# 20. Geoenvironmental Features

By Robert R. Seal II and Nadine Piatak

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**Volcanogenic Massive Sulfide Occurrence Model**

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## Weathering Processes

Modern weathering processes associated with mine wastes from massive sulfide deposits are similar, in many respects, to those operating in the supergene environment after the initial formation of the mineral deposit. Nevertheless, some important differences exist. Acid-mine drainage is one of the most significant challenges associated with these deposits due to the abundance of pyrite, pyrrhotite, or both iron sulfides and the general lack of any significant neutralizing potential or alkalinity. The geochemistry of acid-mine drainage has been reviewed by Nordstrom and Alpers (1999a), and additional aspects of the weathering of a variety of ore and gangue minerals were discussed by Plumlee (1999). Seal and others (2001a), Seal and Hammarstrom (2003), and Seal (2004) have reviewed the geoenvironmental characteristics of volcanic-hosted massive sulfide deposits.

Geochemical aspects of the formation of acid-mine drainage and its burden of metals and other elements of concern can be divided into three broad topics: (1) sulfide oxidation, acid generation, and acid neutralization processes; (2) metal cycling associated with secondary efflorescent sulfate salts; and (3) secondary precipitation of hydroxides and hydroxysulfates and associated sorption of metals.

## Sulfide Oxidation, Acid Generation, and Acid Neutralization Processes

The abundance of pyrite and pyrrhotite in massive sulfide deposits dominates most aspects of the environmental behavior of these deposits and their mine wastes. The acid generated by their oxidative weathering can aggressively attack other ore and gangue minerals, thereby liberating a variety of potentially toxic elements including aluminum and manganese, which are not part of the "typical" ore assemblage of metals but instead are found in silicate and carbonate gangue minerals. These acidic, metal-laden acid-sulfate waters can adversely affect the surrounding surface- and groundwaters. Within the hydrologic system of mine workings or mine wastes, minerals and other compounds, such as lime used in flotation circuits, and even monosulfide minerals, such as sphalerite, can neutralize acid generated by the oxidative weathering of sulfide minerals. Thus, the chemistry of drainage from a mine site is the result of the competing processes of acid generation and acid neutralization.

The oxidation of pyrite or pyrrhotite and other sulfide minerals proceeds with either dissolved oxygen ($O_2$) or dissolved ferric iron ($Fe^{3+}$) as the oxidizing agent. Dissolved oxygen is the most important oxidant at pH values above approximately 4, whereas ferric iron dominates below approximately 4 (Williamson and others, 2006). The aqueous oxidation of pyrite by dissolved oxygen is described by reaction 1:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$

The aqueous oxidation of pyrrhotite by dissolved oxygen is described by reaction 2:

$$Fe_{1\text{-}x}S + (2\text{-}x/2)\ O_2 + x\ H_2O \rightarrow (1\text{-}x)\ Fe^{2+} + SO_4^{2-} + 2x\ H^+ \qquad (2)$$

where *x* ranges from 0.000 to 0.125. Both reactions 1 and 2 actually represent the mass action of numerous intermediate reactions. In the oxidative weathering of pyrrhotite, a common initial reaction is the oxidation of pyrrhotite to either pyrite or marcasite as described by the reaction:

$$2\ Fe_{1\text{-}x}S + (1/2\text{-}x)\ O_2 + (2\text{-}4x)\ H^+ \rightarrow FeS_2 + (1\text{-}2x)\ Fe^{2+} + (1\text{-}2x)\ H_2O \qquad (3)$$

Textural evidence of marcasite replacement of pyrrhotite is common in pyrrhotitic mine wastes (Jambor, 1994, 2003; Hammarstrom and others, 2001).

The aqueous oxidation of pyrite by ferric iron is described by reaction 4:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (4)$$

The aqueous oxidation of pyrrhotite by ferric iron is described by reaction 5:

$$Fe_{1\text{-}x}S + (8\text{-}2x)\ Fe^{3+} + 4\ H_2O \rightarrow (9\text{-}3x)\ Fe^{2+} + SO_4^{2-} + 8\ H^+ \qquad (5)$$

For reactions 4 and 5, where ferric iron is the oxidant, ferrous iron must be oxidized to ferric iron to perpetuate the reaction as described by the reaction:

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O \qquad (6)$$

The rate of the oxidation of ferrous iron to ferric iron is greatly enhanced by the iron oxidizing bacterium *Acidithiobacillus ferrooxidans.* Singer and Stumm (1970) observed that *A. ferrooxidans* increased the rate of oxidation of ferrous iron to ferric iron by a factor of 100,000 compared to the abiotic rate. In the case of both sets of reactions for pyrite and pyrrhotite, additional acid is generated by the oxidation and hydrolysis of the aqueous ferrous iron as described by the reaction:

$$Fe^{2+} + \frac{1}{4} O_2 + 5/2\ H_2O \rightarrow Fe(OH)_3 + 2\ H^+ \qquad (7)$$

which also produces the orange and brown precipitates that typify acid-mine drainage.

Pyrrhotite and other monosulfides, such as sphalerite, can also undergo non-oxidative dissolution under anoxic conditions when exposed to acid, as described by the respective reactions:

$$Fe_{1-x}S + (2-2x)\ H^+ + x\ H_2 \rightarrow (1-x)\ Fe^{2+} + H_2S \qquad (8)$$
$$ZnS + 2\ H^+ \rightarrow Zn^{2+} + H_2S \qquad (9)$$

which, in the case of pyrrhotite, effectively decouples iron and sulfur oxidation. Both of these reactions consume acid.

Ore minerals such as sphalerite, galena, and chalcopyrite react by similar reactions, with dissolved oxygen and ferric iron serving as oxidants. Zinc and copper tend to go into solution, but lead commonly forms secondary phases such as anglesite ($PbSO_4$) or cerussite ($PbCO_3$), depending upon the concentrations of sulfate and carbonate in solution.

Gangue minerals in the host rocks generally react to consume the acid generated by the oxidation of sulfides. Carbonate minerals, such as calcite, consume acid as described by reaction:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (10)$$

Under anoxic conditions, siderite will neutralize acid. However, the oxidation and hydrolysis of the resulting ferrous iron will offset the alkalinity produced. Aluminosilicate minerals such as plagioclase can consume acid, even though they are not as reactive as carbonate minerals (Plumlee, 1999; Jambor and others, 2002). The reaction of these minerals typically adds dissolved constitutes such as aluminum to the water and produces secondary phases.

## Metal Cycling Associated with Efflorescent Sulfate Salts

Evaporative concentration of sulfate-rich mine drainage can produce a series of highly soluble secondary sulfate salts. Evaporative processes can operate during hot arid conditions, within mine workings or other sheltered areas, or in tailings piles beneath snow packs. Common secondary sulfate salts in mining environments include melanterite, rozenite, halotrichite, alunogen, copiapite, goslarite, and chalcanthite, among numerous others (Jambor, 1994; Jambor and others, 2000; Hammarstrom and others, 2001). Gypsum is another common secondary sulfate that can contribute dissolved solids to drainage but does not store acidity or metals. Metal-sulfate salts offer a means of temporarily sequestering acidity and metals for later dissolution during rain events or snowmelt (Jambor, 2003; Jambor and others, 2000; Hammarstrom and others, 2001). The effects of salt dissolution events can be dramatic, cycling through a watershed in a matter of hours.

