

## Chapter L

# GEOENVIRONMENTAL MODELS FOR SEAFLOOR MASSIVE SULFIDE DEPOSITS

Robert R. Seal II, Jane M. Hammarstrom, Nora K. Foley, and Charles N. Alpers

### INTRODUCTION

Massive sulfide deposits have some of the greatest potential for adverse environmental impacts. If improperly exploited, these deposits have high acid-generating potential due to high sulfide content, high heavy metal contents, and low acid-neutralizing potential due to their silicate host rocks, all of which can contribute to deleterious effects on aquatic ecosystems and human health. Massive sulfide deposits are typified by ores that comprise greater than 50 percent sulfide minerals, such as pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena, among others. They can be classified into at least six distinct deposit types on the basis of host rocks, and metal associations. Their potential for deleterious effects is related to their genetic classification in terms of acid-generating potential, associated heavy metal suites, acid-neutralizing capacity of host rocks, weathering products, and natural, pre-mining background characteristics of associated waters and rocks.

The purpose of this paper is to describe the potential behavior of seafloor massive sulfide deposits in relation to their geochemical attributes and in the context of their genetic classification. The link between genetic classification and environmental behavior is established through the compilation of data from site-specific studies. By definition, massive sulfide deposits can be expected to share many common aspects of their environmental behavior. However, significant differences can also be caused by their differences in geochemical characteristics that distinguish the various massive sulfide deposit types. This paper represents an extension and refinement of previous geoenvironmental models for massive sulfide deposits (Taylor and others 1995; Kelley and others 1995; Alpers and Zierenberg 1998).

### CLASSIFICATION OF MASSIVE SULFIDE DEPOSITS

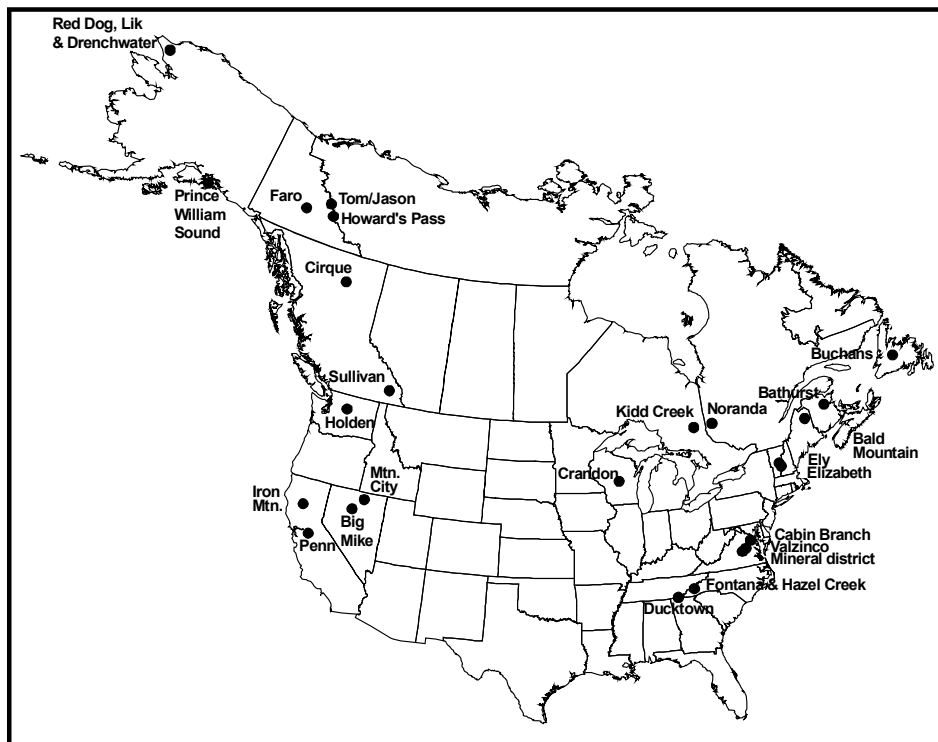
Most massive sulfide deposits form in submarine geothermal systems on or near the ocean floor. These seafloor deposits are dominated by massive accumulations of pyrite and (or) pyrrhotite, with lesser amounts of base-metal sulfide minerals, such as chalcopyrite, sphalerite, and galena. The host rocks for these deposits are typically felsic or mafic volcanic rocks, or siliciclastic sedimentary rocks. Carbonate minerals are typically absent or are a minor component of the host rocks and associated alteration assemblage. Locally, Besshi-type deposits may have carbonate units in the stratigraphic package on a regional scale. Thus, these deposits and surrounding rocks have a high acid-generating capacity and a low acid-neutralizing capacity. Economic geologists have chosen to classify massive sulfide deposits by a variety of schemes that emphasize metal associations, tectonic setting, or host-rock composition, among other characteristics. This paper uses a classification of seafloor massive sulfide deposits based dominantly on host-rock composition, which is a modification and expansion of the classification presented by Franklin and others (1998). This classification emphasizes geochemical controls on metal associations and bulk characteristics of host rocks such as acid-generating and -neutralizing potentials. This paper does not include discussion of types of massive sulfide deposits commonly known as magmatic Ni-sulfide, skarn, and manto deposits, which do not form on the seafloor and are genetically distinct.

Seafloor massive sulfide deposits are divided into six categories based on associated volcanic rocks (or lack thereof) and the relative proportions of volcanic and sedimentary host rocks (Table 1). These six categories, organized from volcanic- to sediment-rich, are (1) Kuroko-type, (2) Noranda-type, (3) Cyprus-type, (4) Bathurst-type, (5) Besshi-type, and (6) Sedimentary-exhalative-type deposits (Franklin and others 1998; Franklin 1993; Goodfellow and others 1993; Slack 1993). Kuroko- (felsic>mafic), Noranda- (mafic>felsic), and Cyprus-type (mafic-only) deposits are dominated by volcanic host rocks. Bathurst- (felsic>mafic) and Besshi- (mafic>felsic) type deposits are characterized by subequal proportions of sedimentary and volcanic rocks, with the dominance of felsic and mafic rocks distinguishing the two types. Sedimentary-exhalative deposits are hosted by dominantly siliciclastic sedimentary rocks with subordinate to no associated volcanic/intrusive rocks. Examples of these deposits are listed in Table 1. Locations of selected deposits in the United States and Canada are shown in Figure 1.

**Table 1.** Classification of seafloor massive sulfide deposits with examples

Volcanic Assemblage	Sediments > Volcanics	Volcanics ≈ Sediments	Volcanics > Sediments
Bimodal Felsic > Mafic		<i>Bathurst (Type 5*)</i> Halfmile Lake & Restigouche, NB	<i>Kuroko (Type 2*)</i> Holden, WA; Penn, CA; Mineral District, VA; Kidd Creek, Ontario; Hokuroko district, Japan
Bimodal Mafic > Felsic	<i>Sedimentary-exhalative</i> Red Dog, Lik, & Drenchwater, AK; Sullivan & Cirque, BC; Balmat, NY; Meggan & Rammelsberg, Germany; Faro, Tom, Jason, & Howards Pass, Yukon Territory; MacArthur River, Mount Isa, Broken Hill, Australia	<i>Besshi (Type 4*)</i> Fontana & Hazel Creek, NC; Ducktown, TN; Elizabeth & Ely, VT; Prince William Sound, AK; Windy Craggy, BC; Besshi, Japan	<i>Noranda (Type 1*)</i> Iron Mountain, CA; Bald Mountain, ME
Mafic and Ultramafic			<i>Cyprus (Type 3*)</i> Prince William Sound, AK; Skouriotissa, Cyprus; Big Mike, NV; Turner-Albright; OR

“(Types)” refer to classification of Franklin and others (1998).



