



LITHOGEOCHEMICAL AND MINERALOGICAL METHODS FOR BASE METAL AND GOLD EXPLORATION

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ABSTRACT

Specific criteria used for exploration for new ore may be derived from genetic models. These might include specific lithological assemblages, fractionation trends, alteration assemblages and ore-controlling structures, for example. Three "lithogeochemical" methods of use in exploration include: diagnostic petrogenetic trends, obtained from geographical or statistical analyses of major and minor element data; diagnostic mineral assemblages, obtained through petrographic and XRD analyses; and specific elemental signatures (gains, losses, and isotopic shifts), also obtained from analytical data.

Volcanogenic massive sulphide deposits formed from high-temperature metalliferous fluids generated in the sub-seafloor through heating (from a subvolcanic intrusion) of downwelling seawater. Both the subvolcanic intrusions and related volcanic rocks have somewhat aberrant petrochemical trends, caused by unusually rapid heat removal to the hydrothermal system; extensive fractionation is evident in both major element and REE trends. Alteration includes lower semi-conformable horizons, albite-epidote-actinolite-quartz zones, and under some deposits, broad carbonatized zones. Alteration pipes vary from those with cores of Fe-chlorite and silica and rims of Mg-chlorite (after smectite), through Mg-chlorite core and sericite-rim pipes, to silica-sericite \pm Fe-carbonate pipes. All are Na-, Ca- and Sr-depleted.

Lode-gold deposits are associated with major transgressive (typically high-angle reverse) fault zones. Vein systems typically occur either in dilational jogs, near fault terminations, or at contacts between units with high ductility contrast. Regional alteration is dominated by CO₂ addition. Iron-dolomite and/or ankerite are most common near the deposits, but dolomite or calcite form the regionally developed alteration assemblage. Sphene occurs distally, but rutile is common near vein systems. Sericite and albite or K-spar occur within a few tens of metres or less of the deposits.

Magmatic sulphide deposits formed by segregation of immiscible sulphide liquid from a parent mafic or ultramafic magma. Deposits occur in intrusions and flows with unusually high Mg/Fe ratios. Nickel is depleted relative to Mg in fertile intrusions. Olivine in "barren" intrusions is rich in Ni, compared with "fertile" intrusions. Because sulphur saturation is promoted by assimilation of sulphur from an external source, Se/S ratios are higher in ore-bearing intrusions. Sulphur isotopes may deviate strongly from mantle compositions because of assimilation, particularly in post-Archean intrusions.

INTRODUCTION

Conventional prospecting and airborne geophysical surveying will have continued importance in finding new mineral resources, but exploration will become increasingly dependent on the application of geological principles, as well as advanced technology. Some regional and local geological elements are critical to locating economic ore deposits: many of these attributes indicate new ore potential, and thus are exploration guides. The genetic model for each ore deposit type is based on extensive field observations, coupled with intensive petrochemical, mineralogical and isotopic investigations. Critical lithological assemblages, specific fractionation trends, and diagnostic alteration assemblages are

examples of attributes that were originally documented during the quest for genetic models, but have important application in exploration for new ore. Before geological indicators of ore potential can be used, the class of deposits being sought must be known. Knowledge is required, prior to application of geologically based exploration tools, of those essential attributes of any specific genetic model that are manifest either by direct observation (i.e., maps or field studies) or laboratory analyses.

The choice of specific lithogeochemical and mineralogical exploration methods is dependent not only on choice of deposit type, but on knowledge of the variability within each type. For example, the well-documented mineralogical and chemical characteristics of alteration associated with porphyry copper/molybdenum, epithermal gold and

volcanogenic massive sulphide deposits have been used very effectively as an exploration tool for many years. Unique fractionation trends, the presence of magmatic sulphide minerals, and anomalous Se/S ratios can be applied in the search for magmatic sulphide ores. Subtle chemical and mineralogical changes point the way to Mississippi Valley-type deposits. Alteration associated with vein-gold deposits, however, has more limited application. For the latter deposit type, a good understanding of structural control has proven to be the most useful tool in finding new resources, particularly in established districts (see Robert and Poulsen, this volume). For each, a brief review of the most commonly accepted genetic attributes is followed by a description of petrogenetic indicators of use in exploration.

VOLCANIC-ASSOCIATED MASSIVE SULPHIDE DEPOSITS

Volcanic-associated deposits occur in terrains dominated by submarine volcanic rocks: the deposits are typically in volcanic strata, but may also be in or near sedimentary strata that are an integral part of a volcanic complex. Volcanic-associated deposits contain variable amounts of economically recoverable copper, zinc, lead, silver and gold that were deposited on or just below the paleo-seafloor, from high-temperature (250–400°C), moderately saline (~3–5 wt.% NaCl) metalliferous fluid. Their close spatial and genetic association with volcanic rocks has prompted the use of the classification term Volcanogenic Massive Sulphide deposits, or VMS deposits as their most common acronym.

VMS deposits in the Precambrian occur as two compositional classes, the copper-zinc and zinc-lead-copper groups (Franklin *et al.*, 1981; Franklin 1995). Phanerozoic deposits also include a copper-rich category characterized by VMS deposits in mafic volcanic dominated terrains (Large 1992). The copper-zinc deposit group has been further divided into two types (Morton and Franklin, 1987): one typified by the deposits in the Sturgeon Lake, Ontario area (*Mattabi-type*); and, the other by deposits at Noranda and Mattagami Lake, Québec. (*Noranda type*). An important sub-group of the zinc-lead-copper deposits are Au-rich VMS deposits (Poulsen and Hannington, 1996), which are typified by Eskay Creek- and Boliden-type deposits. Each type displays distinctive compositional and alteration aspects. Consequently, mineralogical and petrochemical criteria used as exploration guides must be sufficiently extensive to include all sub-types of deposits.

Some of the geological attributes (Figure 1) that are of use in exploring for VMS deposits include:

1. Presence of submarine volcanic strata: paleo-water depth controls some variations in volcanic morphology, as well as alteration assemblages and ore composition. Physical volcanological studies provide useful information to help determine which assemblages and compositions to expect.
2. Presence of a subvolcanic intrusive complex at shallow crustal levels (ca 2 km). These can be any composition represented in the overlying volcanic rocks, and generally: a) are sill complexes that locally transect stratigraphy; b) are texturally variable, composite intrusions, formed through multiple intrusions of the magmas at the same crustal level; c) are [highly] variably fractionated, [with "reverse zonation" common in] felsic intrusions containing abundant xenoliths of earlier mafic intrusions, with mafic portions more abundant along their top (as irregular pods) and ends; or mafic intrusive complexes that are commonly highly fractionated with

well-developed ferro-gabbro and granophyre phases; d) are devoid of a significant metamorphic halo relative to intrusions emplaced at deeper or drier crustal levels; e) are potential hosts to very low-grade porphyry-copper zones that are superimposed on all rock types; and f) may contain extensive sub-vertical breccia zones.

3. Presence of high-temperature reaction zones (one form of semi-conformable alteration) within about 1.5 km of the subvolcanic intrusions. Quartz-epidote-albite alteration, commonly mistakenly mapped as intermediate to felsic rocks, is prevalent under many copper-zinc deposits.
4. Presence of laterally extensive carbonatized volcanic strata that are depleted in sodium near deposits that formed in relatively shallow water (< 1500 m, accompanied by explosion breccia, debris flows, some subaerial volcanic products). These may represent the zone where ambient seawater reacted with the upper part of the hydrothermal reservoir.
5. Synvolcanic faults that are recognizable because they: a) do not extend far into the hanging wall of most deposits; b) commonly contain discrete zones of alteration along their vertical extent; c) are associated with asymmetric zones of growth-fault-induced talus; and, d) may be locally occupied by synvolcanic dykes.

Virtually all of these faults formed in extensional tectonic regimes, and may be listric. Some may be related to caldera margins, and thus curvilinear; others may be margins of elongate axial summit depressions (grabens), and subparallel to the axis of spreading (Kappel and Franklin, 1989).

6. Alteration pipes may extend for thousands of metres in vertical stratigraphic extent and are therefore mappable. The volcanic rocks in virtually all pipes are sodium-depleted, but mineralogical characteristics vary. Most commonly, rocks are silicified directly under the deposits, with broader zones of sericite, Mg- and Fe-rich chlorite or smectite. Less commonly, but important in many Cu-Zn districts, the pipes may have intensely chloritized cores, with more sericitic rims. Peripheral to the distinctive pipes, there is commonly a broad zone of more subtly altered rock; smectite and zeolite minerals may be important. Chemical changes in these latter alteration zones may be very subtle, requiring mineralogical or isotopic studies to detect them.

Metamorphosed pipe assemblages are usually relatively easy to recognize. Typically, rocks in Mg-Fe enriched pipes have been recrystallized to anthophyllite and cordierite. Adjacent, less intensely altered rocks may contain staurolite. Gahnite and Mn-rich garnets may be important accessories. The relatively high ductility of altered volcanic rocks compared with their hosts resulted in exceptional deformation in some districts. They may have become detached completely from their related ore bodies.

7. Strata immediately above deposits may contain indications of mineralization. Hanging-wall volcanic rocks may contain alteration pipe assemblages, most commonly sericite, or at least zeolite-smectite assemblages similar to the peripheral alteration associated with the pipes.

More importantly, hydrothermal precipitates such as ferruginous chert, sulphidic tuff, and products of oxidation of sulphide mounds may be sufficiently laterally extensive to be detected. Base metal contents within these, although of sub-ore grade, may increase towards the deposits.

Table 1: Summary of alteration indices to test for the presence of alteration.

