

AQUEOUS GEOCHEMISTRY IN MINERAL EXPLORATION

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Abstract

Ground and surface waters are important media for the geochemical exploration of many different styles of mineralization. Water-transported (hydromorphic) metals can develop anomalous concentrations and reveal hidden mineralization directly (dissolved phase) and by adsorption/precipitation reactions with suspended and bed-load stream sediments (labile fraction). Groundwater recharges to depth, resulting in greater likelihood of interacting with buried mineralization compared to surface geochemical methods. Advances in the understanding of ore formation processes, water-rock interaction, and metals transport/attenuation in the secondary environment are enhancing the efficacy of aqueous geochemical exploration. Overcoming the issue of false anomalies is aided by traditional and nontraditional isotopic techniques to more directly fingerprint metal sources, in particular through the use of Pb and S isotopes. Advances in analytical technologies should permit such isotopic analyses, traditionally not used by the exploration industry due to cost, to become as routine as elemental analyses are today.

This paper synthesizes the current thinking and state of the art of surficial geochemical methods that are useful to the mineral exploration industry. Examples of how ground and surface waters vector to mineralization are presented for a number of deposit types (volcanogenic massive sulphide, gold, porphyry copper, sedimentary exhalative, unconformity uranium, kimberlite diamond, and Cu-Ni-PGE). The most successful aqueous-phase indicators of mineralization are those that are ore-associated and mobile in solution.

Résumé

Les eaux souterraines et les eaux de surface constituent un important milieu pour l'exploration géochimique d'un grand nombre de styles de minéralisation différents. Les métaux transportés dans l'eau (hydromorphes) peuvent s'accumuler en concentrations anomalies et révéler la présence de minéralisations cachées, soit directement (métaux dissous dans l'eau), soit indirectement par leur association (adsorption ou réaction de précipitation) aux sédiments en suspension ou aux sédiments de la charge de fond des cours d'eau (fraction labile). Les eaux souterraines sont alimentées en profondeur, ce qui fait qu'elles ont plus de chances d'interagir avec les minéralisations enfouies que ne le peuvent les méthodes géochimiques de surface. Les progrès accomplis dans la compréhension des processus minéralisateurs, des interactions entre l'eau et les roches ainsi que du transport ou de l'atténuation des métaux dans le milieu secondaire accentuent l'efficacité de l'exploration hydrogéochimique. Les méthodes isotopiques classiques et nouvelles, en particulier l'utilisation des isotopes de Pb et de S, facilitent l'élimination des fausses anomalies et permettent de caractériser plus directement les sources de métaux. Les progrès réalisés en matière de techniques d'analyse devraient permettre que l'emploi des analyses isotopiques de ce type, jusqu'ici peu répandu dans l'industrie de l'exploration pour des raisons de coût, devienne aussi courant que ne l'est aujourd'hui celui des analyses de la concentration des éléments chimiques.

Cette étude présente une synthèse des idées courantes et d'avant-garde en matière de techniques d'échantillonnage et d'analyse reliées aux méthodes géochimiques de surface, qui présentent un intérêt pratique pour l'industrie de l'exploration minière. Des exemples de la manière dont les eaux de surface et les eaux souterraines peuvent constituer des vecteurs pointant vers des concentrations minérales sont présentés pour un certain nombre de types de gîtes (gîtes de sulfures massifs volcanogènes, gîtes d'or, gîtes porphyriques de cuivre, gîtes de sulfures exhalatifs dans des roches sédimentaires, gîtes d'uranium associés à des discordances, gîtes de diamants dans des kimberlites et gîtes de Cu-Ni-ÉGP). Les meilleurs indicateurs de minéralisations dans l'eau sont ceux qui sont solubles et associés aux minéraux.

Introduction

Aqueous geochemistry (including ground and surface water and stream sediments) has been applied successfully in mineral exploration for some time. However, many surface and near surface deposits have already been discovered. One of the challenges for mineral exploration, then, is to find new deposits, particularly in areas where either thick cover exists (Cameron et al., 2004; Reith et al., 2005) or where past exploration has already discovered shallow mineralization and exploration must extend to greater depth (Goodfellow et al., 2003). Although stream and lake sediment analyses have received the most attention over the last several decades, surface and ground water geochemistry has more recently received consideration (Cameron, 1977, 1978; Miller et al., 1982; Earle and Drever, 1983; Giblin and Snelling, 1983; Taisaev and Plyusnin, 1984; Boyle, 1988; Cidu et al., 1995; Mingqi et al., 1995; Giblin, 1994; Cameron et al., 1997, 2004; Leybourne et al., 1998, 2002; Leybourne et al., 2003;

Phipps et al., 2004), in particular because of significant advances in analytical techniques and the widespread availability of inductively coupled plasma mass spectrometers (ICP-MS). Newer ICP-MS instruments allow routine multi-element analyses with low detection limits (sub-parts per trillion for many elements). Other advances have occurred in ore deposit models, which greatly influence exploration strategies, and in the area 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). Indeed, the relative ease of multi-element analytical techniques has exacerbated the challenge of dealing with very large data sets and being able to extract the most relevant information for mineral exploration.

Because groundwaters penetrate deeply into the earth's crust, hydrogeochemistry offers the potential to explore into

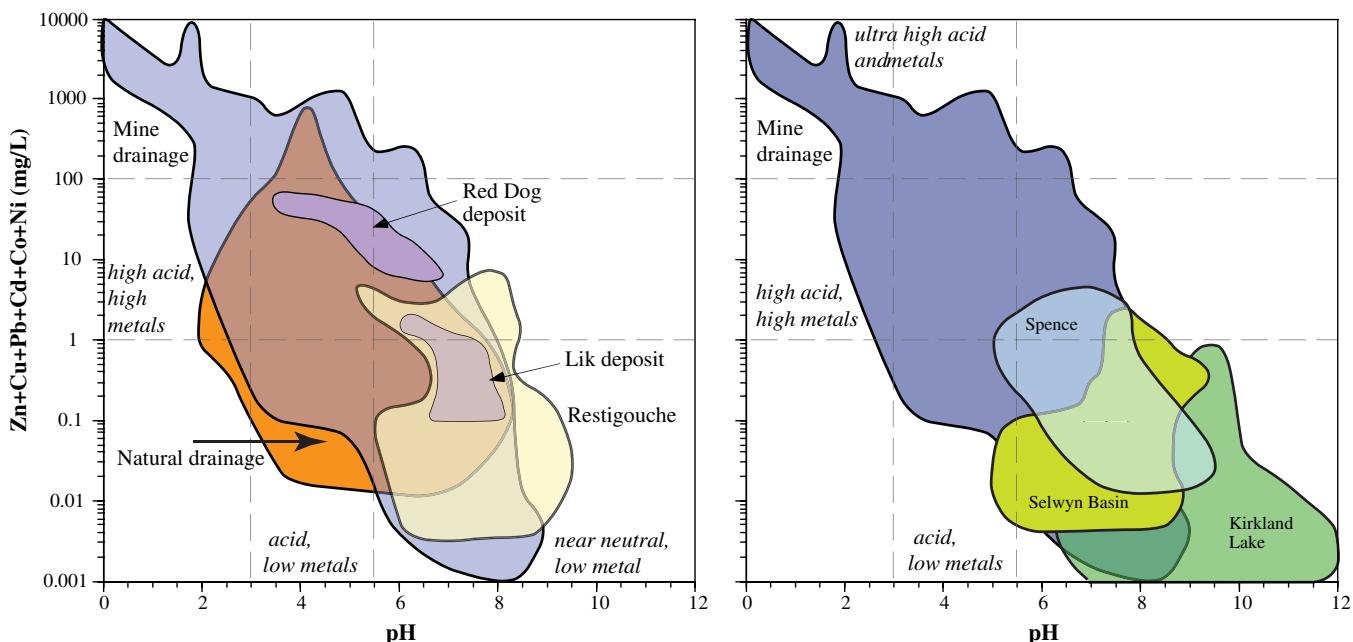


FIGURE 1. Ficklin diagram showing total dissolved metals (Zn, Cu, Pb, Co, Ni, Cd) for natural drainage waters from a variety of deposit types, as compiled by Plumlee et al. (1999). Also shown are fields for ground and surface waters from around the Restigouche (VMS) Deposit, Bathurst mining camp, Canada (Leybourne, 1998), the Spence (porphyry Cu) Deposit, Chile (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006), the XY deposit and Nor occurrence (SEDEX), Selwyn Basin, Yukon (Goodfellow, 1983; Jonasson et al., 1987), the Lik and Red Dog deposits (SEDEX), Alaska (Kelley and Taylor, 1997) and kimberlites from the Kirkland Lake area (Sader et al., 2007). Diagram modified from (Plumlee et al., 1992; Plumlee et al., 1999). Fields are also shown for mine drainage waters for a number of deposit types and natural drainage waters from undisturbed deposits, as compiled by Plumlee et al. (1999). Note that there are a small number of waters in the Plumlee et al. (1999) compilation from Iron Mountain that extend to higher metal loads at negative pH values that are not shown here.

the third dimension and detect deeply buried mineralization, and therefore may prove more advantageous than other superficial geochemical methods. However, despite recent reviews (Giblin, 1994; Taufen, 1997) there are still relatively few detailed studies in the literature. Some of the advantages of using natural waters in mineral exploration include their chemical reactivity, physical mobility, relative ease and rapidity of sampling, greater uniformity compared to other sample media, and the fact that naturally low background values increase anomaly contrast (Giblin, 1994). In addition, because modern analytical methods typically require a sam-

ple in aqueous form, waters require less sample preparation than either sediments or rocks.

This paper synthesizes the current thinking and state of the art with respect to sampling, analysis, and anomaly type in aqueous geochemical methods that are useful to the mineral exploration industry. Although acid mine drainage studies have some utility in terms of understanding element associations between waters and ore, this review places more emphasis on studies around undisturbed mineralization because acid mine drainage represents conditions unlikely to be encountered during mineral exploration owing to greater surface area and generally much lower pH conditions associated with mine waste. However, some of the trends related to metal abundance and pH of ground and surface waters are similar between natural and disturbed systems, with the exception that natural systems do not attain such elevated metal loads and low pH values as some acid mine drainage systems (Fig. 1) (Plumlee et al., 1999). These systems are therefore characterized by the artificially accelerated oxidation of sulphide minerals.

Fundamentally, geochemical techniques for mineral exploration rely on the development of anomalies in the regional geochemical background. Critical to the devel-

TABLE 1. Major components of different deposit types.

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		Cu, Mo, S, Fe, Se, As, Re	Ag, Au
SEDEX	Fe, S, Cu, Zn, Pb	Ag, Au, Ba, Cd	Fe, S, Zn, Cu, C	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, PG	Co, Ni, Cr
Kimberlite (diamond)	Sr, Nb, Ba, Cr, Ni	LILE, HFSE, REE	Sr, LILE	Ba, HFSE, Nb, Cr, Ni, REE
	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 dissolved sulphate owing to insolubility of barite.

HFSE, high-field strength elements; LILE, large ion lithophile elements; REE, rare earth elements.

Table modified after McMartin and McClenaghan (2001).

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	Sulphide-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 et al., 2002; Cameron and Leybourne, 2005; 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	Sulphide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb
Gold (vein)	Au	Se, As, Sb	Activated carbon preconcentration or BrCl (see text) ICP-MS, NAA	Giblin, 2001; Gray, 2001; Carey et al., 2003	
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; Langmuir and Chatham, 1980; Earle and Drever, 1983; Giblin and Snelling, 1983; Dickson and Giblin, 2006	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.

opment of effective exploration strategies is an understanding of the mechanisms of anomaly formation in different settings and for different sample media. There are two different types of anomalies that are pertinent to geochemical exploration. Soil and till geochemical anomalies are developed in areas where there has been mechanical transport of deposit material away from the site of mineralization (i.e. via glacial transport, solifluction, or mass wasting). In contrast, for ground or surface water, any anomalous geochemical signature is fundamentally the result of hydromorphic (water transported) dispersion. Stream sediments (both suspended and bed load) develop geochemical anomalies in two different ways. Analogous to soils, stream sediments may possess anomalous geochemistry as a result of mechanical dispersion of surface or near surface mineralization. In addition, loss of metals from solution results in mass transfer to the sediment phase, resulting in a hydromorphic component to the sediment geochemistry (Leybourne, 2001; Leybourne et al., 2003). Formation of Mn- and Fe-oxides and oxyhydroxides in particular are effective at scavenging trace metals from solution (Bau, 1999). If mineralization is not at or near surface, stream sediments can only develop a geochemical anomaly via hydromorphic dispersion. Thus, there is an important genetic link between stream sediment and stream water geochemical anomalies. However, the fundamental difference between stream sediment and stream water (and groundwater) as sample media is that the former represents a time-integrated signal of the mechanical with or without hydromorphic contributions, whereas the stream water represents a snapshot in time of the state of the geochemical system.

