



Exploration07



Exploration in the new Millennium
5th Decennial International Conference on Mineral Exploration
Toronto, Canada



Workshop 2: Exploration Geochemistry- Basic Principles and Concepts

Convenor: W.B. Coker

September 8, 2007



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Exploration Geochemistry — Basic Principles and Concepts

Convenor: William B. Cooker

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Exploration geochemistry <i>William B. Coker</i>	1
Quality control in overview <i>Barry Smee</i>	9
Geochemical data evaluation and interpretation <i>E. C. Grunsky</i>	13
Regolith mapping, landscape evolution and geochemical applications <i>Simon Bolster</i>	19
Till geochemical and heavy mineral exploration methods in glaciated terrain <i>M. Beth McClenaghan</i>	23
Drainage sampling in British Columbia — stream sediments, lake sediments, water and heavy mineral concentrates <i>Ray Lett</i>	33
Plants: The ultimate selective leach <i>Colin E. Dunn</i>	35
Groundwaters in geochemical exploration <i>Matthew I. Leybourne and Eion M. Cameron</i>	41



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Exploration geochemistry: Basic principles and concepts

William B. Coker

*BHP Billiton World Exploration Inc., Suite 800, Four Bentall Centre, 1055 Dunsmuir Street,
Vancouver, British Columbia, Canada V7X 1L2 (e-mail: William.Coker@bhpbilliton.com)*

INTRODUCTION

Exploration geochemistry¹ utilizes the fact that the chemical characteristics of certain constituents of the natural environment in the vicinity of a mineral deposit commonly differs from those of similar constituents elsewhere. These differences are detected by the systematic measurement of the concentration of individual or, more commonly, suites of elements and/or compounds and/or chemically influenced properties of a naturally occurring material. The material selected for analysis will depend on the local environment, but might include rock, gossan, soil, drainage sediment, glacial sediment, surface water, groundwater, vegetation or soil gases.

Exploration geochemistry relies heavily on certain basic geochemical concepts. Geochemists long ago recognized the general principles underlying element distribution in the natural environment and that elements tend to be associated with one or another of these major phases, or the associated atmospheric and biologic phases, that subsequently developed. Based on these features, elements can be classified (Goldschmidt 1954; Smith & Hallberg 1982) as

1. Siderophile (i.e. affinity for iron) - primarily concentrated in the Earth's core;
2. Chalcophile (i.e. affinity for sulphur) - primarily concentrated in sulphides;
3. Lithophile (i.e. affinity for silicates) - concentrated in the Earth's crust;
4. Atmosphile - present as gas in the atmosphere;
5. Biophile - occurring as biological material.

Thus element distributions in the natural environment are primarily influenced by their fundamental chemical properties. These in turn depend on the element's electronic constitution and hence position in the periodic table.

THE GEOCHEMICAL CYCLE

Geologically and geochemically the Earth constitutes a dynamic system in which material is moved from one place to another and changed in form and composition by a variety of processes, including melting, crystallization, erosion, dissolution, precipitation, vaporization and radioactive decay. The system comprises two major components, primary (deep-seated) and secondary (surficial), which are distinguished by gross differences in pressure, temperature and chemistry. This can be represented in simplified diagrammatic form by the geochemical cycle (modified from Rose *et al.* 1979). See Slide 6 in Coker's PowerPoint presentation on the workshop CD (*rather than reproduce the figures in these workshop notes, the reader will be referred to the slide number in Coker's PowerPoint oral presentation*).

Primary (deep-seated) environment

The primary geological environment extends downward from the lowest levels reached by circulating surface waters to the deepest levels at which normal rocks can be formed. It is characterized by magmatic, metamorphic and diagenetic processes. In magmatic environments, geochemical dispersion may result from exclusively mechanical agencies such as magma injection. More often dispersion results from a combination of chemical and mechanical processes, as for example due to partitioning during crystallization and the separation of aqueous solutions. Components (H₂O, CO₂, H₂S, SO₂, F, Cl, B, and sometimes also Cu, Pb, Zn, Au, etc.), that enter these aqueous solutions commonly undergo significant dispersion.

Metamorphic environments differ from magmatic in that most reactions occur in the solid state. No actual melting is generally involved in metamorphism, except at the very highest temperatures. However, pore fluids rich in water furnish mobile phases into which some rock constituents may be extracted by mineral solution or exchange. Again, both chemical and mechanical processes are important factors in the development of geochemical dispersion patterns.

A wide range of chemical and physical changes occur in sediments during and after burial; changes that alter solid mineral phases and interstitial fluids by a complex series of so-called diagenetic processes. Some of these processes may proceed progressively over extended periods of time. However, the diagenetic history of a sedimentary mass may be punctuated by episodic tectonic events that result in significant modification and/or movement of fluid and dissolved material. In conjunction with normal basinal fluid migration, these episodic processes obviously have a major influence on geochemical dispersion in sedimentary rocks.

Faults, fractures, and intergranular openings provide channelways for dispersion of materials in aqueous solution in a wide variety of primary bedrock environments, especially at shallow to moderate depths.

Secondary (surficial) environment

The secondary environment of weathering, erosion and sedimentation at (or near) the surface of the earth is generally distinguished by low temperatures, nearly constant low pressure, and abundant free oxygen, water and carbon dioxide. On exposure to the surficial environment, as a result of uplift and erosion, most of the minerals developed under deep-seated conditions become unstable. They tend to break down into constituent components and/or be replaced by more stable minerals. These components are redistributed by various weathering agencies (Rose *et al.*

1979; Levinson et. al. 1980) (Slide 8). The dispersion behaviour of individual chemical elements in the surficial environment is strongly influenced by their relative mobility. Immobile elements tend to lag behind with the clastic weathering products, whilst the more mobile elements tend to disperse away from weathering sites as soluble components of surface and ground waters. However, as Slide 8 illustrates, there is generally considerable interchange between aqueous and adjacent clastic phases throughout any dispersal/dispersion processes. Purely mechanical processes, apart from alluvial sorting, usually involve mixing but not differentiation. In contrast, chemical and biochemical processes commonly create fractions of widely differing chemical composition due to the enhanced mobility of specific elements. Consequently, the characteristics of geochemical patterns in the mobile aqueous and relatively immobile solid phases of the surficial environment commonly differ somewhat from those in the primary source materials. It is fortunate, from a mineral exploration point of view, that these changes are generally not sufficient to mask distinctive features related to significant mineralization.

BACKGROUND RANGES AND ANOMALOUS THRESHOLDS

In exploration geochemistry, the normal element abundance level in a non-mineralized earth material is commonly referred to as the geochemical background for that particular material. However, as element distribution in a specific earth material (rock, soil, stream sediment, etc.) is rarely uniform, even when it is derived from an apparently homogeneous source, it is more realistic to visualize background as a range rather than an absolute value. Any departures from the normal range be they positive (i.e. enrichments) or negative (i.e. depletions), are viewed as anomalous. The upper and lower (often defined by the lower detection limit of the analytical method employed) limits above or below which, respectively, values are considered to be anomalous are defined as anomalous thresholds (Slide 10).

TARGET AND PATHFINDER ELEMENTS

In exploration geochemistry, use is frequently made of target (i.e. potentially exploitable) elements as indicators of the presence of mineralization. However, in some situations these may not be particularly effective. Attention is therefore also given to pathfinder (i.e. associated) elements of little or no economic significance that may have useful features (mobility, immobility, easier analysis, particularly low detection limits, low analytical costs, higher concentration, etc.). For example, in gold exploration, despite improvements in the cost, sensitivity and reliability of gold analytical methods, associated elements such as Ag, As, Hg, Sb, etc., which behave very differently to gold in the primary and/or supergene environments, are often also determined. Pathfinder elements can also often provide indications of the possible nature of the bedrock source of the mineralization(s).

GEOCHEMICAL HALOES

Many types of mineral deposit are enveloped in distinct patterns (i.e. haloes) of geochemical enrichment or depletion. These can vary in strength from the strong but sub-economic, down to the weak but detectable trace levels of concentration. Haloes may be of epigenetic (primary) or syngenetic (secondary) origin and sometimes a combination of both. They may include target as well as associated (i.e. pathfinder) elements. They can greatly assist geochemical exploration as they often significantly increase target size and sometimes provide surface indications of blind occurrences (Slide 13).

SECONDARY GEOCHEMICAL ENVIRONMENT

Weathering (Slide 15) involves the transformation of rocks from the massive to the clastic state in response to local surficial conditions that are generally very different to those under which the rocks were formed. It involves both (1) physical and mechanical disaggregation without significant chemical modification of the constituent minerals and (2) chemical weathering resulting in the transformation of primary minerals and the formation of secondary minerals. Chemical-weathering processes generally dominate.

Physical weathering

Physical processes participate in all stages of weathering, with water as the principal and wind and organisms as supporting agents. Gravity and temperature gradients are important contributing factors. The process of physical weathering is generally initiated by uplift and erosion. Differential stresses resulting from the 'unloading' of rocks produce a network of cracks and joints. Further development of cracks and joints is promoted by rapid temperature changes due to rain or fire and, especially in hot arid regions, by diurnal thermal contraction and expansion. Freeze-thaw cycles in percolating surface waters can be important factors in cold deserts and at high altitudes, whilst penetrating plant roots can enhance rock fracturing in a variety of environments. Crystal growth from salt precipitates can widen cracks and cause granular disaggregation. The overall effect of various combinations of these fracturing processes is often reflected by sheeting and exfoliation, especially in massive, poorly jointed rocks such as granite and sandstone. Physical processes generally play a subsidiary role in rock weathering except under certain extreme climatic conditions where chemically reactive percolating water is generally absent. In very cold regions (i.e. at high elevation and/or high latitude), glacial activity can pluck fragments from bedrock surfaces, reduce them in size during transportation and finally deposit them some distance from their points of origin. In desert regions, wind-blown particles tend to be the dominant agent of erosion. Physical weathering can also often play a major role in many areas with steep topography as erosion may cause rock debris to be removed faster than it can be weathered chemically. The increase in reactive surfaces, porosity and, in many cases, permeability resulting from physical weath-

ering can facilitate chemical weathering by active agents in surface as well as ground waters.

Chemical weathering

Chemical weathering in the surficial environment results from percolating water carrying active agents. This leads to the dissolution of rock-forming minerals and the formation of new mineral and/or amorphous and/or soluble phases. Controlling factors include climate, Eh-pH, vegetation, and micro-organisms, which all have a major direct impact on mineral dissolution and synthesis processes. Together with relief, drainage, bedrock geology and mineralogy, these largely control the nature, rate and intensity of chemical weathering.

Climate

Chemical weathering is strongly influenced by climatic factors, in particular temperature and rainfall. High temperatures, especially when they occur year round in conjunction with large volumes of percolating water, provide optimum conditions for chemical-weathering processes. Hence they tend to be particularly important in the humid tropics. Seasonal high temperatures, as for example those found in certain subtropical and Mediterranean regions, tend to be somewhat less conducive to chemical weathering. Cold temperatures are a deterrent to chemical weathering.

Vegetation

Vegetation protects weathered rocks against erosion and limits water evaporation. However, soluble organic compounds with potent weathering properties are produced by chemical leaching of organic matter derived from vegetation and the biochemical activities of micro-organisms. The nature and rate of formation of these soluble organics is primarily controlled by climate (mean temperature, available moisture and degree of aeration), but the character and extent of vegetation and soil mineralogy are important ancillary factors. Soluble organics are active weathering agents in both temperate and humid tropical zones, but obviously not in arid areas. Virgin tropical rain forest soils typically contain approximately 35 tonnes humus/hectare whilst, at the other extreme, desert soils typically contain less than 1% of this amount.

Eh and pH

Due to the pre-eminent role natural aqueous solutions play in the weathering process, mineral solubilities are important factors in weathering. As solution chemistry is dominated by Eh and pH (Slide 19), knowledge of these parameters often permits general predictions of element behaviour in a particular local weathering environment (Hansuld 1967).

Eh is a measurement of the oxidizing or reducing (i.e. redox) potential of a system. As these processes involve transfer of electrons (i.e. oxidation - loss of electrons; reduction - gain of electrons), they can be regarded as electrical properties and expressed in volts or millivolts. It should be noted that redox potential measurements in natural environments are generally only semi-quantitative at best, as some of the reactions that determine the values are very slow. Instantaneous readings with a platinum elec-

trode do not normally provide true equilibrium potential differences. Eh in the natural weathering environment generally falls somewhere in the range of 800 mV to -300 mV (Butty & Chapallaz 1984).

pH is a numerical expression of the relative acidity or alkalinity of an aqueous system. These properties are determined by the relative concentrations of hydrogen and hydroxyl ions in solution. pH is expressed as the negative logarithm (to the base 10) of the hydrogen ion activity. Thus a one unit change in pH represents a ten-fold change in hydrogen ion concentration! Neutrality on the pH scale, which extends from 0 (i.e. extremely acid) to 14 (i.e. extremely alkaline), is defined as the point at which hydrogen and hydroxyl ion activities are roughly equal. With dilute solutions at 25°C and 1 atmosphere pressure, this occurs at a pH value of 7. The majority of pH values in the weathering environment fall in the range of 4 to 8 (Slides 19 & 20). They are generally maintained in this range by natural buffering reactions, such as those involving CO₂ or clay. Dilution and base ion removal by surface and ground waters also assist in this process. Extreme pH values, outside the normal range (Slide 19), occur locally due to the presence of abnormal environments. Strongly acid conditions, (i.e. pH as low as 2 to 3) may result from sulphide weathering or the presence of significant concentrations of organic acids (pH values as low as 3). Conversely, highly alkaline conditions (i.e. pH values of 9 to 11 or more) occur in organic-rich saline lake waters, as for example in parts of the Canadian Shield underlain by carbonate rocks.

Microorganisms

Microorganisms occur extensively in the weathering environment, especially in association with organic matter. Their role in weathering processes, although apparently significant, is poorly understood. However, they are known to play important roles (Butt and Zeegers 1992), such as chemical reaction acceleration (e.g. oxidation of sulphur and iron compounds); environment modification (e.g. change pH); and production of compounds capable of enhancing solubility. Micro-organisms can also derive energy by breaking down large, immobile humic molecules into smaller more mobile ones, thus mobilizing metals associated with the former (Butt and Zeegers 1992).

Relief and drainage

In very mountainous terrain, even in the humid tropics, physical erosion may cause rock debris to be removed faster than it can be weathered chemically. The degree of chemical weathering will therefore tend to be significantly less than it is in geologically and climatically similar areas with more subdued relief. However, low relief and a humid tropical environment does not necessarily guarantee a high rate of chemical weathering, as for example in areas with a high water table and sluggish groundwater movement. In this situation, failure to remove weathering products can, over time, result in a state of virtual equilibrium with little or no ongoing chemical weathering.

Bedrock mineralogy

Common mineral species vary significantly in their resistance to chemical weathering. Minerals that originally crys-

tallized at the highest temperatures, under the most anhydrous conditions, tend to weather more readily than those that crystallized at lower temperatures in more aqueous environments. In general, the susceptibility of ore minerals to weathering tends to increase in the order oxides < silicates < carbonates < sulphides.

Dissolution processes

Chemical weathering of rocks mainly results from reactions between component minerals and surface and near surface waters that often carry a variety of active agents (carbon dioxide, organic acids, oxygen, etc.). It is most active in humid equatorial regions, and becomes less important in cold boreal or alpine climates, as it is, to a large degree, temperature dependent (i.e. at higher temperatures).

Solution

Simple solution processes can be an important factor in chemical weathering under some circumstances. An extreme example is presented by saline deposits and gypsum beds that are readily soluble when exposed to ground or surface waters.

Hydration

In the hydration process, water molecules combine with certain rock minerals. Thus hydration of anhydrite results in the formation of gypsum. Hydration also commonly occurs in conjunction with other weathering processes, as for example during the hydrolysis of aluminosilicate minerals or the oxidation of iron minerals, when the end products are clay and hydrated ferric oxides, respectively.

Hydrolysis

Chemical weathering of rocks containing silicate and aluminosilicate minerals is generally dominated by hydrolysis (i.e. reactions involving the release or consumption of hydrogen ions or hydroxyl groups). The most important proton donor in the near surface environment is normally carbonic acid resulting from the interaction of carbon dioxide and water. The carbon dioxide involved in this process is usually derived from the atmosphere and decomposition of cellulose in plant matter by microbial activity. Particularly strong acid conditions can develop in the vicinity of oxidizing sulphide occurrences. Initial oxidation and hydrolysis of ferrous iron to ferric iron creates much additional acid while producing the goethitic precipitates common to ferruginous gossans. The nature and intensity of hydrolysis is largely dependent on environmental conditions, in particular temperature. The rate of hydrolysis is in fact broadly proportional to the temperature, and any rise in soil water temperature increases the speed of this process (Duchaufour 1978). In temperate, cold and semi-arid regions hydrolysis is generally more gradual than in humid tropical areas.

Chelation

Some of the soluble organic substances (e.g. oxalic and citric acids, and phenolic compounds) produced by the breakdown of organic matter or synthesized by microorganisms are aggressive weathering agents (Duchaufour 1982). This is not only due to the presence of H ions in these com-

pounds, but also their ability to form organo-metallic complexes (i.e. chelates). These chelating agents promote the replacement of metal ions (e.g. aluminum and iron) within the crystalline sheet structures of aluminosilicate minerals (i.e. both primary minerals and certain clays) by hydrogen ions, thereby assisting in their dissolution or transformation (Butty & Chapallaz 1984).

Bio-leaching

Micro-organisms synthesize acids and/or complexing organic compounds, which promotes acid hydrolysis and chelation. They also intervene directly in the oxidation-reduction of iron and manganese, such as in the process of sulphide oxidation, or in the reduction of iron and manganese in anaerobic organic-rich media. Micro-organisms also appear to directly contribute to the destruction of aluminosilicates by selective extraction of nutritive components (N, P, K, etc.) from mineral lattices (Butty & Chapallaz 1984).

Oxidation-reduction (rock-forming minerals and sulphides)

Oxidation is generally considered to be the second most important process (i.e. after hydrolysis) in rock weathering. It is characteristic of the aerated zone above the water table, but can occur in the saturated zone as a result of the presence of descending oxygen-bearing waters. Oxidation reactions are normally sluggish except when catalyzed by the presence of water. The elements most commonly affected by oxidation in the weathering zone are reduced forms of iron, aluminum, manganese and sulphur (i.e. Fe₂, Al₂, Mn₂ and S, respectively) contained in primary minerals (Krauskopf 1979). The chemical reactions involved in the weathering of sulphides are complex with each element present applying some form of influence on the others (Thornber 1982). Sulphides, unlike most silicate minerals, tend to be electrically conductive, and hence subject to rapid movement of electrons (i.e. electrochemical processes) through them in conjunction with electrically induced movement of anions and cations in the adjacent groundwater. These processes are initiated as sulphide bodies are exposed to oxygenated surface and ground water as a result of erosion.

Products

The weathering products of sulphide deposits and common rock types are of importance in exploration geochemistry as the latter can often have a significant influence on the nature and mobility of the former. Both are therefore considered in the following discussion. The major secondary minerals produced by chemical weathering (in particular hydrolysis) of some common primary aluminosilicate minerals, and the sequence and conditions under which they tend to be formed, are fairly well established (Rose *et al.* 1979). The end products mainly comprise clay minerals, oxides of Fe, Al, and, to a lesser extent, Mn and Si. These can all occur, under appropriate conditions, as ultra-fine (colloidal) suspensions in surface and ground waters. In addition to causing hydrolysis, water can also transport the soluble weathering products. It is important to note that the formation of new crystalline mineral phases in the weathering process proceeds either directly

from ions, or more generally from ions or organo-metallic complexes via intermediate amorphous phases (Butty & Chapallaz 1984). The weathering of sulphide deposits typically results in the formation of secondary ore minerals and iron oxides as well as a variety of soluble constituents.