**Figure 1.** Location of selected seafloor massive sulfide deposits in the United States and Canada.

## GEOLOGIC CHARACTERISTICS

### General Characteristics

Seafloor massive sulfide deposits are collectively defined by the fact that they formed syngenetically on or near the ancient seafloor as lens-like or tabular bodies of stratiform sulfide minerals. Their formation resulted from seafloor hot-spring activity. Differences in geologic and tectonic setting among the various types of seafloor massive sulfide deposits cause distinct differences in host-rock compositions, chemistry of the ores, and morphological features of the deposits, all of which affect the environmental behavior of these deposits. Kuroko-, Noranda-, Bathurst-, and Besshi-type deposits form in island-arc settings. Cyprus-type deposits form in mid-ocean-ridge settings. Sedimentary-exhalative deposits form along rifted continental margins.

Kuroko-type deposits are hosted by volcanic rocks that range from basalt to rhyolite in composition. Shales, mudstones, and volcanoclastic sedimentary rocks also are common. Noranda-type deposits are dominated by basaltic host rocks with lesser amounts of felsic volcanic host rocks and subordinate shales. Cyprus-type deposits are dominated by basaltic host rocks with minimal siliciclastic sedimentary rocks. Besshi-type deposits are hosted by turbiditic shales, graywackes, and sandstones, with lesser amounts of basaltic sills and locally minor amounts of dolomitic shales. Bathurst-type deposits are dominantly hosted by rhyolitic volcanic rocks, and siliciclastic sedimentary rocks. Sedimentary-exhalative deposits are hosted by shales, siltstones, and sandstones. Locally, carbonate rocks are important, with igneous rocks, typically basaltic, being absent or comprising up to half of the host-rock package.

### Related Deposit Types

For sedimentary-exhalative massive deposits, deposit types that can be associated on a local to regional scale include bedded barite, Mississippi Valley type lead-zinc, sedimentary manganese, sedimentary phosphate, Besshi massive sulfide, Chinese-type black shale deposits from the models presented by Cox and Singer (1986). The other classes of seafloor massive sulfide deposits are associated with a number of other mineral deposit types. Seafloor massive sulfide deposits are commonly associated with regionally developed iron- and (or) manganese-rich metalliferous sediment and chert developed at the same time-stratigraphic horizon as the massive sulfide deposits. Some Archean deposits may be transitional to volcanic-associated iron formation. All of these related deposit types have strong genetic links to the geochemical environment in which massive sulfide deposits form. There is a common association of seafloor base- and precious-metal massive sulfide deposits with younger low-sulfide quartz-gold vein (mesothermal or "Mother Lode") deposits. The close associations of low-sulfide quartz gold vein deposits with volcanic-associated massive sulfide deposits may reflect the results of the metamorphism of pre-existing metal-rich lithotectonic units.

### Deposit Size

For all classes of massive sulfide deposits, mined deposits are historically in the 1 to 5 million tonnes range, but individual deposits can approach 500 million tonnes (Singer, 1986c, d; Singer and Mosier, 1986). Development of new deposits from all classes in frontier areas likely requires at least 10 million tonnes of reasonably high grade ore. Most Cyprus-type deposits contain less than 15 million tonnes of ore. Most Besshi-type deposits are also fairly small; notable exceptions include the >300 million tonne Windy Craggy, British Columbia, deposit. Kuroko-type deposits, especially those of Precambrian age, can be very large, such as the world class Kidd Creek, Ontario, deposit. Most economic sedimentary-exhalative deposits are between 1.5 and 130 million tons; the median deposit size is 15 million tons (Menzie and Mosier, 1986). The Howards Pass deposit, Yukon Territory, contains 550 million tonnes of ore (Goodfellow and others, 1993).

### Host Rocks

The mineralogy and geochemistry of the host rocks are especially important because of the acid-generating or acid-neutralizing potential of mineable lithologic units. Mafic (basaltic) host rocks typically have sufficient acid-neutralizing capacity, whereas felsic (rhyolitic) host rocks do not. The host rocks of a mineral deposit can also serve to naturally elevate background acidity and aqueous contributions of metals as compared to adjacent rock types. Cyprus-type deposits are hosted by submarine mafic-volcanic rocks, typically in brecciated rocks commonly associated with pillow lavas. Host-rocks for Kuroko-type deposits range from basalt to rhyolite. Host rocks are commonly brecciated and are moderately to highly altered. Some deposits are hosted by associated volcanoclastic or hemipelagic sedimentary rocks that overly

submarine volcanic sequences. Host rocks for Noranda-type deposits are dominated by basaltic rocks, but are otherwise geologically similar to those for Kuroko-type deposits. Besshi-type deposits are typically hosted by turbiditic to hemipelagic graywacke interbedded with or intruded by basalt. Host rocks for sedimentary-exhalative deposits consist of a variety of marine sedimentary rocks such as carbonaceous shale and chert, dolomitic shale or siltstone, and micritic limestone. Turbidites and slump breccias are present locally; minor volcanic rocks, usually mafic, may be temporally, but not necessarily spatially, associated. Sangster (1990) indicates that tuff units are present within ore-hosting sequences at a number of these deposits.

#### Surrounding Geologic Terrane

Mineral deposits form in specific geologic settings, which have certain predictable geochemical attributes. Thus, even though the immediate host rocks of a deposit are devoid of carbonate rocks, such as those associated with Besshi-type massive sulfide deposits, the larger scale lithotectonic terrane can contain significant amounts of limestone and (or) dolomite, which can serve to increase the alkalinity and hardness of watersheds receiving acid drainage from these types of deposits. Also, the structural setting of the deposit can greatly influence the distribution of fractures and associated permeability.

Submarine volcanic activity is a defining characteristic of the environment of formation of volcanic-associated massive sulfide deposits. Most of these deposits, including many ophiolite-hosted deposits of the Cyprus-type, are associated with arc-related volcanism. Local extensional tectonic environments are particularly conducive to deposition of massive sulfide deposits. The geologic terrane surrounding sedimentary-exhalative deposits primarily consists of thick sequences of deep-water marine sedimentary rocks that include fine-grained clastic and carbonate rocks. The formation of these deposits along active plate margins can lead to the juxtaposition of unrelated rock types in compressional regimes.

#### Wall-Rock Alteration

Wall-rock alteration changes the chemistry of the host rock for a significant distance away from the ore zones. Alteration can increase the acid-neutralizing capacity of a rock by introducing carbonate minerals, or it can decrease the acid-neutralizing capacity of a rock by transforming feldspars into clay minerals. In fault zones, footwall alteration associated with volcanic-associated massive sulfide deposits is moderate to locally intense around most deposits. Hanging-wall alteration is typically absent, but may be weakly developed in some deposits. Many deposits that have not been tectonically disrupted are underlain by a stringer-zone of mineralized and altered rock. Stringer-zones are characterized by anastomosing quartz-sulfide veins. Zones of silicification are present near and within mineralized zones. The most common alteration is chloritization, which is less well developed with increasing depth and distance from hydrothermal vent zones. Deposits hosted by felsic rocks typically have extensively developed quartz-sericite alteration. Most altered rocks associated with massive sulfide deposits have low to very low acid buffering capacity. Some massive sulfide deposits are associated with pervasive carbonate alteration in the footwall. These carbonate alteration zones typically have low to moderate abundances of calcitic to ankeritic carbonate minerals (Taylor and others, 1995).

