6 Metal-sulfate Salts from Sulfide Mineral Oxidation

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> *"It is plain that almost all kinds of* atramentum *are made of Earth and Water. At first they were liquid and afterwards solid, and still they can be redissolved, by heat and moisture."*
>
> Albertus Magnus (1205-1280) *Book of Minerals* (transl. D. Wyckoff, 1967)

The observation of "efflorescences," or the flowering of salts, associated with periods of dryness in soils, in closed-basin lakes, in rock outcrops, and in mines and mine wastes has been noted since early antiquity. The formation of metal-sulfate salts, in connection with the mining of metals, was a phenomenon well known to the early Greek and Roman civilizations. Alum, most commonly potash alum $KAl(SO_4)_2 \cdot 12H_2O$, which is from the Latin *alumen*, was extensively mined and used by goldsmiths, dyers, paper manufacturers, and physicians in ancient civilizations. It forms from the oxidation of pyrite in shales and slates and from oxidation of sulfurous gases in geothermal areas. The Greeks and the Romans described stalactites of *atramentum* (soluble metal-sulfate salts) that formed within mines and along rock faces (Agricola 1546, 1556). Furthermore, the toxic effects of these salts on animals were also noted. For example, in *De Natura Fossilium*, Agricola (1546) stated "…I mention the congealed acid juice which usually produces *cadmia*. It is white, hard, and so acrid that it can eat away walls, grills and even destroy all living matter." *Cadmia* is thought to be derived from the oxidation of zinc, cobalt, and arsenic sulfides, such as cobaltite. He goes on to say that "Pyrite, unless it contains sulphates, is either a golden or silver color, rarely any other, while *cadmia* is black, yellow brown, or gray. The former will cure gatherings while the latter is a deadly poison and will destroy any living substance. It is used to kill grasshoppers, mice and flies." These descriptions suggest the presence of arsenic compounds. The range of colors from white to black commonly is caused by different amounts of admixed pyrite with sulfate minerals. From the days of the Greek philosopher Theophrastus (*ca* 325 BCE) and the Greek physician Dioscorides (first century CE), the efflorescent salts *atramentum sutorium virida* or melanterite (also called *melanteria*) and *atramentum sutorium caeruleum* or chalcanthite were well known to form from the corrosion of pyrite and chalcopyrite by moisture (Agricola 1546, footnotes on p. 47-51). By the time of Pliny the Second (Caius Plinius Secundus, 23-79 CE), the names "green vitriol" for melanterite and "blue vitriol" for chalcanthite were in common use and continued to be used from the Middle Ages to the 20th century.

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Today, we know that the formation and dissolution of metal-sulfate salts play an important role in the storage and transport of acids and metals released upon weathering of mineralized rocks, coal deposits, metallic ore deposits, and mine wastes. The composition of the salts reflects the composition of the evaporated waters from which the salts form, including information on whether the waters are acidic, basic, or near neutral. The original composition of the waters reflects water–mineral interactions involving sulfide-mineral oxidation and reactions with non-sulfide gangue minerals, especially carbonates and silicates. Hence, identification of efflorescent salts can provide information about water quality and water–rock interactions.

Oxidation of sulfide minerals in coal and metallic ore deposits typically leads to the formation of both insoluble and water-soluble, metal-bearing sulfates, hydroxysulfates, and hydrous oxides. The reactions generally lead to the generation of acidic solutions. As pH decreases, sulfide oxidation is accelerated because mineral solubilities and metal concentrations increase.

On a global scale, the largest tonnages of metal production are derived from remarkably few primary sulfide minerals. For example, the world's principal sources of Pb, Zn, and Cu are galena PbS, sphalerite (Zn,Fe)S, and chalcopyrite $CuFeS_2$, respectively. If bornite Cu_5FeS_4, chalcocite Cu_2S, and covellite CuS are added as important, albeit minor relative to chalcopyrite, sources of Cu, probably >90% of the world's annual production of Cu + Pb + Zn from mineral deposits would be accounted for. These ore minerals, however, are accompanied by gangue minerals. Although most silicate gangue minerals are environmentally benign, they are commonly accompanied, or exceeded in the case of massive sulfide deposits, by iron sulfides such as pyrite FeS_2, pyrrhotite $Fe_{1-x}S$, and marcasite FeS_2, which produce sulfuric acid upon oxidation and hydrolysis. The last two are locally important, but on a global scale nearly all acid rock drainage, whether natural (as in the development of massive or disseminated gossan, the oxidized equivalent of massive or disseminated sulfide, respectively) or related to anthropogenic activities (as in the generation of wastes from mining and mineral processing) can be traced to the oxidation of pyrite. The metal:sulfur ratio in sulfide minerals plays an important role in determining the amount of sulfuric acid that is liberated by oxidation. Pyrite and marcasite are more S-rich than other sulfides, and consequently produce more acid per mole (Blanchard 1967, Blain and Andrew 1977, Alpers and Brimhall 1989, Plumlee 1999). Two important results from the oxidation of pyrite are (a) the generation of low-pH conditions, and (b) the consequent release of heavy metals into surface and ground waters.

