

Chapter 9

Secondary Minerals and Acid Mine-water Chemistry

C.N. Alpers

U.S. Geological Survey, Room W-2233, 2800 Cottage Way
Sacramento, California 95825

D.W. Blowes

Waterloo Centre for Goundwater Research, University of Waterloo
Waterloo, Ontario N2L 3G1

D.K. Nordstrom

U.S. Geological Survey, 3215 Marine Street
Boulder, Colorado 80303

J.L. Jambor

Department of Earth Sciences, University of Waterloo
Waterloo, Ontario N2L 3G1

9.1. INTRODUCTION

Waters associated with mines and mining waste are geologically unusual fluids and are of interest to geochemists because they accentuate certain types of water—rock interactions. Rates of mineral weathering are greatly accelerated during mining and mineral processing. In particular, the increased accessibility of oxygen enhances the rates of sulfide-oxidation reactions, which produce sulfuric acid and result in highly acidic waters with elevated metal concentrations.

Secondary minerals can form during weathering when solubility products are exceeded in the weathering solutions, so that states of mineral saturation or supersaturation are achieved. Mineral precipitation can take place at the surface of a mineral undergoing incongruent dissolution, or can take place in response to a number of processes that affect the weathering solutions including oxidation, dilution, mixing, evaporation, and neutralization.

Both the formation and the dissolution of secondary minerals can affect the composition of waters associated with sulfide-bearing mine wastes. For example, the formation of insoluble minerals such as anglesite (PbSO_4) can cause significant attenuation of metals close to the source of sulfide oxidation, thereby preventing significant exposure to ecosystems. On the other hand, soluble sulfate minerals formed in arid and semi-arid environments can store metals and acidity during dry periods and then release them during wet periods. This type of cycle can result in dramatic seasonal variations in metal concentrations, with undesirable impacts on biota.

In this Chapter the composition of secondary minerals commonly associated with sulfide mine-wastes are reviewed, and the geochemical and hydrologic processes that contribute to the formation and dissolution of these minerals are discussed. Some examples are given of aqueous speciation—saturation computations for water samples from sites at which secondary minerals are known to occur. This type of computation is a form of geochemical modelling that can be used to evaluate the role of secondary minerals in controlling metal solubility.

9.2. SECONDARY MINERALS AND THEIR RELATIVE SOLUBILITY

Secondary minerals have a wide range in solubility. In the following sections, minerals are discussed in groups, generally starting with the most soluble and progressing toward the least soluble. The groups are: soluble sulfates, less-soluble and insoluble sulfates, metal oxides and hydroxides, carbonates, and secondary sulfides. In addition, there is a section on miscellaneous minerals including arsenates, phosphates, and halides.

Some information is given regarding occurrences of the minerals, generally limited to the direct experience of the authors. Several available reference books and papers contain considerable additional information and references on occurrences, crystallography, crystal chemistry, and other properties of secondary minerals which are known to form in mine-waste environments (*e.g.*, Bandy, 1938; Palache *et al.*, 1951; Sabelli and Trosti-Ferroni, 1985; Williams, 1990).

9.2.1. Soluble Sulfates: Iron Minerals

Pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S) are the most abundant sulfide minerals in mine wastes, so it is not surprising that their oxidized equivalents, iron-sulfate minerals, are among the most abundant secondary minerals in this environment. The geochemistry of iron in the weathering environment is complicated by having both a ferrous (Fe^{II}) and a ferric (Fe^{III}) oxidation state. Table 9.1 lists the end-member compositions of some iron-sulfate minerals, including Fe^{II} sulfates, Fe^{III} sulfates, and mixed Fe^{II} - Fe^{III} sulfates. All of the minerals listed in Table 9.1 are highly soluble; they

form as efflorescent salts from waters containing iron and sulfate, the products of pyrite and pyrrhotite oxidation, by a combination of processes that includes evaporation and Fe^{II} oxidation. The Fe^{II} sulfates occur commonly, whereas the Fe^{II} - Fe^{III} sulfates are known from many fewer localities. Copiapite is the most common of the Fe^{II} - Fe^{III} sulfates; bilinite and voltaite are extremely rare. Among the Fe^{III} sulfates, coquimbite is the most common.

Table 9.1. Selected soluble iron-sulfate minerals

	Mineral	Formula	Color
Fe^{II}	melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	pale blue-green
	ferrohexahydrite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 6\text{H}_2\text{O}$	white
	siderotil	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$	white
	rozenite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$	white
	szomolnokite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot \text{H}_2\text{O}$	white, green
	halotrichite	$(\text{Fe}^{\text{II}})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	white, green
Mixed Fe^{II}-Fe^{III}	copiapite	$\text{Fe}^{\text{II}}\text{Fe}_4^{\text{III}}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	yellow
	bilinite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	orange
	römerite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$	brown, pink
	voltaite	$\text{K}_2\text{Fe}^{\text{II}}_3\text{Fe}_4^{\text{III}}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$	black, green
Fe^{III}	coquimbite	$\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	purple, white
	kornelite	$\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$	pink
	rhomboclase	$\text{HFe}^{\text{III}}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	cream
	ferriccopiapite	$\text{Fe}_3^{\text{III}}(\text{SO}_4)_6\text{O}(\text{OH}) \cdot 20\text{H}_2\text{O}^*$	yellow, orange

* Sabelli and Trosti-Ferroni (1985)

At pH values below about 4, ferric iron is the dominant oxidant of pyrite (Nordstrom, 1982a), by the reaction



Probably the most common of the minerals in Table 9.1 is melanterite $\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$, which forms by combining the first two products of reaction (1). Pure melanterite is pale blue-green, and can occur as stalactites in open mine-tunnels (e.g., Richmond mine, Iron Mountain, California; Alpers and Nordstrom, 1991), or as pore-filling cement in the hardpan layer of sulfide tailings (e.g., Heath Steele, New Brunswick; Blowes and Jambor, 1990). Inclusion of orange-brown Fe^{III} -rich pore water or Fe-hydroxide minerals in melanterite can cause an apparent dark green color, but

the color of the inclusion-free mineral remains pale blue-green.

All of the iron-sulfate minerals listed in Table 9.1 are hydrous compounds, with 1 to 22 waters of hydration per mole. As a result, each mineral has a stability range defined by temperature and water activity (or relative humidity). With increasing temperature and/or decreasing water activity, melanterite may dehydrate to rozenite $\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$ or szomolnokite $\text{Fe}^{\text{II}}\text{SO}_4 \cdot \text{H}_2\text{O}$. The presence of solid-solution substitutions can have an effect on the product. For example, Jambor and Traill (1963) noted that, under identical conditions, copper-free melanterite dehydrated to rozenite, but copper-bearing melanterite transformed to the pentahydrate, siderotil. It should be noted that the preservation of potentially unstable hydrous minerals is facilitated by immersing the samples in mineral oil, which retards dehydration and deliquescence reactions by sharply reducing contact with the atmosphere.

The stoichiometrically simple Fe^{III} -sulfate salts are coquimbite $\text{Fe}^{\text{III}}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and the rare minerals quenstedite $\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$, kornelite $\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, and lausenite $\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. Coquimbite is a relatively common oxidation product of pyrite in highly oxidized environments. In the underground workings of the Richmond mine at Iron Mountain, California, kornelite occurs together with szomolnokite at temperatures of 45–50 °C; these less-hydrous phases are more stable at elevated temperatures caused by the exothermic nature of pyrite oxidation. Such temperatures occur in some massive-sulfide workings and within actively oxidizing waste-rock and leaching, piles (*e.g.*, Cathles, 1994; Guo and Parizek, 1994).

