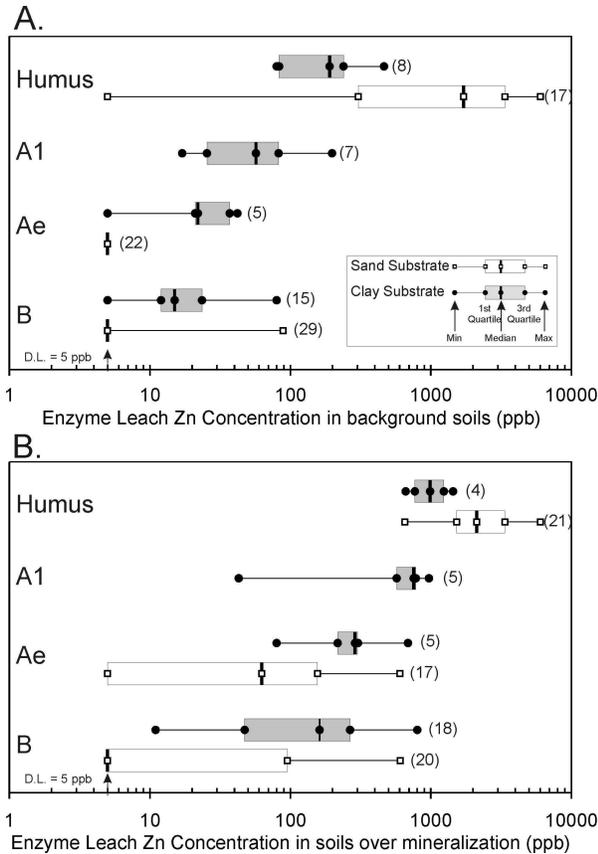


Figure 3: Box and whisker plots showing Enzyme Leach Zn concentrations in various soil media at the Cross Lake VMS deposit. (A) Shows data for samples collected in background areas; (B) Shows data collected over mineralized zones.

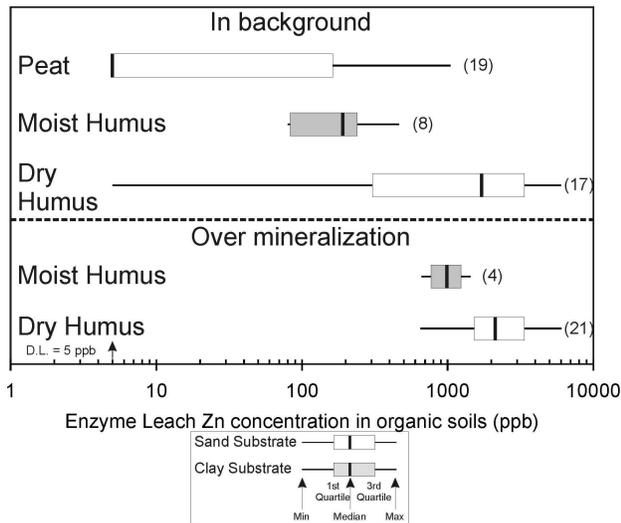


Figure 4: Box and whisker plots showing Enzyme Leach concentrations in organic soils at the Cross Lake VMS. Numbers for each case are shown in parentheses.

No peat was available for collection over mineralization at Cross Lake but other studies have shown that metals responses

occur in peat above sulphide mineralization and kimberlites. Figure 5 shows Zn and Cu by aqua regia and sodium pyrosulphate extractions in peat above the Gemini VMS in northwestern Quebec. Both elements by both digestions show depletion over the projected subcrop of mineralization, enrichments on either side and moderate enrichments over the shallowest down-dip extents of the mineralization. Similar depletions have been noted at a similar sample depth (~25 to 50 cm) in peat by sodium pyrophosphate over a small pyritic syenite-hosted Au vein at the Marsh Zone deposit (Hamilton and Cranston 2000). Like sodium pyrophosphate, sodium pyrosulphate, is a moderately strong leach.

These results show that saturated peat, at least in this depth interval, is an appropriate sample medium for mineral exploration. Despite the relatively low-concentrations of the anomalies in peat, the very low background concentrations for metals result in acceptable anomaly to background contrast.

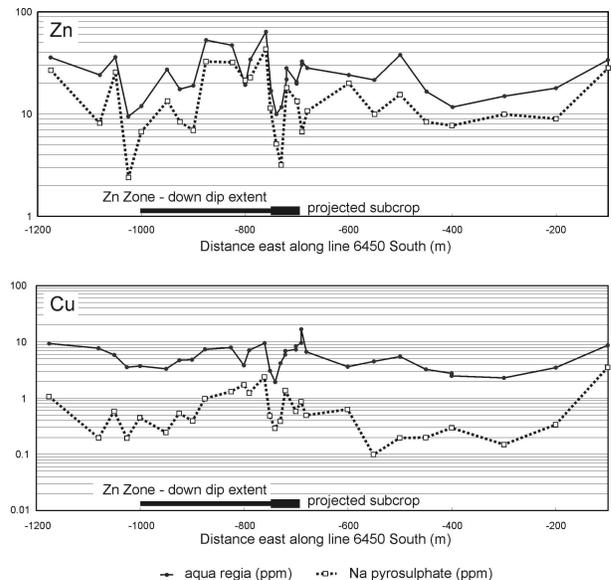


Figure 5: Concentrations of Zn and Cu in ppm by aqua regia and sodium pyrosulphate on a transect across the Gemini VMS deposit, northwestern Quebec. Samples were taken at the 25 to 50 cm interval in peat (from Jackson 2005a).

Selective Leaches and Sampling Depth

Sampling depth in inorganic soil terrain

Sampling depth is very important to a successful selective leach geochemical program. After experimenting with several depth intervals, it was determined during the Camiro Phase 2 study that an interval close to that used in the 'MMI protocol' (Mann et al. 1998) was most appropriate. Figure 6 shows the effect of sampling depth in relatively dry clays in forested terrain at the Cross Lake VMS, where mineralization is covered by 30 to 50 m of glaciolacustrine varved clays, silts and sands. Sampling was carried out on 2 occasions at a total 5 different depth intervals as part of the Camiro Phase 2 study. On the first occasion the B-horizon and humus were sampled and subjected to a variety of analytical extractions, including aqua regia and Enzyme Leach on the B-horizon samples. Samples for MMI

were collected from the 'MMI depth interval' between 10 and 25 cm from the base of the leaf litter. No significant metal response was noted in the humus or B-horizon by any of the leaches but the MMI data showed a multi-sample and multi element (Zn, Cd and Pb) response on both lines sampled.

On the second sampling occasion, the uppermost 10 cm of the B-horizon was collected on both lines and subjected to analysis by aqua regia, MMI, Enzyme Leach and ammonium acetate (the latter is not shown on the figure). On Line 6, the 10 to 20 cm interval of B-horizon was also sampled. On both lines, since the A-horizon was uniformly thin, the uppermost B-horizon interval invariably occurred within the 'MMI depth interval' sampled earlier. It showed an excellent response by both MMI and Enzyme Leach (Figure 6). Interestingly, the 10 to 20 cm interval of B-horizon showed a suppressed response over mineralization with two flanking highs, i.e., a 'rabbit-ear' response. These data indicate that when sampling inorganic soils, sampling both a consistent depth interval and consistent medium are crucial and that the depth interval must be very shallow.

