Chapter 3

The Environmental Geology of Mineral Deposits

G.S. Plumlee
U.S. Geological Survey, Box 25046, MS 964, Federal Center, Denver, CO 80225-0046

INTRODUCTION

Mineral deposits are concentrations of metallic or other mineral commodities in the Earth's crust that result from a variety of complex geologic processes. The natural weathering and erosion of a mineral deposit at the Earth's surface disperses its constituents into the waters, soils, and sediments of its surrounding environment. There, the constituents may be taken up by plants and (or) organisms. The concentrations and chemical, mineralogical, or biological forms of metals and other constituents from a mineral deposit prior to mining in soils, waters, sediments, plants, and organisms are defined here to be the natural environmental signatures of the deposit.

Modern mining and mineral processing activities employ a wide variety of methods to prevent or minimize adverse environmental impacts (Ripley et al., 1996; Plumlee and Logsdon, 1999; references therein). However, if not carried out with appropriate mitigation and prevention practices (as was common in most historical operations), or as a result of accidental releases, mining and mineral processing can disperse potentially deleterious metals, other deposit constituents, and mineral processing chemicals or byproducts into the environment. Mining-related environmental signatures are defined here as the concentrations and chemical, mineralogical, or biological forms of these metals and chemicals *prior to mitigation or remediation* in mining and milling wastes, mine waters, mineral processing solutions and byproducts, and smelter emissions and byproducts.

The geologic characteristics of mineral deposits exert important and predictable controls on the natural environmental signatures of mineralized areas prior to mining, and on the environmental signatures that could result from mining and mineral processing if appropriate preventive and mitigative practices were not followed. A good understanding of the environmental geology of mineral deposits is therefore crucial to the development of effective mining-environmental prediction, mitigation, and remediation practices.

This chapter summarizes the important geologic characteristics of mineral deposits that influence their environmental signatures, how climate and mining and mineral processing methods modify the environmental signatures mandated by deposit geology, and how climate and geology influence the effects of the deposits on the surrounding environment. In addition, the chapter will show how mineral deposit types with similar geologic characteristics have generally similar and predictable environmental signatures, and will discuss the development of empirical geoenvironmental models of various mineral deposit types.

Mineral deposits and mineral deposit types

"Mineral deposits" as considered here include metallic, or hard-rock, deposits (those in which metals such as Au, Ag, Cu, Pb, Zn, Ni, or Co are the dominant commodity), energy mineral deposits (including coal and uranium deposits), and industrial mineral deposits (those which contain mineral commodities such as sand, gravel, zeolites, phosphates, etc.).

"Mineral deposit types" are groups of mineral deposits having similar geologic characteristics, geologic environments of occurrence, and geologic processes of formation (Guilbert and Park, 1986; Cox and Singer, 1986; Bliss, 1992). Different categories of metallic mineral deposit types can be identified based on their mode of formation. Magmatic deposits are those that form directly from magmas, such as Ni-sulfide deposits hosted by layered mafic intrusions. Magmatic hydrothermal deposit types form from fluids expelled from crystallizing magmas, and include types such as porphyry, skarn, and polymetallic replacement deposits. Hydrothermal deposit types form from heated waters circulating in the Earth's crust; common hydrothermal types include volcanogenic massive sulfide, epithermal, polymetallic vein, and Carlin-type sediment-hosted Au deposits. Supergene deposits form from surface and ground waters that weather and redeposit metals from an existing mineral deposit. Residual deposits are formed by the natural weathering of rocks, which removes most of the rock constituents and results in the residual enrichment of economic constituents in the highly weathered rock remnants; these include deposit types such as bauxite Al and laterite Ni. Placer deposits form by sedimentary accumulation of dense minerals eroded from rocks or mineral deposits, and include placer Au and beach-sand Ti deposits.

Industrial mineral deposit types have a broad spectrum of origins, including: chemical (those that form by chemical precipitation from water, such as phosphate and evaporite deposits); sedimentary (those that form by sedimentary processes, such as sand and gravel deposits); metamorphic (those that form by metamorphic processes, such as some garnet deposits); weathering (those that form by weathering of existing rocks, such as some clay deposits); igneous (those that form by igneous processes, such as deposits of perlite in volcanic domes); and hydrothermal (those that form by hydrothermal processes, such as hydrothermal clay deposits).

This discussion will focus primarily on the environmental geology of metallic deposits, but will also include some discussion of the environmental geology of uranium and industrial mineral deposits.

Other sources of geologic information

As part of this discussion, only some of the basic terms and concepts of economic geology will be discussed; for further details the interested reader is referred to general economic geology textbooks such as Guilbert and Park (1986). Holland and Petersen (1995) present an overview of the geologic, economic, and environmental issues related to mineral-resource development. For detailed geologic discussions of particular mineral deposits, mining districts, or mineral deposit types, see general journals such as *Economic Geology* or *Mineralium Deposita*, papers by national geological surveys (for example, U.S. Geological Survey Professional Papers or Bulletins are available for a number of historic U.S. mining districts), and special publications by professional associations such as the Society of Economic Geologists or the Geological Association of Canada (e.g., Kirkham et al., 1993).

There are also a number of journals and volumes available with papers that discuss the environmental aspects of mining from a geologic standpoint, including the journals *Environmental Geology, Applied Geochemistry*, *Journal of Geochemical Exploration*, and *Environmental Geochemistry and Health,* and volumes such as Jambor and Blowes (1994), Kwong (1993), Alpers and Blowes (1994), Pasava et al. (1995), and Ripley et al. (1996). Conceptual models that describe the important geoenvironmental characteristics of a number of mineral-deposit types are presented in du Bray (1995). Many of the papers included in this two-part volume also discuss environmental processes in a geologic context.

ENVIRONMENTAL GEOLOGY CHARACTERISTICS OF MINERAL DEPOSITS

In general, the geologic characteristics of mineral deposits that control their environmental signatures (their environmental-geology characteristics) influence either the chemical or physical response of the deposits to weathering and environmental processes (Table 3.1). Geologic features such as the acid-generating or acid-consuming minerals in the deposit, host rocks, and wallrock alteration are examples of characteristics that influence the chemical response of the deposits to weathering. Other characteristics such as mineral textures, the presence of faults or joints, and the porosity and hydraulic conductivity of the deposit and associated host rocks, ultimately control the access of weathering agents into the deposit and the speed with which the deposit is weathered and dispersed into the environment. Some geologic characteristics such as the mineralogy and trace element content of minerals can affect both the chemical and physical response of the deposit to weathering and environmental dispersion.

Primary mineralogy

Primary minerals are defined as those that form during the original formation of the deposit. The primary ore (economically valuable) and gangue (non-economic) minerals present in a mineral deposit play a key role in determining how readily the deposit's constituents are dispersed into the environment (Tables 3.2–3.5, Figs. 3.1–3.3).

TABLE 3.1—Geologic characteristics of mineral deposits that affect their environmental signatures.

Characteristic	Controls	Remarks
Iron sulfide content	Chemical	Oxidation generates acid; also supplies ferric iron, which is an aggressive oxidant.
Content of other sulfides	Chemical	Many (but not all) may generate acid during oxidation.
Content of carbonates, aluminosilicates and other nonsulfide minerals	Chemical	Many of these minerals can consume acid; iron and manganese carbonates may generate acid under some conditions.
Mineral resistance to weathering	Physical	Function of the mineral (different minerals weather at different rates) and the texture and trace-element content of the mineral.
Secondary mineralogy	Chemical and physical	Soluble secondary minerals can store acid and metals, to be released when the minerals dissolve. Insoluble secondary minerals can armor reactive minerals, thereby restricting access of weathering agents.
Extent of pre-mining or pre-erosion weathering and oxidation	Chemical	Pre-mining oxidation greatly reduces potential for sulfide deposits to generate acid.
Host rock lithology	Chemical and physical	May consume or generate acid. Physical characteristics (porosity, permeability) control access of weathering agents.
Wallrock alteration	Chemical and physical	May increase or decrease the host rock's ability to consume acid. May increase or decrease host rock's ability to transmit ground waters. May also increase or decrease resistance to erosion.
Major-, trace-elements in deposit and host rocks	Chemical	Elemental composition of deposit and host rocks are typically reflected in environmental signatures.
Physical nature of ore body (vein, disseminated, massive)	Physical	Controls access of weathering agents.
Porosity, hydraulic conductivity of host rocks	Physical	Control access of weathering agents.
Presence and openness of faults, joints	Physical	Control access of weathering agents.
Deposit grade, size	Physical and chemical	Controls magnitude of natural, mining impacts on surroundings.

TABLE 3.2—Examples of sulfide oxidation reactions and other mineral dissolution reactions that may generate acid. The reactions depicted are idealized, and likely do not represent the appropriate reaction products for the entire range of ambient chemical conditions in nature. However, they illustrate the range of acid amounts that can be generated (moles acid >0) or consumed (moles acid <0) depending on the mineral, the oxidant (oxygen versus ferric iron) and the reaction products (oxidation state, chemical species, and minerals) produced.

Mineral	Formula	Acid generation/consumption reaction	Moles acid
Pyrite	FeS_2	$FeS_2 + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{=} + 2\ H^+$	2
		$FeS_2 + 3.75\ O_2 + 0.5\ H_2O = Fe^{3+} + H^+ + 2\ SO_4^{=}$	1
		$FeS_2 + 3.75\ O_2 + 3.5\ H_2O = 2\ SO_4^{=} + 4\ H^+ + Fe(OH)_{3\ (s)}$	4
		$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{=} + 16\ H^+$	16
Pyrrhotite	$Fe_{1-x}S$	x = 0.1: $Fe_{0.9}S + 1.95\ O_2 + 0.1\ H_2O = 0.9\ Fe^{2+} + SO_4^{=} + 0.2\ H^+$	0.2
		x = 0.1: $Fe_{0.9}S + 2.175\ O_2 + 0.7\ H^+ = 0.9\ Fe^{3+} + SO_4^{=} + 0.35\ H_2O$	-0.7
		x = 0.1: $Fe_{0.9}S + 2.175\ O_2 + 2.35\ H_2O = SO_4^{=} + 2\ H^+ + 0.9\ Fe(OH)_{3\ (s)}$	2
		x = 0.1: $Fe_{0.9}S + 7.8\ Fe^{3+} + 4\ H_2O = 8.7\ Fe^{2+} + SO_4^{=} + 8\ H^+$	8
Sphalerite,	ZnS, CuS, PbS	$MS + 2\ O_2 = M^{2+} + SO_4^{=}$ (M = Zn, Cu, Pb)	0
Covellite,		$MS + 8\ Fe^{3+} + 4\ H_2O = M^{2+} + 8\ Fe^{2+} + SO_4^{=} + 8\ H^+$	8
Galena	PbS	$PbS + 2\ O_2 = PbSO_4$ (anglesite)	0
		$PbS + 0.5\ O_2 + 2\ H^+ = Pb^{2+} + H_2O + S°$ (native sulfur)	-2
Chalcopyrite	$CuFeS_2$	$CuFeS_2 + 4\ O_2 = Cu^{2+} + Fe^{2+} + 2\ SO_4^{=}$	0
		$CuFeS_2 + 16\ Fe^{3+} + 8\ H_2O = Cu^{2+} + 17\ Fe^{2+} + 2\ SO_4^{=} + 16\ H^+$	16
Enargite	Cu_3AsS_4	$Cu_3AsS_4 + 8.75\ O_2 + 2.5\ H_2O = 3\ Cu^{2+} + HAsO_4^{=} + 4\ SO_4^{=} + 4\ H^+$	4
		$Cu_3AsS_4 + 35\ Fe^{3+} + 20\ H_2O = 3\ Cu^{2+} + 35\ Fe^{2+} + HAsO_4^{=} + 4\ SO_4^{=} + 39\ H^+$	39
Arsenopyrite	FeAsS	$FeAsS + 3.25\ O_2 + 1.5\ H_2O = Fe^{2+} + HAsO_4^{=} + SO_4^{=} + 2\ H^+$	2
		$FeAsS + 3.5\ O_2 + H_2O = Fe^{3+} + HAsO_4^{=} + SO_4^{=} + H^+$	1
		$FeAsS + 13\ Fe^{3+} + 8\ H_2O = 14\ Fe^{2+} + HAsO_4^{=} + SO_4^{=} + 15\ H^+$	15
		$FeAsS + 3.5\ O_2 + 3\ H_2O = SO_4^{=} + 2\ H^+ + FeAsO_4 \bullet 2H_2O$ (scorodite)	2
Native sulfur	S°	$S° + H_2O + 1.5\ O_2 = 2\ H^+ + SO_4^{=}$	2
Realgar	AsS	$AsS + 2.75\ O_2 + 2.5\ H_2O = HAsO_4^{=} + SO_4^{=} + 4\ H^+$	4
		$AsS + 11\ Fe^{3+} + 8\ H_2O = 11\ Fe^{2+} + HAsO_4^{=} + SO_4^{=} + 15\ H^+$	15
Siderite	$FeCO_3$	$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$	-1
		$FeCO_3 + 2\ H^+ + 0.25\ O_2 = Fe^{3+} + 0.5\ H_2O + HCO_3^-$	-2
		$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O = Fe(OH)_3 + H^+ + HCO_3^-$	1
Alunite	$KAl_3(SO_4)_2(OH)_6$	$KAl_3(SO_4)_2(OH)_6 + 6\ H^+ = K^+ + 3Al^{3+} + 2\ SO_4^{=} + 6\ H_2O$	-6
		$KAl_3(SO_4)_2(OH)_6 + 3\ H_2O = K^+ + 3Al(OH)_3 + 2\ SO_4^{=} + 3\ H^+$	3

Acid-generating minerals

Many metallic mineral deposits that form beneath the Earth's surface contain sulfide minerals, a consequence of their formation under relatively reduced conditions out of contact with atmospheric oxygen. Sulfide minerals that are exposed by erosion or mining are unstable in the presence of atmospheric oxygen or oxygenated ground waters. Bacterially catalyzed oxidation of sulfides by oxygenated ground and surface waters is well known as the cause of acid-rock drainage (Nordstrom and Alpers, 1999). However, the amount of acid generated (Tables 3.2 and 3.3) is a complex function of the sulfide minerals present in an ore body, their resistance to weathering (see discussion below and Table 3.4), whether the sulfides contain iron, whether oxidized or reduced metal species are produced by the oxidation, whether other elements such as arsenic are major constituents of the sulfides, whether oxygen or aqueous ferric iron is the oxidant, and whether hydrous metal oxides or other minerals precipitate as a result of the oxidation process. Iron sulfides (pyrite, FeS_2; marcasite, FeS_2; pyrrhotite, $Fe_{1-x}S$), sulfides with metal/sulfur ratios <1, and sulfosalts such as enargite (Cu_3AsS_4), generate acid when they react with oxygen and water. Other sulfides with metal/sulfur ratios = 1, such as sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$) tend not to produce acid when oxygen is the oxidant. However, aqueous ferric iron is a very aggressive oxidant that, when it reacts with sulfides, generates significantly greater quantities of acid than are generated by oxygen-driven oxidation alone (Nordstrom and Alpers, 1999; Tables 3.2, 3.3). Sulfide oxidation by ferric iron also occurs more rapidly than by oxygen alone (Nordstrom and Alpers, 1999). Thus, because of their role in producing aqueous ferric iron, the amounts of iron sulfides present in a mineral assemblage play a crucial role in determining whether acid will be generated during weathering. In general, sulfide-rich mineral assemblages with high percentages of iron sulfides or sulfides having iron as

TABLE 3.3—Common sulfides known or inferred to generate acid when oxidized. Sulfides listed as inferred to generate acid are postulated on the basis of idealized chemical reactions such as those listed in Table 3.2.

Mineral	Formula
Common sulfides known (*inferred*) to generate acid with oxygen as the oxidant:	
Pyrite, marcasite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Bornite	Cu_5FeS_4
Arsenopyrite	FeAsS
Enargite/famatinite	Cu_3AsS_4/Cu_3SbS_4
Tennantite/tetrahedrite	$(Cu,Fe,Zn)_{12}As_4S_{13}/(Cu,Fe,Zn)_{12}Sb_4S_{13}$
Realgar	AsS
Orpiment	As_2S_3
Stibnite	Sb_2S_3
Common sulfides that may generate acid with ferric iron as the oxidant:	
All of the above, plus:	
Sphalerite	ZnS
Galena	PbS
Chalcopyrite	$CuFeS_2$
Covellite	CuS
Cinnabar	HgS
Millerite	NiS
Pentlandite	$(Fe,Ni)_9S_8$
Greenockite	CdS
Common minerals that may generate acid if hydrous oxides are formed:	
Siderite	$FeCO_3$
Rhodochrosite	$MnCO_3$
Alunite	$KAl_3(SO_4)_2(OH)_6$

TABLE 3.4—Factors affecting resistance of sulfide minerals to oxidation, listed in order of increasing resistance from top to bottom of table. The mineral resistance ranking by Brock (1979), is modified to include arsenopyrite (Jambor, 1994) and other sulfides based on the authors' field observations. This ranking is only one of a number of published rankings that are in general agreement, but differ in a variety of specifics. Grain size, texture, and trace element content can substantially shift the relative resistance of the different sulfide minerals; for example, trace element-rich botryoidal pyrite and marcasite generally oxidize much more rapidly than coarse, euhedral sphalerite.

Mineralogy (Brock, 1979; Jambor, 1994)	Grain size	Texture	Trace element content	Resistance to oxidation
Pyrrhotite	Fine	Framboidal	High	Low
Chalcocite		Colloform		
Galena				
Sphalerite		Botryoidal		
Arsenopyrite[1]				
Pyrite,	Medium			Medium
Enargite		Massive		
Marcasite				
Bornite[2]				
Chalcopyrite				
Argentite[2]				
Cinnabar				
Molybdenite	Coarse	Euhedral	Low	High

[1]Based on the observations of Jambor (1994).
[2]Based on the author's observations.

TABLE 3.5—Relative reactivities of common rock-forming and deposit-forming minerals, listed in order of decreasing reactivity. Originally produced by Sverdrup (1990) for soils, and modified by Kwong (1993) and the author (author modifications shown in italics) to include more minerals based on observations of weathering rates observed in mineral deposits. Dissolving minerals are those whose components are taken completely into solution. Weathering minerals are those whose components are partially removed into solution and partially converted to other minerals. For mineral formulas, the reader is referred to standard mineralogic texts such as Deer et al. (1978). Calc-silicates common in skarn deposits (garnet, diopside, wollastonite) are included in the intermediate-weathering group rather than the fast weathering group (as originally classified by Kwong and Sverdrup); the low pH of mine waters that drain some skarn deposits where these minerals are abundant indicate that these minerals do not react readily with acid waters (see Plumlee et al., 1999).

Mineral Group	Typical minerals
Readily dissolving	cerussite, calcite, aragonite, *strontianite*
Less readily dissolving	*rhodochrosite, siderite, dolomite, ankerite, magnesite, brucite, fluorite (?)*
Fast weathering	anorthite, nepheline, olivine, jadeite, leucite, spodumene, *volcanic glass*
Intermediate-weathering	epidote, zoisite, enstatite, hypersthene, augite, hedenbergite, hornblende, glaucophane, tremolite, actinolite, anthophyllite, serpentine, chrysotile, talc, chlorite, biotite, *diopside (?), wollastonite (?), garnet (?), rhodonite (?), hematite (?)*
Slow weathering	albite, oligoclase, labradorite, vermiculite, montmorillonite, gibbsite, kaolinite, magnetite
Very slow weathering	potassium feldspar, muscovite
Inert	quartz, rutile, zircon

a constituent (such as chalcopyrite or iron-rich sphalerite) will generate significantly more acidic waters than sphalerite- and galena-rich assemblages without iron sulfides.

Precipitation of hydrous oxides during the sulfide oxidation process can also lead to the formation of acid (Table 3.2). In fact, some non-sulfide minerals such as siderite ($FeCO_3$) and alunite ($KAl_3(SO_4)_2(OH)_6$) can also generate acid during weathering if hydrous iron or aluminum oxides precipitate.

Acid-consuming minerals

In most mineral deposits, acid-generating sulfide minerals are either intergrown with or occur in close proximity to a variety of carbonate and aluminosilicate minerals that can react with and consume acid generated during sulfide oxidation. However, like the sulfides, the ease and rapidity with which these minerals can react with acid varies substantially (Table 3.5).

Alkaline earth carbonates such as calcite ($CaCO_3$), dolomite [$(Ca, Mg)(CO_3)_2$], and magnesite ($MgCO_3$) typically react with acid according to reactions such as:

$$MCO_{3(S)} + H^+ = M^{2+} + HCO_3^- \quad [1]$$

As discussed previously, if hydrous iron or manganese oxides form as a result of the dissolution of their respective carbonates (siderite and rhodochrosite), then a net generation of acid results;

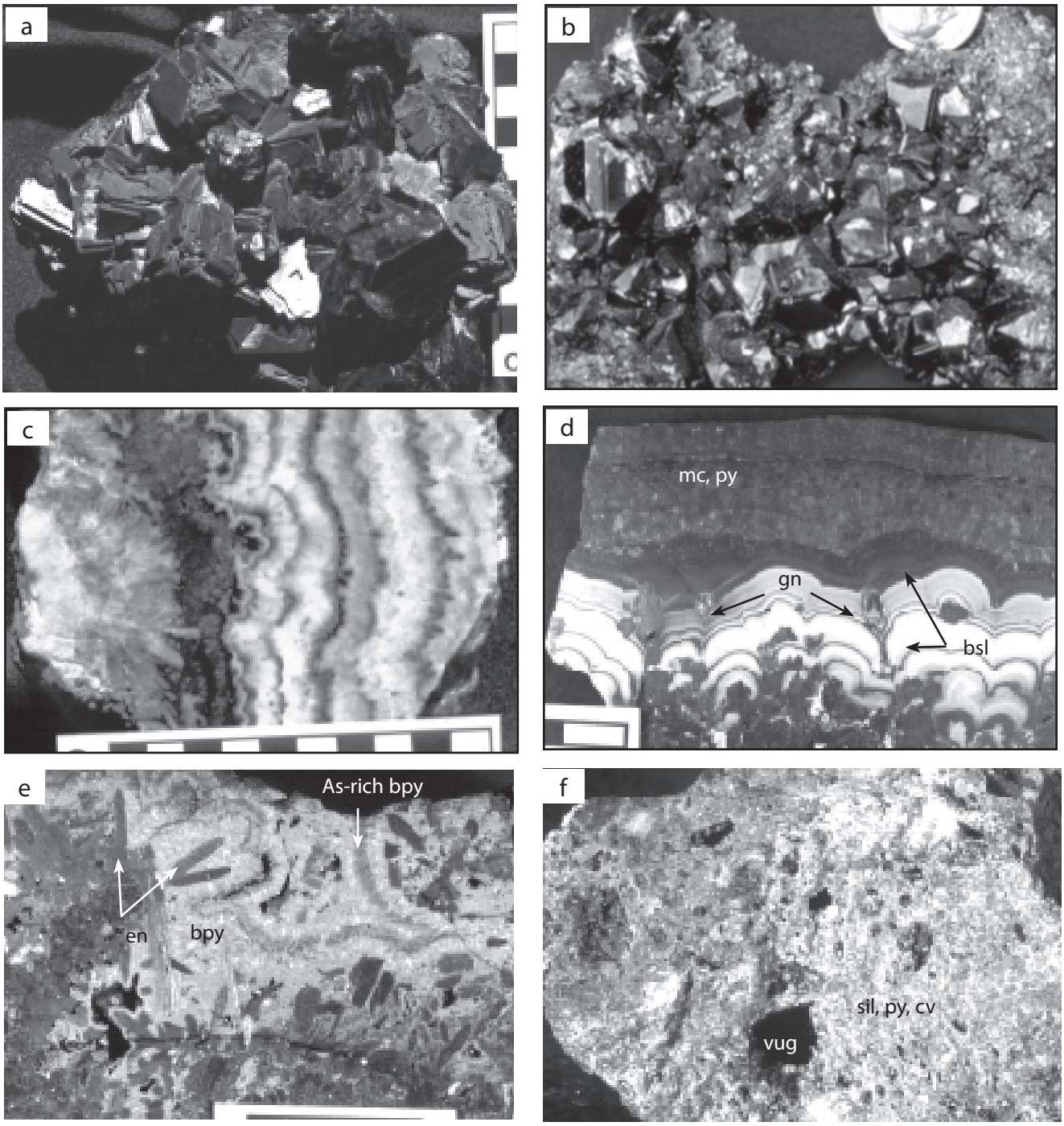


FIGURE 3.1—Examples of sulfide mineral assemblages found in a variety of mineral-deposit types, shown in general order of increasing reactivity and acid-generating potential. (a) Coarse-grained galena, Creede, Colorado. (b) Coarse-grained sphalerite, Creede, Colorado. Dime in upper right for scale. (c) Cut slab of fine-grained sphalerite and galena generations (dark) interbanded with fine- to coarse-grained barite (white). Such banding is termed crustification, and reflects the progressive growth (toward the right in the photo) of successive mineral bands on top of earlier-formed bands. (d) Cut slab of botryoidal marcasite and pyrite (mc, py) coating botryoidal sphalerite (alternating light and dark bands, labeled bsl) with intergrown galena (dark crystals cutting sphalerite bands, labeled gn), Pomerzany mine, Silesia, Poland. The marcasite and pyrite are highly enriched in trace elements, with up to several weight percent As and 1,000 ppm Tl. (e) Cut slab of arsenic-rich botryoidal pyrite (bpy) coating coarse-grained, euhedral laths of enargite (en), Cerro de Pasco, Peru. Scale bars are 1 cm long. (f) Vuggy silica alteration, Summitville, Colorado, with fine-grained silica (sil) replacing the original rock; pyrite (py) and covellite (cv) are disseminated in the silica. Vugs are left by the complete dissolution of a coarse-grained feldspar crystal from the original volcanic rock. Vug is approximately 1.5 cm wide.

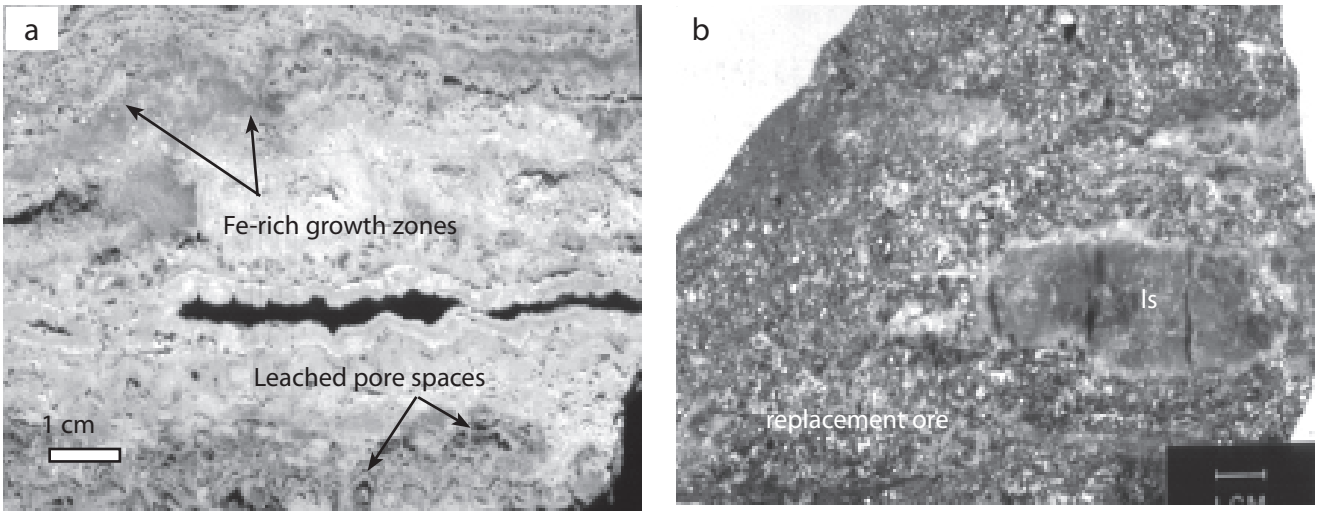


FIGURE 3.2—Examples of acid-consuming mineral assemblages. (a) Banded rhodochrosite, Creede, Colorado. Variations in color in part reflect variations in the Fe content of the rhodochrosite. The Fe preferentially oxidizes on the cut surface of the sample to form Fe-hydroxides. Some of the rhodochrosite growth zones were subsequently leached by hydrothermal fluids, which produced the many dark pores in the sample. The dark open space stretching horizontally across the middle of the sample is a fracture with sides coated by later rhodochrosite that did not completely fill the fracture. (b) Sphalerite-galena-pyrite-calcite-silica ore (labeled replacement ore) replacing limestone, from the polymetallic replacement deposits at Leadville, Colorado. Remnant limestone fragment labeled ls. Due to the high pyrite and sphalerite content, this assemblage would most likely generate near-neutral-pH drainage waters with elevated levels of zinc. Photograph by G. Landis.

acid-base accounting schemes that simply total the amount of carbonate present in minerals can therefore underestimate the acid-generating potential of siderite- or rhodochrosite-bearing mine wastes or soils (see White et al., 1999).

A variety of metal carbonates, such as those of zinc (smithsonite), and copper (malachite and azurite) occur in the oxidized zones of sulfide mineral deposits in dry climates. These minerals are also effective acid consumers.

Aluminosilicate, calc-silicate, and some metal-silicate minerals are common components of many mineral deposits or their host rocks. Reactions of acid with aluminosilicate minerals are a well-known part of the rock weathering process (Stumm and Morgan, 1981). These acid-consuming reactions typically result in the release of some constituents into solution and the transformation of other constituents into more acid-stable and commonly less reactive (Table 3.5) minerals, such as is shown by the reaction below of potassium feldspar with acid to form aqueous potassium and silica and solid hydrous aluminum oxide,

$$KAlSi_3O_8 + H^+ = K^+ + 3\ H_4SiO_{4(aq)} + Al(OH)_{3(s)} \qquad [2]$$

or the reaction of calcium-plagioclase to form kaolinite,

$$CaAl_2Si_2O_8 + 2\ H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_{4(s)} \qquad [3]$$

Calc-silicate minerals such as diopside, wollastonite, and garnets can similarly react to consume acid, as can rhodonite ($MnSiO_3$), a metal silicate common in some types of sulfide-bearing mineral deposits.