An alternative way to write the formula for rhomboclase $\text{HFe}^{\text{III}}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, is $(\text{H}_3\text{O})\text{Fe}^{\text{III}}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, indicating the presence of the hydronium ion. For the latter formula, an overall reaction to form this mineral by pyrite oxidation would be



showing that the acidity from pyrite oxidation (*e.g.*, equation 1) could be stored in solid form until released by subsequent rhomboclase dissolution. Rhomboclase is known from relatively few localities (*e.g.*, Iron Mountain, California; Alpers and Nordstrom, 1991), but possibly it occurs in trace amounts as a receptor for hydronium ions when acid-sulfate waters are evaporated to dryness.

Römerite is a mixed-valence iron-sulfate mineral that forms relatively late in the evolution of evaporating mine-water from the Richmond mine at Iron Mountain (C. Maenz, personal communication, 1994). Crystalline römerite is brown. A fine-grained pink phase that forms as an alteration product of other Fe-sulfate minerals in the laboratory gives a weak X-ray diffraction pattern for römerite, suggesting that this mineral may be stable relative to other Fe sulfates at laboratory conditions. Römerite has been noted to occur in coal spoils (Cravotta, 1994) and in base-metal mine-waste

settings (Alpers and Nordstrom, 1991).

Voltaite is distinct among the iron-sulfate minerals listed in Table 9.1 because it has essential K in its structure. Although rare, it forms abundant, distinctive aggregates of dark green-to-black octahedral crystals in the Richmond mine at Iron Mountain (Alpers and Nordstrom, 1991). Copiapite and ferriccopiapite generally occur as fine-grained yellow crusts. These minerals are occasionally mistaken for jarosite (discussed in a later section) or native sulfur.

Halotrichite, pickeringite, and bilinite are end-member minerals of the halotrichite group of general formula $A^{II}B_2^{III}(SO_4)_4 \cdot 22H_2O$. The divalent site A can be filled by Mg, Fe^{II}, Mn and other transition metals, and the trivalent site B is filled by Fe^{III}, Al, or Cr. Halotrichite-group minerals may occur as very fine acicular needles, or as blanket-like aggregates; microscopically filiform aggregates have been observed as white blooms on sulfate-bearing mine wastes, and halotrichite *per se* is known to occur on coal spoils and coal outcrops. Natural occurrences of soluble iron-sulfate minerals in coals and sulfide ores have been described by numerous authors (*e.g.*, Kossenbergh and Cook, 1961; Bol'shakov and Ptushko, 1971; Cody and Biggs, 1973; Zodrow and McCandlish, 1978; Zodrow *et al.*, 1979; Raymond *et al.*, 1983; Wiese *et al.*, 1987).

9.2.2. Soluble Sulfates: Other Elements

Many elements other than iron can form soluble sulfate minerals. Some of the more common phases and their end-member formulas are listed in Table 9.2. As with the iron sulfates, the various hydration states for each metal sulfate have stability fields that are a function of temperature and water activity.

Table 9.2. Some soluble sulfate minerals

Mineral	Formula	Mineral	Formula
epsomite	$MgSO_4 \cdot 7H_2O$	anhydrite	$CaSO_4$
hexahydrate	$MgSO_4 \cdot 6H_2O$	retgersite	$NiSO_4 \cdot 6H_2O$
goslarite	$ZnSO_4 \cdot 7H_2O$	chalcantithite	$CuSO_4 \cdot 5H_2O$
bianchite	$ZnSO_4 \cdot 6H_2O$	alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$
gunningite	$ZnSO_4 \cdot H_2O$	mirabilite	$Na_2(SO_4) \cdot 10H_2O$
gypsum	$CaSO_4 \cdot 2H_2O$	thenardite	$Na_2(SO_4)$

Formation of the end-member phases in Table 9.2, with the exception of the Ca sulfates, takes place from weathering solutions with relatively low concentrations of Fe²⁺. Otherwise, the divalent metals such as Cu, Zn, Ni, Mg, and Mn are likely to be incorporated as solid-solution components of Fe^{II}-bearing salts. For example, the following melanterite compositions were determined for stalactites from the Richmond

mine at Iron Mountain (Alpers *et al.*, 1994): $\text{Fe}_{.930}\text{Zn}_{.035}\text{Cu}_{.019}\text{Mg}_{.016}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (mean of three analyses), and from another sample, $\text{Fe}_{.534}\text{Zn}_{.281}\text{Cu}_{.142}\text{Mg}_{.043}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (mean of two analyses). No discrete Zn, Cu, or Mg sulfate phases were observed in association with these melanterites.

There are two distinct mechanisms that can lead to the formation of non-FeII-bearing sulfates in mines and mine-waste environments. Oxidation of deposits (or portions thereof) rich in base-metal sulfides containing Cu and Zn with only minor amounts of Fe sulfide present can result in Fe^{2+} -poor waters that may precipitate sulfate minerals such as those in Table 9.2. An alternative process is the oxidation of sulfide deposits containing Fe sulfides, which leads to the formation of Fe^{2+} -rich waters (*e.g.*, reaction 1) also containing other base metals. Metal sulfate minerals in Table 9.2 may precipitate from these waters after the predominant Fe^{2+} is removed from solution, *e.g.*, by oxidation to Fe^{3+} and precipitation as Fe^{III} oxide or hydroxide minerals (see Section 9.2.4.).

Nickel sulfates that form in the weathering environment are morenosite $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, regersite $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (tetragonal), and nickel-hexahydrite (monoclinic, isomorphous with members of the hexahydrite group). None of these minerals has yet been found associated with mine wastes. Solid solution of Ni^{2+} substituting for X in the $\text{XSO}_4 \cdot n\text{H}_2\text{O}$ minerals (Tables 9.1 and 9.2) is expected to occur, but has not yet been documented.

9.2.3. Less Soluble Sulfate Minerals

a. Alunite-jarosite Group

The alunite-jarosite group consists of a large number of isostructural rhombohedral minerals with the general formula $\text{AB}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$, where the A site is filled by monovalent K, Na, H_3O , NH_4 , Ag, or $1/2$ Pb, and the B site is filled by trivalent Fe or Al. End-member formulas corresponding to various combinations of A and B are given in Table 9.3.

Table 9.3. Less soluble sulfates: some minerals of the alunite group

Mineral	Formula	Mineral	Formula
jarosite	$\text{KFe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$	alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$
natrojarosite	$\text{NaFe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$	natroalunite	$\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$
hydronium jarosite	$(\text{H}_3\text{O})\text{Fe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$	ammonioalunite	$(\text{NH}_4)\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$
ammoniojarosite	$(\text{NH}_4)\text{Fe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$	osarizawaite	$\text{PbCuAl}_2(\text{SO}_4)_2(\text{OH})_6$
argentojarosite	$\text{AgFe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$	beaverite	$\text{PbCuFe}_2^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$
plumbojarosite	$\text{Pb}_{0.5}\text{Fe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$		

The derivative phases beaverite and osarizawaite have one mole of Cu^{II} on the B site, with the resulting charge imbalance satisfied with a full mole of Pb on the A site rather than $1/2$ mole as in plumbojarosite. Other members of the alunite family not shown in Table 9.3 include minamiite and its derivatives, which contain $1/2$ mole of Ca or Ba on the A site (Li *et al.*, 1992). Alunite and the other Al-bearing members of the alunite-jarosite group can form either hydrothermally or during weathering. Hydrothermal alunite is an essential component of the acid-sulfate (or advanced argillic) alteration type (Meyer and Hemley, 1967) which is abundant in epithermal systems and in the upper levels of some porphyry copper deposits (*e.g.*, El Salvador, Chile: Gustafson and Hunt, 1975; La Escondida, Chile: Alpers and Brimhall, 1988, 1989). The same duality of genesis applies to jarosite, although hydrothermal occurrences are much rarer than those by weathering. Considerable effort has gone into distinguishing alunite and jarosite formed under hydrothermal (hypogene) *versus* weathering (supergene) conditions, for the purposes of metal prospecting. Such efforts include stable isotopes (Rye *et al.*, 1992) and unit-cell dimensions calculated from powder X-ray diffraction patterns (Stoffregen and Alpers, 1992).