Alteration assemblages associated with sedimentary-exhalative deposits consist of stockwork and disseminated minerals locally present beneath or adjacent to stratiform deposits. These commonly consist of silicified or iron-carbonate altered rocks that locally contain tourmaline, albite, and chlorite, and represent the feeder zones of these deposits. In some deposits, silicification is the dominant or only alteration (Meggen, Germany and Red Dog, Alaska). In others, alteration is less extensive and (or) carbonate-rich (Large, 1981). Large (1983) describes more subtle types of alteration near some deposits, including increased dolomite-calcite ratios (McArthur River, Australia; deposits in Ireland) and increased potassium feldspar-albite ratios in tuffs (McArthur River).

#### Nature of Ore

Volcanic-associated massive sulfide deposits range from lens shaped to sheet-like bodies of sulfide-mineral-rich rock spatially associated with volcanic rocks ranging in composition from basalt to rhyolite. By definition, they contain zones of massive sulfide minerals, many with sulfide mineral contents exceeding 90 volume percent. Most deposits also contain extensive zones of semi-massive sulfide rock (25 to 50 volume percent) that contain economically exploitable ore. Stringer ore zones in the footwall of the massive sulfides typically contain 5 to 20 volume percent sulfide minerals. These are hosted in quartz veins and disseminated in chloritic wall rocks. Disseminated sulfide rock is extensively developed in

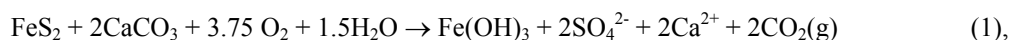
footwall alteration zones; sulfide mineral abundances decrease with depth below the massive sulfide zone horizon. Lateral development of disseminated pyrite can be continuous for large distances at and immediately below the stratigraphic horizon of the massive sulfide lens. In contrast to other volcanic-hosted deposits, many Besshi-type deposits form thin, laterally extensive sheets of pyrrhotite- and (or) pyrite-rich massive sulfide rock.

Sedimentary-exhalative deposits form as lens-like bodies of stratiform sulfide minerals (lead, zinc, and iron) as much as a few tens of meters in thickness and are interbedded with fine-grained dark clastic and chemical sedimentary rocks. These deposits may have large lateral extent (hundreds of meters to kilometers). Mineralized rock varies from a single layer to numerous bodies that may be vertically stacked or be lateral equivalents (Kelley and others, 1995). Within stratiform mineralized rocks of sedimentary-exhalative deposits, sulfide minerals are generally fine-grained, and commonly form nearly monomineralic laminae several mm to cm thick that have continuity over large parts of the deposits. Some deposits are not laminated (Meggen, Germany and Red Dog, Alaska). Sphalerite, galena, and iron-sulfide minerals (pyrite, marcasite, and pyrrhotite) are the most common sulfide minerals, but chalcopyrite and sulfosalt minerals may also be present in minor amounts (Large, 1981; 1983; Lydon, 1983). The most common associated sulfate mineral is barite. It may be peripheral to or stratigraphically above the deposit, or it may form crudely segregated mixtures with sulfide minerals, but many deposits have no associated barite.

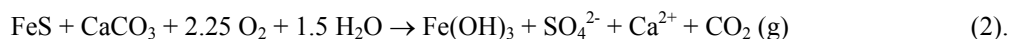
### Primary Mineralogy and Zonation

The primary ore mineralogy defines the suite of heavy metals that may cause potential environmental problems. In addition to pyrite and pyrrhotite, the ore minerals chalcopyrite ( $\text{CuFeS}_2$ ), sphalerite ( $\text{ZnS}$ ), and galena ( $\text{PbS}$ ) are commonly major constituents in these deposits, and are the principal sources of elevated concentrations of Cu, Zn, and Pb in mine drainage. Trace element concentrations in mine drainage are also related to the composition and abundance of trace elements in ore minerals and accessory minerals. For example, elevated dissolved concentrations of Cd are correlated with its substitution into sphalerite. Cadmium rarely forms a discrete mineral in these types of deposits. Arsenic commonly substitutes into pyrite, up to several weight percent, and arsenopyrite ( $\text{FeAsS}$ ) is also a common accessory in some deposit types. Both phases constitute a significant source of As in some deposits. The primary mineralogical characteristics of massive sulfide deposits and associated heavy elements are summarized in Table 2.

The primary and secondary mineralogy of the ores, their solid mine wastes, and associated rock types can affect the acid-base accounting (ABA) calculations. Acid-base accounting is based on the stoichiometric reaction:



which describes acid generation through the oxidation of pyrite and subsequent neutralization by calcite (Sobek and others 1978). Cravotta and others (1990) considered a variation on this reaction where  $\text{CO}_2$  was not exsolved, but contributed carbonic acid. In the case of Besshi-type and some sedimentary-exhalative massive sulfide deposits, pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ; where x ranges from 0.000 to 0.106) is the dominant sulfide mineral. For pyrrhotite, acid-base accounting can be approximated by the simplified stoichiometric reaction:



The net result of the proportion of  $\text{CaCO}_3$  per unit of total S is the same as in reaction 1, but the total S per unit of solid will be lower because pyrrhotite has approximately half of the S of pyrite.

The dominant sulfide mineral in most volcanic-associated massive sulfide deposits is pyrite, but pyrrhotite is dominant in Besshi-type and sedimentary-exhalative. Marcasite, which is present either intergrown with fine grained pyrite or as a replacement product of pyrrhotite, is generally a minor constituent, but locally can constitute a potential source of acidic drainage because of its higher reactivity relative to pyrite. The other dominant phases include sphalerite and chalcopyrite, accompanied by galena in deposits associated with felsic rock. Other ore minerals are present in much lower abundances, but constitute important potential heavy metal sources. The most common accessory sulfide and sulfosalt minerals are those of the tennantite-tetrahedrite series, arsenopyrite, and various lead-antimony-bismuth sulfosalt minerals, particularly in deposits associated with felsic rock. Deposits associated with mafic rock may contain cobalt sulfide or thiospinel. Magnetite is present in some deposits and barite can be very

abundant in Kuroko-type deposits, in which it commonly forms an important ore facies. Gypsum and anhydrite are also abundant in some Kuroko deposits. The most common silicate gangue minerals are quartz and chlorite, which are accompanied by sericite in deposits associated with felsic rocks. Other gangue phases are much less abundant, except in massive sulfide deposits that have been metamorphosed to greenschist or higher metamorphic grades. In these metamorphosed deposits, phases such as anthophyllite and cordierite form from chloritic protoliths (Taylor and others, 1995). In sedimentary-exhalative deposits, the dominant sulfide ore minerals are sphalerite and galena, although minor chalcopyrite, arsenopyrite, and tetrahedrite are present in some deposits (Large, 1983; Kelley and others, 1995). The most common gangue minerals are iron sulfide (pyrite, marcasite, or pyrrhotite) and quartz. Barite may be present. Numerous other sulfide and sulfosalt minerals have been reported in some deposits (Cox and Curtis, 1977; Large, 1983; Taylor and others, 1994).