Sampling depth in peat terrain

In peat terrain a consistent and appropriate sampling depth is necessary for several reasons. Very shallow peat invariably shows elevated concentrations in many metals, particularly within a few 10s of km of historic mining and smelting areas. Fallout from tailings dust, smelting and other anthropogenic sources is partly responsible for this metalliferous zone. Diagenetic metal cycling is also likely a contributing factor since

the highly elevated concentrations always occur in the upper 10 cm, despite variable peat accumulation rates and lengths of time since the local anthropogenic activity started. Figure 7 shows aqua regia concentrations in peat for selected metals at the Marsh Zone. The Pb, Zn and Au responses in very shallow soils are interpreted to be due to dust fallout from Au tailings located less than 1 km to the south. The Hf response, which is similar to that of other lithophile elements, shows an increasing response with depth and is interpreted to be due to entrainment of clastic sediments during an earlier and wetter period of bog development.

Figure 7 shows the importance of sampling at a consistent depth between 25 and 50 cm. If samples are taken from too shallow a depth, the metalliferous zone will be encountered and it is unlikely that a weak signal from depth will be discernable. Sampling too deep may encounter peat with clastics, which can result in a misleading signal.

PH SLURRY TECHNIQUES

Slurry pH measurement is a simple and inexpensive technique that can add value to an exploration geochemical program. For mineral soils, volumetrically equal amounts of sediment and water are mixed into a thin slurry, the pH of which is measured using a standard probe and meter. Mixing, measuring and cleaning between samples takes 3 to 4 minutes and can be done either in the field or in camp the evening after sampling. Saturated peat can be measured directly in a sub-sample, after squeezing out air.

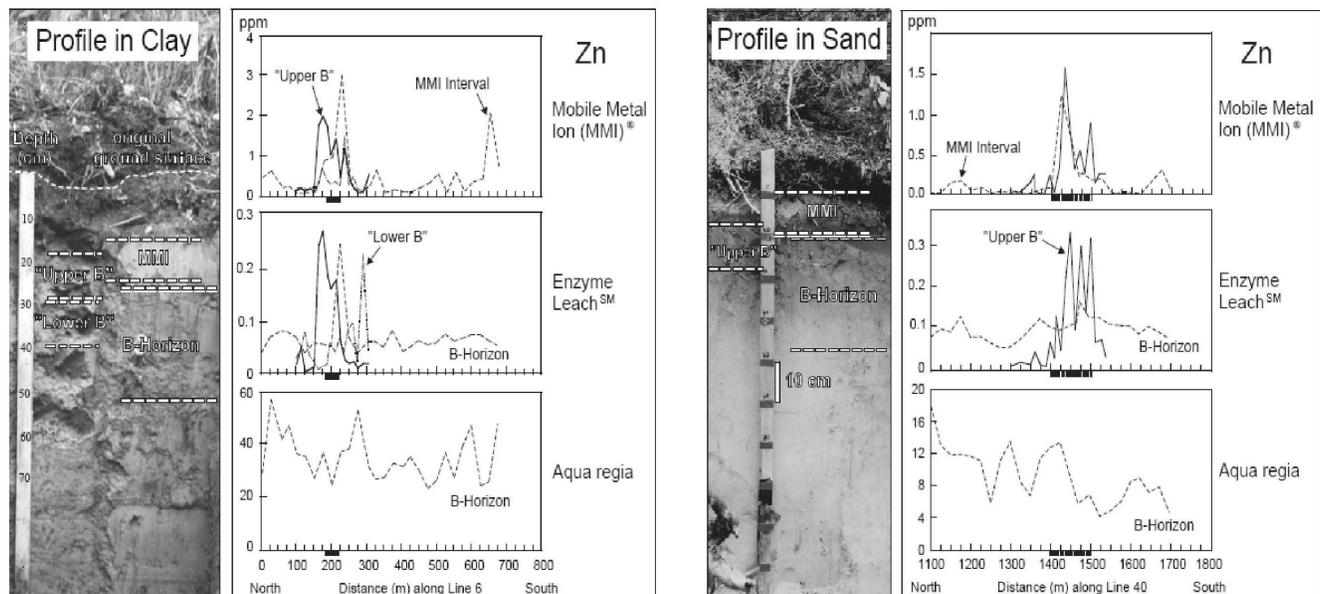


Figure 6: Zn geochemical profiles for MMI, Enzyme, aqua regia leaches of samples from Line 6, covered by ~30 m of clay and Line 40, covered by ~50 m of sand and clay, Cross Lake VMS (from Hall et al. 2004)

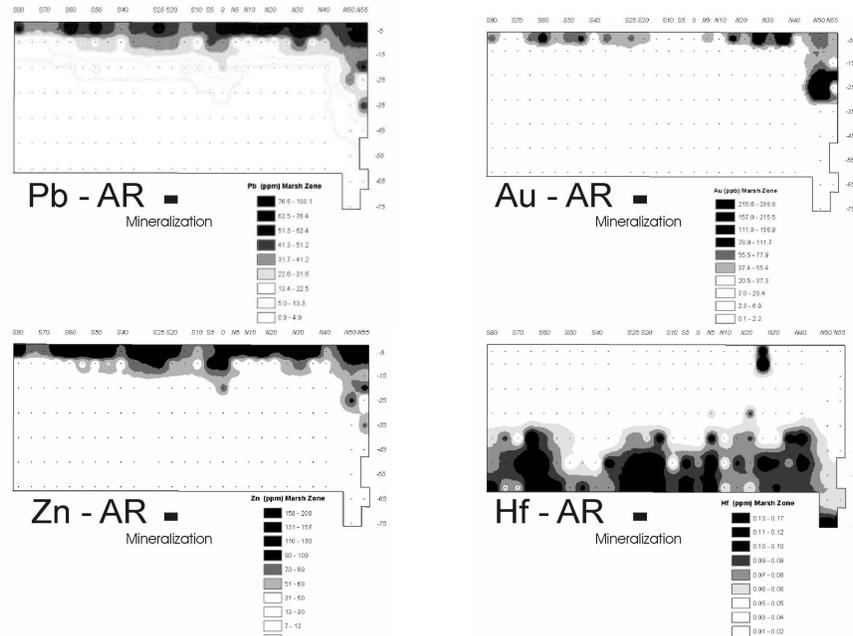


Figure 7: Concentrations of selected elements in peat by aqua regia; Line 15+10, Marsh Zone. Units at top are metres north and south of baseline; units at the side are cm below the top of compressed sphagnum. The elevated concentrations of Zn, Pb and Au at N55 and in Hf at N25 result from contamination by diamond drilling fluids around the drill pads located there. High metal concentrations in very shallow peat are interpreted to be due to dust contamination from tailings located less than 1 km to the south of the site. A metallic response due to the pyritic Au mineralization is not apparent in these data but pH and some metals show a subtle response (From Hamilton et al. 2005).

The measurement of pH allows the detection of several phenomena that can occur in glacial sediments over mineral deposits. Acidic zones have been documented in the unsaturated zone over reduced chimneys and mineral deposits (Hamilton et al. 2004a&b, Jackson 2005a, Gleeson et al. 1988). As discussed, these are postulated to form due to upward movement of reduced metals, followed by their oxidation (Figure 8). Below the water table the reduced chimney itself has an alkaline response relative to adjacent sediments because it suppresses oxidation that occurs in association with weathering reactions (Figure 8).