Metals liberated by sulfide oxidation may precipitate locally as soluble or relatively insoluble sulfate minerals, with the latter acting as solid-phase controls on dissolved metal concentrations. Soluble sulfates generally act only as temporary 'sinks' for the heavy metals, but deposits of chalcanthite, $CuSO_4 \cdot 5H_2O$, of commercial size have been found in arid regions, as at Copaquire, Chile; chalcanthite was also a minor ore in the oxidized zone at Butte, Montana, and was shipped in large quantities from the Bluestone mine, Nevada (Palache et al. 1951). Many of the soluble minerals have the simplified formula $MSO_4 \cdot nH_2O$, wherein M represents divalent Fe, Mn, Co, Ni, Mg, Cu, or Zn, and n ranges from 1 to 7. Mutual substitution among the divalent cations is common, but complete solid solutions have been documented for only a few of the binary systems. Although the soluble sulfate minerals are generally ephemeral, they provide important clues or direct evidence of the pathways of sulfide oxidation and the alteration of the associated mineral assemblages. Where soluble metals salts are present, they provide information about the reactions that have occurred, the composition of the solutions from which they formed, and the types of primary minerals likely to have weathered.

The purpose of this paper is to summarize the occurrence, geochemical properties, and environmental behavior of metal-sulfate salts, in particular those that are readily water-soluble, because these minerals are important in trace-metal cycling and have often been overlooked or ignored. The relatively insoluble sulfate minerals that result from sulfide oxidation are described in three other chapters of this volume. The poorly crystalline, relatively insoluble, hydroxysulfates of iron and aluminum are described by Bigham and Nordstrom (this volume). The well-crystalline minerals of the alunite supergroup, including alunite, jarosite, and related phases, are described by Dutrizac and Jambor (this volume) and by Stoffregen et al. (this volume).

In the following section, variations in the compositions of the more common soluble metal-sulfate salts are reviewed. The sequence begins with the simple hydrated salts of the divalent cations, progresses to salts of the trivalent cations, and thence to those salts that contain both divalent and trivalent cations and (or) monovalent cations. Additional sections in this chapter describe processes of formation, transformation, and dissolution of the soluble salts, including a summary and synthesis of available data on solubility and stability relationships. The chapter concludes with a discussion of the paragenesis of metal-sulfate salts.

COMPOSITIONS AND CRYSTAL CHEMISTRY OF HYDRATED METAL SALTS

Divalent cations

The simple hydrated salts with divalent cations are of the type $M^{2+}SO_4{\cdot}nH_2O$ (Table 1). Numerous experimental studies have shown that n decreases as relative humidity or water activity is decreased, and as temperature or acidity of the mother liquor is increased. The melanterite and epsomite groups are both heptahydrates that are distinguished on the basis of crystal structure. In most compositionally simple solid solutions, the substituting ion is accommodated by various degrees of distortion of the crystal structure of the host mineral. When distortion is too severe, a new structure is formed. For the $M^{2+}SO_4{\cdot}nH_2O$ salts, increasing structure distortion follows the sequence $Ni^{2+} < Zn^{2+} < Mg^{2+} < Co^{2+} < Fe^{2+} < Cu^{2+}$ (Aslanian and Balarew 1977).