Alteration Index	Element Ratios	Alteration Process	Source
Sericite Index	$K_2O / (K_2O + Na_2O)$	replacement of feldspar by sericite	Saeki & Date, 1980
Chlorite Index	$MgO + Fe_2O_3 / (MgO + Fe_2O_3 + 2CaO + 2Na_2O)$	addition of Fe and Mg as chlorite loss of CaO and Na ₂ O by destruction feldspar	Saeki & Date, 1980
Spitz-Darling	Al_2O_3 / Na_2O	sodium depletion (Al_2O_3 conserved)	Spitz & Darling, 1978
Alkali Index	$Na_2O + CaO / (Na_2O + CaO + K_2O)$	loss of CaO and Na ₂ O by destruction feldspar	Saeki & Date, 1980
Hashimoto Index	$MgO + K_2O / (MgO + K_2O + CaO + Na_2O)$	addition of Mg and K as chlorite and sericite loss of CaO and Na ₂ O by destruction feldspar	Ishikawa, 1976 Date <i>et al.</i> , 1983
Modified Hashimoto	$FeO + MgO + K_2O / (MgO + K_2O + CaO + Na_2O)$	as above with addition of FeO	Coad, 1982
Hashigushi Index	$Fe_2O_3 / (Fe_2O_3 + MgO)$	addition of Fe as Fe ₂ O ₃	Hashigushi, 1983
Residual Silica	SiO ₂ vs. Zr/TiO ₂ (silicification)	residual to feldspar fractionation line	Lavery, 1985
Pearce Element Ratios	molar Fe/Zr, Mg/Zr, Mn/Zr, K/Zr, CO ₂ /Zr molar (Na + K + 2Ca - Al/Zr) (alkali depletion) molar (Si/Zr) - 7.5 Al/Zr + 6.25) (silicification)	addition of Fe, Mg etc. relative to conserved Zr residual to feldspar fractionation line residual to feldspar fractionation line	Stanley and Madeisky, 1993
Other	e.g. Zn/Na ₂ O	e.g., sphalerite staining and sodium depletion	
Normative plots	e.g. corundum > .1%, feldspar ratio	Alkali depletion, other	
Mass Balance plots	All major and trace elements, altered vs. unaltered	Addition, loss, metasomatism, volume/mass changes vs. unaltered sample, immobile elements	Gresens, 1967 Grant, 1986 Baumgartner & Olsen, 1995

Petrochemical trends

Recent studies of hydrothermally active sites on the modern seafloor (Embley *et al.*, 1988; Franklin 1996; Hannington *et al.*, 1995) as well as research on subvolcanic and related volcanic rocks associated with ancient deposits (Campbell *et al.*, 1982), have demonstrated the presence of very specific, and possibly unique petrochemical trends that are related to the ore-forming process. Galley (1995) has summarized many of the lithogeochemical methods that are useful exploration tools. Many alteration indices have been developed to test petrochemical data for the presence of alteration (Table 1). While these are useful and simply applied, in many cases, mineralogical data are equally sensitive, and more easily applied (particularly in the field) indicators of ore potential. As described above, an important constituent of the hydrothermal system is the heat source, commonly represented by a subvolcanic intrusion. Compositional variations within these intrusions and their associated volcanic rocks can be affected by the presence of a hydrothermal system in two ways: the rapid removal of heat can cause unusual fractionation to occur within the subvolcanic intrusion, and secondly, hydrothermal fluid may enter into the melt. Hydrothermal signatures are developed through assimilation of previously altered wall rocks. Fracture-controlled alteration is generally sub-solidus and occurs after approximately 80% crystallization (Norton and Knight, 1977).

The presence of anomalously fractionated basaltic sequences has been documented on the Galapagos Ridge (Embley *et al.*, 1988) and at Cyprus (Schmincke *et al.*, 1983). In both cases, fractionation has proceeded from N-MORB through ferrobasalt, Fe-Ti basalt to andesite

(Figure 2). Sulphur and the volatile contents increase with amount of fractionation, although sulphur decreases remarkably in the end-member andesite. Efficient removal of olivine and immiscible-sulphide droplets into the base of shallow magma chambers has occurred during fractionation.

Fractionation [has] may also have affected shallow-level felsic subvolcanic magma chambers, as at Sturgeon Lake (Beidelman Bay intrusion) and Noranda (Flavrian intrusion). Rapid removal of heat may have forced disequilibrium crystallization, causing early formation of anomalous amounts of Ca-plagioclase and ferromagnesian minerals. Irregularly disposed mafic portions of these intrusions are common near their stratigraphic top and lateral terminations. Removal of Ca-feldspar from the melt, or complexing of Eu during catastrophic ingress of seawater could [has] result[ed] in depletion in europium relative to other REE's (Campbell *et al.*, 1982) forming a distinctive REE pattern (Figure 3). However, europium depletion may also be associated with hydrothermal alteration of these high-level complexes.

Although virtually no data exist on the Cl contents of ancient sequences, these data may be useful indicators of the potential for hydrothermal activity to have occurred in an area. Recent data on the Sr isotope and Cl contents of the various members of the fractionated suite at Galapagos indicate that these melts were likely progressively contaminated by seawater. This could have been caused either by assimilation of old crust or ingress of hydrothermal fluid into the melt. Cathles (1990) suggested that the latter process may be important in forming large hydrothermal systems. However, the Galapagos suite could also be the result of progressive melting of previously altered oceanic lithosphere.

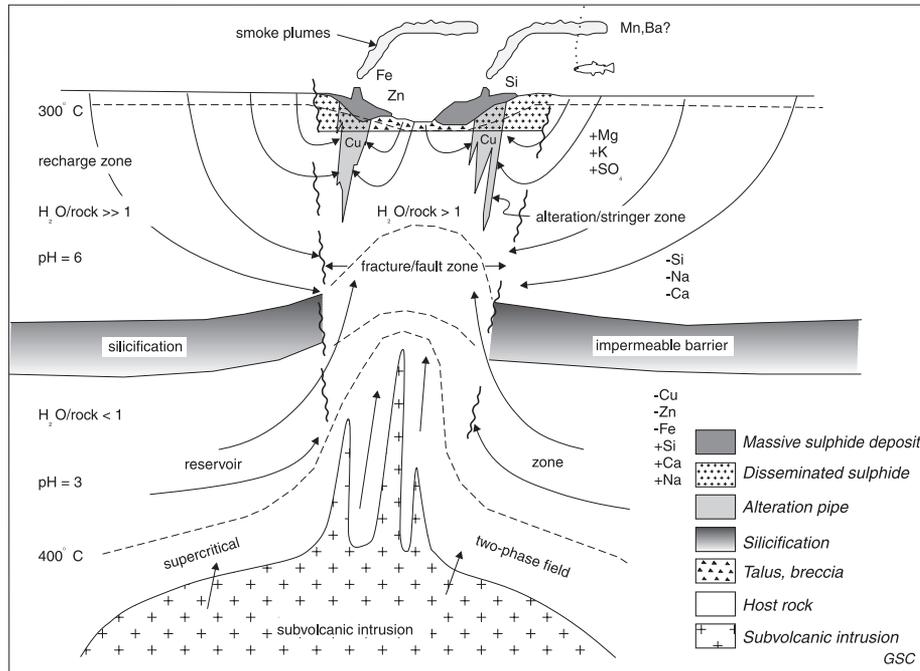


Figure 1: Composite section through a volcanogenic massive sulphide system. Note locally advecting seawater near the deposit, which could form a Na-depleted, Mg-enriched alteration zone. The scale of this alteration depends on the longevity of the system, as well as the physical nature of the footwall rocks.

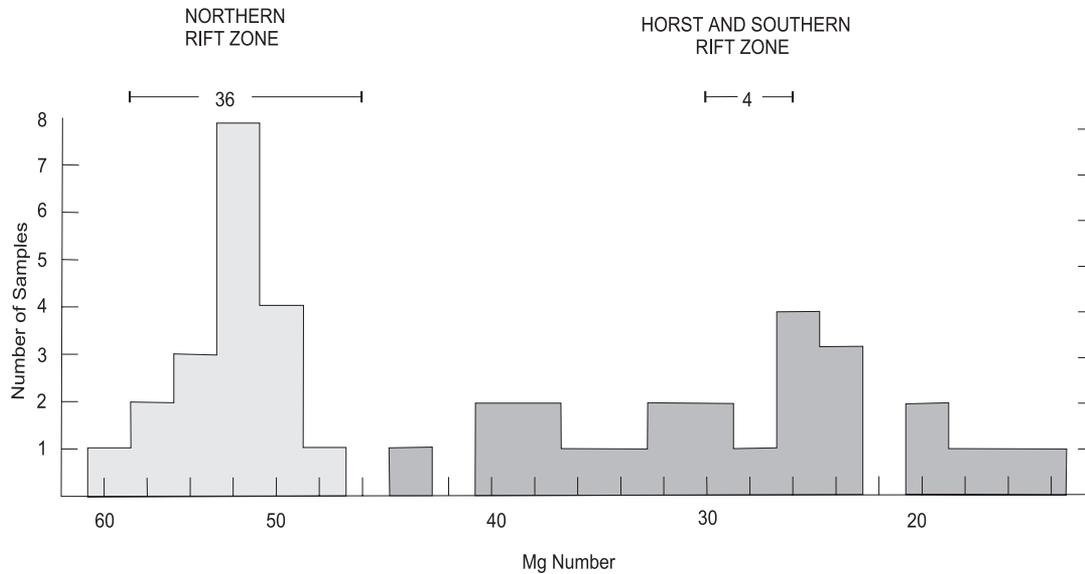


Figure 2: Fractionation index of seafloor basalt near active spreading ridges. Note the high values and relatively narrow range of Mg numbers (Mg/Mg + Fe) for basalts not associated with VMS deposits (Northern Rift Zone), compared with the large range and low values for those rocks associated with deposits (Horst and southern rift zone).