A third possible pH phenomenon can occur over kimberlites and other ultramafic rocks if their interstitial groundwater migrates to the surface. This could occur in areas of thin overburden or coarser-grained sediments. Groundwaters in ultramafic rocks are extremely reducing and alkaline (up to pH 12.4). These waters also contain Ca but no carbonate and if they come in contact with soil zone CO₂, they will rapidly precipitate CaCO₃ (see Hamilton et al., 2002b). Figure 9 shows the slurry pH and Ca by ammonium acetate in soils over 3 kimberlites in northeastern Ontario. The predominant overburden cover material at all three sites is glaciofluvial sand. The samples were all collected at a consistent depth, which resulted on the B-30 kimberlite, in both peat and inorganic sands being sampled. Notwithstanding a bias due to the medium change at B-30, in general soils over the kimberlites clearly show higher pH and Ca than in adjacent areas.

Unfortunately, many soil-forming and other surficial processes affect pH and interfere with pH surveys carried out as part of a geochemical exploration program. Some of the surficial processes that affect pH also cause 'false' anomalies with partial

extractions. A number of the more important interferences are discussed in the interpretation section of this paper.

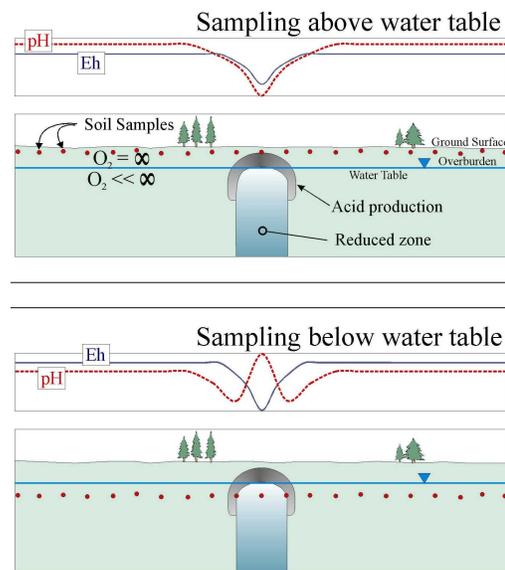


Figure 8: The development of an acidic aureole around a reduced column over mineralisation. The water table is a sharp boundary to the availability of oxidising agents. The contact between the reduced chimney and oxidising agents near and above the water table results in metal oxidation and acid production. Below the water table, suppression of normal B-horizon oxidation processes in the reduced chimney results in a pH high, flanked by minor lows where downward diffusing oxygen reacts with reduced species (From Hamilton et al., 2002a).

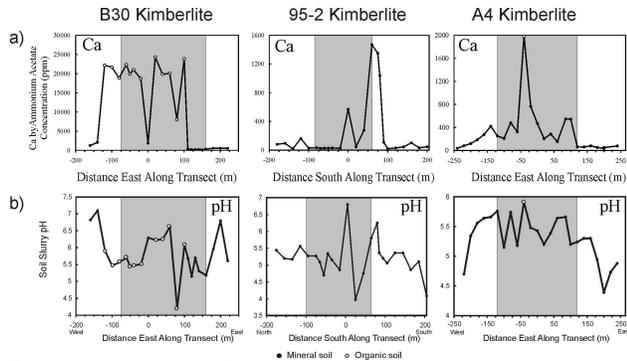


Figure 9: Slurry pH and Ca by ammonium acetate (pH 5) for shallow soils over 3 kimberlites. Note that some of the Ca data show a positive bias in organic soil (peat) samples. All samples were taken at a consistent depth interval 10 to 20 cm below the base of the leaf litter (from McClenaghan et al. 2006).

SOIL HYDROCARBON TECHNIQUES

In recent years, the measurement of hydrocarbons in shallow soils has revealed significant responses over mineralization. Anomalies occur in both the magnitude of hydrocarbon compounds and their assemblages. Two techniques for hydrocarbon analysis of soils were commercially available at the time of our studies: the Soil Gas Hydrocarbon technique by Activation Laboratories in Ancaster Ontario (www.actlabs.com); and the Soil Desorption Pyrolysis technique by SDP Pty Ltd., in Australia (SDP is no longer commercially available). The methods use very different approaches to detect the changes in hydrocarbons (and, in the case of SDP, other gases) associated with buried targets.

Samples for SGH usually consist of B-horizon soils and can be collected at the same depth as pH and selective leach samples. After drying and sieving, approximately 1 g of soil is subjected to an aqueous extraction and analysis by Gas Chromatograph Mass Spectrometry (GCMS). The technique measures 162 hydrocarbon compounds in the C5-C17 range, none of which are gaseous at room temperature. Data are provided in tables of concentrations for the measured compounds. Selected compounds can be plotted individually but as it is the covariability of multiple compounds that is of interest, multivariate techniques such as factor analysis are usually necessary.

An SGH response can consist of elevated concentrations of individual compounds over buried mineralization and kimberlites. However, depletions in other compounds and zones of highly variable (spiky) responses are also common over the target features (Figure 10). The most characteristic SGH signal is a concentric increase in variability of SGH compounds, toward the centre of the buried feature. This is interpreted to be due to changes in the type and quantity of autotrophic organisms occupying the concentric redox/pH regimes in soils over the reduced chimney. Actlabs has a for-cost data interpretation service using Neural-Net Analysis that accentuates this zoned variability of compounds and displays it in plan-view as a single parameter. This method has shown convincing responses in a number of case studies, particularly over kimberlites. For

maximum effectiveness, the interpretation technique requires a continuous set of samples at an even spacing across the deposit. SGH responses over buried targets have been documented in both organic and inorganic soils. Variable sample media is reported to be less problematic for SGH than with selective leach geochemistry and preliminary studies by the OGS and our partners seem to confirm this.

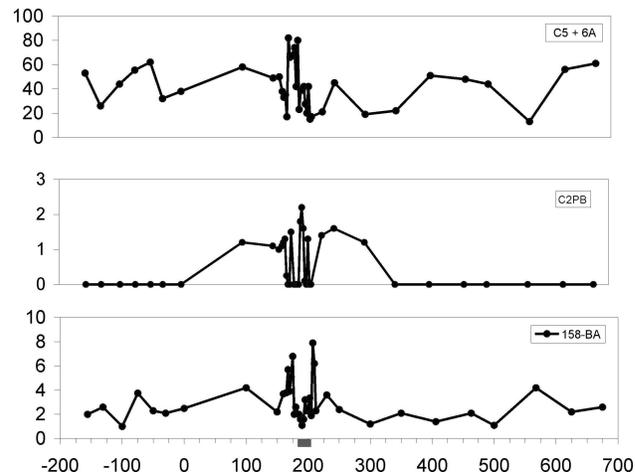


Figure 10: Results for 3 SGH compounds in B-horizon soils over Line 6 at the Cross Lake VMS. Compound C5+6A (a sum of 2 alkanes), shows a wide apical response over mineralization; compound C2PB (a propenyl-Benzene), shows a depletion over mineralization; and compound 158-BA (a branched alkane), shows a mixed and 'spiky' response. Units on the y-axis are parts per trillion (ppt).