## Secondary Precipitation of Hydroxides and Hydroxysulfates

The oxidation of dissolved ferrous iron and neutralization of mine drainage produces a wide variety of secondary Fe or Al hydroxides and hydroxysulfates that are significantly less soluble than efflorescent sulfate salts. These phases range from compounds that are nearly amorphous to those that are well crystalline. Important Fe minerals include ferrihydrite (nominally $Fe_5HO_8 \cdot 4H_2O$), schwertmannite, jarosite, and goethite ($\alpha$-FeO(OH)). Important Al phases include amorphous Al hydroxide ($Al(OH)_3$), gibbsite ($\gamma$-$Al(OH)_3$), and basaluminite ($Al_4(SO_4)(OH)_{10} \cdot 4H_2O$). In mine-drainage environments, neutralization and hydrolysis are the main processes leading to the precipitation of the aluminum phases, whereas oxidation is additionally important for the precipitation of the iron phases. Jarosite tends to form in low-pH (1.5–3.0), high-sulfate (>3,000 mg/L) environments, schwertmannite in moderately acidic (pH of 3.0–4.0), moderate-sulfate (1,000–3,000 mg/L) environments, and ferrihydrite in near-neutral (pH > 5.0) environments (Bigham, 1994; Bigham and Nordstrom 2000; Stoffregen and others, 2000). Aluminum-bearing phases commonly precipitate at pH values above 4.5 (Nordstrom and Alpers, 1999a). An important aspect of the secondary iron hydroxides is their ability to sorb significant quantities of trace metals and remove them from solution. Sorption behavior is pH-dependent. Metal cations such as $Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ generally sorb to a greater extent with increasing pH, whereas most oxyanions, such as arsenate $(AsO_4)^{3-}$ and selenate $(SeO_4)^{2-}$, sorb to a greater extent with decreasing pH (Smith, 1999). Thus, secondary ferric hydroxides and hydroxysulfates can effectively remove metals from solution.

## Pre-Mining Baseline Signatures in Soil, Sediment, and Water

Mine permitting and remediation require an estimate of pre-mining natural background conditions, particularly in regulated media such as groundwater and surface water, soil, and sediment, to serve as a goal for post-mining reclamation. Detailed baseline geochemical characterization prior to the onset of mining is essential. However, for many abandoned mines, baseline characterization was not done prior to mining. Thus, a variety of methods have been used to estimate pre-mining backgrounds for abandoned mines (Runnells and others, 1992, 1998; Alpers and others, 1999b; 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. Mafic-siliciclastic type deposits are typically hosted by sulfide-rich black shales that are enriched in subeconomic 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 mafic-siliciclastic type deposits (Seal and others, 1998b). Available background geochemical data include soil and stream-sediment data from a variety of deposits in Alaska, groundwater and surface-water chemistry in and around unmined bimodal-mafic type and bimodal-siliciclastic type deposits, and surface-water chemistry from watersheds underlain by sulfidic black shale host rocks for which mafic-siliciclastic type deposits are located in adjacent watersheds.

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 from bimodal-felsic type deposits in temperate rain forest on Admiralty Island, Alaska, contain 5–10 wt% iron, as much as 10,000 mg/kg barium, hundreds to several thousand milligram per kilogram zinc, hundreds of milligram per kilogram lead, tens to hundreds of milligram per kilogram arsenic, copper, and nickel, as well as 0–20 mg/kg silver, bismuth, cadmium, mercury, molybdenum, and antimony (Kelley, 1990; Rowan and others, 1990; Taylor and others, 1992). Stream sediment geochemical signatures associated with undisturbed to variably disturbed mafic-ultramafic and mafic-siliciclastic type deposits in the Prince William Sound, Alaska, are similar to those just described. They contain 10–40 wt% iron, several hundred milligram per kilogram barium, hundreds of milligram per kilogram arsenic and zinc, tens to hundreds of milligram per kilogram lead, hundreds to thousands of milligram per kilogram copper, and 0–20 mg/kg silver, bismuth, mercury, molybdenum, and antimony (Goldfarb and others, 1995).

The available data for water associated undisturbed massive sulfide deposits span a range in pH from approximately 3 to 10 and a range of concentrations of dissolved Fe, a dominant cation, from approximately <0.02 to 300 mg/L. The availability of atmospheric oxygen and the position of the groundwater table are two of the most important factors in determining the natural weathering behavior of massive sulfide terranes. Surface waters around exposed deposits generally are more acidic and carry more dissolved Fe than those draining buried deposits (fig. 20–1*A*). The Alaskan sedimentary-exhalative deposits, Red Dog, Lik, and Drenchwater, and the black shales that host the Fontana and Hazel Creek mafic-siliciclastic type deposits in North Carolina are exposed at the surface, whereas the Bald Mountain (bimodal-mafic type) deposit and the Restigouche and Halfmile Lake (felsic-siliciclastic type) deposits are buried beneath glacial overburden or unmineralized rock.

The natural weathering of these host rocks can cause elements of concern for ecosystem health, such as Cu and Zn, to reach concentrations in excess of generic water-quality guidelines for the protection of aquatic life. In the Great Smoky Mountains National Park (North Carolina and Tennessee), watersheds underlain by the Anakeesta Formation, a sulfidic schist that hosts two mafic-siliciclastic type massive sulfide deposits, have dissolved concentrations of Cu and Zn that exceed generic acute toxicity water-quality guidelines (Seal and others, 1998b). Here, the biota in the ecosystem exists despite the concentrations of metals. Similarly, elements of concern for human health, such as As, also can exhibit anomalous background concentrations in groundwaters around unmined deposits. Concentrations of dissolved As reach 430 μg/L, which significantly exceed the drinking-water standards in the United States (10 μg/L), in the vicinity of the undisturbed Bald Mountain bimodal-mafic type deposit in northern Maine (Seal and others, 1998a) and near the undisturbed felsic-siliciclastic deposits in the Bathurst mining camp, New Brunswick (fig. 20–1*B*) (Leybourne and others, 1998). In the compiled dataset, many of the natural background waters have higher As concentrations than mine drainage; the low-pH, high-As waters from Iron Mountain (bimodal-mafic type), California, are an exception (fig. 20–1*B*). The higher concentrations of As in natural background waters compared to those of mine drainage are likely related to a combination of two factors. First, the near-neutral, low-Fe background waters generally remain undersaturated with respect to hydrous ferric oxide, which can sorb significant amounts of As; second, As is an oxyanion, which sorbs to greater extents at lower pH values rather than at higher values (Smith, 1999).