Iron-, manganese-, and aluminum- oxides and hydroxides, such as hematite, magnetite, pyrolusite, and gibbsite can theoretically react with acid, as indicated by the following reactions:

$$Fe_2O_{3(s)}\ \text{(hematite)} + 6\ H^+ = 2\ Fe^{3+} + 3\ H_2O, \qquad [4]$$

$$MnO_{2(s)}\ \text{(pyrolusite)} + 3\ H^+ = Mn^{3+} + 1.5\ H_2O + 0.25\ O_2. \qquad [5]$$

Native silver can also theoretically consume acid; however, it is a relatively stable and trace component of oxidized ore bodies, and so does not readily dissolve in oxygenated surface waters without the availability of complexing agents such as chloride:

$$Ag^{\circ}_{(s)} + H^+ + 0.25\ O_2 = Ag^+ + 0.5\ H_2O. \qquad [6]$$

Quartz, chalcedony, and other silica minerals, however, do not consume acid when they weather:

$$SiO_{2(s)} + 2\ H_2O = H_4SiO_{4(aq)} \qquad [7]$$

Fluorite (CaF_2), a common gangue mineral in a number of mineral deposits, is similarly not an effective acid-consumer:

$$CaF_{2(s)} = Ca^{2+} + 2\ F^- \qquad [8]$$

Mineralogic controls on health effects

Environmental concerns about some industrial minerals stem from their direct effects on health. Mineralogy plays a well-

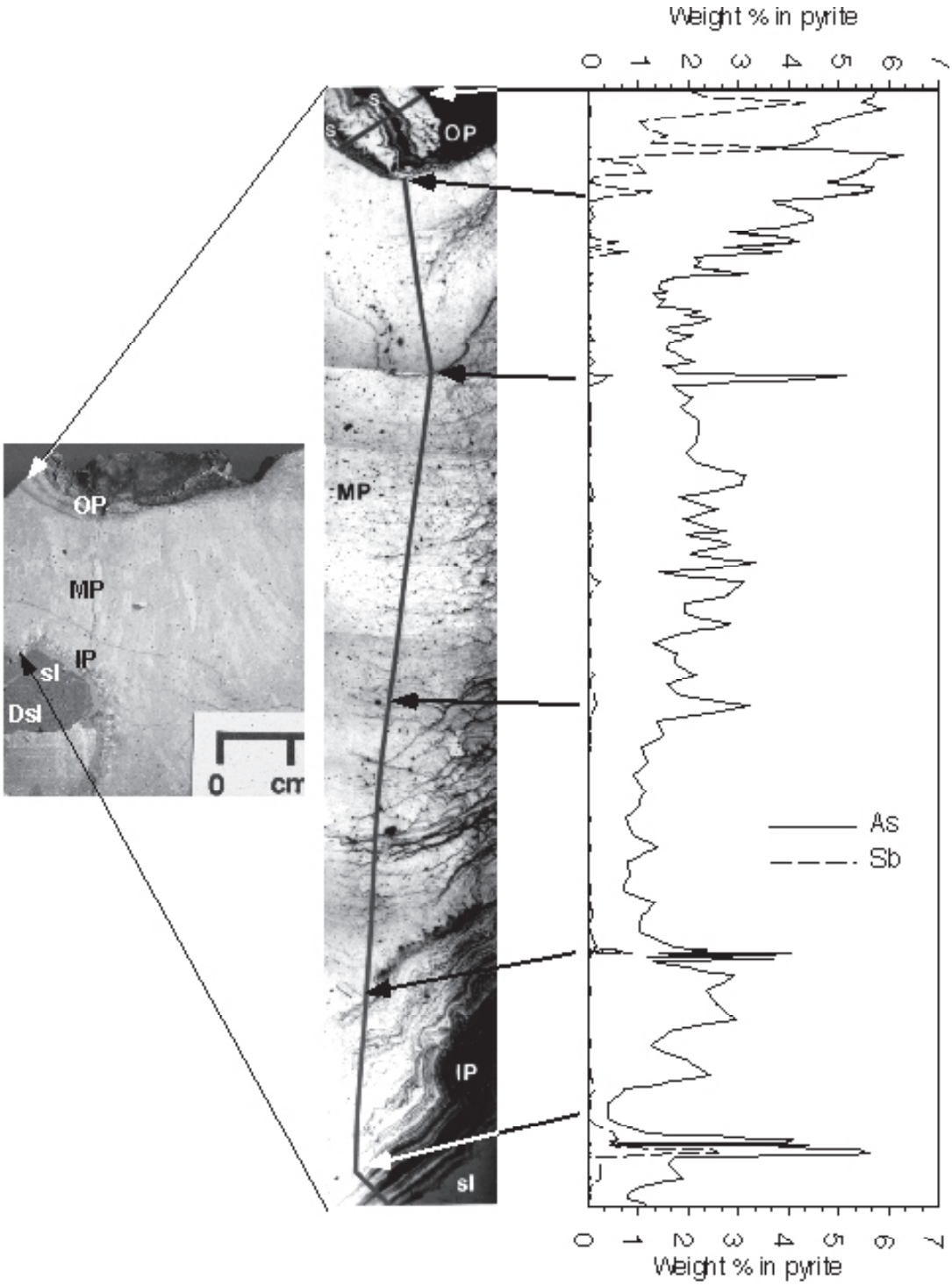


FIGURE 3.3—Relationship between etching rate and trace-element content in a botryoidal pyrite sample from Creede, Colorado. Left photo is photo of cut pyrite slab showing growth of botryoidal pyrite on top of coarse-grained sphalerite (sl, Dsl). Middle photo is composite reflected light photomicrograph across the pyrite stratigraphy. Darker growth zones are those that etched most rapidly when etched for 15 seconds with half-strength reagent-grade nitric acid. Right column shows variations of As, Sb, and Ag across the pyrite stratigraphy; note correlation between highly etched growth zones and elevated As and Sb contents. The etching of polished sulfide slabs with nitric acid and observing the rate of etching appears to be a reasonable proxy for understanding relative sulfide weathering and oxidation rates. Figure modified from Plumlee (1989).

known, important role in determining adverse health effects associated with ingestion or inhalation of asbestos minerals (see Ross, 1999). Chrysotile asbestos, the most common form of asbestos used in industrial applications in the United States, apparently has negligible effects on human cancer incidences. However, crocidolite and amosite asbestos varieties can clearly be linked to greatly increased human mortality rates from certain types of cancer. As another example, resistate minerals (those that are not readily soluble in ground and surface waters) occur in a variety of pegmatite, rare earth, or Ti-bearing beach sand deposits; some of these minerals can contain substantial amounts of radioactive uranium and thorium, which decay to release radon gas that can cause deleterious health effects.

Mineral resistance to weathering

The relative rates at which minerals weather have a major effect on the rates of acid production, acid consumption, and metal release from mineral deposits into the environment. The rates of weathering are a complex function of mineralogy, mineral textures, and trace element contents (Tables 3.4, 3.5).

Sulfide resistance to oxidation

Mineralogy: The relative weathering rates of various sulfide minerals have been evaluated through a variety of laboratory studies (summarized by Nordstrom and Alpers, 1999, and Jambor, 1994) and by field observations. Although the laboratory studies (i.e., Brock, 1979) are generally in overall agreement as to the sulfides which are most (cinnabar, molybdenite) and least (pyrrhotite, chalcocite) resistant to oxidation, they can vary substantially in detail as to whether a particular sulfide is more or less resistant than another sulfide (Jambor, 1994). It is possible that the disagreement between the laboratory studies is due to (at least in part) differences in grain size, texture, and trace element content of the sulfides examined, all of which can greatly influence resistance to oxidation (Table 3.4).

Grain size and textures: Due to greater surface area available for attack by weathering agents, fine-grained (< ~1 mm) sulfides tend to oxidize much more rapidly than their coarser equivalents. Sulfides with framboidal (agglomerations of many microscopic spherules) and colloform (intergrown, radiating crystal fibers) textures grew rapidly under highly supersaturated conditions; due to their very great surface area, they tend to be much less stable during weathering than sulfides having well-developed crystal faces (Figs. 3.1a, b). Using humidity cell tests of sulfide-bearing ores, White and Jeffers (1994) showed that framboidal pyrite weathers much more rapidly than fine-grained, euhedral pyrite, and so contributed to significant acid generation early in the tests; the euhedral pyrite, in contrast, weathered much more slowly, and so released low levels of acid throughout the tests. Botryoidal textures form when crystals grow outward simultaneously from a surface and coalesce; because their outer surfaces are euhedral crystal faces, their reactivity is less than colloform textures. Massive textures form when crystals grow together in a cavity and develop interlocking outer surfaces; due to the lack of pore spaces and crystal faces to weather, massive crystal growths that the author has observed tend to have moderate reactivities (Fig. 3.4).

Trace-element content: Trace elements present in a sulfide (either as impurities within the crystal structure or as minute inclusions of other minerals) cause strain in the crystal structure, and therefore generally tend to diminish the sulfide's resistance to oxidation (Kwong, 1995; Jambor, 1994). Perhaps the best example of this is the occurrence of arsenic in pyrite, which greatly decreases oxidation resistance (Fig. 3.3). As shown on Figure 3.3, the rates at which botryoidal pyrite growth zones are etched by nitric acid (an effective proxy for natural oxidation) are clearly related to the arsenic and antimony content of the growth zones and the botryoidal crystal size (Plumlee, 1989); the higher the arsenic content, the more rapid the etching. A survey of arsenic-rich pyrite and marcasite from a variety of mineral deposits (Plumlee, 1989) indicates that pyrite and marcasite with greater than several weight percent arsenic (which imparts a distinctive bronze tint to the pyrite and marcasite) will weather rapidly even without liquid water, merely from the reactions of the mineral with water vapor in the air (Fig. 3.3); curated pyrite and marcasite samples with high arsenic contents were very easy to identify due to the acid-driven corrosion of their sample containers.

The role of other trace elements in sulfides other than pyrite is less well documented. Kwong (1993) has noted that Cu-bearing growth zones tended to increase pyrite oxidation rates in humidity cell tests of polished sections of sulfide ores, and that sphalerite containing microscopic inclusions of chalcopyrite weathered more rapidly than inclusion-free sphalerite. Jambor (1994) indicates that the presence of iron and other trace elements in sphalerite decreases its stability, and that the presence of Ag, Sb, and Bi in galena similarly decreases its resistance to oxidation.

Not all trace elements decrease a sulfide's resistance to oxidation, however. In his humidity cell study, Kwong (1993) noted that traces of Co and Ni in pyrite tended to increase its resistance to oxidation rather than decrease it. Kwong postulated that elements which substitute for an element to their left on the periodic table (such as Co for Fe), under semiconductor physics theory, should lead to positive effective charge and therefore suppress the electron transfer necessary for sulfide oxidation to occur.

Reactivity of sulfide assemblages: As noted by Kwong (1995), Sato (1992), and Nordstrom and Alpers (1999), sulfides in a mineral assemblage can weather preferentially due to galvanic reactions resulting from differences in their standard electrode reduction potentials. Minerals with low standard electrode reduction potentials (such as pyrrhotite, sphalerite, and galena) can preferentially oxidize when in electrochemical contact (i.e., via ion-bearing waters) with sulfides having higher standard electrode reduction potentials, such as argentite (Ag_2S), and pyrite; the pyrite and argentite are thus "protected" from oxidation by the pyrrhotite, sphalerite, and galena. As noted by other studies cited in Nordstrom and Alpers (1999), however, this galvanic effect is not always discernible.

The presence of readily-weathered sulfides in a mineral assemblage can also increase the reactivity of other, less readily weathered sulfides due to the formation of corrosive acids. For example, the author recently observed monomineralic bornite on one side of a mine drift that has remained unoxidized after 20 years of mining. On the other side of the mine drift, bornite intergrown with reactive marcasite has undergone extensive oxidation to secondary copper sulfate salts. The acid generated by marcasite oxidation has triggered the breakdown of the more resistive bornite. Similar effects were noted by Boyle (1994) in a weathering massive sulfide deposit, where the abundance of readily-weatherable pyrrhotite in the deposit could be directly correlated with the rate at which the intergrown sphalerite and pyrite oxidized.

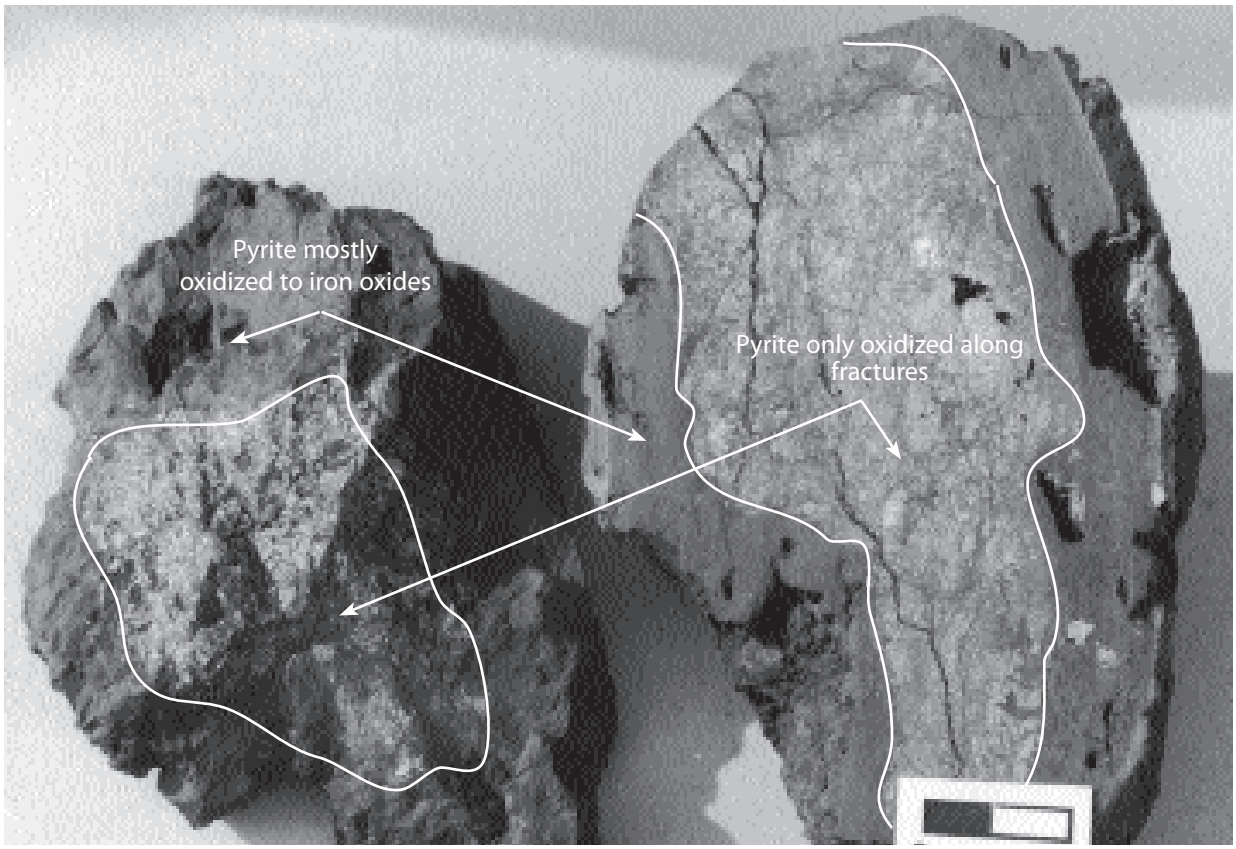


FIGURE 3.4—Massive pyrite sample from the polymetallic replacement deposits at Leadville, Colorado, showing the relative rates of pre-mining and post-mining oxidation. Pre-mining oxidation of the sample replaced the pyrite with iron-oxide minerals in a thick, dark rind around the edges of the samples and in veinlets crosscutting the unoxidized pyrite; this presumably occurred over the thousands of years since the last retreat of glaciers in the area some 10,000 years ago. The post-mining oxidation of the sample on the mine dump produced relatively little oxidation over the course of the ~100 years the sample was on the dump, as shown by the shiny pyrite faces on the uncut surface to the left.

Carbonate- and silicate-mineral resistance to weathering

As with the sulfides, the mineralogy, grain size, and textures of carbonates and silicates greatly influences their ability to react with acid generated during sulfide weathering. Sverdrup (1990) (as cited by Kwong, 1993) classified various rock-forming silicates, carbonates, and oxides according to their relative pH-dependent reactivities; a revised version of the classification provided by Kwong (1993) is shown in Table 3.5. Carbonate mineral reactivity generally decreases in the following sequence:

cerussite, aragonite, calcite > rhodochrosite > siderite > magnesite, brucite

The presence of trace elements may increase or decrease carbonate resistance to weathering. For example, iron-rich growth zones in rhodochrosite can weather more rapidly than the surrounding Mn-rich growth zones, perhaps due to oxidation of the iron; this is illustrated by the development of iron oxide minerals on Fe-rich growth zones in sawed rhodochrosite slabs within a day or two of cutting (Fig. 3.2a).

Variable silicate resistance to weathering is well documented in the literature (for example, Goldich, 1938; Sverdrup, 1990; Kwong, 1993). Minerals that crystallize from magmas at high temperatures, such as olivine, pyroxene, and calcic plagioclase, tend to be more reactive than minerals that crystallize at lower temperatures such as alkali feldspars, biotite, muscovite, and quartz (see summary in Smith and Huyck, 1999). Clay minerals (such as montmorillonite and kaolinite) and zeolites have relatively low reactivity. Volcanic glass and devitrified volcanic glass (a mixture of very-fine-grained aluminosilicate and silica minerals) also can be quite reactive in the ground-water environment. As demonstrated by the high levels (as high as tens of thousands of mg/l or ppm) of aluminum found in acid rock drainage waters (Nordstrom and Alpers, 1999; Plumlee et al., 1999), aluminosilicate minerals do react with the acid generated by sulfide oxidation; however, the great abundances of the aluminosilicate minerals found in most mineral deposits or their host rocks means that the aluminum in the waters was derived from relatively limited acid consumption by the aluminosilicate weathering reactions.

The effects of grain size and texture on carbonate and silicate reactivities can be substantial. For example, mine waters draining pyrite-molybdenite ores and their host coarse-grained granites can

be quite acidic, due to the low reactivity of the coarse-grained feldspars; in contrast, very fine-grained potassium feldspars may consume acid to produce near-neutral mine waters draining Au-Te ores in alkalic volcanic rocks (Plumlee et al., 1999). Effects of climate on silicate weathering rates are discussed below in the section on climate.

Secondary mineralogy

Secondary minerals are those that form at or near the ground surface as mineral deposits are exposed by erosion or mining and weathered by ground waters, surface waters, and the atmosphere. Depending upon their compositions and solubilities, secondary minerals can be beneficial, by restricting access of weathering agents to sulfides, or detrimental, by storing acid and metals in a readily-released form. A detailed discussion is presented by Nordstrom and Alpers (1999) and Jambor (1994), so only a brief discussion is included here. Chemical formulas for minerals discussed here are given in the tables in Nordstrom and Alpers (1999).

Secondary minerals that form in the oxidized zone of weathering deposits

As a mineral deposit is exposed by erosion and weathered by surface waters descending through the unsaturated zone, a near-surface oxidized rind typically results. In this rind, the original constituents of the deposit and its host rocks are either removed in solution or converted to a wide variety of oxygen- and acid-stable minerals. As these minerals tend to be relatively insoluble in most ground and surface waters, they typically reduce the release of metals into the environment; as a result, completely oxidized sulfide orebodies tend to produce relatively non-acidic drainage waters with relatively low concentrations of heavy metals. The oxidized minerals can also form relatively impermeable coatings on remnant sulfides, thereby reducing the rates of sulfide oxidation and acid and metal generation where sulfides are still present in the rock (Nordstrom and Alpers, 1999).

Examples of minerals common in the secondary oxidized zone include: oxides and hydroxides of iron (goethite, lepidocrocite, hematite), aluminum (boehmite, gibbsite, diaspore), manganese (pyrolusite), copper (cuprite, tenorite); sulfates of calcium (gypsum) and lead (anglesite); hydroxysulfates of iron, aluminum, potassium, sodium, and lead (alunite, natroalunite, jarosite, natrojarosite, plumbojarosite); clays (kaolinite, halloysite, dickite); silicates of manganese (psilomelane), copper (chrysocolla), and zinc (hemimorphite); carbonates of copper (malachite and azurite), zinc (smithsonite), and lead (cerussite); phosphates (hinsdalite, turquoise); native metals (Ag, Cu, Au); molybdates (wulfenite); and halides of silver (chlorargyrite, bromyrite, embolite). Soluble sulfate salts of copper (such as chalcanthite) and other metals also can form transiently during dry periods.

Lateritic or residual mineral deposits of Fe, Al, Mn, and Ni are formed as a result of weathering processes of rocks in humid, tropical to subtropical climates (Guilbert and Park, 1986). In general, these deposits result from the residual concentration of the Fe, Al, Mn, or Ni in intensely weathered rocks that were originally somewhat enriched in these constituents. Organic acids released from decaying vegetation play a substantial role in the weathering process, but these deposits are not characterized by acid rock drainage caused by sulfide oxidation. Some transport of Ni in natural and mine-drainage waters does occur however, due to its relatively high mobility and lack of sorption onto particulates (W. Miller, oral commun., 1997; Smith, 1999).

Secondary minerals that form below the water table in weathering sulfide deposits

Some metals leached by waters in the unsaturated zone are re-deposited as sulfides under the reducing conditions present below the water table. This enrichment occurs via the replacement of existing sulfides, and is driven by the relative electrochemical properties of the sulfides (Guilbert and Park, 1986). Copper and silver are the metals most commonly enriched in the reduced supergene zone, and pyrite and the iron sulfides are the sulfides most commonly replaced. A suite of copper and copper-iron sulfides (including covellite, chalcocite, bornite, and djurleite) typically replace iron sulfides. Supergene acanthite (Ag_2S) typically replaces galena, pyrite, and sphalerite, and is itself commonly replaced by native silver.

The predominant environmental effects of the supergene sulfides result from the fact that the supergene process removes acid-generating iron sulfides from the deposit and replaces them with sulfides that commonly generate less acid. However, the supergene process typically does not lead to the complete removal of iron sulfides, and can lead to the precipitation of acid-generating supergene sulfides such as bornite; hence, the potential beneficial effects of supergene enrichment on acid-generating potential are rarely completely realized.

Soluble secondary salts

A complex array of soluble sulfates, hydrous sulfates, and some hydroxysulfates are a common result of sulfide oxidation in the surficial environment (Nordstrom and Alpers, 1999; Jambor, 1994). These soluble salts are of environmental concern because they store acid and metals in the solid phase. During periods of rainfall or snowmelt, their dissolution can result in potentially detrimental flushes of acid and metals into ground and surface waters. For example, seasonal flushing of soluble salts from tailings deposits along the Clark Fork River in Montana has been documented as the cause for seasonal fish kills along the river (see references in Nimick and Moore, 1994). These salts can also be a significant source of dissolved ferric iron which, when released, can trigger further sulfide oxidation.

Sulfates and hydrated sulfates of the major elements calcium (gypsum) and magnesium (epsomite, pickeringite), and the major metals iron and aluminum (melanterite, copiapite, coquimbite, rhomboclase, halotrichite, alunogen, and many others) are generally most abundant, due to the common occurrence of the iron sulfides in many mineral deposits and the abundance of Ca, Mg, and Al in deposit host rocks. Although considered to be relatively insoluble in the secondary oxidized zone of weathering mineral deposits (Nordstrom and Alpers, 1999), jarosite (an Fe-K-Na-H^+ hydroxysulfate) is a common salt in many mine waste materials that readily release acid and metals during rain storms or laboratory leach tests (for example, Plumlee et al., 1995a and b). The abundance of hydrated sulfates of heavy metals such as copper

(chalcanthite, brochantite), zinc (gummingite, zincosite), and nickel (morenosite) varies depending upon the abundance of these metals in the primary sulfides present. As shown by Alpers et al. (1994a and b), these heavy metals can also occur in significant concentrations as impurities within iron- and aluminum-sulfates and jarosite.

Soluble secondary salts are best known to form from the evaporation of acid-drainage waters (Nordstrom and Alpers, 1999). For example, efflorescent crusts are common on the surfaces of mine dumps and on the edges of natural- and mine-drainage streams and puddles. The mineralogy of the product salts can change with progressive evaporation, such as has been observed for hydrous iron sulfates (Nordstrom and Alpers, 1999). In general, the greatest salt growth occurs when the growing crusts are replenished by acid water, such as a flowing drainage stream or waters wicked to the surface of a mine waste dump by capillary action.

The soluble secondary salts can also form as weathering products of sulfides that are not in direct contact with liquid water, but that are in contact with atmospheric moisture; such occurrences are well documented in experimental weathering studies (Borek, 1994; White and Jeffers, 1994) and through field observations. For example, extensive growths of secondary iron and copper salts occur on the ribs of mine workings where there is no source of flowing water to evaporate. As another example, complex intergrowths of secondary salts formed on samples of arsenic-rich botryoidal pyrite from Creede, Colorado while the samples were stored in drawers; the only source of the moisture could have been humidity in the air.

Due to their high solubilities, secondary salts most commonly form where sulfides have been exposed directly to weathering by oxygenated waters. Mine waste piles, mine workings, and mill tailings piles are therefore common hosts for these minerals. However, they can also occur naturally where sulfide mineralization has been exposed at the ground surface by rapid mechanical erosion or glaciation. For example, largely unmined porphyry Cu-Mo systems occur in the Alamosa River basin south and east of Summitville, Colorado. Due to the extreme topographic relief and the highly altered rocks in these areas, physical erosion rates greatly exceed chemical weathering rates, thereby exposing unoxidized sulfides at the ground surface (Figs. 3.5d-f). A water quality study along the Alamosa River (Ortiz et al., 1995) showed that a single rainstorm which affected one of these mineralized areas lead to a transient pulse of acid and metals into the river; the most likely source of this pulse was the dissolution of soluble salts from the sulfide-rich rock material exposed in the mineralized area.

Secondary ferricrete deposits

As Fe-bearing ground waters flow onto the ground surface or mix with surface or near-surface waters, oxidation of the Fe results in the precipitation of Fe hydroxides and hydroxysulfates (Nordstrom and Alpers, 1999; Smith, 1999). In cases where supersaturation is extreme and precipitation is rapid (such as during dilution of acid waters by surface waters, or oxygenation of near-neutral pH waters), suspended particulates are produced (Nordstrom and Alpers, 1999; Smith, 1999). These suspended particulates settle out from surface waters in areas of low flow velocity, but can be easily resuspended and transported downstream in periods of high flow.

In contrast, in environments where supersaturation is less extreme (such as where acid waters flow onto the ground surface and are oxidized), Fe hydroxides precipitate directly on pre-existing surfaces as ferricrete deposits. Ferricrete can occur as a cement around rock fragments in stream channel deposits or talus breccias (Figs. 3.5f, h), or as so-called ferrosinter terraces (Kirkham et al., 1995) on the ground surface (Fig. 3.5g). In most cases, ferricrete and ferrosinter deposits form at or near breaks in topographic slope, where the ground-water table intersects the ground surface or mixes with shallow ground water recharged from streams of different chemical composition. These deposits are typically quite resistant to erosion and form prominent ledges or ridges (Fig. 3.5h). These deposits also have generally low hydraulic conductivities (Fig. 3.5f), and can thus serve as confining beds that restrict the flow of ground water. Paleo-ferricrete deposits are very common around many sulfide-bearing mineral deposits, and are good indicators of naturally degraded ground-water quality for hundreds or thousands of years prior to mining (Furniss and Hinman, 1998).

Extent of sulfide oxidation prior to mining

As indicated in the previous section, pre-mining sulfide oxidation can substantially reduce the potential for a sulfide-bearing mineral deposit to generate acidic, metal-rich mine-drainage waters. The extent of pre-mining oxidation is typically a function of the deposit geology, topography, and climate (discussed subsequently. Oxidation is most extensive in deposits (a) with geologic characteristics that allow easy access to descending oxygenated ground waters (discussed below), (b) that occur in areas of high topographic relief (where the water table tends to be relatively deep), and (c) that occur in dry climates where the water table is deep. Prior to mining, the extent of oxidation should be carefully mapped in an originally sulfide-rich deposit; more than one mine that was planned on the assumption that the sulfides were completely oxidized has turned out to produce pockets of acid-generating, sulfide-bearing ores or wastes that substantially increased the need for and costs of acid-drainage mitigation, and may have affected metal recovery as well.

Host rock lithology

The same mineralogic, textural, and compositional characteristics that influence the environmental geochemistry of a mineral deposit also apply to the minerals making up the rocks that host the mineral deposit (Tables 3.1, 3.5).

Chemical characteristics of host rocks

Host rocks with moderate to high contents of carbonate minerals (for example, limestone, dolomite, marble, carbonate-cemented sandstone, and shale) or contents of reactive aluminosilicate minerals (for example, poorly welded volcanic tuff or ultramafic rocks such as dunite and gabbro) have moderate to very high acid-neutralizing capacity, and so can react directly with acid generated by oxidation of sulfides in the mineral deposit. In addition, ground waters draining these rock types typically have high alkalinities; mixing with and dilution of acid-rock drainage by waters draining these rock types can thus help neutralize the acid and cause some

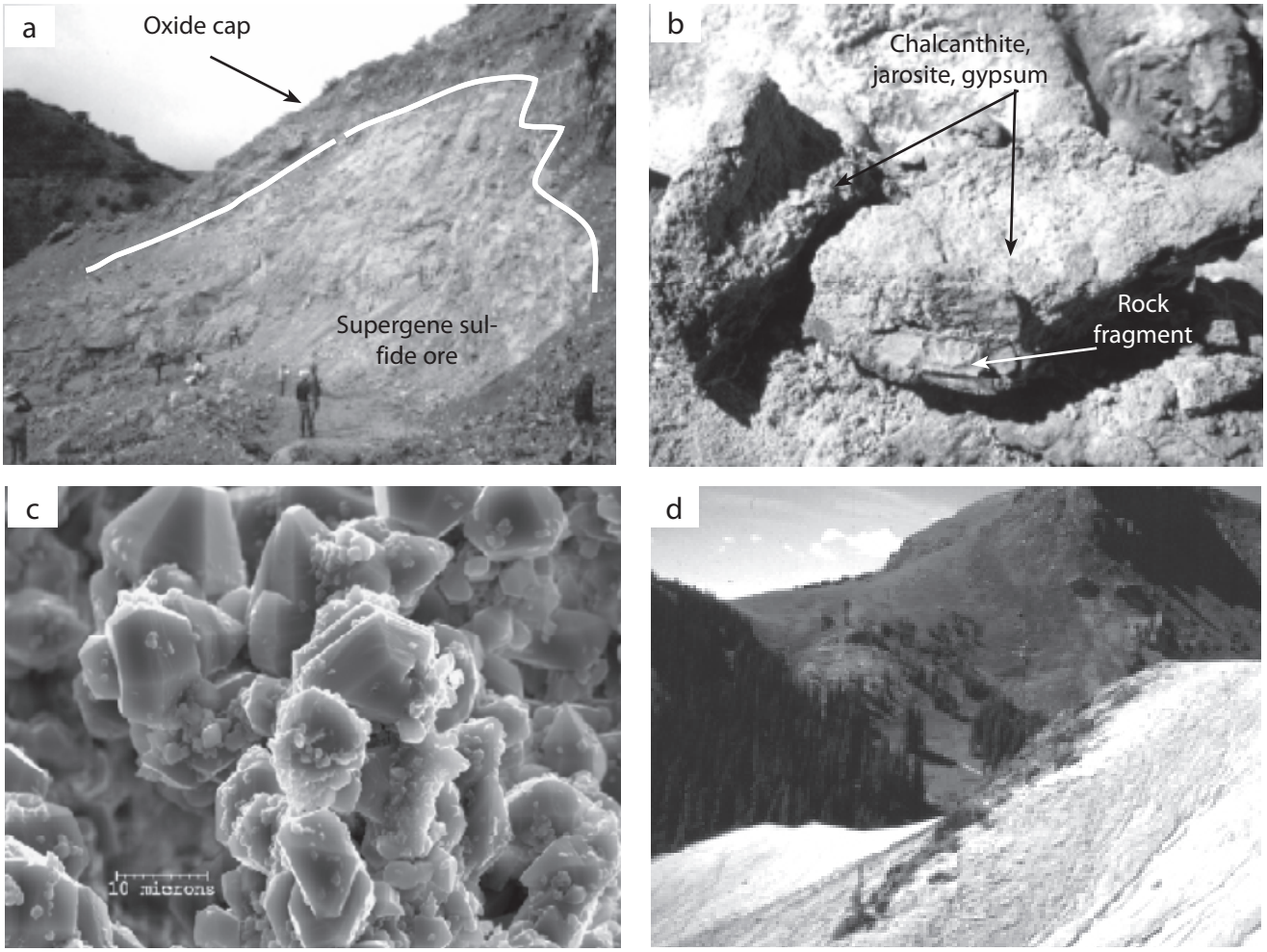


FIGURE 3.5—Examples of weathered mineral deposits. (a) Photographic cross section showing the oxide cap (dark rocks) and supergene sulfide zone (light rocks) of a porphyry-Cu deposit, Bisbee, Arizona. The oxide cap is composed primarily of relatively insoluble secondary oxides of Fe and some oxides and carbonates of Cu. The underlying supergene sulfide zone is characterized by supergene chalcocite replacement of primary pyrite and chalcopyrite stockwork veins and disseminations in altered host rock. After exposure by mining, the sulfides are now weathering to soluble blue Cu sulfates and yellow-orange Fe-sulfates and jarosite. Photo by C. Taylor, USGS. (b) Concrete-like mixtures of chalcanthite, jarosite, and gypsum that form 3–5 cm-thick encrustations in a Cu-sulfide-rich tailings pile, 3-R Mine, Patagonia Mountains, Arizona. The crusts form by the progressive evaporation of acid waters during dry periods. When placed in deionized water, these coatings dissolve nearly completely within an hour, and form a solution with pH < 3 and a blue tint indicative of many hundreds of parts per million dissolved Cu. (c) Scanning electron microscope (SEM) image of copiapite growing on arsenic-rich botryoidal pyrite from Creede, Colorado. All of the growth occurred on a cut slab of the pyrite while the slab was stored in a sample drawer. The growth demonstrates the ease with which reactive sulfides can oxidize simply by reacting with moisture in the air. (d) Argillically-altered rocks (light color in foreground) that formed in the middle to upper levels of a low-grade porphyry Cu-Mo system, Alamosa River stock, south of Summitville, Colorado. The altered rocks erode much more rapidly than the unaltered volcanic rocks in the background; the light color reflects a several centimeter-thick oxidized rind of weathered clays and soluble secondary salts coating unoxidized sulfide-bearing rock.

metals to sorb from solution onto particulates (Smith, 1999; Smith et al., 1994).

Rock types that generally afford little or no acid-neutralizing capacity include coarse-grained, silica-rich intrusive rocks (such as granites or granodiorites), silica-rich sedimentary rocks (such as quartz-rich, silica-cemented sandstones, and arkoses), and carbonate-poor metamorphic rocks (such as quartzites).