Recent advances in weak partial leaches have shown that geochemical anomalies occur in soils and till, in some cases over mineralization that is in excess of 100 m below surface.

These anomalies have been postulated to form by a variety of processes, including capillary migration of ions, vapor transport, ground- and soil-water advection or diffusion, electrochemical transport (Hamilton, 1998), and seismic pumping (Cameron et al., 2002, 2004). Although there has been considerable debate as to which of these mechanisms is responsible for soil anomaly development, it is most likely that most of these mechanisms are viable, and that any one mechanism may be dominant depending on the type of mineralization, characteristics of the overburden, and climate. 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 Cu mineralization (Cameron et al., 2002, 2004). 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 Cu 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.

Aqueous Geochemical Exploration for Specific Deposit Types

This section summarizes key considerations in the geochemical exploration of specific deposit types based on case studies using surface and ground waters. These examples are illustrative rather than comprehensive. In addition, the deposit types discussed are not exhaustive; however, the concepts are applicable to other styles of mineralization. Key geochemical features of the different deposit types discussed are presented in Table 1; key references and findings of

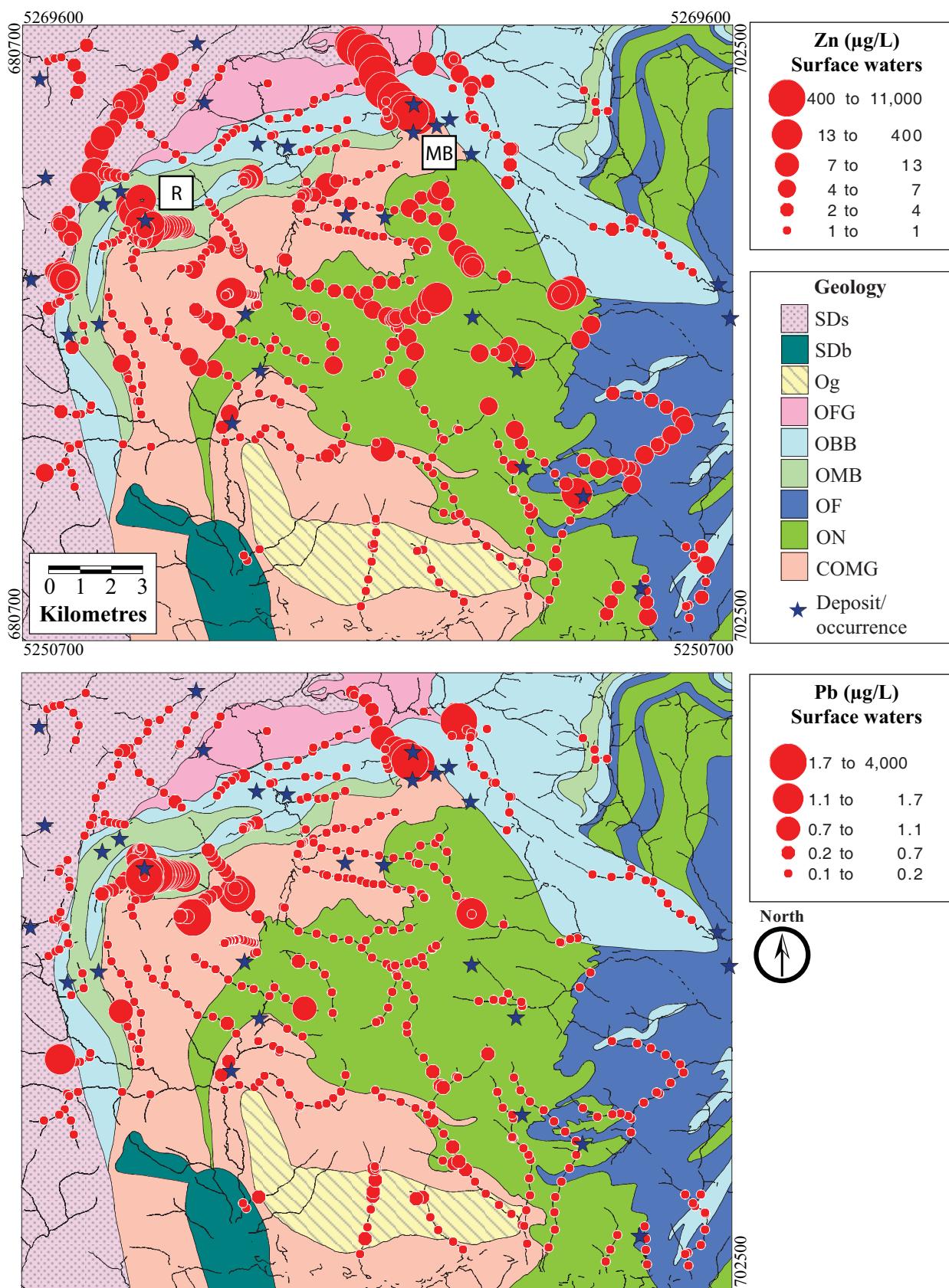


FIGURE 2. Proportional circle maps of Zn and Pb in surface waters of the Bathurst Mining Camp, New Brunswick, Canada. Also shown are deposits and showings/occurrences in the area of $\sim 400 \text{ km}^2$. The two larger deposits are the Restigouche (R) and Murray Brook (MB) deposits, and the former was not mined at the time of sampling. It is only around these two deposits that Zn and Pb anomalies in surface waters are coincident (after Leybourne et al. (2003)). SDs, Silurian-Devonian sandstone/shale; SDb, gabbro/diabase; Og, Ordovician granite; OFG, Fournier Group; OBB, Boucher Brook Formation; OMB, Mount Brittain Formation; OF, Flat Landing Brook Formation; ON, Nepisiguit Falls Formation; COMG, Cambrian-Ordovician Miramichi Group.

aqueous studies around those deposit types are summarized in Table 2. Following these examples, the discussion section summarizes pertinent aspects of aqueous geochemical exploration in terms of what works and some important caveats.

Volcanogenic Massive Sulphide Deposits

Volcanogenic massive sulphide (VMS) deposits are variable in terms of host rock and sulphide compositions, but are characteristically dominated by metal sulphides, in particular by pyrite, pyrrhotite, sphalerite, galena, and chalcopyrite. Details of the geology and geochemistry of VMS mineralization are presented elsewhere in this volume (Dubé et al., 2007; Galley et al., 2007). 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 received moderate attention in terms of studies related to aqueous 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 et al., 1998, 1999, 2002, 2003, 2006a; Leybourne, 2001; Leybourne and Goodfellow, 2003). These studies involved investigation of surface water and coincident stream sediment geochemistry over a moderately large scale (~ 400 km²); samples were taken about every 500 m along all streams in the area (Fig. 2). This study area contains the previously (1989–1992) mined Murray Brook deposit (the gossan cap was mined for Au; in situ massive and supergene sulphides were left largely undisturbed), the smaller undisturbed (at the time of sampling; the deposit was subsequently mined) Restigouche deposit, and a number of other VMS occurrences (Fig. 2). At the Restigouche deposit, surface waters were collected at a denser spacing (Fig. 3) and groundwaters were collected from diamond drillholes within and distal from the deposit (Fig. 4).

For surface waters in the Bathurst mining camp, anomalies are most consistently developed for Zn, but around many occurrences, in addition to the Restigouche deposit, Pb, As, and Cu anomalies are also present. Zinc abundances in surface waters are low compared to other environments (only up to 90 µg/L; low compared to, for example, the Red Dog deposit, Fig. 1) but are clearly anomalous over the regional geochemical landscape (Leybourne et al., 2003) (Figs. 2, 3). Although there are no carbonate rocks in the study area (which is dominated by metamorphosed mafic and felsic volcanic rocks and metasediments derived largely from the felsic rocks), there are sufficient carbonate minerals (calcite, dolomite, and siderite) in veins cross-cutting mineralization and disseminated in the rock matrix to buffer the pH in most surface waters to near-neutral values, restricting the abundance of most metals in solution (e.g. Fig. 1). A result of these pH values is that metal dispersion in surface waters is generally restricted (typically <1 to 2 km), so that hydrogeochemical surveys require fairly tight (<500 m) sample spacing (Leybourne et al., 2003). A further result of this study was that anomalies in the surface waters mirrored those in the stream sediments and partial extractions of the sediments (Leybourne et al., 2003). To illustrate this point, Figure 5 shows detailed chemical profiles for stream waters and sediments in Charlotte Brook, a stream that crosses the

Restigouche deposit close to its surface expression. Both water and sediment samples (and partial extraction) are clearly anomalous in Pb and Zn, with long dispersion trains.

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; Figs. 4, 6). Metals will enter solutions as a result of oxidation of massive sulphide minerals in the deposit. In most cases, oxidation of sulphide minerals occurs where O₂-bearing waters interact with mineralization, although oxidation of sulphides can occur in the absence of dissolved oxygen (Hamilton, 1998). This control by dissolved O₂ is shown by Figure 6, which is a pseudo-cross-section of groundwater geochemical data (Pb, Zn) at the Restigouche deposit. Where wells intersect mineralization at greater depth (e.g. DDH B-80-7), 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 Bathurst mining camp typically have near-neutral pH values, which generally restricts the mobility of base metal cations (Fig. 1A) owing to adsorption, primarily to Fe-oxyhydroxide minerals, and in rare cases due to precipitation of metal-sulphate minerals, e.g., anglesite [PbSO₄] is present in suspended sediments from the Restigouche deposit (Leybourne, 2001).

Based on these studies in the Bathurst mining camp 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 anomalies of other ore-related elements/species, in particular Pb, Cu, As, Mo, Sb, and sulphate. However, some of these elements are relatively immobile under near-neutral conditions, so anomalies of these elements are not always present. Sulphate, although commonly anomalous down-flow 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 sulphide ore have generally low salinity and are oxygenated, which should promote sulphide mineral oxidation. Zinc is the best indicator of massive sulphide 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 (Phipps et al., 2004).

Porphyry Copper and Related Deposits

Porphyry Cu and porphyry Mo deposits are associated with intermediate and felsic intrusive rocks. Classic examples include the Chuquicamata, El Salvador, and Escondida deposits in Chile. Details of the geology and geochemistry of porphyry deposits are presented by Sillitoe (2000) and Sinclair (2007). Key geochemical characteristics include anomalous accumulation of As, Mo, Se, and Re in addition