## Past and Future Mining Methods and Ore Treatment

Mining methods and ore-beneficiation techniques significantly influence the potential environmental impacts of massive sulfide deposits. Both open-pit and underground methods have been used to mine massive sulfide deposits in historical

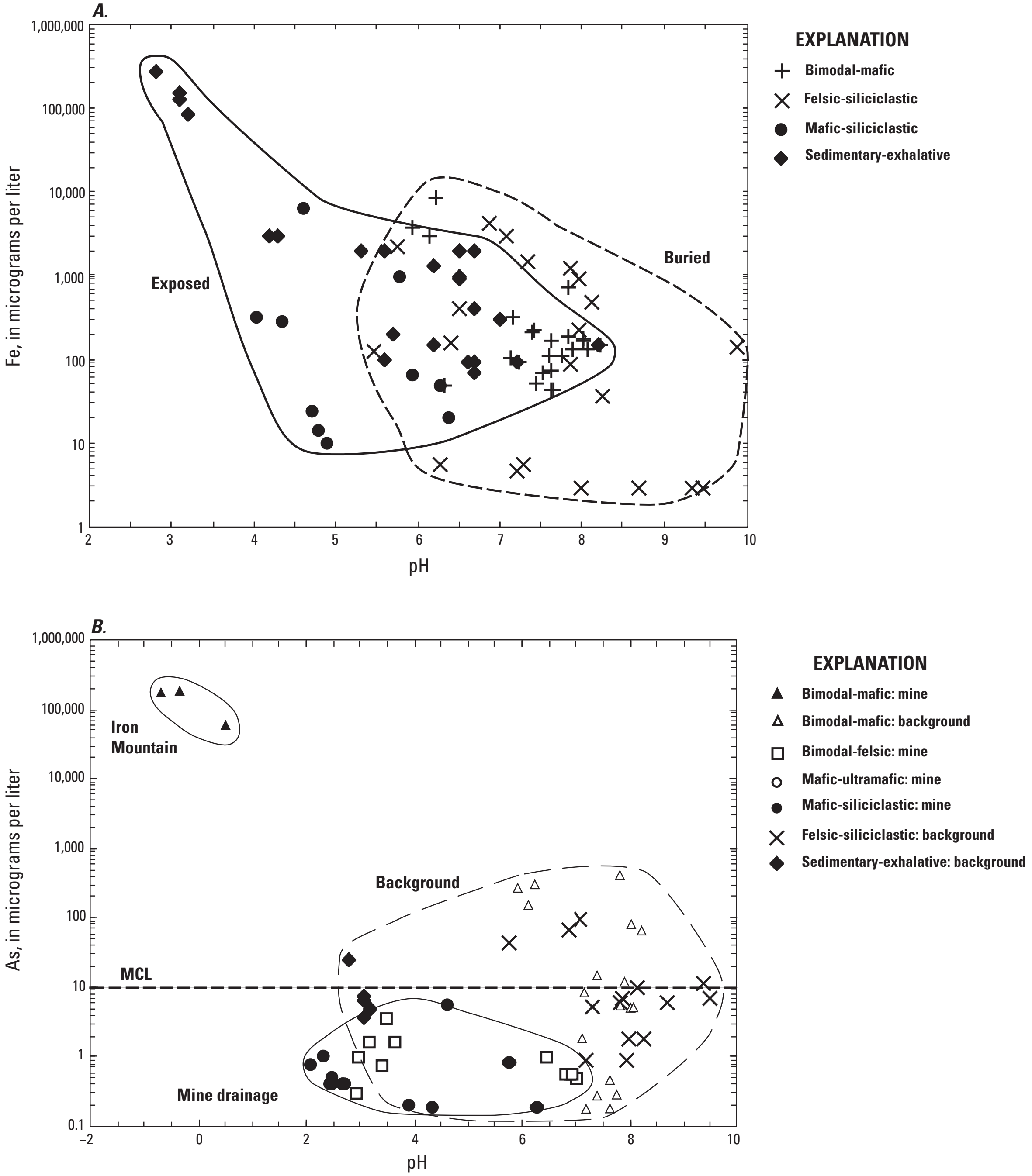

**Figure 20–1.** Geochemical data for waters associated with unmined massive sulfide deposits. *A*, Dissolved iron (Fe) versus pH. Dashed field indicates data from buried deposits, and solid field indicates data from deposits exposed at the surface, highlighting the importance of the availability of oxygen as a control on environmental signatures. *B*, Variation of the concentration of dissolved arsenic (As) with pH for mine drainage. Dashed field indicates natural background waters (unmined deposits), and solid field indicates mine drainage. For reference, MCL (maximum contaminant limit) is the current U.S. Environmental Protection Agency drinking-water limit. [µg/L, micrograms per liter]

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

Mineral processing causes a number of physical and chemical changes to the ore from which the metal concentrates are produced. 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 disposal 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. Some modern mines discharge fine-grained, sulfide-rich tailings into tailings ponds underlain by impermeable linings, but historical tailings impoundments lack impermeable barriers at the base. Thus, many historical mining operations discharged tailings in a manner that has resulted in significant contamination of surface water and shallow groundwater.

Base-metal sulfide minerals are typically separated by froth flotation. Early flotation circuits generally produced copper concentrates and discharged both sphalerite and iron sulfides to tailings ponds. Some surfactants used in the process are toxic, but most are recycled and only relatively minor amounts are discharged to tailings facilities. The flotation properties of various sulfide minerals are affected by pH. Thus, base addition, typically in the form of lime (CaO) or sodium carbonate ($Na_2CO_3$), is a common practice to produce various sulfide-mineral concentrates; other additives to flotation circuits include potassium amyl xanthate, alcohols, ethers, pine oil, sodium cyanide (NaCN), and cupric sulfate ($CuSO_4 \cdot nH_2O$), all of which affect the flotation properties of various minerals (Biswas and Davenport, 1976). Most of these chemicals leave the sites as the tailings piles dewater; however, some may remain and continue to influence drainage chemistry. Other wastes from mineral processing can also be deposited with mill tailings. At the Kidd Creek mine, tailings from the mill are co-disposed with natrojarosite residues that are produced by the zinc processing plant (Al and others, 1994).

The fine grain size, the typically large size of tailings piles, and the addition of a variety of chemicals establish distinct geochemical environments in tailings piles. The fine grain size enhances the reactivity of the sulfide and gangue minerals by increasing surface area, but it also facilitates the formation of hardpan layers that can act as semipermeable to impermeable barriers to oxygen diffusion, thus limiting sulfide oxidation (Blowes and others 1991, 2003). Numerous studies of tailings from a variety of mineral-deposit types indicate that the pH of pore waters in the unsaturated and saturated zones of tailings piles is generally buffered by a predictable series of solid phases. Commonly, pore waters show a step-decrease in pH from 6.5–7.5, to 4.8–6.3, to 4.0–4.3, and finally to <3.5, which corresponds to buffering by calcite, siderite, $Al(OH)_3$, and $Fe(OH)_3$, respectively (Blowes and Ptacek, 1994; Jurjovec and others, 2002; Blowes and others, 2003). Thus, despite being a minor component of many of these mineralized systems, carbonate minerals exert an important control on the geochemistry of anoxic pore waters in tailing piles.

Some historical massive sulfide deposits were mined for their sulfur content. Therefore, much of the sulfide waste has had major to minor amounts of the pyrite or pyrrhotite removed. Roasting of pyrite or pyrrhotite ores for the manufacture of sulfuric acid produces a hematitic calcine waste; the calcine in the Copper Basin, Tennessee, contains variable amounts of sulfate and can generate acid drainage (Moyer and others, 2002). Smelter slag is another important type of mine waste, and the reactivity of slags is significant (Parsons and others, 2001; Piatak and others, 2004). Leaching studies demonstrated that the suite of metals in leachates varies according to the compositional character of the ore (Piatak and others, 2004).