Residual minerals

Quartz and certain accessory minerals (zircon, rutile, ilmenite, tourmaline, etc.) generally weather very slowly and therefore tend to persist in weathered residuum alongside secondary minerals. However, in hot and humid climates quartz is subject to surface corrosion and fine-grained varieties can be almost totally dissolved. Feldspar weathering is influenced by silica content: the higher the content, the slower the weathering. Thus silica-rich varieties, such as orthoclase and microcline, can persist as residual minerals, especially in temperate climates where chemical weathering (i.e. hydrolysis) is only weak or moderate.

Soluble components

Normally soluble components reflect the composition of the parent rock. Thus, the main soluble products of carbonate rocks are Ca^{2+} , Mg^{2+} and CO_3^{2-} . In contrast, silicate rocks can, under suitable weathering circumstances, yield colloidal silica (with a maximum solubility of 100 ppm in aqueous solution), as well as alkalis (Na^+ , K^+ , etc.) and alkali earths (Ca^{2+} , Mg^{2+} , etc.), the relative proportions of which will reflect the general nature of the source rocks. Ca^{2+} and Mg^{2+} will tend to predominate in the case of mafic rocks, whilst felsic rocks should yield higher proportions of K^+ and Na^+ . In general, Ca^{2+} is more likely to be removed in soluble form than is Mg^{2+} , which tends to be strongly adsorbed by clays or incorporated in the structures of chlorites or montmorillonite. Some K^+ may be retained in illite, but Na^+ tends to remain in solution. Iron and manganese only display substantial solubility under reducing conditions. Total hydrolysis of aluminosilicate minerals, of the type observed in the humid tropics, favours the elimination not only of basic cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), but also silica, which is almost as mobile. In contrast, iron and aluminum ions are only slightly mobile and tend to accumulate in situ as hydrous oxides.

It should be noted when considering the weathering products of sulphide mineral deposits that trace metals in natural aqueous systems in the surficial environment are commonly exposed to large numbers of possible interactions with ill-defined dissolved and particulate compounds, and non-equilibrium conditions (Salomons & Förstner 1984). Consequently, concentrations of dissolved species in natural surficial aqueous systems are often significantly less than might be otherwise expected solely on the basis of equilibrium solubility calculations.

Clays

The nature of clays developed in the weathering process ultimately depends on the climatic environment. In equatorial regions, under optimal well drained neutral conditions (i.e. generally at depths where organic acid ions are absent), primary minerals (e.g. micas and feldspars) are sub-

ject to total hydrolysis (i.e. geochemical weathering) and their constituents, particularly silica, alumina and bases, are freed. When the complete elimination of silica is prevented by poor drainage, clay formation by recombination of silica and alumina to form clays (i.e. synthesis) becomes possible. The nature of these clays depends to a large extent on pH, which controls the solubility of the released ions, and drainage conditions, as these determine the rate at which released ions are removed from the weathering zone. Hydrolysis in temperate and cool regions is generally more gradual than in humid tropical areas and clays are in most cases derived from phyllic minerals (e.g. micas, chlorite, kaolinite) by transformation processes in which pH and organic anions (i.e. biochemical weathering) play critical roles. However, mineral synthesis can be of some importance under special circumstances. Conversely, slow transformation can sometimes occur in tropical regions. And, in temperate and some semi-arid regions, acid hydrolysis can result in the transformation of illite into vermiculite.

Organic compounds

Metals may be bound to organic matter in a number of ways. In chelates, a metal atom forms the centre of a complex (organic) ring structure and is attached to one or more carbon atoms of the ring through intermediate N, O, or S atoms. Bonding is generally very strong. On the other hand, in organo-metallic compounds, metal atoms are united directly to the carbon atom of an organic radical resulting in generally strong bonds. Metal atoms may also substitute for the hydrogen of organic acids or similar groups to form salts (e.g. sodium acetate). Many such salts are soluble in water, dissociating to form a metal cation and an organic anion.

Metal oxides

Hydrous iron and manganese oxides are almost ubiquitous in soils and sediments where conditions are not strongly reducing. They occur as coatings on silicate grains and rock fragments, and as discrete particles. Hydrous manganese oxides are often extremely fine grained and have extremely high adsorption capacities and high adsorption affinities for heavy metals. Adsorption by manganese and iron oxides (and solid organic matter) is in fact thought to have a dominant influence on trace metal distribution and dispersion in the supergene aqueous environment.

Silica

Hydrolysis of silicate and aluminosilicate minerals in the weathering environment results in the formation of silicic acid. Much of this silica normally either remains in solution in ground or surface waters, assists in the formation of secondary aluminosilicate minerals (e.g. clays), or is adsorbed by electropositive Fe/Al oxide gels (Butty & Chapallaz 1984).

Secondary 'ore' minerals

In the weathering of sulphide deposits, the more abundant chalcophile elements can, in many circumstances, rapidly exceed their solubility limits and precipitate in the solution cavities as secondary ore minerals (azurite, malachite,

Table 1. Examples of relative element mobilities in various surficial aqueous environments.

Element	Surficial Aqueous Environment			
	Acid	Oxidizing	Neutral-Alkaline	Reducing
Zn	High	High	Very low to immobile	Very low to immobile
Cu, Co, Ni, Hg, Ag, Au	Medium high	Medium high	Very low to immobile	Very low to immobile
Mo	High	High	Very high	Very low to immobile
Fe, Mn	Low	Very low to immobile	Low	Low

goethite, hematite, cerrusite, hydrocerrusite, smithsonite, hydrozincite, etc.) (Nickel 1982).

Gases

It has been clearly shown that oxidation of sulphides, under moist or saturated aqueous conditions, results in the formation of a wide range of hydrocarbon gases and other gaseous compounds (Klusman 1993). It should also be noted that mercury-bearing minerals, including certain sulphides (e.g. sphalerite), also release mercury vapour during oxidation. Gases such as radon and helium are given off during the radioactive decay and weathering of various radioactive minerals.

TRACE ELEMENT MOBILITY

Trace element mobilities in the surficial environment help determine the nature and size of surface geochemical patterns related to outcropping and subcropping mineral deposits. They must therefore be given serious consideration in geochemical exploration program design, and in the interpretation of the resultant analytical data. Numerous field observations have permitted development of certain broad generalizations regarding trace element mobility in the surficial environment (Slides 25 to 30), but these can usually provide no more than general guidance in geochemical exploration programs (Andrews-Jones 1968). Attention must also be given to local chemical, physical and biochemical processes that might affect element mobility, as well as the physical and chemical characteristics of the elements of interest. Mobility in the surficial environment is generally dominated by aqueous transport. Therefore, less attention is given to transport in the biological and clastic environments.

Aqueous media

The extent of the dispersion of water-borne ionic, colloidal, chelated and complexed materials from weathered rocks, including mineral deposits, depends on both the hydrology of the aqueous medium as well as the stability of the transported components in the local aqueous environment.

Solution chemistry is dominated by Eh (oxidation-reduction (redox) potential) and pH (hydrogen ion concentration). Published Eh-pH diagrams (see Slides 19 and 20) permit broad prediction of element behaviour under specific conditions. Some examples of relative mobilities in the surficial aqueous environment are listed in Table 1.

Coprecipitation

Coprecipitation occurs when a dissolved species is incorporated as a minor component in a solid phase as that

phase itself is precipitated (Drever 1982). Within certain commonly encountered ranges of pH values, the solubility of base metals such as Co, Cu, Ni, Pb and Zn is generally significantly reduced in the presence of Fe and/or Mn, which can cause, to varying degrees, these elements to coprecipitate with Fe and Mn hydroxides/oxides. This, in turn, can give rise to false anomalies.

Colloidal chemistry

The mobility and dispersion of many trace elements in surficial aqueous environments are strongly influenced by ion (cation) exchange with, and the adsorption properties of, colloids. These comprise aqueous suspensions of very small particles with diameters typically in the range of 0.001 to 1.000 micron. Colloidal particles become involved in ion exchange and adsorption as they possess large electrical charges relative to their surface areas. In the weathering environment, colloids commonly consist of Fe, Al, and Mn oxides and hydroxides, organic matter, clays and silica. There are fixed negative charges in the silicate layers of clays and fixed surface charges on the oxides of Si, Al, Fe, and Mn, organic matter and edges of clays. Many chalcophile elements are adsorbed onto colloids (i.e. Co, Cu, Zn in presence of Mn and Fe hydroxides/oxides).

Reactions with organic material

Metals may be bound to simple organic compounds in several ways. They may be strongly bonded directly to carbon atoms or to N, O, P, S, etc., or be moderately to strongly bonded by replacement of ionizable H in organic acids. Complex organic compounds, such as fulvic and humic acids, have the ability to adsorb, and chelate metal ions. The relative strength of bonding by chelation is typically $Cu > Ni > Co > Pb = Ca > Zn > Mn > Mg$ (Rose *et al.* 1979). Chelates tend to be fairly stable and consequently have some migration potential. However, as organic complexes tend to breakdown more rapidly at higher temperatures, metals associated with fulvic and other organic acids in the humid tropics and subtropics are often precipitated close to sites of origin (Thomas 1994). Colloidal organic materials may display weak non-specific surface absorption of metals, etc., due to the presence of surface electrostatic charges.

Biological media

Vegetation has a major role in the dispersion of many of the products of weathering. Uptake of available (i.e. soluble) inorganic matter by plant root systems results in its redistribution throughout the various organs of the plants. This provides the basis for the biogeochemical exploration method (Dunn 1991, 2001). During subsequent plant decay, the more insoluble components are concentrated in

the upper part of the soil profile (i.e. humus layer), whilst the bulk of the soluble products tend to be removed by ground and surface waters. However, variable proportions of the latter are often reprecipitated in a zone of accumulation (B horizon) in the soil profile, whilst some re-enters the plant's circulatory system. This sequence of events constitutes a significant portion of the biogeochemical cycle.

Micro-organisms (bacteria, algae, fungi, etc.) are also important factors in metal dispersion, as they are intimately involved in many redox reactions. Micro-organisms also often appear to be capable of assimilating and concentrating certain metals (Southam & Saunders 2005).

Clastic media

Mechanical processes play a major role in the dispersal of clastic weathering products often used as sample media in geochemical exploration programs. Gravity is the principal force responsible for clastic dispersal, acting directly or indirectly (i.e. through water or ice movement) on solid surficial materials. Even on gentle slopes, rock debris and soil continually move downhill under its influence. The presence of moisture acts as a lubricant and helps accelerate this movement, sometimes with catastrophic results. Surface water runoff, in the form of sheetwash and stream flow, is also responsible for the dispersion of large amounts of solid material. Large areas, especially at higher latitudes, have been subject to periods of intensive glaciation in recent geological time. The resulting erosion and deposition has involved a variety of processes that are reflected by an extensive cover of glacially derived clastic surficial materials (i.e. till, glaciofluvial sediments, etc.) (Coker & DiLabio 1989). Erosion and transport of clastic weathering products by wind action is most important in arid and semi-arid areas where there is little or no protective vegetation cover. In desert terrain, this can result in sand cover over large areas, whilst in the vicinity of some arid desert and glaciated areas, deposits of wind-blown dust (loess) are common. Wind is also responsible for the dispersal of man-made contaminants from industrial sites. Substantial amounts of subsurface weathered material are transported to the surface by many burrowing animal species, especially worms and termites. This is particularly important in surficial deposit covered areas where the transport of mineralized fragments to the surface can significantly enhance the surface geochemical response.

Gaseous media

A lot of recent work has documented the vertical migration of gases from concealed mineralization to the near surface and their accumulation in surficial sample media. There is also documentation of gases migrating up faults and fractures. There is ongoing work in this area with respect to the role of various organic gases in the movement of metals to the surficial environment as detected by a variety of selective extraction techniques (Hamilton 1998; Cameron *et al.* 2004; Hamilton *et al.* 2004a, b)

CONCLUSIONS

A good understanding of the aforementioned basic principles and concepts of exploration geochemistry is absolutely

critical to the successful application of geochemistry within mineral exploration.

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Quality control overview

Barry Smee

*Smee and Associates Consulting Ltd., 1010 Seaside Drive, Sooke, British Columbia, Canada V0S 1N0
(e-mail: bwsmee@geochemist.com)*

A full quality control program is now a mandatory component of 'best practices' for mineral exploration in Canada and Australia, and is dictated in Canada by the Canadian Council of Professional Geoscientists guideline *National Instrument 43-101, Standards of Disclosure for Mineral Projects*. However, at one time, only a few companies had an established corporate-wide policy of monitoring sampling and analytical procedures from reconnaissance-stage geochemical sampling through to the warehouse, where a representative portion of the sample was archived.

With a bit of forethought, planning and money, a well designed quality control program can detect contamination, salting, sampling inconsistencies, sampling over-selection, laboratory biases, analytical procedural errors, sample misnumbering or misordering, degraded analytical detection limits and changes in mineralogy. Most importantly, a quality control program can quantify both the accuracy and precision of the entire sampling and analytical process. Knowledge of these two quantities provides an estimate of the potential risk associated with calculating an average grade of a drilled mineral deposit.

EXPLORATION STAGES

The scope, extent and purpose of quality control procedures depend on the stage of exploration; however, there are as many definitions of exploration stages as there are exploration companies. This document refers to three main levels of exploration and attempts to place the most common geological sample type into each stage.

Regional exploration

This stage is intent on discovering previously unknown mineral occurrences or favourable geological horizons and provinces. It is sometimes called "property generation", but well defined land positions are often not the end result of this exploration stage. The usual geochemical methods involve some type of widely spaced sampling.

Follow-up exploration

The purpose of follow-up exploration is to locate the source of, or discover a reason for, 'anomalies' or patterns found during the regional exploration. This stage usually includes more intensive geochemical sampling and/or a change of sample medium. The ultimate goal of this exploration stage is to hold mineral title to a well defined drill target. This stage may include exploratory drilling, but not resource delineation.

Resource delineation

As the name implies, this advanced stage of exploration has the intent of developing an economically viable

mineral resource. This usually involves some type of three-dimensional sampling program.

QUALITY CONTROL PROCEDURES

Quality control in the early stages of exploration, which includes *regional and follow-up exploration* level sampling programs as described above, is primarily focussed on monitoring precision and contamination. Accuracy is of lesser importance. One of the main reasons for this is that less expensive geochemical analytical methods are usually employed. Many laboratories use weaker acid digestions, such as aqua regia, and each lab has their own idiosyncrasies as to dissolution temperature, time, and weight of sample used, thus resulting in data that is biased with respect to other laboratories. Therefore, the main concern with *regional and follow-up exploration* geochemistry is the reproducibility of results and the repetition of patterns (precision), as well as the detection of possible contamination.

Regional and follow-up exploration should therefore include the preparation of blank (barren) samples to monitor contamination and a routine for inclusion of duplicate samples within a sample string to monitor precision. A 'standard' sample can be inserted for piece of mind, however because of inconsistencies with the partial extractions, the main purpose for this standard is to detect analytical biases or drift between sample batches.

Field blanks can be collected for each sample type. For instance, a soil blank can be collected from a property early in the exploration program, and then used for the life of the program. Usually, 40 to 50 kg of blank material is needed, depending on the size of the project. The blank sample must be inserted into the sample stream from the field in such a way as to be invisible to the laboratory. If the blank sample yields a significantly increased concentration of the element being sought, contamination of the sample batch has likely occurred, or the sample sequence has been mixed, either in the field or in the lab. The frequency of insertion depends somewhat on the laboratory batch size. Usually 1 blank in 30 samples is sufficient.

Field duplicate samples are splits of drill core, reverse-circulation cuttings or outcrop samples from the same sampling interval, or stream sediments or soils from the same location, and preferably the same position in the drainage or soil hole. Reverse-circulation (RC) drill duplicates must be obtained directly from the drill sample discharge as drilling is progressing. Duplicates of three-dimensional samples, such as channel samples, cannot be duplicated exactly, but will still provide an estimate of the overall sampling and analytical precision for the commodities of interest.

The frequency of field duplicates depends somewhat on the size of the laboratory batches. One duplicate per labo-

ratory batch should be used. For gold exploration, at least one duplicate sample for every 20 to 40 samples should be inserted into the sample stream. Most laboratories treat base metal analyses in batches of 40 samples, which is the size of a rack of test tubes.

Field duplicate samples must also be blind to the laboratory and treated as normal samples. It is important that the duplicates are taken randomly with no regard to rock type, geographical position, degree of mineralization, or alteration. Any bias in the duplicate sampling program will negate the validity of precision and detection limit calculations.

Field duplicates contain the cumulative uncertainties associated with the entire sampling and analytical process. In addition, the laboratory should periodically split the coarse, jaw-crushed samples (rock) into two *preparation duplicates*, which are then pulverized and analyzed separately. Most laboratories analyze and report a *pulp duplicate* routinely. By compiling the field, preparation, and pulp duplicate types, the geologist can ensure that the overall precision, as well as the source of the greatest uncertainty in the sampling and analytical process, is quantified using recently developed statistical procedures.

Resource delineation drill programs are concerned not only with contamination and precision but must determine the accuracy of the sampling and analytical procedures. These advanced phases of exploration always use a 'total' assay method of analysis, which permits the use of *standards* to quantify accuracy. Accuracy can only be determined by using these standard samples submitted from the field in such a way as to be blind to the analytical lab.

There are different types of standards used during the processing of geological material. Laboratories use artificial aqueous standards to calibrate instruments. Some use artificial solid standards, though most manufacture standards from different geological media. Although those procedures are necessary for the laboratory to monitor itself, the use of these standards does not aid the exploration company whatsoever. If a company does not submit its own set of standards with its samples, no quantitative estimate of accuracy can be given to the analysis of samples submitted during an advanced exploration program.

The best geological standards for the *resource delineation* stage of exploration are property-specific, meaning they contain the same geological matrix as the samples being routinely analyzed. Standards are prepared by collecting material representative of the mineral occurrence being explored. Usually, this material is collected from coarse reject following preliminary drilling or sampling. Composites weighing between 30 and 50 kg are usually made. A common procedure is to prepare three standards for the important economic benchmark grades: one for each of the resource's expected cut-off grade, average grade, and higher grade expected to be mined during the payback period.

These composites should be forwarded to a laboratory specializing in the preparation of standards. Each composite must be crushed, pulverized, and screened through at least 200 mesh. The finely pulverized pulp is placed in a

large mixer for at least a day and as much as a week. Once homogenization tests are performed, at least 60 portions of the pulp are sent for 'round robin' analysis to various laboratories. Results from this analysis are compiled and treated statistically to determine the 'accepted value' and error limits on that value. This process sometimes must be repeated, as laboratories may report unacceptably poor precision, or have significant bias in comparison to other laboratories.

Standards must be packaged either in 1 kg, vacuum-packed and heat-sealed plastic or aluminium foil bags or in individual paper pulp bags that are heat sealed in plastic, then forwarded to the exploration company. Quantities prepared are normally sufficient to last the duration of an exploration program, and may well be used to 'tune up' a mine laboratory. The use of the same standards will ensure that any changes in the laboratory are closely monitored, and that the analyses from a future laboratory will be similar to historical data. As with blanks and duplicates, at least one standard per analytical batch (20 to 40 samples) should be inserted in a sample stream to monitor accuracy.

Many companies routinely submit a subsample of pulp or reject to a second laboratory, with the intent of confirming the 'accuracy' of analyses. This second analysis does not, of course, measure accuracy, but it does establish the reproducibility of analysis and the presence or absence of bias between the laboratories. A well designed quality control program that uses standards to establish the accuracy of all analytical batches does not require a set of confirmatory analyses; however this has been an industry practise and is still required by many mining engineering firms.

