

Groundwaters in Geochemical Exploration: Methods, Applications, and Future Directions

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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 compared to surface geochemical methods, and thus providing a three dimensional perspective. Advances in understanding of ore formation processes, water-rock interaction and metals 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.

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 (Cameron et al., 2004; Reith et al., 2005) and in established mining camps (Goodfellow et al., 2003). Groundwater has the potential to be a powerful mineral exploration tool for several reasons; 1) recent and continuing advances in analytical methods, in particular ICP-MS and, more recently MC-ICP-MS (multi-collector), have resulted in lower detection limits, more rapid sample throughput, and new methods for overcoming mass interferences for key species (e.g., Se, As), 2) groundwaters recharge to depth so that there is potential to penetrate deeply into the earth's crust, with the result that groundwater geochemistry offers the potential to explore into the third dimension and detect more deeply buried mineralization than other geochemical methods, 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 reaction with mineralization, providing a potentially broader exploration target than litho-geochemistry, 5) sample preparation is relatively simple i.e., most modern

analytical techniques operate with a fluid sample, and 6) for many species of interest, background concentrations are low, enhancing anomaly contrast (Giblin, 1994). Although aqueous geochemistry as an exploration tool has been advocated and studied for some time (Cameron, 1977; Cameron, 1978; Miller et al., 1982; Earle and Drever, 1983; Giblin and Snelling, 1983; Taisaev and Plyusnin, 1984; Boyle, 1988; Giblin, 1994; Cidu et al., 1995; Mingqi et al., 1995; Cameron et al., 1997; Leybourne et al., 1998; Leybourne et al., 2002; Leybourne et al., 2003; Cameron et al., 2004; Phipps et al., 2004; Leybourne and Cameron, 2007 in press), there have been relatively few detailed studies, in particular on the utility of groundwaters. Another significant change in mineral exploration since Exploration '97 and the review of aqueous geochemistry in exploration (Taufen, 1997) is the increase in the use of partial (generally weak) extractions of soils and stream sediments, which in some cases have been shown to produce greater anomaly to background contrast than traditional strong-acid (e.g., aqua regia) digestions (Cameron et al., 2004). One of the difficulties of these weak leaches has been the interpretation of the results owing to a lack of understanding of the mechanisms by which ore-related species migrate from depth to the surface environment (Goldberg, 1998; Smee, 1998; Cameron et al., 2004). Processes postulated to account for these surface anomalies over deeply buried mineralization include capillary migration of ions (Mann

et al., 2005), vapor-transport, ground and soil water advection or diffusion, electrochemical transport (Hamilton, 1998), and seismic pumping (Cameron et al., 2004; Cameron et al., 2002). Given the wide variety of terrains and climates that occur, it is likely that no one mechanism will explain soil geochemical anomaly development, and that in many environments, groundwaters will be directly or indirectly involved. 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., 2004; Cameron et al., 2002) (Figure 1). Clearly, some of the postulated mechanisms for these anomalies in soils will have limited applicability to aqueous geochemical exploration, but in some cases, as noted for porphyry copper deposits in Chile, hydromorphic transport is fundamentally important in the development of geochemical anomalies and understanding the aqueous geochemistry of water-deposit interaction can greatly improve our ability to predict styles and composition of surficial anomalies.

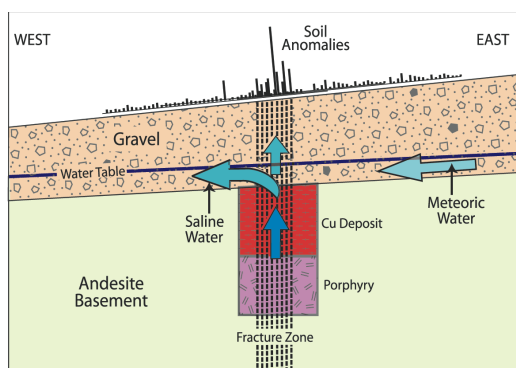


Figure 1: Conceptual model for the development of soil geochemical anomalies via movement of groundwaters to surface during seismic events. In this model, saline fluids interact with porphyry copper mineralization and mix with a more regional shallow groundwater system. The resultant soil geochemical anomalies reflect the composition of the saline groundwaters (in the case of the Spence deposit, Na + Cl) and porphyry copper mineralization (Cu, Se, Re, Mo, As). Modified from Cameron and Leybourne (2005).

This paper synthesizes the current thinking and state of the art with respect to sampling, analysis and anomaly type in groundwater geochemical methods useful to the mineral exploration industry. Some case studies around different styles of mineralization are presented to illustrate different strategies and implications. Although not discussed explicitly, stream and lake water geochemistry can be utilized in similar ways to groundwaters. Indeed, stream waters typically represent baseflow; that is shallow groundwater discharge. For a recent review, see Leybourne (2007 in press).

Fundamentally, 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. Surface geochemical methods rely on development of anomalies by mechanical means (i.e., via glacial

transport, solifluction, or mass wasting), hydromorphic (water transport and precipitation, or metal migration via one of the mechanisms discussed above. In contrast, groundwater geochemical anomalies fundamentally develop by hydromorphic dispersion.

In some environments, such as northern Chile or parts of Australia, grid drilling is common, ideal for the purposes of groundwater geochemical exploration. However, even where exploration wells are not typically drilled, there are a number of ways in which analysis of the geochemistry of groundwaters is practical; 1) in areas where domestic or agricultural wells already exist, 2) springs and seeps represent areas where groundwater returns to surface, and 3) where exploration holes are drilled, the additional cost of adding groundwater chemistry is insignificant relative to the cost of drilling. Because groundwaters flow away from mineralization, there may be geochemical vectors to mineralization even in an apparently barren hole. Drilling is expensive and typically only occurs after a suitable exploration target has been identified. In Western Australia, thick regolith cover is an impediment to geochemical exploration of any kind. In this environment, mineral exploration commonly involves drilling through cover to bedrock. The advantage of groundwater geochemistry is that groundwaters can provide a broader anomaly target than regolith geochemistry, with the result that the density of drill holes can potentially be reduced (Carey et al., 2003). Pauwels et al. (2002) for example used some domestic wells in their surveys around two deposits in the Iberian Pyrite Belt, Spain and were able to use groundwater geochemistry (anomalies in Cu, Zn, Pb and Cd) to vector to known mineralization.

GROUNDWATER SAMPLING TECHNIQUES

There are a number of different ways that groundwaters in exploration holes or other wells can be sampled, with varying degrees of complexity and practicality and resultant information. Some of the more commonly used methods include flow-through bailers, down hole pumps (e.g. double-valve or Grundfos), and straddle-packer systems.

Bailers are commonly used because they are inexpensive, simple to operate, and permit relatively rapid sampling of groundwater. Bailers consist of a PVC tube, generally holding 1-L, with neutrally buoyant stop valves that remain open during bailer descent and close on retrieval. Bailers work best in unconfined aquifers of porous media where there is little variation in hydraulic conductivity with depth. However, bailers are difficult to decontaminate between samples in a well and between wells, the volumes are generally limited (although any given depth can be resampled if needed), and where there are significant hydraulic gradients, the most dominant may be the only one sampled, regardless of depth (Leybourne et al., 2002). Bailers also tend to disturb the well, which can result in an anomalous increase in suspended sediment concentrations. However, analysis of the suspended sediment can prove useful; adsorption of Pb to particle surfaces is typically much greater than is the case for Zn. Leybourne (2001) showed that Pb/Zn ratios of groundwater suspended sediments increased towards VMS (volcanogenic massive sulfide) mineralization.

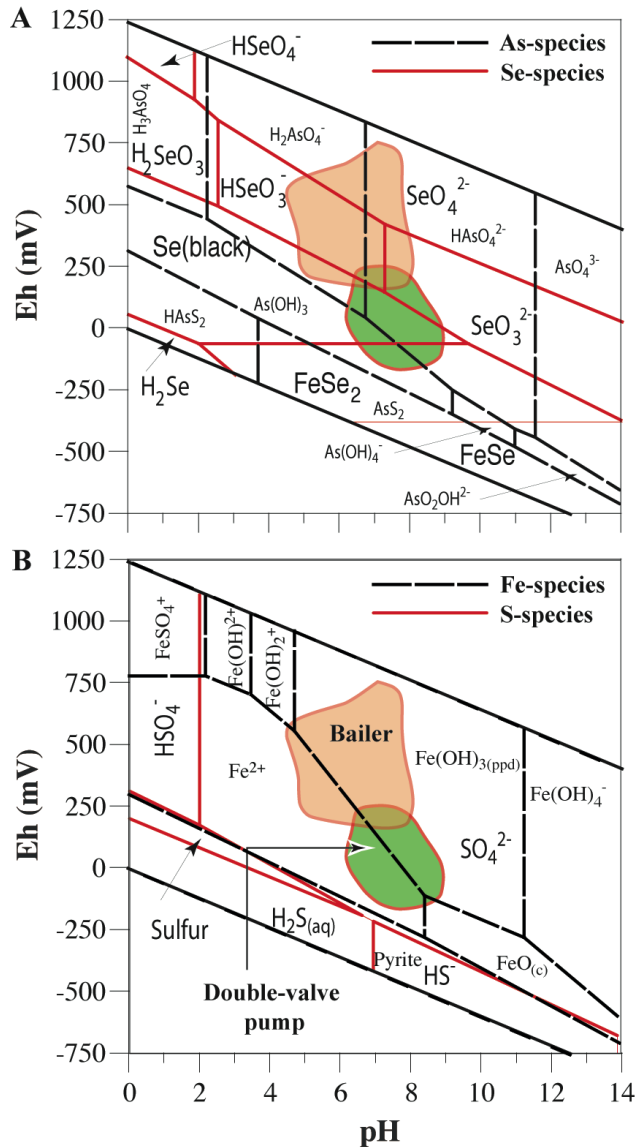


Figure 2: Eh versus pH plots for groundwaters from the Spence deposit, Chile, showing speciation of Se, Fe, SO₄ and As. Note that the samples collected by double-valve pump have generally lower Eh values than flow-through bailer samples. A) Se and As speciation, with [Se] = 10⁻⁶, [As] = 10⁻⁶, [SO₄] = 10⁻², [HCO₃] = 10⁻³, [Fe] = 10⁻⁴. B) SO₄ speciation, with [SO₄] = 10⁻², [HCO₃] = 10⁻³, [Cl] = 10⁻¹. Fe speciation with [Fe] = 10⁻⁵. For the As diagram, formation of realgar, orpiment, scorodite and claudetite was suppressed, as they are kinetically unlikely to form in these waters. For Fe speciation, formation of goethite, magnetite and hematite were suppressed. Plots created using The Geochemists Workbench (Bethke, 1994). Figure modified from Leybourne and Cameron (in review).