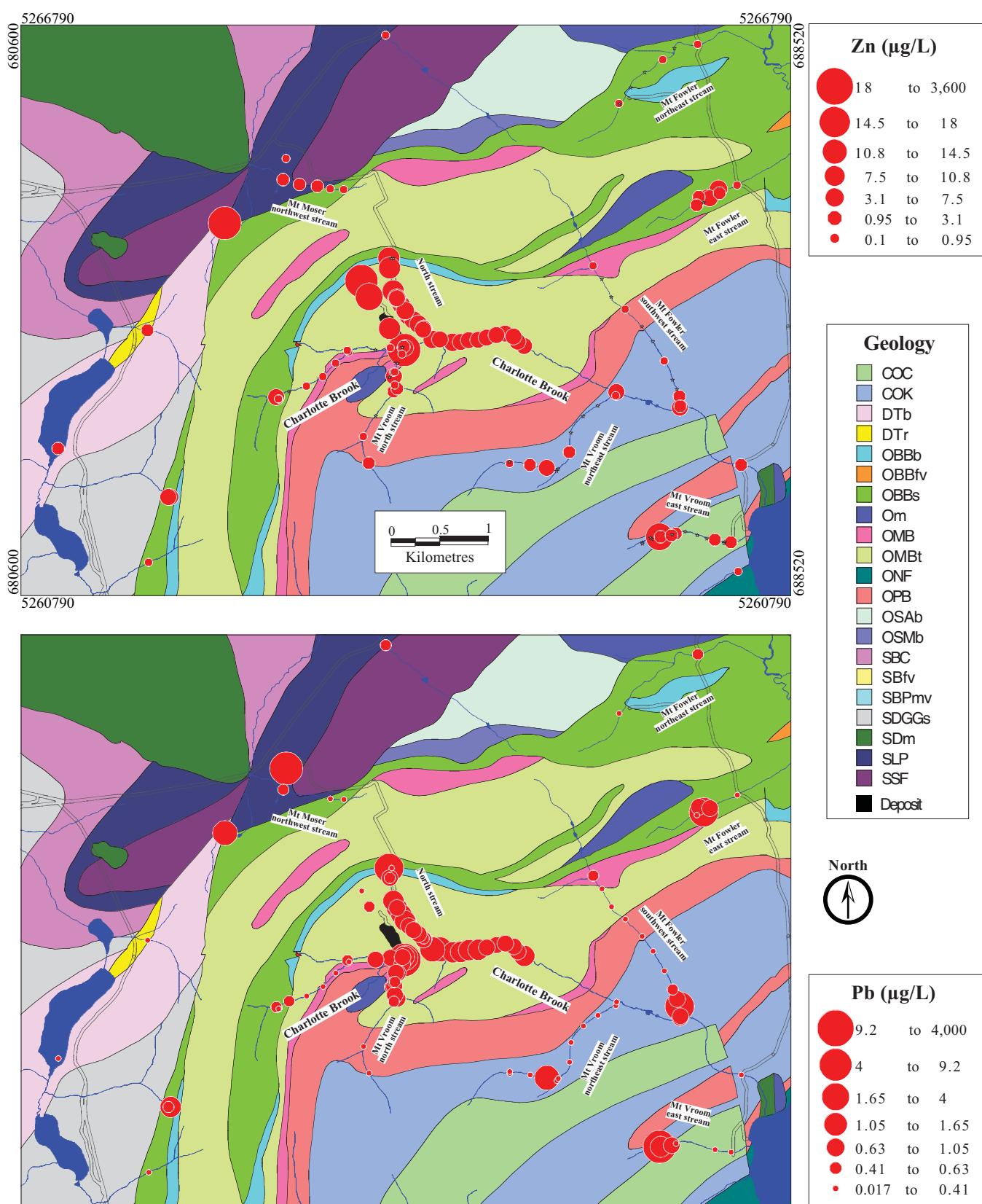


FIGURE 3. Proportional circle maps of Zn and Pb in surface waters around the Restigouche Deposit, Bathurst Mining Camp, New Brunswick, Canada. Modified from Leybourne (1998).

to Cu, and in many deposits Au, Pd, and Pt (Table 1). There have been a small number of studies of the aqueous geo-

chemistry of waters associated with porphyry Cu and Mo deposits (Ficklin et al., 1981; Cameron et al., 2002; Cameron

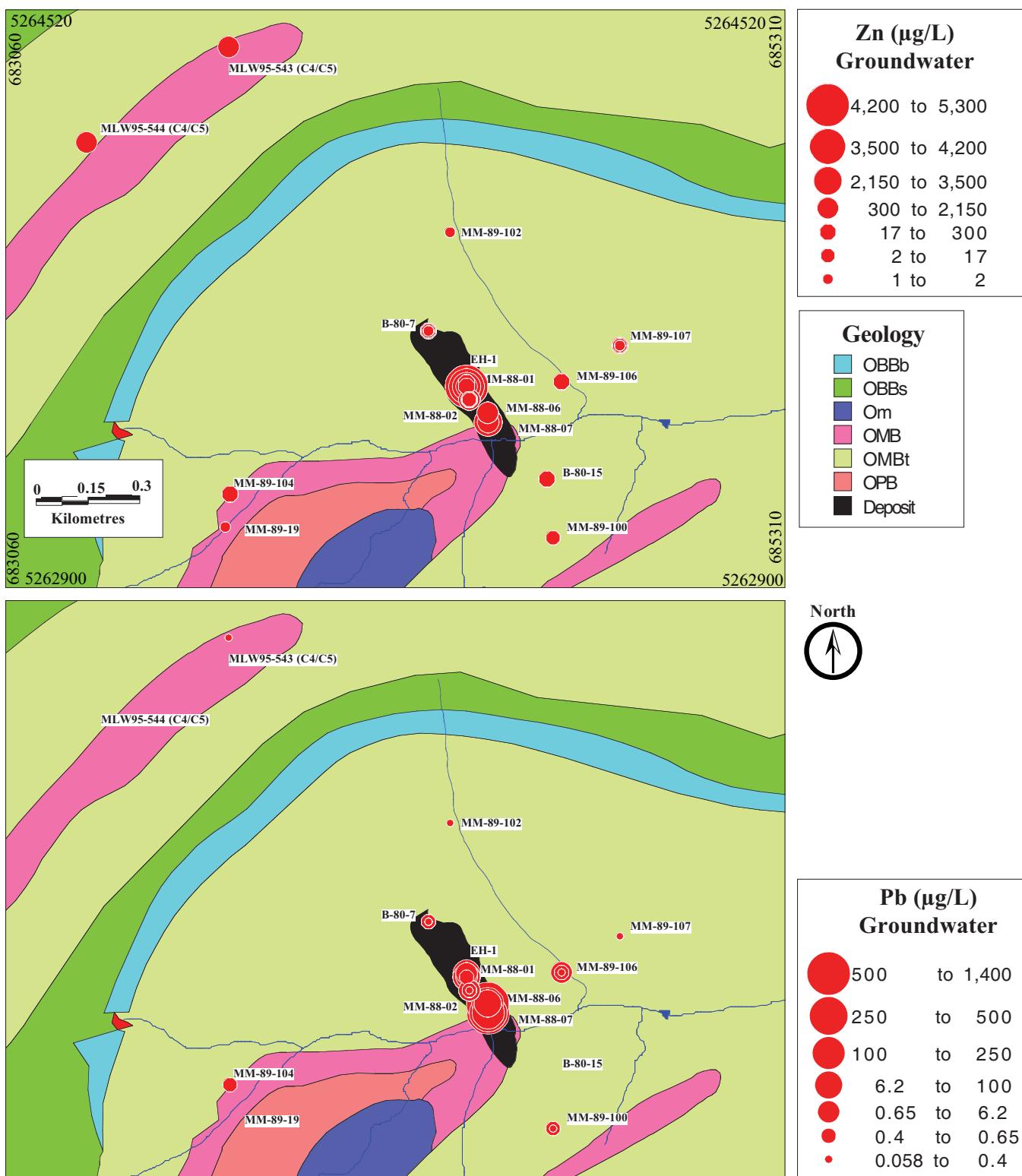


FIGURE 4. Proportional circle maps of Zn and Pb in groundwaters both within and around the Restigouche deposit, Bathurst Mining Camp, New Brunswick, Canada. Modified from Leybourne (1998).

and Leybourne, 2005; Leybourne and Cameron, 2006, in press). Probably the most comprehensive aqueous geochemical studies are those by Cameron and Leybourne (2005) around the Spence deposit in the Atacama Desert of northern Chile. At the Spence deposit, there appears to be two broad groups of waters, a relatively fresh regional groundwater

end-member (with total dissolved solids typically <1000 mg/L) and a saline end-member (with total dissolved solids values up to and in excess of seawater) that has extensively interacted with Spence deposit porphyry Cu mineralization (Cameron et al., 2002; Cameron and Leybourne, 2005; Leybourne and Cameron, 2006) (Fig. 7). Up gradient of the

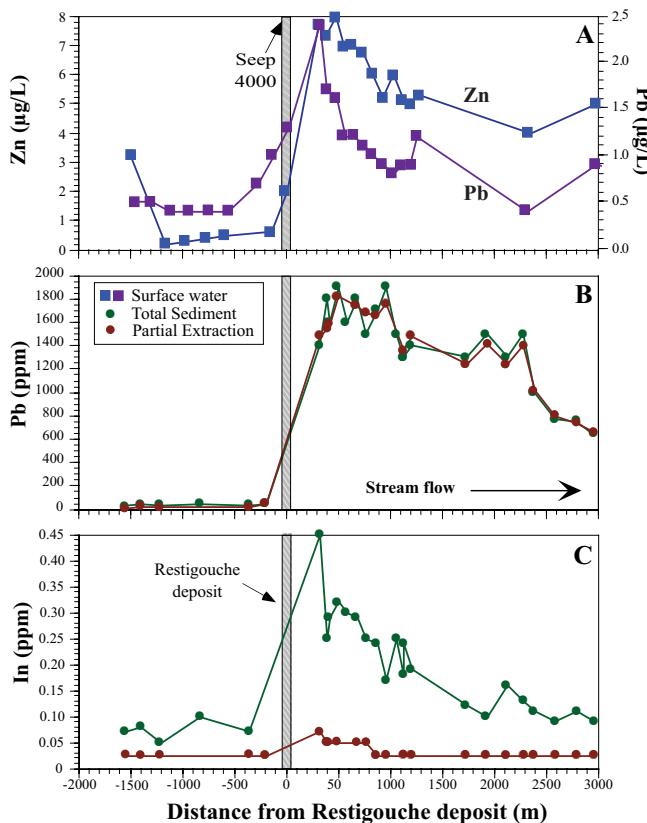


FIGURE 5. Downstream profiles of Zn and Pb (A) in stream waters, and Pb (B) and In (C) in stream sediments from Charlotte Brook draining the Restigouche deposit, Bathurst mining camp, Canada. Charlotte Brook flows across the deposit where it subcrops. Modified from Leybourne et al. (2003). Note the long dispersion for Zn in water and the atypically long dispersion for Pb, especially in the stream sediments. In this case, most of the Pb in the stream sediment is labile (little difference between total and partial extraction values). In contrast, indium is almost entirely transported mechanically, consistent with In being insoluble. For partial extraction analysis, sediments were treated with $0.25 \text{ M } \text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.05 M HCl , using methods outlined in Hall et al. (1996b). See Leybourne et al. (2003) for details.

Spence deposit, groundwaters typically have low concentrations of porphyry Cu-associated elements, e.g., Cu, Mo, Se, Re, and As, and sulphate has isotopic compositions typical of salars and nonmineralized groundwaters in the Atacama Desert (e.g. Fig. 8 shows results for Cu and Se). Oxygen and hydrogen isotopes of these upflow waters are consistent with relatively recent recharge at elevations around 4000 m in the high Andes. Within and down gradient of the deposit, As, Se, Re, and Mo contents increase and remain elevated for at least 2 km from the deposit, owing to the fact that under the present pH and Eh conditions (near neutral, moderately oxidizing), these elements form oxyanions that 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, 2006). In contrast, Cu is clearly anomalous in groundwaters in and around mineralization, but Cu decreases rapidly down gradient, owing to its adsorption to mineral surfaces (compare the results for Cu and Se within and downflow of mineralization, Fig. 8). Base metal contents in Spence deposit groundwaters are limited, as in other environments, by the generally near-neutral pH conditions (Fig. 1B). Thus, at the Spence

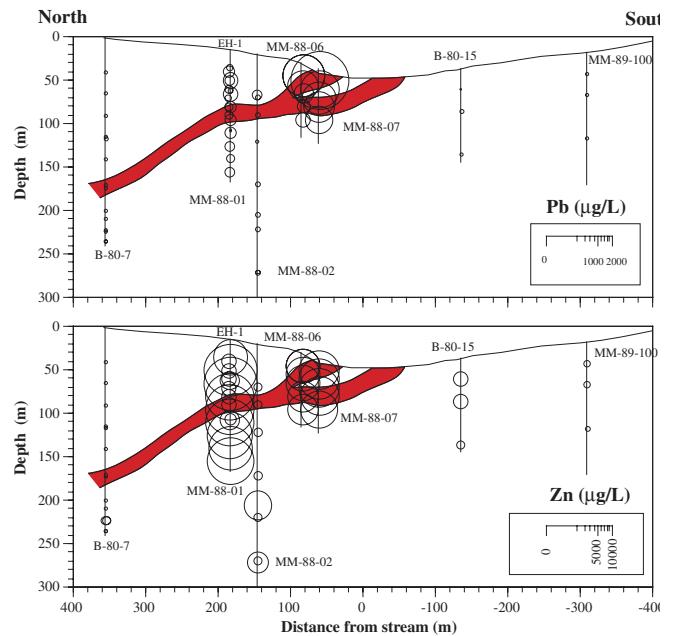


FIGURE 6. Proportional circle plots of Pb and Zn contents of groundwaters in boreholes projected onto a longitudinal cross-section of the Restigouche Deposit, Bathurst mining camp, Canada. Modified from Leybourne and Goodfellow (2003).