Alunite-jarosite minerals of supergene origin are commonly found in the weathered zone of sulfide ore deposits; therefore, it is reasonable to suppose that the deposition of these phases will affect the chemistry of weathering solutions. However, apparent supersaturation of surface waters with respect to alunite and jarosite is commonly observed when speciation—saturation analysis is performed (*e.g.*, Nordstrom, 1977, 1982b; Chapman *et al.*, 1983; van Breemen, 1985). This suggests that kinetic barriers may prevent the rapid precipitation of alunite, jarosite, and related minerals. Alunite has been observed to be actively forming at a small number of localities, including naturally acidic lakes in southeastern Australia (Alpers *et al.*, 1992; Long *et al.*, 1992), and in an acid mine-water mixing with a CO_2 -rich, saline spring discharge in Colorado. These observations suggest that the presence of high ionic strength may help to overcome kinetic barriers to alunite precipitation.

Supersaturation of weathering solutions is less likely to occur for jarosite than for alunite. Thermodynamic calculations of saturation indices should take into account the fact that jarosite-group minerals formed during weathering tend to incorporate 10 to 20 mole percent H_3O on the A site (Kubisz, 1964; Brophy and Sheridan, 1965; Dutrizac, 1983). For example, Alpers *et al.* (1989) described the solubility of a jarosite solid solution $[\text{K}_{0.75}(\text{H}_3\text{O})_{0.20}\text{Na}_{0.05}]\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ from acid mine-water aged 12 years. The erroneous assumption of end-member compositions in saturation-index calculations can lead to errors of more than one order of magnitude with regard to apparent supersaturation (Alpers *et al.*, 1989).

b. Other Hydroxy-sulfate Minerals

Table 9.4 gives formulas for a number of other hydroxy-sulfate minerals of Fe^{III}

and Al. Nordstrom (1982b) provided a detailed discussion of mineral solubility and stability relations in the $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ system. The minerals jurbanite and basaluminite have been found in mine-drainage settings, but the most common phase in this system seems to be an amorphous (or poorly crystalline) Al hydroxy-sulfate of basaluminite stoichiometry (Nordstrom *et al.*, 1984). A common setting for the occurrence of such an aluminous precipitate is the confluence of an acidic ($\text{pH} < 5$), Al-rich surface water with a neutral water that brings the confluent pH to > 5 .

Table 9.4. Other less-soluble iron- and aluminum-sulfate minerals

Mineral	Formula	Mineral	Formula
fibroferrite	$\text{Fe}^{\text{III}}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$	jurbanite	$\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$
amarantite	$\text{Fe}^{\text{III}}(\text{SO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$	hydrobasaluminite	$\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 12\text{-}36\text{H}_2\text{O}$
schwertmannite	$\text{Fe}_8^{\text{III}}\text{O}_8(\text{SO}_4)(\text{OH})_6$	basaluminite	$\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot \text{H}_2\text{O}$

The geochemistry of ferric iron has certain parallels to that of aluminum, including the occurrence of poorly crystalline hydroxy-sulfate phases. Schwertmannite, an iron oxyhydroxide with essential sulfate, is derived structurally from akaganéite, an iron oxyhydroxide with essential chloride (Bigham *et al.*, 1990; Murad *et al.*, 1994; Bigham, this Volume).

Copper also occurs commonly as hydroxy-sulfate minerals of intermediate solubility. Antlerite and brochantite (Table 9.5) are characteristic green-colored copper minerals that occur in oxidized zones. The hydrated minerals with brochantite stoichiometry (*e.g.*, wroewolfeite) are much less common.

Table 9.5. Other less-soluble sulfate minerals

Mineral	Formula
celestite	SrSO_4
anglesite	PbSO_4
barite	BaSO_4
antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$
brochantite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$
langite, wroewolfeite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$
posnjakite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$

The alkali-earth elements generally form poorly soluble to insoluble sulfate minerals. The most notoriously insoluble mineral of this type is barite BaSO_4 , which is used in various analytical schemes as a medium for quantitative precipitation of sulfate from solution. Anglesite PbSO_4 , was mentioned previously as a relatively insoluble compound that is responsible for the attenuation of lead close the source of sulfide

oxidation in many base-metal deposits (*e.g.*, Waite Amulet, Quebec; Blowes *et al.*, 1991). The solid solution of RaSO_4 in other alkali-earth sulfate minerals, including barite and celestite, provides an important mechanism for the attenuation of radium, which carries a significant amount of the radiation in wastes from uranium mining (Landa, 1980; Langmuir and Melchior, 1985).

9.2.4. Metal Oxides and Hydroxides: Iron and Aluminum

Some other similarities between the geochemistry of ferric iron and aluminum are that the two metals have a trivalent charge, similar ionic radii, and form minerals of similar structure and composition. An important difference between the aqueous geochemistry of these elements is the pH at which hydrolysis occurs. The first hydrolysis reaction of aluminum can be written as



Reaction (3) has a $\log K_3$ of -5.00 ± 0.04 at 25 °C, 1 bar, and the standard state of infinite dilution (Nordstrom and May, 1989). For ferric iron, the first hydrolysis reaction



has a $\log K_4$ of -2.2 (Nordstrom *et al.*, 1990) at standard conditions. The mass-action expressions corresponding to reactions (3) and (4) are:

$$K_3 = \frac{[\text{AlOH}^{2+}][\text{H}^+]}{\text{Al}^{3+}} \quad (5)$$

and

$$K_4 = \frac{[\text{FeOH}^{2+}][\text{H}^+]}{\text{Fe}^{3+}} \quad (6)$$

where brackets denote aqueous activity. Inspection of equations (5) and (6) reveals that equal activities of $\text{Al}(\text{OH})^{2+}$ and Al^{3+} are achieved at $[\text{H}^+] = K_3$, or a $\text{pH} = -\log K_3 = \text{p}K_3 = 5.0$. Similarly, equal activities of $\text{Fe}(\text{OH})^{2+}$ and Fe^{3+} are achieved at $[\text{H}^+] = K_4$, or $\text{pH} = -\log K_4 = \text{p}K_4 = 2.2$.

The minerals in Table 9.6 are among the most common of the oxide, hydroxide, and oxyhydroxides of iron and aluminum. Not all of the minerals in Table 9.6 are observed to form readily during weathering. Rather, the table is constructed to emphasize the similarities and differences between the geochemistry of ferric iron and aluminum. Thermodynamic phase relations in the $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ and $\text{Fe}_2\text{O}_3\text{—H}_2\text{O}$ systems are complicated by a large number of metastable phases with similar solubility.