It is important that each exploration office or major project assigns the responsibility of quality control to a geological technician or geologist who compiles and monitors data within 24 hours of receipt of results from the laboratory. Suspect analytical data must be identified immediately, before it is entered into a master database. Each major drilling project should have a dedicated quality control technician or geologist on-site to monitor all aspects of sample collection, quality control sample positioning, database design and updates, sample preparation, laboratory or field failures, data acceptance, and master database updates. This in-house technician or geologist must report to an independent specialist, who can anticipate problems, draw on experience, and independently audit the data.

All on-going quality control data can be summarized into three simple charts: a time-series chart for each standard; a time-series chart for each blank, and an X-Y scatter chart for all duplicates. Additional graphics can be done at a later time, but are used for final presentations or precision calculations rather than real time assessment of data.

Standard charts should begin with the initial round robin results so that the entire history of the standard can be seen at all times. An example of such a chart is shown in Figure 1. Similarly, blanks and duplicates (field, preparation and pulp) should be plotted as each analytical work order is received.

A '*table of logic*' must be developed for each project that clearly outlines the rules for 'passing or failing' for all qual-

Standard 1 Gold Round Robin and Drill Holes

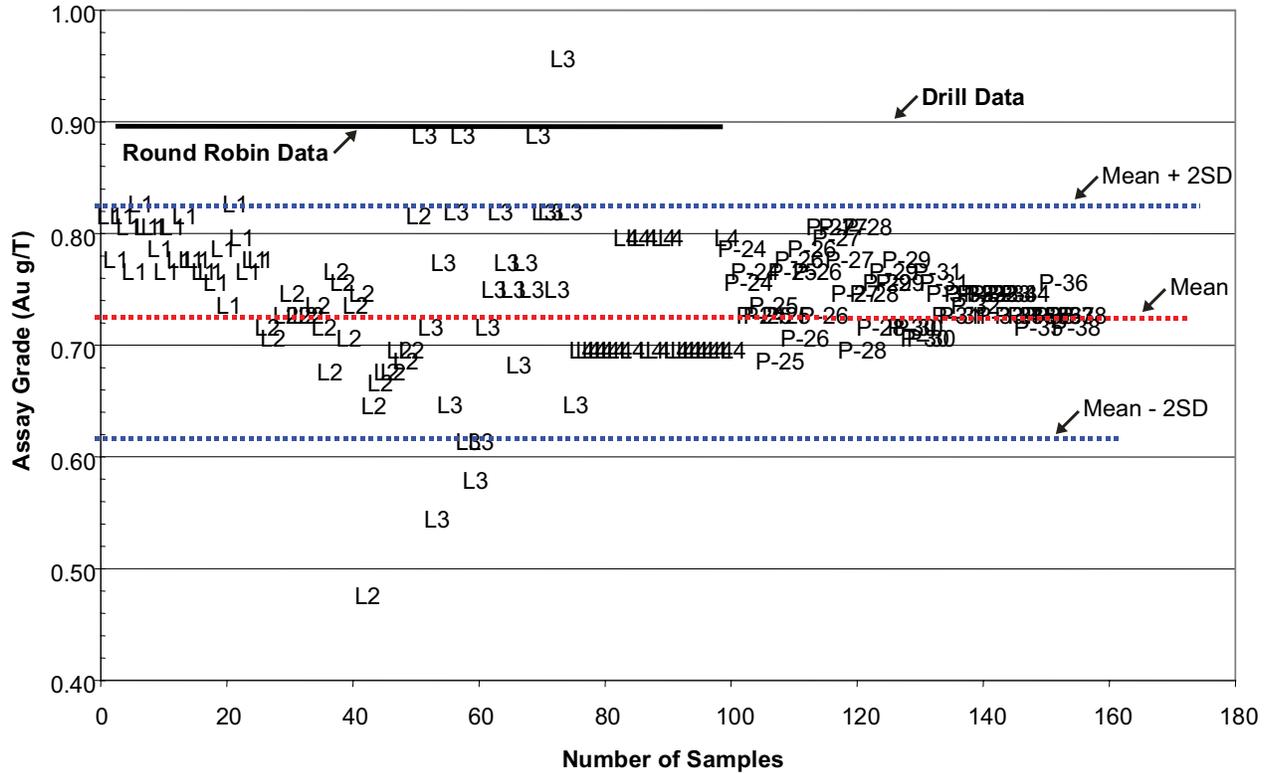


Fig. 1. Chart showing the entire history of a standard, beginning with the initial round robin results.

ity control samples. All failures must be listed in a 'table of failures' so that each failure is listed and the corrective action taken is identified.

Chain of custody in the case of mineral exploration is an assurance that geological samples have been transported in such a manner as to be secure and completely traceable from the field to a commercial laboratory. It is hoped that a proven chain of custody will prevent unusual sample handling or tampering. A well designed chain of custody will certainly add credibility to an exploration program, but it cannot prevent a determined effort to tamper with samples. A chain of custody must be incorporated with all due diligence programs.

An integral part of all quality control programs is the design and security of the database. Multiple copies of a working database can be made but only one copy of the master database should exist, and be under the control of one person. Changes to the master database must be authorised by the senior project geologist or project manager.

No analytical data should be placed into the master database until the data has successfully cleared quality control examination. Additionally, no analytical data received in electronic format should be placed into the database until the work order is marked by the laboratory as being final. Preliminary or partial analyses should never be placed into the master database. In fact, the laboratories should be instructed not to send 'preliminary' data at all.

Senior management must support quality control in mineral exploration. A series of corporate guidelines must be instituted for each stage of exploration, and adhered to. This process costs money and time, and the temptation to cut corners is great, especially if the budget is tight and the will is weak.

A mineral resource database that does not include comprehensive quality control to prove sampling and analytical accuracy, and defines the precision characteristics of the mineralization is essentially worthless for preparing a bankable feasibility study.

Geochemical data evaluation and interpretation

E. C. Grunsky

*Geological Survey of Canada, Natural Resources Canada, 601 Booth Street,
Ottawa, Ontario, Canada K1A 0E9 (e-mail: egrunsky@nrcan.gc.ca)*

This module of the workshop will present methods of processing geochemical data in order to extract information pertaining to the geochemical landscape. Currently, many geochemical surveys consist of thousands of samples that are analyzed for 50 or more elements, which provide a great opportunity to observe a wide range of geochemical processes that may have occurred within a survey area. However, it is often a challenge to examine and interpret the significance of many of the elements, in terms of exploration potential, and even more difficult to observe or understand the relationships between elements. This module will present a number of methods that can be used to help make the data more interpretable. See Grunsky (this volume) for a detailed description of methods used for evaluating geochemical data.

With the availability of affordable desktop mapping systems, geochemical data can now be interpreted together with other data (geology, geophysics, geomorphology) as a basis to provide additional insight into the spatial characteristics of the data. The use of spatial information permits subdivision of the geochemical data into various distinct geographical regions that can be related to the underlying geology and enables a more effective evaluation of the data for exploration purposes.

Prior to carrying out any evaluation of geochemical data for the purpose of identifying samples that are possibly associated with mineralization, it is important to separate samples on the basis of the medium from which they have been collected. The interpretation of mixed sample media can be almost impossible if the differences between the media are significant.

Initially, all data should be examined for analytical reliability and the identification of any suspect analyses (i.e. quality control). This is typically done using a number of exploratory data analysis methods and established procedures that are documented in the geochemical literature. On the basis of subdividing the data into similar sample types and geographically defined areas, the data should then be examined to identify the nature of the distribution, both statistically and spatially, as well as the identification of obvious outliers. This can be achieved using a number of simple graphical techniques such as histograms and probability plots (Fig. 1) and displayed in the geospatial domain (Fig. 2). The preparation of summary tables and maps of the elements helps to identify the character of the data, which often provides insight into which areas contain anomalous or background concentrations and the range of abundances for the various elements. These tables and maps are good comparative tools for assessing the differences between sample media and different areas. In addition, there are a number of statistical and graphical meth-

ods that have been developed to assist in the recognition of anomalous samples.

For large arrays of data, there are a number of multivariate data analysis techniques available (i.e. Fig. 3). These techniques reduce these large arrays of data into a few simple diagrams that often outline the principal geochemical trends within a survey. Typically, the trends that are identified include lithological variation, alteration effects, possible pathfinder signatures and zones of mineralization.

The results of multivariate analysis can be easily rendered in a Geographical Information System that clearly outlines geochemical trends that coincide with geology, alteration zones and mineralized areas. The amount of interpretation that can be inferred is dependent to a large extent on the sampling density of an area. In areas where the sampling density is low, only regional information is likely to be obtained. In areas where the sampling density is high, much information can be obtained about the local variation in the lithologies and the extent and character of alteration and zones of mineralization.

In areas where the nature of the geochemical targets are clearly understood, geochemical reference sets can be created that can be compared against unknown samples. This 'modelled' approach to geochemical data analysis can be useful in detecting samples that may have significant geochemical signatures in large regional datasets.

Geochemical data should be evaluated using a sequence of investigations such as the one suggested below. The use of Geographical Information Systems greatly assists in viewing the geospatial relationships of the data and forms an integral part of any geochemical assessment program.

PRELIMINARY DATA ANALYSIS

Know your data! There is no substitute for spending time evaluating the data using a wide variety of procedures so that associations and structures in the data can be identified.

- Examine each element using histograms, box and whisker plots, Q-Q plots, a scatter plot matrix and summary tables.
- Produce maps of elements showing the range of values using bubble or symbol plots. Interpolated images can be used where appropriate.
- Trim the distribution of each element of gross outliers.
- Investigate outliers for each element; are these the result of analytical error or are they an atypical value?
- Adjust data for censored values if required.
- If measures of association are required (i.e. correlation, covariance), consider the application of logratio transformations (e.g. logcentred, isometric logratio) so that

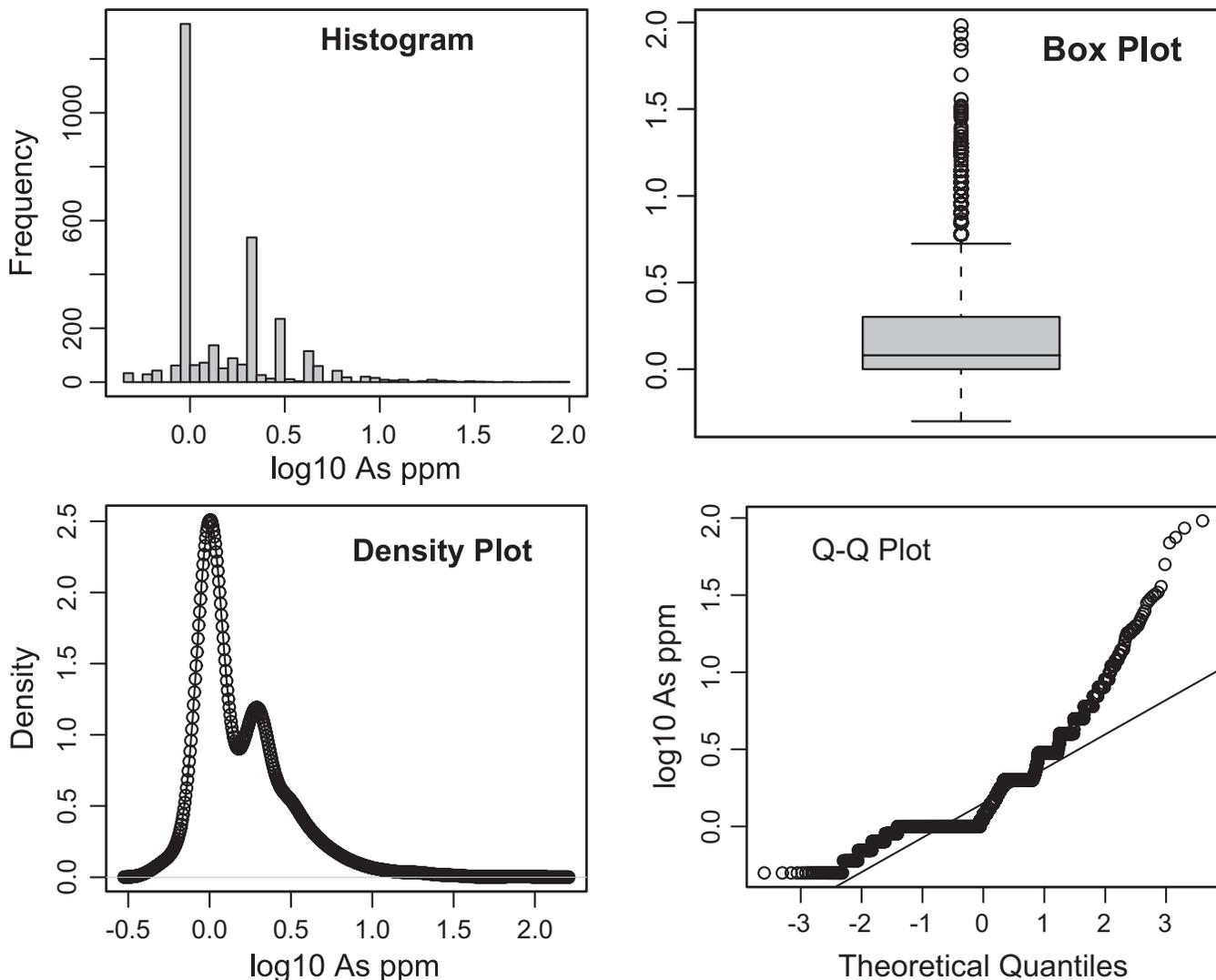


Fig. 1. Exploratory data analysis of arsenic in lake sediments.

compositional data can be evaluated without the effect of 'closure'.

- Apply measures of association using standard measures as well as robust procedures. Examine the differences and scrutinize the outliers.
- Test the data to see if the identification of patterns and outliers are improved by the use of transformations. Use Box-Cox power transformations for observations below the 95th to 98th percentile in order to determine the optimal transformation. The choice of transform parameters can be chosen visually (Q-Q plots, box plots, histograms) or by semi-automatic means.
- Examine scatter and quantile-quantile plots for the presence of multiple populations.
- If assembling data sets, examine the requirement for leveling.

EXPLORATORY MULTIVARIATE DATA ANALYSIS

The follow is a summary of exploratory multivariate techniques:

- Create a scatter plot matrix of the transformed (\log -centred ratios, isometric logratios) data. Look for trends and/or associations.
- Use robust estimates to compute means and covariances to enhance the detection of outliers.
- The application of dimension-reducing techniques, such as principal components analysis, can identify patterns and trends in the data. Other methods, such as non-linear mapping, multi-dimensional scaling and self-organizing maps, may help discover structure in the data.
- Geographic maps of the component loadings can assist in identifying spatially based geochemical processes.
- Methods such as cluster analysis can help to isolate groups of observations with similar characteristics and atypical observations. Specific groups of interest can often be isolated using these methods. Maps of the locations of the groups can help to examine the spatial continuity of the groups.

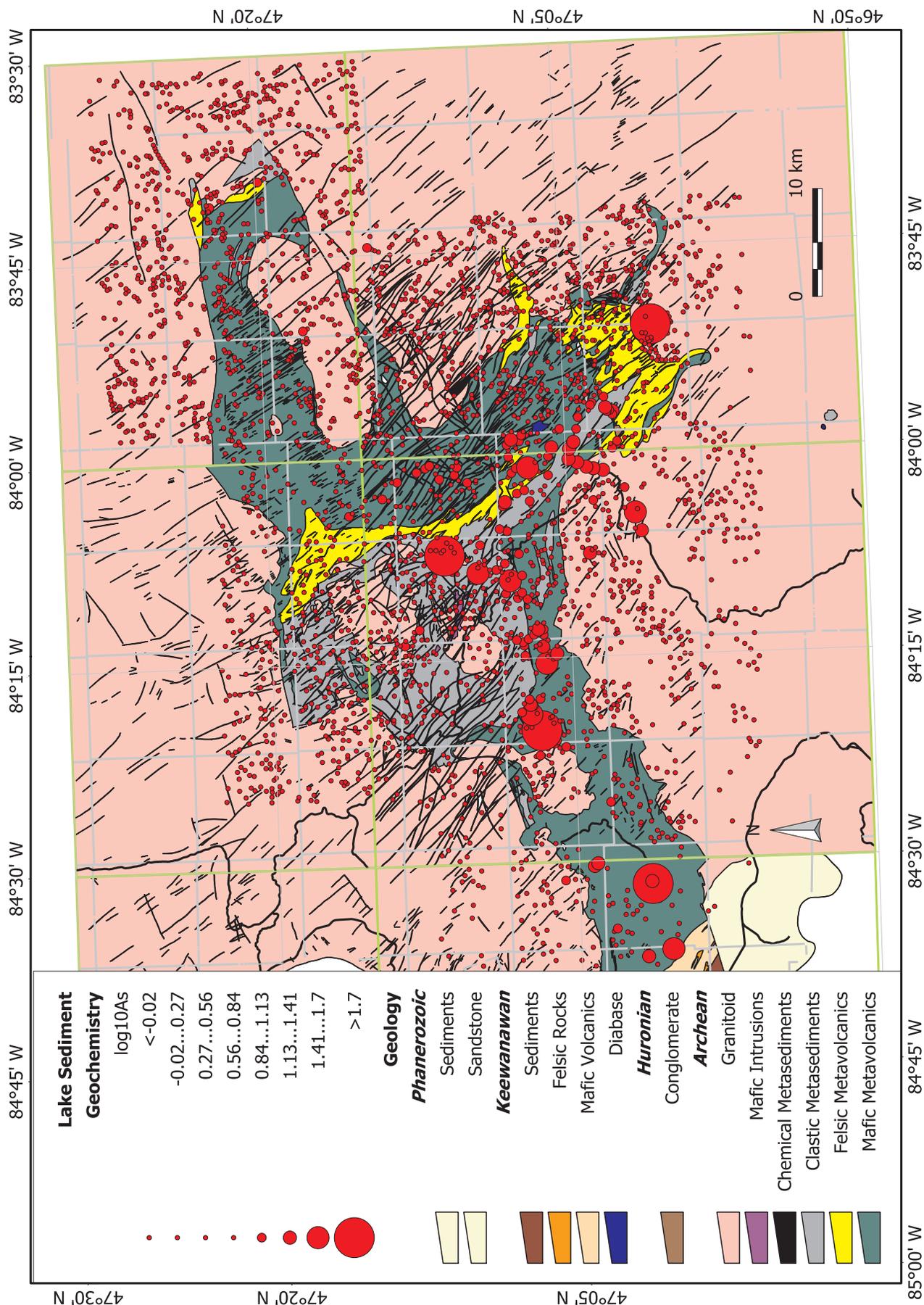


Fig. 2. Arsenic in lake sediments; the geospatial view.