Down-hole pumps are similar to bailers in that they are typically used in an open borehole. In the case of double-valve pumps, a one-way valve is opened by the overlying water column and groundwater flows into the sample chamber. A source of clean gas (compressed air or N₂) is forced down one PVC line closing the valve and returning sample to surface via a

second PVC line. The double-valve pumped can then be evacuated multiple times, effectively purging the well of its standing water until electrical conductivity (as a proxy for salinity), Eh (redox state) and pH reach steady state conditions. Once steady-state conditions are reached, the sample is taken on the assumption that the sample represents groundwaters flowing through the system at the sampled depth (Leybourne and Cameron, 2006a). This repeated sampling to develop the well also serves to decontaminate the sampling apparatus between boreholes or between depths within a well. In some set ups the system can be pressurized prior to deployment in the well, so that the valves do not open until the pump reaches the depth at which the head of the overlying water column exceeds the pressure in the lines (Pauwels et al., 2002). Grundfos pumps operate continuously via a motor, also allowing purging of the standing water in a well, with the added advantage that flow rates can be varied and flow through cells employed to permit real-time monitoring of changes in salinity, pH, and Eh. Both bailer and double-valve pump were used in a study of groundwaters interacting with porphyry copper mineralization in northern Chile (Figure 2). Although there was little difference between the two methods in terms of major ions and ore-related metals and metalloids, significant differences were observed for Eh (Figure 2).

In rocks dominated by fracture-flow, a number of complicate recovery of samples that represent groundwater flow at a specific depth, including; 1) contamination by drilling waters, 2) mixing within open boreholes by groundwaters entering the hole from different depths, and 3) commonly low hydraulic conductivities (1994). Sampling under these conditions is best achieved using a straddle-packer system, which permits sampling of groundwaters from discrete intervals in a borehole (typically 1-3 m in length) (Leybourne et al., 2002). The straddle-packer system is optimal for collecting samples that represent groundwater flow at the sampled depth, but suffers from high cost and time to collect samples. For exploration holes that are older than a few years, groundwater flow should have removed drilling fluids.

Hydrogeochemical methods in general are not used as commonly as they should be by the exploration industry because of perceived complexity of sampling and treatment. Depending on the nature of the exploration program, groundwater geochemical exploration can be carried out in a simple, routine, and easy to train manner. Techniques that are more complex are needed for orientation studies that provide more information but also require more training and equipment. These two approaches are discussed in more detail below. As an example, aqueous geochemists typically filter waters in situ, either to < 0.45 or to < 0.20 μm. These filter pore sizes are operationally defined (Hall et al., 1996), as they do not separate metals that are truly dissolved from those that are bound to fine colloids; many colloids are as small as < 5 nm in size (e.g., Zanker et al., 2002). However, filtering is not always necessary; Cameron et al. (1997) showed that for Canadian northern lakes, pH and suspended sediment contents were sufficiently low that filtering and acidification were not required, with the caveat that analyses were carried out relatively rapidly after collection. In that study, some 5000 samples of lake waters were collected in six weeks. Similarly, Leybourne and Cameron (2000) showed that for groundwaters collected around the Spence porphyry Cu deposit

in northern Chile, many of the species of interest (e.g., S, Se, Re, As, Mo) showed little or no difference between filtered (< 0.45 µm) and unfiltered aliquots, although metal cations (e.g., Cu, Zn) showed large differences owing to adsorption to Fe, Mn and Al oxyhydroxides (Figure 3).

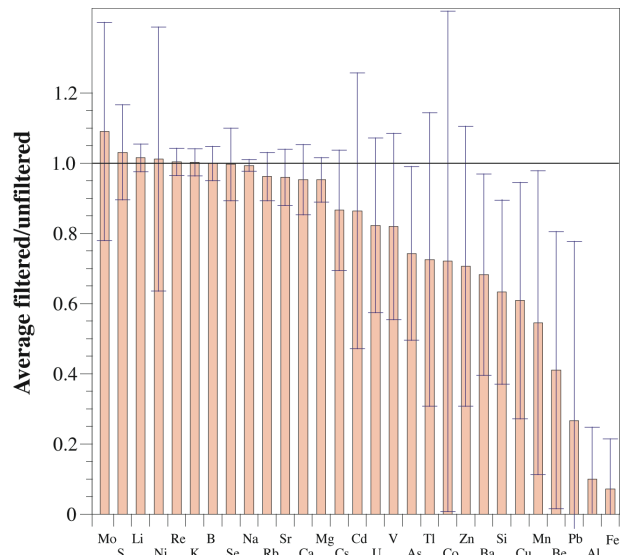


Figure 3: Bar chart showing average elemental values for filtered/unfiltered samples of groundwater from the Spence deposit, Chile. The error bars represent the standard deviation. From Leybourne and Cameron (in review).

HYDROLOGY

In order for a geochemical anomaly to develop in a groundwater, clearly that water must flow through mineralization; therefore interpretation of groundwater geochemistry in mineral exploration is greatly enhanced where there is information regarding the local and regional hydrology (Carey et al., 2003; Leybourne and Goodfellow, 2003; Gilliss et al., 2004). Interpretation of hydrology is simplified in regions dominated by porous flow in unconfined aquifers (e.g., basal gravels in northern Chile that are in direct contact with porphyry mineralization exposed along the underlying basement unconformity and Athabasca sandstone U deposits), and significantly more complicated where flow is fracture-dominated (Leybourne et al., 1998), or where significant density contrasts between different groundwater flow systems exist (Carey et al., 2003). In some cases, faults/fractures that originally focused fluid flow during ore formation may also serve as conduits to groundwater flow into and out of the deposit (e.g., Spence deposit, Figure 1) (Cameron and Leybourne, 2005). Furthermore, the Eh (and concentration of dissolved oxygen) and pH conditions greatly influence the extent and style of ore mineral reaction and the mobility and dispersion of ore-related metals/metalloids. Thus, if the Eh and pH conditions are not conducive to mineral dissolution/replacement and element transport, aqueous geochemical anomalies will be subdued or may not form. For example, Gilliss et al. (2004) investigated the aqueous geochemistry of groundwaters at the Tillex Cu-Zn

deposit in Ontario, Canada and found that conditions proximal to the deposit are characterized by low Eh and near neutral pH. Redox conditions at the Tillex deposit are such that dissolved sulfate is reduced to sulfide, restricting deposit sulfide mineral weathering and preventing the development of a significant aqueous geochemical plume.

Although some types of deposit are stratabound or controlled by faults and fractures, other deposits are channelized. This restriction of mineralization to channels has been noted in particular for some types of Cu-Ni-PGE and unconformity U deposits (Brand, 1999; Pirlo and Giblin, 2004). Channelization of mineralization is an important consideration for aqueous geochemical exploration because the orientation of the channels with respect to local hydrology will determine the extent to which mineralization is in contact with groundwaters. For example, at the Kambalda deposit, Ni-Cu-PGE mineralization is associated with komatiite flows, which were channelized by pre-existing topography. Mineralization at Kambalda forms linear features over 3 km long, but less than 300 m wide, and less than 5 m thick (Brand, 1999).

Another issue is the pre-cover history of the rocks hosting mineralization. Regolith/saprolite development and gossan formation can affect the type of anomaly developed in ground and surface waters. For example, at the Halfmile Lake deposit, Bathurst Mining Camp (BMC), Canada, mineralization crops out as a gossan (Boyle, 2003). As a result of differential mobility in gossan-forming groundwaters (i.e., Zn and Cu are more mobile than Pb), till overlying the deposit has relatively low Zn and Cu contents (Parkhill and Doiron, 2003). Thus, groundwaters interacting with this type of gossan will likely not have Zn and Cu anomalies. At Halfmile Lake, Pb contents are elevated in till down ice, and Pb isotopic ratios demonstrate that the Pb is associated with gossan mineralization over primary VMS mineralization (Hussein et al., 2003).

MAJOR IONS

A full understanding of groundwater geochemistry requires analysis and interpretation of the major ion composition (i.e., for most waters this means Ca, Mg, Na, K, H₄SiO₄, Cl, SO₄ and dissolved inorganic carbon, typically HCO₃). These chemical parameters permit classification and interpretation of, for example, water type, mixing, evaporation, water-rock reaction and recharge. However, some studies have also suggested that the major ion composition of groundwater can provide direct vectors to mineralization, in particular owing to the generally larger target provided by alteration halos around mineralization relative to the size of primary ore mineralization (e.g., Giblin, 1994; Taufen, 1997; Phipps et al., 2004). The major ion chemistry in a hydrogeochemical survey should be interpreted and considered in conjunction with the trace metal data. However, 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) trace element data (Table 1). As an example, soil Br and Cl anomalies develop over some deposit types as a result of electrochemical, gaseous or advective transport (Clark,

1999; Hamilton, 1999). However, it is unclear of the extent to which these elements are diagnostic of mineralized zones. For example, work on groundwaters around the Spence deposit in northern Chile suggests that saline groundwaters migrate to surface along fractures during seismic events (Cameron et al., 2002; Cameron and Leybourne, 2005). Because saline basinal fluids in northern Chile have elevated I, Br, Cl and S, soils over fractures will be anomalous in I and Br regardless of whether or

not the waters have interacted with porphyry copper mineralization. In order to explore effectively using geochemical techniques, the explorationist needs to be able to identify mineralized rocks and be able to distinguish them from non-mineralized rocks of the same composition, so that attention should be placed on what is geochemically distinct about the mineralization (Tables 1, 2).