Samples for SDP consist of *inorganic* soils collected close to surface below obvious organic matter (usually 10 to 15 cm). A consistent sample depth is considered much more important than a consistent sample medium. Samples are dried at 40°C and sieved to obtain a minimum of 0.5 g of the clay fraction (0.2 to 2 μm) for analysis. The analytical method involves pyrolysis to release compounds in the soil sample at high temperatures, followed by analysis of approximately 40 compounds, not all of which are hydrocarbons. The compounds are typically not reported directly, but rather a proprietary mathematical technique derives 2 parameters that can discriminate mineralization and can be plotted on line plots or in plan view.

The data processing requires that a calibration template be obtained by conducting an orientation survey over known mineralization in a similar landscape as in the survey area. Between 60 and 100 samples are collected in the orientation survey, with approximately 1/3 of these collected over and 2/3 off mineralization. Alternately, one of a number of generic templates can be used if studies have been done in the past in similar landscapes over similar deposits.

An SDP-developed mathematical technique compares the behaviour of ratios of compounds over mineralization relative to background areas to establish the nature of a mineralization-related response. SDP Pty. Ltd. describes the purpose of the template thus:

"The template calibration consists of all the gas ratios in a dataset that exceed a threshold defined in terms of their ability to discriminate between "ore" samples and "not-ore" samples in the dataset. This leads naturally to two parameters, the "SDP Sum",

which is the sum of all anomalous ratios in a template, and the "SDP Count", which measures the proportion of the total number of ratios which are anomalous, for a given sample...Broadly speaking, SDP Count measures whether an area in a large survey is anomalous, while the SDP Sum is a measure of how anomalous the area is."

Therefore, the results of SDP analysis are provided in processed form as an SDP sum and an SDP count, both of which can be an indication of the presence of mineralization. Figure 11 shows a plot of SDP sum over VMS mineralization at Cross Lake, using a template developed at that site. Very similar results were obtained using the Noranda template, developed at the Perseverance and Caber deposits in northwestern Quebec, over 100 km away. The developers of SDP now believe (Steve Windle, personal communication, June 2007) that variable such as soil permeability control the localization of some SDP anomalies above mineralization to such an extent that the above-noted template technique is not tenable. For this reason, they no longer endorse the technique, nor do they continue to market it.

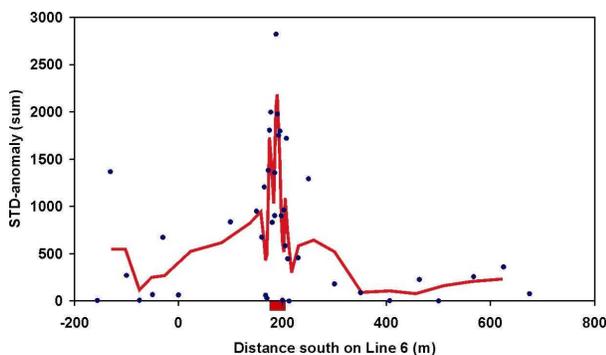


Figure 11: Results of SDP analysis at the Cross Lake VMS, Line 6. Points represent results for samples collected along a line parallel to but displaced from the line by 17 m. Solid line is a 3-point moving average through the data.

As mentioned, the hydrocarbons measured by SGH and SDP are interpreted to be due to the presence of organisms, either directly as microbial biomass or indirectly as the products of microbial exhalation. In soils, groundwater and rock, autotrophic organisms thrive at redox boundaries because they gain metabolic energy from the transfer of electrons from reducing agents to oxidizing agents. Such organisms include sulphur and iron oxidizing bacteria, which oxidize Fe^{2+} to Fe^{3+} and S^{2-} to S^{6+} respectively. Figure 12 shows the correlation between SGH compound variability as measured by the 2nd principal component, and redox, as measured by the oxidation-reduction potential of soil slurries (after the methods of Hamilton et al. 2004a, b). Areas of highest SGH variability correspond to concentric areas of strongly reduced soils that are interpreted to result from the presence of bacterial biomass. A plate count shows that the area over mineralization corresponds to higher plate counts of sulphate reducing bacteria.

The direct measurement of redox using platinum electrodes is expensive and unreliable. However, soil hydrocarbons can be used as a proxy for redox in soils and are therefore capable of detecting the reduced chimneys that are increasingly being reported over buried mineralization and kimberlites.

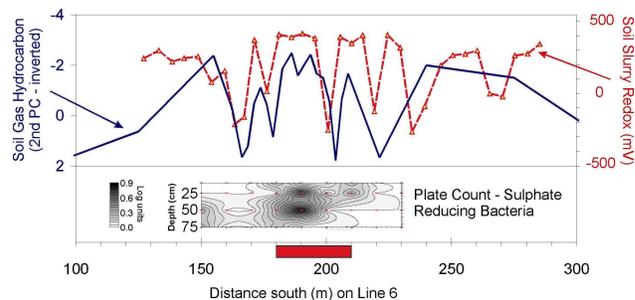


Figure 12: The correlation between (1) SGH variability, as measured by their 2nd principal component of SGH compounds; (2) redox, as measured by the oxidation-reduction potential of soil slurries; and (3) sulphur reducing bacteria (SRB) in soils over mineralization (from Hall et al. 2005).

OPTIMIZED SAMPLING METHODOLOGY

The following methodology is written as a protocol for the use of soil geochemical techniques as a method of discrimination or prioritization of previously identified targets. The initial identification of targets may be by magnetic or electromagnetic methods or it might involve tracing known mineralization into areas of thicker drift cover. The recommended methodology for target discrimination or prioritization would involve one or two transects across the known target and sampling for partial extraction, soil hydrocarbon and pH analysis. In areas of thick glacial overburden, the use of geochemical techniques as a method of generating targets without *a priori* knowledge of their location is not recommended for prospectors or others that lack specialized training in surficial geochemistry. This is because there are many surficial geochemical and soil processes that affect pH and cause mobile metal accumulations and that will lead to 'false' anomalies not related to mineralization.

Selection of sampling transect

Sampling transects must be selected wherein at least half, and preferably two thirds of the sites are to be collected in background, off the target being tested. Ideally, one third of the samples should be taken on either side of the target and one third over it. If numerous targets are being prioritized, georeferenced air photos should be obtained to allow site-selection on the air photo that will transect the target but which will also maximize sample consistency (Figure 13). Sample spacing should not be wider than half the width of the anticipated target and preferably narrower. For instance, for a 400 m wide magnetic target, where kimberlites are the exploration objective a 50 m sample spacing would be appropriate. Ideally, this would result in approximately 8 samples over the target and 8 samples on either side. If a 20 to 30 m wide geophysical conductor is being tested, the ideal sample spacing would be 10 m. Short sample spacing is cost effective provided transects and not grids are being sampled and the object is target discrimination or prioritization and not target generation.