Melanterite group Melanterite, $FeSO_4{\cdot}7H_2O$, is one of the most common soluble sulfate minerals formed in nature, whereas the other four minerals in the group (Table 1) are relatively rare. Boothite, $CuSO_4{\cdot}7H_2O$, for example, has been reported from only a few localities (Palache et al. 1951, Skounakis and Economou 1983), and although the supporting morphological and chemical data are good, no modern description has been made. No numerical X-ray diffraction (XRD) data are available for either natural or synthetic material, although Jambor and Traill (1963) reported that a pentahydrate with Cu:Fe:Zn = 70:24:6, from Alameda County, California, gave a melanterite-type X-ray pattern upon artificial hydration. Similarly, the mineral zinc-melanterite, $(Zn,Cu,Fe)SO_4{\cdot}7H_2O$, is known from fewer than five localities, and no XRD data were available prior to the recent description by Tiegeng Liu et al. (1995). Bieberite, $CoSO_4{\cdot}7H_2O$, and mallardite, $MnSO_4{\cdot}7H_2O$, are not as rare, and both are also well known as synthetic compounds.

Solid solution in binary subsystems of the heptahydrate metal salts has been examined by Aslanian et al. (1972), Balarew et al. (1973), and Siebke et al. (1983). In those studies, supersaturated solutions were prepared at 65-70°C, and crystalline precipitates were obtained by cooling the solutions to room temperature and slowly evaporating the solvent. For the melanterite-group minerals, solid solution between melanterite and bieberite was found to be complete. In the Ni-Fe series, the maximum Ni uptake in solid solution is $(Fe_{0.54}Ni_{0.46})SO_4{\cdot}7H_2O$ (Fig. 1a); analyses of natural materials are within the lower part of the allowable range of Ni substitution (Palache et al. 1951, Rutstein 1980).

Table 1. Simple hydrated sulfate salts of the divalent metal cations.

Melanterite Group (monoclinic, $P2_1/c$)[1]		Rozenite Group (monoclinic, $P2_1/n$)[6]	
melanterite	$FeSO_4{\cdot}7H_2O$	rozenite	$FeSO_4{\cdot}4H_2O$
boothite	$CuSO_4{\cdot}7H_2O$	starkeyite	$MgSO_4{\cdot}4H_2O$
bieberite	$CoSO_4{\cdot}7H_2O$	ilesite	$MnSO_4{\cdot}4H_2O$
mallardite	$MnSO_4{\cdot}7H_2O$	aplowite	$CoSO_4{\cdot}4H_2O$
zinc-melanterite	$(Zn,Cu)SO_4{\cdot}7H_2O$	boyleite	$ZnSO_4{\cdot}4H_2O$
Epsomite Group (orthorhombic, $P2_12_12_1$)[2]			
epsomite	$MgSO_4{\cdot}7H_2O$	Bonattite (monoclinic, Cc)[7]	$CuSO_4{\cdot}3H_2O$
morenosite	$NiSO_4{\cdot}7H_2O$		
goslarite	$ZnSO_4{\cdot}7H_2O$	Sanderite	$MgSO_4{\cdot}2H_2O$
Hexahydrite Group (monoclinic, $C2/c$)[3]		Kieserite Group (monoclinic, $C2/c$)[8]	
hexahydrite	$MgSO_4{\cdot}6H_2O$	kieserite	$MgSO_4{\cdot}H_2O$
chvaleticeite	$MnSO_4{\cdot}6H_2O$	szmikite	$MnSO_4{\cdot}H_2O$
ferrohexahydrite	$FeSO_4{\cdot}6H_2O$	szomolnokite	$FeSO_4{\cdot}H_2O$
nickelhexahydrite	$NiSO_4{\cdot}6H_2O$	dwornikite	$NiSO_4{\cdot}H_2O$
moorhouseite	$CoSO_4{\cdot}6H_2O$	gunningite	$ZnSO_4{\cdot}H_2O$
bianchite	$ZnSO_4{\cdot}6H_2O$		
		Poitevinite (triclinic)[9]	$(Cu,Fe)SO_4{\cdot}H_2O$
Retgersite (tetragonal, $P4_12_12$)[4]			
	$NiSO_4{\cdot}6H_2O$		
Chalcanthite Group (triclinic, $P\bar{1}$)[5]			
chalcanthite	$CuSO_4{\cdot}5H_2O$		
pentahydrite	$MgSO_4{\cdot}5H_2O$		
jôkokuite	$MnSO_4{\cdot}5H_2O$		
siderotil	$FeSO_4{\cdot}5H_2O$		

[1] Baur (1964a); Kellersohn et al. (1991); [2] Baur (1964b); Ferraris et al. (1973); Beevers and Schwartz (1935); [3] Zalkin et al. (1962, 1964); Elerman (1988); Gerkin and Reppart (1988); [4] Beevers and Lipson (1932); [5] Bacon and Titterton (1975); Baur and Rolin (1972); [6] Baur (1962, 1964c); Kellersohn (1992); [7] Zahrobsky and Baur (1968); [8] Le Fur et al. (1966); Hawthorne et al. (1987); Wildner and Giester (1991, 1988); Giester et al. (1994).