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 (2005) also studied soils and waters around a large Cu (soil MMI) geochemical anomaly located in the Pampa del Tamarugal region of

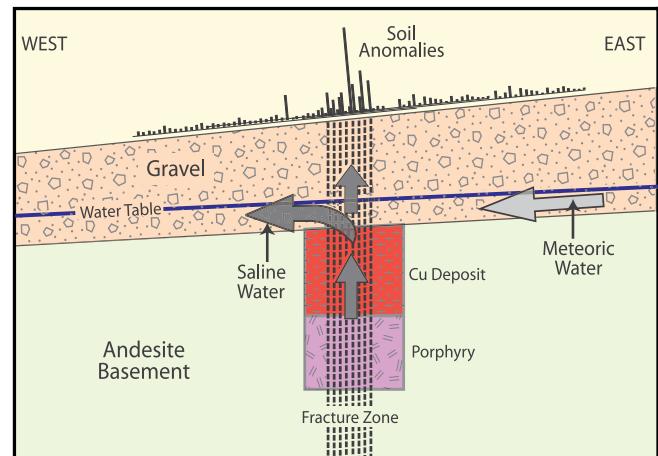


FIGURE 7. Conceptual model for the different groundwater-types and the formation of geochemical anomalies in groundwaters and soils at the Spence deposit. The porphyries and associated mineralization were introduced along a fault zone. Enhanced permeability in the zone permitted the upflow of saline formation fluids from the basement, which have then dispersed down-gradient to the west. Groundwaters of meteoric origin enter from the east and mix with the formation fluids. Reactivation of the fault has created a fracture zone in the overlying gravels. During earthquakes, saline formation fluids from the basement have been pumped to the surface. This has resulted in soil geochemical anomalies that reflect both the formation fluids (e.g. NaCl) and groundwater interaction with the porphyry copper deposit (e.g. As, Se, and Cu). Modified after Cameron and Leybourne (2005).

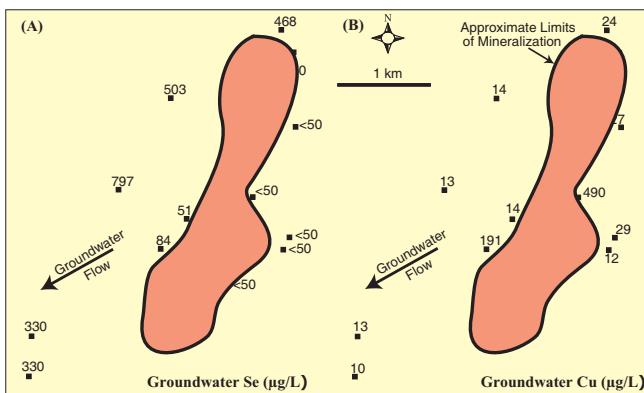


FIGURE 8. (A) Map showing the Se content of groundwater at the Spence Deposit, Atacama Desert, Chile. Note, waters on the upflow side of the deposit have Se abundances less than the detection limit of 50 µg/L. (B) Map showing Cu content of groundwater at the Spence Deposit. Note that elevated Cu is restricted to the immediate area of the deposit. After Cameron and Leybourne (2005).

northern Chile. Although soils here show elevated Cu, analyses of the waters and soils suggests that unlike at Spence, the Cu in the Tamarugal soil anomaly is 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 (Fig. 9D). Note that Se/TDS ratios (where TDS is total dissolved solids) increase more with increasing Se compared to Na/TDS (Fig. 9C), indicating that Se is added in excess of increases in salinity, through interaction with mineralization (Leybourne et al., 2001).

Groundwaters were recovered from around the Casa Grande porphyry Cu-Mo 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. Similarly, Mo is mobile from porphyry Cu mineral-

ization in the wetter climate of western Canada. Discharge of aqueous Mo into lakes via stream and groundwater flow has produced Mo anomalies in lake sediment in British Columbia (Cook, 2000).

In summary, porphyry Cu deposits are good candidates in terms of exploration using water chemistry; these deposits commonly contain anomalous concentrations of species that tend to be relatively mobile in neutral to slightly alkaline, oxidizing 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 through the use of S/Se 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 explains the lack of a Cu anomaly at Casa Grande.

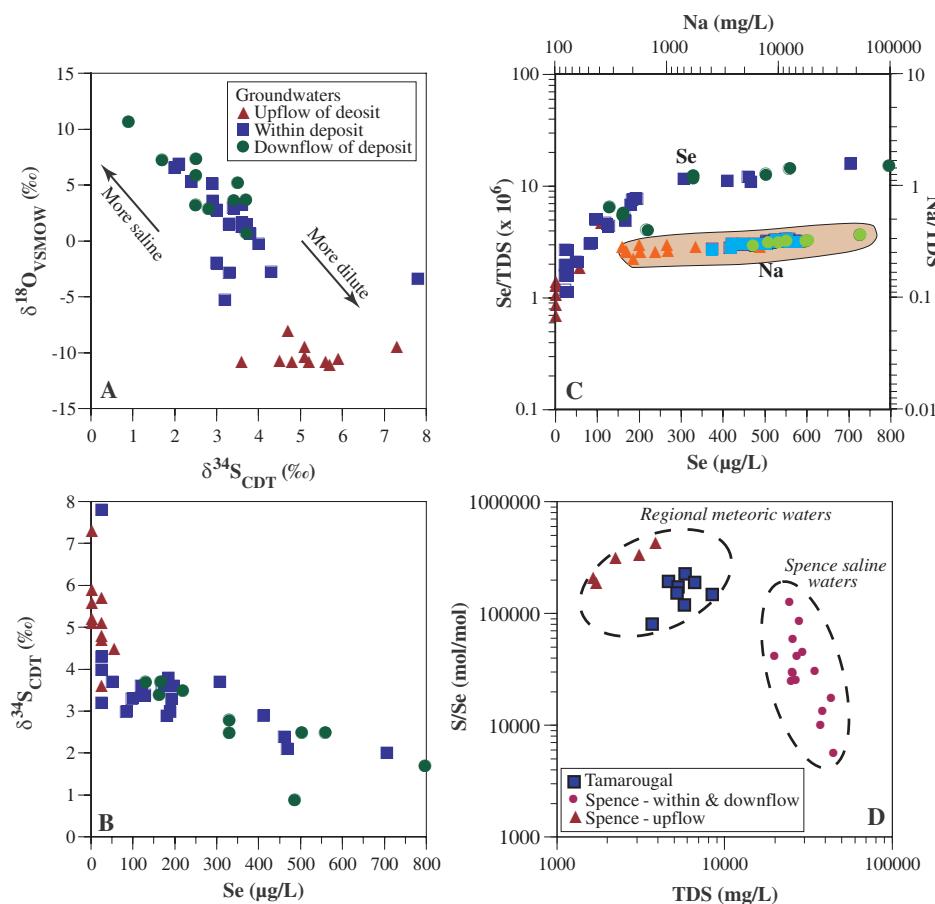


FIGURE 9. (A, B) Stable isotope ratios of S and O, and Se contents of groundwaters flowing into (east of deposit) and through the Spence deposit, Atacama Desert, northern Chile. These data show that groundwaters represent two broad groups, a more dilute upflow (east) groundwater with low Se contents, heavier δ³⁴S values and light δ¹⁸O values (close to meteoric values for northern Chile), and a saline groundwater with δ³⁴S and Se contents largely controlled through interaction with porphyry copper mineralization. Modified from Leybourne and Cameron (2006). (C) Plot of Se/TDS versus Se (bottom and left axes) compared to Na/TDS (Total Dissolved Solids) versus Na (top and right axes). Note that Na, a conservative species, increases only slightly with increasing salinity, whereas Se/TDS increases to a greater extent, indicating that Se is added in excess of changes in salinity, from water-mineralization interaction. Modified from (Leybourne et al., 2001). (D) S/Se versus TDS for groundwaters from the Spence Deposit compared to those from the Pampa del Tamarugal. Despite a large soil geochemical anomaly at Tamarugal for Cu, the S/Se ratios in the waters strongly suggest that the source for the Cu is distal. Modified from Leybourne and Cameron (in press).

Sedimentary Exhalative Deposits

Sedimentary exhalative (SEDEX) deposits are characterized as tabular bodies of sphalerite and galena along with Fe-sulphides hosted in black shale and chert-bearing rocks, and are dominated by Zn, Pb, and Ag as commodities (Goodfellow and Lydon, 2007). Although SEDEX deposits are important as sources of base and precious metals, there are relatively few studies of waters associated with these deposits. Surface waters studies have been carried out around SEDEX deposits in the Selwyn Basin, Yukon (Goodfellow, 1983; Jonasson et al., 1987) and Alaska (Kelley and Taylor, 1997).

Kelley and Taylor (1997) reported the composition of surface waters flowing over three SEDEX deposits in Alaska: the Red Dog, Lik, and Drenchwater deposits. These deposits crop out at or near surface where crossed by streams. Waters downstream of these deposits are anomalous in Al, Fe, Mn, Cd, Co, Cu, Ni, Pb, and Zn (Fig. 1 shows the relationship between total metals and pH for the Lik and Red Dog deposits), although the longest dispersion (up to 1.7 km at Drenchwater and 14 km at Red Dog) are shown by Cd, Co, Fe, Ni, and Zn (Kelley and Taylor, 1997). Both of these deposits are also characterized by low pH waters (e.g. Red Dog, Fig. 1) proximal to and down-flow from mineralization, consistent with the lack of carbonate minerals in the host rocks (mainly black shales). In contrast, the Lik deposit lies within a section that contains platform carbonates in addition to carbonate veins that cross-cut mineralization (Kelley and Taylor, 1997). As a result, waters flowing downstream from the Lik deposit are near neutral and generally low in metals compared to the Red Dog and Drenchwater deposits (Fig. 1). However, one sample proximal to mineralization displayed anomalous Cd, Ni, Mn, and Zn; only Zn remained sufficiently elevated down-flow of the deposit to indicate the presence of mineralization (Zn ranged from 380 to 2000 µg/L, Kelley and Taylor, 1997). Thus, generation of low pH waters and elevated metal contents around these SEDEX deposits is dependent on local geological controls, specifically the buffering capacity of host rocks.

Similarly, Goodfellow (1983) studied surface waters flowing over the Howard's Pass (XY) and Nor SEDEX deposits in the Yukon, Canada. As with the Alaskan examples, where there are significant carbonates in the drainage system, metal contents are suppressed and Zn is the main (or only) pathfinder species (Goodfellow, 1983). Thus, at the XY deposit, only Zn shows a strong increase in abundance towards mineralization, whereas at the Nor occurrence stream waters were also anomalous in Pb and As, with stream sediments showing anomalous Cu, Hg, and Zn (Goodfellow, 1983). The XY deposit differs from the Nor occurrence in that at the XY deposit laminated sulphides are hosted by calcareous shales of the Road River Formation, whereas the Nor occurrence is hosted by pyritic and noncalcareous shales and cherts of the Lower Earn Group.

An important consideration for these examples from Alaska and the Yukon is that the mineralization is at or near surface and exposures are relatively fresh owing to the effects of glaciation (Jonasson et al., 1987; Miller, pers. comm. cited in Plumlee et al., 1999). Glaciation has thus resulted in enhanced weathering and, where buffering of

solutions following water-sulphide interaction is limited, produces more elevated metal contents and longer dispersion than might be expected in unglaciated and intensely weathered terrain.

In summary, SEDEX deposits, like VMS deposits, can be expected to show elevated base metal contents in both ground and surface waters that have interacted with sulphides under oxidizing conditions. Some SEDEX deposits have little or no carbonate in the immediate stratigraphy to mineralization, resulting in multi-element anomalies. Where mineralization is buffered, or more deeply buried with no surface erosion and clastic dispersion, Zn appears to be the dominant anomalous element.