Alteration beneath Cu-Zn massive sulphide deposits

Alteration has been studied more extensively than most attributes of these deposits. Alteration mineral assemblages and associated chemical changes have been very useful exploration guides. Alteration occurs in two distinct zones beneath these deposits (see Figure 1).

1. *Alteration pipes* occur immediately below the massive sulphide zones; here a complex interaction has occurred among the immediate sub-strata to the deposits, ore-forming (hydrothermal) fluids and locally advecting seawater; and,

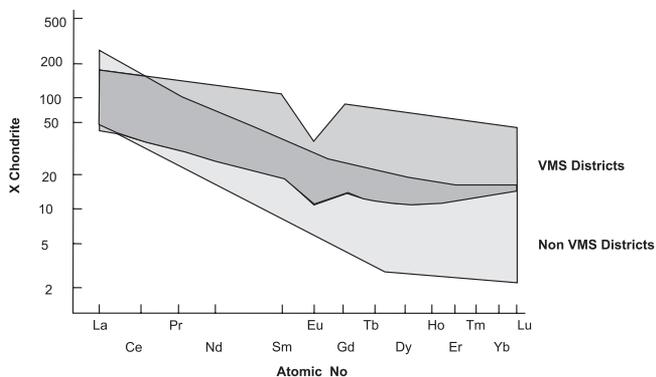


Figure 3: Composite REE patterns for felsic rocks in Archean sequences. Note that the range of patterns displaying a prominent negative Eu^* anomaly is associated with massive sulphide deposits, the relatively flat pattern with “barren” areas.

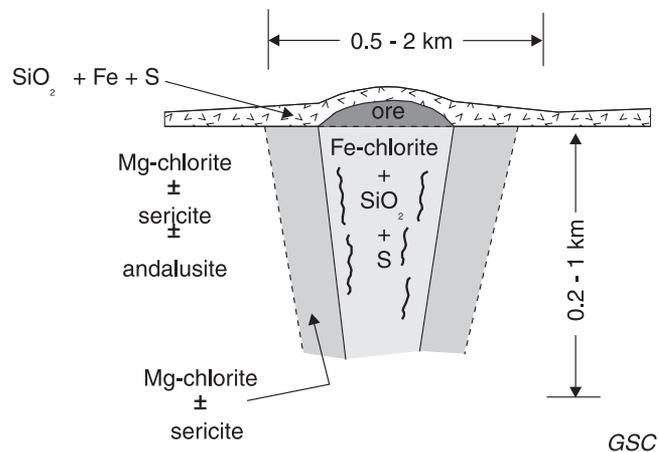


Figure 4: Composite characteristics of a “Noranda-type” alteration pipe.

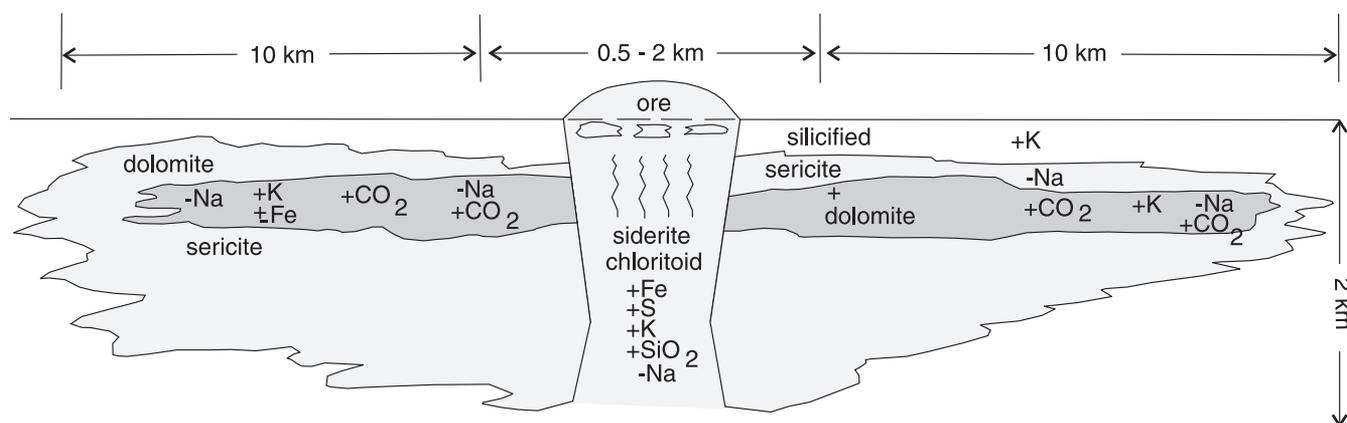


Figure 5: Composite characteristics of local and regional alteration associated with massive sulphide deposits formed in shallow-water (< 2 km).

2. *Lower, semi-conformable alteration zones* (Franklin *et al.*, 1981) occur several hundreds of metres or more below the massive sulphide deposits, and may represent in part the “reservoir zone” (Hodgson and Lydon, 1977) where the metals and sulphur were leached (Spooner and Fyfe, 1973) prior to their ascent to and expulsion onto the sea floor.

Under Precambrian deposits formed in relatively deep water (Noranda-type), alteration pipes typically have a chloritic core, surrounded by a sericitic rim (Figure 4). Some, such as at Matagami Lake, contain talc, magnetite and phlogopite. The pipes usually taper downwards within a few tens to hundreds of metres below the deposits to a fault-controlled zone less than a metre in diameter, but may extend for over 2000 m below the deposits, particularly in the Noranda type. Volcanological evidence suggests that some Noranda-type deposits formed in less than 1000 m of water as hydrothermal explosion breccias. The main differences between Noranda- and Mattabi-type deposits are rock composition and permeability, although the latter were most certainly shallow water deposits.

Beneath deposits formed in shallow water (Mattabi-type), the pipes are silicified and sericitized; chlorite is subordinate and is most abundant on the periphery of the pipes. Aluminosilicate minerals, such as pyrophyllite and andalusite, are prominent (Figure 5).

Alteration pipes under Phanerozoic Cu-Zn deposits are similar to, but more variable than those under their Precambrian counterparts. For example, Aggarwal and Nesbitt (1984) described a talc-enriched alteration core, surrounded by a silica-pyrite alteration halo, beneath the Chu Chua deposit in British Columbia. The Newfoundland, Cyprus, Oman and Galapagos Ridge deposits have Mg-chlorite in the peripheral parts of their pipes, together with illite. Iron-chlorite, quartz and pyrite typify the central parts of the pipes.

Virtually all alteration pipes are characterized by Na depletion. Base metal additions are also ubiquitous, although highly variable in scale. The alteration pipes under deposits such as Millenbach and Ansil extend stratigraphically downwards for hundreds of metres, and contain abundant chalcocopyrite. Under Mattabi, however, only a few metres of the footwall contains abundant chalcocopyrite. As noted above, chlorite spe-

cies varies considerably; the well-known Mg addition under some deposits is by no means a common feature under many other deposits. At Mattabi, for example, Mg is depleted in the footwall (Franklin *et al.*, 1975), but Fe and Mn are enriched. Enrichment in Mn occurs only where syn-depositional carbonate alteration is prominent in the footwall.

The lower semiconformable alteration zones have been recognized under deposits in many massive sulphide districts (Galley, 1993). These include laterally extensive (several kilometres of strike length) quartz-epidote zones, several hundred metres thick, that extend downwards a few hundred metres stratigraphically below the Noranda, Matagami, and Snow Lake deposits of the Canadian Shield. Zones of epidote, actinolite and quartz in the lower pillow lavas and sheeted dykes of the ophiolite sequences at Cyprus (Gass and Smewing, 1973) and in East Liguria, Italy, were explained by Spooner and Fyfe (1973) as due to increased heat flow as a result of convective heat transfer away from the cooling intrusions at the base of these sequences. All of the epidote-quartz zones are depleted in copper, zinc and sulphur (e.g., Skirrow and Franklin, 1994). They represent the zone of high temperature hydrothermal reaction (ca. 400°C), under low water-rock ratio conditions, where the metals and sulphur entered into the ore-forming solution (Richards *et al.*, 1989; Spooner 1977; Spooner *et al.*, 1977a,b).

The albite-epidote-quartz alteration zones are generally metal-depleted. Skirrow and Franklin (1994) show that virtually all of the copper, and one-third of the zinc, has been removed from the albite-epidote-quartz zone in the footwall to the Snow Lake (Manitoba) deposits. Silica and calcium were added, and magnesium was lost. MacGeehan and MacLean (1980) illustrate similar changes for the footwall sequence at Matagami Lake, Québec.

Zones of alkali-depleted, variably carbonatized strata occur directly beneath some deposits (e.g., Mattabi-type deposits, Hudak, 1996). These may extend up to tens of kilometres along strike, and occur in the upper few hundred metres of the footwall (paleo-seafloor) (Figure 6). These zones [probably represent] acted as a sealed cap to the hydrothermal reservoir, and formed through progressive heating of downward percolating seawater, with some possible input CO₂ from an underlying magma chamber, or by pyrolysis of organic compounds in the footwall.