**Table 2.** Mineralogical and metal associations of massive sulfide deposits

	Noranda	Kuroko	Cyprus	Besshi	Bathurst	Sed-Ex
Major metals	Fe, Cu, Zn, (Al)	Fe, Zn, Pb, Cu, (Al)	Fe, Cu	Fe, Cu, Zn, (Al)	Fe, Zn, Pb, (Al)	Fe, Zn, Pb, (Al)
Minor metals	Pb, Cd, As, Ag, Au	Cd, As, Ag, Au	Zn, Cd, Pb, Ag, Au	Pb, Cd, Ag, Ag	Cu, Cd, As	Cu, Cd, Ag
Dominant Fe sulfide	py $\geq$ po	py	py	po $\geq$ py	py	py $\geq$ po
Major ore Sulfides	cpy, sph	sph, gn, cpy	cpy	cpy, sph	sph, gn	sph, gn
Minor sulfide	apy, td	apy, cs, cb, po, td	po, sph	apy, cb, gn, td	cpy, po, apy	apy, cpy, st, td
Primary sulfates	ba	ba, anh			ba	ba
Minor carbonates	sd, cal	cal, dol, sd	cal	ank, cal	cal	cal, dol
Secondary sulfides	en, cv, cc-dg, mc	ac, cv, en	bn	mc, cv, cc-dg		mc
Secondary alkaline earth sulfates	ba, anh	ba, anh		ba, anh		ba, anh
Secondary metal sulfates	ang, gos, hal-pk, mel, roz, cop	ang, gos, aln, chc, eps, hal-pk, mel, roz, cop	chc, eps, Cu-Mg mel, gos	ang, aln, gos, hal-pk, mel, roz, cop		ang, gos, hal-pk, mel, roz
Secondary ferric hydroxide-hydrates	fer, goe, hm, sch, jar	fer, goe, sch, sc	fer, goe, sch	fer, goe, jar, sch		fer, goe

Abbreviations: py: pyrite; po: pyrrhotite; cpy: chalcopyrite; sph: sphalerite; gn: galena; apy: arsenopyrite; td: tetrahedrite-tennantite; cs: cassiterite; cb: cubanite; st: stannite; en: enargite; cv: covellite; cc-dg: chalcocite-digenite; mc: marcasite; bn: bornite; cal: calcite; dol: dolomite; ank: ankerite; sd: siderite; ba: barite; anh: anhydrite; ang: anglesite; gos: goslarite; hal-pk: halotrichite-pickeringite; mel: melanterite; roz: rozenite; cop: copiapite; aln: alunogen; chc: chalcantite; eps: epsomite; fer: ferrihydrite; goe: goethite; hm: hematite; sch: schwertmannite; sc: scorodite; jar: jarosite.

For all deposit types, grain size is highly variable and is generally controlled by primary sulfide mineralogy and the extent of metamorphic recrystallization. Primary sulfide minerals of most zinc-lead-copper deposits are fine grained and intergrown, whereas those of most copper-zinc deposits are coarser grained (Franklin, 1993). The extent of grain size changes depends upon pressure and temperature conditions attained during metamorphism, and on the ductility of sulfide minerals. For example, cataclastic deformation significantly reduces grain-size and therefore reactivity of brittle sulfide minerals such as chalcopyrite and pyrite, but plastically deforms ductile sulfide minerals such as galena. Thermal metamorphism commonly causes sulfide ore to become much coarser grained and develop mosaic or

porphyroblastic sulfide textures (Stanton, 1972). Metamorphism partially or completely replaces primary textures and causes grain size increases. Recrystallization causes porphyroblastic textures in pyrite and sphalerite, barite is recrystallized to an elongate habit, and galena may be remobilized to fill fractures (McClay, 1983).

Metal zoning is well developed in volcanic-associated massive sulfide deposits. Copper abundances are elevated in footwall and stringer ore zones, and zinc content increases upward and outward from the core of hydrothermal upwelling zones. In felsic-associated deposits, lead, arsenic, and antimony abundances are enriched upward and outward from the zinc-rich zones. Barite and silica are also enriched toward the stratigraphic tops and distal edges of most Kuroko-type deposits. In sedimentary-exhalative deposits, relative abundances of major base-metal sulfide minerals vary among deposits and within deposits as a result of zonation. Large (1983) reports that lead-zinc ratios of ore range from approximately 1:1 (Mount Isa, Australia; Sullivan, British Columbia; and Tynagh, Ireland) to 1:8 (Meggen, Germany). The sequence of zonation is generally lead-zinc-(barium-copper) extending outward in laterally zoned deposits and zinc-lead-(barium) extending upward in vertically zoned deposits (Large, 1983; Lydon, 1983). Iron is sometimes enriched at the center of zonation assemblages (Large, 1983), or an iron-manganese halo may encircle the base-metal sulfide minerals (Tynagh, Ireland) (Maynard, 1983).

#### Deposit Trace Element Geochemistry

Massive sulfide deposits of all types are typically dominated by iron, derived from pyrite, pyrrotite, or marcasite. Kuroko-, Bathurst-, and Noranda-type deposits, relative to Cyprus- and Besshi-type deposits, generally have much higher contents of zinc, lead, silver, and antimony, which reflect the composition of their felsic volcanic host rocks. Kuroko-, Bathurst-, and Noranda-type deposits also tend to be underlain by copper-rich stringer zones and commonly have well developed geochemical zonation with progressive zinc, lead, and silver enrichment both vertically and laterally away from vent centers. Besshi-type deposits are typically copper-rich and contain small abundances of lead and other lithophile elements. Sedimentary exhalative deposits are characterized by iron, zinc, and lead, with generally insignificant copper. Thus, in terms of Cu/Zn ratio, these deposits generally decrease in the order Cyprus > Besshi > Noranda > Kuroko > Bathurst > Sedimentary-exhalative.

Deposits associated with mafic rocks, such as Cyprus-, Besshi-, and Noranda-type deposits, can contain anomalous concentrations of gold, silver, and cobalt. In addition to lead, deposits associated with felsic volcanic and sedimentary rocks contain minor to significant concentrations of silver, arsenic, antimony, cadmium, and locally bismuth, tin, and selenium. Cadmium is ubiquitous in all classes of massive sulfides, where it occurs as a solid solution in sphalerite. Concentrations of mercury are high in some deposits, where it is primarily in pyrite, sphalerite, or sulfosalt minerals (Ryall, 1981).

#### MINING AND ORE PROCESSING METHODS

Mining methods have a large influence on the potential environmental impacts of massive sulfide deposits. Both open-pit and underground methods have been used to mine massive sulfide deposits in historic and modern operations. Local climatic and hydrologic conditions influence the acid generating capacity of deposits. Most massive sulfide deposits contain a large excess of iron-sulfide minerals relative to valuable base-metal sulfide minerals. The nature of ore processing and the method of deposition of the sulfide-mineral-rich tailings and waste rocks are critical parameters that influence the scope of environmental impacts associated with mining massive sulfide deposits. Fine-grained and intergrown sulfide minerals may require very fine grinding during the beneficiation process, which can result in highly reactive tailings. Many modern mines discharge fine-grained sulfide-mineral-rich tailings into surface tailings ponds underlain by a number of impermeable linings. Previous mining operations often discharged tailings in a manner that resulted in significant contamination of surface and shallow ground water. In addition, early flotation operations did not separate a zinc concentrate. Thus, older tailings piles are high in zinc. Some active underground mines are able to dispose of essentially all tailings by backfilling and cementing mined stopes; consequently, surface contamination is virtually eliminated. Base-metal sulfide minerals are typically separated by flotation. Some surfactants used in the process are toxic, but most of these surfactants are recycled and only a relatively minor amount is discharged to tailings ponds. Base metal sulfide minerals separated by flotation are usually shipped to smelters as ore concentrates. However, historic flotation circuits and cyanide leach operations add exotic chemicals to mine wastes.

The hydrologic differences between underground and open pit mines are significant, especially at abandoned mines. Evaporative concentration is prominent in open pit settings, particularly in semi-arid to

arid settings. At historic abandoned mines, such as the Elizabeth mine in Vermont, the evolution of ore beneficiation techniques can cause different “vintages” of mine wastes to be variably endowed in metals.