Rocks can themselves be enriched in a variety of trace metals (Thornton, 1995; Rose et al., 1979); however, the ease with which these elements are released into the environment from the rocks during weathering (termed their *geoavailability*; Smith and Huyck, 1999) varies substantially among rock types. Some rock types, such as black shales, sulfidic schists, layered ultramafic intrusive rocks, sedimentary rocks mineralized by migrating basinal brines, and coal beds, contain abundant sulfide minerals as primary constituents. These rock types often have elevated concentrations of trace metals (such as As, Ni, Co, Cu, Zn, Se, etc.) that occur at least in part within sulfides. In many cases, these rocks were mineralized by the same processes that form mineral deposits, but that did not concentrate the metals sufficiently to form a deposit. Depending upon their acid-neutralizing capacity, these rocks, upon weathering, can generate acidic, metalliferous waters or less

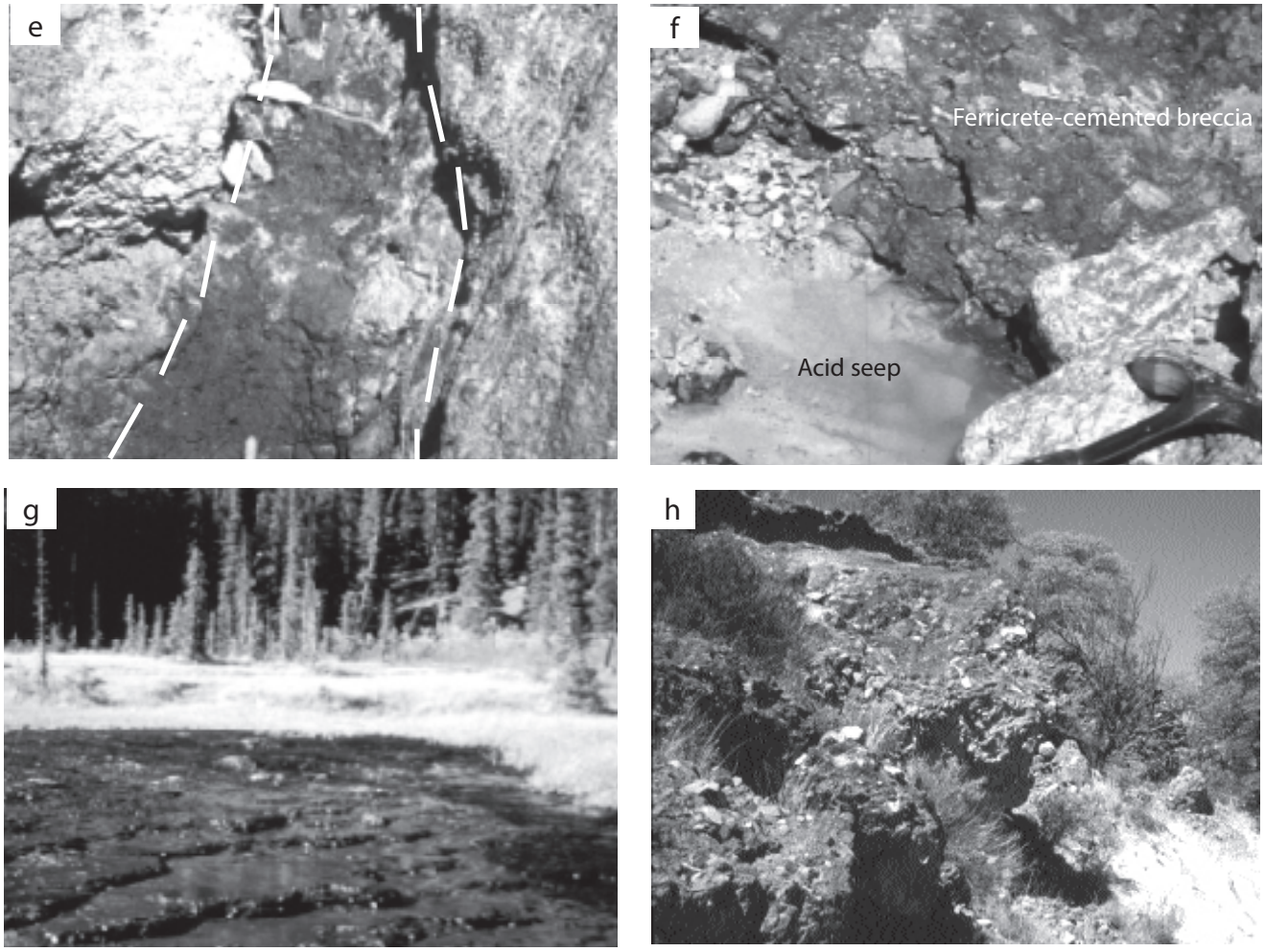


FIGURE 3.5 (Continued)—(e) Fresh sulfides exposed in a rivulet cutting through the weathered rock shown in (d). (f) Ferricrete-cemented breccia that occurs at the base of the altered rock slope shown in (d). The ferricrete has been deposited by acid spring waters since the last period of glaciation some 10–12 thousand years ago. Acid waters still seep from beneath the ferricrete, which serves as an impermeable confining bed. (g) Modern ferrosinter terraces (dark, foreground) being deposited by acid spring waters draining the Alamosa River stock. (h) Ferricrete-cemented breccias (left side of photo) formed in a stream channel on the flanks of a low-grade porphyry-Cu deposit, Patagonia Mountains, Arizona, during a past wet period. The highly cemented ferricrete erodes very slowly and now holds up ridges.

acidic waters with elevated concentrations of metals such as Zn, Se, U, or Ni that are mobile in near-neutral waters. In addition to their limited potential to help chemically mitigate drainage problems from nearby mineral deposits, these rocks can themselves generate a variety of environmental concerns. For example, locally pyrite-rich schists form the mountainous backbone of the Great Smoky Mountains. Exposure of these sulfide-rich rocks by past road building has enhanced natural acid-rock drainage from the schists. As another example, Se-rich black shales in the western foothills of the San Joaquin Valley of California were determined to be the source of Se that was concentrated by agricultural irrigation in the valley, and led to toxic effects on local waterfowl and aquatic life (Deverel and Fujii, 1988; Tidball et al., 1991). Phosphoria Formation phosphate deposits in the northern Rocky Mountains are phosphate-rich, sulfidic black shales that have similarly elevated levels of trace elements such as Se, U, and Ni.

In many rock types, metals occur as trace constituents within the rock-forming minerals, and so their geoavailability depends on the ease with which their host minerals weather. Some rocks such as pegmatites and silica-rich granites have high concentrations of elements such as U, Th, and rare-earth elements (REE). However, in these rock types, these elements typically occur in minerals that are highly resistant to weathering, such as tantalite, zircon, columbite, and monazite. As a result, their geoavailability and environmental mobility is generally quite low. The most significant environmental concern from these rock types is radioactive daughter products, such as radon, that are produced by the radioactive decay of the U and Th (see Landa, 1999, for a discussion of radioactive decay and its environmental effects). As another example, many granites also have elevated levels of Pb that occurs

as a trace element within feldspars; in general, such feldspar-bound Pb is of relatively low geoavailability in most climates.

Physical characteristics of deposit host rocks

The environmentally important physical characteristics of deposit host rocks are those that control ground-water flow to the deposits (Fig. 3.6, Table 3.6) and those that affect the physical susceptibility of the rocks to mass wasting such as slumps and landslides.

Rock characteristics that control ground-water flow: The ability of a rock to transmit ground water is termed its hydraulic conductivity, and is a function of its porosity (the size and number of pore spaces) and permeability (the connectedness of the pore spaces). The porosity and permeability of rock can either be primary (provided by features such as pore spaces within the rocks), or secondary (provided by fractures, joints, etc., that cut the rocks). For a detailed discussion of the porosity and permeability of various rock types, the reader is referred to texts on hydrology such as Domenico and Schwartz (1990), and Freeze and Cherry (1979).

Published hydraulic conductivity values for given rock types can vary over many orders of magnitude (Fig. 3.6), but some generalizations can be made for different rock types. Carbonate rocks such as limestones tend to have low to moderate primary porosity and permeability. However, both limestones and dolomites can have high hydraulic conductivities if they are extensively fractured or have well-developed karst features. Dolomites may have greater fracture densities than limestones because they are more brittle. Karst features are secondary voids formed by the dissolution of carbonate rocks by ground waters flowing along fractures and joints. Karst features can be very large, spatially extensive, and highly irregular in shape and distribution; they can therefore be of potentially great environmental concern due to their ability to transmit ground waters to and from mineral deposits in great volumes and over great distances.

Clastic sedimentary rocks such as sandstone, conglomerate, and breccia have primary porosity and permeability that is a function of the size and interconnection of the pore spaces between their grains. The greatest porosities and permeabilities occur in rocks such as gravels that have the coarsest grain size, greatest sorting (i.e., smallest range in size of the grains), and lowest interstitial cement content.

Due to their clay contents, shales typically do not tend to transmit ground waters. Instead they serve as confining beds that restrict ground-water flow between aquifers. Faults and fractures also tend to be poorly developed in shales, and so do not transmit ground water across shale beds.

In most igneous and metamorphic rocks, ground-water flow occurs along fractures and joints within the rocks. In volcanic flows, brecciated flow tops and bottoms can serve as important sources of primary porosity and permeability, as can lava tubes. Vesicular basalts can also be quite conductive hydrologically (Fig. 3.6).

Rock characteristics that control physical erosion and mass wasting: Processes that lead to gravitational collapse of deposit host rocks can be of environmental concern because the collapses can expose large volumes of potentially mineralized rocks to weathering. In general, rocks with high clay contents are more susceptible to gravitationally driven collapse than those with low clay contents. For example, shales are well known for their susceptibility to landslides and debris flows. Further, recent studies of continental shales in the Colorado Plateau (host rocks to sandstone uranium and copper deposits) have shown that the types of clay minerals present also influence susceptibility to mass wasting; shales with high contents of kaolinite and illite are more prone to landslide generation than those with high smectite contents (Griffiths et al., 1996).

Rocks that have planar geologic structures (such as bedding, lava-flow surfaces, parallel joints, etc.) along which rock failure can occur may be prone to gravitational collapse. For example, the sulfidic schists noted previously in the Great Smoky Mountains National Park are prone to failure where the schistosity surfaces are steeply dipping. During periods of heavy rains, water seeping in along the schistosity surfaces lowers the coefficient of friction sufficiently to enable rock collapse and the formation of debris flows. The debris flows expose fresh sulfides in the schists to weathering and oxidation; the acid and metals released by the sulfide oxidation are toxic to fish and other aquatic organisms in the streams downgradient from the debris flows; the affected populations may require several years to recover.

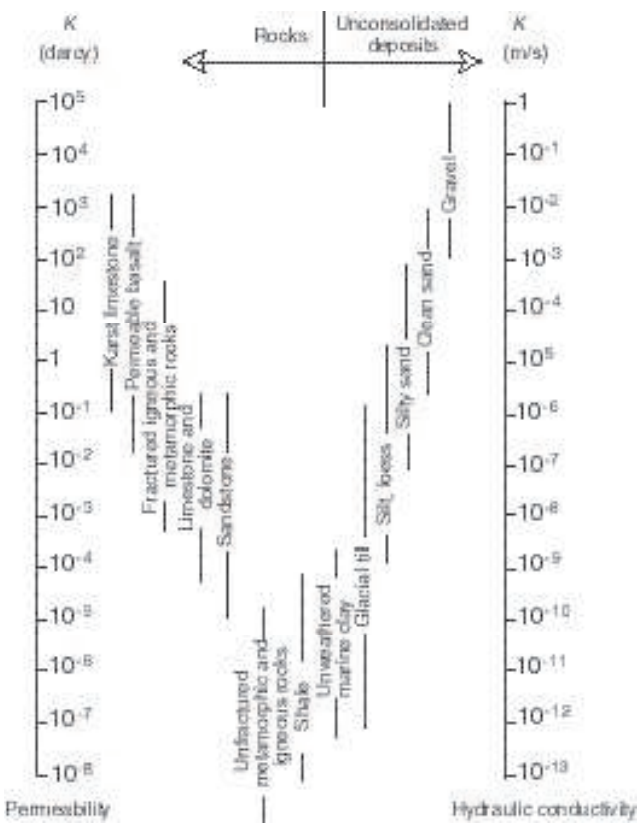


FIGURE 3.6—Hydraulic conductivities of various rock types. Modified from Freeze and Cherry (1979), and Cathles (1997).

TABLE 3.6—Environmental geology characteristics of rock types that commonly host mineral deposits. Acid buffering potential (N.P.) is a combination of the acid-neutralizing capacity of the rock-forming minerals, coupled with their reactivity (modified from Glass et al., 1982). Acid-generating potential (A.P.) is a combination of the sulfide content and reactivities. Rocks with high N.P. and A.P. may generate near-neutral, metal-rich waters. Trace elements from Thornton (1995), Guilbert and Park (1986), and other sources. Physical characteristics from Freeze and Cherry (1979), Domenico and Schwartz (1990).

Rock type	Acid-neutralizing generating potential	Trace elements (geoavailable)	Physical characteristics controlling ground-water flow
Sedimentary			
Limestone	High N.P.	(±F, Mn, Zn). Pb	Karst, fractures, joints
Dolomite	Mod-high N.P.	(± F, Mn, Zn), Pb	Karst, fractures, joints
Calcareous sandstone	Mod N.P.		Moderate intergranular, if little cement; otherwise fractures, joints
Black shales	Low-mod N.P.; low-mod A.P.	(U, Se, S, Ni, Te, Co, Mo, Zn, Cu)[1], P	Generally low permeability
Redbed shales	Mod N.P.	(U, V, Ni, Co, Cu, Se, Te, Mo)[2]	Generally low permeability
Arkose	Low N.P.	(Cu)[1]	Moderate-high intergranular
Chert	Low N.P.		Fractures
Quartzose sandstone	Low N.P.		Low-moderate intergranular, if little cement; otherwise fractures, joints
Igneous intrusive			
Carbonatite	High N.P.; mod A.P. in sulfide-rich rocks	(Cu, Zn, Pb, S)[1], REE, Nb, Ta, Zr, Hf, U, Th, P, Ba	Fractures, joints
Ultramafic (dunite, norite, etc.)	Mod-high N.P.; mod A.P.	Cr, (Co, Ni, S)[1]	Fractures, joints
Granite	Low N.P.	Ba, Li, W, Mo, Sn, Zr, U, Hf, Th, Ti, F	Fractures, joints
Volcanic			
Komatiite	Mod-high N.P.; some A.P.	(Ni, Co, Cu, S)[1]	Fractures, joints
Basalt	Low-mod N.P.	Cu, Zn	Fractures, joints, interconnected vesicles, flow tops and bottoms
Andesites	Low-mod N.P.	Cu, Zn	Fractures, joints, brecciated flow tops
Poorly welded, volcanic tuffs	Mod-high N.P.	(As, Li, Zn, Cu, B)[3]	Low fracture permeability
Highly welded volcanic tuffs	Low-mod N.P.	As, Li, Zn, Cu, Pb	Fractures, cooling joints
Rhyolite flows	Low-mod N.P.	As, Li, Zn, Cu, Pb	Fractures, cooling joints
Metamorphic			
Marble	High N.P.		Fractures, joints
Gneiss	Low N.P.	Ba, Li, W, Mo, Sn, Zr, U, Hf, Th, Ti	Fractures, joints, foliation, remnant bedding
Quartzite	Very low N.P.		Fractures, joints
Sulfidic schists	Low N.P., high A.P.	As, Zn, Co, Ni, Cu, U, Mo, Se	Fractures, joints, foliation, schistosity, remnant bedding

[1]Geoavailable if in sulfides.
[2]Trace elements are typically concentrated at interface between oxidized and reduced ground waters, and are otherwise dispersed elsewhere in the rocks in relatively low concentrations.
[3]These and other trace elements, while not particularly high in concentration, can be relatively geoavailable in fresh volcanic glasses.

Wallrock alteration

Wallrock alteration, a common feature of many hydrothermal mineral deposits, results from the chemical and thermal interaction of hydrothermal fluids or magmas that form the deposits with surrounding wallrock. A number of wallrock alteration types with characteristic mineralogies are recognized in a number of different hydrothermal deposit types (Table 3.7). Wallrock alteration has important environmental consequences because it can affect both the chemical and physical properties of the surrounding rocks.

Chemical effects of wallrock alteration

Wallrock alteration can either increase or decrease the acid-generating capacity and (or acid-neutralizing capacity of a deposit's host rocks. Alteration types that increase the acid-generating capacity (by increasing the content of acid-generating sulfides in the rocks) and (or decrease the acid-neutralizing capacity (by removing minerals that react with acid) of a deposit's host rocks include acid-sulfate (also called advanced argillic), argillic, phyllic (quartz-sericite pyrite), coarse-grained potassic, skarn, and jasperoid. Alteration types that increase the acid neutralizing capacity of host rocks include propylitic, carbonate, and fine-grained potassic.

TABLE 3.7—The environmental characteristics of various wallrock alteration types common to hydrothermal mineral deposits. See discussion in Guilbert and Park (1986) for discussion of alteration origins.

Alteration type	Alteration products	Chemical effects	Physical effects
Acid-sulfate (advanced argillic)	Vuggy silica (+pyrite), quartz-alunite, kaolinite, ± pyrophyllite, dickite	Greatly decreases acid-buffering capacity of host rocks, and increases acid-generating capacity	Vuggy silica zones highly permeable. Surrounding clay alteration zones impermeable
Argillic	Kaolinite, illite, montmorillonite, ± pyrite, ± chlorite	Decreases acid-buffering capacity	Substantially decreases rock and fracture permeability
Phyllic	Quartz, sericite, pyrite	Increases acid-generating capacity	Slightly decreases rock and fracture permeability
Potassic	Potassium feldspar, biotite, anhydrite	Coarse grain size of feldspars decreases rock reactivity	Shifts permeability to fracture permeability
Propylitic	Epidote, chlorite, calcite, albite, ± pyrite	Increases acid-buffering capacity of rock	Chlorite-rich alteration somewhat decreases fracture permeability
Silica	Silica, quartz addition to rock and replacement of rock minerals	Decreases acid-buffering capacity of rock	Decreases rock permeability, porosity. Increases susceptibility of rocks to fracturing
Jasperoid	Silica, quartz replacement of carbonate sedimentary rocks	Greatly decreases acid-buffering capacity	Can increase porosity, permeability of rock; also increases susceptibility of rocks to fracturing
Greisen	Quartz, muscovite, topaz, fluorite, cassiterite, magnetite	Some decrease in acid-buffering capacity, reactivity	Moderate rock permeability, fracture permeability
Skarn	Carbonate rocks alter to calc-silicates, magnetite	Decrease acid-buffering capacity; increase acid-generating capacity	May decrease rock permeability
Dolomitization	Alteration of limestones to dolomites	May decrease acid-buffering capacity	May decrease or increase rock porosity, permeability
Carbonatization	Alteration of rock minerals to carbonates	Substantially increases acid-buffering capacity	Negligible effect
Sulfidation	Alteration of Fe minerals to Fe sulfides	Increases acid-generating capacity	Negligible effect
Decalcification (decarbonatization)	Removal of carbonate from rocks, some replacement by silica	Decreases acid-buffering capacity	Substantially increases porosity, permeability

Acid-sulfate alteration is common in the wallrocks around high sulfidation or quartz alunite-epithermal deposits, and is formed by reactions of acidic magmatic gas condensates with wallrocks. Vuggy silica, in which all of the major host rock constituents are removed except silica, and in which pyrite is introduced into the rock, is the most intense alteration adjacent to fractures; the vugs form from the complete dissolution of feldspar phenocrysts. Progressive neutralization of the acid leads to quartz-alunite-pyrite and quartz-kaolinite-pyrite (± pyrophyllite, dickite) away from the central silica zone. Intense acid leaching of the rocks prior to mineralization essentially removes any capacity the rocks may have had to react with and consume acid generated by sulfide oxidation; hence this alteration type is typically highly acid-generating.

Argillic alteration results in the conversion of rock-forming minerals such as feldspars to various mixtures of clay minerals such as illite, kaolinite, and montmorillonite. Pyrite and other sulfides are also commonly introduced into the rock. As the clay minerals are relatively acid-stable, they do not have any substantial acid-neutralizing capacity. The presence of sulfides typically transforms argillically altered rocks into acid-generating mineral assemblages.

Coarse-grained potassic alteration formed by saline magmatic-hydrothermal fluids in the high-temperature (600–700°C) cores of porphyry copper and other magmatic-hydrothermal deposit types is characterized by the replacement of rock minerals by coarse-grained (up to several centimeters) potassium feldspar, biotite, anhydrite, and sulfides such as pyrite and chalcopyrite. Due to the coarse grain size of the biotite and feldspars, the net result of this alteration is to increase the acid-generating potential of the rock and decrease the acid-neutralizing capacity of the rock. In contrast, potassic alteration formed in epithermal and Au-Te deposits from dilute, near-neutral hydrothermal fluids at temperatures of 250–350°C is characterized by replacement of rock minerals by very fine-grained (<1–2 mm) potassium feldspar. The fine grain size of the feldspars may allow them to react more rapidly with acid generated by sulfide oxidation, and so may increase the acid-neutralizing capacity of the host rocks.

Phyllic alteration is characterized by the replacement of rock minerals by quartz, pyrite, and sericite (a fine-grained mica). Due to the substantial increase in pyrite content and the relatively non-reactive quartz and sericite, phyllic alteration typically has high acid-generating potential. A variation on phyllic alteration that occurs in magmatic-hydrothermal systems enriched in fluorine and tin is greisen alteration, in which tourmaline, fluorite, topaz, cassiterite, and wolframite are also added to the rock in addition to quartz, sericite, and pyrite; greisen alteration is potentially acid generating, depending upon the pyrite content.

Silica alteration, or silicification, is the replacement of rock materials by silica. Because silica minerals are typically nonreactive and do not consume acid, silica alteration generally decreases the acid-neutralizing capacity of the host rocks.

Several of the alteration assemblages mentioned thus far involve sulfidation, the introduction of H_2S into the rock and the reaction of the H_2S with Fe-bearing minerals (such as hematite, magnetite, and Fe-silicates) in the rock. Sulfidation can result in a substantial increase in the acid-generating capacity of the rock.

Propylitic alteration is marked by the conversion of rock

minerals to a mixture of epidote, chlorite, sodium feldspar, carbonates, and pyrite. Due to the presence of carbonates, this alteration type can be an effective acid consumer. The acid-generating potential of the pyrite is generally insufficient to overcome the acid-neutralizing capacity of the carbonates.

Carbonate alteration, or carbonatization, occurs in relatively few mineral deposit types (such as low-sulfide Au-quartz vein deposits and carbonatite deposits), and involves the alteration of host rock silicate minerals to carbonates such as calcite, dolomite, ankerite, and magnesite. The acid-neutralizing capacity of this alteration type is substantial.

Hydrothermal mineral deposits hosted by carbonate-rich sedimentary rocks can have several types of alteration, including skarn alteration, dolomitization, jasperoid alteration, and decalcification/decarbonatization. Skarn alteration is marked by the conversion of calcite and dolomite in the sedimentary rocks to calc-silicate and Fe-rich silicate minerals such as diopside, wollastonite, tremolite, actinolite, and garnets (Guilbert and Park, 1986); sulfides such as chalcopyrite and pyrite, and oxides such as magnetite, also are common. Acidic waters draining skarn deposits indicate that the generally coarse grain size and relatively slow reaction kinetics of the calc-silicate minerals makes them ineffective acid consumers. Jasperoid forms by the extensive replacement of carbonate sedimentary rocks by silica. If few or none of the original carbonate minerals remain in the rock, jasperoid has a very low acid-neutralizing capacity. Dolomitization is the alteration of calcite and aragonite in limestones to dolomite. It generally results in a slight decrease in acid-neutralizing capacity due to the lower reactivity of dolomite. Carlin-type, sediment-hosted Au deposits commonly exhibit decalcification (or decarbonatization) alteration that involves large-scale dissolution of carbonate minerals by acidic hydrothermal fluids, coupled with the residual concentration of the remnant silica minerals originally present in the carbonate sedimentary rocks.

Physical effects of wallrock alteration

Alteration characteristics that control ground-water flow: Wallrock alteration can either increase or decrease the ability of rocks to transmit ground waters, either through rock pore spaces or through joints and fractures (Table 3.7). Alteration that results in extreme leaching of the host rocks, such as vuggy silica alteration in acid-sulfate-altered rocks and the formation of jasperoid in carbonate sedimentary rocks, can lead to increased hydraulic conductivities. Dolomitization may result in increased hydraulic conductivities, due to the volume decrease resulting from the replacement of calcite with denser dolomite; however, in many cases additional dolomite also precipitates in the rock pore spaces, and so results in a net permeability decrease. Decalcification/decarbonatization can result in a substantial increase in hydraulic conductivity of carbonate host rocks, due to the large scale dissolution of the host carbonates during the alteration process.

In contrast, alteration that forms large amounts of clay minerals (such as kaolinite and dickite in acid-sulfate and argillic alteration assemblages) can substantially decrease hydraulic conductivity, as well as decrease the rock's ability to develop hydrologically conductive fractures.

Alteration characteristics that control physical erosion and mass wasting: Various wallrock alteration types can impart varying degrees of resistance to erosion and mass wasting within mineral deposits. Alteration that adds silica to rocks typically increases a host rock's ability to withstand erosion. For example, vuggy silica alteration zones form prominent ledges and topographic highs within quartz-alunite epithermal deposits, and also serve as strong skeletal supports that minimize potential landslides and debris flows within the deposits. In contrast, wallrock alteration that substantially increases the clay-mineral component of wallrocks can greatly weaken the rock's resistance to rapid physical erosion and mass wasting. The argillically altered rocks in the Alamosa River stock shown on Figure 3.5 are an excellent example of this weakening; rapid physical erosion rates compared to chemical weathering rates continually expose fresh pyrite at the ground surface. Drainages in the stock that have oversteepened topography (usually where silicified ledges overlie argillically altered rock) are prone to debris flows during periods of rapid runoff, such as occur during summer thundershowers. As another example, rocks at the upper levels of the Mount Rainier volcano have been extensively altered by magmatic gas condensates to argillic and advanced argillic alteration assemblages very similar to those found at Summitville, Colorado, and other quartz-alunite-epithermal or high-sulfidation deposit types (Zimbelman, 1996; Crowley and Zimbelman, 1997). The structurally weakened, altered rocks at Mount Rainier have been the source areas for large debris flows and mudflows from the mountain, which, due to their high clay contents are very cohesive and can travel great distances downstream (Crandell, 1971; Scott et al., 1995). Detailed links between alteration type and the potential for landslide and debris flow generation remain to be examined.

Major- and trace-element content of deposits and their host rocks

The chemical composition of the geoavailable major and trace elements in mineral deposits is typically manifested in their environmental signatures, with some variability superimposed by geochemical processes such as oxidation, secondary mineral precipitation, and sorption (Nordstrom and Alpers, 1999; Smith, 1999). For example, deposits that are enriched in As (such as those that contain arsenopyrite or enargite) typically produce drainage waters, smelter emissions, etc., that are enriched in As relative to waters or smelter emissions from deposits that are not enriched in As.

Table 3.8 lists some common mineralogic hosts for major and trace elements found in environmental signatures of mineral deposits such as mine-drainage waters and smelter emissions.

The physical characteristics of mineral deposits

Mineral deposits can occur in a wide variety of physical forms, including veins, stockworks, breccias, disseminations, and massive lenses or pods (Fig. 3.7). These different forms influence the extent to which weathering agents can access deposits, either in place within the ground or on mine dumps.

Veins typically form when pre-existing fractures are filled by ore and gangue minerals (Figs. 3.7a, b); crustification sequences often develop in which the vein minerals are added in successive layers (Figs. 3.1c, d, e; Fig. 3.7a). Depending upon the extent to which the fractures are filled with minerals (Fig. 3.7a), veins can either focus or inhibit ground-water flow. Veins with considerable

open spaces can preferentially transmit ground water, and thus enhance the interactions of the waters with vein materials and minimize interaction with wallrock (Fig. 3.7a). In contrast, veins that are nearly completely filled typically transmit ground water only along later fractures within the vein. Unless well-crustified vein fill is permeable (Fig. 3.2a), fractured, or broken and exposed by mining, ground water typically interacts with the outermost coatings of the vein minerals; thus, acid-generating sulfides or acid-consuming carbonates that are coated by later, less reactive minerals may not have as strong an influence on ground-water chemistry.

Stockwork ore bodies (Fig. 3.7c) are composed of many intersecting small veins or veinlets. If the veinlets are at all permeable, they can distribute ground water to a large volume of mineralized rock.

TABLE 3.8—Common primary mineralogic sources for some environmentally important major and trace elements in mineral deposits. For each element, the minerals are listed in general decreasing order of reactivity in the surficial environment. For further details, see discussions in Smith and Huyck (1999) and appendix in Rose et al. (1979).

Element	Common mineralogic sources
Ca	Gypsum, anhydrite, calcite, fluorite, dolomite, calcic plagioclase, calc-silicates
Mg	Dolomite, pyroxenes, amphiboles, chlorite
Na	Sodic feldspars, micas
K	Sylvite, potassium feldspars, micas
Al	Aluminosilicate minerals
Si	Aluminosilicate, silica minerals
Fe	Pyrite, siderite and other carbonates, hematite, mafic silicates (pyroxene, amphibole, biotite), magnetite
Mn	Rhodochrosite, carbonates, aluminosilicate minerals, Mn-silicates
S	Sulfides, sulfosalts, sulfates
F	Fluorite, topaz, silicates
Ba	Feldspars, other aluminosilicates, barite
Zn	Sphalerite, other sulfides and sulfosalts, mafic silicates, Zn-silicates
Cd	Sphalerite, greenockite, other sulfides and sulfosalts
Cu	Cu-sulfides, mafic minerals
Pb	Galena, other sulfides and sulfosalts, feldspars
As	Realgar, orpiment, enargite, arsenopyrite, other sulfides and sulfosalts
Sb	Stibnite, other sulfides and sulfosalts
Ni	Ni-sulfides, other sulfides, olivine and other mafic silicates
Co	Co-sulfides, other sulfides, aluminosilicates
Cr	Mafic silicates, chromite (relatively nonreactive)
Hg	Native mercury, cinnabar, other sulfides and sulfosalts
Mo	Sulfides, molybdenite (relatively non-reactive)
Se	Sulfides, selenides, selenates
U	Uraninite, coffinite, carnotite, apatite, feldspars, zircon, allanite
Rare earth elements	Bastnaesite, silicates, monazite

Disseminated ore is characterized by ore minerals dispersed throughout the host rocks; the ore minerals are therefore available for interactions with ground water over relatively large host-rock volumes. In some deposits such as porphyry-Cu deposits, disseminated sulfides are controlled by microscopic stockwork fractures in the rock that may or may not transmit ground waters. In some sediment-hosted mineral deposits, disseminated sulfides precipitate at the same time as their host sediments are deposited mechanically; if the rate of sulfide precipitation exceeds the rate of host sediment deposition, massive sulfide ore bodies result.

Breccia ore bodies typically form by the filling of open spaces in rocks brecciated by faulting, hydrothermal, or magmatic-hydrothermal processes. Like veins, breccias can either focus or inhibit ground-water flow, depending upon the extent to which their interstices are filled with material (Fig. 3.7e).

Massive ore bodies, as their name implies, are characterized by lenses or pods of massive, intergrown sulfides with few or no intergrown silicates or carbonates (Fig. 3.7f). Ground-water flow is typically along fractures or grain boundaries within the sulfides (Fig. 3.4). Water flowing within massive Fe-sulfide lenses can become quite acidic if flow paths do not intersect wallrocks surrounding the lenses; an example is the extremely acid water draining massive sulfide ore bodies at Iron Mountain, California (Alpers and Nordstrom, 1991; Nordstrom and Alpers, 1999).

Presence and openness of faults, joints

If they are open and interconnected, faults and joints that cross-cut ore bodies can serve as significant conduits for ground waters and their contained weathering agents. In general, flow along faults is generally much more effective than flow across them. The hydraulic conductivity of an open fracture is proportional to the cube of its dilation (or openness).

The openness of fractures is a function of the ability of their host rock to develop fractures, their ambient stress regime (geologic stresses lead to faulting and folding), and the presence or absence of minerals filling the fractures. For example, rocks that are composed of minerals that break rather than deform ductily (such as feldspars and quartz) tend to form more well-developed, open fractures than rocks composed of minerals that deform ductily (such as clays). Different structures in the same rock unit in the same mine can have different degrees of openness as a function of their orientation relative to ambient geologic stress directions; fractures that occur at an angle to compressive stresses tend to be closed, whereas those that are nearly co-planar with compressive stress directions tend to be more open structurally.

If faults and joints are not interconnected or are not open to the ground surface, their influence on ground-water flow is diminished. The interconnectedness of faults can in part be determined through careful structure mapping, but is determined with the greatest certainty through hydrologic testing techniques such as those discussed in Domenico and Schwartz (1990).

A detailed understanding of the structural characteristics of a mineral deposit is crucial to understand the potential role that fractures and joints will play in influencing ground-water flow through the deposit. Such an understanding can only be established through careful geologic mapping of structures, field or mine observations of the orientation and openness of structures, structural analysis, and hydrologic testing.