The distinctive change in carbonate species provides a very important exploration guide. Franklin *et al.* (1975) and Morton *et al.* (1990)

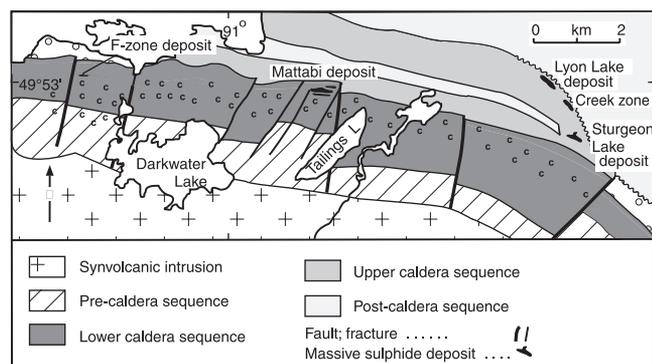


Figure 6: Regional distribution of carbonate alteration in the Sturgeon Lake district, Ontario. Carbonate is shown with "C" symbols. The carbonate-bearing rocks are usually Na-depleted.

have shown that on a regional basis, calcite has been added to the felsic strata, and Fe-dolomite to mafic strata (see Figure 5) in the Sturgeon Lake, Ontario, area. Siderite occurs immediately below and within a few hundred metres of deposits, whereas Fe-dolomite and calcite occur farther away from the deposits. Although the total CO₂ content of the rocks remains essentially unchanged (about 5–10% of the rock), the high Fe content of the mineralizing fluid that passed through these rocks converted the earlier-formed Ca and Fe-Mg-Ca carbonates to siderite. Concomitantly, Mn was incorporated into the siderite. Data on carbonate nodules that are presently forming under the deposits at Middle Valley and Escanaba Trough confirm this transition.

The alkali depletion that is common in many alteration zones is manifest as abundant aluminosilicate minerals (andalusite and, less commonly, kyanite) in areas of abundant carbonate alteration. In the absence of carbonate, margarite (at Snow Lake; Zaleski, 1989) and chlorite replace the feldspar.

Amphibolite-grade metamorphism significantly changes the alteration assemblages under VMS deposits. At upper greenschist facies, chloritoid forms in the carbonatized alteration zones. Although Mg-chlorite remains stable well into amphibolite facies, Fe-chlorite has changed to staurolite in districts such as Snow Lake, Manitoba (Walford and Franklin, 1982) and Manitouwadge (Friesen *et al.*, 1982). In very Fe-rich rocks (and in the absence of potassium) anthophyllite is abundant (Froese, 1969).

The mica species in alteration pipes are poorly documented. At Mattabi, although sericite is the most abundant mica, paragonite is common (but difficult to recognize), even in Na-depleted rocks.

Alteration beneath Zn-Pb-Cu deposits

Alteration associated with Zn-Pb-Cu deposits is typified by that in the Hokuroku district of Japan (Figure 7). Canadian deposits, such as those at Buchans, Newfoundland, Chisel Lake, Ontario, and the Buttle Lake, British Columbia districts, have similar alteration patterns to Hokuroku deposits and those in the Tasman Geosyncline, Australia (Gemmell and Large, 1992). "Lower semi-conformable" alteration zones (cf. Cu-Zn deposits) are well documented under the Bergslagen (Sweden) and Iberian VMS districts.

Four alteration zones (Figure 7) in the Hokuroku district have been described by Shirozo (1974), Iijima (1974), and Date *et al.* (1983). The most intense zone of alteration, zone four, is immediately below the deposits, and consists of silicified, sericitized rock, with a small amount of chlorite. Zone three contains sericite, Mg-chlorite, and montmorillonite, and is not silicified. Feldspar is absent from zones three and four. Zone two consists of sericite, mixed-layer smectite minerals, and feldspar. Zone one contains zeolite (typically analcime) as an essential mineral, with montmorillonite. Outside these four zones the volcanic rocks have been affected by deuteric alteration, which formed clinoptilolite and mordenite. Metamorphism and deformation obscure the alteration minerals associated with zones 1 to 3. At Buttle Lake, for example, zone four alteration is most prominent; carbonate is also present, and is also present distal to the Hokuroku deposits. Although chlorite is much less abundant under Zn-Pb-Cu deposits than under Cu-Zn deposits, the alteration pipe under the Woodlawn deposit (Tasmania) is very chloritic (Peterson and Lambert, 1979). Alteration under the sediment-associated deposits of this group consists of locally distributed sericite-quartz; many deposits do not have obvious alteration zones.

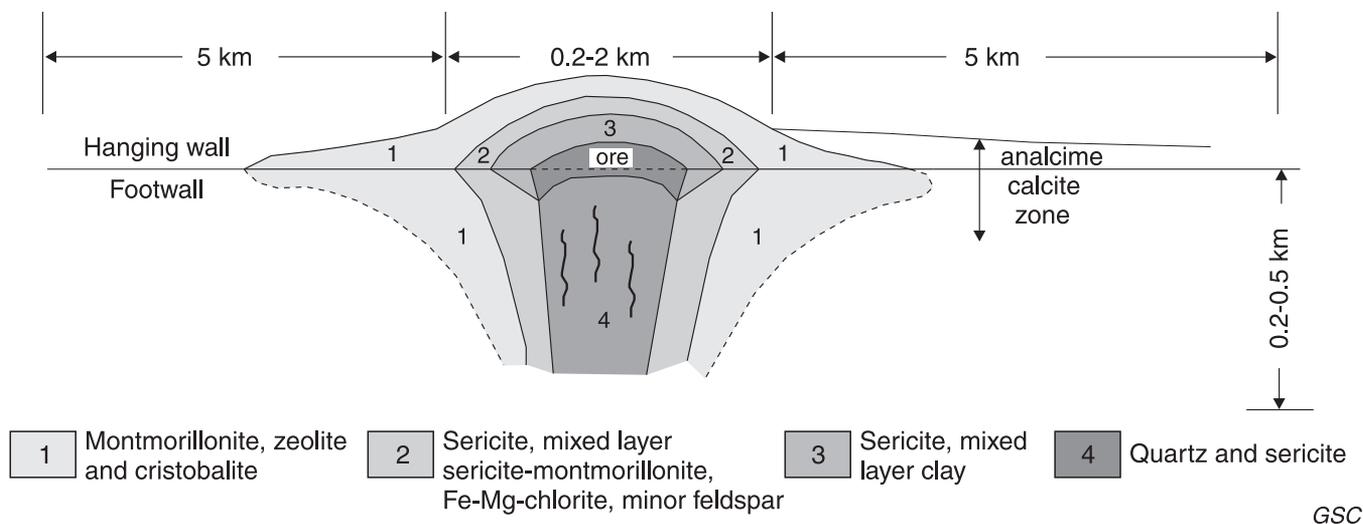


Figure 7: Mineral zonation associated with Zn-Pb-Cu deposits (Kuroko type). After Iijima, 1974. For descriptions of zones see text.

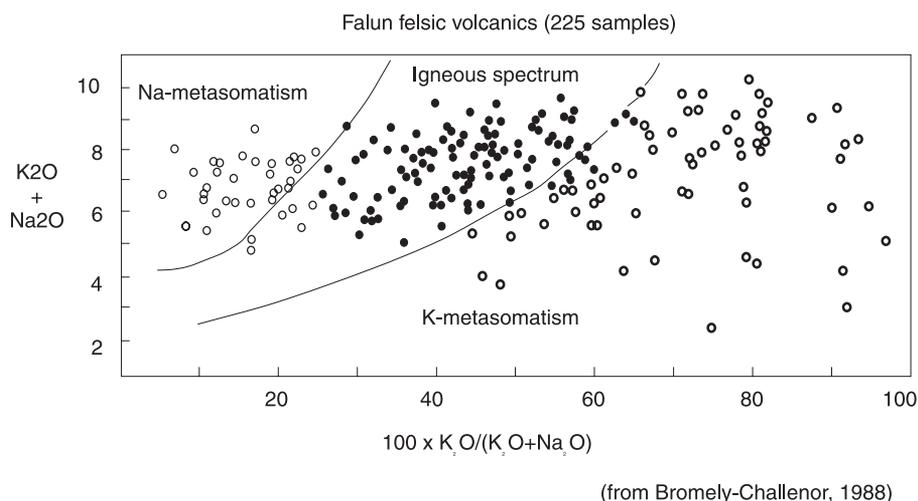


Figure 8: Harker diagram illustrating Na and K metasomatized felsic volcanic compositions in the ergslagen district. Infilled circles represent normal felsic compositions, with K-enriched rocks from the upper part of the semiconformable alterations zone to the right, Na-enriched rocks from the lower zone to the left.

Semi-conformable alteration beneath Zn-Pb-Cu deposits occurs on a very large scale, and thus may be easily misinterpreted. Galley's (1993) review describes the Bergslagen district as having "a broad zone of quartz-microcline, K-enriched alteration, known locally as leptite", with associated K enrichment, underlain by Na-enriched zones. These have been shown by Bromley-Challenor (1988) to lie outside the "normal" compositional range of volcanic rocks (Figure 8).

In the Iberia district, Munha *et al.* (1980, 1986) have shown similarly K- and Na-enriched rocks that were originally classified as "spilites" or "keratophyres". The latter two terms may actually be misrepresentations of primary igneous compositions, and might be applicable only to alteration systems. Munha *et al.* (1980) showed that the most permeable volcanic strata contain intensively altered rocks, with K-feldspar,

smectite-chlorite, zeolite and Mg-carbonate near the top, and albite-chlorite-epidote (or, deeper albite-chlorite-epidote-actinolite) assemblages at lower stratigraphic positions. These latter zones are similar to those in the Snow Lake, Manitoba district (Skirrow and Franklin, 1994).