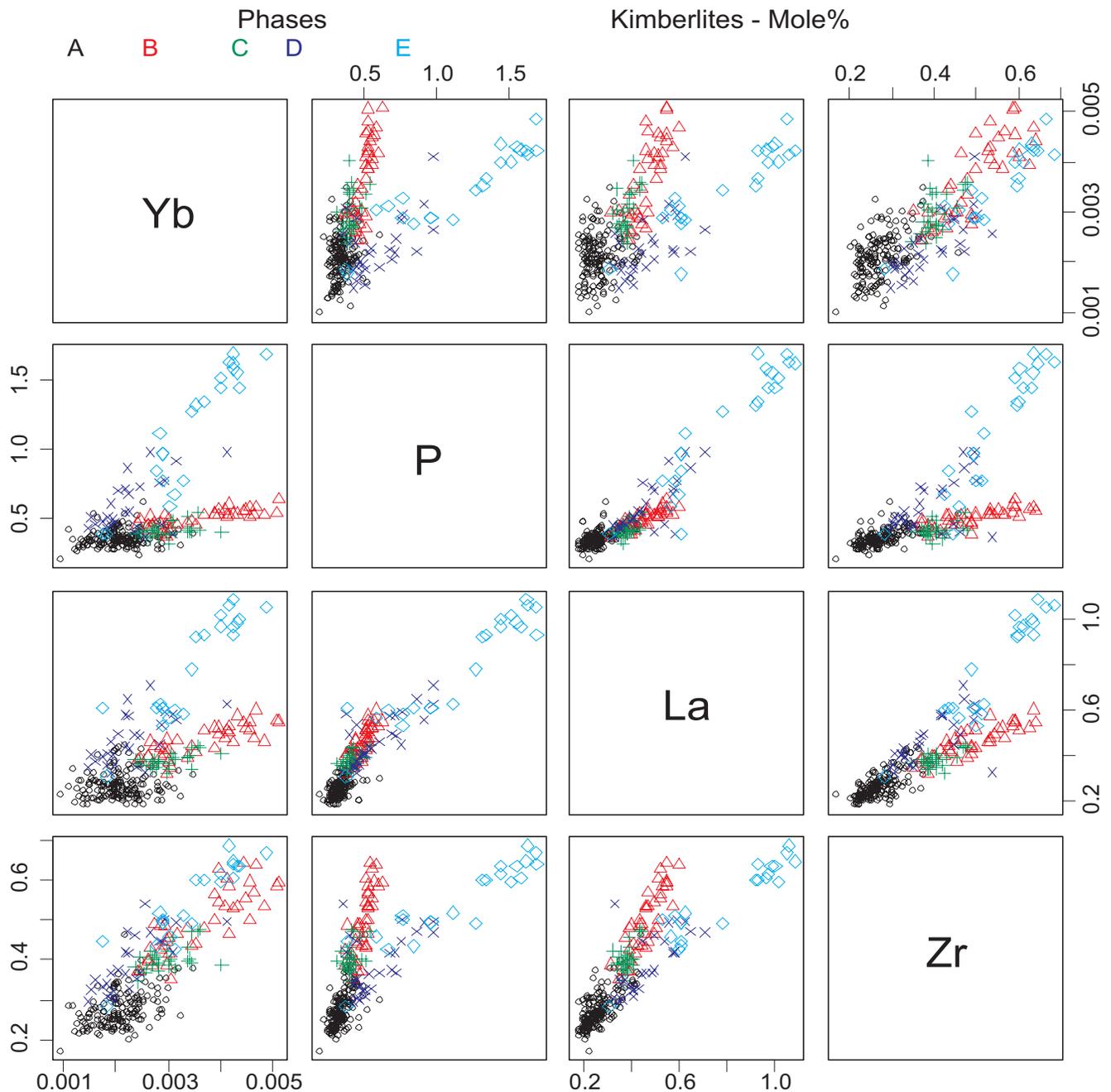


Fig. 3. Scatter plot of selected elements for five kimberlite phases (A, B, C, D, E).

- The use of Mahalanobis distance plots (D^2) applied to transformed data may assist in isolating outliers based on a selected number of elements of interest. Maps of large distances (>95 th percentile) can assist in identifying observations or groups of observations of interest.
- The calculation of specifically tailored empirical indices can be useful in areas where multi-element associations are well understood. The indices are based on a linear combination of pathfinder elements with coefficients that are selected for each area and commodity being sought. Observations with high indices can be investigated for mineralization potential.

SPECIFIC MULTIVARIATE DATA ANALYSIS AND MODELLED MULTIVARIATE ANALYSIS

The calculation of empirically derived geochemical indices can be used as methods which are specifically tailored to areas in which multi-element associations are well understood. The indices are based on a linear combination of pathfinder elements with coefficients that are selected for each area and commodity being sought. Samples with high indices can be investigated for mineralization potential.

- The use of multiple regression can be applied to areas where a linear model of the multi-element association can be computed with good results (i.e. high R^2 coefficient).

cients). Residuals can be examined for the potential of being associated with mineral deposits.

- Establish target groups representing samples that characterize mineralized areas. Establish background groups of samples that represent background lithologies.
- Once target and background groups have been established, the use of analysis of variance and canonical variate analysis can be used to test the statistical uniqueness of the groups. Groups that are statistically distinct can be used as reference groups against which unknown samples can be compared.
- The application of allocation and/or typicality procedures can test the samples being used to make up the reference group populations. Additionally, unknown samples from a regional exploration program can be used to assign the probability of belonging to one of the reference groups. Maps of typicality or posterior probability can be made to indicate group membership.

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Regolith mapping, landscape evolution and geochemical applications

Simon Bolster

*Newmont Mining Corporation, 10 Richardson Street, West Perth, WA 6050, Australia
(e-mail: Simon.Bolster@Newmont.com)*

In mineral exploration, we frequently collect soil and other near-surface geochemical samples to provide information on the underlying bedrock geochemistry. This practice has been successful for a long time and has led to countless discoveries, particularly where the soils are residual and the bedrock is weathered and close to the surface. However, the tenor of a near-surface geochemical response to mineralization is affected by more than just the size of the mineral deposit; a very large mineral deposit does not necessarily have a large surface geochemical expression (Gellatly *et al.* 1995; Cowley 2001). The size and strength of a near-surface geochemical anomaly is a product of bedrock geochemistry +/- regolith +/- geomorphology. The latter two criteria are often completely overlooked, or inadequately factored in when planning geochemical surveys or interpreting the results. As the search for new mineral deposits becomes harder, the need to factor in the regolith and geomorphology will become more critical. This section of the short course describes why geochemists and exploration geologists need regolith maps and the ability to visualize the terrain so they can factor in geochemical dispersion by hydro-dynamic and physical processes if they are to comprehensively sample a project, fully interpret the data and ultimately drill test the best anomalies in the most logical locations.

REGOLITH MAPPING

A simple definition of regolith is 'everything between fresh rock and fresh air'. It follows therefore that regolith includes weathered rock, soils and cover suites, such as alluvium, colluvium and wind-blown sands, glacial material, lacustrine sediments and lateritic weathering products. The ability of the regolith to build-up and maintain a near-surface expression of the bedrock geochemistry depends in part upon the nature and thickness of the regolith as well as the time it has been in place. If the regolith is transported and thick, then the lower the likelihood that surface sampling will be an effective prospecting technique. The geochemical thresholds applied in areas of thick transported cover, or where soils are diluted by aeolian derived sands, have sparse vegetation, or active colluvial wash should be lower than over residual soils. To know where to vary the thresholds, and which geochemical prospecting technique to apply, requires the use of a regolith-landform map.

There are a number of regolith mapping schemes in existence, many of which have developed out of necessity from mineral exploration work in the regolith-dominated Australian terrain (Chan 1988; Anand *et al.* 1993; Craig *et al.* 1993). The author has developed his own mapping scheme and mapping technique with an emphasis on providing a practical sub-division of the terrain, in fast and

cost-effective ways using remote sensing, digital elevation models and terrain evolution models (Bolster 1999). A good regolith-landform map should enable the user to visualise the terrain and to know something about the regolith materials at the surface. Regolith-landform maps have three components to them. These are regolith regimes (chemical environment), landforms (physical dispersion) and cultural features (logistical information). Regolith-landform maps should be produced at the start of an exploration program when they can be used to

- review any historical geochemical data,
- plan orientation surveys,
- plan new geochemical surveys,
- aid remote sensing and some geophysical interpretations and geological mapping.

LANDSCAPE EVOLUTION

Knowledge of how the landscape has evolved is important when constructing a regolith-landform map as it enables the mapper to make predictions about the regolith profile and regolith materials likely to be present within the region. It can be argued that landscape evolution models should be the precursors of geochemical dispersion models. Knowledge of palaeo-climates, tectonic activity and sea-level changes are important for understanding how the terrain has evolved over time and the origin of the regolith available to be sampled and how this material is likely to have been modified or moved around the terrain (Butt 1989; Butt *et al.* 1997).

There are a number of landscape evolution models that are most applicable to regolith mapping, two of which are described below. Which model is applicable depends upon the palaeo-climatic history and maturity of the terrain. Davis' (1905) model was one of the earliest in which he described how terrains evolve by steady denudation and pass through youth, maturity and old age phases as denudation proceeds down to sea level (Fig. 1). Under this type of landscape evolution, soils tend to be residual to proximal, except in the valleys, and the geomorphology is strongly influenced by the geology. Through steady denudation, metals and weather-resistant minerals can accumulate in the soil to give rise to geochemical anomalies that are broader and occasionally stronger than the primary bedrock mineralization. This is particularly true where, for example, gold is hosted in quartz veins or stringers that have a shallow dip. As the country rock is eroded then the quartz and Au drops down into the soil, where it accumulates over time (Fig. 2).

In former tropical weathering environments, such as the Sahel of West Africa, Davis' style of landscape evolution is rarely applicable. Instead, the scarp-retreat landscape evo-

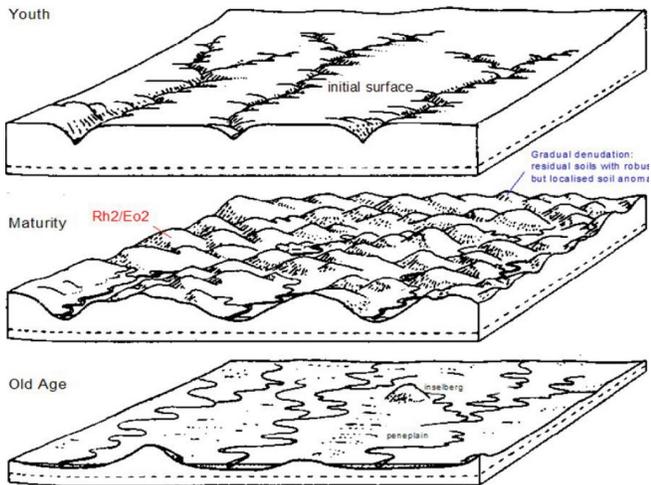
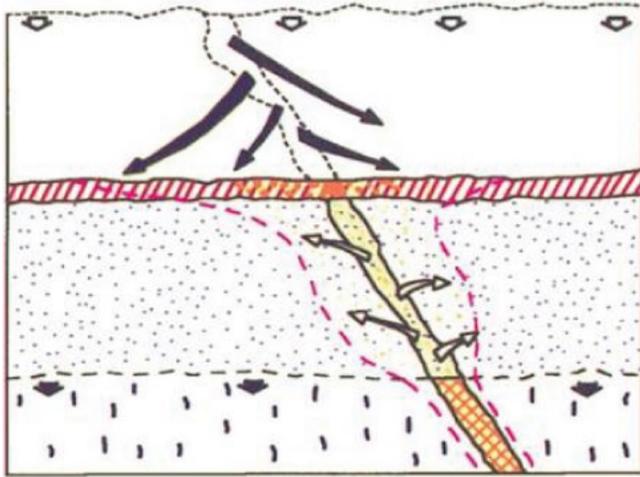


Fig. 1. Landscape evolution model, after Davis (1905), in which the terrain is gradually eroded down to sea level (dashed line). In the maturity phase, the geomorphology is strongly controlled by the geology and many of the soils on the hills will be residual to proximal and therefore ideal for prospecting using stream and soil geochemistry.



Erosion of a mineralized quartz vein

Grade: 2 g/t Au

Width: 1 m

Strike: 100 m

Density: 2.6 g/cm³

Therefore....

100 m x 1 m x 2.6 x 2 ppm = 520 g Au

If denudation over Tertiary = 1 m x 10⁶ years

= 520 g x 60 m

= 31,200 g / 1003 ozs of Au eroded

Fig. 2. The effects of steady denudation on the formation of gold in soil anomaly. Note how a narrow low-grade vein can result in a significant enrichment in the soils despite slow denudation over time.

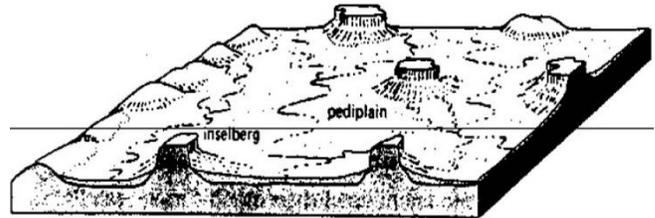
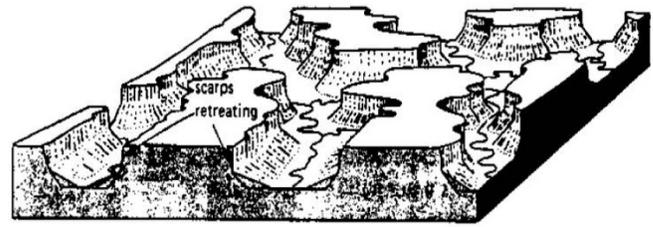


Fig. 3. Scarp-retreat evolution model (after Penck 1920 and King 1953). Lateral retreat rather than vertical surface lowering is the main process and occurs where the surface is armoured by ferruginous duricrust that is underlain by a softer regolith profile. In these terrains, the geochemical assays can change abruptly in direct response to changes in the regolith and unrelated to the underlying bedrock geochemistry (examples of which will be shown during the workshop).

Evolution models, such as those proposed by Penck (1920), King (1953) and others, need to be applied (Fig. 3). The scarp-retreat model is applicable where the surface is armoured by ferruginous duricrust and landscape lowering takes place laterally at an escarpment or breakaway through the undermining of duricrust by erosion of the less competent regolith beneath. This form of terrain evolution gives rise to a stepped terrain with the potential for multiple land surfaces to form. In these terrains, the ferruginous duricrust can be of multiple ages and a mix of residual and transported lateritic weathering products, with implications for whether the geochemical signatures are *in situ*, transported, leached or preserved. Furthermore, predictions can be made about the parts of the terrain where strong geochemical responses should develop (adjacent to breakaways) and where very weak surface responses can be expected (colluvial plains) and therefore appropriate anomalism thresholds can be set.

GEOCHEMICAL APPLICATIONS

Regolith-landform maps should be used to plan and interpret near-surface geochemical prospecting wherever the regolith is complex and variable. The maps are not a substitute for field logs, which have the advantage of being far more accurate and site specific when results need to be interpreted. Using a good regolith-landform map, it is possible to plan an effective geochemical sampling program using several techniques, at a variety of sampling densities. Where the bedrock crops out and a detailed drainage pattern is present, stream sediment sampling often works well as a first-pass exploration tool. Where soils are thin but diluted with aeolian sands in a former lateritized terrain, broadly spaced lag sampling is preferable to drainage or soil sampling (Carver *et al.* 1987). Where the overburden is thick and the vegetation is sparse, the size fraction can be important as can the need for specialized and low-level ana-

lytical techniques or the recognition that the only way to test the bedrock in this part of the terrain for mineralization is to drill down through the cover. If the landscape evolution models are robust, it is possible to predict the nature of the overburden in the channels, and sometimes the probable thickness of cover. This makes it possible to budget for and plan drilling programs with more confidence and place drillholes so they capitalize on up-valley and upstream dispersion.

Through appropriate mapping of the regolith terrain (using remote sensing, field observations and landscape evolution models), it is possible to explore more confidently whilst reducing the chance of leaving holes in the geochemical coverage, or subtle but significant anomalies, for the next generation of explorers who appreciate that near-surface geochemical responses are a product of bedrock geochemistry +/-regolith +/-geomorphology.

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Till geochemical and heavy mineral exploration methods in glaciated terrain

M. Beth McClenaghan

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8
(e-mail: bmcclena@nrcan.gc.ca)

INTRODUCTION

In glaciated terrain, mineral exploration methods often include a till sampling program designed to detect glacial dispersal of mineralized debris. Till is sampled from the least oxidized/ weathered part of the soil profile (typically >0.75 m depth) to avoid changes in geochemistry and mineralogy due to soil formation processes and possible anthropogenic contamination. This paper reviews the collection and analysis of till, focusing on indicator mineral methods and till geochemistry.

During the Pleistocene, between 10,000 and 20,000 years ago, nearly all of Canada, the northern USA, northern Europe and alpine areas of South America were glaciated (Fig. 1). The bulldozing and homogenizing action of flowing ice produced till, a mixture of rock and mineral fragments derived from crushed bedrock and older sediments. Till matrix ranges from sand-rich to clay-rich, depending on the composition of the source rocks and sediments. Till units range from thin beds (~1 m), composed of freshly abraded rock debris deposited near source, to thick beds (>10 m), composed largely of reworked material often transported great distances (>100 km).

Additional information on the application of till sampling to mineral exploration is available in conference proceedings, books and scientific papers, including the Prospecting in Areas of Glaciated Terrain (PAGT) series (e.g. MacDonald & Mills 1988), Drift Prospecting (DiLabio & Coker 1989), Drift Exploration in the Canadian Cordillera (Bobrowsky *et al.* 1995), Drift Exploration in Glaciated Terrain (McClenaghan *et al.* 2001), Regolith Exploration Geochemistry in Arctic and Temperate Terrains (Kauranne *et al.* 1992), Glacial Indicator Tracing (Kujansuu & Saarnisto 1990) and Application of Till and Stream Sediment Sampling to Mineral Exploration (Paulen & McMartin 2007). Although they span a period of more than 30 years, scientific papers by Shilts (1975, 1976, 1993), Coker & DiLabio (1989), DiLabio (1989), McClenaghan *et al.* (2000) and McClenaghan & Kjarsgaard (2007) continue to be informative overviews of till sampling methods in glaciated terrain and provide advice to explorationists.

DISPERSAL TRAINS

Glacial erosion of a distinct or mineralized bedrock source is deposited as till down-ice in a dispersal train or fan (DiLabio 1990a). Dispersal trains are hundreds to thousands of times larger than their bedrock source, making them easier targets to find, are thin in comparison to their length and width, have abrupt vertical and lateral edges, rise within till with increasing distance down-ice, and have

concentrations usually highest at the head of the train and decrease down-ice towards the tail (Fig. 2) (Miller 1984; DiLabio 1990a). The size and shape of a dispersal train are controlled by 1) size and erodibility of the bedrock source, 2) the direction of ice flow(s) and 3) the influence of topography on ice flow in both source and dispersal areas, which can trap dispersal trains in valleys or break them into disjointed segments in rough terrain. In areas affected by continental glaciation, a single ice flow typically produces a ribbon-shaped dispersal train as wide as the bedrock source (Fig. 3), whereas a change in ice flow direction reworks the ribbon into a fan shape (Fig. 4). Reversal of ice flow direction may produce a stellate or amoeboid dispersal pattern. Dispersal trains in glaciated mountainous terrain have higher length-to-width ratios as compared to continental ice sheets (Levson 2001).

Dispersal trains are detected using different size fractions of till: 1) geochemistry is used to detect element concentrations in the clay + silt (<0.063 mm) fraction, 2) indicator minerals are examined in the silt- to sand-sized (0.063 to 2.0 mm) fraction, and 3) specific bedrock lithologies are mapped in the pebble to boulder fractions. Once detected, a train may be traced back to its head and ultimately to its bedrock source. Sampling at spacing of 10s of kilometres will define continental-scale trains that are 100s of km long and consist of distinctive or abundant debris, such as the plumes of distinctive erratics and carbonate rocks dispersed south and southwest of the Hudson Bay Paleozoic carbonate platform (Shilts 1996) or Cr-pyropite from the Lac de Gras kimberlite field (McClenaghan & Kjarsgaard 2007). At the regional scale, 5 to 10 km spacing between samples may detect major lithological units, such as a mineralized belt or kimberlite cluster. Local-scale sampling, such as 1 km spacing, may detect a mineralized environment or the tail of a train, whereas detailed-scale spacing at 100s of metres may be used to find narrow trains (Fig. 3) or to test deposit-scale geophysical or geological targets.

In areas of thick glacial sediments, dispersal trains may be covered by younger till or by glaciolacustrine or glaciofluvial sediments. Buried trains can only be detected by subsurface till sampling using overburden drills (e.g. Geddes 1982; Bird & Coker 1987; Sauerbrei *et al.* 1987). Because dispersal trains generally rise with increasing distance down-ice (Fig. 2), anomalies can be expected at any depth within the till unit. Thus, entire till units should be sampled when drilling, not just the lowermost few metres on bedrock, in order to detect the rising tails of dispersal trains or trains within multiple till sequences.