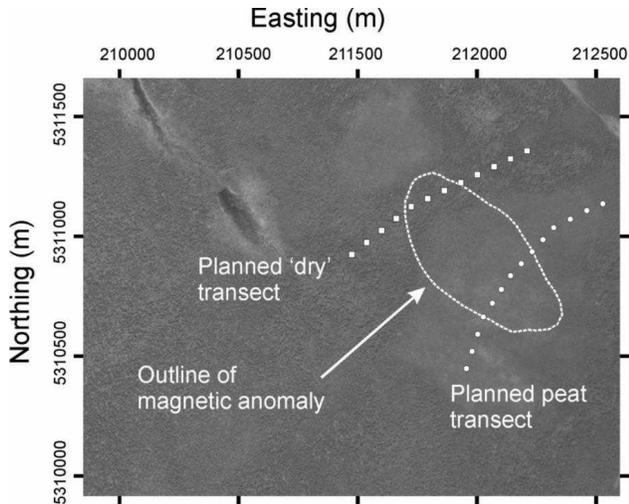


Figure 13: Air photo showing two possible transects over a hypothetical magnetic target. Transect 1 is in 'dry terrain' and the target sample medium is B-horizon. Transect 2 is in peat terrain. Note that the edges of the bog are avoided in the latter transect to avoid possible 'edge effects'.

Sampling Methodology

Sampling depth is as critical as soil type to the successful use of selective leach geochemistry. A protocol was developed for northern Ontario environments that takes into consideration both depth and medium. As part of this protocol, there are only two target media: mineral soil and peat. The mineral soil includes: the Ae horizon, which is the whitish, leached material below the organics; the B-horizon, which is the orange zone of metals accumulation; and the C horizon, which is the relatively unaltered material. It does not include the A1 horizon, which contains significant organic material. Figure 14 shows the common soil types likely to be encountered. Alluvium (Figure 14d) often occurs on slopes and in stream valleys and should not be sampled because of the variable amount of organics and unpredictable age and provenance of the sediments that result in wildly variable metals content.

The primary target medium is the mineral soil but this is not always available within the target depth interval of 10 to 25 cm because much of northern Ontario is covered by peat accumulations of greater than 25 cm. To resolve this problem, we have developed a protocol that collects either mineral soil or peat at a given site and then treats the data as 2 separate media during later interpretation. Notes *must be taken* to differentiate which of the 2 media was collected or interpretation of results will be impossible. In addition, a pH sample or a field pH measurement must also be taken, since pH cannot be properly carried out on a sample pulped and dried for analysis.

Equipment

- 3" diameter Dutch Auger
- Whirl-pac[®] polyethylene bags or equivalent (minimum 5" x 9" bags for selective leach and hydrocarbon samples; smaller bag for pH sample)

- Field pH meter calibrated daily with pH 7 and 4 buffer solution
- Note-book, preferably with pre-printed forms to avoid unrecorded data. Alternatively a Palm-pilot or equivalent digital data entry system could be used.



Figure 14: Soils likely to be encountered during geochemical surveys in northern Ontario. (A) Shows a typical dry podzol soil with a well developed Ae-horizon (whitish) and an underlying B-horizon. (B) Shows a typical B-horizon in a clay substrate. (C) Shows a well humified peat. (D) Shows alluvium (note mottling and organic-rich laminations).

Selection of protocol

At each site the auger is used to extract the top 25 cm of soil (Figure 15). If at least 5 cm of mineral soil is present in the interval from 10 to 25 cm, the "dry protocol" is used. If only peat is available, the "peat protocol" is used. In transitional zones where peat is 20 - 30 cm thick, neither protocol is ideal because clastic matter will likely be entrained in the peat and the mineral soil will be relatively unoxidized and therefore anomalies related to surficial conditions are expected. These problems will affect pH and selective leach samples to a greater extent than hydrocarbon (SGH) samples. A proposed solution to transitional soils is to collect whichever medium has been prevalent on the transect up until that point to maximize consistency. These samples can be submitted for hydrocarbon analysis and analyzed in the field for pH. If very large pH anomalies are associated with the change in medium, it is likely that the selective leach results will be similarly biased. The affected samples can therefore be 'weeded' in the field and not submitted for selective leach analysis.

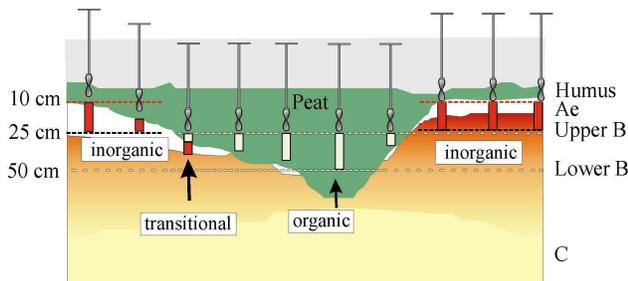


Figure 15: Sampling protocol in variable terrain. Mineral soil should be sampled if available in the upper 25 cm. Where organics are thicker than 25 cm, peat should be sampled in the 25 to 50 cm interval. In transitional areas, where organics are between 20 and 30 cm, the medium that is most prevalent elsewhere on the line should be sampled in order to maximize consistency of the sample medium.

Dry Protocol

The leaf litter at a site is brushed off and the Dutch Auger is used to extract the mineral soil from the 10 to 25 cm depth, measuring from the base of the leaf-litter. If at least 5 cm of mineral soil exists within the 10-25 cm zone, this is collected as the sample for that station. The ideal target medium for the mineral soil sample is the Ae horizon or the uppermost B-horizon if the Ae horizon is not present. Generally, one or the other of these would be developed immediately under the organic soil horizons if they are <25 cm thick. The C-horizon would rarely be encountered in such cases during the sampling, but would be sampled if it was.

Notes must be taken recording (1) the medium (mineral soil); (2) the type of soil material (i.e., sand, etc.), (3) site conditions, especially with respect to drainage and soil moisture. Notes are discussed further below.

Peat Protocol

In northern Ontario if mineral soil does not occur in the first 25 cm, the organic material will almost invariably be peat as opposed to humus and the "peat protocol" must be used.

Avoiding hummocks, stand on level ground and insert the Dutch auger through the compressed sphagnum under which you are standing. The sample should be taken from a consistent depth between 25 and 50 cm. A piece of tape should be put on the auger handle at 35 cm from the centre of the auger sample interval. The sample interval of a Dutch Auger is approximately 20 cm wide and therefore, if the sampler is inserted into the peat until the taped spot is level with the ground, the sample interval will be between 25 and 45 cm.

Samples taken near the base of peat can sometimes have entrained clastic material so if the region has relatively thin peat, the sample depth should be on the shallower end of the range (20 to 30 cm). In thicker peat, the sample can be taken from the deeper part of the interval. After the sample is taken the auger should be inserted to its full length to determine if the base of peat exists within one auger's length and the result should be recorded. Later this will help to discern any geochemical anomalies related to thickness of peat and bog 'edge effects'. Other notes should record the presence of clastic material in the sample and the proximity to creeks that can shed clastics into the peat during flood events.

pH Determination

For peat, the pH probe can be inserted into a sample placed in a cup and the measurement taken in the field. The peat around the probe should be squeezed to exclude air and bubbles and to ensure a liquid contact around the bulb of the probe. The pH readings should be taken after 1 minute of probe immersion. When sampling mineral soil a slurry must be prepared. A consistent amount of distilled water (2 to 5 ml) should be added to a consistent amount of mineral soil (1 to 2 g) and mixed into a paste or slurry. The probe is then inserted into the paste and stirred to ensure complete liquid coverage of the bulb and reference junction (which is a small, circular hole near the bulb that is filled with porous ceramic). Again, the reading should be taken after 1 minute of probe immersion. Because preparing the slurry is a more involved procedure, it may be preferable to carry it out at the end of the day once the fieldwork is completed. A separate sample must be taken for pH, or a subsample removed from the main sample when measurements are being taken at the end of each day.