GEOLOGIC VARIABILITY IN MINERAL DEPOSITS

The previous section outlined the major geologic characteristics of mineral deposits that influence their environmental signatures. It is important to recognize that these characteristics

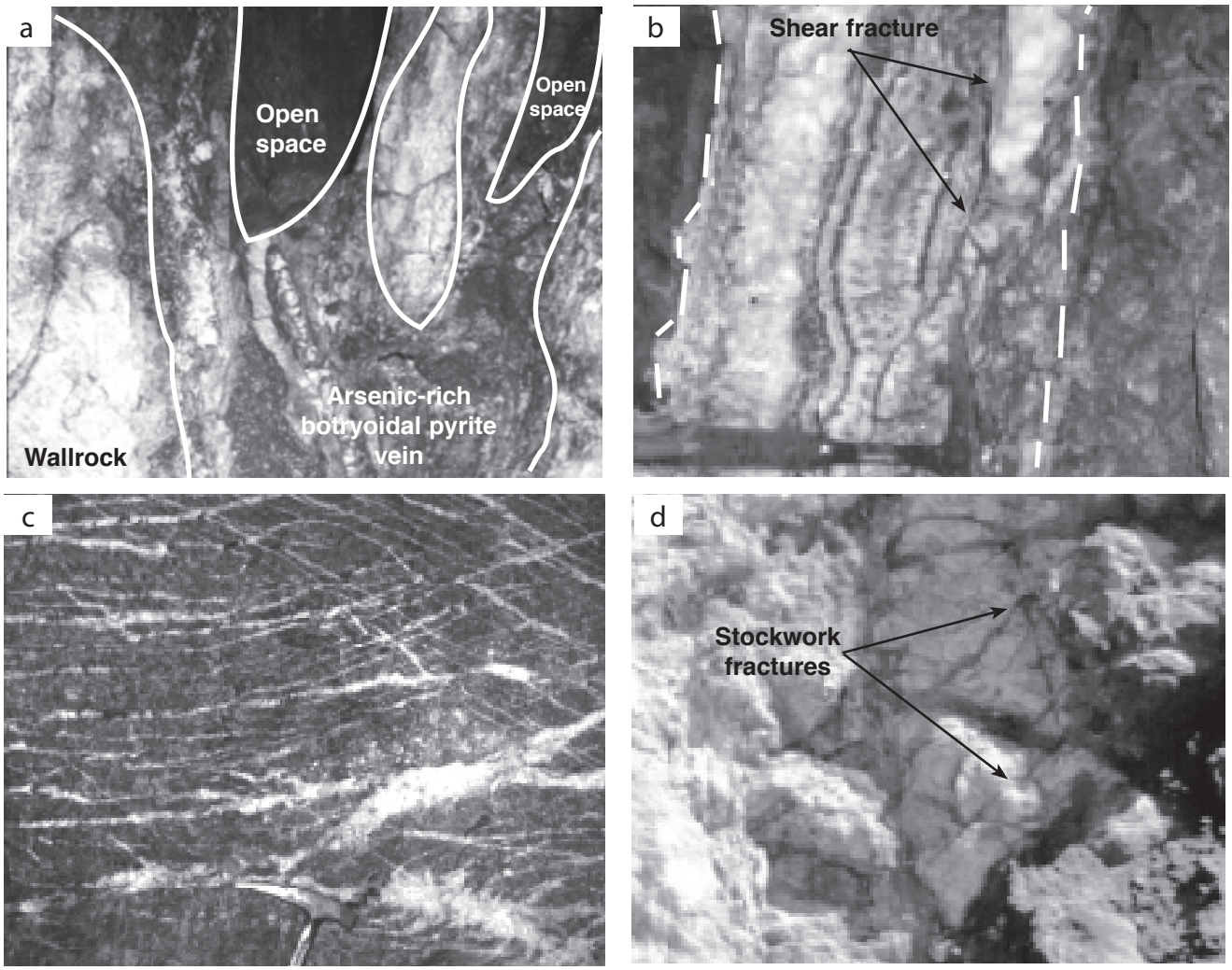


FIGURE 3.7—Examples of different ore types. (a) Vein of crustified, arsenic-rich botryoidal pyrite from Creede, Colorado. The pyrite was deposited in successive layers (a crustification sequence) growing out from the vein walls, completely filling the vein in the lower part of the photograph but only partially filling the vein in the upper part of the photograph. White lines mark approximate edges of vein and open space in the center of the vein. (b) Crustified barite-sulfide vein, Bulldog Mountain mine, Creede district, Colorado. Barite (light) and intergrown sphalerite and galena (dark) generations completely filled the vein, and were later partially truncated by shear fractures. (c) Gold-quartz veinlets in carbonatized wallrock from the low-sulfide gold-quartz vein deposits in the Kensington mine, Juneau, Alaska. The two intersecting sets of parallel veinlets reflect fracture formation along conjugate shear couples. Due to the carbonate alteration of the wallrocks, these deposits tend to have relatively low acid-generating potential, even though they contain several volume % pyrite and arsenopyrite in both the veins and wallrock (Goldfarb et al., 1997). Photo by C. Taylor, USGS. (d) Pyrite-chalcopyrite-quartz stockwork veinlets in altered submarine volcanic host rocks, Rio Tinto, Spain. The stockwork veins formed in the feeder zone for hydrothermal fluids that discharged onto the sea floor and produced massive sulfide deposits overlying the volcanic rocks. Photo by C. Taylor, USGS.

can vary spatially and substantially within most mineral deposits. Thus, one portion of an ore body, mine, or mining district may have significantly different environmental geology considerations than those present in other portions of the same ore body, mine or district.

Primary mineral zoning

The primary minerals making up a mineral deposit commonly show systematic spatial variations, or zoning patterns, that ultimately result from the processes by which the deposit formed. Substantial mineralogic variations can occur on a spectrum of scales ranging from several centimeters within an ore shoot, to tens to hundreds of meters within an ore body, to several kilometers across a mining district (Figs. 3.8, 3.9). From an environmental standpoint, such geologic variability can lead to substantial variations in environmental signatures within a deposit, mining district, or mine.

Creede and Central City, Colorado

Epithermal vein ores in the Bulldog Mountain vein system,

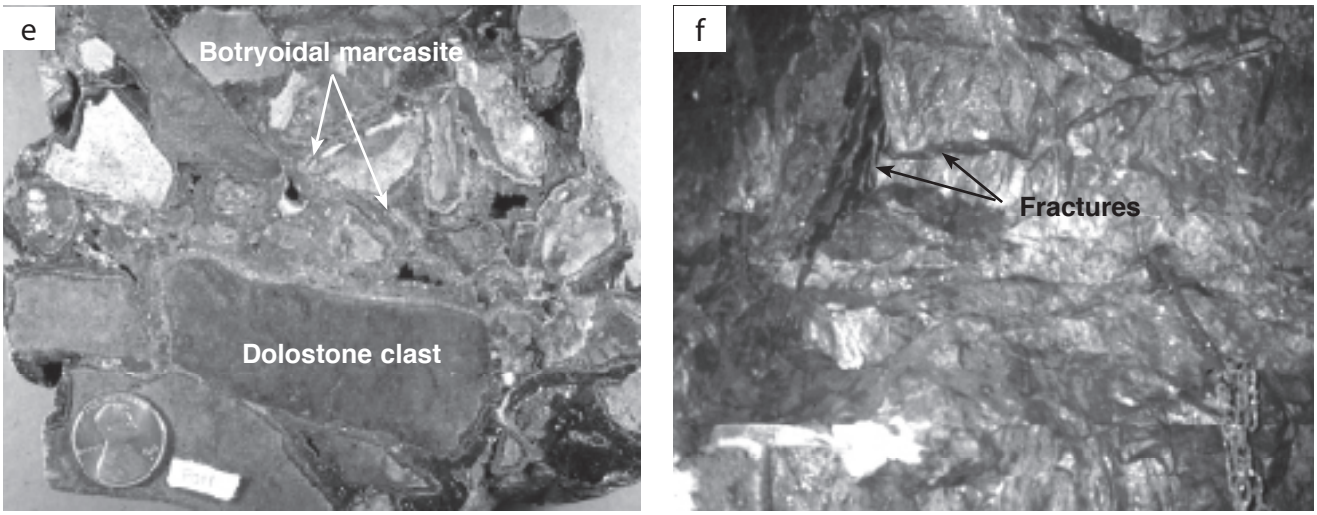


FIGURE 3.7 (Continued)—(e) Sample of a mineralized, partially replaced breccia from Mississippi-Valley-Type (MVT) deposits in the Pomerzany mine, Silesian-Cracow district, Poland. The breccia formed in part by collapse of pre-mineralization karst caverns, and in part by collapse resulting from hydrothermal dolomitization that replaced limestone with dolostone. The dolostone breccia clasts were then partially replaced by fine-grained sphalerite, which was then coated by trace-element-rich botryoidal marcasite. The breccia now has moderate porosity due to infilling of the pore spaces by mineralization. Photograph by D. Leach, reproduced from Leach et al. (1996). (f) Massive sulfide ore body, Windy Craggy deposit, British Columbia, Canada. The entire field of view is composed of massive pyrite-pyrrhotite-chalcopyrite ore. Photo by C. Taylor, USGS.

Creede district, Colorado show complex mineralogic variations (Fig. 3.8) along the major veins in the system. These variations resulted from the geochemical evolution of the hydrothermal fluids that deposited the vein minerals, hydrothermal leaching of some minerals once they were deposited, and progressive closing (and in some cases opening) of the fractures by structural activity during mineral deposition (Plumlee and Whitehouse-Veaux, 1994; Plumlee, 1989).

Polymetallic veins are strongly zoned across Colorado's Central City mining district; pyrite-rich mineral assemblages in the core of the district grade laterally outward into progressively more sphalerite-, galena-, and carbonate-rich ores (Fig. 3.9); this zonation resulted from an overall decrease in formation temperature of the veins toward the lateral fringes of the mineralizing system. In both the Bulldog Mountain and Central City examples, the different mineral assemblages produce quite different environmental signatures, in waters draining both the mine workings and mine waste dumps.

Wallrock alteration zoning

Wallrock alteration assemblages can also vary substantially over the same spectrum of scales at which mineral zoning occurs.

Summitville, Colorado

The high-sulfidation, quartz-alunite epithermal Au-Cu-Ag deposit at Summitville, Colorado, is an excellent example of zoned alteration assemblages (Figs. 3.10–3.13). Summaries of Summitville's environmental geology are presented by Plumlee et al. (1995a, b) and Gray et al. (1994). The deposit formed in the core of a volcanic dome, as part of the waning stages of the dome-forming cycle (Stoffregen, 1987; Rye et al., 1990; Gray and Coolbaugh, 1994). Prior to ore mineralization, magmatic gases released from a crystallizing magma at depth flowed upward along fractures in the dome rocks and condensed at shallow levels in the dome; the highly acidic condensates produced intense, pre-ore acid-sulfate alteration near the fractures (Figs. 3.10, 3.11). On a local scale (Fig. 3.12), progressive neutralization of acid in the condensates, coupled with mixing with ground waters, resulted in laterally zoned alteration assemblages that grade from vuggy silica nearest the fractures to quartz-alunite-pyrite, quartz-kaolinite, illite-montmorillonite, and propylitic farthest from the fractures (Gray et al., 1994, and references therein). On a district-scale (Fig. 3.11), the most intense alteration occurs in the core of the deposit; a central acid-sulfate alteration zone is surrounded by intermediate argillic and distal propylitic alteration zones. Subsequently, hydrothermal fluids deposited pyrite, marcasite, enargite, covellite, native sulfur, barite, and native gold in the central part of the deposit, grading laterally outward to sphalerite and galena. The permeable vuggy silica zones focused hydrothermal fluid flow, causing the bulk of the sulfide deposition to occur in the vuggy silica and adjacent alteration zones, However, some sulfides were also deposited in the argillic zones. Trace-metal zoning is directly related to the overall mineralogic zoning; Cu and As are dominant in the central part of the deposit, and Pb and Zn are more abundant on the lateral fringes of the deposit. Increasing Hg concentrations with increasing elevation resulted from the concentration of Hg in the near-surface levels of the hydrothermal system that formed the deposit; the Hg occurs primarily as a trace metal in sulfides such as pyrite.

Wallrock alteration at Summitville also strongly influenced the deposit's hydraulic conductivity and the way in which the deposit weathered prior to mining. The deepest pre-mining oxidation occurred along permeable vuggy silica zones, to depths

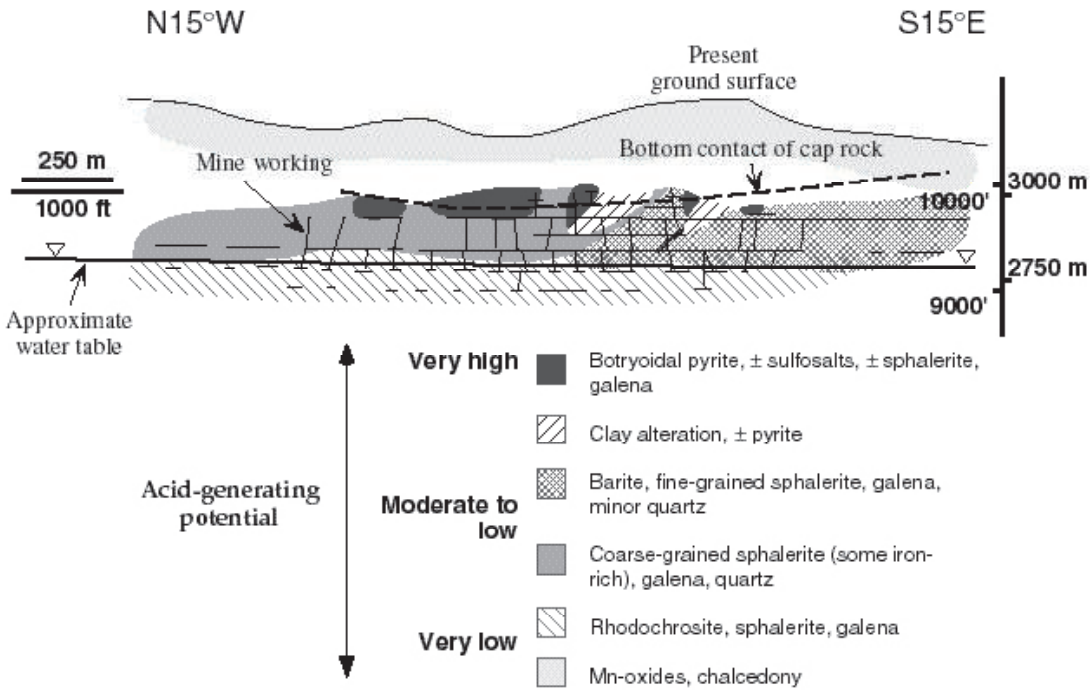


FIGURE 3.8—Longitudinal section of the A Vein, Bulldog Mountain Mine, Creede, Colorado, showing the distribution and environmental characteristics of dominant mineral assemblages along the vein. The pre-mining water table occurred primarily in acid-neutralizing rhodochrosite, and so the mine waters had near-neutral pH and relatively low levels of dissolved metals (R. Boppe, oral. commun., 1982). Acid-generating, arsenic-rich botryoidal pyrite (Figs. 3.3 and 3.7a) persists unoxidized above the water table due to the presence of an illite- and montmorillonite-rich hydrothermal alteration cap and a poorly welded ash-flow tuff above the main ore zone; these features combine to produce low hydraulic conductivity along the vein between the ground surface and the main ore zone. Figure modified from Plumlee and Whitehouse-Veaux (1994) and Plumlee and Nash (1995).

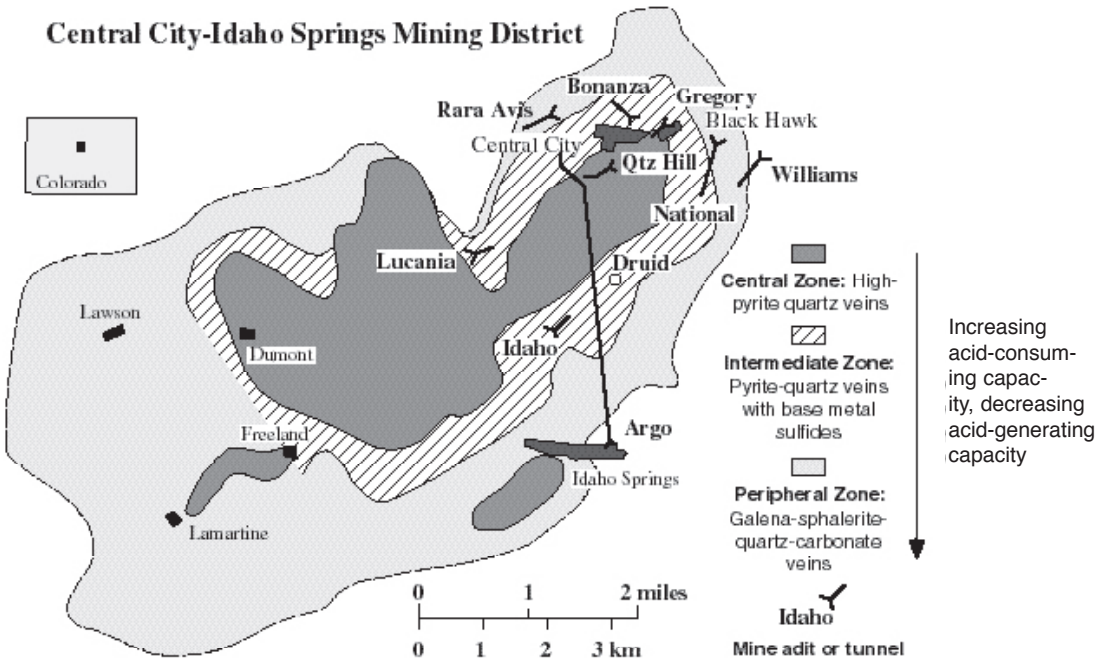


FIGURE 3.9—Map showing primary mineral zoning of polymetallic veins across the Central City-Idaho Springs mining districts, Colorado. Figure modified from Sims et al. (1963). A porphyry Mo deposit is inferred to be present at depth beneath the district.

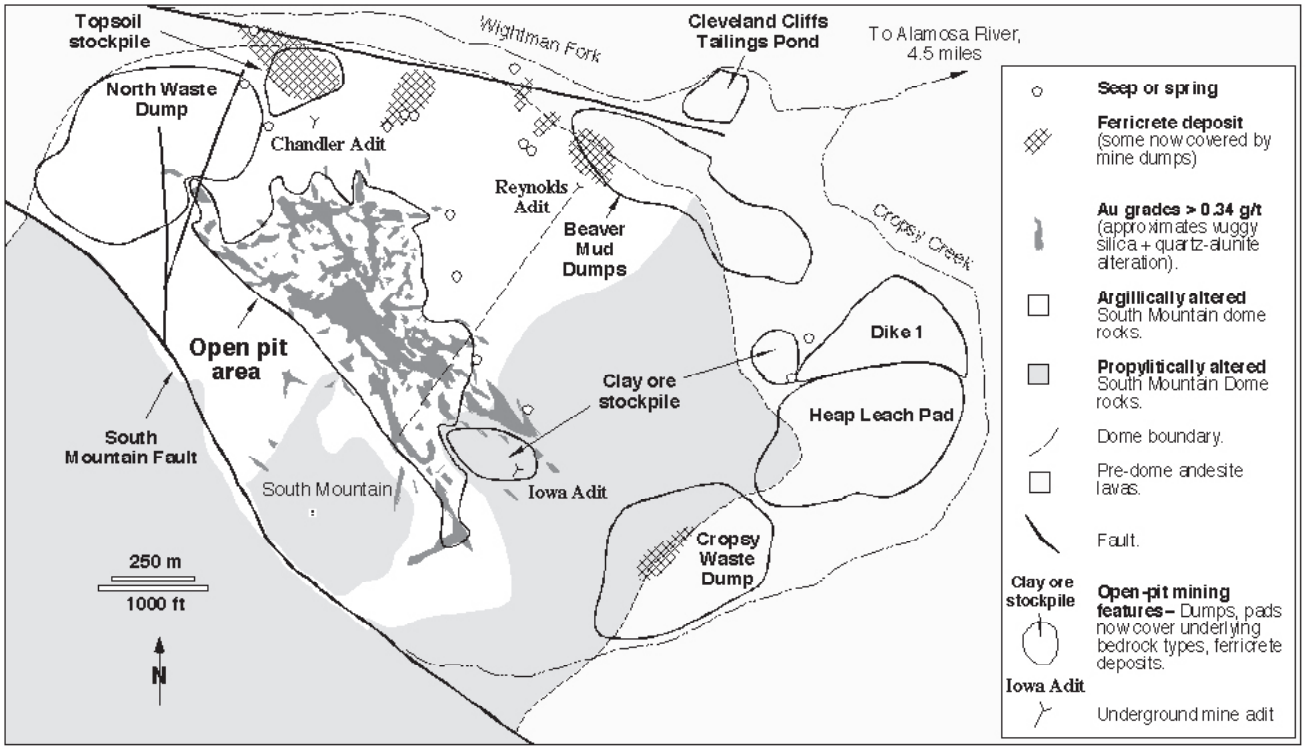


FIGURE 3.10—Geologic map of the Summitville quartz-alunite epithermal, Au-Cu-Ag deposit and mine, SW Colorado, showing the location of major mine features relative to important geologic features. The highest-grade Au ores occurred along vuggy silica alteration zones following original radial fractures in the host volcanic dome rocks. Underground mining in the late 1800s followed the vuggy silica zones. Recent open-pit mining from 1984-1992 used open-pit methods and heap leach processing to extract lower-grade gold ores from the rocks around the highest-grade vuggy silica. The mining company operating the open-pit mine declared bankruptcy in late 1992 as remediation of substantial environmental problems (such as extreme acid-mine drainage) was beginning, and the U.S. Environmental Protection Agency (EPA) took over the site under Superfund Emergency Response Authority. The site was added to the Superfund National Priorities list in 1994.

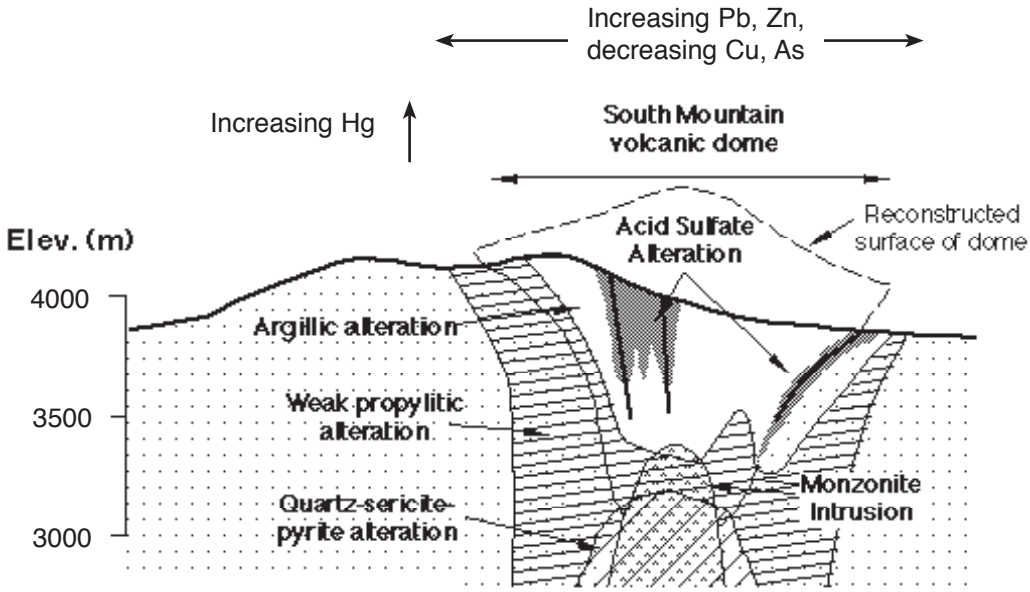


FIGURE 3.11—East-west geologic cross section of the Summitville deposit, SW Colorado, showing deposit-wide alteration and metal zoning. The quartz-sericite-pyrite alteration is associated with a low-grade porphyry-Cu deposit. Figure from Plumlee et al. (1995a), and originally modified from Rye et al. (1990).

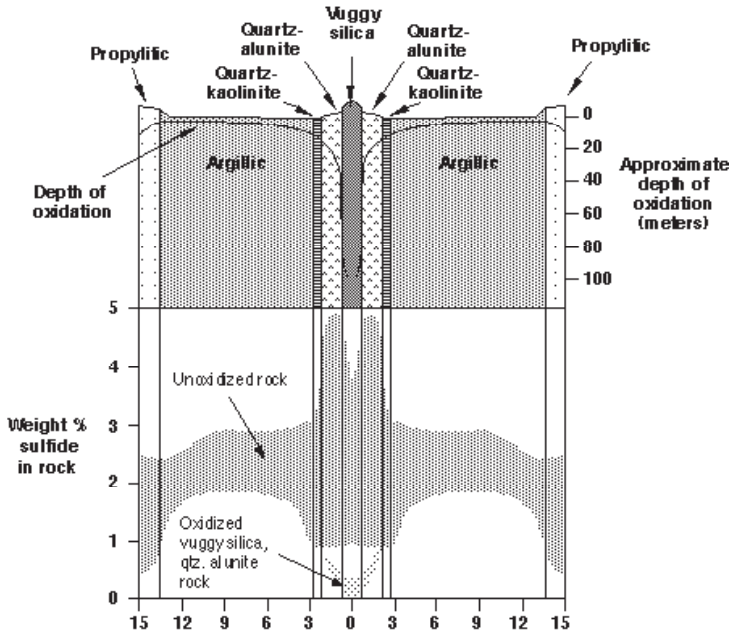


FIGURE 3.12—Schematic diagram showing distribution of alteration zones, sulfide content, and depth of oxidation away from fractures in the Summitville deposit, Colorado. Although the sulfide content of the alteration zones is not extremely high (<5 wt.%), the extreme lack of acid-buffering capacity in the acid-sulfate altered rocks gives the deposit very high acid-generating potential. Figure from Plumlee et al. (1995a), modified originally from a figure in Gray et al. (1994).

as great as 100 m (Figs. 3.12, 3.13; Gray et al., 1994); oxidation concentrated gold in the vuggy silica zones and therefore made the vuggy silica zones the main targets for exploration and mining (Fig. 3.10). In contrast, the clay-rich argillic alteration was much less permeable to descending ground waters, and so oxidation only occurred to depths as shallow as several meters (Figs. 3.12, 3.13). The vuggy silica zones also physically stabilized the deposit and prevented extensive erosion and exposure of sulfides in the argillic alteration zones, such as occurred several kilometers to the south in the Alamosa River stock (Figs. 3.5d-g). The net product of the hydrothermal alteration-mineralization and pre-mining weathering at Summitville was a deposit with very high acid-generating capacity and very low acid-neutralizing capacity in the central (i.e., most mined) part of the deposit. Increased acid-neutralizing capacity of propylitically altered rocks toward the lateral fringes of the deposit is of relatively little environmental benefit due to the lack of mine workings in and ground-water flow through these rocks.

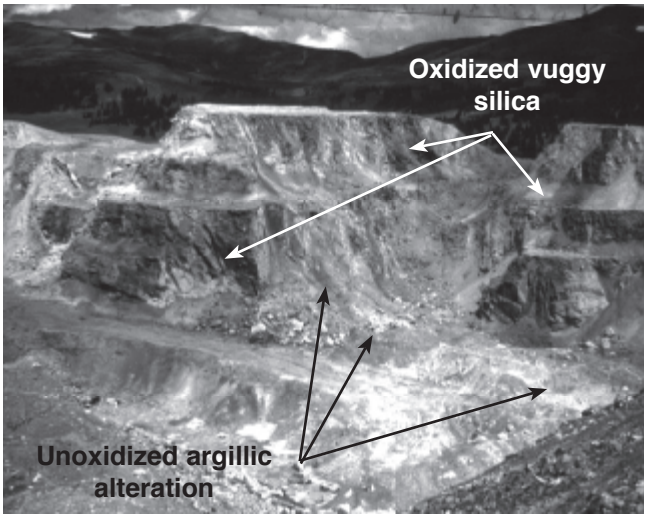


FIGURE 3.13—Photo of the Summitville open pit, taken in August 1993. Dark gray zones are oxidized vuggy silica zones, and lighter gray zones are sulfide-bearing argillic alteration zones.

As at Summitville, district-scale alteration zoning is common in a variety of hydrothermal ore deposit types, including other acid-sulfate epithermal deposits (such as Round Mountain and Goldfield, Nevada), Cordilleran lode deposits (such as Julcani, Peru, and Butte, Montana), porphyry Cu and Cu-Mo, Climax-type porphyry-Mo (such as Climax and Henderson, Colorado), and zoned polymetallic vein systems (such as Central City, Colorado). In nearly all of these deposit types, acid-neutralizing propylitically-altered rocks occur in the distal parts of the deposits. Acid-sulfate epithermal and Cordilleran lode deposits (both are also termed high-sulfidation deposits) contain extensive acid-sulfate or advanced argillic alteration with extreme acid-generating potential in their central portions, and acid-neutralizing propylitic alteration on their distal fringes. Porphyry deposits typically have deep potassic alteration flanked by phyllic alteration and overlain by argillic alteration (Fig. 3.5d) in their central portions (all typically have high acid-generating potential), and distal propylitic alteration. Zoned polymetallic vein deposits also have phyllic and argillic alteration in their central portions, flanked by distal propylitic alteration; such zoning also coincides with the zoning in primary vein mineralogies shown on Figure 3.9.

Jerritt Canyon, Nevada

Carlin-type sediment-hosted Au deposits such as those at Jerritt Canyon, Nevada, also show both local and district-scale alteration and primary mineral zoning patterns. The deposits formed from moderately acidic, H_2S- and As-rich hydrothermal fluids that mixed with cooler, dilute, oxidized ground waters and reacted with Fe-bearing carbonate rocks (Hofstra et al., 1991). The cores of the deposits, where the hydrothermal fluids flowed into the carbonate rocks from feeder fractures (Fig. 3.14), are marked by extensive to complete decalcification of the host rocks and residual enrichment of silica. The decalcification occurred contemporaneously with deposition of hydrothermal quartz, formation of realgar-orpiment veins, and sulfidation of Fe minerals in the host rocks to produce disseminated arsenian pyrite, the main host for the gold (Fig. 3.14a). Grading outward from the feeder zones, the extent of decarbonatization, realgar-orpiment veining, disseminated pyrite, and gold grades progressively decrease; this is accompanied by a progressive increase in the amount of carbonate remaining in the wallrock, as well as an increase in the amounts of pre-ore and ore-stage calcite veins. In the intermediate zones of the deposits, local variations in the extent of decarbonatization can be abrupt, with the transition between extensively decarbonated, quartz-rich rock and carbonate-rich rock occurring over a space of several centimeters (Fig. 3.14b).

From an environmental standpoint, the highest grade ores in Jerritt Canyon and other Carlin-type deposits also have a relatively high potential to generate locally acidic drainage waters, due to the removal of acid-neutralizing carbonate minerals and deposition of reactive, acid-generating arsenian pyrite. However, the abundant carbonate minerals in host rocks surrounding the deposits increase the opportunities for any acid drainage waters that might form to be consumed through reaction with the carbonate minerals or mixing with alkaline waters draining the carbonate rocks. The abundance of As in the deposits, coupled with the mobility of As in higher-pH waters (Smith and Huyck, 1999; Smith, 1999), indicates that As should be the dominant element of environmental concern in this deposit type. However, the formation of Fe particulates in drainage waters should also lead to relatively effective sorption of As in all but the most acidic or alkaline drainage waters (Smith, 1999).

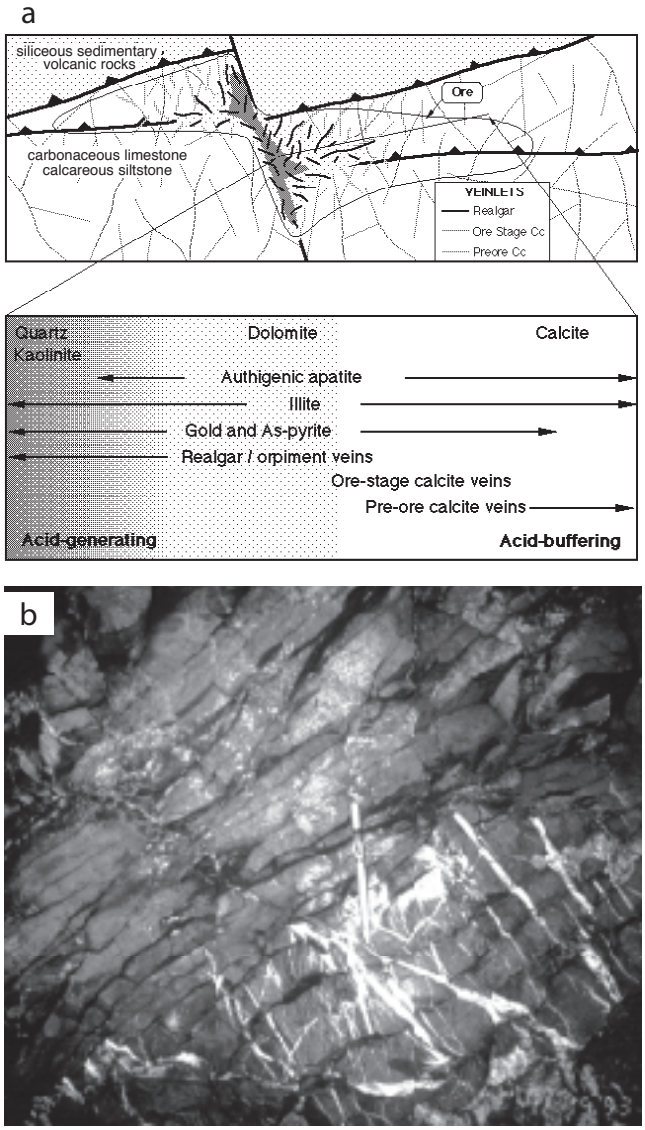


FIGURE 3.14—Spatial variations in alteration and mineralization in a Carlin-type, sediment-hosted Au deposit, Jerritt Canyon, Nevada. (a) Schematic cross section (upper) and primary and alteration mineral zoning patterns (lower) of Carlin-type, sediment-hosted Au deposits, Jerritt Canyon, Nevada. Figure modified from Hofstra et al. (1991). (b) Photo of mine face showing sharp break between highly decarbonated ore with abundant ore-stage realgar-orpiment veins (upper) and unaltered rock containing abundant host-rock carbonate and pre-ore calcite veinlets (white). The decalcification occurred preferentially along bedding planes (dark lines cutting diagonally from lower left to upper right). Photo by A. Hofstra, USGS.