In the Zn-Fe series, the maximum Zn uptake is $(Fe_{0.45}Zn_{0.55})SO_4{\cdot}7H_2O$. The consequence is that two heptahydrate minerals of monoclinic structure are possible, one with formula Fe > Zn, which is melanterite, and the other with Zn > Fe, which is zinc-melanterite (Fig. 1b). Analyses of natural melanterite have shown up to 8.92 wt % ZnO (Palache et al. 1951), which corresponds to $(Fe_{0.69}Zn_{0.30})_{\Sigma 0.99}SO_4{\cdot}6.8H_2O$, and Alpers et al. (1994) reported an analysis with Fe:Zn:Cu:Mg = 53:29:14:4. Only two complete analyses are available for zinc-melanterite; one (Palache et al. 1951) corresponds to $(Zn_{0.44}Cu_{0.43}Fe_{0.08})_{\Sigma 0.95}SO_4{\cdot}6.6H_2O$, and the other (Tiegeng Liu et al. 1995) to $(Zn_{0.57}Fe_{0.35}Mg_{0.10}Ca_{0.01})_{\Sigma 1.03}SO_4{\cdot}6.96H_2O$. The latter slightly exceeds the maximum Zn uptake of 55 mol % in the Zn-Fe binary system; however, the Mg content of the mineral is 10 mol %, and Mg slightly extends the range of substitution within which decreases in Fe are tolerated (Fig. 1c).

Compositions of zinc-melanterite are shown along with other available data for natural metal-sulfate heptahydrates in two ternary diagrams, Fe–Cu–(Zn+Mg) (Fig. 2a) and Fe–(Cu+Zn)–Mg (Fig. 2b). The data points in Figure 2 from Jamieson et al. (1999) for heptahydrate salts from Iron Mountain represent Fe:Cu:Zn ratios from electron microprobe analyses, in which Mg was not analyzed. The Mg contents of other melanterite samples from Iron Mountain are about 2 mol % (Alpers et al. 1994). The Richmond deposit at Iron