Table 9.6. Iron and aluminum oxide and hydroxide minerals

Mineral	Formula	Mineral	Formula
hematite	$\alpha\text{-Fe}_2\text{O}_3$	corundum	Al_2O_3
maghemite	$\gamma\text{-Fe}_2\text{O}_3$	diaspore	AlO(OH)
magnetite	$\text{FeO}\cdot\text{Fe}_2\text{O}_3$	boehmite	AlO(OH)
goethite	$\alpha\text{-FeO(OH)}$	gibbsite	Al(OH)_3
akaganéite	$\beta\text{-FeO(OH,Cl)}$	bayerite	Al(OH)_3
lepidocrocite	$\gamma\text{-FeO(OH)}$	doyleite	Al(OH)_3
feroxyhyte	$\delta\text{-FeO(OH)}$	nordstrandite	Al(OH)_3
ferrihydrite	$\text{Fe}_5\text{HO}_4\cdot 4\text{H}_2\text{O}$, or $5\text{Fe}_2\text{O}_3\cdot 9\text{H}_2\text{O}$		

Efforts to determine stable and metastable phase relations in the Al-O-H system are not straightforward because (Hemingway and Sposito, 1989) "... no single study contains all the information necessary to support the chosen interpretations." According to Hemingway and Sposito (1989), diaspore AlO(OH) is stable relative to the Al-hydroxide phases (*i.e.*, gibbsite, bayerite) in the Al_2O_3 system at 25 °C, 1 bar. Slow growth kinetics of diaspore and gibbsite result in the control of aluminum solubility at pH values above 5.0 by a reaction that mimics gibbsite solubility (Nordstrom and Ball, 1986). Such a reaction may be caused by reversible solubility with a poorly crystalline to amorphous phase of gibbsite or similar composition, or by a surface reaction involving the exchange of Al^{3+} and 3H^+ on any mineral surface containing aluminum.

The $\text{Fe}_2\text{O}_3\text{—H}_2\text{O}$ system is similarly complicated. Hematite and goethite solubilities and stabilities are sufficiently close that grain size and surface Gibbs free energy have an important influence on the phase stability. With regard to coarse-grained minerals, goethite appears to be stable relative to hematite (Langmuir, 1969, 1971, 1972). Both goethite and hematite have slow growth kinetics at surficial temperatures, so the initial solid products from the hydrolysis of Fe^{3+} are poorly crystalline, metastable phases such as ferrihydrite (Chukhrov *et al.*, 1973; Russell, 1979) or microcrystalline goethite.

Leached cappings and gossans represent the *in situ* oxidized equivalents of porphyry-copper and massive-sulfide deposits, respectively. The mineralogy of iron in the oxidized zones of these deposits is dominated by hematite, goethite, and jarosite. The early literature dating back to the 1920s (*e.g.*, Locke, 1926; Tunell, 1930) documented the observations that "deep maroon to seal brown" hematitic iron oxide tends to remain in rocks after oxidation of supergene chalcocite-bearing ores, which

formed as the enrichment product of copper—iron sulfide protores. Increasing amounts of goethite and jarosite correlate with progressively higher ratios of pyrite:chalcocite at depth (Loghry, 1972; Alpers and Brimhall, 1989). The texture of the iron oxides (or “limonites”) also changes systematically from indigenous (in original sulfide cavities) to transported (outside sulfide cavities and in fractures) with increasing pyrite content prior to oxidation (Blanchard, 1968; Loghry, 1972) due to increased acidity and iron mobility after pyrite oxidation.

Although the chemical reaction between goethite and hematite (equation 7) involves only water and not free hydrogen ions,



pH can have an effect on the relative formation of these phases because of kinetic effects. Ferrihydrite has been shown to be the necessary precursor to hematite, to which it transforms by solid-state dehydration reaction (Schwertmann, 1985a,b, and references therein). As this transformation takes place in the presence of water, there is a competing tendency for ferrihydrite to dissolve back into solution and for the ferric iron to precipitate as fine-grained goethite. Schwertmann and Murad (1983) demonstrated that ferrihydrite aged in solutions with a wide spectrum of pH values showed considerable variation in terms of the resulting proportions of hematite and goethite. Goethite was the dominant phase below pH = 6 and above pH = 11; maximum hematite production occurred at pH = 8. These results are relevant to iron in soils, which show increasing proportions of hematite to goethite with increasing pH in the range of 4 to 6 (*e.g.*, Kämpf and Schwertmann, 1982).

Other dissolved ions may also play an important role in determining goethite *versus* hematite formation and preservation. For example, the presence of Ca and Mg in solution has been found to favor the precipitation of hematite rather than goethite, and dissolved sulfate can suppress goethite formation completely under certain conditions (*e.g.*, Torrent and Guzman, 1982). The presence of Cu^{2+} can catalyze the oxidation of Fe^{2+} to Fe^{3+} by oxygen (Thorner, 1985), leading to the precipitation of ferrihydrite-like solids which may convert to hematite if aged under favorable conditions.

Aluminum has been observed to substitute into goethite and hematite, to maximum concentrations of 33 mole % $\text{AlO}(\text{OH})$ and 14 mole % Al_2O_3 , respectively (Yapp, 1983; Schultze, 1984; Tardy and Nahon, 1985; Schwertmann, 1985a). Although both iron and aluminum are highly soluble in acid mine waters, the authors are unaware of any data showing significant aluminum substitution in iron-oxide minerals formed in mine-drainage settings. It is possible that high sulfate concentrations commonly found in acid mine drainage have some effect on minimizing the aluminum content of the resulting iron precipitates.

9.2.5. Oxides and Hydroxides: Other Elements

Ferric oxide, oxyhydroxide, and hydroxysulfate precipitates have been noted at numerous mine-waste sites (Bigham, this Volume). Although geochemical measurements and thermodynamic calculations also indicate conditions favorable for the formation of other metal oxide and hydroxide phases in mine wastes, the authors know of no location where the occurrence of these phases in tailings has been confirmed through mineralogical techniques. The absence of these metal-bearing oxides or hydroxides in mine wastes suggests that other mechanisms limit the concentrations of dissolved metals in mine-waste environments. Field and laboratory studies suggest that coprecipitation or adsorption reactions are the most likely mechanisms of metal attenuation in the absence of discrete sulfate- or carbonate-bearing precipitates. Determination of metal-removal mechanisms in systems in which adsorption or coprecipitation reactions are dominant is an area of active research. Leckie *et al.* (1980) noted that it is difficult to distinguish between coprecipitation and adsorption reactions in some environments in which ferric oxyhydroxide phases are actively precipitating. Farley *et al.* (1985) proposed that a continuum exists between the mechanisms of adsorption and precipitation, and suggested that similar theoretical tools can be used to describe both adsorption and surface precipitation.

The extent of adsorption and coprecipitation is controlled by the intensity of the coulombic attraction between the oxide surface and the dissolved ion, and by the intensity of intermolecular bonds that are formed at the mineral surface. The degree of dissolved-metal adsorption and binding to ferric oxyhydroxide surfaces is dependent on the mineralogical composition of the ferric oxyhydroxide surface and the solution characteristics, including pH, ionic strength, and the concentrations of competing cations and ligands (Davis *et al.*, 1978).

The dependence on pH and ionic strength has been attributed to variations in surface charge that result from changes in the degree of protonation of water molecules coordinated with the metal-oxide surface (Schindler, 1981). As the metal oxide is immersed in solution, water molecules orient and bind to the surface, offsetting the inherent surface charge. Dissociation and protonation of these water molecules occur in a manner that is analogous to the dissociation and protonation of water molecules in the bulk solution. Variations in the protonation of bound water molecules result in changes in the surface charge, and therefore in varying affinities for dissolved metals.