Table 1: Major Geochemical characteristics of different deposit types (modified after McMartin and McClenaghan (2001) and Leybourne (2007 in press))

Type of deposit	Major components	Minor components	Labile components ^A	Relatively immobile components ^B
VMS	Fe, S, Cu, Zn, Pb	Cd, Hg, Au, As, Sb, Ba, Bi, In	Fe, S, Zn, Cu, As, Cd, Hg, Sb	Pb, Bi, In, Au, Ag, Ba
Porphyry Cu ± Mo	Cu, Mo, S	Fe, Ag, Au, Se, Re, As	Cu, Mo, S, Fe, Se, As, Re	Ag, Au
SEDEX	Fe, S, Cu, Zn, Pb	Ag, Au, Ba, Cd	Fe, S, Zn, Cu, Cd	Pb, Ba, Au, Ag
Gold (vein)	Au, Ag	As, Sb, Se, Te, S, Hg	S, Se, As, Hg, Te, Sb	Au, Ag
Ni-Cu-PGE	Ni, Cu, PGE	Cr, Co, S	Cu, S, PGE	Co, Ni, Cr
Kimberlite (diamond)	Sr, Nb, Ba, Cr, Ni	LILE, HFSE, REE	Sr, LILE	Ba, HFSE, Nb, Ba, Cr, Ni, REE
Unconformity uranium	U	Se, Mo, V, Cu, Pb	U, Se, Cu, Mo	U, Pb, V

A. Under oxidizing and near neutral conditions; B. Under normal conditions e.g. Ba is immobile in the presence of S as SO₄
LILE, large ion lithophile elements; HFSE, high-field strength elements; REE, rare earth elements

Table 2: Summary of key aqueous geochemical pathfinders for different deposit types

Type of deposit	Main pathfinders	Secondary pathfinders	Key analytical methods	Key publications	Notes
VMS	Zn	Low pH, Pb, SO ₄	ICP-MS – metals IC, ICP-OES - S	Cameron, 1978; Leybourne et al., 2003; Leybourne and Goodfellow, 2003	Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb
Porphyry Cu ± Mo	Distal – Se, Re, Mo, As Proximal - Cu	Pb, Zn	ICP-MS – metals IC, ICP-OES - S	Cameron and Leybourne, 2005; Cameron et al., 2002; Leybourne and Cameron, 2006, in press	S isotopes also useful as a complimentary vector
SEDEX	Zn	Ag, Au, Ba, Cd	ICP-MS – metals IC, ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes	Goodfellow, 1983; Jonasson et al., 1987; Kelley and Taylor, 1997	Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb
Gold (vein)	Au	Se, As, Sb	Activated carbon pre-concentration or BrCl (see text) ICP-MS, NAA	Carey et al., 2003; Giblin, 2001; Gray, 2001	
Cu-Ni-PGE	Ni, Cu, Pd	As, Cr, Co, S, PGE	ICP-MS – metals IC, ICP-OES - S	Hattori and Cameron, 2004	Pd mobility is enhanced under alkaline conditions relative to other pathfinders
Kimberlite (diamond)	Low Mg, elevated K/Mg, pH » 10	Ni, Co, Cr, high Co/Mg and Ni/Mg	ICP-MS – metals IC, ICP-OES - S	Sader et al., 2003, in press	Also, formation of Mg hydroxides (brucite), silicates (serpentine) and carbonates (magnesite)
Unconformity uranium	Oxidizing – U, radon Reducing – Se, Mo	Se, Mo, As, V, Cu, Pb	ICP-MS – metals IC, ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes	Deutscher et al., 1980; Dickson and Giblin, 2006; Earle and Drever, 1983; Giblin and Snelling, 1983; Langmuir and Chatham, 1980	Radiogenic ²⁰⁷ Pb/ ²⁰⁴ Pb and ²⁰⁶ Pb/ ²⁰⁴ Pb but non-radiogenic ²⁰⁸ Pb/ ²⁰⁴ Pb should prove useful

ICP-MS = inductively coupled plasma mass spectrometry; MC-ICP-MS = multi-collector ICP-MS; OES = optical emission spectroscopy; TIMS = thermal ionization mass spectrometry; IC = ion chromatography.

Certainly, there are instances where there are clear major element changes that are diagnostic of a particular rock type or style of alteration, but these do not necessarily indicate ore mineralization. For example, Sader et al. (2007) showed that groundwaters interacting with kimberlite results in elevated pH and low Eh conditions, with concomitant loss of Mg from solution and increase in dissolved K contents (Figure 4). However, these major ion changes occur regardless of whether the kimberlite is diamond bearing or not; any water-ultramafic rock interaction will likely produce similar changes in major ion chemistry of groundwater. In contrast, Giblin (2001) suggested that waters interacting with ultramafic rocks will have $Mg > Ca, Na, K$.

METAL SATURATION, SPECIATION, AND MOBILITY

Mineral saturation indices and metal speciation calculations are typically carried out using various computer codes. Some of the more popular in the aqueous geochemical literature include PHREEQC (Parkhurst, 1995), MINTEQA2 (Allison et al., 1991), and The Geochemists Workbench (Bethke, 1994). Some geochemical speciation/saturation codes are only available commercially, whereas some are available as free downloads via the Web. Critical to the successful use of geochemical speciation and mineral saturation computer code is the realization that these programs should not be considered black boxes; some understanding of expected output greatly enhances the utility of these programs. In addition, output is only as good as the input data and the internal integrity of the thermodynamic database. In most cases, code is inherently based on equilibrium thermodynamics, so that kinetic (reaction rate) factors are not considered. Finally, much of the information of relevance to exploration is heavily dependent on the input values for pH and the redox state of the system; if these data are incomplete or poorly constrained, these calculations are not worth the effort.

Despite these caveats, calculating mineral saturation and element speciation can be instructive (Giblin, 1994; Leybourne, 1998; Gilliss et al., 2004; Pirlo and Giblin, 2004), for example, to better understand metal mobility or attenuation, and the occurrence of secondary mineralization, such as transported gossan (Boyle, 2003) or secondary copper mineralization. Sader et al. (2007) showed that reaction path modeling of water-kimberlite and water-gneiss interaction enhances understanding of likely meteoric water alteration assemblages, which can also be used as an exploration guide.

The degree to which a water sample will be anomalous with respect to proximal or distal mineralization depends fundamentally on the solubility of the species that reflect that style of mineralization under the prevailing pH, Eh, and salinity conditions (Figure 5). Ideally, the geochemical explorationist would like any sample media 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 (Tables 1, 2). Furthermore, care must be taken to interpret aqueous geochemical data with consideration

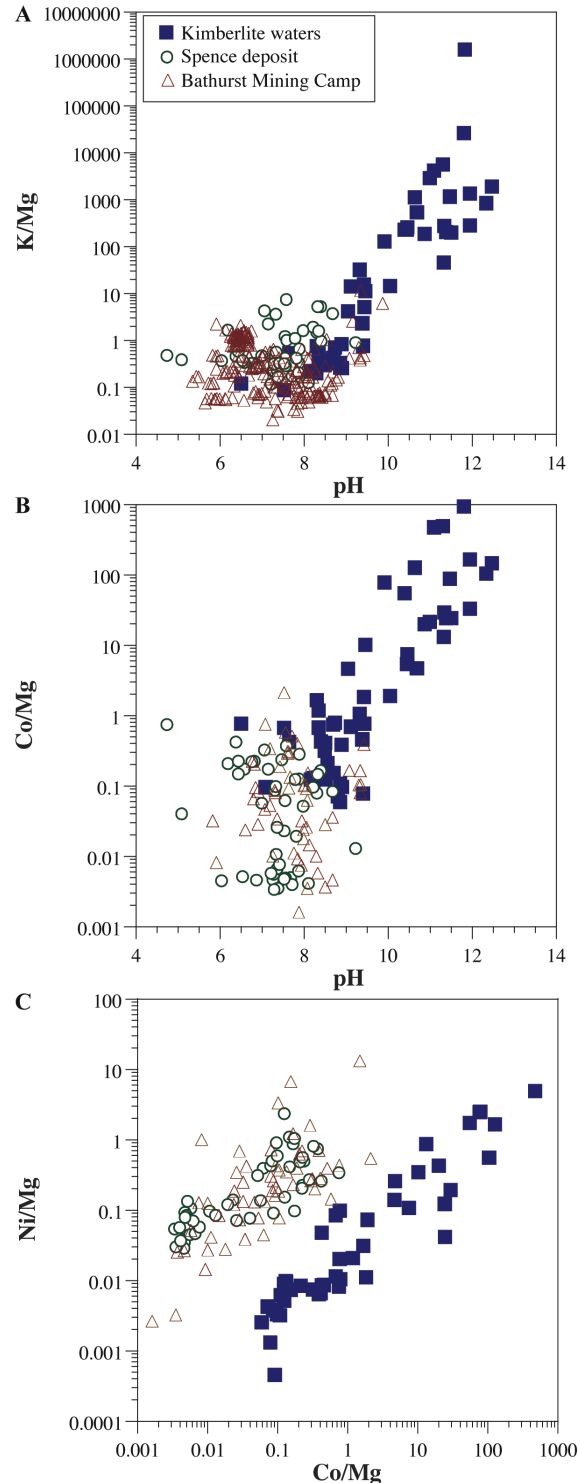


Figure 4: A) pH vs K/Mg, B) pH vs Co/Mg and C) Co/Mg vs Ni/Mg for groundwaters around kimberlites in northern Ontario (Sader et al., 2007), VMS deposits in the Bathurst Mining Camp (Leybourne and Goodfellow, 2003), and porphyry Cu deposits in northern Chile (Leybourne and Cameron, 2006a).

of geochemical theory and analytical constraints. For example, although Ti is elevated in mafic and ultramafic igneous rocks compared to high-Si igneous and sedimentary lithologies, Ti is unlikely to be of much use in groundwater geochemical exploration because; A) Ti is not particularly anomalous in mineralized mafic and ultramafic rocks compared to non-mineralized equivalents, B) Ti is immobile in water, except in very rare cases, and C) analytically, Ti suffers from several potential spectral overlaps in an ICP plasma. Similarly, several studies have suggested that the rare earth elements (REE) may be useful in mineral exploration for non-REE deposits. In some cases, this may be reasonable. For example, metal-rich hydrothermal fluids recovered from active vents at mid-ocean ridge crests show strong positive Eu anomalies, and these anomalies are commonly observed in VMS deposits. In contrast, strong positive Eu anomalies are not common in other geological environments, so that the presence of these Eu anomalies could be used as an exploration guide (Leybourne et al., 2000b; Volesky et al., 2000; Volesky, 2002; Leybourne and Cousens, 2005; Leybourne et al., 2006b). Low-pH groundwaters proximal to VMS mineralization have also preserved the positive Eu anomalies (Leybourne et al., 2000b). Similarly, ground and surface water REE profiles have, in some cases, reflected the host lithology, although this can be complicated by the behaviour of the REE in aqueous systems (Johannesson and Zhou, 1999; Johannesson and Hendry, 2000). Diamond-bearing kimberlites commonly have distinctive large ion lithophile element (LILE) and high field strength element (HFSE), including the REE) associations (McMartin and McClenaghan, 2001). In this case, aqueous anomalies in mobile species (K, Rb, Sr and the REE in some waters) may assist in the distinction between rock types, but may not be as useful in distinguishing mineralized from unmineralized rocks.

ISOTOPIC APPLICATIONS

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 and Leybourne, 2005; Leybourne and Cameron, 2006a; Leybourne et al., 2006a) (Figure 6). 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 (Ehrlich et al., 2004; Johnson and Bullen, 2004; Rouxel et al., 2004; Severmann et al., 2004; Layton-Matthews et al., 2006).