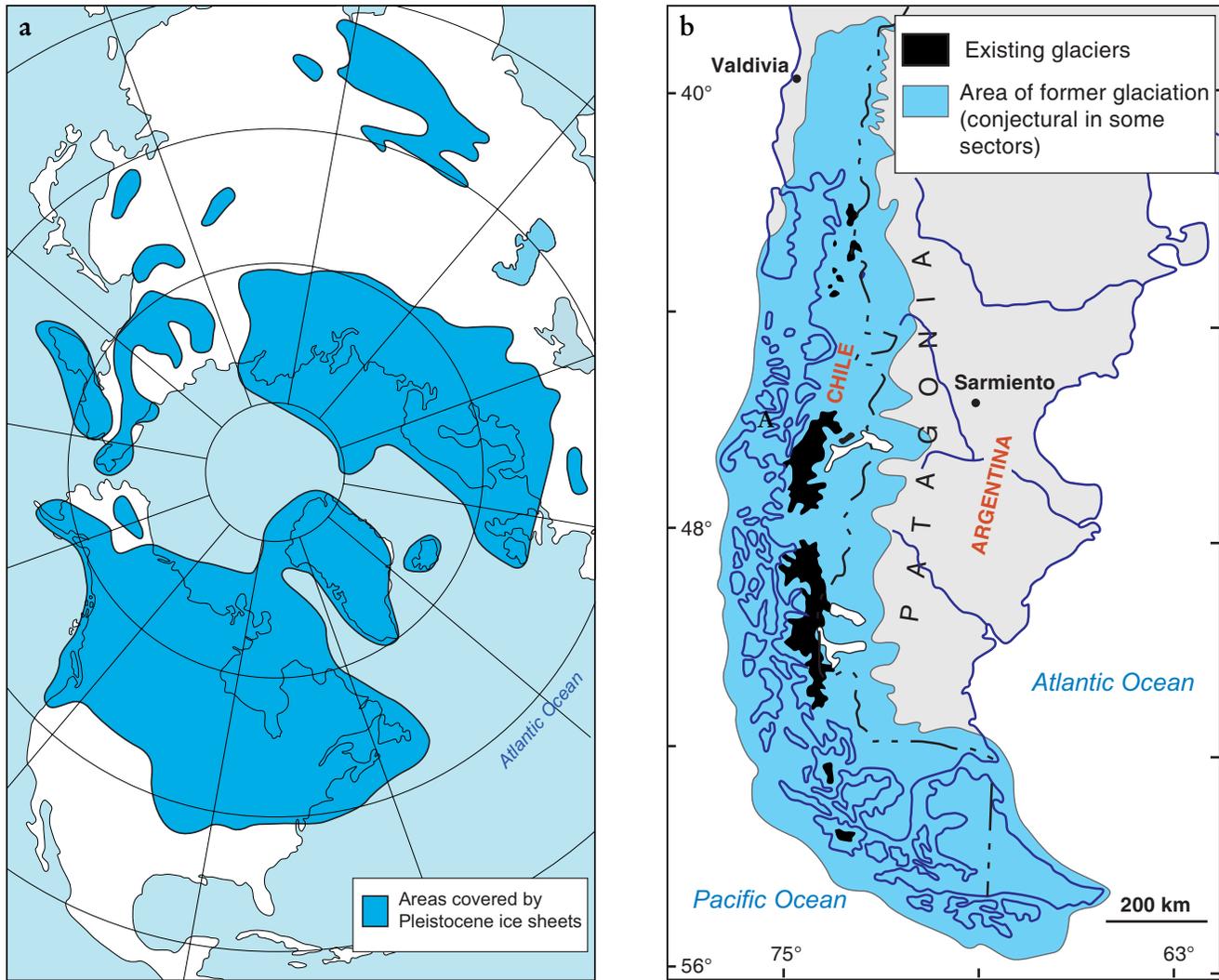


Fig. 1. Regions of the world covered by glaciers during the last glacial maximum (10,000 to 20,000 years ago) in (a) the northern hemisphere (from Ericksson 1992), and (b) southern South America (from Flint 1971).

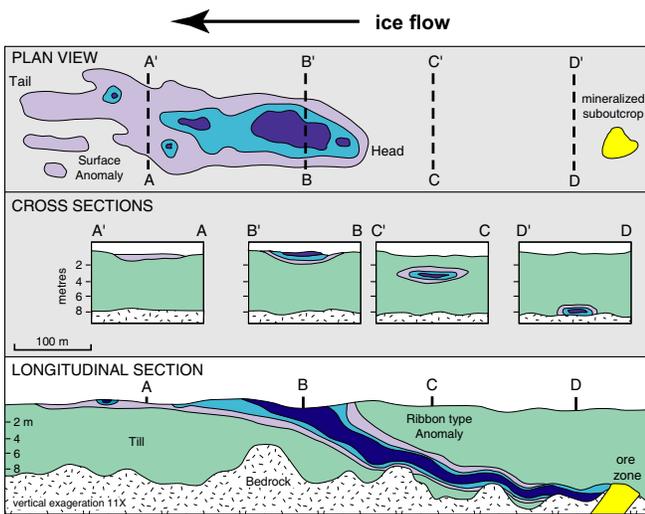


Fig. 2. Idealized model of a glacial dispersal train in till showing longitudinal, cross sections and plan views at four (A to D) selected distances down ice and the location of the head and tail of the train in relation to the bedrock source (modified from Miller 1984).

Ice flow history

To understand complex glacial dispersal trains, ice flow history must be determined from striations on bedrock, striated boulder pavements between tills, the orientation of elongate clasts in till (fabric) and glacial landforms. The final ice-flow phase indicated by glacial landforms, however, may differ from dominant glacial transport paths. Recognition of multiple ice-flow directions in specific areas and in the understanding of their significance to drift exploration in a specific region (e.g. Stea 1994; McMartin & Dredge 2005) is the key to successfully tracing dispersal trains up-ice to their source. For example, systematic measurement of ice-flow features across the Abitibi Greenstone Belt in central Canada (Fig. 5) indicates ice-flow patterns are far more complex (northwest, west, southwest and finally southeast) than previously assumed by companies exploring in the region in the early 1980s (Veillette & McClenaghan 1996).

FIELD METHODS

Till sampling strategies and procedures used in glaciated terrain have been described by Hirvas &

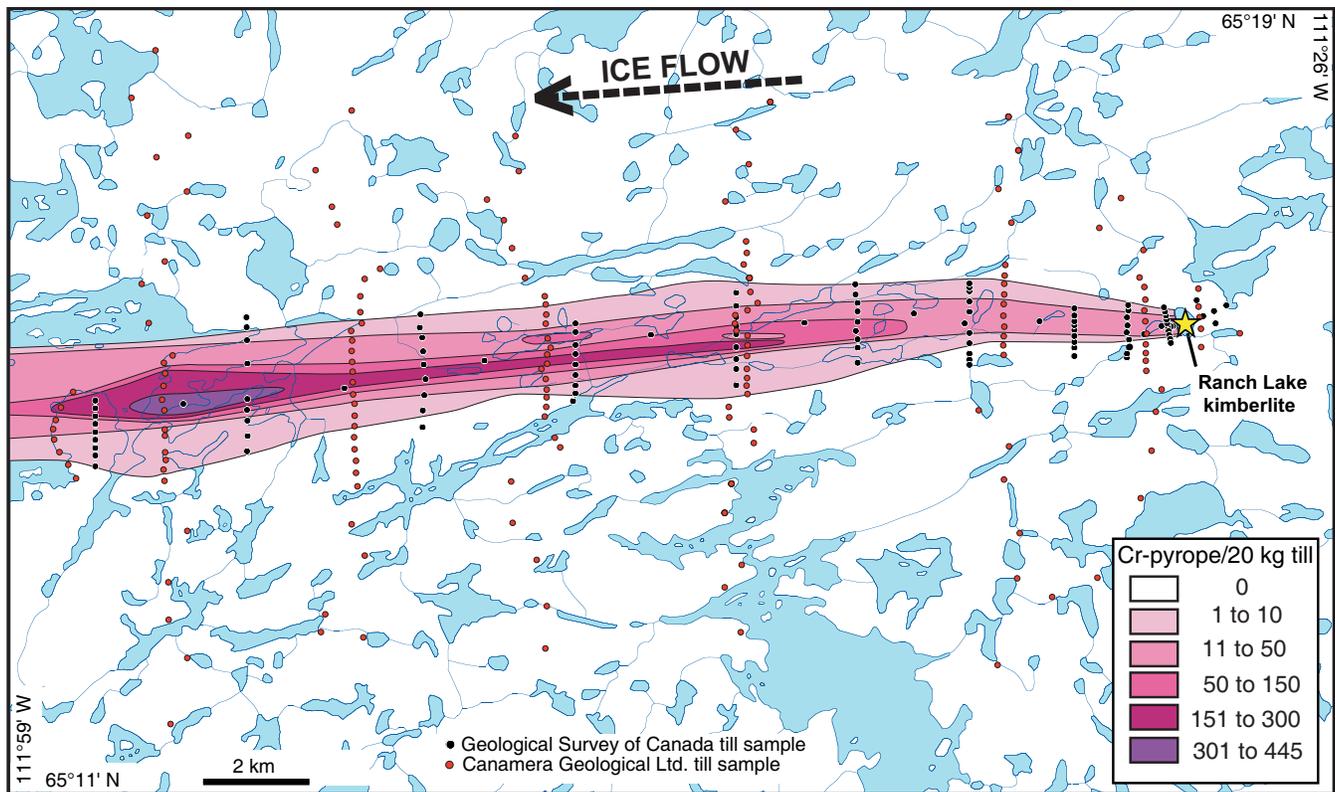


Fig. 3. Ribbon-shaped dispersal train trending westward from the Ranch Lake kimberlite, Lac de Gras as defined by Cr-pyrope concentrations in 20 kg till samples. The train was formed by a single phase of ice flow towards the west (modified from McClenaghan *et al.* 2002).

Nenonen (1990), Kauranne *et al.* (1992), Plouffe (1995), Levson (2001), McMartin & McClenaghan (2001) and McMartin & Campbell (2007). Till sampling grids are designed according to the scale of the survey, the predominant direction(s) of glacial transport, the expected size of the dispersed anomaly, the mineral commodity and the size of the deposit sought, and the analytical methods used to detect dispersal. A sampling grid is often used and can be either a regular grid with similar sample spacing in every direction or a grid where the sampling sites are situated along transverse lines perpendicular to the direction of ice movement, with sample spacing along lines much smaller than the space between lines (McMartin & Campbell 2007). Regular sampling grids are used in areas where ice-flow patterns are not well known or where the character of the buried sources are not well known, which is the case in most regional and reconnaissance-scale sampling surveys. Distribution and/or spacing of sample sites may be constrained by the extent and distribution of the surface till and accessibility. In areas of long distance glacial transport where elongate dispersal trains are expected, sampling lines may be more economical to delineate anomalies at all scales. At least 1 kg of till should be collected for geochemical analysis of the silt + clay (<0.06 mm) fraction and for archiving. For indicator mineral analysis, at least 10 to 20 kg of sandy till and 20 to 40 kg of clay-rich till are required (Averill 1990).

In areas of continuous permafrost, the depth of till sampling is often restricted by the thickness of the active layer,

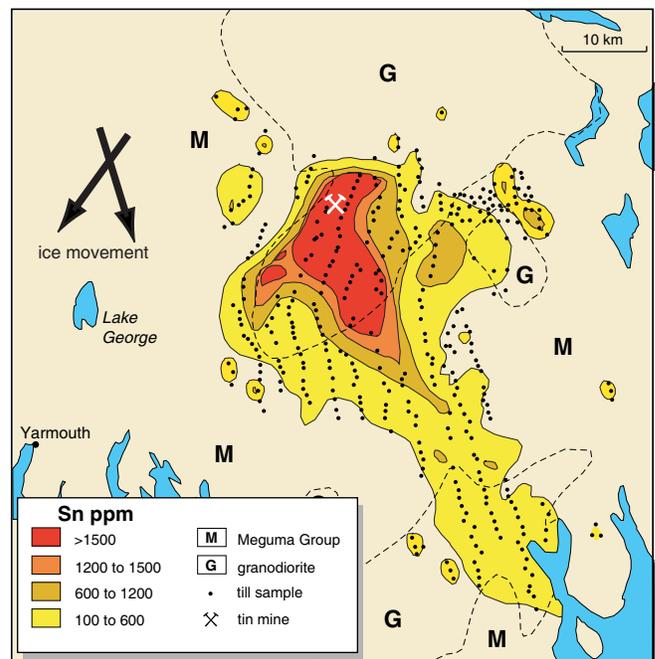


Fig. 4. Fan-shaped East Kemptville dispersal train, Nova Scotia, Canada showing concentration of tin in the sand-sized heavy minerals from till. The train has been shaped by two ice flows, one to the southwest and one to the southeast (modified from Stea *et al.* 1989).

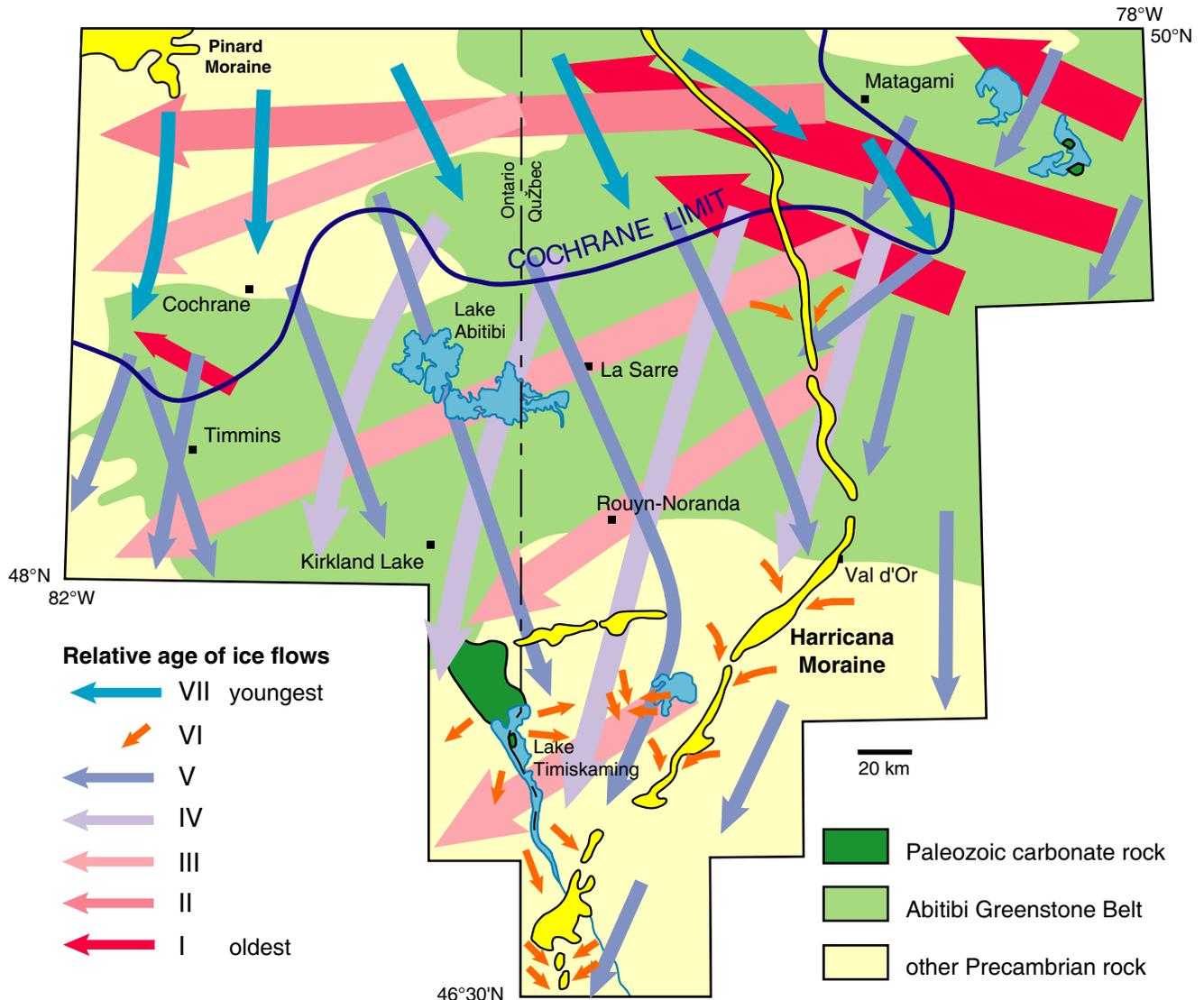


Fig. 5. Regional ice-flow patterns for the Abitibi Greenstone Belt, central Canada, which has been reconstructed from bedrock striations and glacial landforms by Veillette & McClenaghan (1996).

which commonly reaches 1 to 2 m in till during the maximum summer thaw period (McMartin & Campbell 2007). In these areas, freshly extruded till can be sampled from active mudboils (Fig. 6). In non-permafrost areas covered by thin till or where till occurs at surface, samples can be collected from holes that are dug using a hand-held shovel or backhoe excavator, or from sections along rivers, lakes or road cuts. Samples are collected close to the surface (0.5–1.0 m depth) below the B horizon, as the surface part of the till represents a wider source area. In local and detailed surveys, till sampling close to the bedrock surface is most effective because the composition of the till will closely resemble the underlying bedrock. Where glacial sediment thickness exceeds approximately 5 m, drilling is required to reach locally derived till below the surface, to characterize the till stratigraphy and to determine lateral and vertical variations in till geochemistry (Coker & DiLabio 1989). Portable drills are useful for recovering small till samples where boulders do not intervene. Auger and percussion drills recover small till and rock samples. Diamond drills

will core hard, fine-grained till but sand intervals are lost. Reverse circulation drills recover a slurry of till cuttings up to 1 cm in size down to and into bedrock (Averill 1990; McMartin & McClenaghan 2001). Most clay-sized material and approximately 30% of the silt-sized material in till is lost by this drilling method and vertically adjacent samples may contaminate one another in the drilling fluid. The more expensive rotasonic drilling method recovers a 9 cm diameter continuous core of till, through boulders and into bedrock, enabling detailed geology with no loss of fine-grained material (McMartin & McClenaghan 2001). For all drilling methods, brass fittings, diamond drill bits, and tungsten-carbide drill bits can contaminate the heavy mineral fraction of till, and drilling grease can contaminate the finer (<0.063 mm) till fractions with Zn, Pb and Mo (Averill 1990).

LABORATORY METHODS

Heavy minerals found in till are often useful ‘indicators’ of the presence of a particular rock type or mineral

deposit. These minerals should be present in sufficient quantities to be easily detected, are visually and chemically distinct, silt to sand sized, are sufficiently dense to be concentrated by gravity methods, and have survived preglacial weathering and subsequent glacial transport (Averill 2001; McClenaghan 2005). Indicator minerals include native gold, platinum group minerals (PGM), sulphides, uvarovite, scheelite, cassiterite, zirconosilicates, minerals from kimberlite, uranium-bearing minerals and minerals from base metal deposits (e.g. Aumo & Salonen 1986; Peuraniemi 1990; Peltonen *et al.* 1992; Morris *et al.* 1997; McClenaghan & Kjarsgaard 2007). Heavy mineral concentrates are prepared from large (10-40 kg) till samples to concentrate indicator minerals.