Gold Deposits

The main impediment to Au exploration using hydrogeochemistry is the typically low solubility of Au in low-temperature waters (Vlassopoulos and Wood, 1990), because Au solubility is greatly dependent on the availability of suitable ligands. In most natural waters, Au solubility is controlled by the formation of $\text{AuOH}(\text{H}_2\text{O})^0$ complexes, which limits Au solubility to a few parts per trillion (ppt) at best. Solubility is greatly enhanced in the presence of thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and cyanide (CN^-) (Vlassopoulos and Wood, 1990). Bowell et al. (1993) investigated Au in soil pore waters and laterite profiles associated with Au mineralization at Ashanti, Ghana. Although Au was found to be mobile in soil pore waters owing to natural cyanide production (from decomposition of organic matter) and thiosulphate produced by weathering of sulphides, Au was mobile only on scale of a few centimetres (Bowell et al., 1993).

In Western Australia, Au mineralization is typically covered by thick regolith sequences. In this environment, groundwater geochemistry has proven to be successful in some cases, although interpretations of groundwater flow and modeling of water speciation is complicated by the presence of hypersaline waters (Carey et al., 2003). In a study around the St. Isles area, mesothermal Au mineralization is best reflected by elevated groundwater Au contents, which are as high as 52 ng/L, with speciation modeling suggesting that Au occurs primarily as AuCl_2^- and/or AuI_2^- species in these saline waters (Carey et al., 2003). In this study, typical pathfinder elements for Au mineralization (such as Se, As, and Sb) showed no consistent variation with proximity to mineralization (Table 2). Similarly, Gray (2001) in a large study of groundwaters from the Yilgarn Craton of Western Australia found that groundwater Au was the best indicator of Au mineralization. Pathfinders such as As and Sb were only effective at near-neutral pH conditions; saline groundwaters in Western Australia are commonly acidic (acid-sulphate waters), resulting in adsorption of elements that form oxyanions (Gray, 2001). Various studies of groundwater Au contents in Australia indicate that Au is typically present at concentrations in excess of that predicted by equilibrium calculations (Giblin, 2001). Giblin (2001) suggested that this apparently enhanced Au solubility was either a consequence of Au-organic complexing not being taken into account in speciation calculations or to the propensity for Au to form fine colloids. In a study of Au contents of stream waters in the Bathurst mining camp, Canada, Leybourne et al. (2000a) used ultrafiltration (samples were unfiltered, filtered to

<0.45 µm, and <0.004 µm) to show that even in the presence of large amounts of cyanide, a strong Au-complexing agent, a maximum of 50% of the Au that passed the <0.45 µm filter passed the 0.004 µm filter and could be considered to be present in dissolved (non-colloidal) form.

In Nevada, groundwater Au contents are elevated (up to 4700 ng/L) proximal to mineralization under oxidizing conditions, whereas pathfinder species (As, Sb) are elevated in groundwaters where reducing conditions prevail (Grimes et al., 1995). Similarly, Cidu et al (1995) found for stream and spring waters in Sardinia, Italy, that Au was the best indicator of mineralization, although As and Sb were also typically anomalous close to mineralization. Sahoo and Pandalai (2000) studied groundwaters associated with Au mineralization in the Hutt-Maski schist belt of India. Although these authors apparently did not determine aqueous Au contents, they found that groundwater As and Sb contents delineated areas of Au mineralization (Sahoo and Pandalai, 2000).

Thiosulphate forms relatively strong complexes with Au at neutral to alkaline pH conditions (Webster, 1986). As Au mineralization is commonly associated with sulphide minerals, Au can be dispersed if ground and surface water conditions remain neutral (Benedetti and Boulègue, 1990, 1991). Indeed, the intermediary species formed during oxidation of sulphide to sulphate have been suggested as a prospecting tool in waters draining sulphide-bearing mineralization (Kondratenko, 1997).

In summary, the studies discussed above indicate that for ground and surface waters, 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).

Magmatic Cu-Ni-PGE Deposits

The geological and geochemical characteristics of magmatic Cu-Ni-PGE deposits are reviewed by Eckstrand and Hulbert (2007) and Layton-Matthews et al. (2007). There has been little research into aqueous geochemical exploration for magmatic Ni-Cu-PGE mineralization. Some comments can be made, as there is good potential for water chemistry in this regard, in particular for those deposits that are sulphide-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 Pd the most mobile (Wood, 2002; Hattori and Cameron, 2004). Hattori and Cameron (2004) have suggested that Pd is mobile in surface waters around the Lac des Iles PGE deposit as hydroxide complexes (e.g. $\text{Pd}(\text{OH})_2^0$, $\text{Pd}(\text{OH})_3^-$, and $\text{Pd}(\text{OH})_4^{2-}$); the low SO_4 and Cl^- contents of these waters precludes sulphate and chloride forming significant Pd complexes. 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). The Lac des Iles mineralization is sulphide poor (Hattori and Cameron, 2004). In contrast, many Ni-Cu-PGE deposits have abundant Ni and Fe sulphides. In sulphide-rich deposits, Pd (and other PGE) mobility in solution should be enhanced, in particular where pyrrhotite is abundant, as dissolution of Fe sulphides 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 deposits with minor Fe-sulphides, 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 sulphides 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 common (Table 2).

Kimberlite and Lamproite Diamonds

Diamonds are primarily extracted from ultramafic kimberlite and lamproite lithologies. Mineralogically these rocks are characterized by olivine, Cr-diopside, enstatite, Cr-poor Ti-pyrope garnet, Mg-ilmenite, and phlogopite (McClennahan and Kjarsgaard, 2001). Kimberlites and lamproites are derived by small degrees of partial melting at significant depth (150–200 km) in the asthenospheric and/or subcontinental lithospheric mantle (Kjarsgaard, 2007). As such, they have distinctive geochemical signatures compared to most other mantle partial melts, with enrichment in the incompatible elements Sr, Ba, light REE (La, Ce, Pr, Nd, Sm), Nb, Ta, Hf, Zr, P, and Ti along with elevated Mg, Cr, Ni, and Co (McClennahan and Kjarsgaard, 2001). Although it is a relatively simple task to geochemically distinguish these ultramafic rocks from their host rocks (typically felsic-dominated rocks of old shield areas), the distinction between diamond-bearing and barren kimberlite and lamproite is more problematic. Given this constraint, the use of aqueous geochemistry to explore for kimberlite in general and diamondiferous kimberlite more specifically, is therefore also geochemically challenging.

There have been almost no research studies specifically utilizing water chemistry for 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). New research in geochemical exploration for diamonds has involved groundwater geochemistry (Sader et

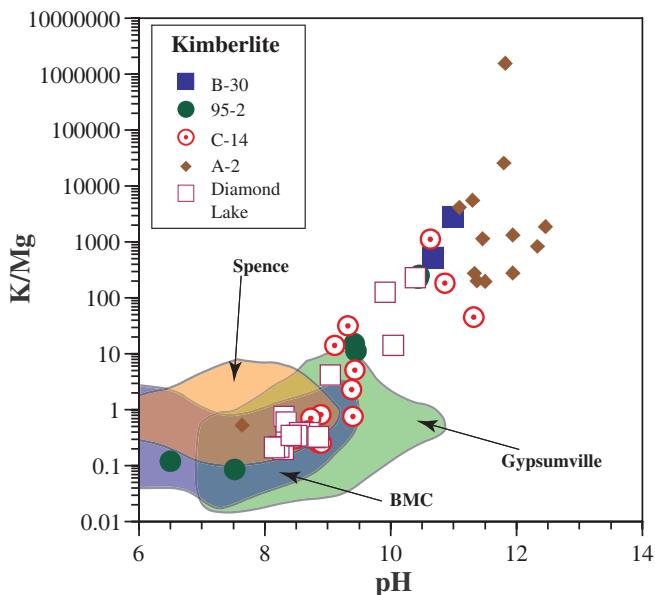


FIGURE 10. Plot of pH versus K/Mg ratio for groundwaters interacting with five different kimberlites from the Kirkland Lake area of northern Ontario, Canada. As increasing pH is due to hydrolysis reactions involving olivine and pyroxene, Mg is progressively buffered out of solution by brucite and magnesite precipitation (Sader et al., 2007). Shown for comparison are fields for groundwaters interacting with VMS mineralization in the Bathurst mining camp, New Brunswick, Canada (Leybourne and Goodfellow, 2003), groundwaters interacting with the Spence porphyry copper deposit, Atacama Desert, Chile (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006), and from carbonate and crystalline rock aquifers around Gypsumville, MB, Canada (Leybourne, unpublished data).

al., 2003a,b, 2007). Where groundwater interacts with ultramafic rocks, hydration reactions of olivine and clinopyroxene result in elevated groundwater pH values, up to in excess of pH 12 (Fritz et al., 1992; Sader et al., 2007). These hydration reactions have the consequence of essentially buffering Mg out of solution in the formation of brucite [$Mg(OH)_2$] and/or serpentine minerals; groundwaters that have interacted extensively with kimberlites in northern Ontario are thus characterized as having elevated pH and highly atypical K/Mg ratios (Fig. 10). 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 elevated pH (Figs. 1, 10), anomalously low Mg and elevated K/Mg ratios in waters (Fig. 10) and the presence of key alteration minerals down-flow may assist exploration. 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 (Table 2).

Unconformity (Sandstone-Hosted) Uranium

Details related to the geology and geochemistry of unconformity uranium deposits is presented elsewhere in this volume (Jefferson et al., 2007). Exploration for uranium using groundwater geochemistry was investigated in the 1970s and early 1990s (e.g. Langmuir, 1978; Dyck, 1979; Langmuir and Chatham, 1980; Runnels 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). Further insights into the relationships between water chemistry and U deposits can be gained

from studies investigating the formation of uranium deposits and the long term stability of these deposits as proxies for the stability of buried nuclear waste materials (Yanase et al., 1995a,b; Arthur et al., 2006). Pirlo and Giblin (2004) provide a good summary of the history, strengths, and weaknesses of hydrogeochemistry with respect to uranium exploration. Previous studies of groundwater U exploration have focused on elemental determinations, U-series isotopes, He and He isotope anomalies, and the calculation of U-related mineral solubilities (Langmuir, 1978; Dyck, 1979; Deutscher et al., 1980; Langmuir and Chatham, 1980; Runnels and Lindberg, 1981; Earle and Drever, 1983; Giblin and Snelling, 1983; Toulhoat and Beaucaire, 1991; Singh et al., 2002; Pirlo and Giblin, 2004; Dickson and Giblin, 2006).

There are some significant challenges to the use of hydrogeochemistry to explore for U mineralization, in particular because of the strong redox control over U solubility and transport, and because U is a common trace element in a variety of rock types (Kotzer and Kyser, 1995; Dickson and Giblin, 2006). Despite these problems, many of the studies cited above suggest that the best aqueous indicator of U mineralization remains dissolved U contents (Table 2), assuming oxidizing conditions; other potential pathfinders are more problematic. In a large study of groundwaters in India (more than 600 groundwater samples), Singh et al. (2002) showed that U anomalies over known U-mineralization were coincident with anomalies in Na, K, Cl, SO_4 , HCO_3 , and TDS. However, none of these additional species are in any way diagnostic of U mineralization, limiting their utility. Similarly, Dickson and Giblin (2006) suggested that anomalous U contents were coincident with high Mg/total cations in groundwaters from the Pine Creek area, with REE, PO_4 , F, and Cu in groundwaters from Olympic Dam, and with neutral pH, equilibrium with carbonate minerals and carbonaceous matter in groundwaters from sedimentary paleochannels in South Australia. Again, these coincident pathfinders are in no way diagnostic of U deposits. Finally, several studies have shown that calculation of mineral saturation indices (via geochemical software, see discussion) can provide vectors to U mineralization (e.g. Pirlo and Giblin, 2004; Dickson and Giblin, 2006); the issue remains that these calculated minerals (e.g. phengite) are not diagnostic. These calculations are useful additional sources of information for full data interpretation, but are unlikely to be successful in the absence of other pathfinders.

In summary, 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 deposits. Clearly, exploration success will be enhanced if there are coincident anomalies in other elements (e.g. Se, V, Mo, and Cu; Table 2) that are typically enriched in U deposits. Molybdenum and Se may be especially useful in sulphide-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 the potential application of Pb and/or U-series isotopes in U exploration (Earle and Drever, 1983; Toulhoat and Beaucaire, 1991; Yanase et al., 1995b). Toulhoat and Beaucaire (1991) studied the Pb isotope geochemistry of groundwaters as an exploration tool for detecting buried U deposits. In this approach,

groundwaters that have most interacted with U mineralization have the most radiogenic Pb isotopes with respect to $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (from ^{235}U and ^{238}U decay, respectively) but not in $^{208}\text{Pb}/^{204}\text{Pb}$ (from ^{232}Th decay), owing to U deposits having anomalously high U/Pb but lower than typical Th/Pb.