Variations in geology that affect hydraulic conductivity and ground-water flow

In addition to variations in hydraulic conductivity imparted by its alteration, Summitville is also an excellent example of the variations in hydraulic conductivity imparted by fractures and rock contacts. The location of ferricrete deposits and acid seeps in and around the deposit (Fig. 3.10) show that the primary geologic features which focus ground-water flow are the vuggy silica alteration zones, the South Mountain fault bounding the deposit on its western side, fractures within the dome (which follow dominant N30°W, N60°W, N5°W, and N30°E trends; Gray et al., 1994; Gray and Coolbaugh, 1994), and the contact between the dome rocks and the surrounding andesite volcanic rocks. The andesites surrounding the Summitville dome have very low fracture and joint permeability (M. Roeber, oral commun., 1993), and so minimize ground-water flow from the dome into the surrounding rocks. Prior to the development of the Reynolds adit (which was installed in the early 1900s to drain the underground workings, ground-water recharge into the deposit was most likely from the South Mountain fault and the vuggy silica zones, and discharge was primarily along the dome-andesite contact and fractures that intersect the ground surface. The Reynolds adit short-circuited

the natural flow paths, and focused all discharge from most of the deposit. Plugging of the Reynolds adit in 1994 during environmental restoration at the site resulted in the predictable reactivation of the natural discharge seeps (Fig. 3.10), which will continue to serve as long-term, but relatively low-level, sources of acid drainage from the site.

In other deposit types, geologic variations in host rocks, alteration, faults, joints, and other geologic features can combine to create complex controls on porosity, permeability, and therefore hydrology. This again underscores the need for careful, integrated geologic and hydrologic site characterization prior to mining and remediation, in order to better understand the geologic controls on fracture-dominated ground-water flow.

Variations in deposit type within a mining district or mineralized area

In addition to local- to district-scale geologic variations within a given deposit type noted previously, many mineralized areas and mining districts can contain more than one deposit type, each with its own particular range of geologic characteristics. In many cases, these multiple deposit types are genetically-related parts of a larger mineralizing system. More rarely, they may be entirely unrelated in age or processes of formation.

One example of genetically-related, multiple deposit types in a given district is the occurrence of a low-grade porphyry-Cu deposit with stockwork pyrite-chalcopyrite veins and phyllic alteration at depth beneath the Summitville quartz-alunite epithermal deposit (Fig. 3.11). The porphyry deposit formed during the crystallization of the host monzonite intrusion. It is unclear whether the intrusion and the porphyry-Cu mineralization are truly contemporaneous with either the pre-mineralization acid-sulfate alteration or the hydrothermal mineralization in the Summitville quartz-alunite epithermal deposit; however, both clearly formed in the late stages of the Summitville volcanic dome formation (Gray and Coolbaugh, 1994; Rye et al., 1990). Quartz-alunite epithermal deposits and their deeper equivalents, Cordilleran lode deposits (such as Butte, Montana) commonly form in the upper levels and (or) late stages of porphyry-Cu or porphyry-Mo-Cu mineralizing systems; both require crystallization of magmas to produce magmatic-hydrothermal fluids that form the porphyry deposits, and the magmatic gases and magmatic heat source for the hydrothermal system that produce the acid-sulfate alteration and high sulfidation mineralization.

Another example of multiple deposit types occurring within a single district is shown on Figure 3.15, a schematic cross section of porphyry, skarn, breccia, igneous-hosted polymetallic vein, and sediment-hosted polymetallic vein and replacement deposits associated with the crystallization of a magmatic intrusion into a sedimentary rock sequence. Examples of such systems include Leadville and Gilman, Colorado; and New World, Montana. Districts developed on such deposit systems can have a wide range in environmental geology characteristics depending upon the deposit type(s) in which particular mines are developed. For example, the igneous-hosted porphyry deposits (with quartz-pyrite-chalcopyrite stockwork veins and disseminations) and polymetallic vein deposits (pyrite-sphalerite-galena, with occasional calcite) generally have high acid-generating capacity but low acid-neutralizing capacity. The breccia (sulfides cementing igneous or sedimentary rock breccias), skarn (sulfides and calc-silicate minerals replacing carbonate rocks), and sediment-hosted polymetallic vein (pyrite-sphalerite-galena-±calcite) and replacement deposits (massive pyrite-marcasite-sphalerite-galena-±calcite) can display a variety of acid-generating and acid-neutralizing capacities, depending upon factors such as the carbonate content of the sedimentary host rocks, the reactivities of the calc-silicate skarn minerals, the thickness and permeability of the massive sulfide lenses, and the amount of calcite present in the ores. Metal contents can also vary substantially, with Cu typically enriched in the deeper porphyry and skarn deposits, and Pb and Zn enriched in the more shallow polymetallic vein and replacement deposits. Hence, environmental signatures such as natural- or mine-drainage compositions may vary greatly within these districts, depending upon which of the deposit types have been exposed at the surface by pre-mining erosion, and which have been mined.

THE ROLE OF CLIMATE AND MINING/ MINERAL PROCESSING METHOD

Climate and mining/mineral-processing method also influence the environmental signatures produced by weathering mineral deposits and by mining and mineral processing activities. However, the effects of climate and mining/processing methods generally serve to modify the environmental signatures that are ultimately governed by the deposit geology and geochemistry.

Effects of climate

Three main aspects of climate exert important controls on rock weathering and related environmental processes: temperature, humidity, and the amount of precipitation (rain + snow) relative to evapotranspiration (the combined evaporation from soils, rocks, and surface waters, and transpiration from plants).

Temperature and humidity influence potential evapotranspiration (the maximum possible evapotranspiration that could occur in an area), the rate of vegetation growth, and the rates at which weathering occurs.

In wet climates where precipitation exceeds evapotranspiration, abundant water is available to promote rock weathering, vegetation growth, and ground-water recharge. With increasing aridity, evapotranspiration increases and overtakes precipitation, and so less and less water becomes available for weathering, ground-water recharge, and vegetation growth. In most climates, precipitation and potential evapotranspiration vary as a function of season (Domenico and Schwartz, 1990), leading to significant variations in recharge, weathering rates, and vegetation growth over the course of a year. Relative precipitation and evapotranspiration can also vary seasonally on a regional and local basis. For example, the basins of northern Nevada are quite cool in late fall and winter and receive most of their precipitation in the form of snow in the early winter and spring; however, they are quite hot and dry during the summer months (Shevenell, 1996). The mountain ranges, due to their higher elevation and orographic precipitation effects, have higher precipitation and lower evapotranspiration than the adjacent valleys in the wet seasons. In contrast, southern Nevada receives its precipitation in the form of both winter rains and summer monsoonal rains; however, the basins of the area are hot enough throughout the year for potential evapotranspiration to predominate greatly over precipitation, and so the overall climate is quite arid (Shevenell, 1996). Local scale variations in precipitation relative to evapotranspiration can also

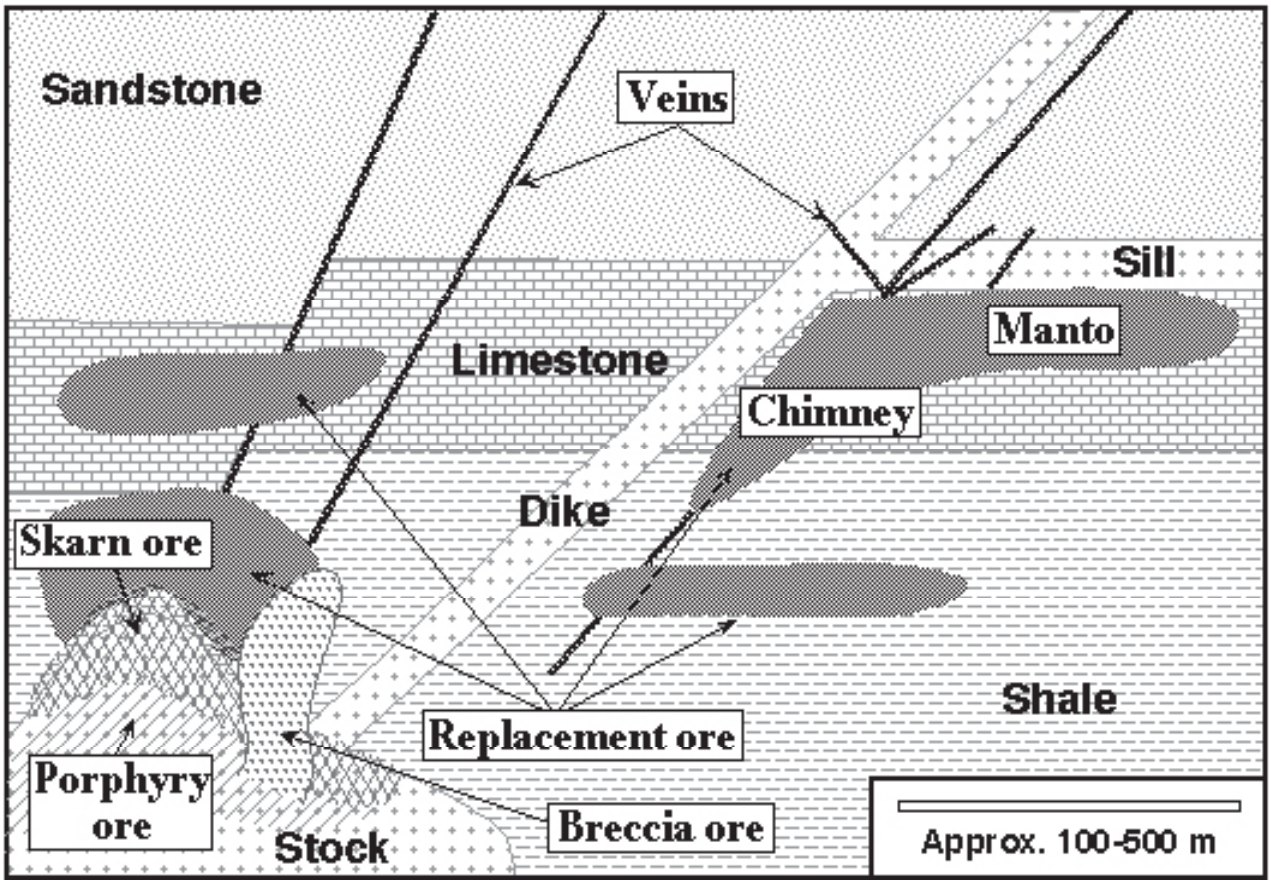


FIGURE 3.15—Schematic cross section of mineral-deposit types that may form from the intrusion of a magmatic stock into a sedimentary-rock sequence containing carbonates, shales, and sandstones.

result from variations in topography and the direction slopes face relative to the dominant sun direction. For example, in the eastern foothills of the Colorado Rocky Mountains, Douglas fir (indicative of relatively abundant water) grow on the shaded north-facing slope of a hill, whereas ponderosa pines and scrub junipers (indicative of less available water and higher evapotranspiration rates) grow on the sun-baked south-facing slopes, even though the overall precipitation rates are the same on both sides of the hill.

Links between climate, mineral-deposit geology, and environmental processes

The major links between climate, geology, and the environmental effects of mineral deposits are best known from studies of soil (FitzPatrick, 1980), hydrologic studies (Domenico and Schwartz, 1990, and references therein), and studies of supergene enrichment of ore deposits (Guilbert and Park, 1986). However, systematic studies of the environmental geology and geochemistry of mineral deposits as a function of climate are in their infancy. Nonetheless, some generalizations can be made.

In general, the water table is shallow in wet climates with high precipitation relative to evapotranspiration, and deep in semi-arid to arid climates with high evapotranspiration relative to precipitation. Deep weathering and sulfide oxidation profiles therefore tend to develop in semi-arid climates due to the generally deep water tables. In wetter climates, shallow water tables tend to preclude very deep oxidation. However, even in semi-arid and wet climates, depths to water table and resulting depths of weathering can be quite variable depending upon the local topography and geologic conditions. For example, the depth to water table in individual mining districts in the mountain ranges of the semi-arid U.S. southwest can vary from 0 to several-hundred-meter depths, depending upon proximity to incised canyons.

Weathering of, and element leaching from, rocks and mineral deposits tend to be intense in humid tropical climates, due to the warm temperatures and organic acids generated by the abundant decaying vegetation. In contrast, element leaching and weathering rates are much less intense in arid deserts and cold arctic regions. In humid to semi-arid climates, leaching and transport tends to be downward, whereas in arid climates, evaporation-driven upward movement of water by capillary action becomes a significant process.

High rates of evaporation in arid and semi-arid climates also result in increased alkalinity in surface waters and ground waters in the unsaturated zone. Carbonate-rich waters can produce extensive carbonate cements and weathering rinds in soils and alluvial sediments in semi-arid to arid climates.

As shown by Plumlee et al. (1999), mine waters draining sulfide-mineral-bearing deposit types that generate acid mine waters

tend to have lower pH and higher metal contents in dry climates than in wet climates due to lesser dilution by fresh waters and greater evaporative concentration of acid and metals. Evaporative processes can also have important effects in wet climates that have seasonal wet and dry periods; as discussed previously, evaporation of acid waters to dryness triggers the formation of soluble metal sulfate salts, which then dissolve readily during the next rain or snowmelt. However, data summarized by Plumlee et al. (1999) indicate that relative shifts in pH and metal content for a given deposit type in different climate settings are generally less than shifts due to differences in geologic characteristics.

Very cold climates can have several consequences for mineral environmental processes. First, weathering rates decrease substantially in very cold climates. For example, unweathered sulfide minerals may be abundant at the ground surface where climate favors permafrost formation. However, during short warmer summer seasons in areas dominated by otherwise very cold climate, weathering of sulfide minerals exposed at the ground surface can lead to formation of highly acidic water, depending upon the mineral-deposit geology (i.e., Kelley and Taylor, 1997). Partial freezing of acid waters can also lead to increased acidity and metal contents in the residual waters (W. Miller, oral commun., 1994).

Climate effects on environmental impacts downstream from mineral deposits can be significant. For example, downstream dilution (and therefore environmental mitigation) of acid mine water by dilute water draining unmineralized areas is much more efficient in wet climates than in dry climates. In contrast, downstream mitigation is enhanced in dry climates by the increased acid-neutralizing capacity of solid material in stream beds and soils, coupled with the generally higher alkalinities of surface waters draining unmineralized areas.

Effects of mining and mineral processing methods

The techniques used to extract and process ores can substantially affect the nature, volumes, and compositions of mine wastes, waters, byproducts, and airborne emissions needing treatment to prevent or minimize environmental impacts.

A wide variety of mining and mineral processing methods are currently in use; even more have been used over the course of historic mineral extraction activities. Ultimately, mining and mineral processing methods used to exploit a deposit are strongly dependent on the geologic and mineralogic characteristics of the ore. For example, vein ores continue to be most economically extracted by underground tunnels, adits, and stopes. In contrast, disseminated and stockwork deposits such as porphyry-Cu and -Mo deposits are at present most economically extracted using either surface open-pit methods or large-volume underground methods such as block caving. The large-scale underground and open pit mining methods have only become technologically feasible and widely used in the last 40–50 years.

The biggest environmental effect of mining method (open-pit vs. underground block caving vs. underground tunnels, stopes and adits) is in the amount of disturbance generated and the amount of mineralized rock exposed to weathering. Abundances of acid and metals in mine waters draining deposits with similar geologic characteristics tend to progressively increase from waters draining underground workings, to those draining mine dumps and mill tailings, to those which collect in open pits (Plumlee et al., 1999). This trend is due to increasing access to weathering agents (water and atmospheric oxygen), increased surface area of sulfide minerals exposed to weathering, and increased opportunities for evaporative concentration.

Mineral processing methods have also evolved as new technological advances have been made, enabling the economic processing of lower-grade ores in higher volumes. As with mining method, however, the geologic nature of the ores controls the optimum mineral processing method used to extract metals from ore. In the past century, physical crushing and sorting methods, such as jig crushers, were followed by roasting or smelting to extract metals contained in sulfide ores, and amalgamation was used to extract Au from oxidized or pre-roasted ores. Cyanidation milling became popular for the treatment of Au ores in the early 1900s. In the 1950s and 60s, froth flotation of sulfides allowed economical processing of large volumes of sulfide-bearing porphyry ores. Cyanide heap leach methods (Smith and Mudder, 1999) have become economically in the last several decades to extract gold from oxidized low-grade ores. Heap leach solvent extraction (where the sulfide or oxide ores are treated with sulfuric acid to leach the metals, and the metals remove from the acid solution with organic solvents) have been used in the last decade to process lower-grade Cu ores.

The size of particles produced by milling and beneficiation processes can dramatically influence their environmental impacts. Particles in finely milled ore and tailings have very high surface areas and abundant broken crystal edges, which greatly enhance mineral reactivities relative to those of mined rock and waste rock. Thus, sulfide oxidation and acid-generation rates can increase substantially. In addition, tailings particles are more likely to be distributed by wind and water than their more coarse-grained equivalents in waste-rock piles.

One important way in which mineral processing techniques influence potential environmental impacts relates to the way in which potentially environmentally-problematic chemicals were utilized. For example, mercury amalgamation was widely used as a gold extraction technique in the United States in the last century. As a result, soil and sediments may be mercury-contaminated at many sites where amalgamation was practiced historically, but would not otherwise be characterized by elevated mercury abundances in the deposits themselves.

ENVIRONMENTAL SIGNATURES THAT ARE INFLUENCED BY DEPOSIT GEOLOGY

As discussed in previous sections, significant differences in the environmental-geology characteristics may exist between mineral deposits of different types, and within a given mineral deposit. These differences are clearly discernible in the environmental signatures produced during the natural weathering of mineral deposits and by the mining and processing of the mineral deposits. In this section, the links between the environmental-geology characteristics of mineral deposits and their environmental signatures will be discussed.

Drainage water compositions

Geologic controls on the compositions of mine waters and natural waters draining a number of mineral-deposit types are interpreted in detail by Plumlee et al. (1999), and so will only be

discussed briefly here. Other studies examining the roles of deposit geology in controlling drainage-water compositions include Runnells et al. (1992), Price et al. (1995), Barry (1996), and Kelley and Taylor (1997). A subset of data presented by Plumlee et al. (1999) are summarized graphically on Figure 3.16 using element-pH plots, in which dissolved mine- and natural-water compositions are grouped according to the geologic characteristics of the specific ore types drained by the waters. This type of graphical portrayal is useful to examine compositional similarities of waters draining specific ore types that occur in more than one deposit type, such as waters draining propylitically altered rocks in porphyry, epithermal, and polymetallic vein systems.

The data show that, without considering geologic characteristics, both mine and natural drainage waters span a broad range of pH values (>9 pH units) and dissolved metal concentrations (for some metals, ranging ten orders of magnitude, from less than a part per billion [ppb] to tens of thousands of parts per million [ppm]). However, when grouped according to the dominant geologic characteristics of the ore types they drain, the drainage water compositions cluster in groups having much smaller ranges in pH (generally <several pH units) and metal concentrations (generally <several orders of magnitude). While clearly not sufficiently detailed to permit a precise and accurate prediction of the pH and metal concentrations of a specific water draining a specific ore type or deposit type, this type of graphical representation nicely illustrates the role of geology in influencing drainage compositions.

The groupings of data by geologic characteristic illustrate the integrated role of both deposit geology and geochemical processes in controlling drainage compositions. The overall trend of increasing metal content and decreasing pH results from the increasing acid-generating capacity (pyrite, sulfide content) and decreasing acid-neutralizing capacity (amounts and types of carbonates) of the deposits. For waters with a given pH, metal contents increase with increasing pyrite and sulfide content, and increasing exposure of Zn-, Cu-, and other metal-sulfides near the ground surface. The relative abundances of Zn, Cu, As, and U in the deposits are also manifested in their concentrations in the drainage waters.

Geochemical controls such as the solubility of Fe and sorption onto Fe particulates are also manifested in the plots. Waters with elevated Fe concentrations at near-neutral pH values have low dissolved oxygen levels, which preclude the formation of hydrous ferric oxide and hydroxysulfate particulates. Near-neutral pH waters with elevated Zn are due to high amounts of pyrite in sphalerite-galena ore bodies, coupled with the lack of Zn sorption onto particulates (Smith, 1999). The steep trends of decreasing U and As concentrations with increasing pH below pH 5 are due to sorption onto particulates, and the increasing abundance of particulates; however, both U and As show increasing concentrations with increasing pH above pH 5–6. For U, this results from desorption caused by the formation of aqueous uranyl carbonate complexes (Wanty et al., 1998, 1999). For As, this results from both desorption and the lack of Fe particulates to sorb the As in near-neutral waters with low dissolved oxygen.

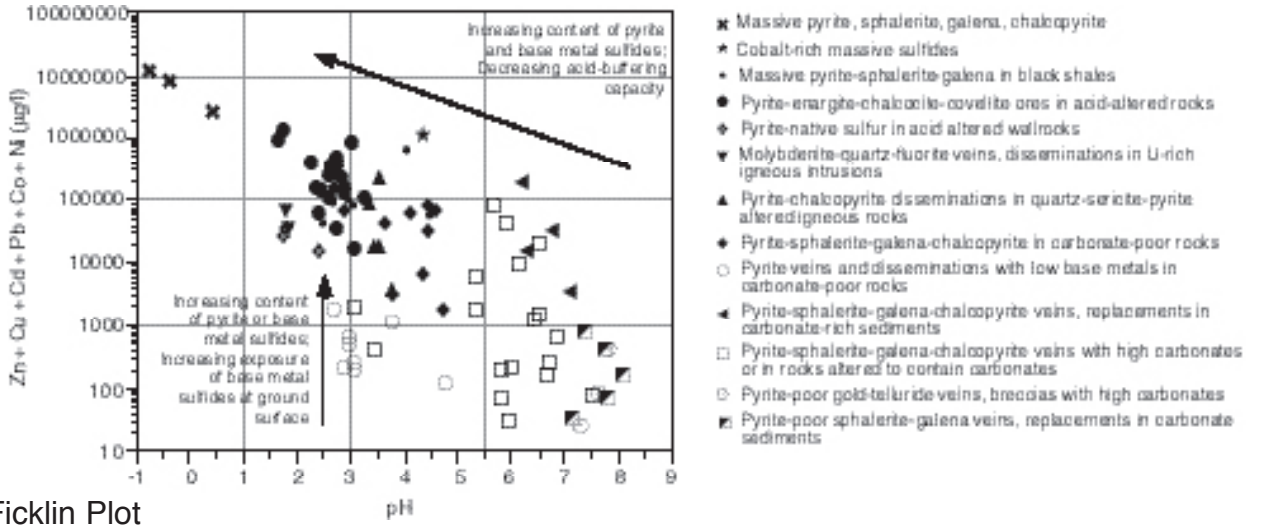
As shown in detail by Plumlee et al. (1999), systematic variations in drainage composition can be linked to variations in geologic characteristics within mineral deposits. Figure 3.17 shows that the different mineralogic zones of the Central City-Idaho Springs, Colorado, mining district (Fig. 3.9) are marked by characteristic and fairly distinct ranges in metal concentration and pH.

Natural and mine waters draining deposits of the same type and same geologic characteristics within a deposit type also have fairly characteristic and predictable ranges in pH and metal concentrations. Figure 3.18 depicts the compositions of mine waters (Summitville and Red Mountain Pass, Colorado; 3R mine, Patagonia Mountains, Arizona) and natural waters (Mt. Macintosh, B.C., Canada) draining quartz alunite epithermal deposits. Mine waters draining the core acid-sulfate alteration zones of these deposits all are highly acidic and metalliferous. Waters draining the intermediate argillic and distal propylitic alteration zones have progressively lower metal concentrations and higher pH values, resulting from progressively greater acid-neutralizing capacity.

In addition to the Al, Fe, Zn, and Cu found in most mine-drainage waters, the waters draining the advanced-argillic alteration zones of Summitville and other quartz-alunite epithermal deposits also have quite high dissolved concentrations of a number of more exotic elements such as Cr, Co, Ni, Be, and rare-earth elements (REE) (Fig. 3.19). It is likely that the elevated concentrations of these metals result from both release of trace metals via sulfide oxidation, and the partial dissolution of the altered host rocks. For example, Co, Ni, and Cr are unusually enriched in the volcanic host rocks in the area (T. Steven, oral commun., 1992), and so their elevated concentrations in mine waters most likely result from acid-attack of wallrock minerals containing these elements.

Waters draining the unmined quartz-alunite epithermal deposit at Mt. Macintosh, B.C., have similar ranges in pH and concentrations of Al and Fe as their mine-water counterparts, but have lower concentrations of Cu, Zn, As, and other trace metals (Fig. 3.18). Similar differences between natural water compositions and mine-water compositions are present in other mineral-deposit types where sulfides are not exposed at the ground surface. However, in unmined deposits where sulfides have been exposed at the ground surface by glaciation (i.e., SEDEX deposits in Alaska; Kelley and Taylor, 1997) or by rapid physical erosion (i.e., the Alamosa River stock, Colorado; Fig. 3.5e) the concentration ranges of Zn, Cu, and other trace metals are nearly identical to those measured in mine waters draining the same deposit types.

A plot of Cu concentrations in adit and seep outflows from Summitville in the 11 years following inception of open-pit mining (Fig. 3.20) illustrates both the rapidity with which acid-mine waters can develop if sulfides are reactive, and the major effect that dissolution of soluble salts can have on mine-drainage compositions. The soluble salts form in the historic underground mine workings and rock fractures beneath the open pit during dry periods in mid-summer and fall, and then are flushed out by snowmelt waters in late spring. In addition to Cu, the adit waters have very high concentrations of Fe^{2+} and many other metals, which mimic the concentration variations shown by Cu. Soluble Cu-sulfates and ferrous sulfates such as melanterite, and their contained trace elements are the likely sources for these metals (Nordstrom and Alpers, 1999). The dramatic increase in metal loadings from the Reynolds adit, especially during spring snowmelt (flows in excess of 1,000 gallons per minute were common in late May and early June of 1993), prompted the plugging of the adit as part of Superfund site remediation. The Chandler adit (located some 800 m north of and 80 m higher than the Reynolds; Fig. 3.10) was also plugged, but developed a substantial leak within 6 months of the Reynolds plugging, as the waters backed up in the underground workings. The Chandler adit was re-plugged in 1995, resulting in a substantial decrease in Cu loads leaving the site. However, the pre-mining seeps (Fig. 3.10) reactivated by the adit plugging had,



Ficklin Plot

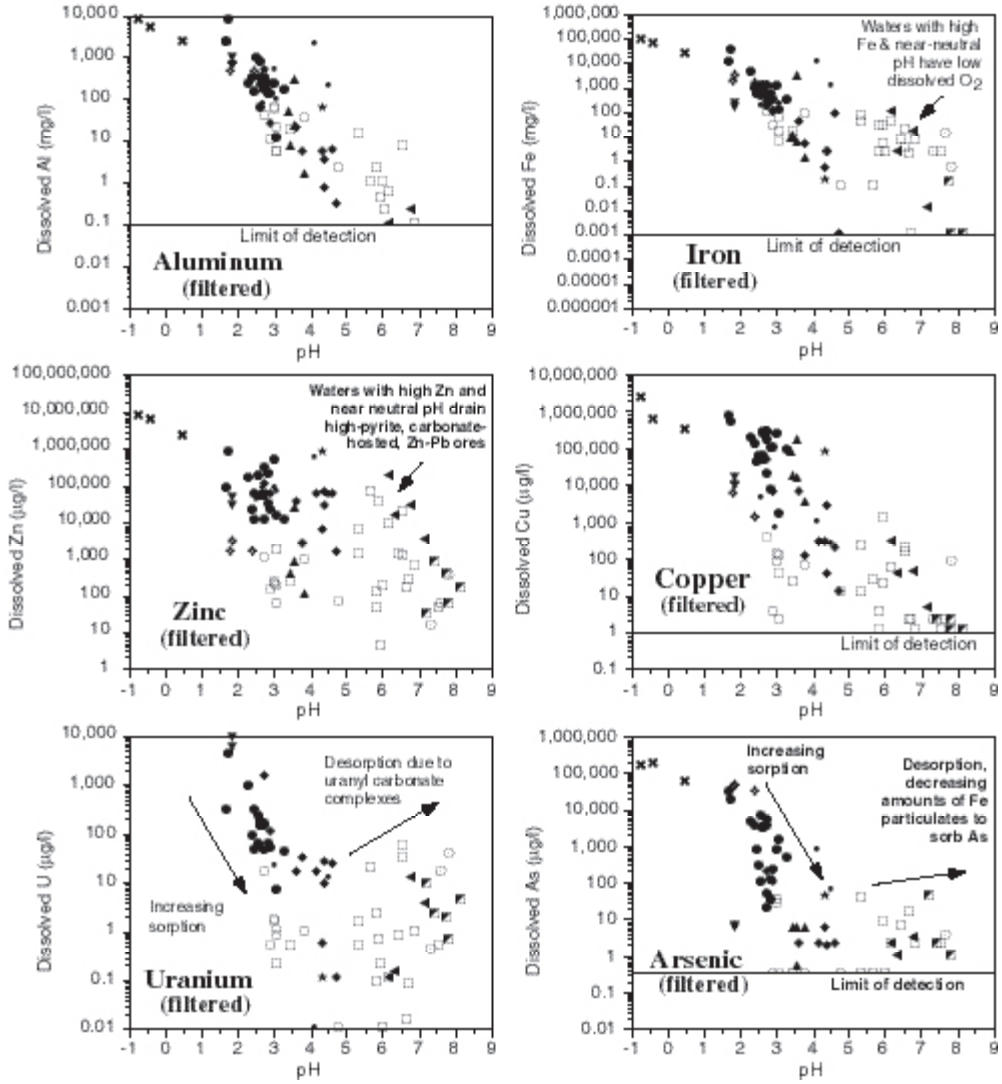


FIGURE 3.16—Plots showing the metal-pH compositions of mine waters and natural waters from mineralized areas, grouped according to the geologic characteristics of the ore types, alteration zones, etc., that they drain. The plots are from Smith et al. (1994), and show a subset of the data presented by Plumlee et al. (1999). The Ficklin plot at the top of the page shows the sum of base metals Zn, Cu, Cd, Pb, Co, and Ni, the generally predominant trace metals found in mine waters and natural waters draining unmined mineral deposits. See discussion in Plumlee et al. (1999) regarding metal concentration units used for the plots.

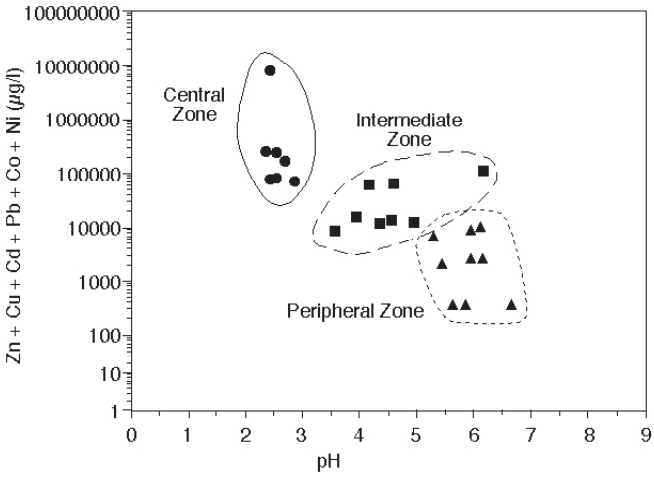


FIGURE 3.17—Ficklin plot showing the composition of mine waters draining different mineralogic zones of the Central City-Idaho Springs mining districts, Colorado (Fig. 3.9). Data from Plumlee et al. (1999) and Wildeman et al. (1974).