Syndepositional indicators of ore potential

Many massive sulphide districts have "sedimentary" or distal, syn-depositional strata that reflect the ore-forming process. For example, the various sulphidic tuff horizons at Noranda (Kalogeropoulos and Scott, 1983, 1989), and at Bathurst (Peter and Goodfellow, 1996), the Key Tuffite horizon at Matagami Lake (Davidson, 1977), the ochre at Cyprus

(Herzig *et al.*, 1991), and the shale beds associated with several deposits (Kidd Creek, Uchi, West Arm) were all deposited penecontemporaneously with VMS deposits, or slightly pre-date them. Some exhalites have no apparent relationship with known VMS, and represent a period of extensive, but shallow, low temperature hydrothermal convection. Modern sea-floor hydrothermal sites also have hydrothermal sediments surrounding them (Hannington *et al.*, 1990). Finally, many VMS deposits have thin, laterally extensive "tails" leading away from the economic sulphide deposits; these may extend for hundreds of metres or more. They usually contain sub-economic metal contents; most are composed of "barren" pyrite.

The "near-field" sedimentary strata may be divided into two groups; those that contain sulphide as at least an accessory mineral, and those that contain oxide minerals. The origin of each of these is somewhat complex. Sulphidic sediments may have incorporated fallout particles from hydrothermal plumes. They may also have formed from the discharge of poorly focussed low-temperature hydrothermal fluids in areas surrounding the high temperature vents. The oxide zones may be formed from the oxidation of sulphides (Hannington *et al.*, 1990; Kalogeropoulos and Scott, 1983), or by direct precipitation of oxide minerals (i.e., iron formation).

The geochemical aspects of these two types of deposits that pertain to exploration have only been examined in a few districts. Some preliminary findings are as follows.

For sulphidic sediments:

1. Base metal contents increase towards the ore zone, although rather irregularly (Kalogeropoulos and Scott, 1989).
2. The silver contents of disseminated sulphides in any type of VMS-related sedimentary rock are higher than in pyrite from strata where the sulphide was generated biogenically (Elliot, 1984). At Kidd Creek, for example, disseminated sulphide in the hanging-wall graphitic shale unit contains 60 ppm Ag, in comparison with the silver content of pyrite from unmineralized black shale of 18 ppm. Pyrite from VMS-related sedimentary rocks also has lower Ni and Co contents (200 and 120 ppm, respectively) than the abundances in biogenic pyrite (2000 and 650 ppm).
3. The sulphur isotopic composition of sulphides in sediments associated with Precambrian VMS mineralization typically has a very narrow range ($\pm 1\%$), clustered around 0‰, in contrast to sulphides in shale not associated with VMS deposits, which are probably biogenic (Goodwin *et al.*, 1976), and have very wide ranges (typically -8 to +8‰).

For oxide-rich sediments derived through degradation of VMS sulphides, only a few indicators are noteworthy.

1. Hannington *et al.* (1988) have demonstrated that gold is enriched by a factor of 10 to 100, by a secondary process in the oxidized sulphidic sediments at the TAG field (Mid Atlantic Ridge) and in the ochres at Cyprus (Herzig *et al.*, 1991). This enrichment may only be present where bottom water was oxidizing, i.e., in Phanerozoic open-ocean areas.
2. The lead isotope composition of oxidized sulphide material is conserved from the primary deposit composition, and is much less radiogenic than the lead in oxides generated by weathering of ferruginous (non-sulphide) rocks, or from iron formation (Gulson and Mizon, 1979).

LODE-GOLD DEPOSITS

Lode gold deposits occur in close association with major deformation zones, and can occur in virtually any rock type (Keays *et al.*, 1989). The general characteristics of Archean examples of this deposit type have been summarized by Kerrich (1983), Colvine *et al.* (1988), Card *et al.* (1989) and Robert and Poulsen (this volume). Lode gold deposits occur in sequences of all ages, although they may be more plentiful in Archean rocks; Superior Province has produced 142 million ounces of gold, only surpassed by the paleoplacer deposits of the Witwatersrand (Card *et al.*, 1989). Otherwise their geological characteristics are similar regardless of age.

The lode-gold group of deposits includes both vein and disseminated (or sulphidic schist) types. These two types account for the majority of the gold produced in Canada. They are associated with major fault zones, and are themselves structurally controlled. They appear to form very late in the geological history of their regions, typically after the peak of metamorphism.

Some geological attributes useful for exploring for this deposit type (after Poulsen, 1996; Robert, 1996) are:

1. Areas containing significant volumes of mafic volcanic rocks and a major fault zone, especially near the edge of a volcanic domain are most favourable. Shear zones or faults demonstrating high-angle reverse to reverse oblique motion contain the largest deposits (Sibson *et al.*, 1988).
2. Gold deposits do not normally occur in the first-order fault or shear system, but in subsidiary fault and shear zones.
3. Favourable segments of fault or shear zones are those intersecting favourable host rocks such as small felsic intrusions, iron formations, and iron-rich rocks. Also, portions of a shear or fault system where splays or deviations from the overall trend are evident are more productive.
4. Rocks surrounding the deposits are commonly (but not ubiquitously) carbonatized.

Petrochemical trends

As gold deposits formed well after nearly all of their host rocks, little if any information on the petrogenesis of these rocks has relevance to the deposits. A hypothesis has been presented (e.g., Callan and Spooner, 1989) for a genetic relationship between the tonalite-trondhjemite-granodiorite magmatic assemblage and gold deposits. The isotopic data used in their argument do not provide a unique resolution of this hypothesis. Although the common association of small albitic porphyry intrusions with gold deposits also provides some possibility for a genetic relationship, age data (Anglin *et al.*, 1988; Marmot and Corfu, 1989), as well as petrogenetic arguments (the porphyry bodies usually pre-date the metamorphic peak, the veins postdate it; Robert, 1996) make any genetic relationship virtually impossible.

Rock *et al.* (1989) and Wyman and Kerrich (1989) noted the association of gold deposits with shoshonitic (typically lamprophyric) intrusions. Although no direct genetic (or temporal) connection with this magmatic suite has been confirmed, the age of these intrusions is similar to ages determined for some gold veins (Bell *et al.*, 1989). This similarity may reflect some common source attributes for gold-bearing fluids and alkaline rocks, but no more direct genetic relationship has been established.

Alteration

Alteration associated with gold deposits has a very complex genesis. Only a few “diagnostic” features have been observed, and these must be treated with some caution (Fryer and Franklin, 1982).

Alteration is caused by two processes.

1. Dynamo-thermal alteration, usually on a regional scale, accompanied the formation of most major shear and fault zones. Feldspar destruction (yielding a mica) was commonly accompanied by dissolution of some components, leading to volume loss within a shear zone (Beach, 1976). Alkali elements may have been gained, through mica formation, or lost, through feldspar destruction. Typically, ferromagnesian components are conserved. Fluid movement through shear zones caused hydration, and possible re-setting of isotopic systems. All of these alteration processes can combine to yield a geochemical signature with no relevance to the ore-forming process. Almost any shear zone will be mineralogically and chemically modified; caution must be exercised in using these changes to determine ore potential.
2. Ore-related fluid movement through the area of gold mineralization imparted mineralogical and geochemical change at two scales (Figure 9). Many aspects of alteration associated with gold deposits are reviewed by Colvine *et al.* (1988).
3. At a local scale, sulphidation, alkali (either K or Na) and carbonate metasomatism, boron enrichment, and hydration are very common. The scale of alteration is typically from a few centimetres to a few metres adjacent to veins. The area affected by alteration is controlled by the fracture-induced permeability of the rocks. Per-

vase alteration is present in schistose deformation zones, but much more defined (and possibly equally extensive) alteration is observed adjacent to extensional veins. For example, at the Doyon Mine (Guha *et al.*, 1982) vein and disseminated gold mineralization occurs within a broad envelope of highly sheared, sericitized volcanic rocks. In contrast, Robert and Brown (1986) documented very well defined alteration zones, typically a few metres wide, adjacent to the veins at the Sigma Mine.

Mass balance studies (Robert and Brown, 1986; Ames *et al.*, 1991; Dubé 1990; Clark *et al.*, 1989; Kerrich, 1983) yielded results that demonstrate a lack of consistency in alteration styles for lode gold deposits. A few generalities can be drawn.