At least daily calibration of the pH probe is essential and records should be kept after each calibration. Probes used for slurry measurements have a shorter life than probes used for water measurements. Generally a probe will last a field season but care should be taken to replace the probe if calibration becomes difficult, as this is an indication of probe degradation.

Recording of field data

Notes must be taken when sampling because the two media are treated separately at the data interpretation stage. Notes should include the following:

Dry protocol:

- Medium, i.e., mineral soil
- Moisture and drainage conditions, i.e., wet / dry, "near creek", "on slope"
- The type of material sampled, i.e., sand, silt, clay or alluvium, till

- The predominant soil horizon sampled, i.e., Ae (the whitish leached zone), B (the zone of iron oxides, C (relatively unaltered parent material).

Peat protocol:

- Medium, i.e., peat; dry peat; humus
- Peat thickness (up to the length of the auger).
- The presence of any clastic material in the peat such as sand, silt, or clay.
- Presence of watercourses.

INTERPRETATION OF GEOCHEMICAL RESPONSES OVER BURIED FEATURES

Outlined below are descriptions of the types of responses expected due to a variety of buried features and 2 major classes of 'false anomalies' that result from surficial processes. It draws from multiple sources related to the projects outlined in Table 1.

Halos responses over reduced chimneys & acidic caps

As discussed, halo responses in shallow soils can surround a reduced chimney and the acidic cap that often overlies it. The solubility of most elements and minerals depends on pH and Eh, and since these two parameters are starkly different above the chimney/cap relative to adjacent soils, very different assemblages of mobile ions are found in and adjacent to these features. In Ontario, as discussed above, the most common halo responses occur in elements associated with carbonate – Ca, Mg and Sr. Others include the halogens, Cl, Br and I and rare earth elements. Activation Laboratories have identified an empirical 'oxidation suite' of elements that often form halos around deposits. This suite comprises Cl, Br, I, V, As, Se, Mo, Sb, Te, W, Re, Au, Hg, Th and U. These elements are interpreted to be captured at the pH/redox boundary at the edge of reduced chimneys (Hamilton 2000) although many likely do not originate from the ore deposit itself but rather from overburden. Elements mobile in oxidized environments (e.g., U, V), may originate in background areas and are captured in the more reduced and acidic environment over the buried feature whereas those mobile in reduced and/or acidic environments (e.g., Cu, Ca) may be mobilized away from overburden above mineralization and accumulate in peripheral areas. Therefore, these are responses that result from secondary geochemical processes, such as acid generation, which are related to the primary process of upward metal dispersion. Halo responses and 'rabbit-ear' anomalies (a single-transect expression of a halo response) can be indicative of a buried reduced feature and hence, proper identification of this type of anomaly can provide important information to the explorationist.

Hydrocarbon responses have been documented over mineralized targets and at least one barren target (an accumulation of $H_2S_{(aq)}$) that have associated reduced chimneys. As mentioned, it is the redox anomaly that is postulated to indirectly cause the hydrocarbon anomaly through the proliferation of autotrophic bacteria in strong redox gradients.

Therefore, soil hydrocarbon anomalies that accompany selective leach halo responses and/or a pH response support the presence of a reduced chimney, but not necessarily the presence of economic mineralization. To determine the nature of the buried feature, the data interpreter has several options. The magnitude of the pH and hydrocarbon (redox) anomalies provide some indication, since some features such as kimberlites have stronger responses than others. However, the most important evidence regarding the nature of the buried feature is the assemblage of anomalous metals in shallow soils. Wide apical anomalies over the target are of particular interest because elements originating from the target most often form this type of response.

Kimberlites

Kimberlites overlain by coarser-grained sediments such as glaciofluvial sands are most likely to show positive pH responses as groundwaters in kimberlite rock are hyper-alkaline. In this case, carbonate precipitation that occurs as the fluids contact the soil zone may result in accompanying apical Ca, Mg and Sr responses that may or may not be enhanced above the edges of the target. However, the alkaline response will only occur if the fluids reach the soil zone. If the dominant transport mechanism is electrochemical, as is usually the case in clayey overburden, the fluids will not reach the soil zone and upward transported reduced metals are likely to produce an acidic pH response.

In addition to the possibility of a high pH-Ca-Mg-Sr response, other elemental assemblages have been noted over buried kimberlites and/or ultramafics. These include the light (La, Ce, Pr, Nd, Sm, Eu) and heavy rare-earth elements (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), which are often respectively summed. They also include Nb, Hf, Ni and K.

Based on our limited testing of soil hydrocarbon techniques and other reported case studies, kimberlites appear to show the strongest responses of any buried feature. As would be expected, the highest contrast responses occur near the edges of the reduced chimney over the kimberlite. On larger targets, a concentric pattern of hydrocarbon variability is often observed, which further supports a biogeochemical explanation for the responses.

It is important to note that the pH, hydrocarbon and metals assemblages observed over kimberlites are likely to be similar for any buried ultramafic rock, especially if it occurs in a felsic or sedimentary country rock. We currently cannot distinguish between kimberlites and ultramafic rocks such as dunite. In future, users that routinely test many magnetic targets may find that kimberlitic responses can be isolated from those of other ultramafics but to do so will require maximum consistency of sampling methodologies and analytical methods and careful maintenance of a database of the results of past projects.

Volcanogenic Massive Sulphide Mineralization

In case studies to date, sulphide mineralization has generally shown acidic pH responses in shallow unsaturated soils and shallow saturated peat. In deeper peat and saturated overburden

more than 1 m below the water table, basic responses have been noted within reduced chimneys relative to adjacent areas. The acidification of overburden has produced strong halo anomalies in elements such as Ca, Mg, Sr, Cl, and Br. Zn-Cu-Pb VMS mineralization in drier terrain produced wide, apical, commodity element responses in Zn, Cd and Pb but notably not in Cu. In drier terrain, Cu has a frustrating tendency to not accumulate in shallow soils, probably due to downward leaching in the acidified area. There is evidence that Cu does accumulate below the acidified zone at > 1 m depth but this is too deep for routine sampling. At the only VMS so far sampled in peat terrain (Jackson 2005a) the recommended 25 to 50 cm sample interval shows Cu and Zn depletions but these are accompanied by enrichments in both Cu and Zn on either side.

Barren Sulphides

Sampling has been carried out over sulphides consisting of pyrite or pyrrhotite in both peat and dry terrain (Hamilton et al. 2005). Responses in various metals were noted in both media but the responses were muted relative to those over the VMS. In the case of peat overlying (Au-bearing) pyritic syenite at the Marsh Zone property near Matheson, Ontario, metals strongly correlated with pH. Where pyrrhotitic sulphides are overlain by thick sands, the B-horizon showed a pH response and a moderately high Ni and Cu response, possibly due to sources of these metals in the mineralization. In general, however, barren sulphides should be expected to produce a soil hydrocarbon response (due to the redox anomaly), and pH as well as associated secondary responses, but with low base metal signals.