Analytical considerations include the ease of sampling, storing, sample processing and cost of determination. For example, traditionally, Sr and Pb isotope analyses have been

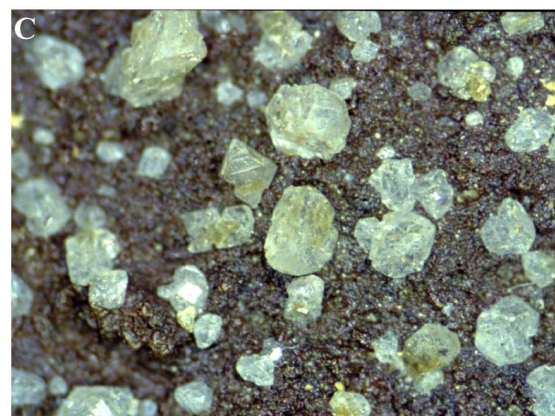
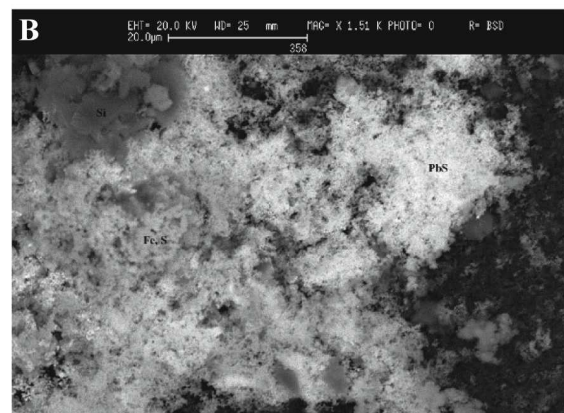
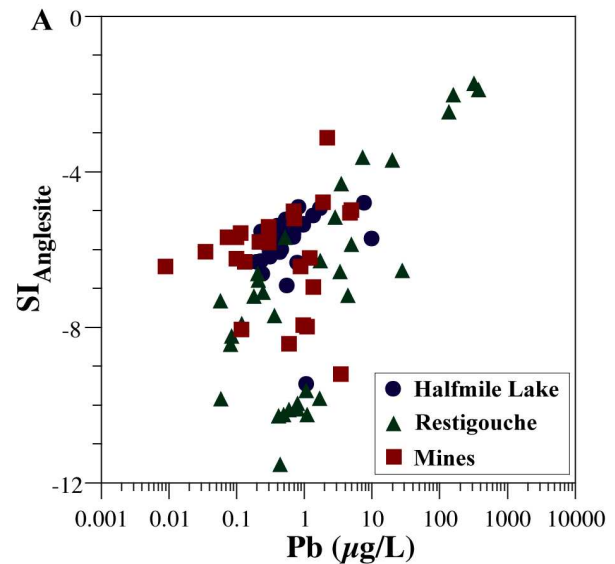


Figure 5. A) Solubility of anglesite (PbSO_4) in groundwater, Bathurst Mining Camp, Canada. Waters collected in the mineralized zone are closest to saturation. B) Precipitates of Pb and Fe sulphates on filter paper from waters closest to anglesite saturation (from Leybourne, 2001). C) Anglesite crystals in gossan from the Restigouche deposit.

carried out by thermal ionization mass spectrometry (TIMS). Although Pb isotopes have received some attention (Gulson, 1986; Gulson et al., 1988; Gulson et al., 1992; Bell and Franklin, 1993; Leybourne et al., in review), measurement by TIMS is time consuming owing to the need for chemical separation of the species of interest. Newer quadrupole (especially those with reaction cells; DRC), high resolution (HR) and multi-collector ICP-MS instruments allow Pb isotopes to be measured with accuracy and precision in some cases rivaling that of TIMS, with significantly less sample preparation and greater throughput.

Stable isotopes are a critical component in many aqueous geochemical studies because they provide important information regarding water sources, groundwater flow history, water-rock reactions, and groundwater evolution. For a good recent summary of the light stable isotopes in aqueous studies, see Clark and Fritz (1997). Stable and radiogenic isotopes have not found much application in exploration, owing to cost and perceived difficulty in interpretation. Although stable isotope determinations are not overly expensive per isotope, especially compared to commercial rates for Pb and Sr by TIMS, adding a full suite (e.g., O, H, C, S) to an exploration program would significantly add to the cost of a survey, with additional resources required for sample collection, preparation, and data interpretation. However, although the light stable isotopes may not become routine, they can be a very useful addition to an orientation or more detailed study. For example, future successes in surficial geochemical exploration will rest with the ability of groundwaters to penetrate to depth, with subsequent return of pathfinder element-bearing fluids to surface. In that context, sampling of overland or shallow soil water flow following storm events will not be as useful as sampling base-flow conditions for stream water surveys, or deeper groundwater flow in the case of springs. In a study of stream, seep, and ground waters from two undisturbed VMS deposits in the Bathurst Mining Camp, Leybourne et al. (2006a) showed that surface waters were similar to shallow groundwaters based on the ^{18}O and 2H compositions, indicating that surface water flow represented shallow groundwater discharge. In addition, saline groundwaters at the Restigouche deposit were found to be isotopically distinct from shallow groundwaters, consistent with the interpretation that the saline waters were paleowaters (Leybourne et al., 2006a). These saline waters were also Zn, Co and Ni-rich, but enhanced metal contents were a function of increased Cl-complexing and, possibly, to deeper mineralization unrelated to VMS mineralization at the Restigouche deposit (Leybourne and Goodfellow, 2003). Studies of groundwaters recovered around the undisturbed Spence porphyry copper deposit, in the hyper-arid Atacama Desert of northern Chile have shown using O and H isotopes that saline waters interacting with copper mineralization (as shown by elevated Cu, As, Se, Re, Mo and low ^{34}S ; Figure 6 shows Se and ^{34}S) are paleowaters, possibly derived from sedimentary basin brines. These paleowaters have mixed with regional groundwater flow, derived by recharge in the high Andes (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a). Understanding the recharge history of groundwater and whether sampled waters are modern meteoric or paleowaters is important in terms of understanding local hydrology, in particular where groundwater composition is being used to vector to mineralization.

In contrast to the isotopes of O and H, which are unlikely to yield relationships directly linked to mineralization, sulfur isotopes can provide vectors to mineralization in addition to aiding interpretations of water sources and rock reactions. For example, Whitford et al. (1997) suggested that groundwater sulfur isotopic compositions provides a vector to gold mineralization in Australia. Similarly, analysis of the sulfur isotopic composition of groundwaters at the Spence porphyry copper deposit in Chile show that groundwater ^{34}S values decrease from values typical of regional waters and salars (Pueyo et al., 2001; Rech et al., 2003; Rissmann, 2003) to values closer to those typical of porphyry copper mineralization as waters flow into and through mineralization (Leybourne and Cameron, 2006a). This increasing influence on groundwater sulfur isotopic composition is also evident in Se (Figure 6) in addition to Re, Mo, and As). Recent work in the area that hosts the giant Broken Hill SEDEX deposit in Australia has also suggested that the S and O isotopic composition of dissolved sulfate can be used to vector to mineralization and provide a broader halo than groundwater base metal (Zn, Pb, Cu) contents (de Caritat and Kirste, 2005).

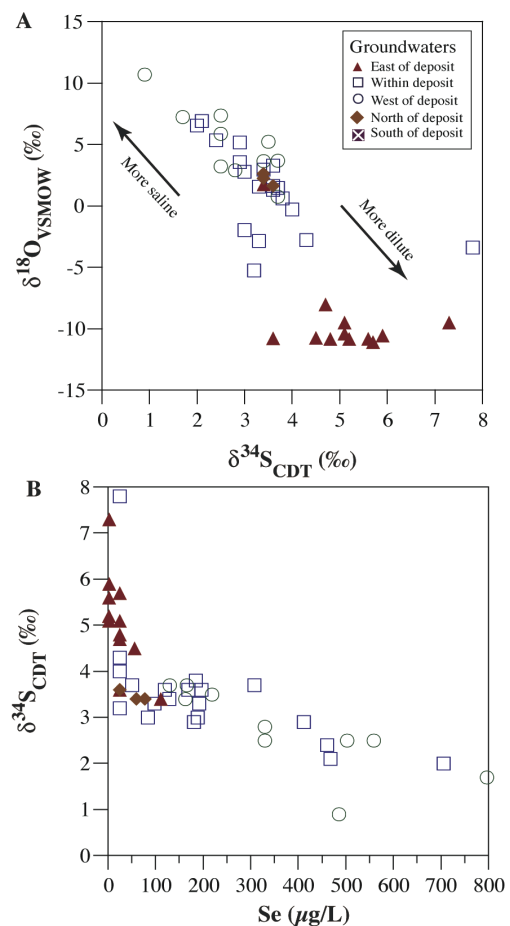


Figure 6: Stable isotopes of S and O and Se concentrations in groundwaters from the Spence porphyry Cu deposit, Chile. These data are consistent with mixing between deep saline waters and regional dilute meteoric waters. Increase in Se indicates reaction with Cu mineralization. After Leybourne and Cameron (2006a).

The generally low solubility of Pb in most waters means that ground and surface water Pb contents may not be sufficiently elevated proximal to mineralization to warrant consideration, in particular where pH values are buffered and/or mineralization is more deeply buried. However, because sulfide minerals do not incorporate U and Th into their structure, Pb derived from sulfide minerals will retain the isotopic composition of the ore-forming fluids, whereas Pb from surrounding U- and Th-rich host rocks will typically have more radiogenic Pb isotopic compositions. Therefore, Pb isotopes can “fingerprint” Pb sources, and indicate subsurface mineralization, even where aqueous Pb contents are low (Leybourne, 1998; Leybourne et al., in review) (Figure 7).

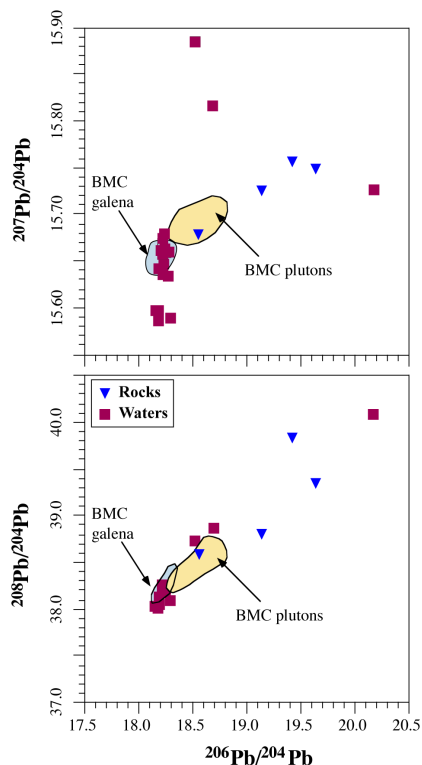


Figure 7: Plots of Pb isotopes for BMC waters and host rocks, galena (Thorpe et al., unpublished data) and local Ordovician granitoids (Whalen et al., 1998). Modified from (Leybourne et al., in review). Groundwaters can provide a useful vector to mineralization, even where Pb concentrations are low.