1. The complexity of chemical gains and losses increases as the ore-bearing veins are approached.
2. Alteration mineral assemblages, as well as chemical gains and losses, are furthermore a function of pre-alteration mineral assemblages. The latter generally reflect the primary rock type, but metamorphic modification of the pre-ore mineral assemblage can significantly affect the final alteration assemblage. For example, an ultramafic rock that was already converted to a talc-chlorite assemblage will react quite differently during alteration in comparison with a rock composed of olivine, pyroxene and plagioclase.
3. Either Na_2O or K_2O (but rarely both) are the most extensively added components. K_2O addition is most common. Sericite and biotite are common alteration minerals, particularly, but not exclusively in disseminated-type deposits. Paragonite may also be present (Ames *et al.*, 1991). Albite or K-feldspar is more common adjacent to veins which occupy brittle fractures. At Hemlo, how-

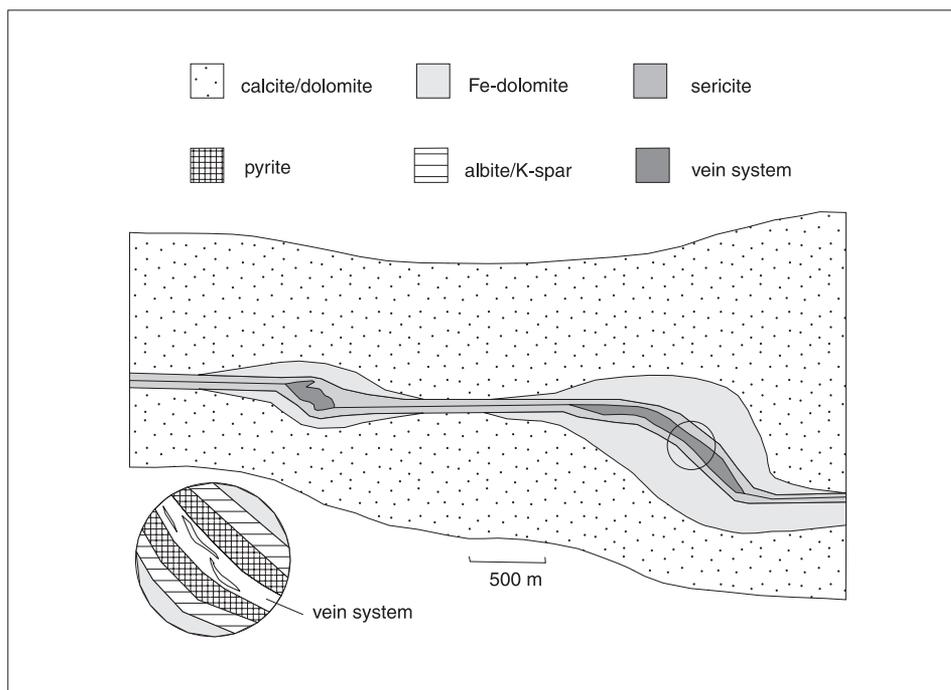


Figure 9: Schematic illustration of alteration associated with lode-gold deposits.

ever, K-feldspar (microcline) is extensively developed around the ore (Kuhns, 1986), with sericite alteration peripheral to the microcline zones.

Elemental additions most diagnostic of gold mineralization are (in approximate order of importance) Au, S, CO₂, K, Rb, SiO₂, Na, As, Sb, W, B, Mo and Pb (Davies *et al.*, 1982; Andrews *et al.*, 1986 and references therein). A few elements, notably Ca and Sr, may be depleted, due to feldspar destruction. Given that volume reduction may have occurred during deformation, some immobile elements (e.g., Al₂O₃, TiO₂, Zr) display *apparent* increase, but mass balance calculations may confirm that such changes occur through volume or mass change, rather than real gain or loss. The size of geochemically anomalous zones of these elements is variable, from centimetres to hundreds of metres away from ore. Typically, the zones of geochemically measurable alteration are about the same width as the ore deposits themselves, and are symmetrical to the ore zone.

4. Sulphide minerals (commonly pyrite) typically have overgrown and replaced ferromagnesian minerals. Iron was added at the Victory Mine (Clark *et al.*, 1989), but sulphidization was prominent at the San Antonio and Norbeau deposits (Ames *et al.*, 1991; Dubé 1990). Sulphidization is probably a particularly important indicator of gold mineralization, as reduction in the sulphur content of the gold-bearing fluid probably destabilized the Au-bisulphide complex, inducing very efficient deposition of gold.

Pyrite (or, less commonly pyrrhotite) is most abundant where gold-bearing fluids have interacted with iron-rich rocks. Sulphidized iron formation (e.g., Geraldton, Ontario; Anglin and Franklin, 1986) and sulphidized Fe-basalt are important hosts to gold mineralization. As noted by Kerrich *et al.* (1977), the Fe²⁺/Fe³⁺ ratio increases towards gold veins, largely in response to pyrite formation.

5. Alumina appears to have been mobile on a very local scale. Silicification is most common in broad shear zones, where silica-sericite-pyrite alteration assemblage typifies many disseminated-type deposits.
6. Tourmaline, scheelite, and arsenopyrite are all locally abundant in some deposits. In addition, very minor amounts of base metal sulphides occur in some veins; molybdenite and chalcopyrite seem most common, but sphalerite and galena are recorded at several deposits (Hodgson and MacGeehan, 1982). Virtually none of these minerals is sufficiently abundant to provide an indication of ore potential, although all may occur as weathered and transported products in overburden.

Regional scale alteration is well developed in some districts, such as Timmins (Davies and Whitehead, 1982), Red Lake (MacGeehan and Hodgson, 1982), and Geraldton (Anglin and Franklin, 1986), less well developed at Bissett (Ames *et al.*, 1991), and not prominent or even absent at others, such as Hemlo, and the Thompson Bousquet–Doyon (Malartic) group of deposits. Apart from shear-related mica alteration that may be widely distributed, depending on the breadth of any particular shear zone, the principal alteration type is carbonatization.

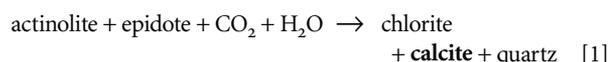
Carbonate alteration has been intensively examined at the Victory Mine area in Western Australia (Clark *et al.*, 1989), the Timmins district (Davies *et al.*, 1982), the Chibougamau area (Dubé, 1990), Red Lake (Andrews *et al.*, 1986) and Bissett, Manitoba (Ames *et al.*, 1991).

Summarizing their work, the principal changes at a regional scale are as follows:

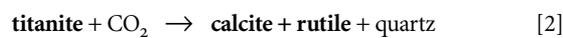
1. Virtually all rock types are affected by addition of CO₂ only. Other components of the carbonate minerals are derived through metasomatic alteration of the host rock.
2. The species of carbonate mineral present is a function of both the mole fraction of CO₂ (X CO₂) of fluids and the pre-alteration mineral assemblage. Clark *et al.* (1986) demonstrated at the Victory mine in the Yilgarn Block of Western Australia that close to the mineralization, ferruginous dolomite/ankerite is the prevalent carbonate species, whereas further from the deposit, calcite predominates. Significantly, silicate and oxide assemblages also reflect varying amounts of alteration. The equations presented by Clark *et al.* (1986) and Ames *et al.* (1991) are instructive. These represent a progressive set of reactions, describing the effect of an H₂O–CO₂ fluid on a metagabbro or metabasalt. They are written here in generalized form:

In metagabbro, the reactions are (Ames *et al.*, 1991):

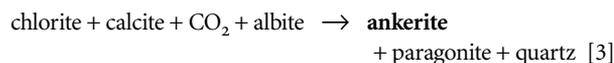
At a scale of tens of metres or more away from the vein systems, two reactions describe the principal changes:



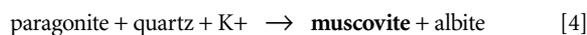
The specific reaction affecting titanite to form leucocoxene produces a mineral assemblage that is readily visible:



At a scale of 2–5 m away from the veins, ankerite appears in the alteration assemblage:

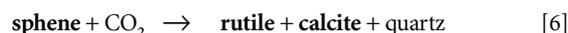
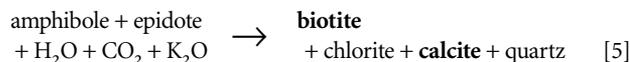


Immediately adjacent to the veins (~0.5 m), K is added:



In gabbroic rocks where potassium was added (either from the alteration fluid or prior to carbonatization), the reactions described by Clark *et al.* (1986) pertain:

On a regional scale (10's or more metres):



With increasing X CO₂ (i.e., closer to the veins):



The important aspects to note are the presence of rutile (rather than sphene) as a result of CO₂ metasomatism, and that with increased X CO₂, the biotite–chlorite–calcite assemblage produced in reaction [5]

changes to dolomite–muscovite–quartz (reaction [7]). Knowledge of the titanium mineral species, as well as the mica species and carbonate composition can provide some estimate of “closeness” to a gold-bearing (hopefully!) system of conduits (i.e., faults/shear zones). This type of mineral determinative work can be done by x-ray diffraction, an inexpensive and rapid method. The carbonate species can effectively be determined by staining methods.

Discriminating Au-related from VMS-related alteration

As noted above, both vein-gold deposits and VMS deposits may have significant carbonate alteration associated with them. How does the exploration geologist, confronted with carbonate alteration in the field, determine which deposit type is likely to be associated with the alteration? Besides the obvious field criteria (structural observations, regional setting), the answer lies in understanding the processes of alteration. As demonstrated above in the discussion of vein-gold related alteration, the carbonate species are formed through a metasomatic process, where only CO_2 is added to the rock. The other constituents of the carbonate minerals were derived from the host rocks, and thus the species is to some extent a function of host-rock composition. Carbonate alteration associated with massive sulphide mineralization was derived entirely from the hydrothermal fluid. All constituents were added to the rock, and metasomatism was probably unimportant.

In order to discriminate between these types of mineralization, mass balance studies should be undertaken. Using complete whole-rock analysis (including volatile elements), preferably with specific gravity measurements (not necessary if using Grant's (1986) method), it is necessary to simply determine whether only CO_2 was added to the rock (and therefore vein-gold mineralization is likely present) or all of the carbonate constituents were added (Fe, Mg, Ca as well as CO_2), indicating the potential presence of hydrothermal-exhalative (VMS or possibly epithermal) type of mineralization. A similar approach for sulphur should also work, and could be used as corroborating evidence.

MAGMATIC SULPHIDE DEPOSITS

Magmatic sulphide deposits form by the segregation of an immiscible sulphide liquid from a parent silicate magma. The magma is generally of mafic or ultramafic composition and the elements of economic interest which concentrate in the molten sulphide include nickel, copper, cobalt and the platinum group elements (PGEs). The most important examples of this category in Canada are the world class deposits at Sudbury, Ontario and in the Thompson Nickel Belt in Manitoba. Other significant deposits occur at Shebandowan and Timmins in Ontario, Lynn Lake in Manitoba, and the Ungava belt in Québec.