## ENVIRONMENTAL GEOCHEMISTRY

### Secondary Mineralogy

The secondary mineralogy associated with the weathering of a deposit or its mine wastes tends to sequester metals and (or) acidity on either a long-term or short-term basis. Hydrated ferric oxides can sorb metals on a somewhat refractory substrate, whereas efflorescent metal sulfate salts, such as melanterite, serve as a means of stored metals and acidity during dry periods. These salts readily dissolved during rain storm or spring melt of snow and deliver their metals and acidity to the surrounding watershed. For many deposit types, pre-mining oxidation of primary ores was a major contributing factor in enriching some deposits to economic grades. Secondary minerals also have important implications for acid-base accounting. General secondary mineralogical features of massive sulfide deposits are summarized in Table 2.

Oxidation of massive sulfide minerals results in the formation of iron-rich gossan zones, both initially on the seafloor and later, in subaerial surface environments. Sedimentary-exhalative deposits typically form in anoxic seafloor environments (Goodfellow and others, 1993); therefore, sulfide oxidation is restricted to the more recent history of these deposits. Intermediate stages of oxidation also can result in the formation of a wide range of iron- and base-metal sulfate and sulfate-hydrate minerals. Secondary minerals formed in temperate climates include goethite, crystalline and amorphous silica, jarosite, a variety of metal-bearing hydroxy-sulfate minerals (beudantite, plumbojarosite, argentojarosite, woodhouseite, beaverite, meta-aluminite, hinsdalite, and brochantite), scorodite, native gold, native silver, native bismuth, barite, anglesite, litharge, covellite, chalcocite, digenite, enargite, luzonite, and acanthite (Taylor and others, 1995). Anglesite and cerussite are the most abundant secondary lead minerals but coronadite, mimetite, nadorite, pyromorphite, and lanarkite have also been reported (Kelley and others, 1995). Secondary zinc minerals are rare, with the exception of goslarite. Rock may be oxidized to 100 m below the surface, and may extend to 300 m adjacent to major faults and shear zones. Oxidation depth is controlled partly by fracture density near orebodies and presence of pyrrhotite, which is highly reactive with oxygenated ground water (Taylor and others, 1984).

Soluble sulfate salt minerals derived from weathering and oxidation of sulfide minerals in mine dumps and tailings piles represent a potential source of metal contamination and acid generation. As surface and ground water evaporates during dry periods or winter freeze, efflorescent metal-sulfate salt minerals form on and below the surface of waste piles, which effectively stores acidity and metals from mine drainage. Subsequent rainfall or snowmelt is likely to release a highly concentrated pulse of acid mine water. Secondary minerals associated with waste piles include a variety of less soluble iron oxyhydroxides (goethite, lepidocrocite, akaganeite, maghemite, and ferrihydrite), and sulfates (jarosite, hydronium jarosite, anglesite). More soluble secondary minerals include gypsum, bassanite, melanterite, goslarite, ferroxahydrite, epsomite, hexahydrite, siderotil, rozenite, alunogen, and copiapite. Secondary sulfide minerals that can form include marcasite, covellite, and native sulfur (Jambor, 1994).

From an acid-base accounting perspective, significant differences are found among the various deposit types with regard to the speciation of sulfur in primary ores, host rocks and mine wastes. Sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, and sphalerite dominate the primary mineralogy of these deposits (Table 2) and contribute to the maximum potential acidity. Secondary metal-sulfate salts that commonly accumulate as intermediate products of sulfide oxidation also will contribute acidity (Alpers and others 1994a; Cravotta 1994). For example, melanterite, rozenite, copiapite, and halotrichite, among others, are quite common and highly soluble; less soluble sulfate minerals such as jarosite and schwertmannite also are common in mining environments (Table 2). In contrast, alkaline earth-sulfate minerals such as barite and anhydrite also are common as both primary and secondary minerals (Table 2), but do not contribute acidity even though their S content will be reported in total S determinations. The most prominent differences in secondary sulfur mineral speciation among mine wastes from the different deposit types are found in their metal-sulfate salts, particularly in the presence or absence of chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), goslarite ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), Cu-Mg melanterite ( $\text{Cu, MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and alunogen ( $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ ), among others.

Various carbonate minerals, most of which contribute neutralizing potential, are associated locally with primary alteration assemblages of some of these deposit types. Calcite and ankerite ( $\text{Ca(Fe,Mg)CO}_3$ ) dominate the carbonate mineralogy (Table 2). Sedimentary-exhalative deposits may have dolomitic shales in their host rocks, and siderite, which has no net neutralizing potential (Alpers and Zierenberg 1998), in



their alteration assemblages. Post-mineralization tectonism can introduce late calcite veinlets into the rock units surrounding these deposits, such as at the Big Mike Cyprus-type deposit in Nevada, where pit waters have neutral pH.

#### Soil and Sediment Signatures

Pre-mining soil and stream sediment signatures may be useful for establishing pre-mining backgrounds. Also, soils around abandoned mine sites represent a significant sink for metals. The elemental suite and magnitude of geochemical anomalies in soil and sediment collected from undisturbed massive sulfide deposits depend upon a number of factors, including deposit type, extent of ore outcrop or overburden, climate, and topography, among others. Stream sediment samples collected downstream Kuroko-type deposits in temperate rain forest on Admiralty Island, Alaska, contain 5 to 10 weight percent iron, as much as 10,000 ppm barium, hundreds to several thousand ppm zinc, hundreds of ppm lead, tens to hundreds of ppm arsenic, copper, and nickel, as well as 0 to 20 ppm silver, bismuth, cadmium, mercury, molybdenum, and antimony (Kelley, 1990; Rowan and others, 1990; Taylor and others, 1992; C.D. Taylor, unpub. data, 1995). Stream sediment geochemical signatures associated with undisturbed to variably disturbed Cyprus- and Besshi-type deposits in the Prince William Sound, Alaska, are similar to those just described. They contain 10 to 40 weight percent iron, several hundred ppm barium, hundreds of ppm arsenic and zinc, tens to hundreds of ppm lead, hundreds to thousands of ppm copper, and 0 to 20 ppm silver, bismuth, mercury, molybdenum, and antimony (R.J. Goldfarb, unpub. data, 1995).

Stream sediment samples (<0.2 mm and <0.5 mm fractions) associated with sedimentary-exhalative deposits in cold semi-arid settings in Alaska contain anomalous concentrations of many metals, including as much as 10 ppm silver; 10s of ppm arsenic, cadmium, and antimony; 100s of ppm copper and nickel; 1000s of ppm manganese, lead, and zinc; and hundreds to thousands of ppm barium (Theobald and others, 1978; Kelley and others, 1992). Soil that overlies mineralized rock contains hundreds to tens of thousands of ppm lead, hundreds to thousands of ppm barium and zinc, tens of ppm silver; and tens to hundreds of ppm copper, but concentrations of other metals, including <2 ppm cadmium, hundreds of ppm manganese, and tens of ppm nickel are low relative to stream sediment abundances (Briggs and others, 1992; Meyer and Kurtak, 1992). Soil overlying sedimentary-exhalative deposits in warm semi-arid settings in Australia contains hundreds to thousands of ppm copper, lead, and zinc, and tens of ppm silver (Cox and Curtis, 1977).

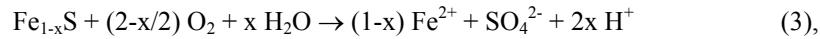
#### Hydrology

The hydrologic setting, especially relative to the water table, is a key variable in determining the magnitude of mine drainage problems. The extent of mineralized outcrop and (or) mine-related excavations exposed to the atmosphere or oxidized groundwater, and their position relative to the water table, are hydrologic factors that can significantly influence the intensity and scale of environmental problems related to massive sulfide deposits. Availability of oxidizing water is a controlling factor for acid generating potential and dissolved metal carrying capacity of water interacting with massive sulfide deposits or their mine-related products. Similarly, the geologic setting of a deposit can influence the distribution of fracture-controlled permeability.