RECOMMENDATIONS FOR SAMPLING AND ANALYTICAL PROTOCOLS OF WATERS IN MINERAL EXPLORATION

From the above discussion and the case studies discussed below, there are clearly a large number of parameters that can be used to aid the detection of undiscovered mineralization and that there are a number of potential issues and pitfalls that need to be avoided. Despite these issues, groundwater geochemistry can be a powerful tool for the exploration geochemist for the reasons outlined in the introduction. In this section, recommendations

are made regarding sampling and analysis that should aid exploration geochemists in realizing this relative simplicity. The collection and analysis of groundwaters in mineral exploration can be broken down into two different approaches, here referred to as the “routine exploration” (Figure 8) and “exploration research” (Figure 9) approaches. Giblin (2001) also provides useful guidelines for groundwater sampling in geochemical exploration. The routine approach is applicable in areas where some knowledge of the geochemical landscape and, ideally, the hydrology already exists. In areas where this knowledge base does not exist, or where techniques require refining, the research approach should be adopted in an orientation survey.

Ideally, plastic gloves (cheap, disposable) should be worn during collection of water samples to ensure uniformity in sampling and prevent contamination. Some measurements are best made in the field because the parameters are unstable (pH, Eh) and because they can provide useful guides during exploration. For example, large changes in pH may indicate the presence of unbuffered sulfide oxidation (decrease) or proximity to ultramafic igneous rocks (increase). Similarly, changes in electrical conductivity (i.e., salinity) may reflect additions of different, potentially deeper, groundwater. For routine exploration, conductivity can serve as a proxy for total dissolved solids. Where possible, S should be measured by ICP-OES if anions are not determined by ion chromatography. Meters for the determination of pH and conductivity are relatively robust, inexpensive, and simple to calibrate. Cameron et al. (1997) showed that using portable anode stripping voltammetry (ASV) to measure dissolved Zn was useful in guiding the exploration program; waters were analyzed immediately following each days’ collection. Comparison of these field Zn analyses with subsequent ICP-MS analyses showed effectively no difference for Zn > 1 µg/L.

GROUNDWATER GEOCHEMICAL EXPLORATION: CASE STUDIES

This section presents some case studies of groundwater exploration related to several deposit types. The case studies presented here present concepts and methodologies that are applicable to other styles of mineralization. Table 1 indicates the major geochemical characteristics of the deposit types discussed below, and Table 2 summarizes the key results of aqueous studies around those deposit types summarized in Table 2.

Porphyry Copper Deposits

Porphyry copper and porphyry molybdenum deposits are typically associated with intermediate to felsic intrusive igneous rocks. Although common, large porphyry copper systems are particularly abundant in Chile and include the giant Chuquibambilla, El Salvador and Escondida deposits. Recent reviews of porphyry deposits include those by Sinclair (2007, in press), Richards (2003), and Sillitoe (2000). Key geochemical characteristics include anomalous accumulation of As, Mo, Se, and Re in addition to Cu, and in many deposits Au, Pd, and Pt (Table 1). There have been a small number of studies of the aqueous geochemistry of waters associated with porphyry deposits, with the most detailed around the Spence deposit in the

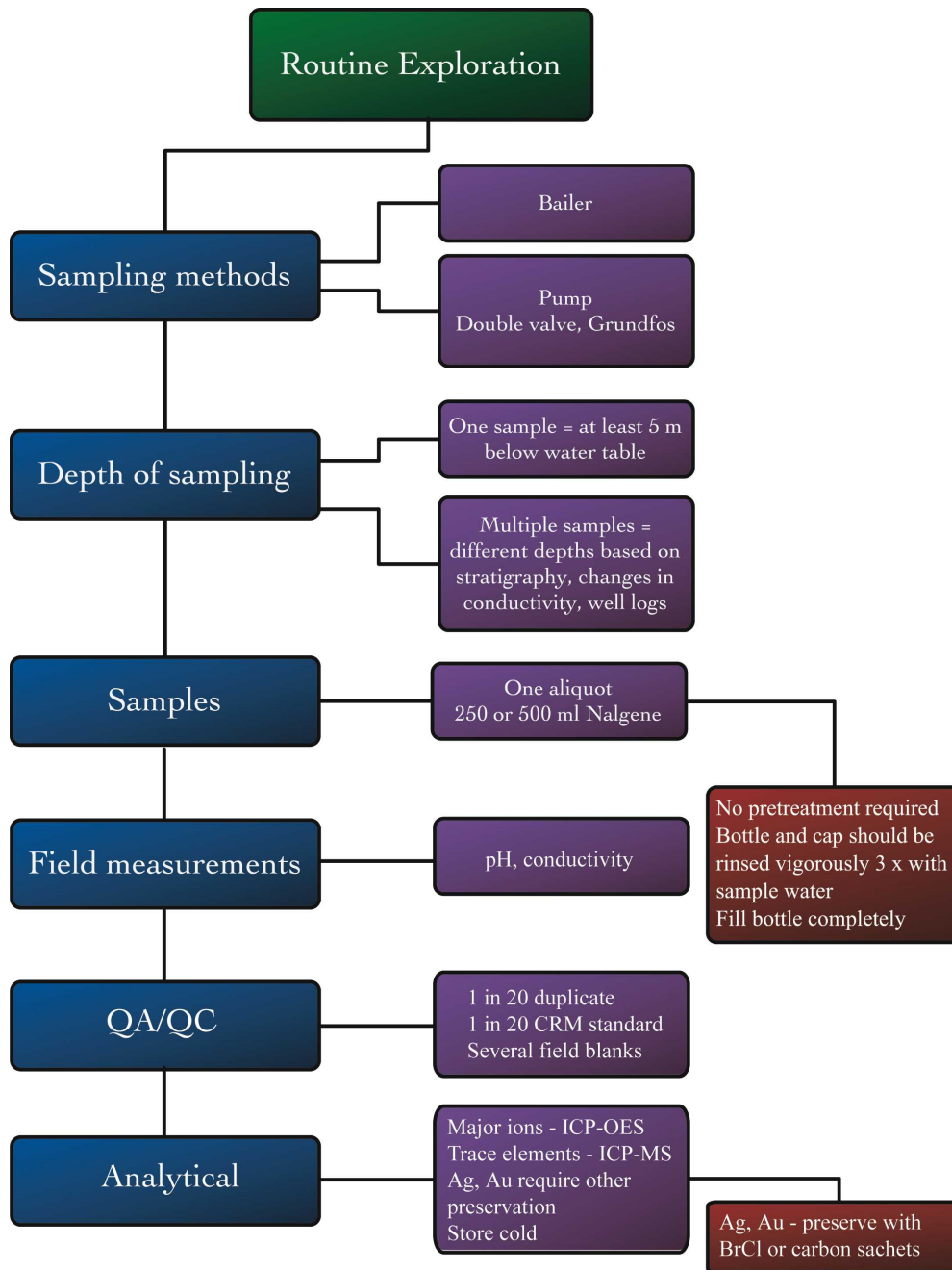


Figure 8: Flowchart illustrating the major aspects of a groundwater geochemical exploration program for “routine exploration”.

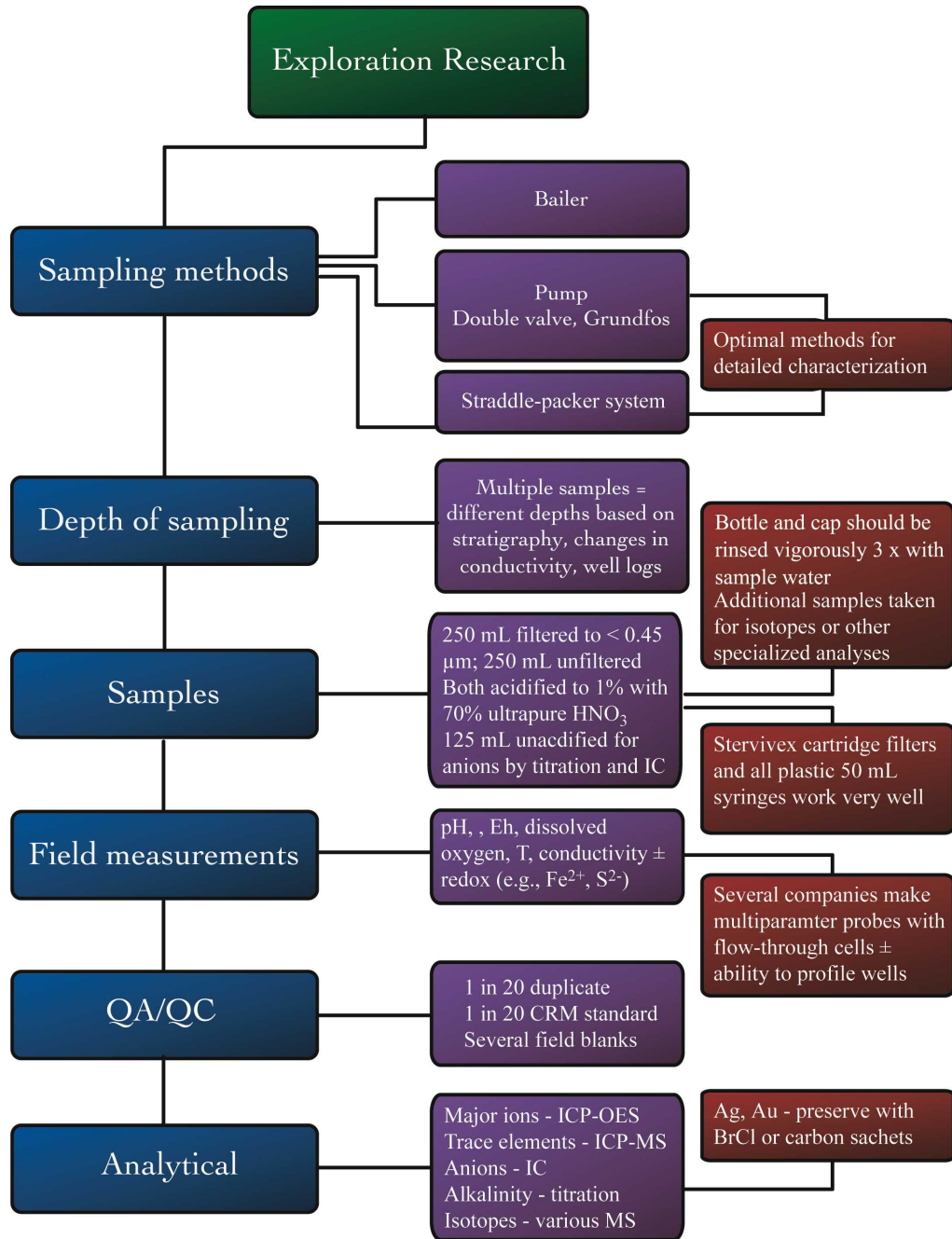


Figure 9: Flowchart illustrating the major aspects of a groundwater geochemical exploration program for “exploration research”.