A number of lithogeochemical approaches have been suggested for the exploration for magmatic sulphide deposits (Leshner and Stone, 1996) but few of these have found wide application. Probably the most useful application of lithogeochemistry has been in the delineation of the stratigraphy within igneous intrusions or sequences of volcanic rocks. Lithogeochemistry can also be used as a direct indicator of the presence of magmatic sulphides but these methods require more research and development before they can be used routinely.

Delineation of igneous stratigraphy

Magmatic sulphide deposits are, by definition, syngenetic with the igneous bodies in which they occur. Sulphides segregate at specific times during magmatic differentiation and are therefore associated with particular phases or stratigraphic units within an intrusion or volcanic succession. While these units are normally defined on petrographic criteria including mineralogy and texture, their chemical compositions are often more distinctive than subtle petrographic differences. Moreover, petrographically homogeneous units commonly display significant compositional variations (i.e., cryptic variation). Finally, ultramafic rocks in particular are very susceptible to alteration, which may completely obliterate any primary minerals and texture, leaving lithogeochemistry as the primary means of identifying the protolith.

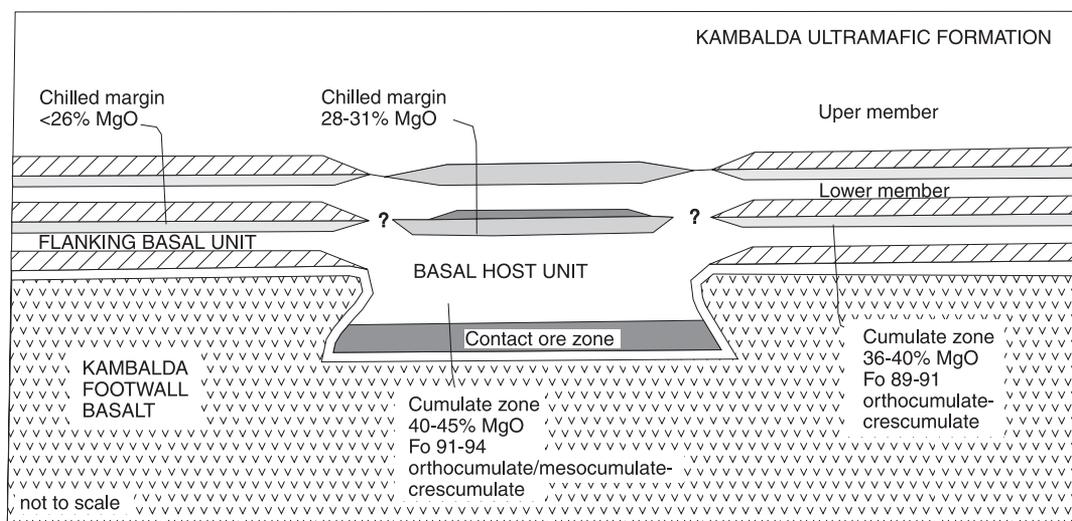


Figure 10: Schematic cross section of a typical Kambalda “ore shoot” showing the MgO contents of the ore-bearing and barren komatiite units (after Leshner and Groves, 1984).

For these reasons alone, lithogeochemistry should form part of any exploration program for magmatic sulphide deposits. The compositional parameters which will be most useful will depend on the circumstances in each case. However, as a general rule, some attention should be given to defining a "differentiation index". For example, in mafic and ultramafic rocks where fractional crystallization of olivine and pyroxene is a dominant differentiation process, the magnesium number (the magnesium number, sometimes abbreviated as Mg# or *mg*, is simply the atomic ratio $Mg/(Mg+Fe)$) is frequently used for this purpose. In the case of ultramafic volcanics (komatiites), the absolute MgO content, recalculated on a volatile-free basis, serves as a practical differentiation index.

Komatiite-associated nickel sulphide deposits provide one of the best examples of the use lithogeochemistry for this purpose. These deposits are associated with extrusive komatiites in Archean greenstone terranes in Australia, Canada and Zimbabwe. Gresham and Loftus-Hills (1981) give an excellent review of the characteristics of deposits in the type area of Kambalda, Western Australia. The sulphide accumulations occur in the lower parts of thick komatiite sequences with the bulk of the ore occurring at the base of the lowermost flow-unit. The ore-bearing units average 50 m but may exceed 100 m in thickness whereas flows in the lower part of the sequence but remote from ore are typically 15–20 m thick. The ore-bearing and barren flow units are also compositionally distinct. The thick basal flows are richer in magnesium, averaging 40–45% MgO as compared with 36–40% in the barren flows (Figure 10). The fine-grained, flowtop spinifex-textured peridotites in these units tend to contain from 28–32% MgO whereas elsewhere they have less than 26%. This provides a very useful exploration guideline.

Presence of magmatic sulphide

The formation of a magmatic sulphide deposit requires that the parent magma be at least locally saturated with sulphide for a finite period of time. Saturation leads to the segregation of droplets of immiscible sulphide liquid, which then must accumulate to some degree if economic concentrations are to be formed. Since it is virtually impossible for the accumulation process to operate with anything approaching 100% efficiency, some significant proportion of immiscible sulphide will remain dispersed and ultimately become trapped in the silicate host rocks. The presence of magmatic sulphide grains in an igneous rock is thus an indication of a potentially "fertile" magma.

Magmatic sulphide grains can sometimes be recognized in mafic and ultramafic rocks that are not too badly altered. Such grains are commonly minute and may not be readily distinguished from secondary sulphides without microscopic examination. They are characterized by a polymineralic composition (commonly pyrrhotite-chalcopyrite-pentlandite) and their textural relationship to primary silicate minerals (globular or cusped appearance where they are moulded around silicates). Duke and Naldrett (1976) give some of these criteria in their description of magmatic and secondary sulphides in the Main Irruptive at Sudbury.

Cameron *et al.* (1971) applied a lithogeochemical approach to detect the presence of small quantities of such "residual" magmatic sulphide in ultramafic rocks. They determined the concentrations of S and of sulphide-bound Ni, Cu and Co, and found that all four elements were enriched in ore-bearing as compared with barren rock suites. Copper and sulphur were the most significant factors in the discriminant function which distinguished the two populations. A practical consideration here is that Cu and particularly S tend to be mobile during alteration of

ultramafic rocks. This means that a relatively large number of samples from each body should be analysed.

Sulphur isotopes and Se/S ratios

It is widely believed that a significant component of the sulphur in most massive accumulations of magmatic sulphides is of crustal rather than mantle derivation. The parent magma from which these accumulations segregated presumably became saturated with sulphide by assimilation of crustal sulphur. This applies to komatiite-associated nickel sulphides (i.e., Kambalda-type deposits), deposits in intrusions of continental flood basalt affinity (e.g., Noril'sk, Duluth Complex, Insizwa), and the ores of the Thompson Nickel Belt, among others. It is important to note, however, that the sulphur in many disseminated magmatic sulphide deposits (e.g., the strata-bound platinum "reefs") is largely of mantle origin.

These observations suggest another lithogeochemical approach to the exploration for massive Ni-Cu sulphide ores. It was noted above that the presence of minute quantities of magmatic sulphides in an igneous rock is indicative of a "fertile" intrusion or lava sequence. Taking this one step further, geochemical parameters may be used to determine the likely source of the sulphur in these magmatic sulphide grains. A strong supracrustal signature would indicate that the parent magma had assimilated sulphur, which in turn suggests that the body in question would have some potential to host a massive sulphide accumulation.

Two parameters that are indicative of the source of sulphur are the sulphur isotopic composition and the Se/S ratio. The quantity $\delta^{34}S$ is close to zero in sulphur of mantle origin but often very different from zero in supracrustal sulphur (at least in post-Archean rocks). Similarly, rocks of mantle derivation typically have lower Se/S ratios in the range of $250\text{--}350 \times 10^{-6}$ whereas the ratio in supracrustal rocks is typically less than 100×10^{-6} (e.g., Eckstrand *et al.*, 1990).

Chalcophile element depletion

Chalcophile elements (Cu, Ni, Co, PGEs, etc.) partition strongly into molten sulphide in preference to silicate liquid, and magmas from which sulphide has segregated will be depleted in these elements. Chalcophile element depletion, as revealed by lithogeochemistry, is therefore a potentially useful indicator of igneous bodies that have crystallized from sulphide-saturated magmas (Naldrett *et al.*, 1984).