Ions attracted to mineral surfaces participate in complexation reactions or ligand-exchange reactions with surface species. Reactions at the mineral surface can be described by association constants that are analogous to those used to describe the formation of aqueous complexes (Westall, 1986). Numerous mathematical models have been developed to describe the electrostatic attraction and chemical bonding of dissolved metals to mineral surfaces (Davis *et al.*, 1978; Hohl *et al.*, 1980; Dzombak

and Morel, 1986). Although these mathematical models are based on different conceptualizations of the oxide—water interface, several are able to describe well the laboratory adsorption data (Westall and Hohl, 1980), indicating a need to characterize the nature of metal binding at the mineral surface. Current research focuses on developing more accurate descriptions of the adsorption mechanism at the mineral surface (Dzombak and Morel, 1991), and on the application of adsorption models to natural materials (Honeyman, 1984; Fuller *et al.*, 1993; Waychunas *et al.*, 1993).

a. Formation of Nickel Hydroxides

The most widespread secondary mineral of nickel in ore deposits is violarite Ni_2FeS_4 , but a variety of secondary sulfates, carbonates, and combinations that include Ni with other elements is known. For secondary oxides or hydroxides, however, only three minerals have been characterized (Table 9.7): bunsenite NiO , theophrastite $\text{Ni}(\text{OH})_2$, and jamborite $(\text{Ni}^{2+}, \text{Ni}^{3+}, \text{Fe})(\text{OH})_2(\text{OH}, \text{S}, \text{H}_2\text{O})$ (Morandi and Dalrio, 1973). No discrete secondary nickel hydroxide or oxide phases have been found in tailings impoundments or as acid mine drainage (AMD) precipitates. It could be argued, as in the case for aluminum, that secondary nickel hydroxides are likely to be X-ray amorphous, as occurs with laboratory precipitates unless special precautions are taken. Energy-dispersion analyses of altered tailings, however, do not show nickel to be sufficiently concentrated to indicate the presence of a discrete secondary nickel phase, regardless of whether it is crystalline or amorphous.

Table 9.7. Some other oxide and hydroxide minerals, and native metals

Mineral	Formula	Mineral	Formula
pyrolusite	MnO_2	cuprite	Cu_2O
hausmannite	Mn_3O_4	delafossite	CuFeO_2
manganite	$\gamma\text{-MnO}(\text{OH})$	bunsenite	NiO
pyrochroite	$\text{Mn}(\text{OH})_2$	theophrastite	$\text{Ni}(\text{OH})_2$
todorokite	$(\text{Mn}^{\text{II}}, \text{Ca}, \text{Mg})\text{Mn}_3^{\text{IV}}\text{O}_7 \cdot \text{H}_2\text{O}$	jamborite	$(\text{Ni}^{2+}, \text{Ni}^{3+}, \text{Fe})(\text{OH})_2(\text{OH}, \text{S}, \text{H}_2\text{O})$
rancieite	$(\text{Ca}, \text{Mn}^{\text{II}})\text{Mn}_4^{\text{IV}}\text{O}_9 \cdot 3\text{H}_2\text{O}$	native copper	Cu
tenorite	CuO	native silver	Ag

The Copper Cliff tailings area at Sudbury, Ontario, contains millions of tonnes of tailings from the processing of Ni and Cu ore, with the metals occurring predominantly as pentlandite and chalcopyrite, respectively. The precipitation of secondary nickel in these tailings provides a good example of what has been found to occur for nickel and several other elements, such as Si and Al, in an oxidizing tailings environment. Figure 9.1 shows a backscattered-electron image of the remnants of a large grain of pyrrhotite, surrounded by its alteration products. In the accompanying X-ray image for Fe, the pyrrhotite grain is outlined well because of its high Fe content; the surrounding alteration material is also rich in Fe, and is predominantly goethite.

The whiteness of the dot-maps reflects the element concentrations, and as the ideal formulas for pyrrhotite and goethite have similar Fe contents (63.5 and 62.8 wt%, respectively), they should also have a similar whiteness. The pattern for goethite, however, is considerably weaker because it has been "diluted", probably mainly by excess H_2O , but also by the presence of appreciable quantities of Si and Al (not shown). As well, the X-ray map for S shows that the goethite is S-bearing, probably as sulfate. The X-ray map for Ni reveals that the pyrrhotite is slightly nickeliferous, and that Ni is dispersed in the surrounding goethite.

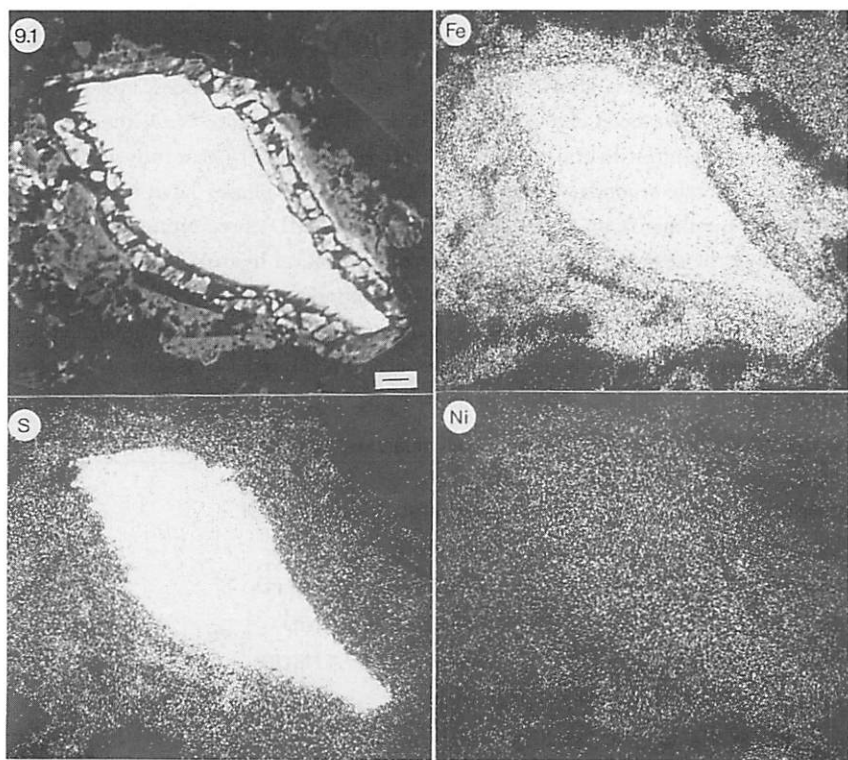


Figure 9.1. Backscattered-electron image of a margin-altered grain of pyrrhotite in a polished section of tailings from Copper Cliff, Ontario. Corresponding X-ray maps show the distributions of Fe, S, and K. Bar scale represents 10 µm.

Not all pyrrhotite or goethite is nickeliferous, but all pentlandite is. Nevertheless, the same picture emerges when pentlandite alteration rims are examined. The geochemical and mineralogical results suggest that part of the nickel remains in solution, a small part is taken up by vermiculite and associated mixed-layer phyllosilicates that form by the alteration of biotite, possibly some occurs as the expected but as-yet-undetected violarite, and the bulk is deposited with goethite.

b. Coprecipitation of Other Metals

The coprecipitation of other elements in association with secondary hydrous Fe oxides follows the same pattern as that described above for nickel. Some examples of the association are given for tailings from the Delnorte minesite, which is a former gold producer in the Timmins area of northern Ontario. Examples from any of the impoundments examined to date could have been chosen to illustrate the element associations with oxyhydroxides, but Delnorte was selected because arsenopyrite is present in the tailings, and significant amounts of pore-water arsenic generated by the dissolution of arsenopyrite and arsenic-bearing pyrite were precipitated with goethite.