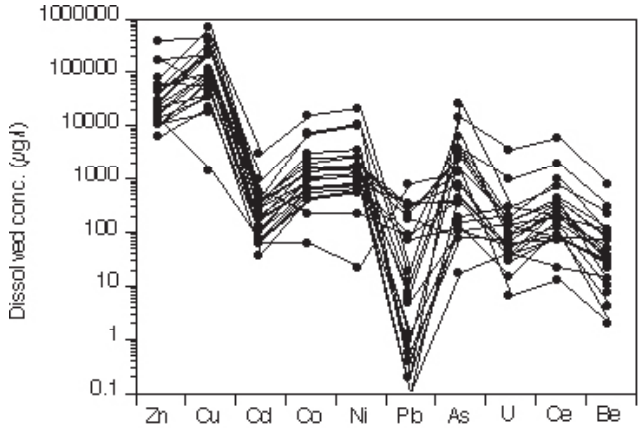


FIGURE 3.19—Concentrations of metals in waters draining acid sulfate alteration zones of quartz-alunite epithermal deposits. Data from Plumlee et al. (1999). Figure modified from Plumlee et al. (1995c).

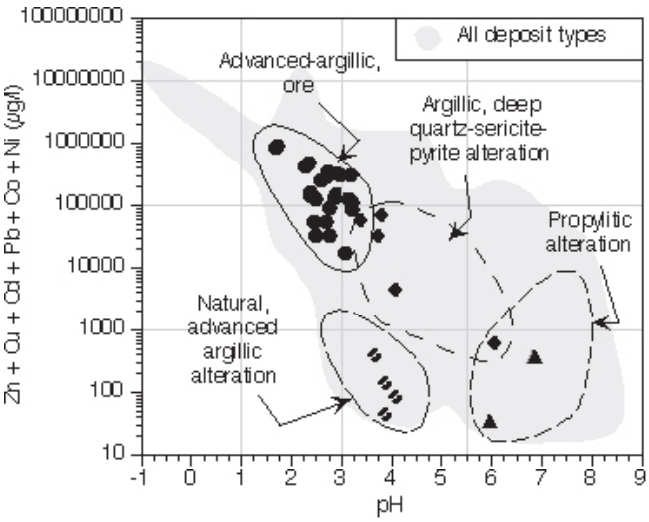


FIGURE 3.18—Ficklin plot showing the compositions of mine and natural waters draining quartz-alunite epithermal deposits. Data from Plumlee et al. (1999). Figure modified from Plumlee et al. (1995c) and Plumlee et al. (1999).

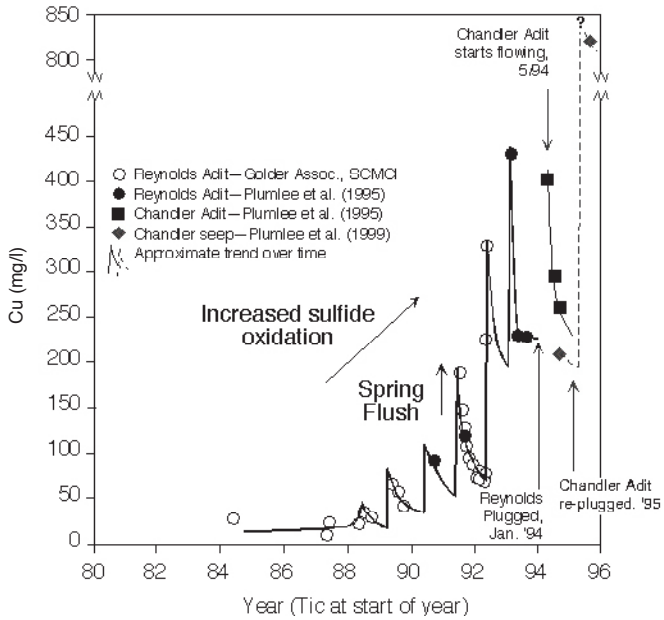


FIGURE 3.20—Plot of copper concentrations in adit and seep outflows from the area beneath the Summitville open pit since the start of open-pit mining in 1985. Figure modified from Plumlee et al. (1995b). The hollow symbols show data collected by Golder and Associates for the mining company, Summitville Consolidated Mining Co., Inc. (SCMCI on figure) prior to the bankruptcy of the company in 1992.

as of 1995, higher Cu concentrations than the adit waters.

Simple loading and price calculations indicate that the gross (pre-extraction) value of major metals leaving Summitville in solution via Reynolds adit waters during 1993 peak spring flow was in excess of $20,000 U.S. per day (Fig. 3.21). At present, Cu is the only one of these metals that might have been economically extractable from the Summitville mine waters; Cu-rich mine waters have long been viewed as economic resources in many porphyry-Cu mines, which commonly extract the Cu with shredded auto parts and other scrap steel. In the future, mine-waters draining geologically favorable mineral deposit types such as Summitville may at some point (with appropriate advances in metal extraction technology) be viewed as economic resources for a variety of metals, rather than as environmental liabilities.

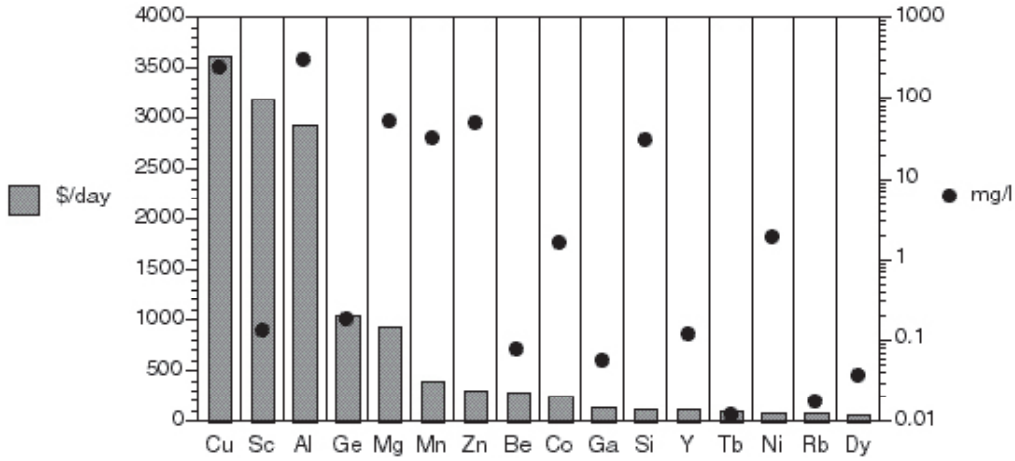


FIGURE 3.21—Concentrations and calculated gross (pre-extraction) values of various metals in Reynolds adit waters during peak spring flow, early June 1993. The values were calculated using estimated metal prices for that general time period. Mine-drainage data from Plumlee et al. (1995b). Flow value of 1000 gallons per minute was used to estimate total loadings of metals per day carried by the waters.

Mine-drainage data from polymetallic vein and replacement deposits at Leadville, Gilman, and Silverton, Colorado, New World, Montana, and Nabesna, Alaska, illustrate the range in water compositions that can be produced by different deposit types in a given district (Fig. 3.22). Waters draining igneous-hosted polymetallic vein ores and skarn ores with low carbonate contents produce the most acidic waters, resulting from the lack of acid-neutralizing reactions with the igneous wallrocks and skarn calc-silicate minerals. Sediment-hosted skarn, vein, and replacement deposits can also produce mine waters with a wide range in metal content and pH, depending upon the carbonate content of the sediments, the extent to which the waters react with the carbonates, and the pyrite content of the ores.

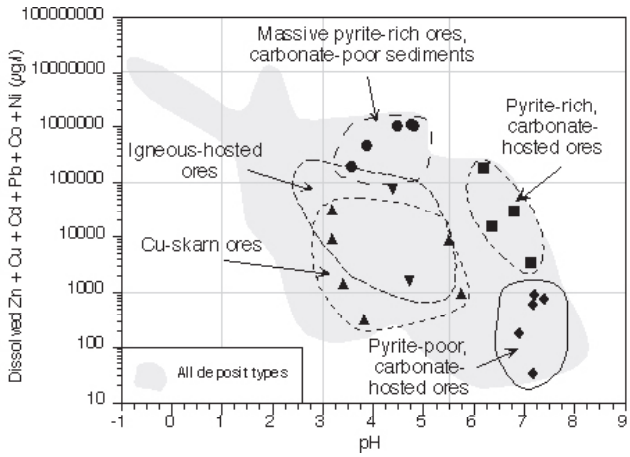


FIGURE 3.22—Ficklin plot comparing the concentrations of mine waters draining different ore types that are found in polymetallic vein and replacement deposits. Data are from Leadville, Gilman, and Bandora, Colorado (polymetallic replacements); New World, Montana (Cu-skarn; Pioneer Technical Services, 1994); Nabesna (Au skarn; Eppinger et al., 1997). Data are listed in Appendix of Plumlee et al. (1999).

Climate and mining method controls on drainage compositions

The data presented on Figures 3.16–3.22 also illustrate the generally subordinate controls that climate and mining method exert on natural and mine-drainage compositions. For example, the data for pyrite-enargite-covellite ores in acid-sulfate altered rock (Fig. 3.16) include compositions from Summitville and Red Mountain Pass, Colorado (waters draining adits, mine waste piles, and open pit ponds in wet, cool mountainous climates). Data from the 3-R Mine, Arizona, located in a hot, semi-arid climate, are not shown on Figure 3.16 (Plumlee et al., 1999), but fall within the same range of pH and metal contents as those of Summitville and Red Mountain Pass. Although the compositions of the 3-R waters are similar to those of Summitville and Red Mountain Pass, their effects on the surrounding surface water environment are not; they flow for only a portion of the year, and when they do flow they do not persist far downstream due to loss by evaporation and loss into the vadose zone below the stream beds.

As discussed by Plumlee et al. (1999), waters draining mine waste piles and tailings impoundments can be quite acidic and metal-bearing in deposit types with large amounts of carbonate minerals. This likely results from the large surface area of sulfides exposed in the waste-rock piles and tailings impoundments, the lack of reaction with acid-neutralizing carbonates that are armored by secondary hydrous Fe- and Al-oxides, and the dissolution of soluble sulfate salts from sulfide surfaces by rain and snowmelt waters.

Mineral processing waters

There are a variety of mineral processing (beneficiation) methods that use water-based reagents to either physically concentrate ore minerals or chemically extract ore elements from the surrounding gangue material. For a detailed discussion of the chemical reagents used in mineral beneficiation, the reader is referred to general texts on the subject (e.g., Ripley et al., 1996). Although the chemical compositions of mineral processing solutions are

largely controlled by the complex chemical reagent mixtures needed for the specific beneficiation processes, the solutions can be modified chemically through reactions with the ore and gangue materials, and thus can be influenced by the mineralogy and trace-element compositions of the ore being processed.

Froth flotation waters

Froth flotation processing of sulfide ores uses a variety of soap-like organic chemicals with high surface tension that, when frothed, create bubbles to which the milled sulfide particles adhere. Other reagents such as cyanide may also be added to the processing solutions to enhance the process. Although processing solutions are recycled repeatedly, they eventually end up in tailings impoundments, where the reagents may be isolated by impoundment reclamation, diluted by rainfall, concentrated by evaporation, or gradually degraded by bacterial, photolytic, or other geochemical processes. As the processing solutions react with the ore and gangue minerals, they can pick up dissolved heavy metals. In sulfide-rich tailings impoundments, the processing solutions, which typically are maintained to relatively alkaline pH during the beneficiation process, may be acidified by oxidation of sulfides and dissolve heavy metals from the sulfides. Due to the organic chemical degradation and sulfide oxidation, tailings impoundment waters can therefore eventually develop compositions that are quite similar to those draining mine dumps and mine workings of their deposit type (see above).

Cyanidation and cyanide heap-leach processing waters

Cyanidation milling and cyanide heap leach processing both use cyanide solutions to chemically extract gold and (or) silver (Smith and Mudder, 1999). Cyanidation solutions and heap leach processing solutions typically are maintained at pH values near 10 using lime in order to maximize CN^- concentrations and gold extraction efficiency. If the ores are very low sulfide or are completely oxidized (either naturally by pre-mining oxidation, or by pre-cyanidation roasting), then the process waters are composed primarily of free cyanide and gold- and silver-cyanide complexes, and gold extraction efficiency is greatest. Concentrations of Fe, Cu, and other metals are generally low because their oxides are relatively insoluble in the alkaline processing waters.

If appreciable amounts of sulfides are present in the ores being treated, then sulfide oxidation can reduce solution pH. It can also produce elevated concentrations of thiosulfate (derived by reactions of cyanide with intermediate oxidation-state sulfide species) and cyanide complexes with a variety of other metals (such as zinc, copper, cobalt, and nickel). In general, the concentrations of these metals in the processing solutions mimic their abundances in the ores. For example, heap leach processing of Cu-rich, sulfide-bearing ores at Summitville, Colorado (Plumlee et al., 1995b), produced processing waters with quite elevated thiocyanate and copper concentrations (as high as several hundred ppm), and relatively high concentrations of iron, cobalt, and nickel (several ppm). Although iron sulfides are abundant in the Summitville ores, Fe concentrations were typically limited to several ppm by the precipitation of insoluble hydrous iron oxides or Fe (±Cu) cyanides. In contrast to the Summitville heap leach solutions, a solution produced during cyanide heap-leach testing of sphalerite-bearing polymetallic vein ores from Central City, Colorado, had several hundred ppm Zn, Ag, and thiocyanate (G. Plumlee, unpub. data). Experimental studies by Ficklin et al. (1995) showed that alkaline heap leach solutions are effective at extracting As from realgar, orpiment and other As-bearing minerals. Thus, heap leach solutions from As-rich deposits (such as Carlin-type sediment-hosted Au deposits) may contain up to several ppm As.

Heap-leach, solvent-extraction processing waters

In recent years, heap-leach processing and solvent-extraction/electrowinning have been used to extract copper from both oxide and sulfide ores. The ores are placed on a heap leach pad and treated with sulfuric acid, which dissolves metal sulfide, oxide, sulfate, and carbonate minerals from the ores. The Cu is then extracted from the processing waters using organic solvents, and the Cu extracted from the solvents using electrowinning. Due to the use of sulfuric acid, these processing waters develop compositions that are lower in pH but similar in their contained metals to acid-mine drainage. However, metal concentrations of the leach waters are substantially higher than those of mine waters, due to the repeated cycling of the processing waters through the heap leach. For example the leach waters may contain very high to extreme concentrations of Fe, Al, and sulfate (thousands of ppm), and Cu and Zn (many hundreds to low thousands of ppm).

Processing waters and byproducts from some industrial mineral deposits

Some industrial mineral deposits, such as phosphate deposits, rare earth deposits, and titanium deposits, have significant environmental considerations that result directly from mineral processing. The processing liberates and concentrates potentially deleterious trace elements contained in the ores as waste byproducts.

Rouse (1974) summarized the environmental issues related to the mining and processing of the phosphate deposits in Florida. The deposits are chemical sediments composed largely of nodules of apatite (a calcium phosphate mineral) that commonly contains high concentrations of U, F, Cl, REE, and Cr as trace impurities. The phosphate concentration process involves initial washing to remove fine phosphate particles as slimes, followed by amine flotation to remove silica sand particles. The phosphate concentrate is then ground and acidulated, where it is reacted with sulfuric acid to produce either a mixture of superphosphate and gypsum, or phosphoric acid and waste byproduct gypsum. The byproduct gypsum is a substantial waste product that is stored in large piles near the processing plants. Prior to the mid-1970s, environmental considerations such as the release of fluorine into the atmosphere from processing plants, disposal of highly acidic, F- and P-rich waste waters, dust, and SO_2 emissions from sulfuric acid plants were recognized and being largely remediated. However, the issue of potential radiochemical releases was largely not recognized until the 1970s (Rouse, 1974). Due to the high levels of U in the original ore, the radioactive decay of U and its daughter products, primarily radium-226 and radon-222, in the waste processing waters, slimes, and gypsum byproducts were recognized to be of potentially significant environmental concern. As a result, new environmental mitigation measures were needed, such as better waste disposal procedures, and the prohibition of the use of

byproduct gypsum in the manufacture of wallboards.

Titanium processing uses sulfuric acid to dissolve resistate minerals such as ilmenite and rutile. The processing also releases a variety of trace metals into the sulfuric acid. For example, Schuiling and van Gaans (1997) and van Gaans and Schuiling (1997) measured compositions of acid-discharge waters from a TiO_2 processing plant in the Ukraine, and found a pH of 0.85 and extreme concentrations of Fe, Na S, and Cl (tens of thousands of mg/l); Al, Ca, Ti, P, Si, Mn (hundreds of mg/l); Cu, Cr, Ce, V, Sr, and Ni (tens of mg/l). Although these studies did not determine concentrations of radionuclides such as U, Th, Ra, and Rn, it is possible that they may also be present in elevated concentrations. Placer sand deposits, the most common source of Ti ore, commonly contain other resistate minerals such as monazite, columbite, zircon, and tantalite that are enriched in these radionuclides (see, for example, Eisenbud, 1987; Filippidis et al., 1997; and references therein).

Effects of mine-drainage, natural-drainage, and mineral-processing waters on ground- and surface-water quality

The geochemical and biological effects of waters draining unmined mineral deposits and, if released into the environment, mine waters and mineral-processing waters, are a complex function of many interrelated factors. The composition and flow (volumes) of a poor-quality water relative to those of ground or surface-waters with which it mixes affects how rapidly and effectively the chemical effects of the degraded water are mitigated downstream. Other processes such as chemical precipitation (formation of particulates), sorption, photochemical processes (i.e., photoreduction of iron), physical processes (physical settling or resuspension of particulates), and biogeochemical processes (i.e., bacterially catalyzed reactions such as iron oxidation) also play important roles in the downstream mitigation of degraded waters (Nordstrom and Alpers, 1999; Smith, 1999).

As acid-rock drainage flows into a fresh stream, it is progressively diluted by the stream waters. This dilution triggers an increase in pH of the acid drainage, which leads to the precipitation of orange hydrous ferric oxide colloids and particulates; the precipitation of the iron particulates also results in part from the gradual oxidation of ferrous iron in the acid waters by oxygen in the oxygenated stream waters. Once the pH of the mixture rises above 4.5–5, white aluminum colloids and particulates form. As shown by Smith (1999), suspended Fe and Al particulates can effectively sorb most trace elements (As, Pb, and most Cu) in the manner and order discussed previously; Zn, Cd, Ni, and, to a lesser extent, Cu, are not as effectively sorbed. Suspended particulates settle as they reach low-velocity areas downstream, form coatings on the rocks and sediment in the stream bed, and remove (at least temporarily) their sorbed trace metals from the surface water system. Particulate-rich bed sediments are relatively ineffective at sorbing metals from the waters flowing over them, and are easily eroded from the stream bottom during periods of high flow. Seasonal changes in water chemistry may lead to desorption of trace metals from the uppermost bed sediments and resuspended particulates. Process such as photoreduction of iron may also lead to dissolution of some of the particulates.

The controls of watershed geology

Geology (with the modifying effects of climate) can play an important role in controlling the downstream or down-gradient effects of mine- or natural-drainage waters. The influence that geologic characteristics of mineral deposits have on the compositions of mine, natural-drainage, and mineral-processing waters has been discussed previously. Similarly, the geologic characteristics of the rock units in a watershed around a mineral deposit can influence the compositions of the ambient ground and surface waters in the watershed, including their alkalinities, major-element concentrations, and trace-element concentrations. The compositions of these ambient waters influence the downstream chemical and biological effects of acid-mine drainage and mineral processing waters. For example, as discussed previously, the higher the alkalinity of a stream- or ground-water, the more effective a given volume of the water is at reacting with and consuming the acid in acid-mine waters. Hence, watersheds with carbonate-rich rocks (such as limestones or dolomites), or reactive silicate rocks (for example, ultramafic rocks such as dunites or serpentinites) generally produce surface waters with higher alkalinities and acid buffering capacities than watersheds with carbonate-poor, less-reactive rocks such as many granites.

The role of climate

Climate can substantially affect the acid-buffering capacities of waters in a watershed. In drier climates, high evaporation rates tend to increase the alkalinities and acid-buffering capacities of waters draining most rock types, including those with low carbonate contents or reactivities (W. Miller, oral commun., 1996). Thus, smaller volumes of alkaline surface waters draining many rock types in dry climates can mitigate the effects of acid drainage waters as effectively as larger volumes of less alkaline waters draining similar rock types in wetter climates.

A comparison of two watersheds affected by acid-rock drainage

The effects of watershed geology on the downstream impacts of acid-mine drainage can be seen by comparing two mineralized watersheds in southwestern Colorado, the Animas and Alamosa River basins (Fig. 3.23). Both watersheds originate in intermediate to felsic volcanic rocks of the San Juan volcanic field. Both are characterized by extensive mineralization in their headwaters, including quartz-alunite epithermal deposits (Summitville on the Alamosa, and Red Mountain Pass on the Animas) that produce highly acidic mine-drainage waters (Fig. 3.18) and polymetallic to adularia-sericite epithermal vein deposits that produce, depending upon the carbonate content of the veins and wallrock alteration, variably acidic and metalliferous drainage waters. Both also have their headwaters in high mountains with high precipitation (in excess of 1 meter annually); both have high snowfall in winter and intermittent thundershowers and dry conditions in summer. Both flow from the mountains into adjacent lowlands that are very dry, with less than 10–20 cm total annual precipitation.

However, there are important geologic differences between the watersheds. The Animas drains extensive areas of propylitically altered volcanic rocks in its headwaters, and drains carbonate-rich

sedimentary rocks downstream from its headwaters. In contrast, the Alamosa River drains several large, predominantly unmined areas of pyritic alteration that produce extensive natural acid drainage; although propylitically altered rocks are present on the fringes of the pyritically altered areas, they are relatively minor in volume. The Alamosa River also drains volcanic rocks throughout most of its length, and does not drain carbonate-rich sedimentary rocks.

As a result of the differences in their watershed geology, waters in the Alamosa and Animas Rivers have very different chemical compositions. Tributaries of the Animas River that drain the Red Mountain Pass mineralized systems are quite acidic and metalliferous; however, once these waters mix with waters from numerous other tributaries draining carbonate-bearing, propylitically altered rocks, and the carbonate-rich sedimentary rocks downstream, the pH of the Animas River rises to near-neutral levels, abundant Fe-, Al-, and Mn-rich colloids and particulates form, and most metals other than Zn and Cd sorb onto the particulates.

The Alamosa River water is quite acidic and metalliferous in its headwaters, due to largely natural acid rock drainage from the pyritically altered areas (Kirkham et al., 1995). Creek names such as Iron, Alum, Bitter attest to the naturally degraded water quality in the headwaters of the Alamosa. Few tributaries drain unmineralized rocks, and those that do are generally of relatively low volume. Thus, Alamosa River has a relatively limited capability to mitigate the effects of acid rock drainage. The tremendous increases in acid-rock drainage that resulted from recent open-pit mining at Summitville thus flowed into a river that was already quite acidic during most times of year. As a result, especially during dry periods when dilution from unaffected tributaries was minimal, quite acidic waters can persist well downstream. For example, in late summer, 1994 (when significant volumes of untreated acid waters were leaving the Summitville site), irrigation waters drawn from the Alamosa River some 60–70 km downstream from Summitville had pH values as low as 3.9 and dissolved Cu concentrations near 1 ppm (Fig. 3.24).

Possible downstream effects of cyanide heap leach solutions: Summitville as an example

Accidental releases of cyanide heap-leach processing solutions have occurred at several mine sites in recent years. The potential downstream environmental effects of cyanide-bearing processing solutions are influenced in part by the composition of the processing solutions (i.e., whether the cyanide is present as free cyanide, weak-acid dissociable cyanide complexes, or complexes that do not dissociate readily in weak acids) (Smith and Mudder, 1999). Geochemical and biogeochemical processes such as volatilization, bacterial degradation, precipitation of insoluble cyanide solids, and photolytic degradation influence how rapidly cyanide is degraded once in the environment (Smith and Mudder, 1999). In general, degradation is most rapid in systems open to the atmosphere, either in surface waters or in the vadose zone above the water table. As with acid-mine drainage, the climate and geology of the watershed into which the heap solutions are released play an important role in the downstream persistence and environmental effects of the cyanide, most importantly by controlling the volumes and compositions of the waters with which the heap leach solutions interact. Summitville is an example of one extreme, in which heap leach solutions interacted with highly acidic waters affected by acid-mine drainage.

Summitville perhaps received more public attention for several accidental releases of cyanide heap leach processing solutions from the site during mining than it did for its acid-rock drainage problems. However, the exact number, magnitude, and sources (heap leach pad versus the french drain beneath the pad) of cyanide releases from Summitville are not well documented, nor are their actual downstream effects on surface water quality.

In an attempt to interpret the possible fate of cyanide accidentally released into the environment from Summitville, Plumlee et al. (1995b) carried out laboratory experiments in which they mixed samples of heap leach solutions from Summitville with water collected from the Wightman Fork of the Alamosa River (Fig. 3.25). The experiments were designed to simulate the chemical evolution of the Wightman Fork waters after receiving an influx of cyanide-bearing solutions from the heap leach impoundment. The mixing experiments were carried out in the sun (to take into account photolytic cyanide degradation), and compressed air was bubbled into the mixed solution to simulate the churning of the Wightman Fork waters as they flowed over the ~8-km course to the Alamosa River.

The experimental results suggest that, depending on the time of year and the magnitude of the release, acidic waters from Summitville may have helped degrade cyanide accidentally released from the heap-leach impoundment. Further, the alkaline heap leach solutions may have improved downstream water quality by neutralizing the acid Wightman Fork waters. The experimental results indicate that acid in the Wightman Fork waters broke down the Cu-cyanide complexes to form hydrogen cyanide, which then volatilized and caused water pH to increase further. In addition, ferric iron from the acid-mine drainage also likely combined with the Cu-cyanide complexes to precipitate insoluble Cu-Fe-cyanide solids. Copious orange (presumably hydrous ferric oxide) and white (presumably aluminum hydroxysulfate) precipitates also formed in the experiments, which helped to sorb Cu, Pb, and other metals from solution. The relatively positive effects indicated by these experiments may not have occurred, however, if: the flow volumes of heap leach solutions released were substantially greater than the flow volumes of Wightman Fork water at the times of release; if the releases occurred during winter when ice cover over the Wightman Fork inhibited cyanide volatilization; or if the cyanide releases were of acidic mixtures of heap leach waters and acid drainage from the french drain system underneath the heap leach pad.

In watersheds where acid drainage is not present, the likelihood increases that cyanide accidentally released into the environment will persist for appreciable distances downstream. The persistence and environmental effects of the cyanide will depend on the relative flow volumes of the released solutions versus those of the local surface waters, the degree of turbulence in the local surface waters, and the compositions of the local surface waters (a function of climate and watershed geology). Dilution of alkaline heap leach solutions by near-neutral surface waters (in most temperate climates) or acidic surface waters (in wet climates where decay of organic matter generates humic acids) will eventually lead to breakdown of weak cyanide complexes and cyanide volatilization (see Smith and Mudder, 1999). However, metals complexed by the cyanide may persist in solution if particulate matter is not present to sorb the metals. As with the experiments conducted by Plumlee et al. (1995b), the potential downstream effects of heap leach solutions from a site may be evaluated experimentally by mixing

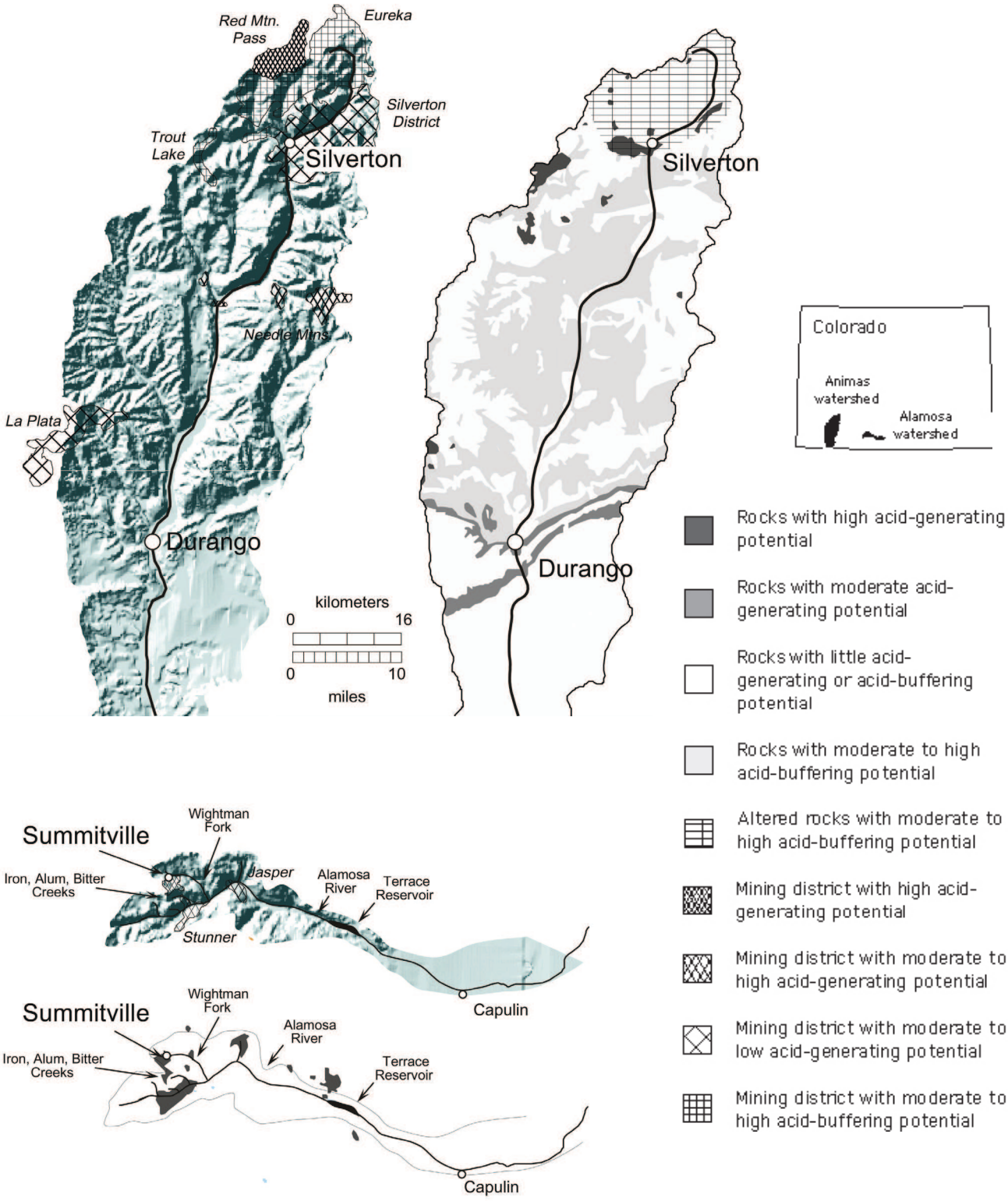


FIGURE 3.23—Maps comparing the environmental geology and mining districts of the Animas (upper) and Alamosa (lower) watersheds, southwest Colorado, that are affected by both natural acid rock drainage and mine drainage. The environmental geology of the watershed rock units is recompiled from the Colorado state geologic map (Tweto, 1985; Green, 1992). Mining districts are from Plumlee et al. (1995d) and references therein.

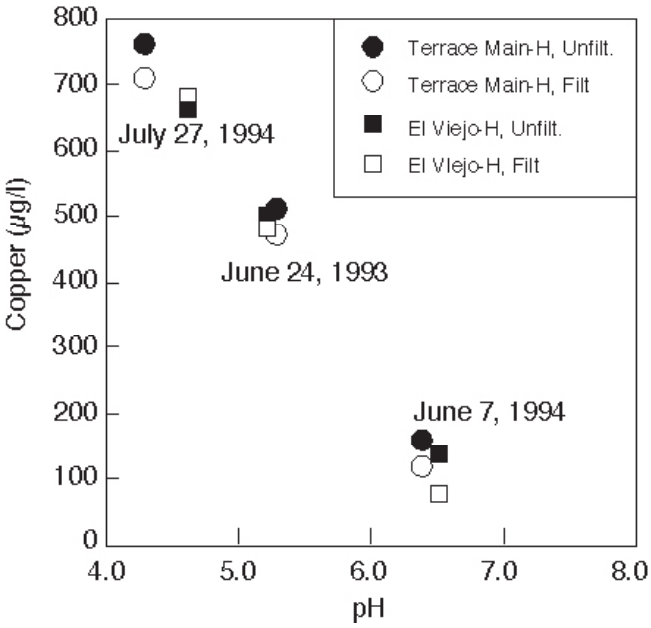


FIGURE 3.24—Plot of the pH and copper concentration in filtered (filt.) and unfiltered (unfilt.) irrigation waters taken from irrigation ditch headgates along the Alamosa River in 1993 and 1994, during the peak impacts of acid drainage resulting from open-pit mining at Summitville. The collection points for the water are some 60–70 km downstream from Summitville, and thus demonstrate the Alamosa River watershed's lack of capacity to self-mitigate significant influxes of acid-rock drainage. Figure modified from Smith et al. (1995).

samples of the heap leach solutions and local surface waters.