# Volume of Mine Waste and Tailings

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, 1986a, b; 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 mafic-ultramafic type deposits contain less than 15 million tonnes of ore. Most mafic-siliciclastic type deposits are also fairly small; notable exceptions include the >300 million tonne Windy Craggy, British Columbia, deposit. Bimodal-felsic type deposits, especially those of Precambrian age, can be very large, such as the world class Kidd Creek, Ontario, deposit. Because ore grades typically reach several percent at most, the tonnage of tailings is similar to the tonnage of ore. However, the amount of waste rock will vary mostly on the basis of mining method. Open-pit mines may need to strip significant amounts of subeconomic, but potentially problematic, waste rock, whereas the amount of waste rock generated by underground mines is typically less.

# Mine Waste Characteristics

## Mineralogy

Seafloor massive sulfide deposits are collectively defined by the fact that they formed syngenetically on or near the ancient seafloor through hot spring activity as lenslike or tabular bodies of stratiform sulfide minerals, dominantly pyrite or pyrrhotite. By definition, the deposits contain massive zones of sulfide minerals, many with sulfide mineral contents exceeding 90 vol%. Most deposits also contain extensive zones of semimassive sulfide rock (25–50 vol%) that contain economically exploitable ore. Quartz- or carbonate-rich stringer ore zones in the footwall of the massive sulfides typically contain 5–20 vol% sulfide minerals, hosted in quartz veins and disseminated in chloritic wallrocks. 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 ($CuFeS_2$), sphalerite ($ZnS$), and galena ($PbS$) 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 of ore minerals and accessory minerals also contribute to environmental impacts of massive sulfide deposits, even though many of these elements do not occur as distinct mineral species. For example, elevated dissolved concentrations of cadmium typically are correlated with its substitution into sphalerite. Cadmium rarely forms a discrete mineral in these types of deposits. Mercury can also be an important solid-solution component of sphalerite and tetrahedrite. Schwartz (1997) observed that sphalerite has higher Hg concentrations (4–4,680 mg/kg) in Proterozoic massive sulfide deposits than in Phanerozoic massive sulfide deposits (0.3–548 mg/kg). Arsenic commonly substitutes into pyrite in concentrations up to several weight percent, and arsenopyrite is also a common accessory mineral in some deposit types; both minerals constitute a significant source of As in some deposits. Cobalt probably resides in pyrrhotite or pyrite (Craig and Vaughan, 1990) but also occurs locally as cobaltite ($CoAsS$), glaucodot ($(Co,Fe)AsS$), or carrollite ($CuCo_2S_4$). Nickel can also be an important component of pyrite and pyrrhotite. The primary mineralogical characteristics of massive sulfide deposits and associated heavy elements are summarized in table 20–1.

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 ($Ca(Fe,Mg)CO_3$) dominate the carbonate mineralogy. Sedimentary-exhalative deposits may have dolomitic shales in their host rocks and siderite, which has no net neutralizing potential, in their alteration assemblages. Post-mineralization deformation can introduce late calcite veinlets into the rock units surrounding these deposits, such as at the Big Mike mafic-ultramafic type deposit in Nevada, where pit waters have neutral pH.

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 dissolve during rain storm or spring melt of snow and deliver their metals and acidity to the surrounding watershed. Secondary minerals also have important implications for acid-base accounting. General secondary mineralogical features of massive sulfide deposits are summarized in table 20–1.

Secondary minerals formed in temperate climates include goethite, crystalline and amorphous silica, jarosite, a variety of metal-bearing hydroxysulfate 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.

## Acid-Base Accounting

The primary and secondary mineralogy of the ores, their solid mine wastes, and associated rock types can affect the acid-base accounting (ABA) calculations. A series of static-test methods has been developed to predict the acid-generating potential of mine wastes as a tool to assist in waste disposal. These tests are known as acid-base accounting or ABA (Sobek and others, 1978; White and others, 1999), which is discussed in detail by Jambor (2003). Acid-base accounting is based on the stoichiometric reaction:

$$FeS_2 + 2CaCO_3 + 3.75\ O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2(g) \tag{11}$$

which is simply the sum of reactions 1 and 10 to eliminate $H^+$ as a constituent. It describes acid generation through the oxidation of pyrite and subsequent neutralization by calcite (Sobek and others, 1978). In the case of mafic-siliciclastic type and some sedimentary-exhalative massive sulfide deposits, pyrrhotite ($Fe_{1x}S$; 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:

$$FeS + CaCO_3 + 2.25\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + Ca^{2+} + CO_2(g) \tag{12}$$

The net result of the proportion of $CaCO_3$ per unit of total S is the same as in reaction 11, but the total S per unit of solid will be lower because pyrrhotite has approximately half of the S of pyrite.

From an ABA perspective, the various types of massive sulfide deposits can differ significantly with regard to the speciation of sulfur in primary ores, host rocks, and mine wastes (table 20–1). Sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, and sphalerite dominate the primary ore mineralogy of these deposits 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; Hammarstrom and others, 2001). For example, melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), copiapite ($Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$), and halotrichite ($Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$), among others, are common and highly soluble; less soluble sulfate minerals such as jarosite and schwertmannite ($Fe_8O_8(SO_4)(OH)_6$) also are common in mining environments (table 20–1). In contrast, the alkaline-earth sulfate minerals,

**Table 20–1.** Selected common mineralogical characteristics of volcanogenic massive sulfide deposits with a comparison to sedimentary-exhalative deposits.

[X, major; x, minor]

| | Mafic-ultramafic | Bimodal-mafic | Bimodal-felsic | Mafic-siliciclastic | Felsic-siliciclastic | Sedimentary-exhalative |
|---|---|---|---|---|---|---|
| Primary sulfide minerals | | | | | | |
| Pyrite | X | X | X | X, x | X | X |
| Pyrrhotite | x | X, x | x | X | X | X, x |
| Chalcopyrite | X | X | X | X | X | x |
| Sphalerite | x | X | X | x | X | X |
| Galena | x | x | X | x | X | X |
| Arsenopyrite | | x | x | | x | |
| Tetrahedrite-tennantite | | x | x | | | x |
| Cinnabar | | | | | | x |
| Primary sulfate minerals | | | | | | |
| Anhydrite | | | X | | | X |
| Barite | | X | X | | X | X |
| Primary carbonate minerals | | | | | | |
| Calcite | x | x | x | x | x | X |
| Dolomite | | | x | x | | X |
| Ankerite | | x | | x | x | x |
| Siderite | | x | x | | x | x |
| Primary oxide minerals | | | | | | |
| Magnetite | x | x | x | | x | x |
| Hematite | x | x | x | | | |
| Secondary sulfide minerals | | | | | | |
| Marcasite | | x | x | x | | x |
| Covellite | | x | x | x | | |
| Chalcocite | x | x | | x | | |
| Enargite | | x | x | | | |
| Secondary sulfate minerals | | | | | | |
| Gypsum | | x | x | x | | x |
| Barite | | x | x | | | |
| Melanterite/rozenite | x | x | x | x | | x |
| Copiapite | | x | x | x | | |
| Halotrichite | x | | x | x | | x |
| Alunogen | | | x | x | | |
| Epsomite | x | | | x | | |
| Chalcanthite | x | | | x | | |
| Goslarite | x | x | x | x | | x |
| Anglesite | | x | x | | | x |
| Secondary carbonate minerals | | | | | | |
| Siderite | | | | | | |
| Cerussite | | | | | | x |