Atacama Desert northern Chile (Cameron et al., 2002; Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a). These studies around the Spence deposit also highlight the utility of stable isotopes in process interpretation.

RioChilex discovered the Spence deposit in 1996-1997 by grid drilling through piedmont gravels that cover the deposit, which displays a typical supergene-enriched sequence (Figure 10). Reserves recoverable by open-pit mining comprise 50 Mt of oxide ore with 1.4% Cu, 200 Mt of enriched sulfide ore with

1.3% Cu, and 150 Mt of primary sulfide ore with 0.6% Cu. Ore is associated with three quartz-feldspar porphyry bodies intruded along a northeast axis into andesitic volcanic rocks. Intrusions are cut by tourmaline-quartz-sulfide hydrothermal breccias. The irregular deposit surface is covered by 30-180 m of gravels. Groundwaters were sampled in and around the Spence deposit in exploration and definition wells in 1999 and 2000, using a combination of flow-through bailer and downhole pump, as described above. This groundwater study was undertaken to

enhance understanding of geochemical anomalies in the soils overlying the Spence deposit, which are similar to surficial anomalies elsewhere in northern Chile (Cameron et al., 2002). As such, this groundwater study can be considered an example of a “research exploration” survey (Figure 9). Thus, samples were collected for all major and trace metals, anions, stable isotopes (O, H, C, S), and both filtered (< 0.45 μm) and unfiltered aliquots (Cameron et al., 2002; Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a).

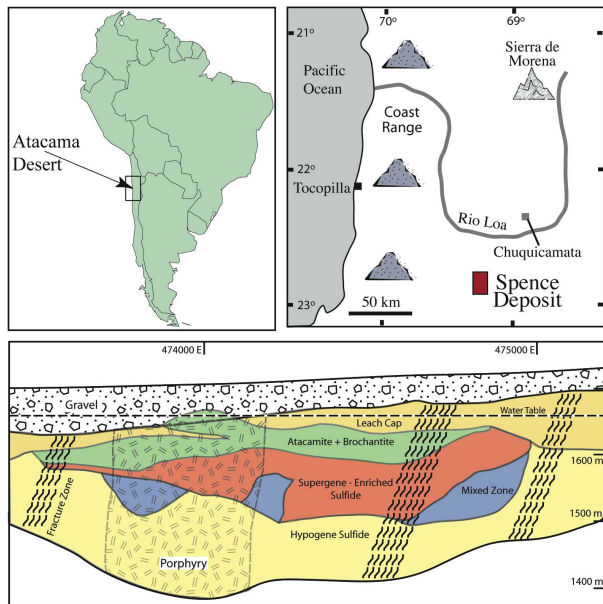


Figure 10: Location of the Spence deposit, Atacama Desert, Chile. W-E cross section of the southern part of the Spence deposit. Intermediate porphyry intrudes andesites. After Cameron et al (2007).

Groundwaters at the Spence deposit are variable between two end-members; a relatively fresh regional groundwater end-member (with TDS typically < 1000 mg/L) and a saline end-member (with TDS values up to and in excess of seawater; Figure 11) that has clearly extensively interacted with Spence deposit porphyry copper mineralization (Cameron et al., 2002; Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a) (Figure 6). Up gradient of the Spence deposit, groundwaters typically have low concentrations of porphyry copper-related species, such as Cu, Mo, Se, Re, As and sulfate has isotopic compositions typical of salars and non-mineralized groundwaters in the Atacama Desert (Figure 6). Oxygen and hydrogen isotopes of these upflow waters are consistent with relatively recent recharge at elevations around 4000 m in the high Andes (Figure 12). Within the deposit, As, Se, Re and Mo contents increase and remain elevated for at least 2 km down gradient from the deposit, owing to the fact that under the pH and Eh conditions present (near-neutral, moderately oxidizing), these elements form oxyanions, which are less readily adsorbed to oxyhydroxide or clay mineral surfaces than the metal cations (Cameron et al., 2002; Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a). The water table shallows in a salar (salt pan) 5 km down gradient from the deposit, and salar

sediments are strongly enriched in these porphyry indicator elements (Leybourne and Cameron, 2006b). In contrast, Cu is clearly anomalous in groundwaters in and around mineralization, but Cu contents decrease rapidly down gradient, owing to adsorption of this cation to mineral surfaces. Base metal contents in Spence deposit groundwaters are limited, as in other environments, by the generally near-neutral pH conditions. Thus, at the Spence deposit, mineralization can be detected for long distances downflow of mineralization (at least several km) by anomalous contents of As, Se, Re and Mo, with local definition of the target based on coincident anomalies in Cu abundance and S isotopes. Cameron and Leybourne also studied soils and waters around a large Cu (soil MMI) geochemical anomaly located in the Pampa del Tamarugal region of northern Chile (Leybourne and Cameron, 2006b). Although soils here show elevated Cu, analyses of the waters and soils suggest that unlike at Spence, the Cu in the Tamarugal anomaly soils are the result of long periods of accumulation owing to evaporation of Cu-bearing waters from a distal source. S/Se ratios of these waters are similar to the regional waters upflow of the Spence deposit, and significantly elevated compared to waters that have clearly interacted with Spence mineralization.

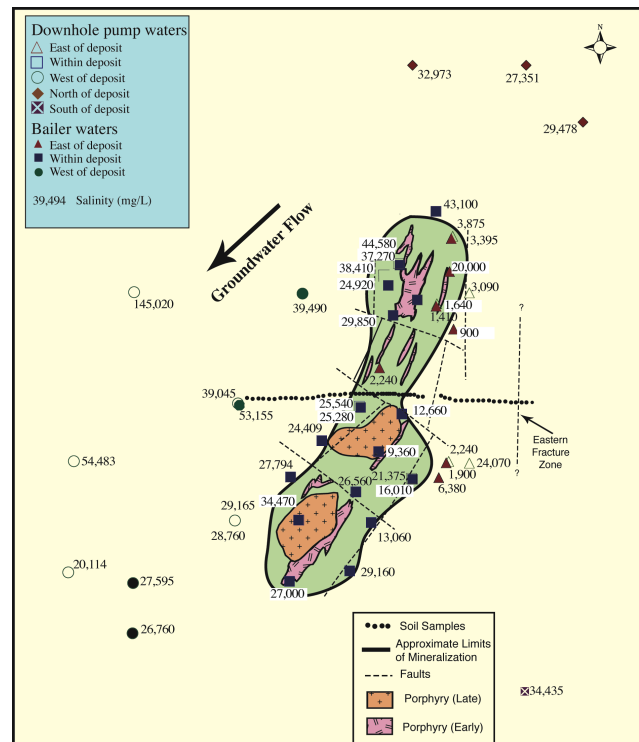


Figure 11: Outline of the Spence deposit, including location of major porphyries, groundwater sample locations, soil sample traverse and generalized groundwater flow. After Leybourne and Cameron (2006a). Salinities indicated next to well location.

There has been relatively little research on groundwater geochemistry around porphyry copper deposits elsewhere; groundwaters were recovered from around the Casa Grande porphyry copper-molybdenum system, Arizona (Ficklin et al.,

1981). Groundwaters at Casa Grande appear to be anomalous in Mo, As, K and SO₄ proximal to mineralization, although As anomalies are displaced from Mo and SO₄ anomalies, complicating interpretation in the absence of groundwater flow data. Groundwater Cu contents are not anomalous (Ficklin et al., 1981; Taufen, 1997). Waters around Casa Grande appear to have very similar characteristics in terms of metal association as waters from the Spence deposit. In summary, porphyry copper deposits appear to be excellent candidates for groundwater geochemical exploration; these deposits commonly contain anomalous concentrations of species that tend to be relatively mobile in neutral to slightly alkaline, suboxic solutions e.g., As, Se, Re and Mo. As shown at the Spence deposit in Chile, these species form oxyanions and therefore migrate downflow for significant distances, providing a broad exploration target. Anomalies in these oxyanions can be refined using S/S_e ratios and S isotopes, to aid distinction from far-traveled saline fluids. Copper migration is typically restricted owing to adsorption to hydroxide surfaces, which also likely explain the lack of a copper anomaly at Casa Grande.

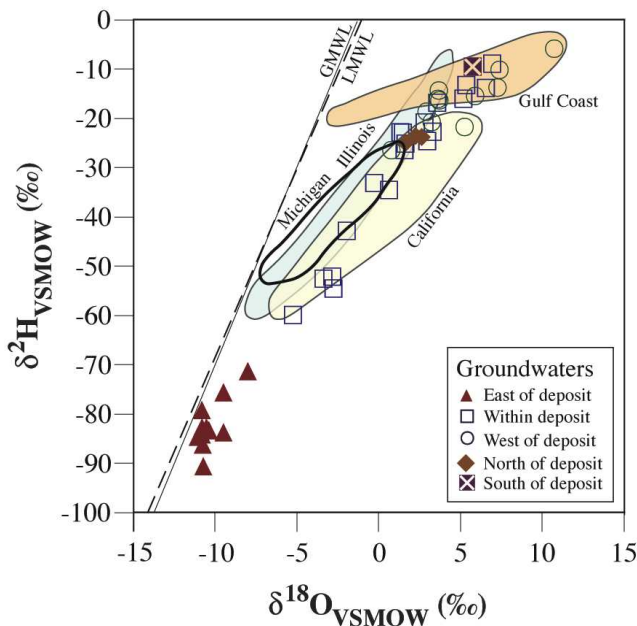


Figure 12: Stable isotope of oxygen and hydrogen for Spence deposit groundwaters. GMWL = global meteoric water line of Craig (1961), and local MWL after Aravena et al (1999). Note that the most saline waters at the Spence deposit are similar to basinal brines; fields based on data from Hoefs (2004) and Taylor (1974). Figure after Leybourne and Cameron (2006a).

Volcanogenic Massive Sulfide Deposits

Volcanogenic massive sulfide (VMS) deposits are variable in terms of host rock and sulfide compositions, but are characteristically dominated by metal sulfides, in particular by pyrite, pyrrhotite, sphalerite, galena and chalcopyrite. Details of the geology and geochemistry of VMS mineralization are presented elsewhere (Barrie and Hannington, 1999; Galley et al.,

2007, in press). These deposits are dominated by Fe, Zn, Pb, and Cu, with generally minor Cd, Hg, Au, As, Sb, Ba, Bi, and In (Table 1).