Soil and sediment compositions

The mineralogic and geochemical compositions of soils that form on and stream sediments that are deposited downstream from a weathering mineral deposit are the complex result of many interacting geologic, geochemical, biological, and climatic processes. The byproducts of human resource extraction activities (such as mining and processing wastes, smelter emissions, etc.) add many more layers of geologic and geochemical complexity to interpret. However, there are a number of ways that geologic and geochemical information can be used to interpret the relative contributions to and environmental significance of multiple natural and anthropogenic sources in the overall makeup of soil or stream-sediment samples. Many examples are presented in the exploration geochemistry literature (see Rose et al., 1979, and the *Journal of Geochemical Exploration*, for example), and in the burgeoning literature on environmental geology (see, for example, the journals *Environmental Geology*, and *Environmental Geochemistry and Health*).

Soil compositions

Soils that form by the weathering of underlying rocks mimic in large part the original mineralogic and geochemical makeup of the rock, but also in part result from various aspects of the weathering process that are controlled by non-geologic factors (such as topography, rain and snowfall amounts, ambient temperature, vegetation types and amounts, etc.). Soils developed on unmineralized rocks that are not enriched in any trace metals tend to have low natural concentrations of metals of environmental concern (such as Hg, As, Cu, Zn, Pb, etc.). In contrast, metal concentrations in soils developed on trace-element-rich bedrocks or directly on weathering mineral deposits can have extremely high concentrations of many of the same elements enriched in the mineral deposits. For example, Chaffee (1987) measured very high total concentrations of Pb (as high as 10,000 ppm) and Zn (as high as 30,000 ppm), and moderate to high concentrations of Cu (up to 500 ppm) and Sb (up to 400 ppm) in soils developed on mineralized carbonate host rocks of the polymetallic Pb-Zn-Cu replacement deposits, Eureka district, Nevada.

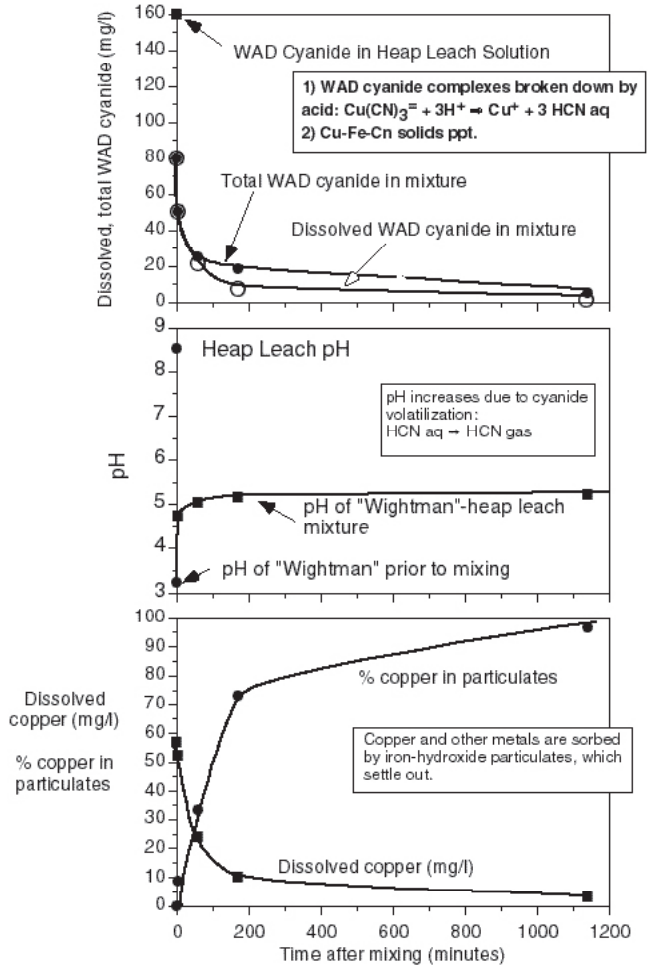


FIGURE 3.25—Plots of cyanide concentrations (upper), pH (middle), and dissolved copper (lower) over time in a mixing experiment simulating the mixing cyanide heap leach solutions from Summitville with Wightman Fork waters. "WAD"-weak acid-dissociable aqueous cyanide complexes (such as those with Zn and Cu). "Ppt."-precipitates. Figure modified from Plumlee et al. (1995b).

Stream sediment compositions

Stream sediments downstream from a weathering mineral deposit typically contain a mixture of minerals, including: the less easily weathered primary minerals of the deposit and host rocks (i.e., quartz, some feldspars, clays, and resistates such as Fe- and Fe-Ti-oxides, native Au, columbite, apatite, zircon, etc.); secondary minerals formed during the weathering process (clays, hydroxides, insoluble metal carbonates or sulfates); and secondary minerals precipitated from the surface waters (Fe-, Al-hydroxysulfates and hydrous oxides that contain sorbed metals). In drainages where sulfides are exposed at the surface by glaciation or high erosion rates, sulfides can comprise a significant portion of the stream sediment package as well. Organic detritus can also be present in trace to major amounts.

Natural concentrations of metals derived from a weathering mineral deposit can be quite high in stream sediments close to the deposit, but decrease with increasing distance downstream due to dilution by sediments from other sources. For example, pre-mining stream sediments downstream from polymetallic replacement deposits at Leadville, Colorado contained thousands of ppm lead in the form of secondary cerussite; in fact, the polymetallic nature of the deposits at Leadville was discovered because a heavy mineral that was greatly decreasing placer gold recovery was identified as cerussite. In the last several decades, stream sediment geochemistry surveys of unmined mineralized areas have been responsible for the discovery of a number of economic ore deposits.

Where mining and mineral processing activities have released material into the environment, still more complexities are added to the bulk geochemical compositions of stream sediments. Physical transport of solid materials from mine-waste dumps and mill-tailings adds a variety of minerals originally present in the deposit; these minerals add high concentrations of the metals that, depending upon the mineral, may be released into solution or taken up by plants and organisms. Secondary minerals (such as yellow- to orange hydrous ferric oxides and iron hydroxysulfates, and white aluminum hydroxysulfates) precipitate through chemical reactions such as dilution. These secondary particulates can settle out in slow-flow portions of the stream and contribute significantly to the composition of the stream sediments. Because they effectively scavenge other metals and As (Nordstrom and Alpers, 1999; Smith, 1999) these secondary precipitates can contribute significant concentrations of these elements in a readily-liberated form to the stream sediments.

A number of regional stream sediment geochemistry surveys were carried out as part of the United States National Uranium Reconnaissance Evaluation (NURE) program in the mid 1970s. Interpretations of the NURE data illustrate the combined effects of naturally elevated metal concentrations in stream sediments around mineralized areas and elevated metal concentrations in stream sediments resulting from human activities such as mining, mineral processing, smelting, and automobile use. In Colorado (Fig. 3.26), elevated lead concentrations in stream sediments highlight historic mining districts such as Leadville (which contributed metal loadings to the stream sediments both naturally prior to mining and as a result of mining), locations of smelters, and other sources of lead such as particulate lead contributed by burning of leaded gasoline prior to the 1970s (prevalent in metropolitan areas). Areas with moderate lead concentrations in soils in some cases result from weathering of lead from lead-rich rocks such as granites.

The geoavailability of metals from soils and sediments

Surveys such as those depicted on Figure 3.26, which measure total metal concentrations in stream sediments, do not give an indication of how readily the metals may be taken up from the sediments by waters, plants and animals (i.e., how geoavailable they are; Smith and Huyck, 1999). However, geochemical surveys can be carried out that measure not only total metal concentrations but also concentrations released in each of a series of sequential chemical extractions (see Crock et al., 1999). Such extractions subject soil or sediment samples to sequential leaches of increasingly strong acids and other reagents, which dissolve increasingly resistant, less readily-weathered mineral phases. Such leaches commonly dissolve metals tied up in (listed in general order of decreasing geoavailability) (a) water-soluble minerals (such as soluble sulfate salts), (b) colloids, (c) poorly crystalline, fine-grained hydrous Fe- and or Al oxide and hydroxysulfate particulates, (d) carbonates, (e) sulfides and organics, (f) silicates, and (g) resistate minerals such as ilmenite, rutile, zircon, columbite, and others.

When coupled with detailed mineralogical studies of the sediments, these sequential extraction studies provide important insights into how readily the metals contained in stream sediments downstream from a mining district may be released into the environment. For example, Church et al. (1997) demonstrated that a significant component of the lead, zinc, copper, and arsenic in stream sediments in the Animas River watershed, Colorado are stored in readily available form, sorbed onto colloidal and more crystalline but fine-grained particulates. When ingested by invertebrates, the metals tied up in these particulates may be present in concentrations high enough to be toxic (Church et al., 1997).

The geoavailability of metals from soils and stream sediments also may be determined by directly measuring the amounts of metals taken up by waters, plants, or organisms that come in contact with or ingest the sediments. For example, Dwyer et al. (1988) studied metal uptake by longear sunfish living in a part of the Big River near Deslodge, Missouri, which had large amounts of Pb-, Zn- and Cd-rich mill tailings incorporated into its stream sediments as a result of accidental releases from a tailings impoundment. Dwyer et al. (1988) found elevated levels of Pb, Cd, and Zn in blood and muscle tissues of the fish, as well as biochemical indicators of the effects of these metals on the biologic activity of the fish.

Techniques to discriminate natural from anthropogenic contributions to metal concentrations in soils and sediments

It is generally very difficult to discern the relative geochemical contributions of multiple geologic and anthropogenic sources for soil or stream sediment samples, based solely on the concentrations of major and trace elements in the samples. However, a variety of statistical and isotopic techniques have been developed that, when used in conjunction with surficial geology and geomorphology studies, significantly improve the chances of successfully differentiating relative contributions from multiple sources.

Multivariate statistical techniques such as factor analysis (i.e., Johnston, 1980) have been developed that can discriminate, for a

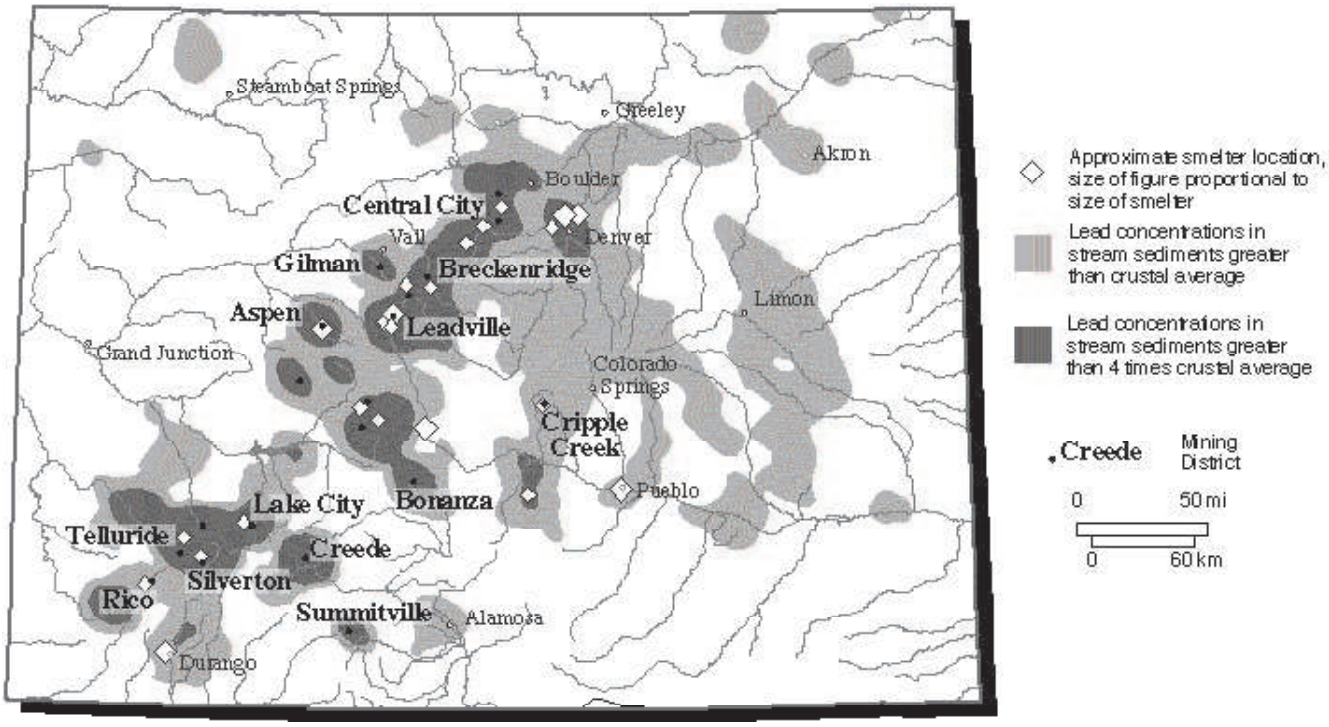


FIGURE 3.26—Map of Colorado showing contours of lead concentrations in stream sediments collected throughout the state as part of the NURE program. Names of mining districts are shown in bold dark text, and cities in plain text. Locations and relative sizes of some historic smelters (taken from Fell, 1979) are also shown.

sufficiently large population of samples, different suites of elements that are statistically associated. The analysis also estimates the relative proportions of different element suites, or factors, contained in a given sample of the population. The technique can be used for samples collected regionally, or locally within a smaller area such as a mining district.

Tidball et al. (1995) measured the geochemical compositions of soils, stream overbank sediments, and aeolian (windblown) sediments collected from throughout the San Luis Valley, Colorado, in order to examine the effects of acid-mine drainage and materials eroded from Summitville on soils and stream sediments in the southwestern part of the valley near the Alamosa River. They collected samples on a grid with spacing between samples varying from 2–5 km, and from 0–30 cm depth in the soil profile; they analyzed then analyzed these samples for 40 elements. Soil paste pH was also measured for each sample. The results were then interpreted with the aid of factor analysis. Seven factors, or geochemical associations of elements, were identified (Table 3.9), and then scores for each factor at each sample site were plotted and contoured on a map of the valley (see, for example, Fig. 3.27). Factors 1, 2, and 5 were interpreted to result from sediments derived primarily from volcanic or igneous rocks of various origins. Samples with high scores for these factors occur primarily on the margins of the valley, on or near alluvial fans whose rivers drain areas underlain by these rock types in the adjacent mountains. Factors 3 and 5 result from geochemical enrichments caused by evaporation of shallow ground waters, and are greatest in samples collected in the central parts of the valley where evaporation rates are greatest. Factors 4 and 7 indicate high contributions from mineralized areas. Samples with high factor 4 scores occur on or near alluvial material deposited by streams draining Pb-Zn mining districts such as Creede and Bonanza to the west of the valley. Factor 7 scores are greatest in soils collected on the Alamosa River fan and in the floodplain of the Alamosa River, and therefore indicate a high contribution of elements from Summitville (Tidball et al., 1995) and other mineralized areas in the Alamosa River watershed.

In a soil geochemistry survey of the Eureka district, Nevada, Chaffee (1987) used factor analysis to help identify soils in and near the district that were not contaminated by heavy metals emitted from local smelting. Samples with anomalously high levels of a variety of heavy metals (Ag, As, Au, Mo, Hg, Pb, Cu, Zn, and others) occur both in soils derived from weathering of the mineralized rocks and in soils near smelters. In contrast, Ba, Co, Mn, and V are anomalous over mineralized areas but not near the smelters; elements with high factor scores for this association were therefore interpreted as having minimal smelter contamination. Factor analysis also identified two soil geochemical associations that Chaffee interpreted as being derived from two distinct mineral-deposit types in the district, including the polymetallic-replacement deposits from which the bulk of the district's historic production came, and sediment-hosted Au deposits previously unidentified in the district. These results show that factor analysis is not only useful in a mineral exploration context, but also can be used to help establish pre-mining baseline geochemical conditions in districts having significant historic mining and smelting impacts.

A number of studies have successfully used radiogenic

TABLE 3.9—Compositions of element suites (or factors) determined by Tidball et al. (1995) using factor analysis for a large set of soil, aeolian sediment, and stream overbank sediment samples collected from the San Luis Valley, Colorado. For each factor, the elements that make up the factor are listed in decreasing order of dominance, based on the correlation between the factor scores and the concentrations of elements in the samples. Interpreted origins for each factor are also shown (from Tidball et al., 1995).

Correlation coefficients						
Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Nd, 0.953	Fe, 0.965	Mg, 0.917	Pb, 0.922	Cr, 0.895	Na, 0.882	As, 0.705
Ce, 0.942	V, 0.922	Ca, 0.849	Zn, 0.858	Ni, 0.882	K, 0.651	Cu, 0.616
La, 0.934	Ti, 0.892	Sr, 0.662		Co, 0.635		
Nb, 0.827	Co, 0.870	S, 0.456		Sc, 0.632		
Y, 0.822	Sc, 0.809					
Th, 0.683	Ga, 0.631					
Yb, 0.647						
Rhyolitic, granitic source	Andesitic source	Alkaline evaporative salts	Pb-Zn ores	Basalt source	Saline evaporative salts	High-sulfidation mineralization

isotopes to help understand the sources and their relative contributions to the geochemical makeup of stream sediments or soils. Lead isotopes have proven extremely useful in identifying multiple sources of lead in mineralized watersheds, including different mining districts and different rock units that each have distinctive lead isotopic signatures (i.e., Church et al., 1993, 1997, 1999; Östlund et al., 1995). For example, the lead isotopic composition of stream sediments upstream and downstream from the Penn Mine, California (Church et al., 1999) clearly shows the significant contribution of lead (as much as 71%) and other related metals from the Penn Mine ores relative to contributions of lead from rocks upstream in the drainage basin.

Stratigraphic sampling of overbank or lake sediments, coupled with ^{210}Pb (Robbins, 1978), ^{137}Cs (Ritchie and McHenry, 1984) or other isotopic or geomorphic dating of the sediments, also provides an indication of variations in metal concentrations in stream sediments over time. If the sedimentary record is long enough, such techniques may permit determination of pre-mining baseline concentrations of metals in the sediments. For example, Horowitz et al. (1996) examined the bed-sediment geochemistry of Terrace Reservoir, located on the Alamosa River downstream from Summitville (see the location of the reservoir on Fig. 3.27). They found that the onset of enrichment of many metals (Cu, Pb, Zn, Cd, As, Hg, Fe, and Al) in the reservoir sediments substantially predates the open-pit mining at Summitville, and that the open-pit mining may have marginally increased the concentrations and fluxes of some of these metals in the reservoir sediments.

Mobility of metals from solid mine and mineral-processing wastes

Metals may be liberated from solid mine wastes and mineral processing wastes by weathering, sulfide oxidation, and dissolution of soluble secondary salts. In addition, animals or aquatic organisms that directly ingest the solids may take up metals into their systems. As discussed in the previous section on geologic controls on mine-drainage compositions, the mineralogy of the waste material plays an important role in controlling how readily metals are liberated from the wastes into the environment. Waste rock piles with large amounts of soluble secondary salts (which therefore usually have high contents of reactive sulfides) will have a greater likelihood of producing acidic, metalliferous waters during storm or snowmelt events. Tailings solids, due to their fine grain size resulting from crushing and grinding, are likely to be more reactive than geologically similar waste rocks, and hence are likely to have greater potential metal mobility than the mine wastes.

There are a number of tests, including humidity cell tests (White and Jeffers, 1994), column tests (Filipek et al., 1999), tank tests (Logsdon and Basse, 1991), and leach tests (Montour, 1994), that may be used to help estimate potential metal mobility in aqueous form from solid mine and mineral processing wastes.

The extent of metal uptake directly by an organism that ingests solid mine or processing waste particles also is a function of the mineralogy of the wastes, coupled with the chemical conditions inside the organism's gastro-intestinal tract. Experiments have been developed to simulate metal mobility in gastro-intestinal tracts of some organisms such as rabbits (Davis et al., 1992). Metal uptake by organisms can also be evaluated by measuring the concentrations of metals in organism tissues and blood (for example, Dwyer et al., 1988).

Smelter slag and emissions

Sulfide ore smelting results in the formation of waste slag (through the reaction of iron in the ores with silica flux), and gaseous emissions containing both sulfur dioxide (an acid-generating gas) and particulates with high concentrations of the metals contained in the ores. Although modern smelters have scrubbers that remove much of the sulfur dioxide and metal-bearing particulates, emissions from past smelters lacking the scrubbers are a significant environmental concern in the areas immediately around and downwind from the smelters. Metal mobility from slag, although commonly low, may be potentially important at some sites.

A number of mineralogical and geochemical studies of smelter slag piles (e.g., Lasmanis et al., 1997) and of the soils and plants affected by particulate smelter emissions (e.g., Chaffee, 1980, 1987; Montour, 1994; Maskall et al., 1996; Karczewska, 1996) have been conducted. These studies show that the slags and soils are generally enriched in many of the same metals that were present in the ores being smelted, and that the metals can occur in very high concentrations from several hundreds to several thousands of

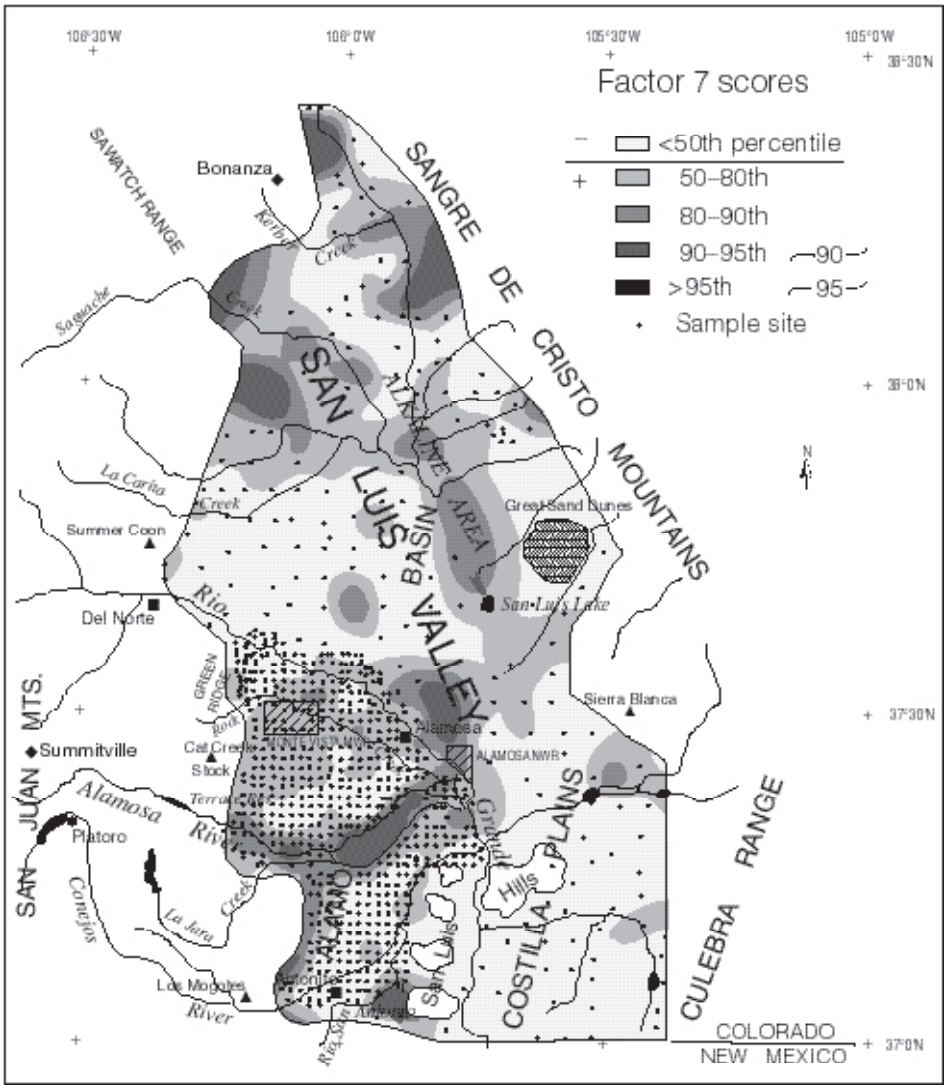


FIGURE 3.27—Map of the San Luis Valley, south-central Colorado, showing contours of factor 7 scores in soil samples for the As-Cu element association, as determined by R-mode factor analysis of the soil geochemistry data. Darker shades within contours indicate a greater component of the As-Cu element association in the geochemical makeup of soils. Note the very high levels in the floodplain sediments and soils of the Alamosa River alluvial fan in the SW corner of the valley. Figure modified from Tidball et al. (1995).

ppm. The availability of the metals from slag is a function of the slag mineralogy, the degree to which more reactive minerals are encapsulated by less reactive phases, and the way in which the slag is cooled. The metal content of slag can be provided by remnant sulfides of the metals contained in the ores (Montour, 1994), or by less reactive oxide minerals, silicate minerals, or glass phases (Parsons et al., 1998). Slag poured on the ground surface to cool generally has lower metal availability than slag frothed into the air to cool (J. Drexler, oral commun., 1993). Metal availability in soils affected by particulate smelter emissions is a function of the clay, organic, and moisture contents of the soil (e.g., Karczewska, 1996), coupled with the mineralogical form and geochemical properties (Smith and Huyck, 1999) of the metals in the emissions.

Plant compositions

A number of plant species can take up trace metals from waters and from the soils in which they grow. A number of studies of metal uptake by plants, as well as the application of plant chemistry as a mineral prospecting technique, are summarized by Rose et al. (1979), other exploration geochemistry textbooks, journals such as the *Journal of Geochemical Exploration*, and textbooks such as Kabata-Pendias and Pendias (1984). Methods used to prepare plants for chemical analysis and to analyze the metal contents of plants are presented by Crock et al. (1999), and in the references cited in the following discussion.

Many trace elements (such as Cu, Zn, Mn, Fe, and Mo; Rose et al., 1979) are essential nutrients for plants. For example, Cu

is involved in a variety of photosynthetic, respiration, oxidation-reduction, and other metabolic processes (Gupta, 1979). Zinc also has a variety of plant physiological functions, and is commonly associated with plant proteins and enzymes. However, excessive abundances of many otherwise beneficial trace metals may have an overall toxic effect upon a plant.

Trace metal uptake from a soil depends upon: the nutritive requirements of the different plant species growing in a soil (different plant species take up metals in greatly different amounts); the depth to which the plant roots penetrate (some plants may penetrate soil and underlying bedrock to depths of many tens of feet); the concentrations and geoavailabilities of the different trace elements in the soil or rocks in which the plant is growing; and the geochemical conditions within the soil (pH, soil moisture, oxidation state, organic matter content, etc.). Once taken up, trace elements may be stored in different concentrations in different parts of a plant such as the leaves, twigs, roots, and bark of a tree.

Many trace elements (such as Cu) are essential nutrients for plant-eating animals. However, the concentrations of particular trace elements in plants growing on mineralized rocks may reach sufficiently elevated levels that the plants become toxic to the animals that consume them. For example, selenosis and molybdenosis are two diseases in cattle that develop as a result of the cattle eating Se-rich (selenosis) or Mo-rich, Cu-poor (molybdenosis) forage.

The potential effects of acid-mine drainage from open-pit mining at Summitville on the metal contents of San Luis valley crops irrigated with Alamosa River water were a substantial concern in the years immediately following the mine closure. To address these concerns, studies were carried out in 1993 to measure the metal contents of SW San Luis valley alfalfa (Erdman et al., 1995, 1997), barley (Stout and Emerick, 1995), and wheat and potatoes (Cardon et al., 1995). Crops irrigated with Alamosa River water were found to have concentrations of various metals (such as Cu, Ni, and Mn) that were statistically higher than those of SW San Luis valley crops irrigated with near-neutral pH water from other sources (see Fig. 3.28 for the study results for alfalfa). However, the concentrations of these metals were also found to be well within the ranges of metal concentrations measured in these crops from throughout the United States. In the case of alfalfa (Fig. 3.28), the 1993 metal concentrations were well below levels considered toxic to cattle (Erdman et al., 1995). However, later sampling carried out in 1994 and 1995 (Erdman et al., 1997) indicated that concentrations of Cu in the alfalfa were increasing and beginning to approach potentially toxic levels for sheep, underscoring the need for environmental remediation at Summitville, and continued crop monitoring.

Gough et al. (1995) measured the metal content of tree rings in aspens and cottonwoods growing along the Alamosa River, to chart the spatial and temporal variations in metal contents of the river waters. Although the temporal trends (across ~30 years of tree rings) and spatial trends proved inconclusive for most elements measured, Gough et al. (1995) concluded that the analytical method used and the approach of dendrochemical trace element measurements hold promise for tracking metal variations over time, in spite of processes such as metal translocation across tree rings that tend to blur temporal metal variations. Gough et al. (1995) also list a number of useful references on trace metal uptake by trees and dendrochemical analytical methods.

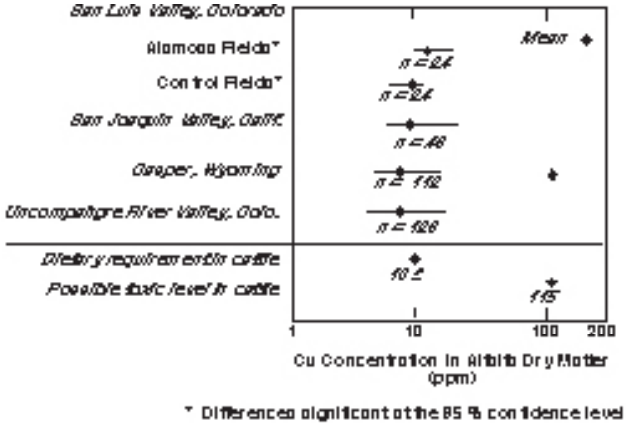


FIGURE 3.28—Plot comparing the Cu concentrations of alfalfa from fields irrigated with Alamosa River water ("Alamosa Fields") to those of alfalfa from SW San Luis Valley fields irrigated with water from other sources ("Control Fields"), and alfalfa from elsewhere in the United States. Also shown is the dietary requirement for Cu in alfalfa fed to cattle, and the possible level of Cu in alfalfa that is toxic to cattle. Figure modified from Erdman et al. (1995). References for other data sources included on figure are also given in Erdman et al. (1995).

GEOLOGY-BASED GEOENVIRONMENTAL MINERAL DEPOSIT MODELS

As shown by the discussion in the preceding sections, the same geologic characteristics that allow economic geologists to classify or type mineral deposits also play key roles in controlling the pre-mining and mining-related environmental signatures of mineral deposits. In the same way that economic geologists can develop deposit models for diverse mineral-deposit types (Cox and Singer, 1986; Kirkham et al., 1993), geology-based geoenvironmental models can also be developed for the same mineral deposit types (Plumlee and Nash, 1995; du Bray, 1995) that interpret the deposits' environmental characteristics in a geologic context.

A preliminary compendium of descriptive geoenvironmental deposit models developed by the U.S. Geological Survey is presented in du Bray (1995). The geoenvironmental models are based on and extend the mineral deposit models originally included in Cox and Singer (1986) and Bliss (1992). The working definition of a geoenvironmental mineral deposit model given by Plumlee and Nash (1995) in the introduction of the du Bray volume is: "A compilation of geologic, geochemical, geophysical, hydrologic, and engineering information and data pertaining to the environmental behavior of geologically similar mineral deposits (a) prior to mining, and (b) resulting from mining, mineral processing, and smelting."

For a given deposit type the geoenvironmental models included in du Bray (1995) summarize:

- Pertinent environmental geology characteristics, such as sulfide mineralogy, textures, and resistance to weathering; gangue mineralogy, textures, and resistance to weathering; wallrock alteration; host rock lithology; mineral zoning; trace element contents of the deposit and its host rocks; structural, lithologic controls on ground-water flow; and the nature and extent of

pre-mining oxidation.

- Pertinent information on potential past and present mining methods (i.e., open-pit, underground, or block caving) and processing methods (froth flotation and roasting or smelting; jig concentration; mercury amalgamation; crushing, roasting, and cyanidation; crushing and cyanide heap leaching).
- As a function of climate, empirical data (where available) on environmental signatures from all mineralogic zones or ore types, including: pre-mining baseline geochemical conditions (compositions of seeps, soils, and stream sediments); compositions of mine-drainage, tailings, or cyanide heap leach waters; metal mobility from mine dumps, tailings, or smelter slag; smelter signatures in soils; and environmental effects on the surrounding ecosystem or watershed (which are a function of geology and climate).
- Useful geophysical techniques to identify, delineate, and monitor, environmental signatures associated with mined and unmined mineral deposits.
- Geoscientific guidelines for potential remediation/mitigation strategies.

Although the preliminary geoenvironmental mineral deposit models originally presented in du Bray (1995) are still evolving in concept and content (see Wanty et al., 1999 in press), they provide a very useful way in which to interpret and summarize the environmental signatures of mining and mineral deposits in a systematic geologic context. They cannot and should not be used to predict the absolute pH and metal concentrations that will develop from a particular mine dump in a particular ore zone of a particular mineral-deposit type. The models also should not be used in place of field characterization and study of mine sites. Rather, the models are best used as a series of geologic guidelines about the potential range of environmental signatures that may have been present in a district prior to mining, that may exist in a mining district as a result of historic mining activity, or that may develop as a result of mining a particular deposit (and therefore need to be accounted for in prevention and mitigation strategies).