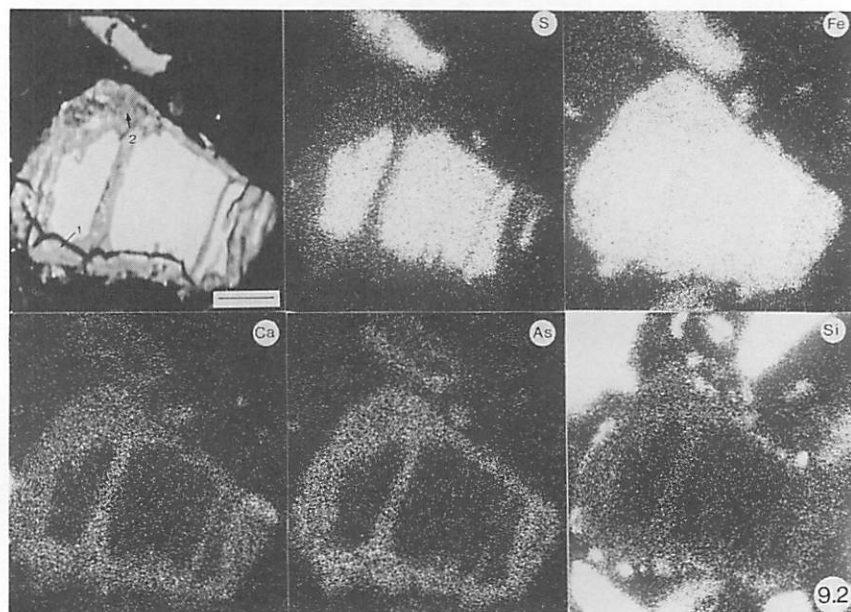
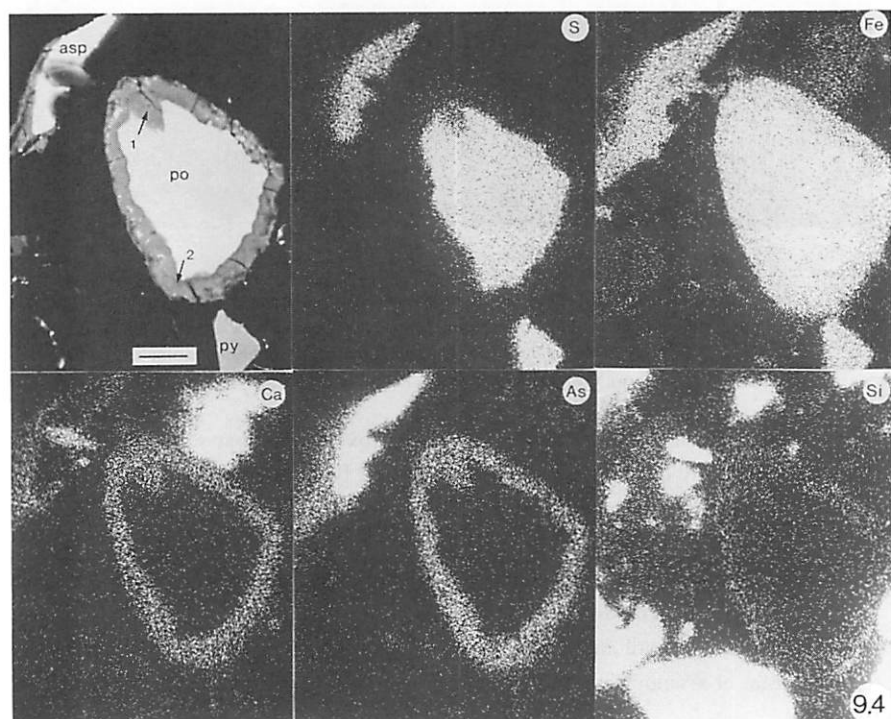
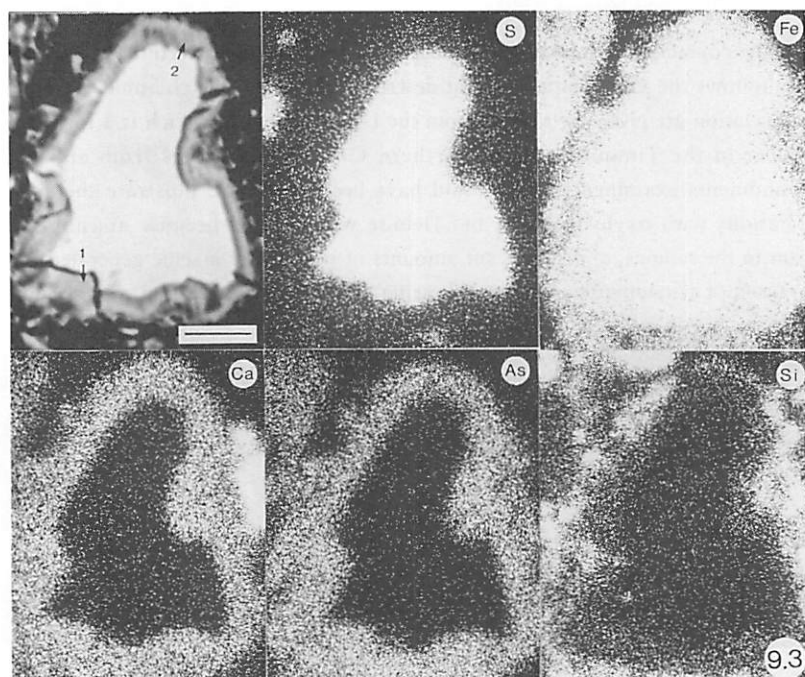


Figure 9.2. Backscattered-electron (BSE) image of a pyrrhotite grain, rimmed and veined by arsenic-rich goethite, in a polished section of tailings from the Delnorte impoundment, Ontario. Arrows point to microprobe-analyzed areas as given in Table 9.8. X-ray maps for S, Fe, Ca, As, and Si match the BSE image. Smaller, less altered grain above the pyrrhotite is pyrite. Bar scale represents 10 μm .

Figures 9.2, 9.3, and 9.4 show iron oxyhydroxide rims that surround grains of pyrrhotite. As X-ray diffraction patterns of rims and bulk, altered grains from Delnorte consistently indicate the presence of goethite, but no other iron oxyhydroxides, the rims are referred to here as goethite. Each of the pyrrhotite grains in Figures 9.2, 9.3, and 9.4 is accompanied by corresponding X-ray dot-maps to show the distributions of S, Fe, Ca, As, and Si. The distribution patterns are similar in indicating an association of Ca, As, Si, and a small amount of sulfate with the goethite. Figure 9.4 has a partly replaced grain of arsenopyrite, and its rim has element associations similar to those for



the rims on pyrrhotite.

Electron-microprobe analyses of the rims are given in Table 9.8. The results show that the sum of Ca, Si, As, and S (as oxides) ranges from 12.7 to 19.5 wt%, and averages 16.4 wt%. Substitutions of these elements at such magnitudes cannot be accommodated in the goethite structure. The arsenic content alone is much too high to be structurally incorporated, thus indicating a physical rather than a solid-solution association. The calcium content is too low to suggest the presence of a calcium arsenate, but the presence of an iron arsenate is a possibility. As no iron arsenate has been identified mineralogically, the phase is assumed to be amorphous. This assumption is reasonable in that, unlike the association of iron with other anions, iron and arsenic commonly combine to form poorly crystalline to amorphous compounds in oxidation zones.

Table 9.8. Electron microprobe analyses of goethite rims, Delnité mine, Ontario

		Figure 9.2		Figure 9.3		Figure 9.4	
		area 1	area 2	area 1	area 2	area 1	area 2
wt%	Fe ₂ O ₃	74.6	73.1	75.1	74.8	73.8	68.9
	CaO	2.1	1.4	3.2	3.4	3.4	3.1
	SiO ₂	1.5	1.7	0.0	0.9	0.9	0.9
	As ₂ O ₃	7.2	7.4	10.0	10.6	10.9	13.0
	SO ₃	<u>3.5</u>	<u>2.2</u>	<u>2.7</u>	<u>2.7</u>	<u>2.2</u>	<u>2.5</u>
	sum	88.9	85.8	91.9	92.4	91.2	88.4

Figure 9.3. BSE image and corresponding X-ray maps for a pyrrhotite grain and alteration rim, as in Figure 9.2. Bar scale represents 10 µm.