Prior to indicator mineral processing, small 500 g subsamples are often removed from the bulk till samples for geochemical analysis of the silt+clay fraction and archiving. The remaining material is disaggregated and the gravel fraction (> 2 mm) is removed for lithological analysis (pebble counts). The < 2 mm fraction is then preconcentrated using density methods either in the field or in the lab, depending on shipping costs and time constraints (e.g. jig, table, spiral, dense media separator, Knelson Concentrator, pan). Screening to recover the medium to very coarse sand-sized fraction, or rejection of non-paramagnetic minerals, principally quartz and feldspar, may be used instead of density preconcentration if recovery of precious and base metal grains is not a priority. Final density concentration is commonly completed using heavy liquids such as methylene iodide or a Magstream® separator using a threshold of specific gravity 3.2 g/cm³ to ensure more complete recovery of the kimberlite indicator minerals Cr-diopside and forsteritic olivine (McClenaghan & Kjarsgaard 2007). The ferromagnetic fraction is removed using a hand magnet or roll separator, weighed and either examined or stored. The non-ferromagnetic heavy mineral concentrate is most commonly examined for indicator minerals. Indicator minerals are selected during a visual scan, in most cases, of the 0.25 to 0.5 mm (medium-sand) fraction. Depending on regional bedrock mineralogy, paramagnetic sorting may be required, especially for the 0.25 to 0.50 mm till fraction, in order to reduce the volume of material to be scanned. Indicator minerals are visually examined (shape, surface features) to obtain information on glacial transport directions and distances, and chemically analyzed to confirm their identification and to provide insight into the character and potential value of their bedrock source. For example, kimberlite indicator minerals include Cr-pyrope (Fig. 3), eclogitic garnet, Cr-diopside, Mg-ilmenite, Cr-spinel, and forsteritic olivine. Microprobe analysis of these grains provides important information about the composition of the kimberlite and mantle sources and a kimberlite's diamond potential (McClenaghan & Kjarsgaard 2007).

Gold and platinum group minerals (PGM) may be panned from a heavy mineral concentrate to determine their abundance, morphology and for compositional analysis (e.g. Nikkarinen 1991). The degree of rounding, polishing and bending of the gold grains in till can provide information about glacial transport distance. DiLabio (1990b)

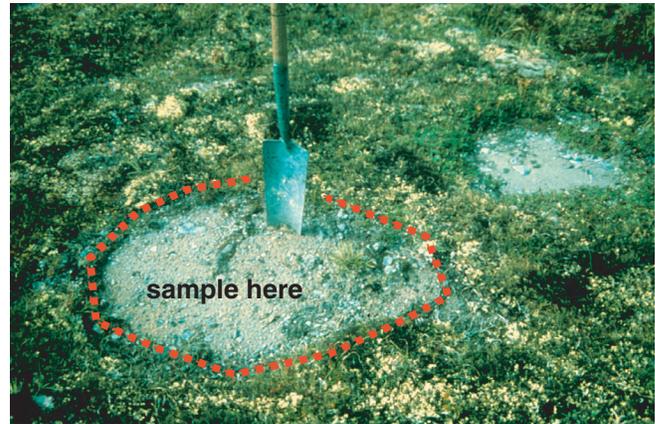


Fig. 6. Photograph of an active mudboil (dashed line) developed in till in the permafrost terrain of northern Canada showing freshly extruded till in the centre surrounded by vegetation and stone rims (from McMartin & McClenaghan 2001).

proposed a classification scheme (pristine-modified-reshaped) for describing shapes and surface textures of gold grains related to glacial transport distance.

Similar methods are used to recover indicator minerals from glacially dispersed cobbles and boulders, with the exception that they often require crushing to 2 mm prior to sample processing.

Samples for geochemical analysis of the silt+clay (< 0.06 mm) fraction are dried at < 40° C to prevent the loss of volatile elements such as Hg, and sieved using stainless steel or nylon screens to recover the fine fraction. Averill (1990) noted the tendency for gold grains to pass through sieves preferentially, thus a complete screening of a split, rather than the rapid recovery of a small portion, is advisable. Geochemical methods commonly used to analyze till are summarized by Hall (1997), Kauranne *et al.* (1992), and Lett (1995). Most exploration programs and regional geochemical surveys use strong partial digestions such as aqua regia, although both total and partial digestions or instrumental neutron activation analysis (INAA) have been used for some regional surveys to investigate a broad range of commodity potential (e.g. Lahtinen *et al.* 1993). PGE and Au are often determined by fire assay/ICP-MS. Uranium and Th are often determined by 4-acid digestion/ICP-MS. Five to 15% of each analytical batch should comprise in-house and certified geological reference materials, as well as field and post-preparation duplicates to monitor analytical accuracy and precision (Smeets this volume).

DATA PLOTTING AND INTERPRETATION

To evaluate anomalies and plan follow up strategies, till geochemical and/or indicator mineral data may be plotted on maps using proportional dots or contouring (Fig. 7) and interpreted when these are combined with ice-flow information, bedrock geology, geophysical data, and topography. Subsequently, more rigorous multivariate data interpretation can be carried out using methods described by Grunsky (this volume).

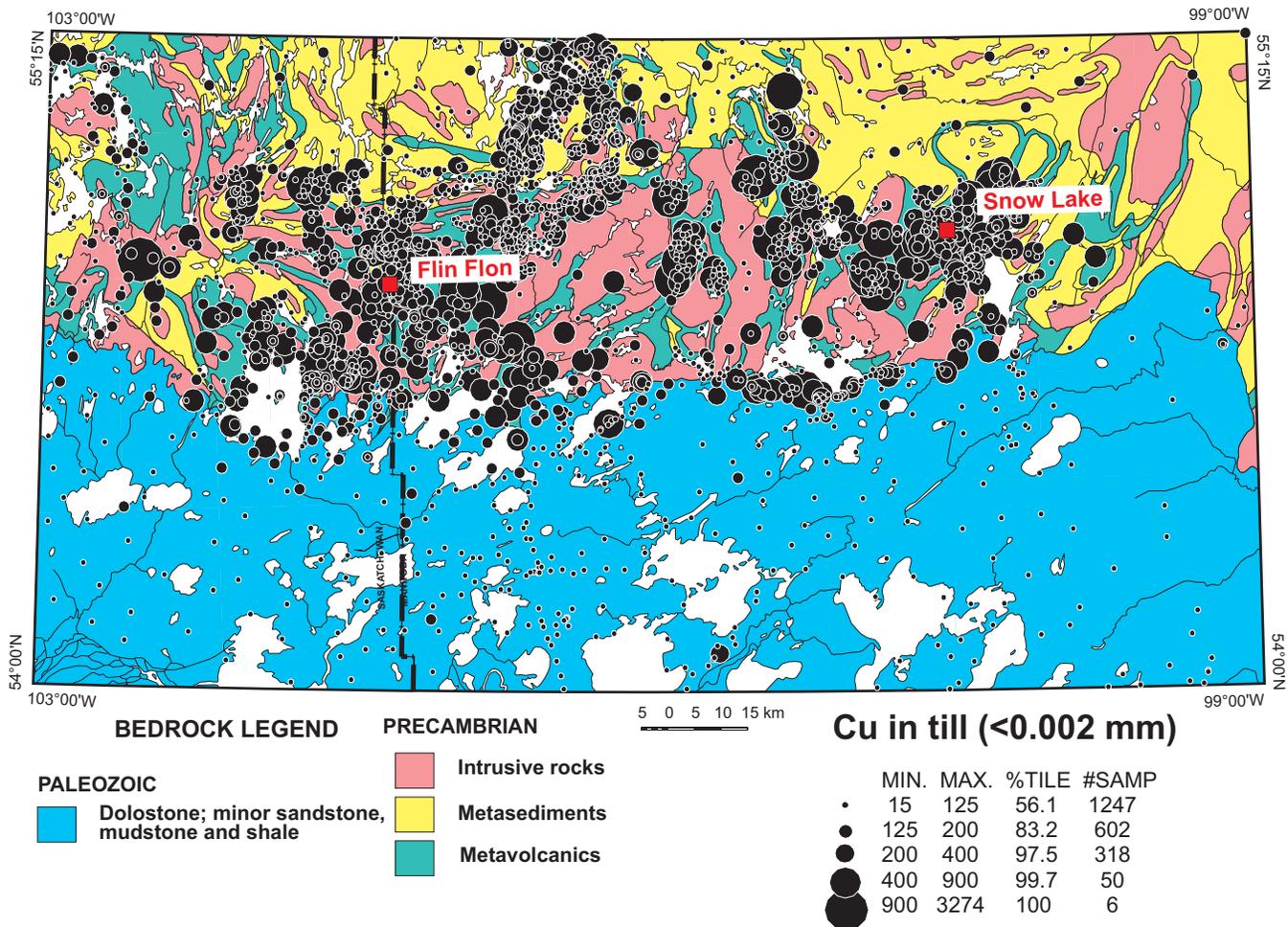


Fig. 7. Regional distribution of Cu (ppm) in the <0.002 mm fraction of till in the Flin Flon area, northern Manitoba (from McMartin *et al.* 1996).

EXPLORATION CASE HISTORIES

Numerous case histories and regional till surveys have been conducted in support of exploration for a broad range of commodities over the past 50 years, including Au, PGE, Sn, REE, U, base metals and diamonds. Published reports and scientific papers provide useful insights into various options for sampling techniques, sample spacing and weight, processing methods and analytical techniques. Many of these publications are listed in the *Exploration 87* and *97* conference proceedings (DiLabio & Coker 1989; McClenaghan *et al.* 1997). Gold exploration in glaciated terrain has used both gold grain (indicator minerals) and till geochemical methods for over 100 years (e.g. Prest 1911; McClenaghan 2001) and as a result a significant volume of the drift prospecting literature relates to gold exploration. Results from numerous case studies (e.g. Averill & Zimmerman 1987; Saarnisto *et al.* 1991; Huhta 1993; Sibbick & Fletcher 1993; Bird & Coker 1987; Brereton *et al.* 1988; Chapman *et al.* 1990; McClenaghan 1999) as well as regional till surveys have been published (e.g. Bernier & Webber 1989; Hartikainen & Nurmi 1993; McClenaghan *et al.* 1998).

Tracing of mineralized float boulders has contributed to significant base metal discoveries in the past 100 years,

including the deposits at Bathurst (Dreimanis 1958), Buchans (Klassen & Murton 1996) and Outokumpu (Aumo & Salonen 1986). The application of till geochemistry to base metal exploration is well established and has 50+ year history (e.g. Ermengen 1957; Driemanis 1960; Fortescue & Hughes 1965; Shilts 1975; DiLabio 1981; Hoffman & Woods 1991; Kaszycki *et al.* 1996; Parkhill & Doiron 2003). In recent years, a suite of sulphide, oxide and silicate indicator minerals has been identified that can significantly increase the effectiveness of till sampling for base metal exploration (e.g. Averill 2001, 2007).

A few publications describe the application of till geochemistry to PGE exploration (e.g. Coker *et al.* 1990, 1991; Cook & Fletcher 1994; Bajc & Hall 2000; Tardiff 2000; Searcy 2001). Until very recently, indicator minerals in till were not used for PGE exploration, however case histories reported by Kojonen *et al.* (2005), Averill (2007), Ames *et al.* (in press) and Barnett & Averill (in press) demonstrate that specific PGE, oxide and silicate minerals recovered from till can be useful indicators. Diamond exploration in glaciated terrain differs from precious or base metal exploration in that indicator minerals (e.g. Fig. 3) are the prime methodology, instead of till geochemistry (Golubev 1995; Morris & Kaszycki 1997; McClenaghan & Kjarsgaard

2001, 2007; Lehtonen *et al.* 2005). Till geochemistry can assist diamond exploration and a few recent case histories document kimberlite geochemical signatures in till (McClenaghan *et al.* 1999, 2002, 2004; Wilkinson *et al.* 2001).

Numerous published reports and scientific papers dealing with drift exploration for U exploration were published in the 1970s and 1980s, with most focused on tracing glacially dispersed U-rich boulders (e.g. Lundberg 1973; Ramaekers *et al.* 1982; Steele 1988; Hirvas & Makinen 1989; Kirchner & Tan 1994; Earle 2001). Geddes (1982) described the use of till geochemistry and indicator minerals to explore for U deposits. Iron Oxide-Copper-Gold (IOGC) deposits may also contain significant contents of U, as well as base metals and Au. Recognition of the IOGC deposit type and its genesis is relatively recent compared to other mineral deposit types. As a result, no exploration case histories using till geochemistry and indicator minerals have been published for this deposit type. Corriveau *et al.* (in press), however, suggest a suite of potential indicator minerals that may prove useful for till sampling in glaciated terrain: oxides (hematite, magnetite, rutile, spinel, uraninite); silicates (allanite, amphibole, epidote, garnet, titanite, tourmaline, vesuvianite, zircon); phosphates (monazite, xenotime); and sulphides (bismuthinite, cobaltite). Till geochemistry may also prove useful for exploration of IOGC deposits, including the use of pathfinder elements such as U, Au, Bi, and Co.

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Drainage sampling in British Columbia — stream sediments, lake sediments, water and heavy mineral concentrates

Ray Lett

Geological Survey, British Columbia Ministry of Energy, Mines & Petroleum Resources, 5th Floor, 1810 Blanshard Street (PO 9333 Stn Prov Govt), Victoria, British Columbia, Canada V8W 9N3 (e-mail: Ray.Lett@gov.bc.ca)

Government agencies and mining companies commonly use drainage sediment geochemistry for evaluating the mineral resources over a large area based on the premise that the sediment chemistry and mineralogy reflect the bedrock and surficial geology of the drainage catchment area upstream from the sample site. Fluvial sediment forms by the physical and chemical weathering of bedrock within the catchment basin. In the absence of mineralization, the sediment geochemistry reflects normal or background element concentrations typical of the source bedrock. Mineralized bedrock, if present, will be revealed by the presence of elevated metal and/or indicator mineral contents in sediment. Ideally, the metal content of sediment collected at intervals along a stream channel will display both a peak value close to the entry point of the metal into the drainage basin and a downstream asymptotic decay curve that reflects dilution of the mineralized material. This dilution is caused by barren bedrock, surficial material or fluvial material. At some point along the dilution curve, the anomalous geochemical signal of the mineralization will merge with the geochemical background. While this simple model describes element dispersion in the sediment weathered from a small catchment basin, it is less reliable for predicting dispersion from a larger catchment basin where the stream becomes decoupled from the surrounding valley slopes and the sediment is less representative of bedrock geochemistry (Fletcher 1997). Drainage anomaly length is also constrained by the point where anomalous values can be reliably distinguished from the geochemical background. Anomaly strength (i.e. contrast) is the ratio of the peak value to background.

The mountainous terrain and well developed drainages typical of British Columbia make it a region especially suited for using stream sediment geochemistry to find new mineral resources. As a result, the British Columbia Geological Survey started a regional stream sediment and stream water geochemical survey (RGS) in 1976 as part of the Geological Survey of Canada National Geochemical Reconnaissance (NGR) Program. This survey now covers about 70 percent of the province with field and analytical data from the collection and analysis of over 50 000 stream sediment, lake sediment and surface water samples.

The main objective of the RGS is to identify regions of high mineral potential based on elevated element concentration in drainage sediment. The survey has also created a high-quality, seamless geochemical database that can be used for mineral exploration, environmental monitoring and land use evaluation. Much of the applied research by government and non-governmental agencies and universi-



Fig. 1. Stream sediment and water collection during a helicopter-supported regional geochemical survey in northwestern British Columbia. One sampler is collecting sediment from a point bar that is sufficiently large enough to allow a field duplicate to be easily taken. The second sampler is taking a water sample and will record information about the site on a field form.

ties has focused on understanding how fluvial processes, surface geochemistry, catchment basin morphology and geology contribute to the formation of a stream sediment anomaly. The objective of the research is to improve drainage survey design. For example, the basic strategy of the British Columbian RGS is to collect stream sediment samples at an average density of 1 sample per 13 km² from active first- or second-order streams approximately 60 m upstream from a confluence, a possible source of contamination (e.g. forestry, mining, residential) or a tidal influence if the stream flows into the ocean. Since the survey aims to detect elements with a range of physical and chemical properties (e.g. density, solubility), the collected sample is ideally of fine-textured sand and silt collected from a relatively low-energy fluvial environment (Fig. 1). While this survey strategy can generally outline regions of higher mineral potential, it is less effective for detecting individual mineral deposits or where the sediment is less representative of the source area, such as in low-relief terrain or in larger catchment basins. Modifications to survey design have been made in different areas of British Columbia to improve the ability of stream geochemistry for detecting mineralization, the simplest of which is increasing sample density. This approach has helped identify primary geochemical zones surrounding massive sulphide deposits south of Terrace, British Columbia (Alldrick & Jackaman 2002).



Fig. 2. Stream sediment sampling in a high-energy stream in northwestern British Columbia. The samplers are returning from what is clearly a difficult collection from a mid-stream bar. This site would be ideal for collecting a bulk sample for heavy mineral concentration.

Sampling moss-captured sediment solved the problem of finding insufficient fine-grained sediment sample in torrential streams, which are typical of Vancouver Island where annual rainfall exceeds 100 cm. High-density minerals, such as Au, are also preferentially captured by moss, thereby improving anomaly contrast. However, the mechanism of sediment transport and accumulation by moss is still uncertain and warrants more research (Matysek & Day 1988). In northwestern and central British Columbia, analyzing a heavy mineral concentrate (HMC) prepared from a bulk sediment sample collected at a high-energy stream site improves the ability of geochemical surveys to detect mineralization at a lower sample density (Fig. 2). Concentrate mineralogy and mineral grain shape can also aid in estimating the proximity of an anomaly to the source (Lett & Friske 2006). Drainage systems are poorly developed, but lakes are common in low-relief areas, typical of central British Columbia, and therefore lake sediments are collected as an alternative to stream sediments (Cook & McConnell 2001). Stream and lake water samples collected routinely at the same time as sediment are used to

measure such parameters as water pH and, in some areas, the dissolved metal content of the water.

The systematic recording of information about the sample site is important for data interpretation. Field forms are designed for helicopter-supported stream and lake surveys where careful collection and accurate recording of field information must be balanced against maintaining survey efficiency. Quality control is vital in order to maintain a high-quality database. The RGS quality-control scheme monitors sampling and analytical variability by randomly inserting field and analytical duplicate samples and control reference samples into each batch of 20 samples collected. The analytical duplicate and control reference samples are inserted after sample preparation. Field duplicates are two separate samples collected at the same site, generally several metres apart from sediment that has similar characteristics. The minus 80-mesh fraction of sediment samples is routinely analysed for a range of elements by a combination of instrumental neutron activation (INAA), aqua regia digestion followed by inductively coupled plasma mass spectrometry (ICP-MS), loss on ignition (LOI) at 500°C, and specific ion electrode for flouride. Samples with anomalous Au concentrations are routinely checked by a second Au analysis.

While drainage survey design, quality control, sample preparation and sample analysis will be discussed in this workshop presentation, sampling techniques, illustrated by case histories, will be described in more detail.

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Plants: The ultimate selective leach

Colin E. Dunn

Consulting Geochemist, 8756 Pender Park Drive, Sidney, British Columbia, Canada V8L 3Z5
(e-mail: colindunn@shaw.ca)

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INTRODUCTION

Plants are capable of accumulating all chemical elements. Once we can identify those species and those parts of species that are most consistent in accumulating elements of relevance to a particular type of mineral deposit, we can apply this valuable geochemical technique to the exploration for metals concealed beneath a wide range of different types of cover.

METAL UPTAKE, ACCUMULATION AND BARRIERS

Each species of plant has a different requirement for, and tolerance to, the full spectrum of chemical elements. Some plants are capable of accumulating metals to extraordinary concentrations – these are known as ‘hyperaccumulators’. An extreme example is the ‘Sève Bleue’ (*Sebertiana spp.*) from New Caledonia that has sap containing up to 11% Ni, fresh weight.

The most basic of life forms are bacteria and fungi. Table 1 shows experimental data on the phenomenal concentrations of metals within these primitive species.

The data in Table 1 were derived from laboratory experiments. In the natural environment, it has been established that macrofungi can accumulate high levels of metals from soils that contain background levels of metals. A few examples of concentrations in dry tissue are given in Table 2.