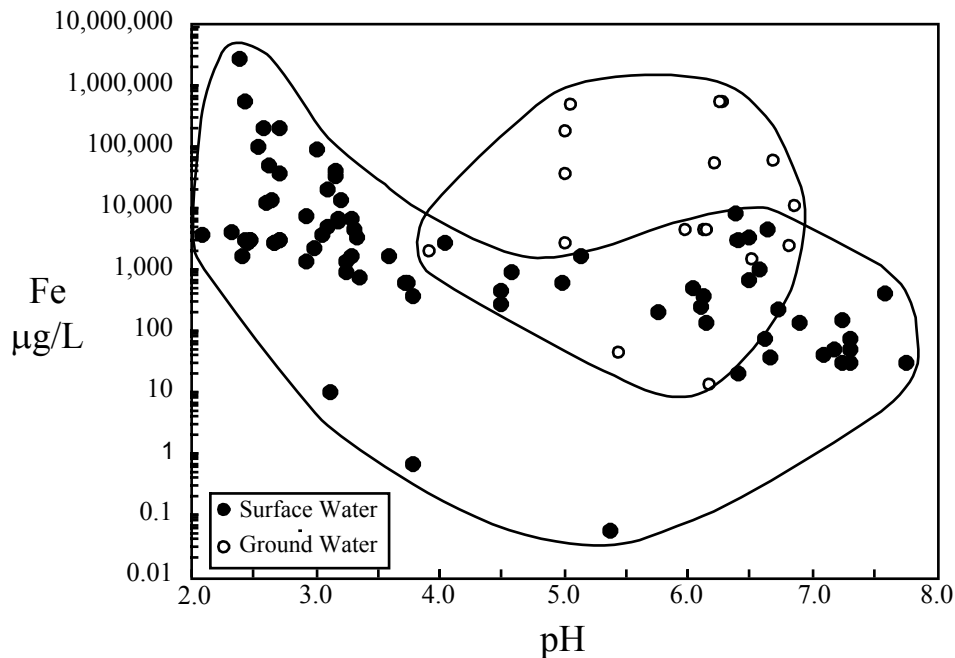
A comparison of mine drainage from pyritic ores at Iron Mountain (Noranda-type) and the Penn mine (Kuroko-type), California emphasizes the importance of the location of the deposit relative to the water table. Both deposits are situated in similar climatic settings. At Iron Mountain, the deposit is mostly located above the water table, whereas at the Penn mine, the deposit is mostly below the water table, but has waste piles above the water table that contribute to water-quality degradation (Alpers and others 1994b; 1999). At Iron Mountain, pH values range as low as -3.4 and total dissolved solids concentrations exceed 100,000 mg/L (Alpers and others 1994b; Nordstrom and Alpers 1999). In contrast, pH values of mine waters from the Penn mine range as low as 3.1 and total dissolved solids concentrations reach a maximum of approximately 5,500 mg/L (Alpers and others 1999).

Mine drainage from the pyrrhotitic Elizabeth mine (Besshi-type), Vermont also emphasizes the importance of hydrologic setting. Two dominant hydrologic settings are present at Elizabeth: one dominated by surface flow over mine wastes, and one dominated by ground water flow through tailings piles. In these two environments, the relationship of dissolved Fe to pH varies significantly. Surface waters show a general negative correlation between dissolved Fe and pH; in contrast, waters flowing through the tailings piles are near-neutral to slightly acidic, but carry amounts of dissolved Fe that are comparable to those in the surface waters (Fig. 2; Seal and others 1999). The geochemical differences between these two

environments can be related to the presence of pyrrhotite as the dominant Fe-sulfide mineral. The oxidation of pyrrhotite by dissolved oxygen can be described by the reaction:



where one mole of pyrrhotite generates from 0 to less than 0.25 moles of acid depending on the composition of the pyrrhotite. In contrast, the similar oxidation reaction for pyrite yields 2 moles of acid for each mole of pyrite. Under acidic conditions,  $\text{Fe}^{3+}$  can be an important oxidizer of pyrite and generates 16 moles of acid for each mole of pyrite. Likewise, at low pH values capable of carrying significant amounts of  $\text{Fe}^{3+}$ , the acid-generating potential of pyrrhotite is enhanced. However, at Elizabeth, precipitation and regional ground waters that infiltrate the tailings pile are slightly acidic to near-neutral. The addition of lime in mineral processing circuits prior to disposal may also contribute to the present-day near neutral pH of ground waters emerging from the tailings pile. Therefore, pyrrhotite oxidation is dominated by dissolved oxygen, which has limited acid-generating capacity. Because of the near-neutral pH, the ground waters flowing through the tailings do not have elevated concentrations of heavy metals such as Cu, Zn, and Cd. Upon emerging from the base of the tailings pile, Fe in the ground waters undergoes rapid oxidation from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , followed by hydrolysis and a concomitant drop in pH. Despite the decreased pH, the Cu, Zn, and Cd concentrations are low because of the prior history of these waters.



**Figure 2.** Fe versus pH for filtered mine drainage samples from Besshi-type deposits. Note that ground waters (seeps) from this deposit type have elevated Fe concentrations at comparable pH values relative to surface waters because of the higher solubility of ferrous iron found in ground waters.

#### Drainage Signatures

The geology of a deposit exerts a major influence on both pre-mining background water compositions and on mine drainage. In general, increases in total dissolved base metals generally correlate with increases associated pyrite content, decreases in acid-neutralizing capacity, and increases in base metal content of deposits (Plumlee, 1999).

Natural backgrounds: Mine permitting and remediation require an estimate of pre-mining natural background to serve as a goal for post-mining reclamation. A variety of methods have been used to estimate pre-mining backgrounds for abandoned mines (Runnells and others 1992; 1998; Alpers and others 1999; Alpers and Nordstrom 2000). Baseline data from undisturbed mineral deposits are useful for comparing and contrasting geochemical signatures among different types of massive sulfide deposits. These comparisons illustrate the importance of using a geochemically based classification of massive

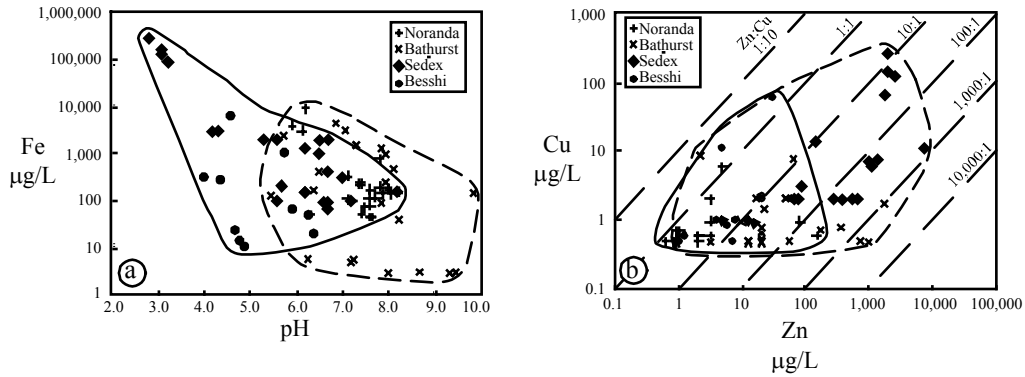
sulfide deposits in selecting an appropriate baseline. Besshi-type deposits are typically hosted by sulfide-rich black shales that are enriched in sub-economic concentrations of heavy metals and which formed through many of the same geochemical processes responsible for massive sulfide mineralization. Thus, drainage from watersheds underlain by these black shale units provides useful background data for Besshi-type deposits (Seal and others 1998a). In this paper, we compile data from in and around undisturbed Noranda-type (Seal and others, 1998b), Bathurst-type (Leybourne and others 1998), and sedimentary-exhalative deposits (Kelley and Taylor 1997). Comparison of these data with data from black shale terranes that host Besshi-type deposits (Seal and others 1998a) illustrates several important points about natural backgrounds.