Discussion: Aqueous Geochemistry in Mineral Exploration

Ground and Surface Water Sampling Techniques and Strategies

One of the limitations in using groundwater geochemistry in mineral exploration is the availability of suitable boreholes. In many areas of interest to mineral exploration, there are insufficient domestic or agricultural water wells for effective use of groundwater in an exploration program. Drilling is expensive and typically only occurs after a suitable exploration target has been defined. In Western Australia, thick regolith cover is an impediment to geochemical exploration of any kind and mineral exploration in this environment 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 drillholes can potentially be reduced (Carey et al., 2003). In other environments, however, once drilling has commenced, groundwater composition may be useful in vectoring towards possible new targets and choosing locations for additional drillholes. 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. Given the great expense of drilling exploration holes and the fact that groundwaters flow, there is only a small addition in cost to a drilling program to include an aqueous geochemical component, which may greatly enhance the value of the drilling, especially in the case of an apparently barren hole.

In areas where exploration holes or domestic wells are available, the sampling method requires some consideration. The principal sampling methods are bailer, down hole pump (e.g. double-valve or Grundfos), and straddle-packer systems (Figs. 11, 12). Flow-through bailers typically consist of a PVC tube (commonly around 1 litre in volume) with one or two stop-valves that permit the flow of water through the tube during bailer descent in the well, because of the neutral buoyancy of the stop-valves. The valves are closed and the groundwater is trapped during retrieval of the bailer. The bailer method has the advantage that it is rapid, inexpensive, and easily learned for new users. The disadvantages of the bailer are 1) it is difficult to decontaminate the apparatus between samples and wells; 2) there is a fixed volume, which may not always be sufficient; and 3) the standing water column in a well is sampled, which may not represent the full variability of the well, in particular in crystalline rocks where groundwater flow is fracture dominated (Fig. 11). Another disadvantage of the bailer is that the method commonly results in disturbance of borehole walls and/or fracture zones, so that suspended sediment loads are typically greater than is the case for the packer (Leybourne, 2001).

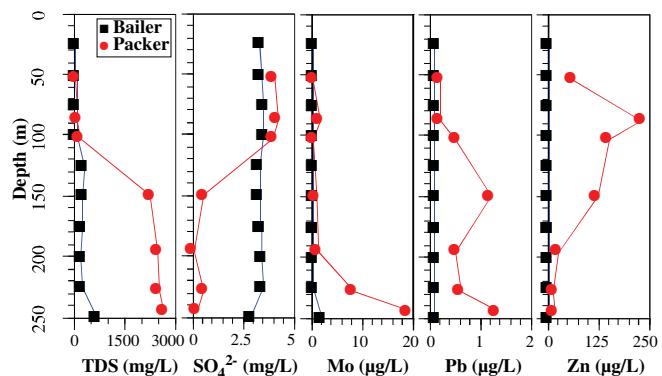


FIGURE 11. Down-hole variation plots of selected parameters for borehole MM-89-106 from the Restigouche deposit, Bathurst Mining Camp, New Brunswick, Canada. These plots illustrate the differences between samples collected using a bailer system and those using a straddle-packer system. In this case, the bailer samples indicate that there are significant chemical changes down hole, but do not reflect the full magnitude of those changes. Modified after Leybourne (1998).

Double-valve pumps operate in a similar fashion to bailers in that the pump head is lowered down the hole to the desired depth (typically at least 5 m below the water table) and the height of water column overlying the pump-head (i.e., the hydraulic head) results in groundwater flow into the chamber and up the PVC tubing to the static head level. Nitrogen gas or clean compressed air is then forced down one PVC tube into the sample head, resulting in return of groundwater to surface via another PVC tube. The advantage of the pump over the bailer is that successive samples can be taken until steady state conditions are reached for electrical conductivity (as a proxy for salinity), Eh (redox state), and pH. Once steady-state conditions are reached, the assumption is made that the system is sampling groundwaters that are representative of the borehole at that depth and the sample is taken (Leybourne et al., 2001; Leybourne and Cameron, 2006). This process not only allows greater confidence as to the degree to which the sample represents flow at the depth sampled, but also serves to decontaminate the sampling apparatus between boreholes. In some setups, 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).

Bottomley et al. (1994) noted that sampling of depth-representative groundwaters in low-permeability fractured rock is difficult due to contamination by waters used in drilling the boreholes, mixing within open boreholes by groundwaters entering the hole from different fractures at different depths, and because fractures commonly have low hydraulic conductivities. These problems can be at least partly mitigated by the use of 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.

Surface waters are typically collected from the most actively flowing part of a stream. Samples are taken directly



FIGURE 12. (A) Sample chamber for a straddle-packer system, constructed at the Geological Survey of Canada. There is a unidirectional 1 psi cracking valve at the bottom of the sample chamber. (B) Upper sliding head packer. The packer is inflated when at the desired depth and seals the well. Note the white tubing at the base, which leads to the intake section. (C) Straddle-packer tubing spool and pressure apparatus. Constructed at the Geological Survey of Canada. All three photographs from the Restigouche deposit in the Bathurst Mining Camp, New Brunswick, Canada. (D-F) Down-hole pump apparatus. Note the tank of N₂ gas used to force sample back to surface. These photographs show sampling of groundwaters from kimberlites in the Kirkland Lake area of Northern Ontario, Canada.

from the stream into a sample bottle, or may be sampled using a peristaltic pump. The elemental budget of any stream can be parsed into the dissolved load, the suspended load, and the bed load.

Aqueous geochemists typically filter waters *in situ*, either to 0.45 or 0.20 µm. These filter pore sizes are operationally defined (Hall et al., 1996a), 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). To separate truly dissolved aqueous species from those that may be associated with colloids requires ultrafiltration using either tangential flow or centrifuge techniques (Leybourne et al., 2000a; Zanker et al., 2002).

Most stream sediment studies only consider bed load geochemistry (Telmer et al., 2002). However, because metals undergo differential partitioning between the dissolved and particulate fraction (Leybourne, 2001), the suspended load is also a viable medium for geochemical exploration (Telmer et al., 2002). For example, Siegel (1990) investigated stream-suspended and bed load sediments in drainages associated with Mississippi Valley-type (MVT) Zn-Pb mineralization in Virginia, USA, and found that Zn formed the most consistent geochemical anomalies and that the suspended (>0.45 µm) sediment provided superior anomaly to background contrast compared to bed load sediments. One major disadvantage of using the suspended load is the difficulty of sample collection, especially for first- and second-order streams, which commonly have a very minor suspended component (Leybourne et al., 2003). For the study of suspended sediments over MVT mineralization, Siegel (1990) filtered approximately six litres of stream water per sample; this volume of filtration is impractical in large surveys (see below).

In geochemical exploration surveys where groundwaters are sampled, the groundwater suspended load may also be used; metals that are sparingly soluble in the dissolved load may be partitioned into the suspended sediment load and be more amenable to analysis, as was shown for groundwaters around undisturbed VMS deposits in the Bathurst mining camp (Leybourne, 2001). For example, suspended sediments in wells from the Bathurst mining camp commonly have Pb/Zn ratios that are greater than the aqueous phase and primary massive sulphide mineralization (Leybourne, 2001).

Depending on the nature of the survey, filtering may not be 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. Similarly, Leybourne and Cameron (2000a) showed that for groundwaters collected around the Spence porphyry Cu deposit in northern Chile, many of the elements of interest (e.g. S, Se, Re, As, and Mo) showed little or no difference between filtered (<0.45 µm) and unfiltered aliquots, although metal cations (e.g. Cu and Zn) showed large differences owing to adsorption to Fe, Mn, and Al oxyhydroxides.

Hydrology

For optimal interpretation of aqueous geochemical results in an exploration program, some understanding of the

hydrology is required (Carey et al., 2003; Leybourne and Goodfellow, 2003; Gilliss et al., 2004). In order to develop either a surface geochemical anomaly or a distal groundwater geochemical anomaly of a deeply buried deposit, the hydrology must be conducive to return flow to the surface environment. In some cases, faults and/or 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, Fig. 7; Cameron and Leybourne, 2005). Furthermore, the Eh and pH conditions control, to a large extent, how ore minerals behave during water-rock interaction 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 not be formed. 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 Tillex are such that dissolved sulphate is reduced to sulphide, restricting deposit sulphide mineral weathering and preventing the development of a significant aqueous geochemical plume (Gilliss et al., 2004).

Although some types of deposits 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).

Streams are referred to as gaining or losing (i.e. influent and effluent) where shallow groundwater discharges into the stream or the stream recharges the shallow groundwater, respectively. Clearly, detection of buried mineralization will be more problematic where a losing stream crosses mineralization compared to a gaining stream. For example, the Restigouche deposit in the Bathurst mining camp crops out where Charlotte Brook crosses mineralization. Although stream waters show clear anomalies in ore-related elements across the deposit (e.g. Pb, Zn, Cu, and As; Fig. 5 shows Zn and Pb), sulphate contents are only slightly anomalous at best, consistent with Charlotte Brook being a losing reach proximal to mineralization at the time of sampling (Leybourne et al., 2003). In contrast, sediments are anomalous in Zn, Pb, and Cu for three kilometres downstream from the Restigouche deposit, indicating that Charlotte Brook is a gaining stream for at least part of the year (Fig. 5 shows water and sediment Pb contents).

Because of the temporal variability in surface water chemistry, stream water sampling is sensitive to timing of sampling with respect to perturbation in stream flow as a

result of rainfall. In contrast, groundwaters typically integrate an annual to multi-annual signal, as revealed by the stable isotopes of oxygen and hydrogen (see Clark and Fritz, 1997). Surface waters primarily represent base flow (i.e. shallow groundwater discharge), combined with increases in discharge owing to rainfall or snowmelt. In areas with vegetation cover, the increase in stream discharge during a storm event may still be dominated by base flow (Caissie et al., 1996). In general, the stable isotopic composition (H, O) of precipitation varies significantly as a function of season, owing to the strong temperature dependence on the fractionation of these isotopes (Craig, 1961; Clark and Fritz, 1997). Thus, winter precipitation is typically depleted isotopically compared to summer precipitation.

Major Ions

Some studies have suggested that the major ion composition of ground and surface waters may provide useful vectors to mineralization, owing to the generally larger target provided by alteration halos around mineralization relative to the size of primary mineralization (e.g. Giblin, 1994; Taufen, 1997; Phipps et al., 2004;). Although the major ion chemistry of waters in a hydrogeochemical survey should be interpreted and considered in conjunction with the trace metal data, because of the complexity of water-rock reactions, cation exchange reactions, and the formation of secondary minerals, the major element composition of water should be used with great caution as an exploration guide in the absence of other (i.e. deposit-diagnostic) chemical data (Table 2). Some workers have suggested that soil Br and Cl anomalies develop over some deposit types as a result of electrochemical, gaseous, or advective transport (Clark, 1999; Hamilton, 1999). However, focusing on these anomalies is likely to cause more problems than it solves, simply because these elements are less likely to be diagnostic of mineralized zones. For example, work on groundwaters around the Spence deposit (Cameron et al., 2002; Cameron and Leybourne, 2005) suggests that in northern Chile saline groundwaters migrate to surface along fractures during seismic events. Because saline basinal fluids in northern Chile have elevated I, Br, Cl, and S contents, soils over fractures will be anomalous in I and Br regardless of whether or not the waters have interacted with porphyry Cu 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, therefore attention should be placed on what is geochemically distinct about the mineralization (Table 1).

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 mineralization. For example, Sader et al. (2007) showed that groundwaters interacting with kimberlite results in elevated pH and low Eh conditions, with a concomitant loss of Mg from solution and an increase in dissolved K contents (Fig. 10). 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 the major ion chemistry of groundwater. In con-

trast, Giblin (2001) suggested that waters interacting with ultramafic rocks will have Mg > Ca, Na, K.

Mineral Saturation and Speciation Calculations

Mineral saturation indices and metal speciation calculations are typically carried out using various software packages that include PHREEQC (Parkhurst, 1995), MINTEQA2 (Allison et al., 1991), and The Geochemists Workbench (Bethke, 1994). Some of the geochemical speciation/saturation computer programs are only available commercially, whereas other packages 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.