Figure 9.4. BSE image and corresponding X-ray maps for a pyrrhotite grain and its alteration rim, as in Figure 9.2. Also present are a smaller arsenopyrite grain (asp), and a small pyrite grain (py). The X-ray map for As shows that the arsenic concentrations in the goethite around the arsenopyrite and pyrrhotite are similar. Bar scale represents 10 µm.

The above example illustrates the significant role that goethite and other iron oxyhydroxides, especially ferrihydrite, can play in acting as “sinks” for various elements in an AMD environment. In a vertical oxidation zone, such as occurs in a tailings impoundment, the sink-type goethite is more amenable to dissolution than is pure goethite. With prolonged oxidation the dissolution—precipitation cycle is repeated so that the various elements gradually move downward in the oxidizing zone.

9.2.6. Carbonate Minerals

Acid neutralization by carbonate minerals is discussed by Blowes and Ptacek (this Volume). Table 9.9 lists various carbonate minerals; the most common in ore deposits and mine wastes are calcite, siderite, dolomite, and ankerite. All of the hydroxyl-bearing carbonates in Table 9.9 are secondary minerals formed by the oxidation of Zn-Cu-Pb ores.

Table 9.9. Some carbonate minerals

Rhombohedral		Double	
Mineral	Formula	Mineral	Formula
calcite	CaCO_3	dolomite	$\text{CaMg}(\text{CO}_3)_2$
magnesite	MgCO_3	kutnohorite	$\text{CaMn}(\text{CO}_3)_2$
siderite	FeCO_3	ankerite	$\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$
rhodochrosite	MnCO_3	minrecordite	$\text{CaZn}(\text{CO}_3)_2$
smithsonite	ZnCO_3		
otavite	CdCO_3		
gaspeite	NiCO_3		
sphaerocobaltite	CoCO_3		
Orthorhombic		Hydroxyl	
Mineral	Formula	Mineral	Formula
aragonite	CaCO_3	malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
strontianite	SrCO_3	azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
witherite	BaCO_3	hydrocerussite	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
cerussite	PbCO_3	hydrozincite	$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$
		aurichalcite	$(\text{Zn,Cu})(\text{CO}_3)_2(\text{OH})_6$

9.2.7. Supergene and Diagenetic Sulfides

The supergene enrichment process is important to mine-waste geochemistry from two points of view: (1) it is necessary to recognize whether ores and associated wastes may be enriched or partly enriched, as the resulting mineralogy and its oxidation properties will be distinct from primary ores and protores, and (2) enrichment

processes may become established in oxidizing waste-piles, resulting in redistribution of iron, copper, sulfur, and other elements.

Alteration of copper- and nickel-sulfide deposits results in significant enrichment of ore grades by a process involving oxidation and leaching above the water table, followed by transport of metals to a zone of more reducing conditions where secondary sulfides are formed. Table 9.10 lists the formulas of some of the copper and nickel minerals found in the supergene environment. The recent paper by Sato (1992) provides a discussion of metastable sulfide assemblages and their persistence in the oxidized zone. Reviews of supergene copper enrichment have been given by Bateman (1950), Anderson (1955), Brimhall and Crerar (1987), and Alpers and Brimhall (1989). Supergene nickel enrichment is described by Thornber (1975, 1985).

Table 9.10. Some supergene sulfide minerals

Mineral	Formula	Mineral	Formula
chalcocite	Cu_2S	spionkopite	$\text{Cu}_{1.39}\text{S}$
djurleite	$\text{Cu}_{31}\text{S}_{16}$	yarrowite	$\text{Cu}_{1.12}\text{S}$
digenite	$(\text{Cu},\text{Fe})_{1.8}\text{S}$	covellite	CuS
anilite	$\text{Cu}_{1.75}\text{S}$	violarite	Ni_2FeS_4
geerite	$\text{Cu}_{1.60}\text{S}$	millerite	NiS

Diagenesis represents the chemical, physical, and mineralogical changes that occur when sediments are buried. The diagenetic environment is generally reducing, and can be a favorable site for the reduction of sulfate and the formation of secondary sulfide minerals. Iron-sulfide minerals reported from this environment are listed in Table 9.10. Secondary iron sulfides formed in diagenetic environments are almost always fine grained, and some occur in raspberry-shaped aggregates known as framboids. There is an abundant literature on geochemical processes related to formation of sulfide minerals in the diagenetic environment, especially in tidal marshes. Some of the key publications are by Berner (1964, 1967a,b, 1980, 1984), Howarth (1979), Luther *et al.* (1982), Howarth and Giblin (1983), Canfield (1989), and Canfield and Des Marais (1991, 1993).

Iron is usually the most abundant transition metal and therefore is the most likely metal to combine with H_2S formed by sulfate reduction to produce secondary sulfides in diagenetic environments. Other divalent metals present in pore water will also tend to form sulfide minerals, as indicated in Table 9.11. The relative solubility of metal sulfides, starting from the most soluble is: $\text{MnS} > \text{FeS} > \text{NiS} \sim \text{ZnS} > \text{CdS} \sim \text{PbS} > \text{CuS} > \text{HgS}$ (DiToro *et al.*, 1991). The fixation of metals in anoxic wetlands and lake bottoms may be related to the formation of diagenetic metal sulfides.

Table 9.11. Diagenetic sulfide minerals

Mineral	Formula	Symmetry
amorphous FeS	FeS (with coprecipitated Zn, Cd, Mn, Cu, Ni, As)	—
mackinawite	(Fe,Ni) ₉ S ₈	tetragonal
smythite	(Fe,Ni) ₉ S ₁₁	trigonal
greigite	Fe ^{II} Fe ^{III} ₂ S ₄	cubic
pyrite	FeS ₂	cubic
marcasite	FeS ₂	orthorhombic

Conventional lime neutralization tends to form hydroxide and carbonate phases as the pH is raised by addition of CaO or Ca(OH)₂. A high-density-sludge process involves the addition of H₂S as a way to fix metals as secondary sulfides. The resulting sludge has improved dewatering properties. The high-density-sludge process has been chosen at Iron Mountain, California, for treatment of AMD so that the available disposal capacity for sludge in an open pit can be more efficiently utilized (U.S. EPA, 1992).

9.2.8. Miscellaneous Minerals: Arsenates, Phosphates, Halides

Secondary arsenates, phosphates, and halide minerals can form naturally in oxidized zones of *in-situ* sulfide deposits as well as in weathered zones of tailings and waste rock. Some of the more common minerals are listed in Table 9.12. The most common arsenate mineral is probably scorodite Fe^{III}AsO₄·2H₂O, which forms as an alteration product of arsenopyrite. Mansfieldite AlAsO₄·2H₂O is the aluminum analogue to scorodite and can be found in aluminum-rich environments such as the advanced argillic alteration at Summitville, Colorado (R. Stoffregen, personal communication). The solubility of scorodite has been discussed by Dove and Rimstidt (1985), Robbins (1987), and Nordstrom and Parks (1987).

Another relatively common group of arsenate minerals is the beudantite group, isostructural with alunite and jarosite. The arsenate ion AsO₄³⁻ contains the most oxidized form of arsenic, As(^v). Substitution in beudantite of AsO₄³⁻ for one of the sulfate groups in jarosite creates a charge imbalance which is satisfied by the presence of a full mole of Pb on the A site, similar to that which occurs in beaverite (Table 9.3.).