Ni and Ni-Cu-PGE Mineralization with Sulphides

The OGS has conducted one partial extraction study on a Ni-Cu-PGE deposit (Dyer and Barnett, *in press*) but no studies yet over Ni sulphide mineralization. The results showed significant Cu, Ni and Cr responses that may have been displaced due to groundwater transport. No PGE responses were noted. This supports anecdotal evidence from others that suggests the mobility and abundance of Ni and Cu in rocks that host such mineralization may present a problem when using selective leaches for exploration. Layered intrusions and komatiites contain abundant Ni and Cu in mafic minerals such as olivine that are easily weathered and may result in elevated background concentrations in soils that might obscure the signal from mineralization. However, sulphide-rich Ni deposits should potentially produce reduced chimneys and associated pH and soil hydrocarbon responses and geochemical methods should be considered as an exploration tool for these deposits.

Buried Graphitic Targets

Earlier suggestions (Hamilton, 1998) that graphite might produce reduced chimneys due to upward conduction of electrons and reduction of oxidizing agents in overlying

sediments have not been supported by subsequent observations. Several sites with graphitic conductors have been tested using partial extractions and pH. In one case (Cross Lake north grid, Hamilton et al. 2005) a graphitic conductor with few sulphides under peat showed no response in either pH or metals. Likewise, a graphitic conductor with nearby sulphides (Cross Lake south grid, Hamilton et al. 2005) showed no significant response due to the graphite. Graphite is highly conductive but is not easily oxidizable in the surface environment. It appears that the buried feature must itself be oxidizable to generate an overlying reduced chimney and the concomitant upward metal transport. This suggests that the proposed 3-component soil geochemical program has merit as a discriminator of sulphides from graphitic deposits, provided there is a sufficiently low percentage of pyrite in the graphite.

Gold mineralization

Soil geochemical studies over Au deposits in glaciated terrain have been only partially successful, because they generally show geochemical responses in other elements but only weak responses have been noted in Au. Two studies recently sampled surface soils over Au mineralization: the Marsh Zone (Hamilton et al. 2004a, Hamilton et al. 2005) and the 180-East Project (Closs 2005). The former study showed a weak pH-related multi-metallic response in peat (see under 'Barren Sulphides', above) but a null result for Au by sodium pyrophosphate, Enzyme Leach and aqua regia, partly because airborne gold tailings contamination in the upper peat obscured any possible signal.

The study at the 180-East Property was in dry pine-forested terrain over pyritic Au mineralization covered by thick glaciofluvial sands. Humus was analyzed by aqua regia and Na-pyrophosphate. B-horizon sediments were analyzed by MMI-B and Enzyme Leach. By far the best response was noted in B-horizon soils by Enzyme Leach, which showed multi-metallic (plus As) halo responses over the extent of mineralization that usually took the form of depletions with flanking enrichments (rabbit-ear responses). Convincing halo responses were also noted in Br and I, suggesting the presence of a reduced chimney. Unfortunately neither pH nor soil hydrocarbons were measured as part of this project. Halo responses in As were noted by Enzyme Leach in the B-horizon. Although humus was sampled at a lower density and had fewer background samples, humus by Na-pyrophosphate and aqua regia appeared to show similar patterns as those of the B-horizon as measured by Enzyme Leach. Au in the B-horizon was non-detectable by Enzyme Leach and MMI but an anomaly was noted in humus by aqua regia. The ZARG leach performed on the B-horizon showed spiky and poorly reproducible responses.

A compilation report (Jackson 1995b) describing geochemical responses over 6 Au properties in glaciated terrain showed similar general results to those at 180-East. These included dominantly halo-type responses in many elements, including As, evidence for the presence of reduced chimneys and acidic responses over mineralization and weak Au responses in organic media, where they exist at all.

In summary, responses over Au deposits appear to be associated with the presence of reduced chimneys, and likely acidic caps, which suggest most of the response may be due to the associated sulphides. Without the presence of sulphides it is possible there would be no surface response to Au, because without the reduced chimney, there ought to be no electrochemical transport. In the cases described, Au appears to be mobile in an unknown form and developing weak anomalies in the uppermost organic material. With such weak anomalies, As may be a more important pathfinder element than Au itself.

Moisture-related ‘false’ anomalies in dry terrain

Variable soil moisture can cause false anomalies in both mineral and organic soils. Figure 16 shows the effect of a wetter area on the pH of both mineral soil and organic media. Elsewhere on the line, conditions are dry and show humus developed over a soil profile that includes a B-horizon. In the moist area a thin peat unit has developed over mineral soil that shows minimal weathering and oxidation and no B-horizon development. Both the organics and mineral soils show lower pH (more acidic) conditions in the dryer areas. Figure 17 shows the effect of moisture on metal concentrations in soils. Anomalously high Cu concentrations occur in the mineral soil in the wet area because there has been less oxidative weathering and consequently less leaching of the primary Cu in the soil parent material. Conversely, anomalously low metal concentrations occur in the peat for a number of metals, relative to humus on either side of the line. For selective leach metals in general, moist conditions cause false positives in B-horizon soils whereas dry conditions cause false-positives in peat.

Clastic-Related False Anomalies in Peat Terrain

Elements depleted in clay due to oxidation in upland areas can be transported laterally into a bog. On the periphery of bogs, metals can also be transported up from shallow clays into shallow peat. Both of these can result in a bog 'edge effect' in the geochemistry, which is a serious and common type of false anomaly. Elements transported hydromorphically into bogs can be captured by organic material or by the sudden change in redox and pH. Most of this capture would occur in peripheral areas resulting in large enrichments in some elements in peat at the flanks of the bog. Cu and U are examples of elements commonly input into bogs from adjacent areas (Figure 18). Stream input and episodic surface-flow can result in mechanical transport from flanking areas and also produce edge effects. Episodic input by surface flow from adjacent areas is suggested by elements that show elevated aqua regia concentrations in peat at the periphery of the bog, particularly in the *upper* peat. These are predominantly lithophile with a few chalcophile elements (e.g Ag, Al, As, Cd, Cs, Mg, Pb, Rb, Se, Th, Ti, Y, Zn, Zr, REEs). Corresponding increases in the mobile element concentrations for these elements may be due to release of the element from the entrained clastic phase after deposition in the peat.

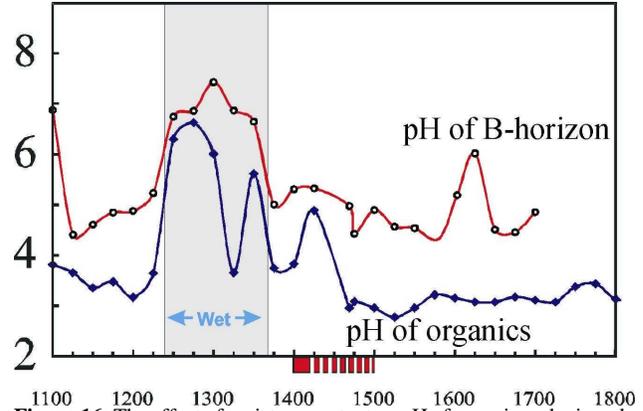


Figure 16: The effect of moisture content on pH of organic and mineral soils. The organic soils include humus and peat; the inorganic soils are B-horizon (from Hamilton et al., 2002a).