Metal Mobility and Solubility

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. 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 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 geochemical exploration because Ti is not particularly anomalous in mineralized mafic and ultramafic rocks compared to non-mineralized equivalents, Ti is particularly immobile in water, except in very rare cases, and 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 explo-

ration 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 also 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 (Volesky et al., 2000; Volesky, 2002; Leybourne and Cousens, 2005; Leybourne et al., 2000b, 2006b). Low-pH groundwaters proximal to VMS mineralization have also preserved the positive Eu anomalies (Leybourne et al., 2000b). Diamond-bearing kimberlites commonly have distinctive large ion lithophile elements (LILE) and high field strength elements (HFSE) (+ rare earth element) associations (McMartin and McClenaghan, 2001). In this case, aqueous anomalies in mobile species (K, Rb, Sr, and REE in some waters) may assist in differentiating between rock types, but may not be as useful in distinguishing mineralized from unmineralized rocks.

False anomalies may be produced in stream sediments owing to the accumulation of background metal concentrations by Fe- and Mn-oxyhydroxides. However, where stream sediment surveys reveal elevated Fe and Mn contents in association with anomalous ore-indicator metals, it would be wrong to assume that the results obviate the presence of mineralization. Firstly, Mn contents do increase towards the core of some hydrothermal systems, such as VMS (Large et al., 2001), so that high-Mn contents may also indicate proximal mineralization. Secondly, because the hydrology is so important in controlling the localization of hydromorphic anomalies, even relatively low-metal contents may indicate proximal mineralization. As discussed below, some isotopic systems can be used to more quantitatively assign a mineralization association where anomalous metal contents are associated with elevated Mn contents.

Pre-Cover, Cover, and Post-Cover History

Another issue is the pre-cover history of the rocks hosting mineralization. For example, 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, 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).

Stable and Radiogenic Isotopes

A variety of isotopic systems are traditionally not used in routine mineral exploration. Most of these are unlikely to become standard in mineral exploration, but discussion is warranted because there are cases where stable and/or radiogenic isotopic data may assist in data interpretation or the understanding of metal and water sources, and because advances in analytical methods are such that the cost of iso-

tope analyses continues to decline and the simplicity of sample preparation increase. Isotopes of potential use in mineral exploration include the traditional stable isotopes (O, H, C, S), radiogenic isotopes (Pb, Sr), in addition to newer non-traditional isotope systems, such as Fe, Se, and Cu.

Analytical considerations include the ease of collecting, storing, and processing samples, and the cost of measuring element abundance. For example, traditionally Sr and Pb isotopes have been analyzed by thermal ionization mass spectrometry (TIMS). Measurements by TIMS are time consuming owing to the need for chemical separation of the species of interest. As such, application of these systems to mineral exploration has been limited, and most research studies have focused on Pb isotopes (Gulson, 1986; Gulson et al., 1988; Gulson et al., 1992; Bell and Franklin, 1993; Leybourne, 1998). However, recent advances in ICP-MS instrumentation, including dynamic reaction-cell ICP technologies (DRC-ICP-MS), high-resolution ICP-MS (HR), and multi-collector ICP-MS (MC), have resulted in the potential to more routinely and cost-effectively analyze geological samples for radiogenic and some light stable isotopes. For example, Doherty et al. (1997) used a standard quadrupole ICP-MS to measure Pb isotopes of till from the Restigouche deposit in the Bathurst mining camp. Although ICP-MS Pb isotope determinations are less precise than those by TIMS, for the purposes of detecting massive sulphide mineralization in the Bathurst mining camp and thus fingerprinting the Pb source, the ICP-MS had sufficient precision, with less sample preparation and analytical time compared to TIMS analyses on the same samples (Doherty et al., 1997). New multi-collector ICP-MS instruments are opening up new areas of research in non-traditional isotopes, some of which may find application in mineral exploration. These include the stable isotopes of Fe (Rouxel et al., 2004; Severmann et al., 2004), Cu (Ehrlich et al., 2004), and Se (Johnson and Bullen, 2004; Layton-Matthews et al., 2006).

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 the 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 superficial 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 baseflow 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 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 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 enriched in Zn, Co, and Ni, 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). Similarly, O and H isotopes in groundwaters recovered around the undisturbed Spence porphyry Cu deposit in the hyper-arid Atacama Desert of northern Chile indicate that saline waters interacting with Cu mineralization (as shown by elevated Cu, As, Se, Re, Mo, and low $\delta^{34}\text{S}$; Fig. 9B) are paleowaters, possibly derived from sedimentary basin brines, and have mixed with regional groundwater flow, derived by recharge in the high Andes (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006). 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, sulphur 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 sulphur isotopic composition provides a vector to gold mineralization in Australia. Similarly, analysis of the sulphur isotopic composition of groundwaters at the Spence porphyry copper deposit in Chile show that groundwater $\delta^{34}\text{S}$ 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, 2006). This increasing influence on groundwater sulphur isotopic composition is also evident in Se abundances (Fig. 9B; in addition to Re, Mo, and As, not shown). 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 sulphate can be used to vector to mineralization and provides a broader halo than groundwater base metal (Zn, Pb, Cu) contents (de Caritat and Kirste, 2005).

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 sulphide minerals do not incorporate U and Th into their structure, Pb derived from sulphide 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).

Partial and Sequential Extraction Techniques

A large number of schemes have been suggested in the literature, but essentially all reduce to the same basic idea; different extractions are designed to remove metals from different portions of the sediment (e.g. Chao, 1984; Hall et al., 1996b, 2003; McCarty et al., 1998; Gray et al., 1999). Most sequential extraction schemes have been designed for and applied to soils and till. However, a smaller number of studies have applied these partial leaches for stream sediments (Martin et al., 1984; Evans and Davies, 1994; Borovec, 1996; Leybourne et al., 2003). Most leaches are weak, designed to remove the more labile components in a sediment compared to more aggressive leaches such as aqua regia or total dissolution (e.g. fusion or HF-HClO₄-HCl-HNO₃ digestion).

Partial leaches have utility in geochemical exploration because they commonly result in an enhanced anomaly to background contrast. Furthermore, they provide insights into the speciation or binding sites of metals in soils and sediments. These insights are key to an improved understanding of the processes of metal migration in the secondary environment and the formation of geochemical anomalies (Hall et al., 1996b; Cameron et al., 2004). In addition, partial leaches can also aid in understanding metal bioavailability, metal sources, and the potential for metal remobilization with changes in surface conditions, especially pH (Hall et al., 1996b). Such changes resulting from a change in the pH conditions are especially important where mining of Fe-sulphide-rich deposits is being considered. In soils, loosely bound metals (weakly adsorbed, extracted with deionized water or weak acetate) may be attributable to a buried source of mineralization and/or to anthropogenic influences via atmospheric transport (Hall, 1998).

There are two areas in which these analytical schemes have application to aqueous geochemical exploration. Firstly, one of the principle reasons for using partial leaches is to try and capture the fraction of a till or soil elemental budget that has been transported in some way from buried mineralization to surface and added to the soil profile, either adsorbed to mineral surfaces or organic matter, precipitated/incorporated into pedogenic calcite or gypsum, or incorporated into oxyhydroxides of Fe and Mn. Although a variety of transport mechanisms have been proposed (Cameron et al., 2004), the processes by which these surface geochemical anomalies form is still not well understood. However, understanding groundwater geochemistry has greatly improved interpretations of metal transport processes in arid gravel-covered regions like Chile (Cameron et al., 2002) and glaciated terrains in Canada (Cameron et al., 2004). Secondly, although not all the proposed leaches are applicable to stream sediments, leaches that target the amorphous Mn- and Fe-oxyhydroxides can improve anomaly to background contrast, and also provide information regarding mechanical versus hydromorphic metal transport, which will help interpretations regarding vectoring to mineralization (e.g. compare the response of In and Pb in stream sediments from the Bathurst mining camp, Fig. 5).

TABLE 3. Advantages and disadvantages of surficial geochemical methods - EXTECH II, BMC, Canada.

Method	Advantages	Disadvantages	Reference
Surface waters	Ease of sampling; limited sample preparation (already in solution) for ICP analysis; instantaneous geochemical signature	Risk of contamination; potential of low background contrast; limited mobility of certain metals in near neutral pH waters	Leybourne, 1998; Leybourne et al., 2003
Groundwaters	Strong anomaly/background contrast, multiple samples can be taken at variable depths; hydrological information can be used to vector towards mineralization; potential for accessing deep mineralization	Expense of drilling holes, need to understand hydrology; depth specific samples difficult to collect except with expensive/time consuming packer system	Leybourne and Goodfellow, 2003
Stream sediments (total)	Ease of sampling; information about lithological variations	Post sample preparation (drying, sieving, dissolution); dilution of hydromorphic components by detrital components	Leybourne et al., 2003
Stream sediments (partial)	Separates hydromorphic from detrital contributions; generally greater dispersion than soils	Greater sample handling and preparation; more expensive than total analysis	Leybourne et al., 2003
Soil (total and sequential)	Deposit-related metals may be transported through thick cover (weak leaches)	Weak-leach soil anomalies may be difficult to interpret	Hall et al., 2003
Till	Glacial dispersion provides larger exploration target compared to other methods	Glacial movement may be complex; requires surface deposit; post collection sample preparation (drying, sieving, dissolution)	Parkhill and Doiron, 2003
Biogeochemistry	Tree roots may penetrate to tap more deeply buried mineralization; some plant species may preferentially take up ore-related metals	Optimally requires a single species of similar age over entire study area; metabolic requirement of plants for some metals may complicate interpretations	Leybourne et al., 1999
Gossans	Derived directly from original massive sulfide	Requires surface or near surface deposit; preservation of gossan during glaciation; distinguishing from gossan developed over non-sulphide Fe-rich rocks	Boyle, 2003

Recommendations for Sampling and Analytical Protocols of Waters in Mineral Exploration

From the above discussion and the examples presented, one can see that there are a large number of parameters that can be used to aid the detection of undiscovered mineralization and that there are a large number of potential issues and pitfalls that need to be avoided. However, it should be emphasized that despite these issues, aqueous geochemistry is a powerful tool because it is a relatively simple and if surveys are well designed, robust. In this section, recommendations are made regarding sampling and analysis to aid exploration geochemists in realizing this relative simplicity. Table 3 provides a summary of geochemical exploration techniques that were used in the Bathurst mining camp and indicates the strengths and weaknesses of the different approaches employed in that study (for all papers in this Bathurst mining camp study, see Goodfellow et al., 2003).

The collection and analysis of ground and surface waters in mineral exploration can be broken down into two different approaches, which, for the sake of this discussion, shall be termed the “routine exploration” and “exploration research” 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.

Routine Exploration

1. Groundwaters can be sampled rapidly with a bailer. If only one sample is to be taken from a well or drillhole,

the sample should be taken at least 5 metres below water level. Surface waters are sampled directly from the actively flowing part of a stream. Ideally plastic gloves (cheap, disposable) should be worn during collection of water samples to ensure uniformity in sampling and prevent contamination. In any case, jewelry and watches should not be worn during sample collection.