The models underscore the utility of and need for the compilation and interpretation of empirical environmental data in a geologic context. An empirical study of mine waters draining diverse mineral deposit types presented by Plumlee et al. (1999) in the accompanying volume illustrates the utility of this empirical approach. However, the geoenvironmental models of specific mineral deposit types as presented in du Bray (1995) or Plumlee et al. (1999) do not provide on their own a complete estimation of potential environmental impacts of a mine site, mineral processing site, or unmined mineralized area on its surrounding ecosystem or watershed. These impacts are not only a function of the geology, climate, and mining/processing methods used for the particular deposit, but also of the bedrock geology, climate, and other characteristics of the surrounding watershed. An important next step in the development of geoenvironmental mineral-deposit models will therefore be the shift to a watershed- or ecosystem-based focus, where the deposits are considered not only in the context of their geology, but also in the context of their surrounding watersheds (Wanty et al., 1999).

SUMMARY

This paper has summarized many key geologic characteristics of mineral deposits that control their environmental signatures and their effects on the surrounding environment, both prior to mining and that may result from mining and mineral processing. Careful attention to the environmental geology of mineral deposits is crucial to all aspects of mineral-resource development, from grass-roots exploration through mine development, closure, and remediation:

- *Establishment of pre-mining baseline conditions:* It is more cost-effective, technologically feasible, and realistic to remediate mine sites to the background conditions that existed in a mineralized area prior to mining, rather than to remediate to conditions found in unmineralized areas. Geologically constrained baseline data are crucial to establish reasonable pre-mining conditions for diverse deposit types in various climates. These baseline models can then be used to establish analogues for pre-mining conditions in districts where historic mining activities obscure pre-existing baseline conditions.
- *Mineral exploration:* Knowledge of the likely environmental effects associated with development of particular deposit types can be integrated into grass-roots exploration efforts. For example, development of deposit types with high geologic potential to generate very acidic mine drainage with extreme metal contents will have the lowest environmental mitigation expenses in arid climates, in deposits with extensive to complete pre-mining oxidation, or in geologic terranes with abundant carbonate rocks. Conversely, development of such acid-generating deposits in wet climates may require such expensive environmental mitigation measures as to either require high ore grades or make development non-profitable.
- *Mine planning and development:* Improved predictive capabilities provided by geologic knowledge enable mine planners to better anticipate, plan for, and mitigate potential environmental problems, rather than to try to treat (with much greater technical difficulties and costs) the environmental problems after they occur. Similarly, geologic characteristics of a particular deposit can be exploited to help mitigate potential environmental problems. For example, carbonate-bearing wallrock alteration that is often present on the fringes of deposits, or carbonate sediments that occur in the proximity of some deposits, may be useful in helping to mitigate acid drainage from sulfide-rich ore zones.
- *Remediation:* Accurate geological, geochemical, and hydrologic information (such as geologic controls on ground-water flow and ore mineralogy) is needed by engineers to develop the most effective remediation plans at mine sites. Many remedial plans implemented in the past ignored or dangerously oversimplified important geologic information. For example, adit plugging has been used or is proposed to reduce acid drainage from a number mine sites. Detailed geologic characterization is crucial to identify the location of faults or other hydrologic conduits that might reduce the effectiveness of adit plugging as a remedial solutions.
- *Abandoned mine lands issues:* Although mineral resource extraction has been carried out for several millennia, relatively little attention has been given until the last several decades to minimizing the effects of such extraction on the environment. As a result, a number of historic (meaning they were operated prior to the last several decades) mining and mineral processing sites that were abandoned once the profitable ores ran out are now potential or ongoing sources of environmental contamination. In the United States, land management agencies are currently faced with the daunting task of identifying and

prioritizing for remediation all abandoned mine sites on public lands; although a large majority of these sites will not require remediation, the total number of sites to be investigated and prioritized for remediation is likely in excess of several hundred thousand. Geologic information provides land managers with a low-cost screening technique to help identify, prioritize for study, and remediate potentially hazardous mine sites on public lands.

- *Mineral deposits in a holistic context:* In the future, as metal extraction technologies improve (such as techniques to remove metals from waters) mineral deposits may be treated in a more holistic context. For example, acid-mine waters may be viewed as economic resources rather than as environmental liabilities. Techniques to extract metals in situ, or to extract environmentally problematic metals from solid mine wastes or mineral processing wastes may reduce the need for mining with physical extraction techniques, and may turn former wastes into ores. Geologic characterization and mineral-environmental deposit models will help identify mineral deposits or mineral deposit types amenable to such a holistic treatment.

Quite simply, geologic knowledge is a fundamental and critical component of environmentally friendly mineral-resource development.

REFERENCES

Alpers, C.N., and Blowes, D.W. (eds.), 1994, Environmental geochemistry of sulfide oxidation: American Chemical Society Symposium Series 550, 681 pp.

Alpers, C.N., and Nordstrom, D.K., 1991, Geochemical evolution of extremely acid mine waters at Iron Mountain, California—Are there any lower limits to pH?, Proceedings, 2nd Internatl Conference on the Abatement of Acidic Drainage: MEND (Mine Environment Neutral Drainage), Ottawa, Canada, v. 2., pp. 321–342.

Alpers, C.N., Blowes, D.W., Nordstrom, D.K., and Jambor, J.L., 1994a, Secondary minerals and acid mine-water chemistry; *in* Jambor, J.L., and Blowes, D.W. (eds.), Short course on environmental geochemistry of sulfide mine-wastes: Mineralogical Association of Canada, Short Course Handbook, v. 22, pp. 247-270.

Alpers, C.N., Nordstrom, D.K., and Thompson, J.M., 1994b, Seasonal variations of Zn/Cu ratios in acid mine water from Iron Mountain, California; *in* Alpers, C.N., and Blowes, D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation: American Chemical Society Symposium Series 550, pp. 324-344.

Barry, T.H., 1996, The geochemistry of natural waters draining hydrothermally altered and mineralized terrains in the upper Alamosa River basin, Colorado: Unpub. M.S. thesis, Auburn Univ., 220 pp.

Bliss, J.D., 1992, Developments in mineral deposit modeling: U.S. Geological Survey Bulletin 2004, 168 pp.

Borek, S.L., 1994, Effect of humidity on pyrite oxidation; *in* Alpers, C.N., and Blowes, D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation: American Chemical Society Symposium Series 550, pp. 31–44.

Boyle, D.R., 1994, Oxidation of massive sulfide deposits in the Bathurst mining camp, New Brunswick—natural analogues for acid drainage in temperate climates; *in* Alpers, C.N., and Blowes, D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation: American Chemical Society Symposium Series 550, pp. 535–550.

Brock, T.D., 1979, Biology of microorganisms, 3rd ed.: Prentice-Hall, Inc., Englewood Cliffs, N.J., 802 pp.

Cardon, G.E., Ali, A.Y., McCann, J., and Lorenz, A., 1995, Metal content of wheat and potato tissue and associated soils irrigated with Alamosa river water; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 281–285.

Cathles III, L.M., 1997, Thermal aspects of ore formation; *in* Barnes, H.L. (ed.), Geochemistry of Hydrothermal Ore Deposits, Third Edition: John Wiley and Sons, New York, pp. 191-228.

Chaffee, M.A., 1980, Interpretation of geochemical anomalies in soil samples from a smelter-contaminated area, Eureka mining district, Nevada [abs.]: Technical Program, American Institute of Mining, Metallurgical, and Petroleum Engineers Annual Meeting, February, 1980, Las Vegas, Nev., pp. 56–57.

Chaffee, M.A., 1987, Application of R-mode factor analysis to geochemical studies in the Eureka mining district and vicinity, Eureka and White Pine counties, Nevada; *in* Elliott, I.L., and Smee, B.M. (eds.), GEOEXPO/86, Exploration in the North AMerican Cordillera: The Association of Exploration Geochemists, Vancouver, Canada, pp. 94–108.

Church, S.E., Holmes, C.W., Briggs, P.H., Vaughn, R.B., Cathcart, J., and Marot, M., 1993, Geochemical and Pb-isotope data from stream and lake sediments, and cores from the upper Arkansas RIver drainage—effects of mining at Leadville, Colorado, on heavy-metal concentrations in the Arkansas River: U.S. Geological Survey Open-File Report 93–534, 61 pp.

Church, S.E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J., and Vaughn, R.B., 1997, Source, transport, and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado: U.S. Geological Survey Open-File Report 97–151, 135 pp.

Church, S.E., Alpers, C.N., Vaughn, R.B., and Briggs, P.H., 1999, Use of lead isotopes as natural tracers of metal contamination—a case study of the Penn Mine and Camanche Reservoir, California; *in* Filipek, L.H., and Plumlee, G.S. (eds.), The Environmental Geochemistry of Mineral Deposits, Part B. Case Studies and Research Topics: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 567–582.

Cox, D.P., and Singer, D.A. (eds.), 1986, Mineral deposit models: U.S. Geological Survey Bulletin 1693, 379 pp.

Crandell, D.R., 1971, Postglacial lahars from Mount Rainier volcano, Washington: U.S. Geological Survey Professional Paper 677, 75 pp.

Crock, J.G., Arbogast, B.F., and Lamothe, P.J., 1999, Laboratory methods for the analysis of environmental samples; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 265–287.

Crowley, J.K., and Zimbelman, D.R., 1997, Mapping hydrothermally altered rocks on Mount Rainier, Washington, with Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) data: Geology, v. 25, pp. 559–562.

Davis, A., Ruby, M.V., and Bergstrom, P.D., 1992, Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district: Environmental Science and Technology, v. 23, pp. 461–468.

Deer, W.A., Howie, R.SA., and Zussman, J., 1978, An introduction to the rock-forming minerals: Longman Group, Ltd., London, 528 pp.

Deverel, S.J., and Fujii, R., 1988, Processes affecting the distribution of selenium in shallow ground water of agricultural areas, western San Joaquin Valley, California: Water Resources Research, v. 24, pp. 516–524.

Domenico, P.A., and Schwartz, F.W., 1990, Physical and chemical hydrogeology: John Wiley and Sons, New York, 824 pp.

du Bray, E.A. (ed.), 1995, Preliminary descriptive geoenvironmental models of mineral deposits: U.S. Geological Survey Open-File Report 95–231, 272 pp. (also available online at at http//:minerals.cr.usgs.gov)

Dwyer, F.J., Schmitt, C.J., Finger, S.E., and Mehrle, P.M., 1988, Biochemical changes in longear sunfish, *Lepomis megalotis*, associated with lead, cadmium, and zinc from mine tailings: Journal of Fisheries Biology, v. 33, pp. 307–317.

Eppinger, R.G., Sutley, S.J., and McHugh, J.B., 1997, Environmental geochemical study of the Nabesna gold skarn and Kennecott strata-bound copper deposits, Alaska; *in* Dumoulin, J.A., and Gray, J.G. (eds.), Geologic Studies in Alaska by the U.S. Geological Survey, 1995: U.S.

Geological Survey Professional Paper 1574, pp. 19–40.
Eisenbud, M., 1987, Environmental Radioactivity from Natural, Industrial, and Military Sources: Academic Press, San Diego, 475 pp.
Erdman, J.A., Smith, K.S., Dillon, M.A., and ter Kuile, M., 1995, Impact of Alamosa river water on alfalfa, southwestern San Luis valley, Colorado; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 263–269.
Erdman, J.A., Smith, K.S., and ter Kuile, M., 1997, Impact of the lower Alamosa river water on alfalfa, southwestern San Luis valley—1995 follow-up study of effects from the Summitville mine: U.S. Geological Survey Open-File Report 96–034, 32 pp.
Fell, J.E., Jr., 1979, Ores to Metals, The Rocky Mountain Smelting Industry: University of Nebraska Press, Lincoln, 341 pp.
Ficklin, W.H., Plumlee, G.S., and McHugh, J., 1995, Reactions of arsenic minerals and gold ores with alkaline cyanide solutions; *in* Morganwalp, D.W., and Aronson, D.A. (eds.), U.S. Geological Survey Toxic Substances Hydrology Program, Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20–24, 1993: U. S. Geological Survey Water Resources Investigations Report 94–4015.
Filipek, L.H., VanWyngarden, T.J., Papp, C.S.E., and Curry, J., 1999, A multi-phased approach to predict acid production from porphyry copper-gold waste rock in an arid montane environment; *in* Filipek, L.H., and Plumlee, G.S. (eds.), The Environmental Geochemistry of Mineral Deposits, Part B. Case Studies and Research Topics: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 433–445.
Filippidis, A., Misaelides, P., Clouvas, A., Godelitsas, A., Barbayiannis, N., and Anousis, I., 1997, Mineral, chemical, and radiological investigation of a black sand at Touzla Cape, near Thessaloniki, Greece: Environmental Geochemistry and Health, v. 19, pp. 83–88.
FitzPatrick, E.A., 1980, Soils—Their formation, classification, and distribution: Longman, London, 353 pp.
Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Prentice Hall, Englewood Cliffs, N.J., 604 pp.
Furniss, G., and Hinman, N.W., 1998, Ferricrete provides record of natural acid drainage, New World District, Montana; *in* Arehart, G.B., and Hulston, J.R. (eds.), Water-Rock Interaction, Proceedings of the 9th Internatl Symposium on Water-Rock Interaction, Taupo, New Zealand: A.A. Balkema, Rotterdam, Brookfield, pp. 973–976.
Glass, N.R., Arnold, D.E., Galloway, J.N., Henry, J.R., Lee, J.J., McFee, N.W., Norton, S.A., Powers, C.F., Rambo, D.L., and Schofeld, C.L., 1982, Effects of acid precipitation: Environmental Science and Technology, v. 16, pp. 162A–169A.
Goldich, S.S., 1938, A study in rock weathering: Journal of Geology, v. 46, pp. 17–58.
Goldfarb, R.J., Taylor, C.D., Meier, A.L., d'Angelo, W.M., and O'Leary, R.M., 1997, Hydrogeochemistry of mine-drainage waters associated with low-sulfide, gold-quartz veins in Alaska; *in* Dumoulin, J.A., and Gray, J.E. (eds.), Geologic Studies in Alaska by the U.S. Geological Survey, 1995: U.S. Geological Survey Professional Paper 1574, pp. 3–18.
Gough, L.P., Yanosky, T.M., Lichte, F.E., and Balistrieri, L.S., 1995, Preliminary interpretation of spatial and temporal trends in the chemistry of tree rings downstream from the Summitville mine; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 236–243.
Gray, J.E., and Coolbaugh, M.F., 1994, Geology and geochemistry of Summitville, Colorado—An epithermal acid-sulfate deposit in a volcanic dome: Economic Geology, Special Issue on Volcanic Centers as Exploration Targets, v. 89, no. 4., pp. 1906–1923.
Gray, J.E., Coolbaugh, M.F., Plumlee, G.S., and Atkinson, W.W., 1994, Environmental geology of the Summitville mine, Colorado: Economic Geology, Special Issue on Volcanic Centers as Exploration Targets, v. 89, no. 4., pp. 2006–2014.
Green, G.N., 1992, The digital geologic map of Colorado in ARC/INFO Format: U.S. Geological Survey Open-File Report 92–507A–O, 9 pp. (http://greenwood.cr.usgs.gov/pubs/maps/maps.html)
Griffiths, P.G., Webb, R.H., and Melis, T.S., 1996, Initiation and frequency of debris flows in Grand Canyon, Arizona: U.S. Geological Survey Open-File Report 96–491, 35 pp.
Guilbert, J., and Park, C., 1986, The Geology of Ore Deposits: W.H. Freeman and Co., New York, 985 pp.
Gupta, U.C., 1979, Copper in agricultural crops; *in* Nriagu, J. (ed.), Copper in the Environment: John Wiley and Sons, New York, pp. 255–288.
Hofstra, A.H., Leventhal, J.S., Northrop, H.R.L., Andis, G.P., Rye, R.O., Birak, D.J., and Dahl, A.R., 1991, Genesis of sediment-hosted disseminated gold deposits by fluid mixing and sulfidization—chemical-reaction-path modeling of ore depositional processes documented in the Jerritt Canyon district, Nevada: Geology, v. 19, pp. 36–40.
Holland, H.D., and Petersen, U., 1995, Living Dangerously—The earth, its resources, and the environment: Princeton University Press, Princeton, 490 pp.
Horowitz, A.J., Robbins, J.A., Elrick, K.A., and Cook, R.B., 1996, Bed sediment-trace element geochemistry of Terrace Reservoir, near Summitville, southwestern, Colorado: U.S. Geological Survey Open-File Report 96–344, 41 pp.
Jambor, J.L., 1994, Mineralogy of sulfide-rich tailings and their oxidation products; *in* Jambor, J.L., and Blowes, D.W. (eds.), Short Course on Environmental Geochemistry of Sulfide-Mine Wastes: Mineralogical Association of Canada, Short Course Handbook, v. 22, pp. 59–102.
Jambor, J.L., and Blowes, D.W. (eds.), 1994, Short course on environmental geochemistry of sulfide mine-wastes: Mineralogical Association of Canada, Short Course Handbook, v. 22, 438 pp.
Johnston, R.J., 1980, Multivariate statistical analysis in geography: Longman, London, 280 pp.
Kabata-Pendias, A., and Pendias, H., 1984, Trace Elements in Soils and Plants: CRC Press, Inc., Boca Raton, Fla., 315 pp.
Karczewska, A., 1996, Metal species distribution in top- and sub-soil in an area affected by copper smelter emissions: Applied Geochemistry, v. 11, pp. 35–42.
Kelley, K.D., and Taylor, C.D., 1997, Environmental geochemistry of shale-hosted Ag-Pb-Zn massive sulfide deposits in northwest Alaska—Natural background concentrations of metals in water from mineralized areas: Applied Geochemistry, v. 12, pp. 397–409.
Kirkham, R.D., Sinclair, W.D., Thorpe, R.I., and Duke, J.M. (eds.), 1993, Mineral deposit modeling: Geological Association of Canada Special Paper 40, 770 pp.
Kirkham, R.M., Lovekin, J.R., and Sares, M.A., 1995, Sources of acidity and heavy metals in the Alamosa River basin outside of the Summitville mining area, Colorado; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 42–57.
Kwong, Y.T.J., 1993, Prediction and prevention of acid rock drainage from a geological and mineralogical perspective: MEND Project 1.32.1, 47 pp.
Kwong, Y.T.J., 1995, Influence of galvanic sulfide oxidation on mine water chemistry; *in* Hynes, T.P., and Blanchette, M.C. (eds.), Proceedings of Sudbury '95—Mining and the Environment, v. 2, May 28–June 1, 1995, Sudbury, Ontario: CANMET, Ottawa, pp. 477–484.
Landa, E.R., 1999, Geochemical and biogeochemical controls on element mobility in and around uranium mill tailings; *in* Filipek, L.H., and Plumlee, G.S. (eds.), The Environmental Geochemistry of Mineral Deposits, Part B. Case Studies and Research Topics: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 527–538.
Lasmanis, R., Norman, D.K., and Cannon, B., 1997, Preliminary study of minerals in Tacoma smelter slags: Washington Geology, v. 25, no. 3, pp. 19–25.
Leach, D.L., Viets, J.G., and Powell, J.W., 1996, Textures of ores from the Sliesian-Cracow zinc-lead deposits, Poland—clues to the ore-forming environment; *in* Górcka, E., Leach, D.L., and Kozlowski, A. (eds.), Carbonate-hosted zinc-lead deposits in the Silesian-Cracow area, Poland: Prace Panstowowego Instytutu Geologicznego, Warsaw, Poland, pp. 37–50.

Logsdon, M.J., and Basse, B., 1991, Quantitative evaluation of Pb-Zn mine wastes for subgrade disposal—Characterization versus classification in a Superfund environment: Proceedings of the 1991 AIME Annual meeting, Denver, Colorado, Environmental Management for the 1990's, pp. 207–212.

Maskall, J., Whitehead, K., Gee, C., and Thornton, I., 1996, Long-term migration of metals at historical smelting sites: Applied Geochemistry, v. 11, pp. 43–51.

Montour, M.R., 1994, Aqueous leachability of solid forms of lead in mining and smelting wastes, Leadville, Colorado: M.S. thesis, Univ. of Colorado, Boulder, 234 pp.

Montour, M.R., Hageman, P.L., Meier, A.L., Theodorakos, P., Briggs, P.H., 1998, Leachate chemistry data for solid mine waste composite samples from Silverton and Leadville, Colorado: U.S. Geological Survey Open-File Report 98–621, 46 pp.

Nimick, D.A., and Moore, J.N., 1994, Stratigraphy and chemistry of sulfidic flood-plain sediments in the Upper Clark Fork valley, Montana; *in* Alpers, C.N., and Blowes, D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation: American Chemical Society Symposium Series 550, pp. 276–288.

Nordstrom, D.K., and Alpers, C.N., 1999, Geochemistry of acid mine waters; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 133–160.

Ortiz, R.F., von Guerard, P.B., and Walton-Day, K., 1995, Effect of a localized rainstorm on the water quality of the Alamosa River upstream from Terrace Reservoir, south-central Colorado, August 9–10, 1993; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Proceedings, Summitville Forum '95: Colorado Geological Survey Spec. Pub. No. 38, pp. 171–177.

Östlund, P., Torssander, P., Morth, C.M., and Claesson, S., 1995, Lead and sulfur isotope dilution during dispersion from the Falun mining area: Journal of Geochemical Exploration, v. 52, pp. 91–95.

Parsons, M.B., Einaudi, M.T., Bird, I.K., and Alpers, C.N., 1998, Geochemical and mineralogical controls on trace-element release from base-metal slag deposits at Penn Mine, Calaveras County, California: EOS, Transactions, American Geophysical Union, v. 79, no. 45, supplement, pp. F354.

Pasava, J., Kribek, B., and Zak, K. (eds.), 1995, Mineral deposits—from their origin to their environmental impacts, Proceedings, 3rd Biennial SGA Meeting, Prague, Czech Republic, August 1995: A.A. Balkema, Rotterdam, 1018 pp.

Pioneer Technical Services, 1994, Abandoned hardrock mine priority sites, summary report: Montana Department of State Lands, Abandoned Mines and Reclamation Bureau, Engineering Services Agreement DSL-AMRB No. 004, 314 pp.

Plumlee, G.S., 1989, Processes controlling epithermal mineral distribution in the Creede mining district: Unpub. Ph.D. thesis, Harvard University, 379 pp.

Plumlee, G.S., and Logsdon, M.J., 1999, An earth-system science toolkit for environmentally friendly mineral resource development; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 1–27.

Plumlee, G.S., and Nash, J.T., 1995, Geoenvironmental models of mineral deposits—fundamentals and applications; *in* du Bray, E.A. (ed.), Preliminary compilation of descriptive geoenvironmental mineral deposit models: U.S. Geological Survey Open-File Report 95–831, pp. 1–9.

Plumlee, G.S., and Whitehouse-Veaux, P. H., 1994, Mineralogy, paragenesis, and mineral zoning along the Bulldog Mountain vein system, Creede District, Colorado: Economic Geology, Special Issue on Volcanic Centers as Targets for Mineral Exploration, v. 89, no. 8, pp. 1883–1905.

Plumlee, G.S., Smith, K.S., Ficklin, W.H., Briggs, P.H., and McHugh, J.B., 1993, Empirical studies of diverse mine drainages in Colorado—implications for the prediction of mine-drainage chemistry: Proceedings, 1993 Mined Land Reclamation Symposium, Billings, Mont., v. 1, pp. 176–186.

Plumlee, G.S., Gray, J.E., Roeber, M.M., Jr., Coolbaugh, M., Flohr, M., and Whitney, G., 1995a, The importance of geology in understanding and remediating environmental problems at Summitville; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 13–22.

Plumlee, G.S., Smith, K.S., Mosier, E.L., Ficklin, W.H., Montour, M., Briggs, P.H., and Meier, A.L., 1995b, Geochemical processes controlling acid-drainage generation and cyanide degradation at Summitville; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 23–34.

Plumlee, G.S., Smith, K.S., Gray, J.E., and Hoover, D.B., 1995c, Epithermal quartz-alunite deposits; *in* du Bray, E.A. (ed.), Preliminary compilation of descriptive geoenvironmental mineral deposit models: U.S. Geological Survey Open-File Report 95–831, p. 162–169.

Plumlee, G.S., Streufert, R.K., Smith, K.S., Smith, S.M., Wallace, A., Toth, M., Nash, J.T., Robinson, R., Ficklin, W.H., 1995d, Geology-based map of potential metal-mine drainage hazards in Colorado: U.S. Geological Survey Open-File Report 95–26. (also available online at http://minerals.cr.usgs.gov)

Plumlee, G.S., Smith, K.S., Montour, M., Ficklin, W.H., and Mosier, E.L., 1999, Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types; *in* Filipek, L.H., and Plumlee, G.S., (eds.), The Environmental Geochemistry of Mineral Deposits, Part B. Case Studies and Research Topics: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 373–432.

Price, J.G., Shevenell, L., Henry, C.D., Rigby, J.G., Christensen, L.G., Lechler, P.J., Desilets, M.O., Fields, R., Driesner, D., Durbin, B., and Lombardo, W., 1995, Water quality at inactive and abandoned mines in Nevada: Nevada Bureau of Mines and Geology Open-File Report 95–4, 73 pp.

Ripley, E.A., Redmann, R.E., Crowder, A.A., 1996, Environmental Effects of Mining: St. Lucie Press, Delray Beach, Fla., 356 pp.

Ritchie, J.C., and McHenry, J.R., 1984, Application of radioactive ^{137}Cs for measuring soil erosion and sediment accumulation rates and patterns—a review: Journal of Environmental Quality, v. 19, pp. 215–233.

Robbins, J.A., 1978, Geochemical and geophysical applications of radioactive lead isotopes; *in* The Biogeochemistry of Lead in the Environment: Elsevier/North Holland Biomedical Press, Amsterdam, pp. 285–383.

Rose, A.W., Hawkes, H.E., and Webb, J.S., 1979, Geochemistry in mineral exploration, 2nd ed.: Academic Press, New York, 657 pp.

Ross, Malcolm, 1999, The health effects of mineral dusts; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 339–356.

Rouse, J.V., 1974, Radiochemical pollution from phosphate rock mining and milling; *in* Hadley, R.F., and Snow, D.T. (eds.), Water Resources Problems Related to Mining: American Water Resources Association Proc. No. 18, pp. 65–71.

Runnells, D.D., Shepherd, T.A., and Angino, E.E., 1992, Metals in water—determining natural background concentrations in mineralized areas: Environmental Science and Technology, v. 26, pp. 2316–2323.

Rye, R.O., Stoffregen, R., and Bethke, P.M., 1990, Stable isotope systematics and magmatic and hydrothermal processes in the Summitville, CO, gold deposit: U.S. Geological Survey Open-File Report 90–626, 31 pp.

Sato, M., 1992, Persistency-field diagrams for sulfides and their application to supergene oxidation and enrichment of sulfide orebodies: Geochimica et Cosmochimica Acta, v. 56, pp. 3133–3156.

Schuiling, R.D., and van Gaans, P.F.M., 1997, The waste sulfuric acid lake of the TiO_2-plant at Armyansk, Crimea, Ukraine. Part II. Modeling the

chemical evolution with PHRQPITZ: Applied Geochemistry, v. 12, pp. 187–201.

Scott, K.M., Pringle, P.T., and Vallance, J.W., 1995, Sedimentology, behavior, and hazards of debris flows at Mount Rainier Washington: U.S. Geological Survey Professional Paper 1547, 56 pp.

Shevenell, L., 1996, Statewide potential evapotranspiration maps for Nevada: Nevada Bureau of Mines and Geology Report 48, 32 pp.

Sims, P.K., Drake, A.A., Jr., and Tooker, E.W., 1963, Economic geology of the Central City district, Gilpin County, Colorado: U.S. Geological Survey Professional Paper 359, 231 pp.

Smith, A.C.S., and Mudder, T.I., 1999, The environmental geochemistry of cyanide; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 229–248.

Smith, K.S., 1999, Metal sorption on mineral surfaces—An overview with examples relating to mineral deposits; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 161–182.

Smith, K.S., and Huyck, H.L.O., 1999, An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 29–70.

Smith, K.S., Plumlee, G.S., and Ficklin, W.H., 1994, Predicting water contamination from metal mines and mining waste; Notes, Workshop No. 2, Internatl Land Reclamation and Mine Drainage Conference and 3rd Internatl Conference on the Abatement of Acidic Drainage: U.S. Geological Survey Open-File Report 94–264, 112 pp.

Smith, K.S., Mosier, E.L., Montour, M.R., Plumlee, G.S., Ficklin, W.H., Briggs, P.H., and Meier, A.L., 1995, Yearly and seasonal variations in acidity and metal content of irrigation waters from the Alamosa River, Colorado; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 293–297.

Stoffregen, R.E., 1987, Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado: Economic Geology, v. 82, pp. 1575–1591.

Stout, P.R., and Emerick, J.C., 1995, Metal uptake by Moravian III barley irrigated with water affected by acid mine discharge in San Luis valley, Colorado; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 272–280.

Stumm, W., and Morgan, J.J., 1981, Aquatic chemistry—An introduction emphasizing chemical equilibria in natural waters: John Wiley and Sons, New York, 780 pp.

Sverdrup, H.U., 1990, The kinetics of base cation release due to chemical weathering: Lund University Press, Lund, 246 pp.

Thornton, I., 1995, Metals in the global environment—facts and misconceptions: Internatl Council on Metals in the Environment, Ottawa, 103 pp.

Tidball, R.R., Severson, R.C., Presser, T.S., and Swain, W.C., 1991, Selenium sources in the Diablo Range, western Fresno county, California; *in* Severson, R.C., Fisher, S.E., and Gough, L.P. (eds.), Proceedings of the 1990 Billings Land Reclamation Symposium on Selenium in Arid and Semi-arid Environments, Western United States: U.S. Geological Survey Circular 1064, pp. 107–114.

Tidball, R.R., Stewart, K.C., Tripp, R.B., and Mosier, E.L., 1995, Geochemical mapping of surficial materials in the San Luis Valley, Colorado; *in* Posey, H.H., Pendleton, J.A., and Van Zyl, D. (eds.), Summitville Forum Proceedings: Colorado Geological Survey Spec. Pub. No. 38, pp. 244–262.

Tweto, O., 1979, Geologic map of Colorado: U.S. Geological Survey Geologic Map, 1:500,000 scale, 1 plate.

van Gaans, P.F.M., and Schuiling, R.D., 1997, The waste sulfuric acid lake of the TiO_2-plant at Armyansk, Crimea, Ukraine. Part I. Self-sealing as an environmental protection mechanism: Applied Geochemistry, v. 12, pp. 181–186.

Viets, J.G., Leach, D.L., Lichte, F.E., Hopkins, R.T., Gent, C.A., and Powell, J.W., 1996, Paragenetic and minor- and trace-elements studies of Mississippi Valley-Type ore deposits of the Silesian-Cracow district, Poland; *in* Górcka, E., Leach, D.L., and Kozlowski, A. (eds.), Carbonate-hosted zinc-lead deposits in the Silesian-Cracow area, Poland: Prace Panstowowego Instytutu Geologicznego, Warsaw, Poland, pp. 37–50.

Wanty, R.B., Miller, W.R., Zielinski, R.A., Plumlee, G.S., Bove, D.J., Lichte, F.E., Meier, A.L., and Smith, K.S., 1998, Uranium mobility in surface waters draining mineralized areas in the western U.S.; *in* Arehart, G.B., and Hulston, J.R. (eds.), Water-Rock Interaction, Proceedings of the 9th Internatl Symposium on Water-Rock Interaction, Taupo, New Zealand: A.A. Balkema, Rotterdam, Brookfield, pp. 1013–1016.

Wanty, R.B., Miller, W.R., Briggs, P.H., and McHugh, J.B., 1999, Geochemical processes controlling uranium mobility in mine drainages; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 201–213.

Wanty, R.B., Berger, B.R., and Plumlee, G.S., 1999 in press, Geoenvironmental models; *in* Fabbri (ed.), Proceedings, 1998 NATO Advanced Studies Institute Workshop on Geoenvironmental Models of Mineral Deposits: L. Kluwer Academic Publishers.

White, W.W., III, and Jeffers, T.H., 1994, Chemical predictive modeling of acid mine drainage from metallic sulfide-bearing waste rock; *in* Alpers, C.N., and Blowes, D.W. (eds.), Environmental Geochemistry of Sulfide Oxidation: American Chemical Society Symposium Series 550, pp. 608–630.

White III, W.W., Lapakko, K.A., Cox, R.L., 1999, Static-test methods most commonly used to predict acid-mine drainage—Practical guidelines for use and interpretation; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 325–338.

Wildeman, T.R., Cain, D., and Ramiriz, R.A.J., 1974, The relation between water chemistry and mineral zonation in the Central City Mining district, Colorado; *in* Hadley, R.F., Snow, D.T. (eds.), Water Resources Problems Related to Mining: American Water Resources Association Proc. No. 18, pp. 219–229.

Zimbelman, D.R., 1996, Hydrothermal alteration and its influence on volcanic hazards—Mount Rainier, Washington, a case history: Ph.D. thesis, University of Colorado, Boulder, 384 pp.