From data such as these, it is apparent that there are some key stages of metal acquisition that take place in the micro-environment of plant roots, where organic acids can have a pH as low as 1 at the interface between the root surfaces and the surrounding substrate (soil, water and rock).

It is probable that all plants *require* mycorrhizal fungi on their root surfaces to effectively transfer nutrients into their structures. This micro-environment can be highly corrosive. Furthermore, roots will take the path of least resistance and first accept elements in gaseous form, then those in solution, then seek out additional requirements by selectively extracting labile elements, i.e., those loosely bonded to soil surfaces, such as the amorphous manganese oxide coatings to which metals are known to be adsorbed and which form the basis of various selective extraction techniques applied to soils. Once the above elemental sources have been exhausted, then further requirements of the plants will be met by attacking the less labile components of the substrate – the crystalline phases of soils and bedrock.

Many metals impact cell physiological function, altering physicochemical properties of the cytoplasm, the ‘poros-

Table 1. Concentrations of metals in primitive life forms (experimental data) (from Dunn (2007), modified after Lepp (1992)).

	Bacteria	Conc. %	Fungi	Conc. %
Ag	<i>Thiobacillus ferrooxidans</i>	35	<i>Rhizopus</i>	5.4
Cd	<i>Zooglea ramigera</i>	40	<i>Rhizopus</i>	3
Co	<i>Zooglea sp.</i>	25		
Cr			<i>Rhizopus</i>	3.1
Cu	<i>Zooglea ramigera</i>	40	<i>Rhizopus</i>	1.6
Hg			<i>Rhizopus</i>	5.8
Ni	<i>Zooglea sp.</i>	13		
Pb	<i>Micrococcus luteus</i>	35	<i>Rhizopus</i>	10.4
Zn			<i>Rhizopus</i>	2

ity’ of the trans-plasma membrane, and consequently ion fluxes. These impacts affect various activities, such as transport function, cytoplasm enzymes, and metal tolerance mechanisms. The net result is the creation of **barrier mechanisms** to the uptake of elements by plants (Fig. 1; see Kovalevski 1987 for more detail).

Regardless of the characteristic curve, uptake is by one of two mechanisms:

- **Active**, requiring energy by the plant to get the element,
- **Passive**, requiring no energy expenditure on the part of the plant.

Table 2. Average concentrations of selected elements in common plants compared to highest concentrations recorded in macro-fungi growing in soils containing background levels of these elements (from Dunn (2007), modified after Lepp (1992) with supplementary data).

	Average Plant Concentration (ppm)	Highest Fungal Concentration (ppm)	Genus	Common Name
Ag	0.02	1253	<i>Amanita</i>	Death-cap mushroom
As	0.1	427	<i>Amanita</i>	Death-cap mushroom
Au	0.2 ppb	2250 ppb	<i>Lepiota</i>	‘Shaggy-stalked parasol’
Cd	0.05	300	<i>Amanita</i>	Death-cap mushroom
Cu	5	469	<i>Amanita</i>	Death-cap mushroom
Hg	0.02	80	<i>Agaricus</i>	mushroom
Sb	0.1	1423	<i>Chalciporus</i>	Peppery bolete
Se	0.02	55	<i>Boletus</i>	Edible mushroom
V	0.5	700	<i>Amanita</i>	Death-cap mushroom

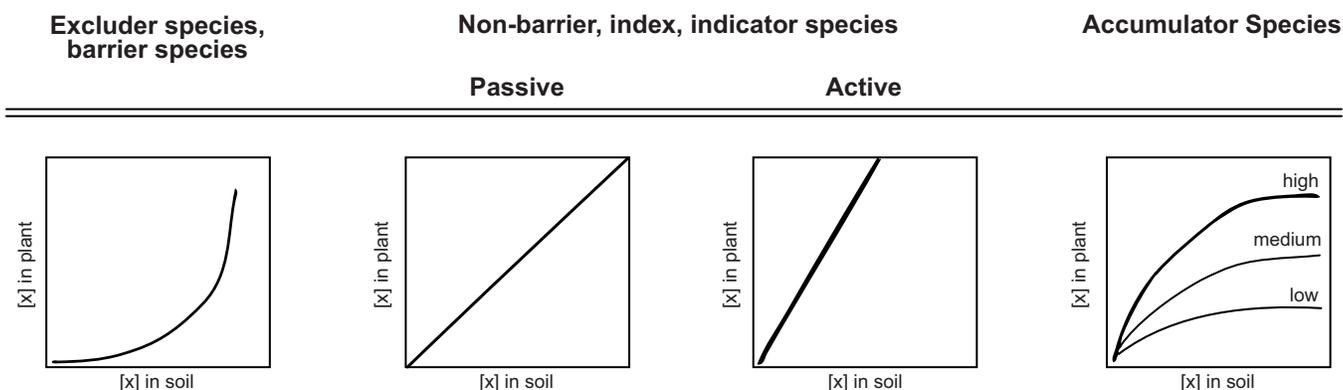


Fig. 1. Metal uptake by plants exhibiting different barrier mechanisms.

ELEMENT VARIATIONS AMONG SPECIES

Each plant species establishes a different barrier to the uptake and translocation of elements. As an example, Table 3 shows concentrations in ash of several elements in a variety of species, all collected within a radius of 5 m from an undeveloped occurrence of gold mineralization.

ELEMENT VARIATIONS AMONG TISSUES WITHIN A PLANT

An individual plant is typically highly selective in its extraction and distribution of elements throughout its structure. Table 4 is an example of a single Lodgepole Pine rooted in tourmalinized massive sulphide. Note that some elements are concentrated in the roots, whereas others are concentrated in the treetop.

In short, plants are complex structures that apply extraordinarily sophisticated mechanisms to select those elements that they require for efficient metabolic function, whilst tolerating other elements and sequestering them out of harm's way, and actually excluding other elements that could have significant toxic effects. Each species of plant is unique in its chemical composition and, therefore, its value for biogeochemical exploration. We need to unravel the mysteries of the plant kingdom in order to take full advantage

of the remarkable amount of information on the substrate that they have to impart.

SELECTIVE EXTRACTION FROM THE SUBSTRATE

A good positive correlation between plant and soil chemistry may not always occur, because a plant integrates the geochemical signature of a large volume of soil. Where there is a positive correlation, it is not usually with the surface sediments. Table 5 shows correlation coefficients (r) between Au and As in bark ash and their concentrations in different soil horizons. The data show that for both the Douglas fir and the Engelmann spruce the correlation between the bark and C-horizon soil is considerably stronger than between the bark and other soil horizons. The implication is that the root systems of these trees have absorbed Au and As, mostly from the C-horizon, and transferred these metals to the trees' extremities.

Commonly, in areas of exotic overburden (e.g. glacial till, loess) a biogeochemical anomaly is not derived from the exotic overburden, but from an underlying 'critical mass' of mineralization, i.e., the biogeochemical anomaly is closer to the source of mineralization.

Table 3. Distribution of elements among tissues of common species from a single location near Au mineralization at Doctor's Point, Harrison Lake, southern British Columbia.

Tree	Tissue	Au ppb	As ppm	Mo ppm	Sb ppm
Douglas fir	Twig	35	1600	<1	1
Douglas fir	Needle	23	130	<1	2
Douglas fir	Bark	53	250	<1	8
Western	Twig	200	710	<1	8
Western Red Cedar	Twig	7	11	4	1
Western Red Cedar	Needle	5	6	<1	1
Western Red Cedar	Bark	8	12	<1	1
Western Cedar	Bark	31	46	<1	11
Red Alder	Twig	14	4	57	0.5
Red Alder	Bark	<5	4	4	0.3
Douglas Maple	Twig	12	6	4	1

Table 4. Concentrations of several elements in the ash of different tissues from a single Lodgepole pine rooted in massive sulphide-bearing tourmalinite near the Sullivan Pb/Zn mine, Kimberley, southern British Columbia.

	Top Stem	Lower Twigs	Outer Bark	Roots
Ag ppm	1	3	13	77
As ppm	9	9	52	190
Au ppb	<5	<5	20	19
B ppm	1150	400	260	580
Ba ppm	48	310	1000	500
Cd ppm	52	95	143	135
Cr ppm	6	18	18	10
Cs ppm	110	9	5	38
Cu ppm	400	180	158	190
Mn ppm	13000	27000	4230	63000
Ni ppm	180	22	14	24
Pb ppm	150	2950	4900	16400
Sb ppm	2	3	13	5
Zn ppm	6100	7350	5700	12800

Table 5. Correlation coefficients (r) between Au and As in bark ash and underlying soil horizons: near the Nickel Plate Au mine, Hedley, southern British Columbia.

Soil Horizon	Douglas Fir Bark n = 12		Engelmann Spruce Bark n = 13	
	Au	As	Au	As
Forest Litter	0.13	0.1	0.48	0.58
A - Horizon	0.63	0.63	0.65	0.65
B - Horizon	0.6	0.55	0.79	0.8
C - Horizon	0.76	0.64	0.9	0.88

SAMPLE COLLECTION

The first step in preparing to conduct a biogeochemical survey is to look for the most widespread species within the area of interest, then determine from published information if it is likely to be informative (i.e. which parts accumulate the elements of interest). If published information is not available, an orientation survey should be conducted. The survey area should always be reconnoitred prior to sample collection to assess which species are dominant.

There are only a few additions required to the usual field equipment of the geologist:

- a pair of pruning snips, preferably Teflon-coated and anvil type rather than the scissor type;
- a pair of leather gloves for the tough thorny species typical of many arid environments;
- for bark surveys, a paint scraper (or hunting knife) and either a dustpan or paper bag for collecting the flakes of bark; 'kraft' soil bags are suitable for bark samples;
- fairly large bags for twigs (about 20 x 30 cm) made either of non-fungicide-treated cloth (preferable) or heavy duty coarse brown paper if conditions are dry (e.g. 16 lb [7 kg] hardware bags); a roll of masking tape to close paper bags;
- a large back pack, because if twigs are the chosen sample medium the volume of material collected soon becomes quite large (but not heavy). For large surveys bring along some heavy duty orange garbage bags - these can be left at the ends of cut lines to be picked up at the end of the day;

- a x10 hand lens to help in species identification, and in counting growth rings on twigs.

As a basic premise, the same type of plant tissue should be collected from the same species of tree or shrub at all sample stations, unless there is prior knowledge that no significant chemical differences occur between two or more species. Most heavy metals, especially the precious metals, concentrate in the extremities of plants, i.e., the outer bark, the twig ends, and plant tops. Laboratory studies by Girling & Peterson (1978) using radioactive gold have shown that gold also accumulates in the tips of leaves. Recent hydroponic work by CSIRO in Australia has demonstrated Au accumulation near the outer part of twigs, coating Ca-oxalate crystals (M. Lintern pers. comm. 2007). Many metals collect in the roots but these are impractical to collect. An effective biogeochemical survey needs to be simple and practical (see Table 6).

SAMPLE PREPARATION AND ANALYSIS

Samples from dusty areas should be washed. Samples from many areas of the northern and temperate forests need not be washed because they are regularly rinsed by rain, and washing can remove some elements. Table 7 shows results of washing sagebrush collected from an area of dry temperate climate, with little dust, in southern British Columbia. Clearly, in this case there is no advantage in washing the samples. The situation requires an on-site judgement call.

Once the moisture has been removed (air or oven dry), it is a simple process (for most species) to remove the foliage from the twigs by pummeling the bag, then removing the foliage. Hands should be thoroughly washed and *rings* removed (to avoid precious metal contamination) before doing this. This separation procedure is always advisable because, as noted above, the chemistry of the different tissue types is not the same, and the density of foliage may vary from one sample to the next (therefore the ratio of twig to foliage will vary, providing the potential for false anomalies).

Bark needs no further separation, since any separation of inner from outer bark should have been performed in

Table 6. Basic rules to be applied at each sampling station when conducting a biogeochemical survey.

Basic Rules	Reason
1. Collect same species.	Every species has a different chemical composition, and trace element requirements and tolerances.
2. Collect same plant organ.	Each plant organ has a different capacity to store trace elements.
3. Collect same amount (i.e. age and diameter) of growth, from the same horizontal area of a tree or shrub, preferably from all sides.	There are chemical variations along and across a twig. Heterogeneity in bark scales can be minimised by scraping from around the tree.
4. Try to collect samples from plants of similar age and appearance.	This is the basic inter-site consistency that is required for any geochemical sample medium.
5. If living tissue is the selected medium, collect at same time of year (preferably conduct a survey in 2-3 week period).	For some elements there are significant seasonal changes in plant chemistry.
Dead tissue (e.g. outer bark) can be collected at any time.	No appreciable seasonal change.
6. Do not return to a previously sampled tree or shrub and expect to obtain exactly the same analyses.	This is unrealistic in view of the heterogeneity of element distributions and seasonal variations in composition (and to a lesser extent annual variations). Be satisfied if an anomaly is the same order of magnitude.

Table 7. Effects on the chemical composition of different plant tissues of thorough washing in distilled water (1 hour in ultrasonic bath).

	Sagebrush Twig		Sagebrush Leaf		Lodgepole Pine	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed
Au (ppb)	270	294	279	267	293	298
As (ppm)	100	95	50	64	150	160
Ba (ppm)	330	300	140	150	590	590
Co (ppm)	4	4	2	2	11	10
Fe (ppm)	6300	5500	2500	2800	17600	17200
K (%)	26.3	24.3	17.4	13.2	3.2	1.5
Mo (ppm)	11	10	9	11	2	3
Sb (ppm)	1.7	1.5	0.7	1.1	4.2	4.3
Zn (ppm)	570	550	530	610	1300	1400

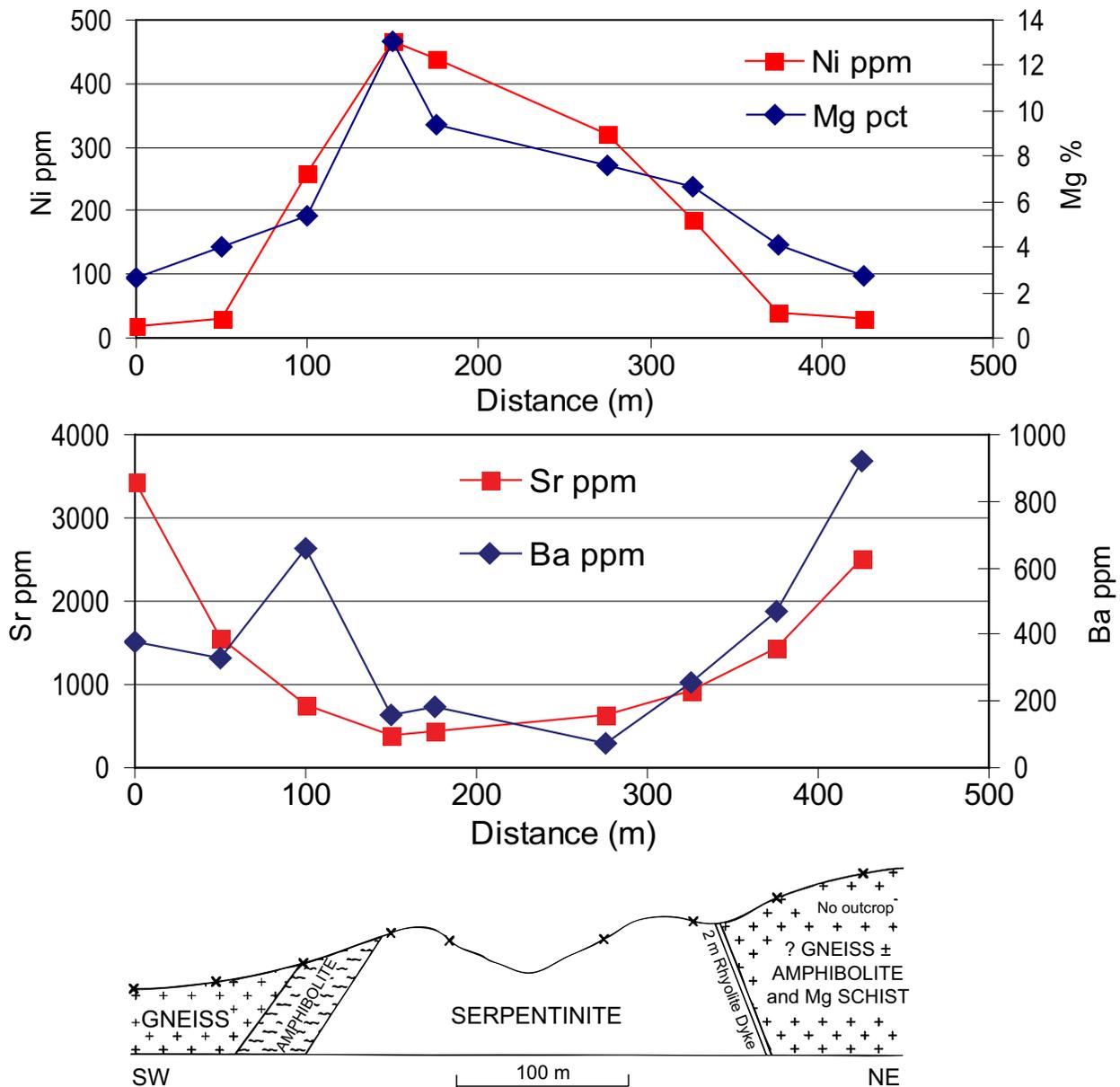


Fig. 2. Response of vegetation chemistry to underlying bedrock; *Baccharis trimera* from Cerro Mantiqueira, southern Brazil. *Baccharis* has many common names, notably ‘Tholas’ and ‘carqueja’, and is widespread throughout much of South America.

the field. It is much easier to do this separation when the samples are moist as drying bakes the layers together. The dried and separated material is then ready for either milling to a fine powder and direct analysis by a suitable analytical technique, of which ICP-MS is now the preferred method for obtaining data for many elements in a single pass and at remarkably low cost. In order to preconcentrate elements that are typically present at very low levels (e.g. PGEs, Be, Bi, In, Re, Te, V, W), samples can be reduced to ash prior to analysis. However, this results in loss of highly volatile elements, such as Hg, and partial losses of other elements, such as As and Cr.

Whichever analytical method is employed, it is *essential* for adequate quality control that at least one standard sample of known composition (and similar matrix) and one duplicate pair are inserted within every batch of 20 'regular' field samples. These samples provide control on the accuracy (using standards) and precision (determined from duplicates) of the data.

BEDROCK AND STRUCTURE

Judicious evaluation of a biogeochemical data set can provide valuable information on the underlying substrate. Of importance, it seems that the signature derived from biogeochemical surveys is spatially more closely related to the underlying source than the signature derived from sampling exotic material, such as glacial deposits or wind-blown sediments. This equates the value of biogeochemical data to that of data derived from various selective leaches of soils. However, careful consideration must be taken of the fact that plants *require* certain elements for their very existence. For example, high levels of Zn in plants (e.g. birch) do not necessarily reflect a rich source of mineralization; 2000 ppm Zn in ash is not uncommon. Other plants *scavenge* metals from the ground; Douglas fir has an affinity for arsenic and can concentrate substantial amounts without showing any signs of toxicity.

That said, a lot of biogeochemical patterns can be interpreted in much the same manner that you would apply to more 'conventional' geochemical data in order to determine structure and bedrock, but with the added advantage that you may detect concealed mineralization that is difficult, if not impossible, to find by other methods (especially where soils are absent or frozen and therefore not available for selective leaching).

Figure 2 shows the response of vegetation chemistry to changes in the underlying lithology, using as an example a simple transect from gneiss into an ultramafic body and back into gneiss.

Additional examples will be presented that demonstrate the use of plant chemistry to help to elucidate bedrock structure, faulting and underlying mineralization.