**Table 20–1.** Selected common mineralogical characteristics of volcanogenic massive sulfide deposits with a comparison to sedimentary-exhalative deposits.—Continued

[X, major; x, minor]

| | Mafic-ultramafic | Bimodal-mafic | Bimodal-felsic | Mafic-siliciclastic | Felsic-siliciclastic | Sedimentary-exhalative |
|---|---|---|---|---|---|---|
| | | | Secondary oxyhydroxide minerals | | | |
| Ferrihydrite | x | x | | x | | x |
| Goethite | x | x | | x | | x |
| Schwertmannite | x | x | | x | | |
| Jarosite | | x | | x | | |
| Amorphous Al(OH)3 | | | | | | |
| Basaluminite | | | x | x | | |
| Jurbanite | | | | | | |

such as barite, anhydrite, and gypsum, also are common as both primary and secondary minerals (table 20–2), but they do not contribute acidity even though their sulfur content will be reported in determinations of total sulfur. The most prominent differences in secondary sulfate-mineral speciation among mine wastes from the different types of massive sulfide deposits are in their jarosite and metal-sulfate salts, particularly in the presence or absence of chalcanthite ($CuSO_4 \cdot 5H_2O$), goslarite ($ZnSO_4 \cdot 7H_2O$), Cu-Mg melanterite ($(Fe,Cu,Mg)SO_4 \cdot 7H_2O$), and alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$), among others. Modifications to the original ABA procedures attempt to accommodate these problems (White and others, 1999).

Net neutralization potentials for both bimodal-felsic and mafic-siliciclastic type tailings are generally net acid. Bimodal-felsic type tailings range from -142.0 to 17.2 kilograms calcium carbonate per ton (kg $CaCO_3$/t) (Seal and others, 2009). Net neutralization potentials for two samples of mafic-siliciclastic type deposits are -324.0 kg $CaCO_3$/t for coarse tailings and -282.5 kg $CaCO_3$/t for fine tailings (Seal and others, 2009).

## Element Mobility Related to Mining in Groundwater and Surface Water

The quality of mine drainage is controlled by the geological characteristics of the mineral deposit modified by the combined effects of the mineralogy, the mining and ore-beneficiation methods used, the hydrologic setting of the mine workings and waste piles, and climate. Fewer published geochemical data for mine drainage are available for mafic-ultramafic and felsic-siliciclasic type deposits than for bimodal-felsic, mafic-siliciclastic, bimodal-mafic, and sedimentary-exhalative type deposits, for which data are available from several deposits in different climatic settings.

Mine drainage associated with massive sulfide deposits shows a general negative correlation between dissolved metals and pH for most metals, such as Fe, Al, Cu, Zn, Ni, Co, Cd, and Pb, and sulfate (figs. 20–2, 20–3). Iron is typically the dominant cation, and sulfate is the dominant anion. The correlations among pH, metals, and sulfate reflect acid generation dominantly through the aqueous, oxidative weathering of pyrite, pyrrhotite, and associated ore sulfides. For the divalent metals and for Fe and Al, mine-drainage compositions overlap significantly with natural background compositions but extend to higher metal concentrations and lower pH values. Increases in total dissolved base metals and iron in mine drainage generally correlate with increases in pyrite content, decreases in acid neutralizing capacity, and increases in base-metal content of deposits (Plumlee, 1999). However, the presence of anoxic conditions in tailings and other waste piles may result in seepage waters that have high concentrations of Fe at near-neutral pH values because the iron is dominantly in the more soluble ferrous state than in the less soluble ferric state (Seal and others, 2001b).

The geochemistry of mine drainage from massive sulfide deposits shows clear evidence of primary controls based on deposit type, as well as mineralogical controls for individual metals. In terms of dissolved Cu and Zn, the data correlate 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. 20–4*A*). The Zn:Cu ratios (mass basis) for waters associated with the Cu-rich mafic-ultramafic type deposits range from approximately 1:10 to 10:1, whereas those associated with Cu>Zn mafic-siliciclastic type deposits range from approximately 1:10 to more than 100:1, and those associated with Zn>Cu bimodal-felsic type deposits are the highest, ranging from 1:1 to 10,000:1. Correlations between Cu and Pb are less distinct, presumably due to the saturation of Pb with respect to anglesite. 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. 20–4*B*). The overlap reflects the fact that Cd occurs primarily in all massive sulfide deposits as a minor solid-solution element in sphalerite.

**Table 20–2.** Environmental guidelines relevant to mineral deposits.

[mg/kg, milligram per killigram; mg/L, milligram per liter]

| Element | Human health | | | | Aquatic ecosystem | |
|---|---|---|---|---|---|---|
| | Residential soil[1] mg/kg | Industrial soil[1] mg/kg | Drinking water[1] mg/L | Drinking water[2] mg/L | Acute toxicity[1] mg/L | Chronic toxicity[1] mg/L |
| Aluminum (Al) | 77,000 | 990,000 | 200 | | 750 | 87 |
| Arsenic (As) | 23 | 160 | 10 | 10 | 340 | 150 |
| Cadmium (Cd) | 70 | 810 | 5 | 3 | 2* | 0.25* |
| Chromium (Cr) | 280 | 1,400 | 100 | 50 | 570* | 74* |
| Copper (Cu) | 3,100 | 41,000 | 1,300 | 2,000 | 13* | 11* |
| Iron (Fe) | 55,000 | 720,000 | 300 | | | 1,000 |
| Mercury (Hg) | 6.7 | 28 | 2 | 6 | 1.4 | 0.77 |
| Manganese (Mn) | 1,800 | 23,000 | 50 | 400 | | |
| Molybdenum (Mo) | 390 | 5,100 | | 70 | | |
| Nickel (Ni) | 1,600 | 20,000 | | 70 | 470* | 52* |
| Lead (Pb) | 400 | 800 | 15 | 10 | 65* | 2.5* |
| Selenium (Se) | 390 | 5,100 | 50 | 10 | | 5 |
| Uranium (U) | 230 | 3,100 | | 15 | | |
| Zinc (Zn) | 23,000 | 310,000 | 5,000 | | 120* | 120* |

*Hardness-dependent water-quality standards; value is based on a hardness of 100 mg/L CaCO3.

[1] U.S. Environmental Protection Agency (2006)

[2] World Health Organization (2008)

Cobalt also can be an important trace element in drainage from mafic-siliciclastic type mines and mine wastes. Elevated concentrations of Co (up to 7.2 mg/L) in drainage at the Elizabeth and Ely deposits are probably derived from the weathering of pyrrhotite and Co sulfides (Seal and others, 2001b).

The hydrologic setting, especially relative to the water table, is another 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 oxygen-rich groundwater and the position relative to the water table are hydrologic factors that can influence significantly the intensity and scale of environmental problems related to massive sulfide deposits. Availability of dissolved oxygen is a controlling factor for the acid-generating potential of massive sulfide deposits and their wastes.