The availability of atmospheric oxygen and the position of the ground-water table are key related factors in determining the natural weathering behavior of massive sulfide deposits. The Alaskan sedimentary-exhalative deposits and the black shales that host the Fontana and Hazel Creek Besshi-type deposits in North Carolina are exposed at the surface of the Earth, whereas the Bald Mountain (Noranda-type) deposit and the Restigouche and Halfmile Lake (Bathurst-type) deposits are buried beneath glacial overburden and unmineralized rock. Surface waters around exposed deposits generally are more acidic and carry more dissolved iron than those draining buried deposits (Fig. 3a).

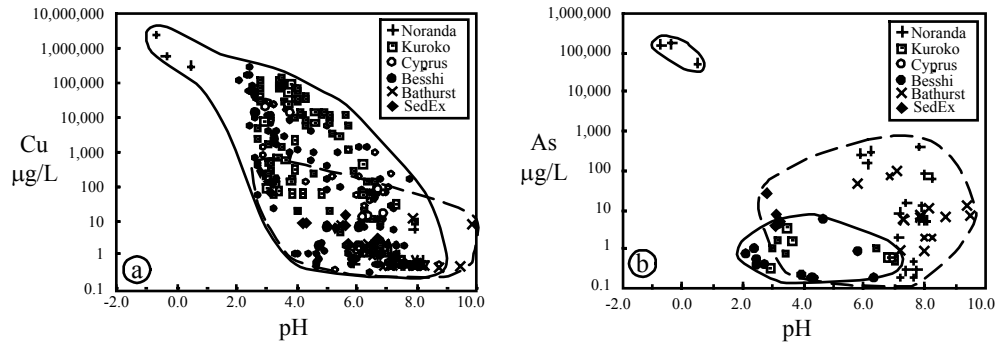
Significant differences can be found in the metal ratios of natural ground and surface waters around undisturbed deposits that can be related to the primary character of the deposits. The Zn:Cu ratio of waters around sedimentary-exhalative and Bathurst-type deposits is generally greater than 1:1 and can exceed 1,000:1, consistent with the Zn-rich/Cu-poor character of these deposits; in contrast, the Zn:Cu ratio of waters associated with Cu-rich Besshi- and Noranda-type deposits is generally between 1:10 and 10:1, but can reach 100:1 (Fig. 3b). An important implication of this observation is that natural background data from a sedimentary-exhalative deposit such as Red Dog (Alaska) may not represent an appropriate proxy for natural backgrounds that might be expected around a Noranda-type deposit such as Iron Mountain (California).

Mine drainage: Mine-drainage data compiled in this study include studies at the Elizabeth and Ely mines (Besshi-type), Vermont (Seal and others 1999), the Fontana and Hazel Creek mines (Besshi-type), North Carolina (Seal and others 1998a), the Prince William Sound district (Cyprus- and Besshi-type), Alaska (Goldfarb and others 1995), the Holden mine (Kuroko-type), Washington (Kilburn and others 1999), the Mineral district (Kuroko-type), Virginia (R.R. Seal, II, unpub. data, 1999), the Penn mine (Kuroko-type), California (Alpers and others 1999), and Iron Mountain (Noranda-type), California (Alpers and others 1994b). Mine drainage associated with massive sulfide deposits tend to show a general, negative correlation between dissolved metals and pH for most divalent metals such as Cu (Fig. 4a), Zn, Ni, Co, Cd, and Pb, and sulfate. Likewise, Fe and Al also exhibit increased solubility with decreased pH. The correlations between pH, metals and sulfate reflect acid generation dominantly through the aqueous, oxidative weathering of pyrite and (or) pyrrhotite and associated ore sulfides. For the divalent metals, Fe, and Al, mine-drainage compositions overlap significantly with natural background compositions, but range to higher heavy metal concentrations and lower pH values (Fig. 4b). Relative to the divalent metals, limited data on As presents an intriguing contrast. With the exception of the low-pH, high-As waters from Iron Mountain, California (Noranda-type), the natural background waters tend to have higher As concentrations than mine drainage (Fig. 4b). Data for the Bald Mountain deposit (Noranda-type) have established that the development of an ancient goethite gossan was an important controlling factor on As distribution in the deposit, which presumably was reflected in ancient ground-water compositions (Foley and Flohr 1998). The most likely explanation for higher concentrations of As in natural background waters compared to mine drainage is that the near-neutral, low-Fe background waters tend to remain undersaturated with respect to hydrous ferric oxide, which can sorb significant amounts of As (Smith and others, 1998). Thus, any proposed remediation plan should carefully consider As behavior and mobility relative to Fe geochemistry.

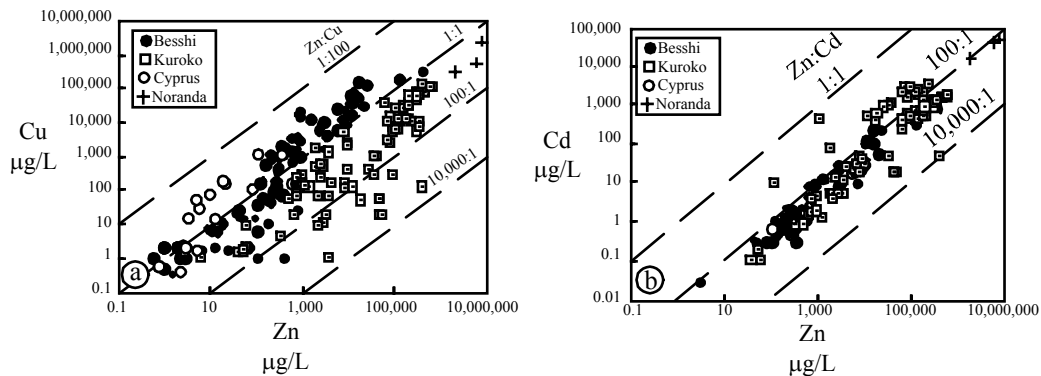
The dissolved chemistry of mine drainage from massive sulfide deposits shows clear evidence of both primary controls based on deposit type and mineralogical controls for individual metals. In terms of dissolved Cu and Zn, the data are correlated positively with individual deposit types falling at distinct ranges of Zn:Cu ratios, which are directly related to the primary character of the ores (Fig. 5a). Zn:Cu ratios (mass basis) associated with the Cu-rich Cyprus-type deposits range from 1:100 to 10:1, whereas those associated with Cu>Zn Besshi-type deposits range from 1:10 to more than 10:1, those associated with Zn>Cu Kuroko-type deposits are the highest, ranging from 1:1 to 10,000:1. Correlations between Cu and



**Figure 3.** Natural background geochemical data for filtered ground and surface waters around massive sulfide deposits. a. Fe vs. pH. Data outlined by solid line are from deposits exposed at the surface; data outlined by dashed line are from buried deposits. b. Cu vs. Zn. Dashed lines represent Zn:Cu ratios (mass basis). Note that waters from Zn-rich deposits (Sedimentary-exhalative and Bathurst) range to higher Zn:Cu ratios than Cu-rich deposits (Noranda and Besshi).



**Figure 4.** Comparison of filtered mine drainage waters with natural background waters. Data outlined by solid lines are mine drainage; data outlined by dashed lines are natural backgrounds. a. Cu vs. pH. The general negative slope of the data is typical of most divalent metals. b. As vs. pH. Note that many of the natural background samples have higher As concentrations than the mine drainage samples.