VMS deposits have been studied in variable detail in terms of surface and groundwater geochemical exploration. Ground and surface waters were investigated for their efficacy in exploring for more deeply buried mineralization in the mature Bathurst Mining Camp, New Brunswick, Canada (Leybourne, 2001; Leybourne et al., 2003; Leybourne et al., 2006a; Leybourne and Goodfellow, 2003; Leybourne et al., 1998, 1999, 2002). These studies involved investigation of surface water geochemistry over a moderately large scale (~ 400 km²) with comparison to coincident stream sediments, with samples taken about every 500 m along all streams in the area. At the Restigouche and Halfmile Lake deposits, groundwaters were collected from diamond drill holes within and distal from the deposits (Figure 13).

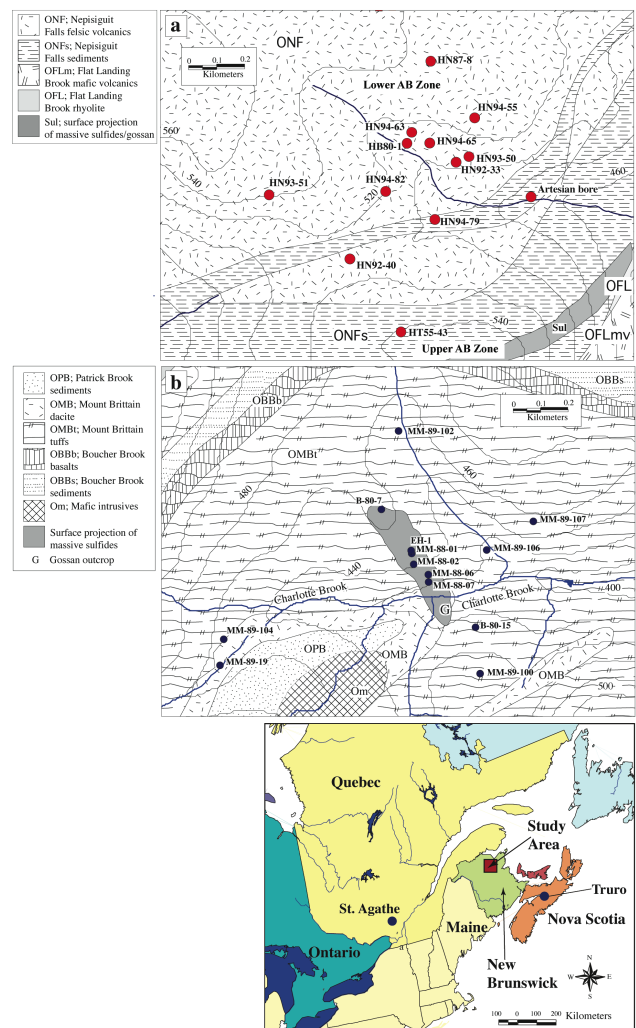


Figure 13: Geology of the Halfmile Lake deposit (A) and Restigouche deposit (B), Bathurst Mining Camp, Canada, showing the location of the boreholes sampled. Inset map shows the location of the study area in northern New Brunswick. After Leybourne et al. (2006a).

Groundwaters proximal to the Restigouche deposit have elevated As, SO₄ and metal (Zn, Pb, Cu, Mo, Sb, Cd) contents that are significantly greater than local surface waters and groundwaters distal from mineralization (Leybourne and Goodfellow, 2003) (e.g., Zn, Pb; Figures 14-17). Metals will enter solutions because of oxidation of massive sulfide minerals in the deposit. In most cases, oxidation of sulfide minerals occurs where O₂-bearing waters interact with mineralization, although oxidation of sulfides can occur in the absence of dissolved oxygen (Hamilton, 1998). This control by dissolved O₂ is shown by figure 17, which is a pseudo-cross section of groundwater geochemical data (Pb, Zn) at the Restigouche deposit. Where wells intersect mineralization at greater depth, metal contents are low in the waters recovered from those depths indicating that O₂-bearing waters do not penetrate to these depths. As with the surface waters, groundwaters around undisturbed VMS deposits in the BMC typically have near-neutral pH values, which generally restricts the mobility of base metal cations owing to adsorption, primarily to Fe-oxyhydroxide minerals, and in rare cases due to precipitation of metal-sulfate minerals (e.g., anglesite [PbSO₄] is present in suspended sediments from the Restigouche deposit) (Leybourne, 2001) (Figure 5).

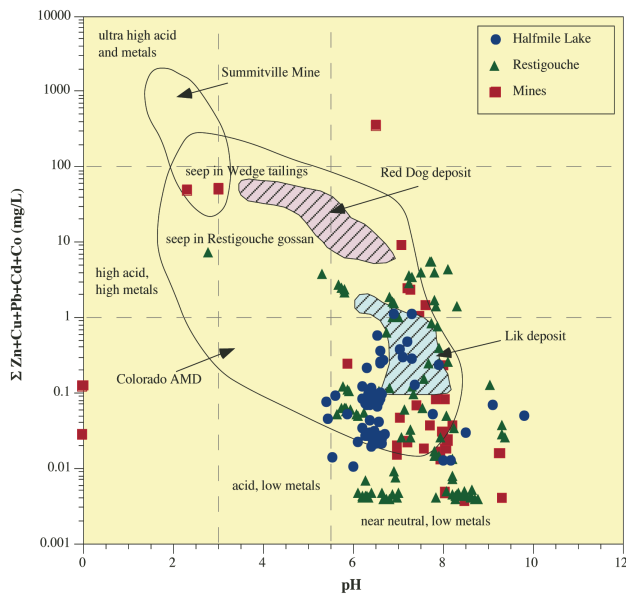


Figure 14: Plot of pH vs total metal load (Ficklin diagram) for groundwaters in the Bathurst Mining Camp. The majority of the groundwaters from the undisturbed Halfmile Lake and Restigouche deposits are near-neutral with low to moderate metal loads. Also shown are waters from the Red Dog and Lik deposits (Kelley and Taylor, 1997) and acid-mine drainage (Plumlee et al., 1999).

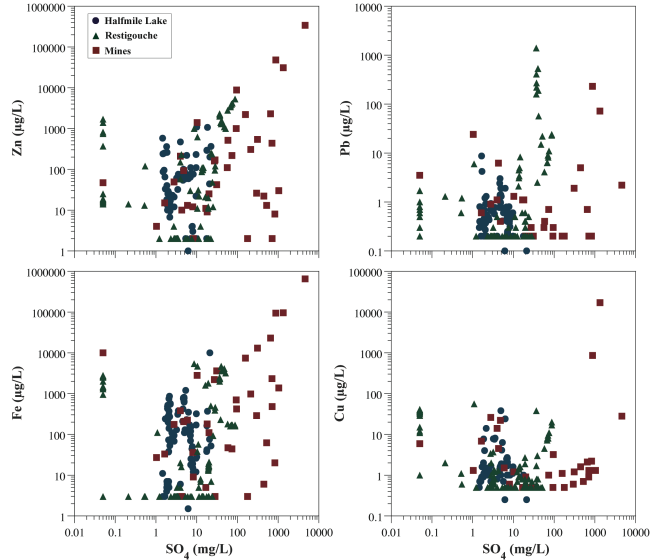


Figure 15: Sulphate versus metals for groundwaters from the Bathurst Mining Camp, Canada. Lead concentrations are highest in Restigouche deposit groundwaters closest to where the orebody crops out (see Figures 16, 17).

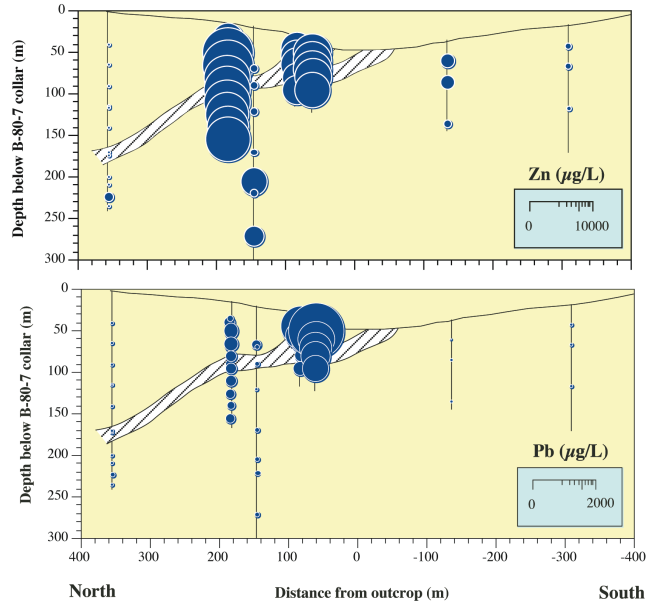


Figure 17: Proportional circle plots of Zn and Pb concentrations in groundwaters at the Restigouche deposit, Bathurst Mining Camp, Canada. Modified from Leybourne and Goodfellow (2003).