Substitution of phosphate PO₄³⁻ for SO₄²⁻ in alunite has a similar effect as for arsenate, resulting in the corkite group of minerals (Table 9.12). Other phosphate-bearing members of the extended alunite group are svanbergite, woodhouseite, and crandallite, which tend to contain Sr and (or) Ca rather than Pb. The source for phosphate in these phases is likely the destruction of primary apatite by sulfuric acid

solutions (Stoffregen and Alpers, 1987). An excellent example of compositional variability in supergene alunite-jarosite-beudantite-corkite assemblages in gossans was presented by Scott (1987). Other discussions of gossan mineralogy, textures, and geochemistry are given by Blain and Andrew (1977), Andrew (1980), and Boyle (1994).

Table 9.12. Selected phosphate, arsenate, and halide minerals

Mineral	Formula
vivianite	$\text{Fe}_3^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
strengite	$\text{Fe}^{\text{III}}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$
variscite	$\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$
berlinite	$\text{Al}(\text{PO}_4)$
crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$
svanbergite	$\text{SrAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$
woodhouseite	$\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$
corkite	$\text{PbFe}_3^{\text{III}}(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$
pyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
pseudomalachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$
scorodite	$\text{Fe}^{\text{III}}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$
mansfieldite	$\text{Al}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$
pharmacosiderite	$\text{KFe}_4^{\text{III}}(\text{AsO}_4)_3(\text{OH})_4 \cdot 6\text{--}7\text{H}_2\text{O}$
beudantite	$\text{PbFe}_3^{\text{III}}(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$
chlorargyrite	$\text{Ag}(\text{Cl}, \text{Br}, \text{I})$
bromargyrite	AgBr
boleite	$\text{Pb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$
atacamite	$\text{Cu}_4\text{Cl}_2(\text{OH})_6$
paratacamite	

Other common phosphate minerals of aluminum and iron may form when acidic water containing Al and Fe mix with phosphate-rich waters. An example is waters with high nutrients such as sewage effluent.

Supergene halides have been exploited as a high-grade surficial weathering product of sulfide ores. Many halide minerals are quite soluble, whereas others such as chlorargyrite are extremely insoluble. Halides tend to persist only in extremely dry climates, and may be present as ephemeral phases in the dry season where Cl, Br, or I are present from natural causes (*e.g.*, sea spray) or anthropogenic factors (*e.g.*, road salt).

9.3. DETERMINATION OF SOLUBILITY CONTROL

The precipitation and dissolution of secondary minerals can effectively limit the maximum aqueous concentrations of dissolved metals associated with inactive mine wastes. The approach to equilibrium can be described by the saturation index (*S.I.*) through the relationship

$$S.I. = \log \frac{I.A.P.}{K_{sp}} \quad (8)$$

where *I.A.P.* is the ion activity product determined from observed solution concentrations following the appropriate activity and speciation calculations, and K_{sp} is the theoretical solubility product adjusted to the observed water temperature. An *S.I.* <0 indicates water undersaturated with respect to a mineral phase, *S.I.* >0 indicates supersaturation, and *S.I.* = 0 indicates equilibrium conditions. Equilibrium conditions with respect to an observed mineral phase suggest that precipitation or dissolution of that phase controls the dissolved concentrations of the components contained in the phase.

Solubility controls on aqueous concentrations of dissolved metals have been inferred at many mine sites. An example is the Heath Steele mine tailings impoundment, near Newcastle, New Brunswick (Boorman and Watson, 1976; Blowes *et al.*, 1991, 1992, 1994). Oxidation of the sulfide-rich tailings has released high concentrations of dissolved metals to the tailings pore-waters, including up to 60 g/L Fe(II), 95 g/L SO₄, 6 g/L Zn, and 15 g/L Pb. Geochemical calculations conducted using PHRQPITZ (Plummer *et al.*, 1988) and MINTEQA2 (Allison *et al.*, 1990) indicated that pore-water samples collected from near the depth of a cemented hardpan layer approach saturation with respect to melanterite FeSO₄·7H₂O, gypsum CaSO₄·2H₂O, and anglesite PbSO₄ (Blowes, 1990). Mineralogical study has confirmed the presence of these phases in the shallow tailings near the depth of the hardpan layer.

Precipitation and dissolution of the sulfate-bearing secondary minerals melanterite, gypsum, and anglesite are rapid and seem to limit the dissolved concentrations of Fe(II), Ca, Pb, and SO₄. Melanterite is a soluble sulfate mineral, and high concentrations of Fe(II) >60 g/L are observed. Gypsum is less soluble, and dissolved concentrations of Ca are consistently <800 mg/L. Anglesite is relatively insoluble, and relatively low concentrations of Pb (<20 mg/L) are maintained by anglesite solubility. In contrast to anglesite, one of the more common zinc-bearing sulfate minerals, goslarite ZnSO₄·7H₂O, is very soluble, and dissolved Zn concentrations in excess of 6 g/L are observed in the shallow tailings. Below the hardpan layer the carbonate content of the tailings pore-water approaches saturation with respect to siderite FeCO₃ (Pracek and Blowes, 1994). The occurrence of siderite in the tailings has been confirmed through mineralogical study.

Precipitation and dissolution reactions can have both beneficial and detrimental effects in mine wastes. Precipitation of relatively insoluble minerals, such as anglesite, can maintain low concentrations of dissolved metals in the tailings pore-water while an increasing mass of the metal accumulates in the tailings solids. After the most intense period of sulfide oxidation and dissolved-metal release has passed, the dissolution of secondary precipitates can contribute dissolved metals to the tailings pore-waters for long periods of time. Dissolution of secondary minerals may result in increases in the concentrations of dissolved metals if the concentration of the anion contained in the mineral decreases. This may occur in a tailings impoundment as the rate of sulfide oxidation slows and SO_4 concentrations decrease. In this situation, there is potential for increases in dissolved-metal concentrations.

9.4. CONCLUDING REMARKS

This Chapter has reviewed several groups of secondary minerals that influence water chemistry in the vicinity of mine wastes. Soluble sulfate minerals of iron and other transition metals form readily from acid-sulfate drainage in virtually all climates during periods of drying. Evaporation is clearly an important mechanism in the formation of these salts and is most likely to occur at interfaces between saturated and unsaturated conditions in the presence of air.

Rapid dissolution of soluble salts occurs during wetting events and can result in significant increases in certain metal concentrations (*e.g.*, Cu, Al) during high-flow flushing events, with severe effects on ecosystems. Aqueous speciation—saturation computations can aid in interpretation of water chemistry by indicating the minerals likely to dissolve or to precipitate from water of a known composition.

Less-soluble sulfate minerals, including the hydroxy-sulfate minerals of the alunite-jarosite group, can also incorporate transition metals in solid-solution substitution. These minerals, because of their relatively slow dissolution rates, are less likely than the soluble sulfates to affect water quality adversely.

Iron and aluminum oxyhydroxide and hydroxysulfate minerals commonly precipitate from acid drainage in response to a variety of reactions, most commonly either by neutralization in response to mineral hydrolysis (see Ptacek and Blowes, this Volume) or by mixing with waters of higher pH. Oxidation of iron from Fe^{2+} to Fe^{3+} is also an important factor in the formation of secondary iron minerals. The mineralogy of secondary Fe^{III} precipitates is complex and depends on solution composition, pH, temperature, and the rate of Fe^{2+} oxidation.

Concentrations of transition metals (*e.g.*, Cu, Zn, Cd, Ni) and semi-metals (*e.g.*, As) in acid drainage are commonly affected by sorption and coprecipitation with hydrous Fe^{III} oxides. Substantial progress has been made in modelling metal sorption

processes on monomineralic substrates in the laboratory, but much work remains to be done in the quantitative application of sorption models to complex natural systems.

9.5. DISCLAIMER

This Chapter is not an authorized publication of the U.S. Geological Survey and has not received approval from the Director.