A comparison of mine drainage from pyritic ores at Iron Mountain (bimodal-mafic type) and the Penn mine (bimodal-felsic type) in California emphasizes the importance of the location of the deposit relative to the water table. Although both deposits are in similar climatic settings, Iron Mountain is mostly located above the water table; the Penn deposit, however, is mostly below the water table, but waste piles above the water table contribute to water-quality degradation (Alpers and others, 1994b, 1999a). At Iron Mountain, pH values are as low as -3.4 and concentrations of total dissolved solids exceed 100,000 mg/L (Alpers and others, 1994b; Nordstrom and Alpers, 1999b; Nordstrom and others, 2000). In contrast, pH values of mine waters from the Penn mine vary to a low of 3.1 and total dissolved solids reach a maximum of approximately 5,500 mg/L (Alpers and others, 1999a). Mine drainage from the pyrrhotitic Elizabeth mine also emphasizes the importance of hydrologic setting. Two dominant mine-waste hydrologic settings are present at Elizabeth: one dominated by surface flow over mine wastes, and the other dominated by groundwater flow through tailings piles. In these two environments, the relationship of dissolved Fe to pH varies significantly. Surface waters show a general negative correlation of dissolved Fe, Al, Cu, and Zn, among other metals, and pH. In contrast, waters emerging from the base of the tailings piles are anoxic and near-neutral to slightly acidic (pH of 6.1–6.9) but carry amounts of dissolved Fe (14.0–904.0 mg/L) and sulfate (1,300–3,800 mg/L) that are comparable to those in the surface waters. However, dissolved concentrations of Al (<0.001–0.5 mg/L), Cu (<0.5–20 µg/L), and Zn (5.0–100.0 µg/L) are comparatively low (Seal and others, 2001b). The geochemical differences between these two environments can be related to several factors. The low concentrations of aluminum are a reflection of the near-neutral pH and the low solubility of aluminum under these conditions. In contrast, the copper concentrations are well below their theoretical maximum solubilities under these conditions, which attest to the efficiency of the ore-beneficiation technique or to the role of sorption at the oxic/anoxic interface near the top of the tailings. Oxidative weathering of pyrrhotite involving dissolved oxygen, as

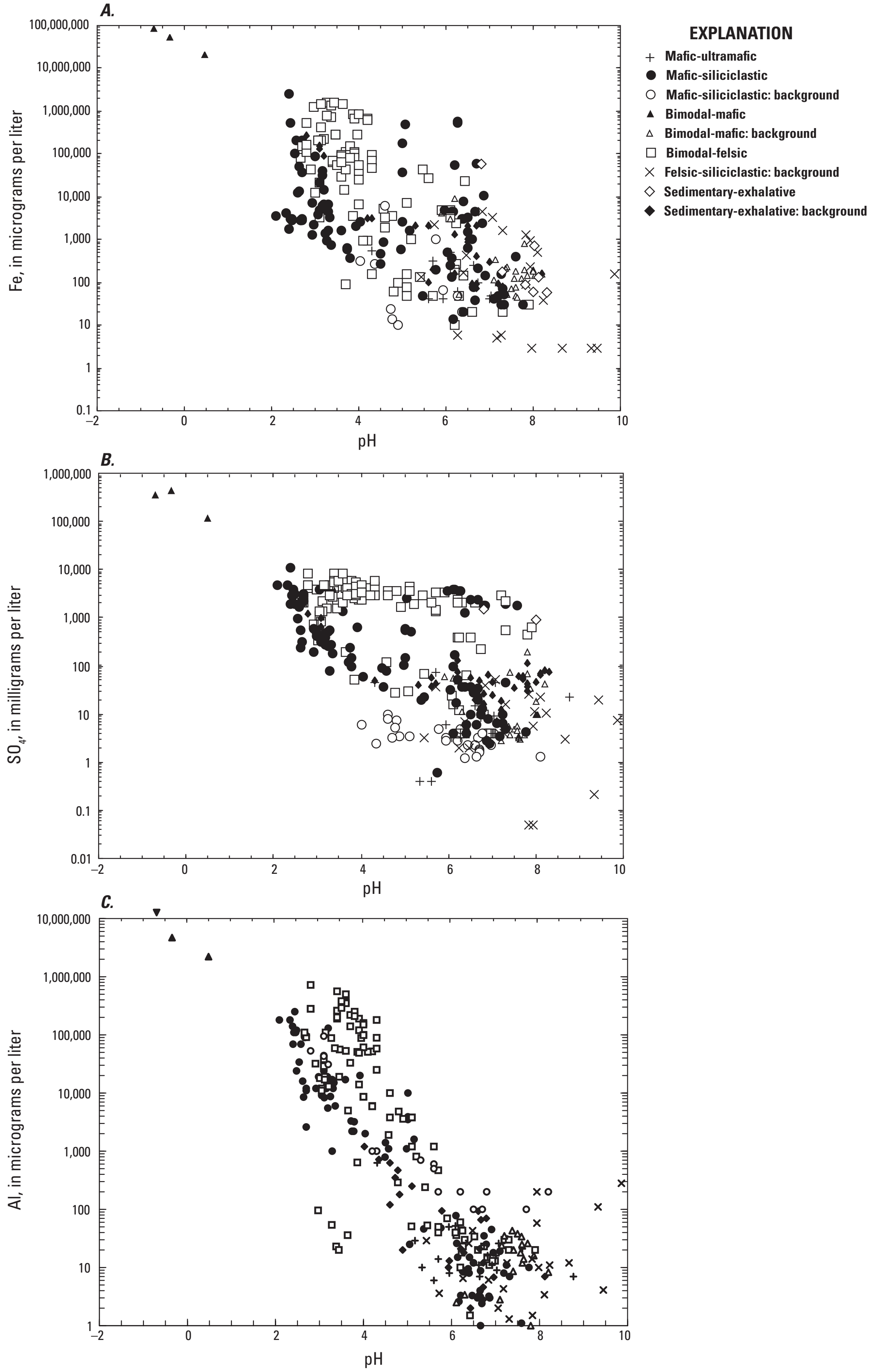

**Figure 20–2.** Geochemical data for major constituents in mine drainage associated with massive sulfide deposits. *A*, Iron (Fe) versus pH. *B*, Sulfate ($SO_4$) versus pH. *C*, Aluminum (Al) versus pH. Note the general negative correlation between pH and dissolved constituents. [µg/L, micrograms per liter; mg/L, milligrams per liter]