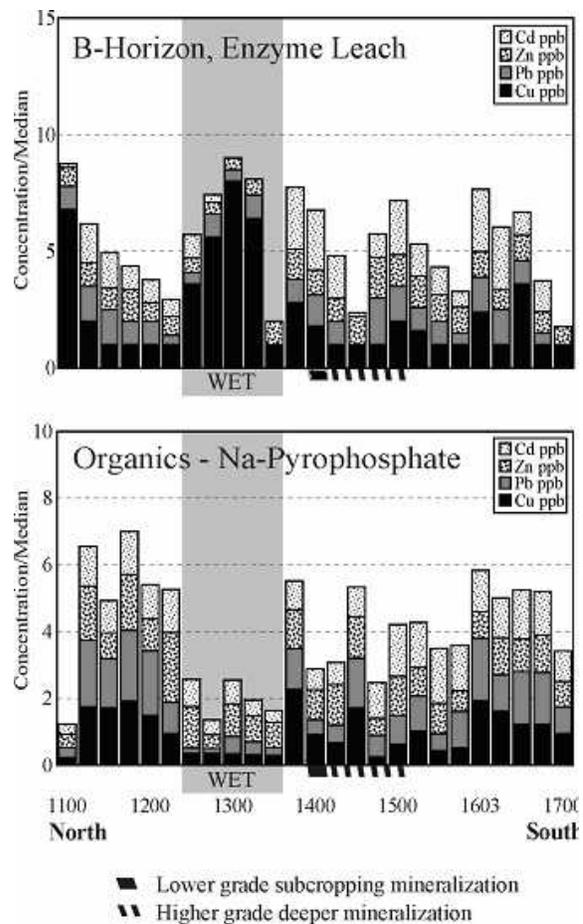


Figure 17: The effect of moisture content on metals concentrations in B-horizon and organic soils. Moist conditions cause anomalously high concentrations of Cu in mineral soil, by Enzyme Leach, due to suppressed weathering. Conversely, peat in the wet area has anomalously low concentrations of Cu, Zn, Pb and Cu, by Na-pyrophosphate, relative to adjacent humus (from Hamilton et al. 2002a), probably due to an decrease in available sorption sites in wet organic material vs. dry.

Even very low gradient streams can result in mechanical transport of clay, silt and sand, especially during spring melts, which can drastically alter the total-element chemistry of the peat. Although most prominent at the periphery of the bog, false anomalies due to stream alluvium can extend as far into the bog as the stream extends. Clastics in the peat may or may not be visible in the field and can extend laterally for many 10s of metres away from the water course as a result of spring flooding.

Mechanical and chemical processes that input elements from peripheral areas occur simultaneously for many elements and differentiation between the two processes may not always be possible. Regardless of the cause, it is important that field observations be comprehensive enough to allow later identification of possible edge effect false anomalies.

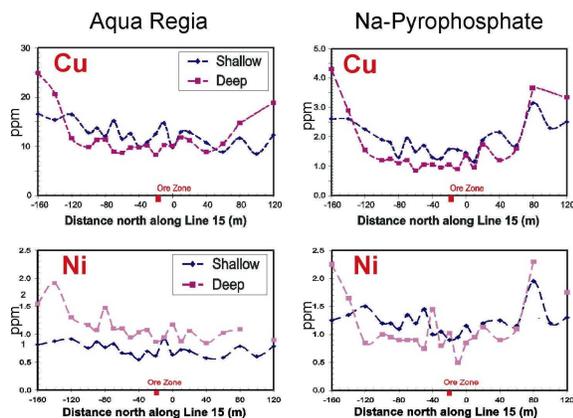


Figure 18: Edge effects in deep and shallow peat due to thinning of the peat and entrainment of clastic material near the edge of the bog (data source: Cameron, 2002, Abitibi 1999 database).

SUMMARY AND CONCLUSIONS

After more than 10 years of research by the OGS and our government, academic and industrial partners, we conclude that if used properly and under suitable conditions, soil geochemistry can detect and discriminate certain buried bedrock features through at least 50 m of fined-grained glacial sedimentary cover. Studies carried out over kimberlites, Zn-Cu-Pb VMS deposits, sulphidic Au deposits, barren sulphides and one PGE deposit have shown responses that diminish in strength approximately in the order listed. Three classes of soil geochemical methods are available: selective leaches, soil hydrocarbon techniques and pH slurry measurement. Using all three methods at once will improve the likelihood of success as they each detect a different aspect of a single, large-scale geochemical process that occurs over buried mineralization. This is the process of vertical migration of chemically reduced metals from the buried feature to surface, which results in 'reduced chimneys' in the saturated zone, 'acidic caps' in the unsaturated zone and metals accumulating in a very shallow 'metal accretion zone' in soils.

Selective leaches target the 'metal accretion zone' and are designed to selectively dissolve the mobile component of metals adhering to soil grains, i.e., the component most likely to have originated from mineralization in exotic sediments. The two most common selective leaches, Enzyme Leach and MMI were

extensively tested and found to detect buried mineralization better than stronger leaches such as ammonium acetate, weak HCl and Na-pyrosulphate. Ideally, sampling targets the metal accretion zone, which in dry terrain occurs beneath organic matter but never deeper than 25 cm from the base of the leaf litter. In peat terrain sampling should be carried out at depths deeper than 25 cm (and less than 50 cm) to avoid a diagenetic and anthropogenic layer of very high metal concentrations that typically occurs in the uppermost 10 cm, especially in historic mining areas.

Two methods of soil hydrocarbon analysis are commercially available: SHG and SDP. Soil hydrocarbons are thought to form within, and be indicative of, reduced chimneys. Data indicate they are directly measuring either, or both, the biomass or the exhalative products of autotrophic bacteria that thrive in the strong redox gradients above mineralization. SGH does not appear to be as adversely influenced by variable soil media as the other methods (SDP was not tested). Their advent is a particularly important development because they are the only reliable and inexpensive way to approximate redox that has, to date, been demonstrated to be effective in young glacial sediments.

Slurry pH is the simplest and cheapest of the three recommended soil geochemical techniques. Normally it targets the 'acidic' cap that often occurs above reduced chimneys. However, in some cases an alkaline response is observed, such as when kimberlite-influenced groundwater reaches the soil zone, and therefore any strong pH anomaly that correlates with metal and hydrocarbon responses is of interest.

Notwithstanding their potential, there are many possible sources of error when using soil geochemical methods in glacial sediments. The geochemical signal from mineralization is usually subtle and many surficial processes can produce equivalent or stronger responses, particularly in metals and pH. The most likely source of error in drier terrain is variable moisture content. Drier soils are associated with more acidic pH and higher background metal concentrations - both in humus and mineral soils. In peat, the addition of clastic material by minor watercourses or at the edge of bogs can cause very strong responses in metals. Airborne fallout in areas of historic mining is another possible source of spurious responses that is best avoided by using an appropriate (i.e., slightly deeper) and consistent sample depth.

The three-component geochemical technique just described is most appropriate for target discrimination (e.g., distinguishing kimberlite from magnetic granite) and prioritization of numerous geophysical targets. Using soil geochemistry this way could result in higher success rates and lower drilling costs, especially in remote areas where drill costs are very high. However, soil pH and selective leaches in particular, are less suitable for target generation, i.e., the sampling of large grids, because the required short sample spacing elevates costs and because of the numerous 'false anomalies' related to variable surficial conditions. With the aid of soil hydrocarbon techniques, the sampling of grids is feasible but interpretation of selective leach and pH data may require expertise in surficial geochemistry. In general, conscientious samplers, good field notes and, during interpretation, a basic knowledge of surficial geochemical processes are critical success factors when using soil geochemistry.

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