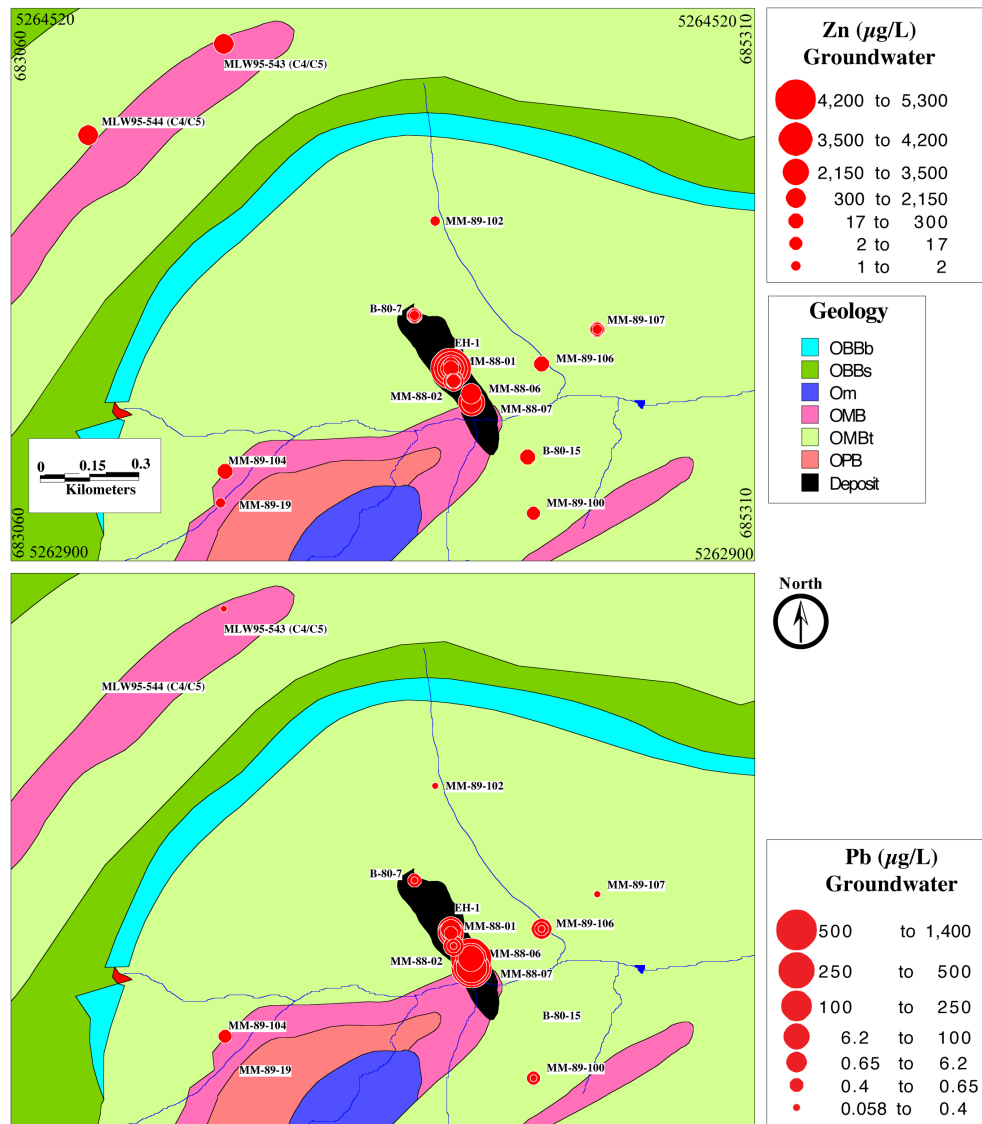


Figure 16. Proportional circle maps of Zn and Pb in groundwaters within and around the Restigouche deposit, Bathurst Mining Camp, Canada. After Leybourne (2007 in press).

Based on these studies in the BMC and on other studies around VMS mineralization, it appears that the best and most widely dispersed indicator of this type of mineralization in both ground and surface waters is Zn. In many cases, there are coincident anomalous concentrations of other ore-related species, in particular Pb, Cu, As, Mo, Sb and sulfate. However, some of these species are relatively immobile under near-neutral conditions, so anomalies in these species are not always present. Sulfate, although commonly anomalous downflow of VMS deposits, is not in itself a reliable indicator of mineralization, given that it is a major anion in many waters. Similar results were found for groundwaters associated with the Myra Falls deposit, Vancouver Island, Canada (Phipps et al., 2004). The mountainous terrain and well-developed fracture network has resulted in rapid recharge so that groundwaters interacting with ore have generally low salinity and are oxygenated, which

should promote sulfide mineral oxidation. Zinc is the best indicator of massive sulfide mineralization, with a threshold value of 20 µg/L (Phipps et al., 2004). Zn anomalies at Myra Falls are commonly associated with more subtle anomalies in a suite of pathfinder elements associated with primary VMS mineralization and hydrothermal alteration, including Cu, Pb, Cd, Mn, As, Sb, Ba and U.

Other Deposit Types

The main impediment to Au exploration using hydrogeochemistry is the typically low solubility of Au in low temperature waters (Vlassopoulos and Wood, 1990). Despite this, several studies in various environments have found that the best predictor of Au mineralization is aqueous Au (Cidu et al.,

1995; Grimes et al., 1995; Gray, 2001; Carey et al., 2003). These studies indicate that aqueous Au contents provide the most consistent vectors to Au mineralization, although confidence in Au anomalies may be increased with coincident As and/or Sb anomalies. Water samples can be difficult to preserve for Au and Ag analyses, as these species tend to adsorb strongly to the walls of HDPE bottles acidified with nitric acid (Leybourne et al., 2000a). A separate aliquot can be acidified to 1% with BrCl; this keeps the Au, Ag and Hg in solution, which can then be analyzed by ICP-MS to < 2 ng/L. Alternatively, Au (and Ag) can be preconcentrated in the field using sachets of activated carbon, followed by analysis by NAA for detection limits of around 1 ng/L for Au and 1 µg/L for Ag (Giblin, 2001; Gray, 2001).

There has been little research into aqueous geochemical exploration for magmatic Ni-Cu-PGE mineralization. There is good potential for water chemistry in this regard, in particular for those deposits that are sulfide-poor (especially in pyrrhotite) and therefore do not present a good geophysical target (Hattori and Cameron, 2004). The PGE are variably mobile in low-temperature aqueous systems with palladium the most mobile (Wood, 2002; Hattori and Cameron, 2004). Palladium is mobile in surface waters around Lac des Iles PGE mineralization as hydroxide complexes (e.g., Pd(OH)₂⁰, Pd(OH)₃⁻ and Pd(OH)₄²⁻); the low SO₄ and Cl contents of these waters precludes sulfate and chloride forming significant Pd-complexes (Hattori and Cameron, 2004). As discussed above for porphyry copper systems, where metals and metalloids are complexed as neutral or negatively charged species, adsorption to clays and Fe- and Mn-oxides and oxyhydroxides is inhibited at neutral to slightly alkaline pH conditions (owing to surface charge considerations), consistent with the potential for significant aqueous dispersion of Pd (Hattori and Cameron, 2004). In contrast to Lac des Iles, many Ni-Cu-PGE deposits have abundant Ni- and Fe-sulfides. In this case, Pd (and other PGE) mobility in solution should be enhanced, in particular where pyrrhotite is abundant, as dissolution of Fe-sulfides promotes more acidic conditions, which in turn will result in greater leaching of the PGE (Hattori and Cameron, 2004). Given the mafic-ultramafic rock association of magmatic Ni-Cu-PGE deposits, typically water-rock reactions can be expected to result in relatively elevated pH values as a result of hydration of mafic Mg- and Fe-bearing minerals (Fritz et al., 1992; Stefánsson et al., 2001; Sader et al., 2007). In the case of PGE mineralization in the absence of significant Fe-sulfides, pH values are likely to remain elevated (i.e. up to pH 10 or so), and Pd may prove to be the optimal pathfinder in solution, along with S and As, owing to their likely occurrence as oxyanions (Cameron and Hattori, 2003). Where significant Fe-sulfides are present, as at most Cu-Ni-PGE deposits, pH values are likely to be anomalously low compared to waters more distal from mineralization, and the lower pH values will likely promote solution of Ni and Cu in addition to the PGE, so that multi-element anomalies should be more significant (Table 2).

There has been almost no research investigating the use of groundwater chemistry in diamond/kimberlite exploration, although there have been a number of studies that have investigated the geochemical consequences of water-ultramafic rock interaction (Fritz et al., 1992; Allen and Seyfried, 2004; Palandri and Reed, 2004; Pokrovsky and Schott, 2004). Sader et

al. (2007) have shown that where groundwater interacts with kimberlite (in one instance, diamond-bearing), hydration of olivine and clinopyroxene produces elevated groundwater pH, up to in excess of pH 12, and result in loss of Mg and increase in K (Figure 4). Further work is needed to better define trace element and/or isotopic anomalies in groundwaters that might provide vectors towards diamond-bearing ultramafic bodies, although preliminary data (Sader and Leybourne, unpublished) suggests that some kimberlite waters are enriched in Co and Ni and have elevated Co/Mg and Ni/Mg ratios (Figure 4).

Exploration for uranium using groundwater geochemistry was investigated in the 1970's and early 1980's (e.g., Langmuir, 1978; Dyck, 1979; Langmuir and Chatham, 1980; Runnells and Lindberg, 1981; Earle and Drever, 1983; Giblin and Snelling, 1983) and has received renewed interest in the last few years (Singh et al., 2002; Pirlo and Giblin, 2004). Despite the fact that U is immobile under reducing conditions, in terms of elemental abundances, U appears to be the best indicator of unconformity-type U mineralization. Clearly, exploration success will be enhanced if there are coincident anomalies in other species that are typically enriched in U deposits, such as Se, V, Mo, and Cu (Table 2). Mo and Se may especially be useful in sulfide-poor reducing waters. There is some indication that waters are uncommonly Mg-rich and in equilibrium with phengite (Yanase et al., 1995a; Dickson and Giblin, 2006). One avenue that requires more research is through the use of Pb and/or U-series isotopes (Earle and Drever, 1983; Toulhoat and Beaucaire, 1991; Yanase et al., 1995b).

FUTURE DIRECTIONS

The role of bacteria in controlling sulfide oxidation and silicate hydrolysis as well as metal mobility and attenuation is not well understood. In recent years there has been increasing appreciation that many reactions that were previously considered inorganic, are now recognized as at least being facilitated, if not controlled, by biological processes. Recent studies have suggested that alteration of mid-ocean ridge basalt glass is bacterially mediated (Torsvik et al., 1998). For example, Reith et al. (2005) suggest that there is an association between Au mineralization and *Bacillus cereus* in soils in Australia. Supergene sphalerite mineralization was recently identified at the Mike deposit in Nevada (Bawden et al., 2003). Here, sulfur isotopes of framboidal sphalerite are very negative (as low as -70 ‰ δ³⁴S), illustrating the control of sulfur reducing bacteria on this unusual mineralization (> 400,000 tonnes of Zn).

One of the important challenges for surficial geochemical exploration methods is to move beyond deposit scale reconnaissance surveys (although, as is obvious from the preceding, more of these are needed) towards application of the methods in areas of prospective, but unknown, mineralization.

Greater emphasis needs to be placed on distinguishing real from false geochemical anomalies, in particular development of better models that relate redox and pH conditions of ground and surface waters with the element associations that can be expected given different styles of mineralization.

There will likely be increased use of non-traditional stable and radiogenic isotopes both in terms of deposit characterization

and in aqueous media for mineral exploration. For example, Cu and Se isotopes are relatively new systems being investigated. At the current state of understanding of these isotopes, we are still characterizing potential fractionations and cataloging values associated with different environments. However, in the future these systems may become understood sufficiently that they may become useful in mineral exploration. In addition, more research is needed on analytical methods that lower the cost, sample preparation steps, and speed of isotope analyses.

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.

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.

CONCLUSIONS

The following recommendations can be made with respect to the use of groundwater geochemistry in mineral exploration:

1. 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.
2. Determine the type of sampling apparatus to be used; routine 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.
3. 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.

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