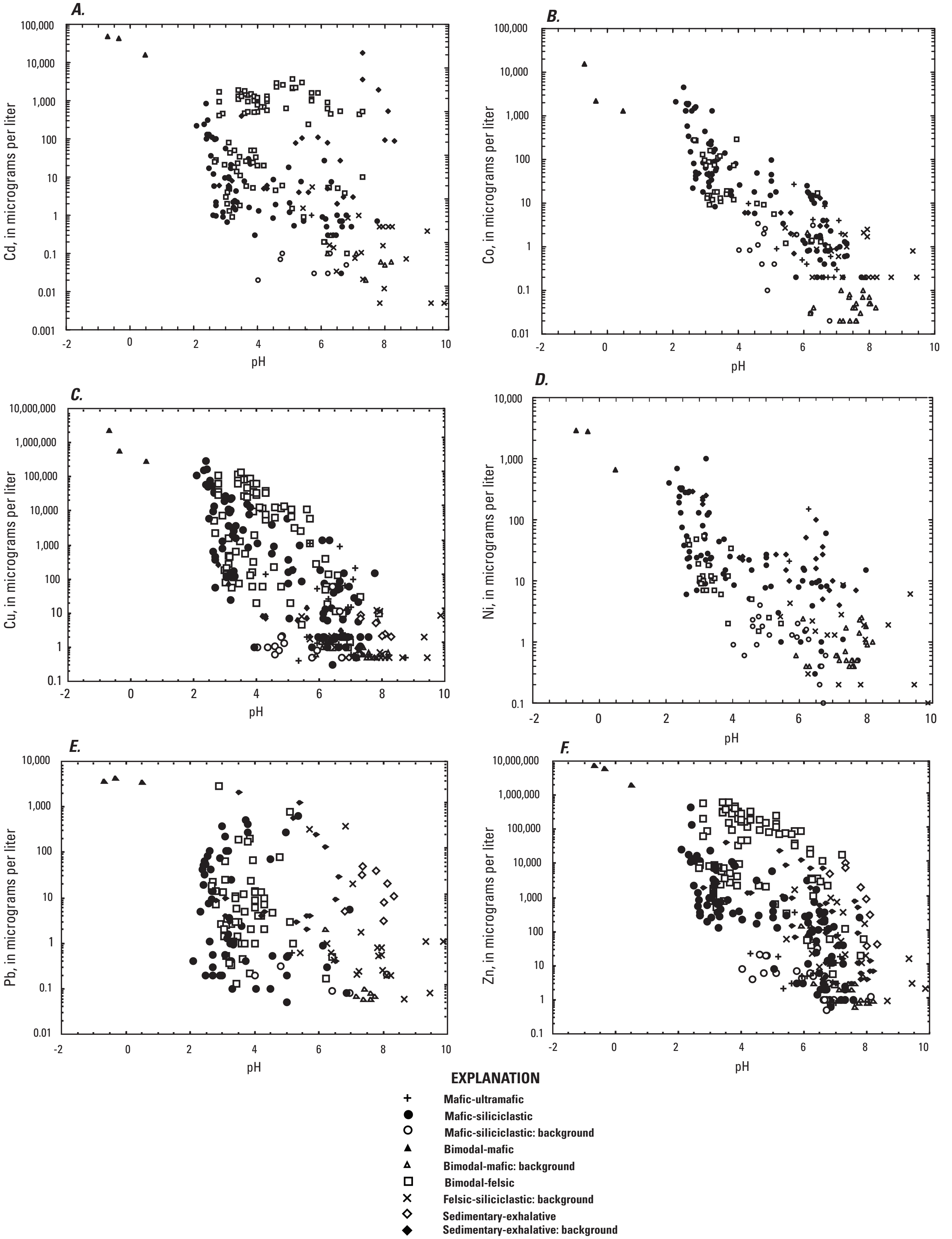

**Figure 20–3.** Geochemical data for minor constituents in mine drainage associated with massive sulfide deposits. *A*, Cadmium (Cd) versus pH. *B*, Cobalt (Co) versus pH. *C*, Copper (Cu) versus pH. *D*, Nickel (Ni) versus pH. *E*, Lead (Pb) versus pH. *F*, Zinc (Zn) versus pH.

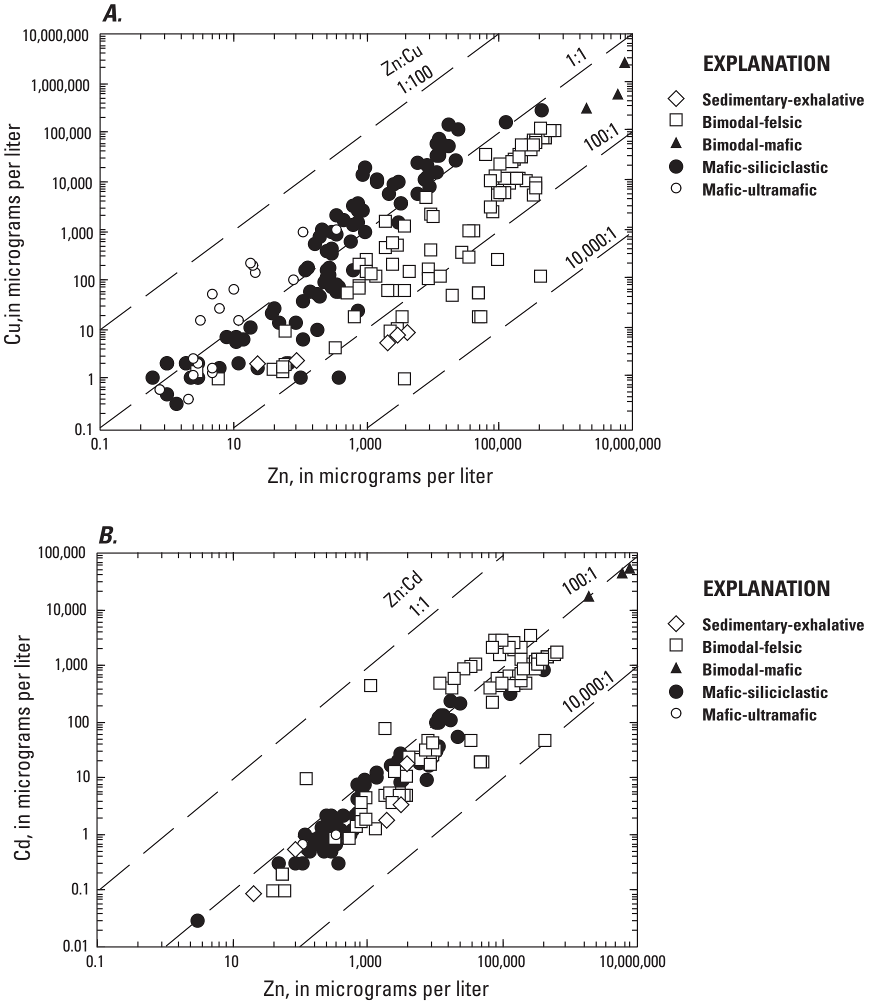

**Figure 20–4.** Geochemical data for dissolved metals in drainage associated with massive sulfide deposits. *A*, Copper (Cu) versus zinc (Zn). *B*, Cadmium (Cd) versus zinc. [µg/L, micrograms per liter]

described by reaction 2, develops minor acid in an oxygen-limited environment such as the subsurface of the tailings pile. The presence of minor amounts of carbonate minerals in the host rock and the addition of lime in mineral-processing circuits prior to disposal may also contribute to the near-neutral pH of groundwaters emerging from the tailings pile. Likewise, under anoxic conditions, pyrrhotite can consume acid to produce ferrous iron and $H_2S$ (reaction 8). High concentrations of iron can be attributed to the high solubility of ferrous iron. Because of the near-neutral pH, the groundwaters flowing through the tailings do not have elevated concentrations of metals such as Al, Cu, Zn, and Cd. Sorption of divalent metals on hydrated ferric oxides in the oxidized, upper portions of the tailings pile may explain the lower concentrations of Cu, Zn, and Cd. High flotation recoveries of the ore minerals may also explain the lower concentrations of Cu. Upon emerging from the base of the tailings pile, ferrous iron in the groundwaters undergoes rapid oxidation to $Fe^{3+}$, followed by hydrolysis and a concomitant drop in pH. In contrast, under oxygenated conditions, such as in the surface waters at Elizabeth, the iron commonly occurs in both valence states. Under these conditions, acidic pH values are required to carry significant concentrations of iron in the drainage.