2. If only one aliquot is taken, a 250 or 500 mL Nalgene HDPE bottle should be used. No pretreatment of Nalgene bottles is required, though the bottle and cap should be rinsed vigorously three times with sample water prior to filling the bottle (Cameron, 1978). For consistency, and assuming that samples will not be acidified, the bottle should be completely filled and stored in a cool place. If a separate aliquot is taken for anion and alkalinity determination, 125 or 60 mL bottles are sufficient.
3. Some parameters that are useful or critical to measure in the field are cheap and require minimal training of personnel. These field analyses should include, as a minimum, pH and conductivity. pH is very useful in subsequent data interpretation, but is also a useful guide in the field; large drops in pH values during a survey may indicate the presence of unbuffered sulphide oxidation, and sample density can be increased appropriately. Similarly, although the electrical conductivity of a water sample is only a rough measure of its salinity, sudden changes in salinity likely reflect additions of different, potentially deeper, groundwater. In addition, if all anions will not be measured, the conductivity can be used as a proxy for total dissolved solids. Meters for the

- determination of pH and conductivity are relatively robust, inexpensive, and simple to calibrate.
4. In order to ensure internally consistent data that can be used with confidence by all members of the program, the following QA/QC procedures should be followed. Within every batch of twenty samples, a duplicate sample should be taken. If only small numbers of samples are being collected, a duplicate should be taken for every ten samples collected. Within every batch of twenty samples a bottle should be left empty, but given a sample number. Prior to submission to a laboratory, this bottle should be filled with a standard or, ideally, a certified reference material. Finally, several field blanks should be taken (bottle filled with deionized water) to test for any contamination in the bottles.
 5. Because in a routine exploration survey samples do not need to be filtered or acidified, samples should be kept cold and analyzed as soon as feasible. For this kind of survey, ICP is the analytical method of choice, ideally a combination of ICP-MS and ICP-OES. The former permits the determination of essentially all of the trace species of interest in mineral exploration, with the exception that Au and Ag are not stable in solution in unpreserved bottles. ICP-OES permits the determination of major cations, metals that are present in high abundance (especially Fe, Mn, and Zn), and S (although note that not all commercial ICP-OES instruments operate at low enough wavelengths to measure S, around 185 nm). Although detailed interpretation of ground and surface waters requires full anion analyses, for a routine survey it may not be necessary to determine Cl or alkalinity (typically primarily carbonate alkalinity), whereas dissolved sulphate contents are useful as a secondary vector.
 6. Cameron et al. (1997) showed that using a portable anode stripping voltammeter (ASV) to measure dissolved Zn was useful in guiding the exploration program; waters were analyzed immediately following each day's collection. Comparison of these field Zn analyses with subsequent ICP-MS analyses showed effectively no difference for $Zn > 1 \mu\text{g/L}$ (Cameron et al., 1997).

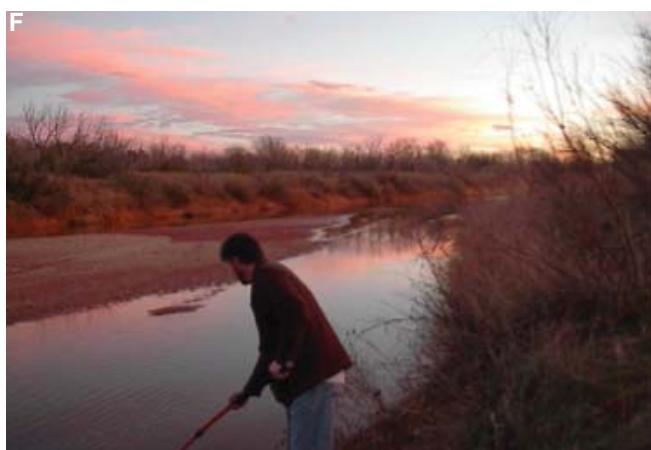
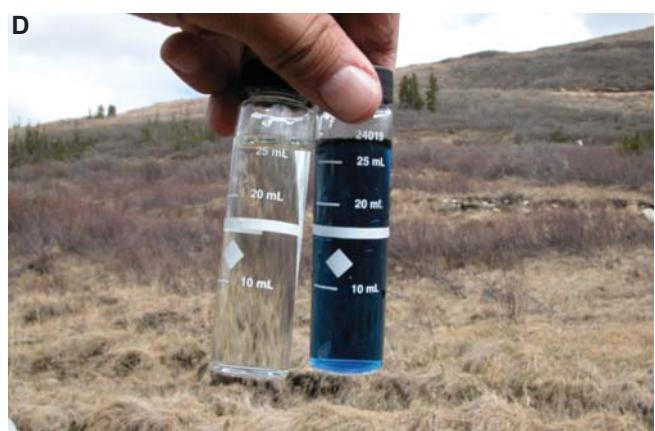
Exploration Research

1. Although groundwaters can be collected using a bailer, for optimal results in an exploration research study a down-hole pump or, ideally, a straddle-packer system or equivalent should be used. As noted above, optimal results are obtained when samples can be collected from a specific depth, especially in fracture-flow dominated systems. In the case where down-hole pump or packer is used, sample return lines can be fitted to a flow-through

cell to permit determination of field parameters (below) without exposing the groundwater to atmospheric oxygen. Surface water samples are collected in the same manner as above, using plastic gloves and taking the sample from the active part of the stream.

2. Field analyses should be more extensive in a more research-focused program. In addition to pH and conductivity, measurements should be made that try to capture the reduction-oxidation (redox) state of the aqueous system under study. There are a number of ways to measure redox, the most common being through the use of an Eh or ORP probe. Eh probes typically employ a Pt electrode. Unfortunately, Eh measurements performed this way are commonly only measure the redox state of a few species to which the platinum electrode responds. For example, Pt-Eh probes do not respond to the $\text{O}_2-\text{H}_2\text{O}$ couple, so that there is typically little correlation between Eh measurements and the amount of dissolved oxygen. However, Pt-probes do respond well to the $\text{Fe}^{3+}-\text{Fe}^{2+}$ couple, which given the common occurrence of Fe sulphides in many types of ore deposits, makes Eh measurements worthwhile. There are multiprobe meters that permit most or all of these measurements to be made simultaneously (Fig. 13). In addition, some are sufficiently narrow and can be fitted with long cables to permit in situ profiling of wells and/or boreholes. In situ profiling is useful because zones can be identified where changes in EC, pH, T, and Eh occur (Pauwels et al., 2002), information that can then be used to determine optimal sampling depths. However, these meters can cost several thousand dollars so care must be taken when deploying these down an exploration drillhole. Alternatively, these meters can also be fitted with flow-through cells, so that where groundwater samples are collected by pump or packer, pH, Eh, and DO can be measured without exposing the sample to the atmosphere. There are some other very simple tests of the redox state of a groundwater that can be measured in the field that are useful for full geochemical interpretation; these being measurements of dissolved ferrous (Fe^{2+}) iron and dissolved sulphide. These tests involve the use of a field spectrophotometer. The presence of dissolved ferrous Fe or sulphide is indicated by colour changes to a water sample the 1, 10 Phenanthroline method (Fe^{2+}) or the Methylene Blue method (HS^-) (e.g. Fig. 13).
3. For the research approach, a larger number of samples should be taken to allow the optimization of a more routine study in an area. Cameron and Leybourne (2000a,b, 2001, 2005) found that analyzing both an unfiltered and filtered ($<0.45 \mu\text{m}$; Fig. 13) aliquot was useful in demonstrating the different behaviour in species that behaved as cations (Cu, Fe) from those that were com-

FIGURE 13. (A) Measuring pH, T, conductivity, dissolved oxygen and Eh simultaneously with a multiprobe, Wichita River, Texas (photo courtesy of N. Miller). (B) Sterivex filters; the lower two filters were used to filter a groundwater with $0.75 \text{ mg/L } \text{Fe}^{2+}$ and 0.21 mg/L HS^- at the Kudz Ze Kayah deposit, Yukon, Canada (Layton-Matthews and Leybourne, unpublished data). (C) Example of a groundwater with significant Fe^{2+} , which develops a strong orange colour. Kudz Ze Kayah deposit, Yukon, Canada (Layton-Matthews and Leybourne, unpublished data). (D) Similarly, groundwaters with significant dissolved sulphide develop a blue colour, with depth of colour increasing with increasing HS^- . Kudz Ze Kayah deposit, Yukon, Canada (Layton-Matthews and Leybourne, unpublished data). (E) In situ measurement of pH, T, conductivity, dissolved oxygen, and Eh simultaneously with a multiprobe, Wichita River, Texas (photo courtesy of N. Miller). (F) For larger streams where it may be difficult to reach the active portion, a sample bottle can be fixed to the end of an extendable pole. Wichita River, Texas. (G) An example of precipitate that formed rapidly upon addition of BaCl_2 to a high- SO_4 water sample from the Wichita River, Texas (photo courtesy of N. Miller).



plexed as anions in northern Chile groundwaters (e.g. Se, As, Re, and Mo). Therefore, it is recommended that at least a filtered (to 0.2 or 0.45 µm) cation sample be taken, though an unfiltered aliquot should also be taken if resources permit. Use disposable cartridge filters (especially Millipore Sterivex-HV filters, catalog# SVHV010RS) and all-plastic syringes (no rubber stoppers, as these commonly contain significant Zn). A new filter and syringe should be used for each sample; filter the cation sample first and then the anion sample. The same filter and syringe can be used for both the cation and anion samples. Plastic gloves should be worn at all times during sampling; new gloves for every sample. Bottles should be rinsed with 20 to 30 mL of filtered water three times before filling the bottle.

4. The cation sample should be acidified to 1% by volume with 70% ultrapure nitric acid as soon as feasible. Because more detailed analyses will be performed, a 250 or 500 mL Nalgene bottle should be used. For the cation aliquot(s), sufficient headspace should be left in the bottle to permit addition of nitric acid. In contrast, an aliquot should also be taken for anion and alkalinity determination; this sample should be filtered, but otherwise is untreated, so the bottle should be completely filled. Additional samples should be taken based on the types of analyses to be performed. For sulphur isotope determination, BaCl₂ is typically added to a separate aliquot of sample. The BaCl₂ is highly soluble, whereas BaSO₄ is highly insoluble; if the sample has dissolved sulphate, it precipitates rapidly. The sample is allowed to sit for a few hours so that the BaSO₄ settles to the bottom and the remaining fluid is decanted, preserving the precipitate for isotopic analysis. This is also a useful field test in that the almost instantaneous formation of precipitate indicates the presence of dissolved sulphate and the amount of precipitate is obviously dependent on the concentration of sulphate. In a Au exploration program, an additional sample should be taken. Gold can either be preconcentrated in the field using sachets of activated carbon (Giblin, 2001; Gray, 2001) or by preservation to 1% with BrCl (Leybourne et al., 2000a).
5. As full a set of analyses should be performed as is practical. However, at a minimum, the analytical program should include determination of alkalinity by titration, anions (Cl, SO₄, PO₄, Br, F, NO₃) by ion chromatography or liquid chromatography, major species by ICP-OES (e.g. S, Si, Fe, Mg, Ca, Na, K, B, Mn, Sr, Zn, and Cu), and trace elements by ICP-MS (Be, Li, Ti, Ag, Bi, Co, Cr, Cs, In, Fe, Mn, Pb, Rb, Sb, Tl, U, V, Al, Ba, Cd, Cu, Mo, As, Ni, Se, Zn, Sr, Re, Th, Y, and the REE). In many media, S and Cl are the dominant anions and their peaks on an ion chromatogram may mask those of less abundant species, or dilution may be required such that these minor peaks are too small to be resolved. In these cases, Br, I, and PO₄ can also be measured by ICP-MS, and F and NO₃ by ion specific electrode or calorimetric methods. Some species of interest are difficult to measure by quadrupole ICP-MS (e.g. Se, As in the presence of significant Cl) owing to mass overlaps by species that form in an ICP plasma. Where these species are required at low detection limits, hydride generation ICP-MS can

be performed to improve detection limits and remove interferences (Hall and Pelchat, 1997a,b; Layton-Matthews et al., 2006).

Future Directions and Knowledge Gaps

1. The role of bacteria in controlling sulphide oxidation and silicate hydrolysis as well as metal mobility and attenuation is not well understood. In recent years, there has been an increasing appreciation that many reactions that were previously considered inorganic, are now recognized as 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, sulphur isotopes of frambooidal sphalerite are very negative (as low as -70 ‰ δ³⁴S, illustrating the control of sulphur-reducing bacteria on this unusual mineralization (>400,000 tonnes of Zn) (Bawden et al., 2003).
2. 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.
3. 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.
4. 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 well enough understood that they may become useful in mineral exploration. In addition, more research is needed on analytical methods, lowering the cost, sample preparation, and the speed of isotope analyses.
5. 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.
6. Accurate hydrological models are needed in a study area in order to connect surface aqueous geochemistry to groundwater flow and metal sources.
7. One of the great advantages of collecting ground and surface water 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 hydrogeochemistry 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 the characterization of groundwaters (via wells, springs), surface waters and partial leaches of stream (and groundwater suspended) sediments.
2. For groundwaters, 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, in order to provide optimal understanding of the redox state of the groundwater system.
3. For surface waters, sampling should be carried out when base-flow conditions operate, i.e., in the dry season.
4. In stream sediment surveys, if resources are available, significant additional information on hydromorphic versus mechanical transport (and therefore potential depth to mineralization) can be gained by addition of partial leach schemes to bed load sediment samples.
5. 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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