CONCLUDING REMARKS

Plants are complex entities that, over the past 420 million years of evolution, have become extraordinarily sophisticated in their abilities to select those elements that they need for metabolic function, whilst developing ingenious methods to exclude other elements or tolerate their presence by sequestering them in tissues (commonly their extremities) out of harm's way.

Root systems extract elements selectively from the substrate, initially by following the lines of least resistance: first elements carried in gaseous phases, then those in solution, then labile phases (cf. elements loosely bound to amorphous oxide coatings on soils) and finally by attacking with their strong chemical and physical powers any further requirements for elements structurally bound in crystal lattices. Thus, they perform the 'ultimate selective leach'. We need to continue to unravel the mysteries of the plant kingdom in order to harness the power of plants with respect to their value to assist in geological mapping and exploring for minerals.

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Groundwaters in geochemical exploration

Matthew I. Leybourne¹ and Eion M. Cameron²

1. GNS Science, P.O. Box 30-368, Lower Hutt, New Zealand (e-mail: m.leybourne@gns.cri.nz)

2. Eion Cameron Geochemical Inc., 865 Spruce Ridge Road, Carp, Ontario, Canada K0A 1L0

INTRODUCTION

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

BACKGROUND

Because many surface and near-surface mineral deposits have been discovered, the challenge for mineral exploration is to find new, more deeply buried deposits, particularly in areas where thick cover exists (Cameron *et al.* 2004; Reith *et al.* 2005) and in established mining camps (Goodfellow *et al.* 2003). Groundwater has the potential to be a powerful mineral exploration tool:

- Recent and continuing advances in analytical methods, in particular ICP-MS and, more recently MC-ICP-MS (multi-collector), have greatly lowered detection limits for water samples and have the potential to revolutionize the use of isotopes in geochemical exploration.
- Groundwaters recharge to depth so that there is potential to penetrate deeply into the Earth's crust, with the result that groundwater geochemistry offers the potential to explore into the third dimension and detect more deeply buried mineralization than other geochemical methods.
- Groundwaters are chemically reactive with mineralization and host rocks, in particular where waters are O₂-bearing.

- Groundwater flows away from the site of reaction with mineralization, providing a potentially broader exploration target than litho-geochemistry.
- Sample preparation is simple, i.e. most modern analytical techniques (ICP) operate best with a fluid sample.
- For many species of interest in geochemical exploration, background concentrations are low, enhancing anomaly contrast.

Although aqueous geochemistry as an exploration tool has been advocated and studied for some time (Cameron 1977, 1978; Miller *et al.* 1982; Earle and Drever 1983; Giblin & Snelling 1983; Taisaev & Plyusnin 1984; Boyle 1988; Giblin 1994; Cidu *et al.* 1995; Mingqi *et al.* 1995; Cameron *et al.* 1997; Leybourne *et al.* 1998; 2002; 2003; Cameron *et al.* 2004; Phipps *et al.* 2004; Leybourne and Cameron 2007; Leybourne in press), there have been relatively few detailed studies in particular on the utility of groundwaters. Another significant change in mineral exploration since *Exploration '97* and the review of aqueous geochemistry in exploration (Taufen 1997) is the increase in the use of partial (generally weak) extractions of soils and stream sediments, which in some cases have been shown to produce greater anomaly-to-background contrast than traditional strong-acid (e.g. aqua regia) digestions (Cameron *et al.* 2004). One of the difficulties of these weak leaches has been the interpretation of the results owing to a lack of understanding of the mechanisms by which ore-related species migrate from depth to the surface environment (Goldberg 1998; Smee 1998; Cameron *et al.* 2004). Processes postulated to account for these surface anomalies over deeply buried mineralization include capillary migration of ions (Mann *et al.* 2005), vapor-transport, ground and soil water advection or diffusion, electrochemical transport (Hamilton 1998), and seismic pumping (Cameron *et al.* 2002, 2004). Given the wide variety of terrains and climates that occur, it is likely that no one mechanism will explain soil geochemical anomaly development, and that in many environments, groundwaters will be directly or indirectly involved. For example, recent work in the Atacama Desert of northern Chile has indicated that seismic pumping of groundwaters interacting with mineralization is a viable mechanism for producing significant anomalies in soils and gravels over porphyry copper mineralization (Cameron *et al.* 2002, 2004) (Fig. 1). Clearly, some of the postulated mechanisms for these anomalies in soils will have limited applicability to aqueous geochemical exploration, but in some cases, as noted for porphyry copper deposits in Chile, hydromorphic transport is fundamentally important in the development of geochemical anomalies and understanding the aqueous geochemistry of

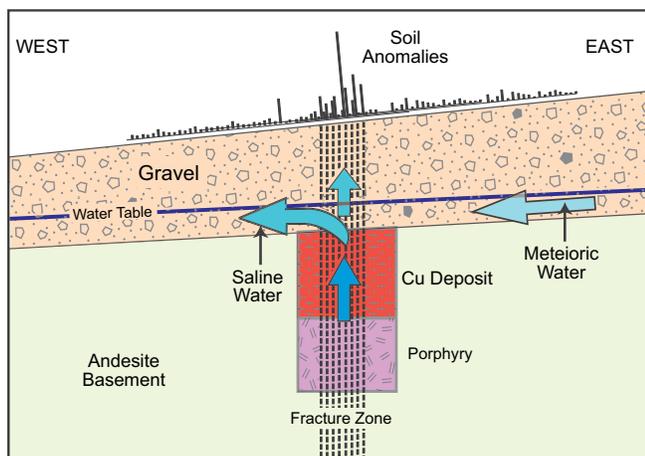


Fig. 1. Conceptual model for the development of soil geochemical anomalies via movement of groundwaters to surface during seismic events. In this model, saline fluids interact with porphyry copper mineralization and mix with a more regional shallow groundwater system. The resultant soil geochemical anomalies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

water-deposit interaction can greatly improve our ability to predict styles and composition of surficial anomalies.

Fundamentally, geochemical techniques for mineral exploration rely on the development of anomalies in the regional geochemical background. Critical to development of effective exploration strategies is an understanding of the mechanisms of anomaly development in different settings and for different sample media. Surface geochemical methods rely on development of anomalies by mechanical means (i.e. via glacial transport, solifluction, or mass wasting), hydromorphic (water) transport and precipitation, or metal migration via one of the above mechanisms. In contrast, groundwater geochemical anomalies fundamentally develop by hydromorphic dispersion.

KEY CONSIDERATIONS

In some environments, such as northern Chile or parts of Australia, grid drilling is common, which is ideal for the purposes of groundwater geochemical exploration. However, even where exploration wells are not typically drilled, there are a number of ways in which analysis of the geochemistry of groundwaters is practical: 1) in areas where domestic or agricultural wells already exist; 2) springs and seeps represent areas where groundwater returns to surface (indeed, stream waters generally represent base-flow, which is shallow groundwater discharge); and 3) where exploration holes are drilled, the additional cost of adding groundwater chemistry is insignificant relative to the cost of drilling; because groundwaters flow, there may be geochemical vectors to mineralization even in an apparently barren hole. Sampling techniques range from simple down-hole bailers to complicated straddle-packer systems; the choice depends to a great extent on the objectives of the sampling program and the nature of the hydrology.

A geochemical anomaly develops in groundwater by flow through mineralization. Interpretation of groundwater geochemistry in mineral exploration is greatly enhanced where there is information regarding the local and regional hydrology (Carey *et al.* 2003; Leybourne & Goodfellow 2003; Gilliss *et al.* 2004). Interpretation of hydrology is simplified in regions dominated by porous flow in unconfined aquifers (e.g. basal gravels in northern Chile that are in direct contact with porphyry mineralization exposed along the underlying basement unconformity and Athabasca sandstone U deposits), and significantly more complicated where flow is fracture-dominated (Leybourne *et al.* 1998), or where significant density contrasts between different groundwater flow systems exist (Carey *et al.* 2003).

A full understanding of groundwater geochemistry requires analysis and interpretation of the major ion composition (i.e. for most waters this means Ca, Mg, Na, K,

Table 1. Summary of key groundwater 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 & Goodfellow 2003; Leybourne <i>et al.</i> 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 <i>et al.</i> 2002; Cameron & Leybourne 2005; Leybourne & Cameron 2006a,b	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 <i>et al.</i> 1987 Kelley & 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 Br Cl (see text) ICP-MS, NAA	Giblin 2001; Gray 2001; Carey <i>et al.</i> 2003	
Cu-Ni-PGE	Ni, Cu, Pd	As, Cr, Co, S, PGE	ICP-MS – metals IC, ICP-OES – S	Hattori & 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 <i>et al.</i> 2003, 2007	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 <i>et al.</i> 1980; Langmuir & Chatham 1980; Earle & Drever 1983; Giblin & Snelling 1983; Dickson & Giblin 2006	Radiogenic ²⁰⁷ Pb/ ²⁰⁴ Pb and ²⁰⁶ Pb/ ²⁰⁴ Pb but non-radiogenic ²⁰⁸ Pb/ ²⁰⁴ Pb should prove useful

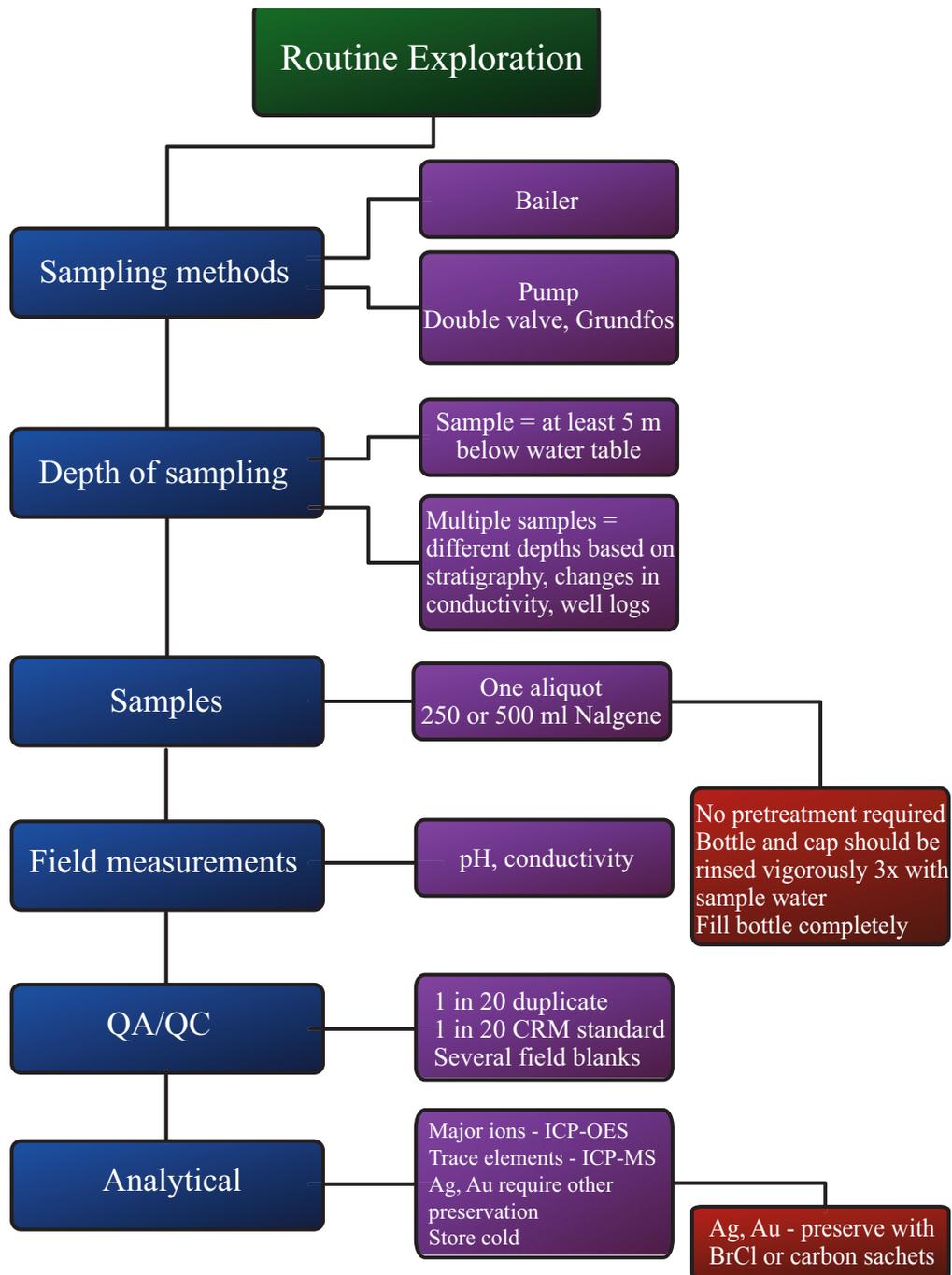


Fig. 2. Flowchart illustrating the major aspects of a groundwater geochemical exploration program for “routine exploration”.

H_4SiO_4 , Cl, SO_4 and dissolved inorganic carbon, typically HCO_3^-). These chemical parameters permit classification and interpretation of, for example, water type, mixing, evaporation, water-rock reaction and recharge. However, some studies have also suggested that the major ion composition of groundwater can provide direct vectors to mineralization, in particular owing to the generally larger target provided by alteration halos around mineralization relative to the size of primary ore mineralization (e.g. Giblin 1994; Taufen 1997; Phipps *et al.* 2004). Although the major ion chemistry of waters in a hydrogeochemical survey should be interpreted and considered in conjunction with

the trace metal data, owing to the complexities of water-rock reactions, cation exchange reactions and formation of secondary minerals, the major element chemistry of water should be used with great caution as an exploration guide in the absence of other (i.e. deposit-diagnostic) chemical data (Table 1).

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

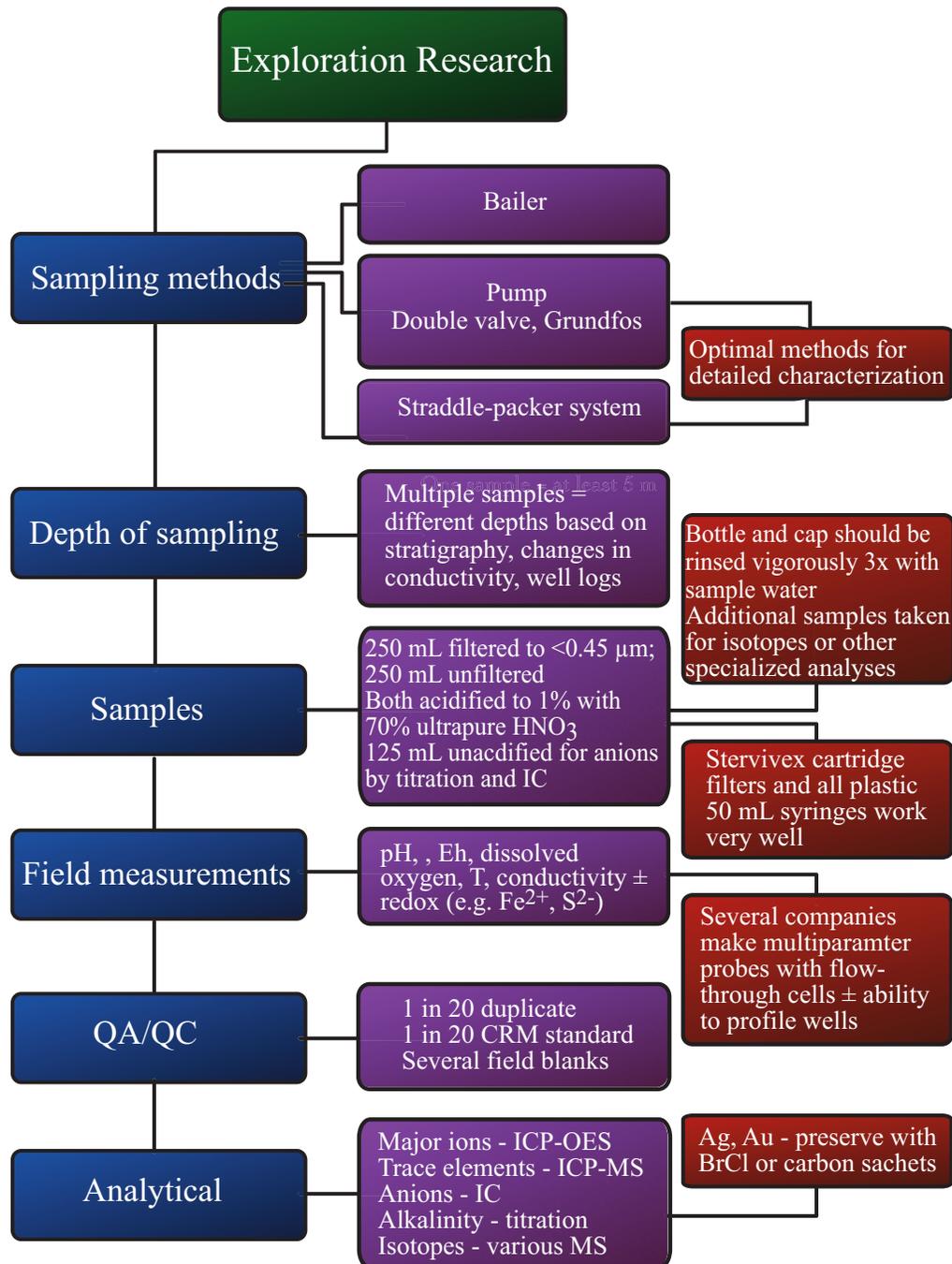


Fig. 3. Flowchart illustrating the major aspects of a groundwater geochemical exploration program for “exploration research”.

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 (Table 1).

Traditionally, stable and radiogenic isotopes have not been used in routine mineral exploration programs. Use of isotopes has been hampered by cost, additional requirements for sampling and perceived difficulties in data interpretation. Although this underutilization of isotopes in exploration is unlikely to change for large exploration programs, there are applications that warrant their incorpora-

tion. The light stable isotopes (e.g. O, H, S) can greatly assist in the interpretation of water sources, mixing and water-sulphide interaction (Cameron & Leybourne 2005; Leybourne & Cameron 2006; Leybourne *et al.* 2006). In addition, advances in analytical methods, in terms of detection limits, sample throughput and lower costs, are such that some isotope systems may become as routine as ICP-MS elemental analyses are today. Isotopes of potential use in mineral exploration include the traditional stable isotopes (O, H, C, S), radiogenic isotopes (Pb, Sr), and non-traditional isotope systems, such as Fe, Se and Cu (Ehrlich *et al.* 2004; Johnson & Bullen 2004; Rouxel *et al.* 2004; Severmann *et al.* 2004; Layton-Matthews *et al.* 2006).

GROUNDWATER GEOCHEMICAL EXPLORATION APPROACHES

From the discussion and case studies presented in this workshop, there are clearly a large number of parameters in groundwater geochemistry (and aqueous geochemistry more generally) that can be used to aid the detection of undiscovered mineralization and there are also a number of potential issues and pitfalls that need to be avoided. Despite these issues, groundwater geochemistry is a powerful tool for the exploration geochemist for the reasons outlined above. The collection and analysis of groundwaters in mineral exploration can be broken down into two different approaches, here referred to as the “routine exploration” (Fig. 2) and “exploration research” (Fig. 3) 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.

CONCLUSIONS

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

1. 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. In addition, accurate hydrological models are needed in a study area in order to connect surface aqueous geochemistry to groundwater flow and metal sources.
2. 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) sediment.
3. Determine the type of sampling apparatus to be used; routine exploration may only require a flow-through bailer, whereas, more detailed studies will likely need some form of down-hole pump or straddle-packer system, particularly in fractured-rock media, to provide optimal understanding of the redox state of the groundwater system.
4. 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.

5. One of the great advantages of collecting groundwater samples during exploration is that the data are also critical in establishing local and regional geochemical baselines should the program be successful in finding mineralization and the decision made to initiate mining.

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