## Pit Lakes

Studies of pit lakes associated with volcanic-hosted massive sulfide deposits are limited. A small pit lake at the abandoned Elizabeth mine, a mafic-siliciclastic type deposit, in Vermont has moderately low pH and moderate total dissolved solids (Seal and others, 2006). The ephemeral pit lake at the Big Mike mine, a mafic-ultramafic type deposit, has slightly alkaline pH and low total dissolved solids (Shevenell and others, 1999).

## Ecosystem Issues

Ecosystem threats are dominantly produced by acid mine drainage, which targets aquatic environments. The oxidative weathering of pyrite ($FeS_2$) and pyrrhotite ($Fe_{1-x}S$), is described by reactions 1 to 5. The lower pH values generated by the oxidation of pyrite and pyrrhotite enhance the solubility of base metals such as Cu, Zn, Cd, Co, Ni, and Pb and the ability to attack silicate-gangue minerals, thus liberating Al, Mn, and other elements. Most metals show greater solubility at lower pH values; however, aluminum and ferric iron have solubility minimums at circumneutral pH values, with greater solubility at both lower and higher pH. Once liberated, the metals and acidity can affect downstream aquatic ecosystems. Downstream effects can be localized or can extend at least 100 km from mine sites. Metal contamination can also be dispersed downstream by the erosion and transport of tailings, which subsequently release metals to the water column.

The toxicity of the metals Cd, Cr, Cu, Pb, Ni, Ag, and Zn to aquatic ecosystems is dependent on water hardness; higher concentrations of metals are needed to exceed toxicity limits at higher hardness values (U.S. Environmental Protection Agency, 2006). Hardness is a measure of the concentrations of Ca and Mg. The concentration of hardness is expressed in terms of an equivalent concentration of $CaCO_3$, typically in milligrams per liter. The U.S. Environmental Protection Agency (USEPA) has presented hardness-dependent expressions for both acute (one-hour exposure) and chronic (four-day exposure) toxicity and limits independent of hardness for cyanide, Al, As, Sb, Fe, Hg, Se, and Tl (table 20–2) (U.S. Environmental Protection Agency, 2006).

## Human Health Issues

Human-health impacts of massive sulfide deposits are generally associated with either the inhalation or the ingestion of metals. Ingestion may be in the form of drinking water or as particulates. The USEPA has set primary maximum contaminant levels (MCLs) for cyanide, Sb, As, Cu, Cd, Cr, Hg, and Ni, among other compounds, for drinking water (table 20–2) (U.S. Environmental Protection Agency, 2009). Groundwaters around mineral deposits, both from undisturbed and disturbed settings, can exceed drinking-water standards. For example, the concentration of dissolved As in groundwaters around the unmined Bald Mountain massive sulfide deposit in northern Maine reaches a maximum of 430 µg/L, whereas the USEPA drinking water standard is 10 µg/L (fig. 20–1*B*) (Seal and others, 1998a). The unmined deposit contains minor amounts of both primary arsenopyrite and secondary enargite. Likewise, a shallow groundwater well near the abandoned Elizabeth mine in Vermont has high concentrations of Cu and Cd (Hathaway and others, 2001).

Risks are generally related to ingestion of Pb-rich mine waste through incidental contact. Studies have demonstrated that the relative bioavailability of Pb in the digestive tract varies according to mineralogy. Lead in galena and anglesite ($PbSO_4$) is considered to be less bioavailable than Pb in cerussite ($PbCO_3$) (U.S. Environmental Protection Agency, 1999). At the Valzinco mine in central Virginia, fine-grained flotation tailings exposed to wind and water contain up to 4,000 mg/kg Pb, well in excess of USEPA residential and industrial soil criteria (400 and 750 mg/kg Pb, respectively). For bimodal-felsic type massive sulfide deposits such as Valzinco, Pb is present as galena and its weathering product, anglesite. Thus, because of the geochemical character of the bimodal-felsic type massive sulfide deposits, Pb remains speciated in solid forms that are less bioavailable. For all Pb-bearing deposits, the fine grinding required for concentration by flotation increases the risk of inhalation because of the airborne transport of Pb-bearing dust. This phenomenon is most likely to occur in semiarid to arid regions in which strong winds prevail.

Mercury risks are generally related to the consumption of Hg-contaminated fish and the contamination of drinking water. Mercury occurs as several aqueous species, with methylmercury the one of greatest environmental concern. Methylmercury is a potent neurotoxin that bioaccumulates with increasing trophic level in aquatic and terrestrial ecosystems (Gehrke and others, 2011). The primary pathway for human-health impacts is through the consumption of fish and other higher organisms in Hg-contaminated environments. The United States Food and Drug Administration issues fish-consumption advisories for Hg concentrations in fish tissue above 1,000 ng/g (wet basis). Thus, Hg derived either from past amalgamation use or from solid solution in minerals, such as sphalerite, may affect human and other animals if it becomes methylated and enters the foodweb.

In semiarid to arid areas, the human-health risks associated with Hg are more likely related to drinking-water supplies that are obtained from shallow groundwaters. The surficial weathering of mine wastes, especially during the rainy season, may liberate metals to the local groundwater. In the case of sedimentary-exhalative ores, the most likely metals of concern in drinking water are Pb, Zn, Cd, As, and Tl in addition to Hg (table 20–2).

## Climate Effects on Geoenvironmental Signatures

Climate plays an especially important role in the potential environmental impact from mines that exploit massive sulfide deposits (Nordstrom, 2009). However, its effect is difficult to quantify systematically because insufficient data are available for a given deposit type in a wide spectrum of climatic settings. Nevertheless, temperature and humidity are the prime variables that control evaporation. Evaporation can be expected to limit the amount of water in semiarid to arid climates. Evaporation can concentrate solutes in all climates. Acidity and total metal concentrations in mine drainage in arid environments are typically several orders of magnitude greater than in more temperate climates because of the concentrating effects of the evaporation of mine effluent and the resulting "storage" of metals and acidity in highly soluble metal-sulfate salt minerals. 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 may continually flush existing tailings and mine dumps. Although metal-laden acidic mine water does form, it may be diluted to benign metal abundances within several hundred meters of mixing with a higher order stream.

The importance of climate as a variable can also be demonstrated by comparing seasonal variations in the chemistry of effluent from two abandoned mines that exploited massive sulfide deposits in the eastern United States—one with a winter-long snow pack, the Elizabeth mine in Vermont, and one without a winter-long snow pack, the Valzinco mine in Virginia. At Elizabeth, concentrations of dissolved Cu in surface waters peak during spring melt and are interpreted to reflect the dissolution and flushing of efflorescent salts or brines formed in the subsurface of the tailings pile during the winter. In contrast, concentrations of dissolved Cu in the drainage from the Valzinco mine reach a peak in the summer as the flow approaches base conditions, possibly with some evaporative concentration. The absolute differences in the peak concentrations of Cu between the Elizabeth and Valzinco mines reflect the Cu-rich character of the Elizabeth ores and the Zn-rich character of the Valzinco ores. In both settings during the summer, the concentrations of Cu and other dissolved constituents can spike because of the dissolution of efflorescent salts during rain storms.

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