The magnitude of this depletion will depend upon a number of factors including the partition coefficient of the element, the relative masses of sulphide and silicate melts, and the mechanism by which the two liquids equilibrate. Komatiitic sequences provide an ideal situation in which to apply the chalcophile element depletion approach to exploration because they usually include spinifex-textured peridotites which have compositions equivalent to magmatic liquids. Duke and Naldrett (1978) quantitatively modelled the depletion patterns of Ni, Cu, and Co in komatiitic magmas, and predicted that these could be used as an exploration guide for Kambalda-type deposits. Subsequent studies have shown that the spinifex-textured peridotites at Kambalda (Leshner *et al.*, 1981) and Scotia (Stolz, 1981) are indeed depleted in Ni. In each case, the entire komatiite sequence shows evidence of depletion (Figure 11) which means that this lithogeochemical approach would be useful in identifying fertile komatiite successions but not in detailed exploration within these sequences. In applying this approach, it is important to

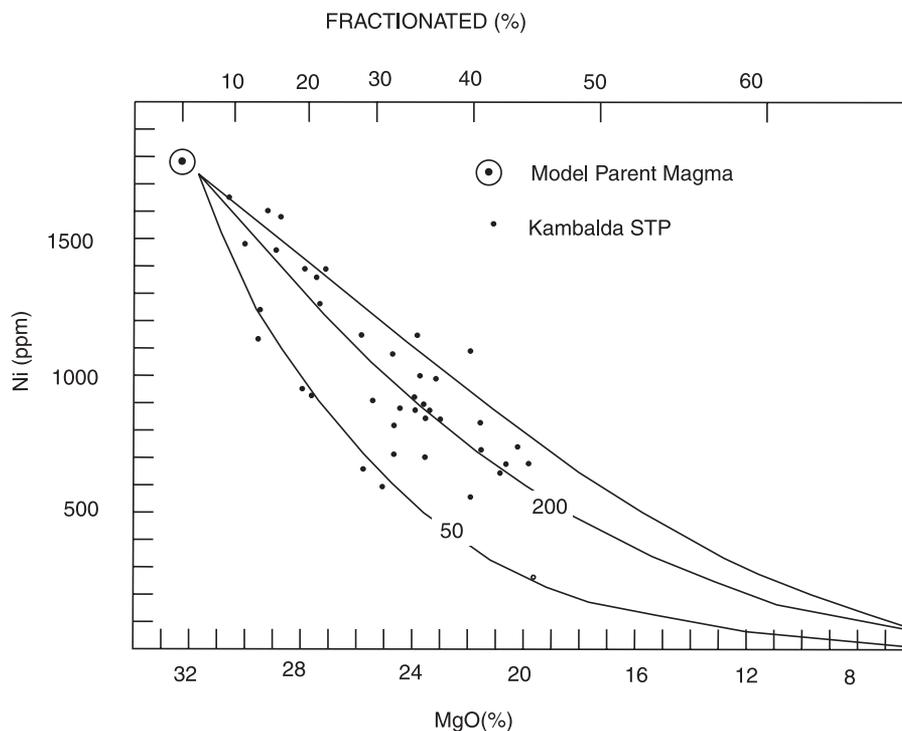


Figure 11: Ni-depletion in the ore-bearing komatiite succession at Kambalda, Western Australia. The solid line represents the model compositional trend produced by fractional crystallization of olivine; the dashed lines show the effect of removal of olivine and sulphide in 200:1 and 50:1 ratios (Duke 1979). The dots give the compositions of spinifex-textured peridotites (STP) from Leshner *et al.* (1981).

sample the fine-grained spinifex in the flow-top, that will most closely approximate the initial liquid composition.

In dealing with plutonic rocks, it is only rarely possible to identify rocks which have "liquid-equivalent" compositions. However, the chalcophile element depletion concept also applies to minerals which crystallized from sulphide-saturated magmas. Olivine is the most useful mineral in this respect because it normally contains readily detectable concentrations of Ni. Naldrett *et al.* (1984) have described a number of examples of nickel depletion in olivine from mineralized intrusions including the Insizwa Complex of South Africa, the Moxie and Katahdin intrusions in Maine, and the Dumont Sill in Québec. Paktunc (1989) has documented Ni-depleted olivines in the St. Stephen intrusion in New Brunswick which hosts a number of zones of magmatic Ni-Cu mineralization.

Chromite compositions

Leshner and Groves (1984) reported that chromites from mineralized komatiite sequences at Kambalda contain significantly higher levels of Zn than those from unmineralized sequences, specifically, 0.6 to 2.2 atomic % as compared to less than 0.6 atomic %. Chromites from ultramafic host rocks to ore at Thompson, Manitoba were found to contain similar high levels. The suggestion of Leshner and Groves (1984) that this enrichment is due to concentration of Zn in the silicate liquid during sulphide segregation is inconsistent with the inferred silicate/sulphide mass ratio (see Duke [1990] for a discussion of the silicate/sulphide ratio which may

have prevailed at Kambalda). A more likely explanation may lie in the fact that the magmas from which the sulphides segregated almost certainly assimilated significant quantities of sulphidic sediments which were also Zn-rich. Whatever the explanation, however, the elevated Zn content of chromites from some mineralized sequences may be a useful indicator.

SUMMARY

Alteration associated with both lode-gold and volcanogenic massive sulphide deposits results from interaction of high-temperature fluid with wall rocks. The fluids responsible for both deposit types probably had about the same range of temperatures (ca 300–400°C). Judging from their respective products, lode-gold-related fluids had very low base metal contents relative to VMS-forming fluids. Major districts containing either of these deposit types had fluids associated with them that contained high CO₂ contents; these CO₂-rich fluids may not have been the actual ore-forming fluid in either case, although these relationships have not been clarified.

Precipitation mechanisms of the ore constituents (and certainly depositional environments) were very different. Gold deposits formed through cooling on expansion of the fluid (e.g., in dilational structures; Sibson *et al.*, 1988) or through reduction of the sulphur content of the fluid, by reaction with iron in the wall rocks to form pyrite. The latter reaction effectively reduces the solubility of gold if it was being transported in a bisulphide complex. Deposition probably occurred about 4 km below the erosional surface of the time (Robert, 1996). Precipita-

tion of metals from a VMS-forming fluid occurred primarily through cooling, either on contact with cold seawater at the sea floor or by heat-conduction in the immediate footwall.

In the case of gold deposits, water, sulphur and CO₂ are the primary constituents added to the wall rocks. Potassium and Na were also added, but the "reservoir" of these elements is presumed to be the hydrothermal fluid responsible for mineralization; this fluid had limited amounts of these alkali elements. In contrast, much of the alteration associated with VMS deposits was formed from locally advecting (and progressively heated) seawater. Retrograde solubility of Mg, and the virtually unlimited reservoir of Mg and K, provided the opportunity for much more extensive addition of these elements to the footwall. Iron, sulphur and silica are derived from the ore-forming fluid, however, and usually are added only in the immediate footwall area.

One of the more important aspects of alteration associated with these two deposit types is carbonatization at a regional scale. How can carbonatization related to gold deposits be discriminated from that related to VMS deposits? Some guidelines are:

1. Carbonatization associated with gold deposits typically post-dated the peak of metamorphism. Also, the carbonatized rocks were not subjected to alkali-depletion, as was the case of the footwall sequences associated with VMS deposits. Consequently, the carbonate alteration associated with gold deposits was not metamorphosed, or if it was, this metamorphism occurred in rocks with "normal" alkali contents; metamorphosed alteration assemblages might contain diopside (or even secondary olivine, if temperatures were high enough). Metamorphosed carbonate alteration assemblages associated with VMS deposits probably contain chloritoid (Lockwood and Franklin, 1986) or staurolite, due to the alkali-deficient nature of the rocks. Also, the latter rocks are strongly per-aluminous, and typically contain andalusite (or sillimanite at higher metamorphic grades).
2. Mass balance studies of each alteration type should indicate that Ca, Mg, Fe and CO₂ were added in VMS-related carbonate alteration, but only CO₂ (and locally, possibly some K or Na) was added during gold-related alteration.
3. The "local" alteration assemblages associated with gold mineralization (e.g., ankerite and paragonite) may be much more regionally developed under VMS deposits. Although little is known about the source of CO₂ associated with VMS deposits (it could either be part of the hydrothermal fluid, a degassing product of an underlying subvolcanic magma chamber, or formed from downward-advecting, progressively heated seawater), there is no indication of X CO₂ gradients associated with its formation.

RECOMMENDATIONS

A few admonitions may be worth considering:

1. Geological models for ore deposition are based primarily on empirical field observations, and refined using laboratory data. The field observations typically include some recurring, somewhat extraordinary assemblages of rocks, alteration patterns, or structures. Careful examination of geological information, or prefera-

bly, mapping, should be the most powerful exploration tool. Where outcrop is sparse, geophysical or geochemical remote sensing methods, if applied with the full knowledge of the characteristics of ore deposits and their alteration assemblages, should provide guidance.

2. Petrochemical trends can be useful indicators of ore potential for magmatic and sea-floor-hydrothermal deposits, but are of little use for most types of vein deposits. High precision analytical data are needed if reliable petrogenetic indicators are to be used. These data should include determination of the volatile (CO₂ and S) and halogen elements and compounds, and REE. Indiscriminate determination of a large suite of volatile and trace elements could be expensive. Where possible, sampling should be done with the best geological knowledge at hand.
3. Alteration mineral assemblages provide excellent exploration guides for VMS and lode gold deposits. Some of these can be determined in the field, others with a petrographic microscope, and only a few require x-ray diffraction analyses. All of these techniques are inexpensive, readily available, and usually unambiguous. Mineral assemblages as exploration guides are under-used as techniques in the exploration arsenal. Some useful staining methods are available for determining the composition of carbonate minerals in the field. In the case of magmatic sulphides, on the other hand, alteration often obscures primary trends making the interpretation of lithochemistry more difficult.
4. Lithochemistry as an exploration technique has been used widely, and, unfortunately, indiscriminately. The exploration geologist armed with some knowledge of alteration processes could use subtle variations in the chemical composition of a rock to good advantage. For example, Na is lost where the water/rock ratio was high in an alteration zone (i.e., near a VMS deposit), but gained where this ratio was low (i.e., in the high temperature reaction zone, 1–2 km below the deposits). Both types of anomaly can be useful guides to ore, but must be applied with full consideration of stratigraphic implications. Analysis of the mineral assemblages in such rocks will yield much more information than the chemical data alone. "Cook-book" applications of lithochemical prospecting methods are potentially very misleading.

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