**Figure 5.** Filtered mine drainage geochemical data. a. Cu vs. Zn. Note the separation of deposit types by Zn:Cu ratio (mass basis), which reflects primary differences in deposit types. b. Cd vs. Zn. Note the overlap among deposit types in terms of Zn:Cd ratios (mass basis), which reflects the common source control of Cd as a trace element in sphalerite.

Pb are less distinct, presumably due to the saturation of Pb with respect to anglesite ( $\text{PbSO}_4$ ). Unlike Cu and Zn, the systematics of dissolved Cd and Zn are different; the fields for all massive sulfide types overlap in a range of Zn:Cd ratios (mass basis) that scatter about 100:1 (Fig. 5b). The overlap reflects the fact that Cd occurs primarily in all massive sulfide deposits as a minor element in sphalerite as a solid solution.

Pore water from tailings impoundments associated with the Heath Steele, New Brunswick, deposit is acidic (pH 1.8 to 5.2), have Eh of 280 to 580 mV, and contain significant dissolved metal abundances, including 0.3 to 600 mg/L copper, 0.8 to 11 mg/L lead, 23 to 4,880 mg/L zinc, 1,200 to 36,000 mg/L iron, and 600 to 67,600 mg/L sulfate (Boorman and Watson, 1976). Similarly, pore water from tailings impoundments associated with the Waite Amulet, Quebec, deposit are acidic (pH 2.5 to 6.0), have Eh of 200 to 700 mV, and contain significant dissolved metal abundances, including as much as 65 mg/L copper, as much as 5 mg/L lead, as much as 250 mg/L zinc, as much as 8,000 mg/L iron, and as much as 20,000 mg/L sulfate (Blowes and Jambor, 1990). Finally, pore water from tailings impoundments associated with the Kidd Creek, Ontario, deposit are acidic (pH 3.5 to 7.5), have Eh of 50-500 mV, and contain significant dissolved metal abundances, including 0 to 38 mg/L copper, 0 to 2 mg/L lead, 0 to 6,200 mg/L zinc, 0 to 350 µg/L arsenic, 1 to 990 mg/L iron, and 1,860 to 27,000 mg/L sulfate (Al and others, 1994).

### Climatic Effects

Climate plays an important role in the environmental behavior of mineral deposits. Differences in temperature, amount of precipitation, and humidity are probably the most important climatic variables (Plumlee, 1999). From the perspective of massive sulfide deposits, this factor is probably the least well understood because of the limited data for specific deposit types that span different climatic settings.

Temperature and humidity are the prime variables that control evaporation. Evaporation limits the amount of water in semi-arid to arid climates. Evaporation can concentrate solutes in all climates. Acidity and total metal concentrations in mine drainage in arid environments are several orders of magnitude greater than in more temperate climates because of the concentrating effects of mine effluent evaporation and the resulting "storage" of metals and acidity in highly soluble metal-sulfate-salt minerals. However, minimal surface water flow in these areas inhibits generation of significant volumes of highly acidic, metal-enriched drainage. Concentrated release of these stored contaminants to local watersheds may be initiated by precipitation following a dry spell. In wet climates, high water tables may reduce exposure of abandoned orebodies to oxidation and continually flush existing tailings and mine dumps. Although metal-laden acid mine water does form, it may be diluted to benign metal abundances within several hundred meters of mixing with a higher order stream. Winter freezing conditions can lead to seasonally episodic fluctuations in drainage chemistry.

### POTENTIAL ENVIRONMENTAL CONCERNS

Potential environmental concerns associated with mineral deposits can generally be divided into three broad categories: (1) human health risks; (2) ecosystem risks; and (3) physical hazards. All of these concerns are ultimately established in the geologic framework of the mineral deposit. Human-health risks (exclusive of physical hazards) generally focus on metals, such as lead, arsenic, selenium, and mercury, associated with various mineral deposit types, and elements and compounds used in ore processing, such as mercury or cyanide. Ecosystem risks are associated with acidity and several metals, such as Al, Cu, Zn, Cd, Se, Hg, and others. Physical hazards such as open shafts and open pits are related to the mining required to exploit specific mineral deposit types.

Human health risks: Human health risks associated with massive sulfide deposits are most prominent in terms of their contained lead and arsenic, and cyanide used in some recovery circuits. In addition, smelting may produce SO<sub>2</sub>-rich and metal-rich emissions, which may increase acidity and foster accumulation of heavy metals in downwind areas. Lead risks are generally related to ingestion of lead-rich mine waste through incidental contact. Extreme fine grinding required for beneficiation of enhances airborne transport of lead-bearing dust. This phenomenon is most probable in semi-arid to arid regions in which strong winds prevail. Data compiled by Gulson and others (1994) around the Broken Hill sedimentary-exhalative deposit documented the relationship between lead in soil near smelters and blood lead in children. Arsenic risks are generally related to contamination of ground waters. Seal and others (1998) documented ground water As concentrations up to 430 µg/L around the undisturbed Bald mountain deposit, Maine. Tailings ponds below mills can contain significant cyanide and other reactants used in flotation and recovery circuits (Taylor and others, 1995).

Ecosystems risks: The most significant ecosystem impacts related to massive sulfide deposits are through acid mine drainage. Mine drainage can reach extreme acidity and high heavy metal-rich compositions due to the abundance of metallic sulfide minerals in mine wastes and the lack of carbonate minerals in the mineralized rocks. Ecosystem impacts can result from low pH, and dissolved Fe, Al, Cu, Zn, Pb, Cd, and

As. The alkalinity and hardness of waters receiving mine drainage can be highly variable. Thus, natural mitigation and attenuation processes can be highly variable. Downstream effects can be very localized or can extend at least 100 km downstream from mine sites. Heavy metal contamination can also be dispersed downstream by the erosion and transport of tailings.

Atmospheric contamination can also occur because highly pyritic-pyrrhotitic orebodies that are exposed to oxidation by air circulating through open adits, manways, and exploration drill holes may evolve SO<sub>2</sub> gas; in some cases, spontaneous combustion can cause sulfide ore to burn. "Hot muck", the spontaneous combustion high sulfide ore in mine workings, is an environmental concern associated with processing ore from deposits with high pyrrhotite orebodies. The primary environmental concern is evolved sulfur dioxide. Fires are ignited by the build-up of heat, caused by ore oxidation, in stock piles, or may be triggered by blasting in areas of previously broken ore. Periodically, air emission can exceed 9.5 ppm SO<sub>2</sub> (Brown and Miller, 1977; Good, 1977); SO<sub>2</sub> release can acidify water in areas downwind from release site. Because hot muck is easily avoided by proper blasting techniques, it does not pose significant risks in modern mining operations.

### CONCLUSIONS

Seafloor massive sulfide deposits show significant variations in their environmental behavior based on differences in deposit types within this class of mineral deposit. As a class, these deposits have high acid-generating potential, and low acid-buffering capacity due to the sulfide-rich and carbonate-poor nature of the ores and host rocks. Some metal ratios of mine drainage and natural background waters reflect the primary character of the ores, whereas others reflect the mineralogical host of heavy metals in the deposits. Secondary processes, such as precipitation of secondary minerals and sorption obscure the primary geochemical controls in mine drainage for some elements like Pb and As. The magnitude of the potential environmental impact is strongly dependent upon the hydrologic setting of each individual deposit and its solid wastes. Climate, as it relates to variables such as temperature, amount of precipitation, and seasonality of precipitation, among others, is undoubtedly an important variable but difficult to assess because of the limited amount of data available for individual deposit types from various climatic settings.

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