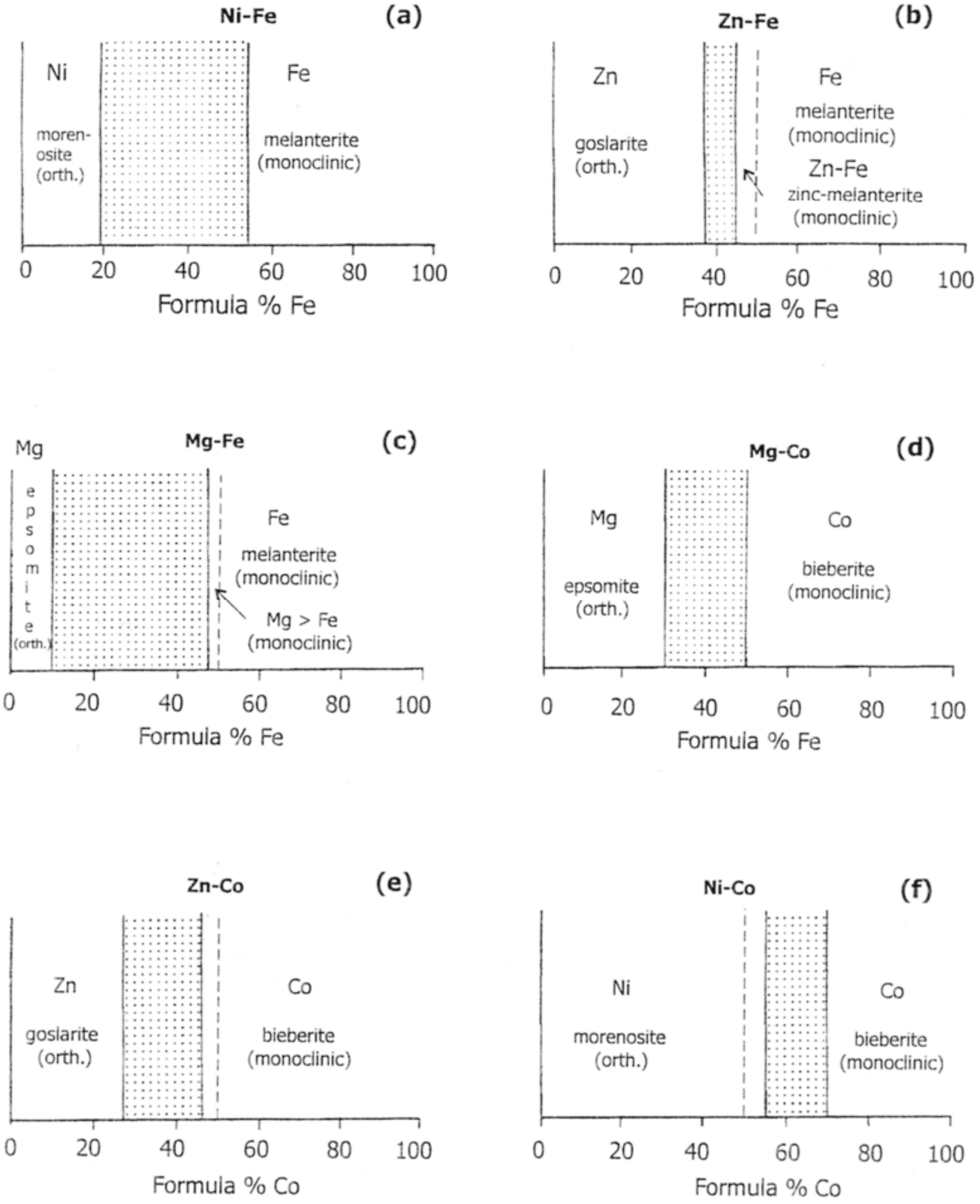


Figure 1. Binary solid solutions among the synthetic metal-sulfate heptahydrates precipitated at room temperature (data from Aslanian et al. 1972, Balarew et al. 1973, and Siebke et al. 1983). Dotted pattern shows the miscibility gaps in the solid-solution series: (a) Ni-Fe; (b) Zn-Fe, vertical dashed line at 45 mol % Fe (55 mol % Zn) represents the maximum solid solution of Zn in monoclinic $M^{2+}SO_4 \cdot 7H_2O$, where M = Fe,Zn. At 0-50 mol % Fe in $(Fe,Zn)SO_4 \cdot 7H_2O$ the equivalent mineral is melanterite, and at >50 mol % Zn in $(Zn,Fe)SO_4 \cdot 7H_2O$ the equivalent mineral is zinc-melanterite; (c) Mg-Fe; (d) Mg-Co; (e) Zn-Co; (f) Ni-Co. Note that, as for zinc-melanterite, narrow fields are available for the Mg-dominant analog of melanterite, the Zn analog of bieberite, and the orthorhombic Co analog of morenosite.

Mountain is a massive sulfide that hosts extremely acidic mine waters, some with negative pH values (Nordstrom and Alpers 1999a,b; Nordstrom et al. 2000). Some of the melanterite from the Richmond mine precipitated from mine water with a pH of -0.7 (Alpers et al. 1994, Nordstrom et al. 2000). The Mattie deposit at Iron Mountain is located adjacent to the Richmond deposit, and is accessed by a common tunnel. Mine waters associated with melanterite and zinc-melanterite formation in the Mattie deposit have pH values in the range of 3-4 (Alpers and Nordstrom, unpublished data).

The diagram for Fe-Mg solid solution (Fig. 1c) shows that Mg can be accommodated up to $(Fe_{0.47}Mg_{0.53})SO_4 \cdot 7H_2O$. Theoretically, therefore, the Mg analog of zinc-melanterite could exist as a mineral. Magnesium-rich melanterite was previously called 'kirovite,' a name no longer in good standing. However, an analysis reported by Palache et al. (1951) contains 7.45 wt % MgO and the corresponding formula is $(Mg_{0.48}Fe_{0.47}Al_{0.07}Zn_{0.02}Cu_{0.01}Mn_{0.01})_{\Sigma 1.06}SO_4 \cdot 6.80H_2O$, which is (barely) the Mg analog of zinc-melanterite. A Mg-dominant mineral was also described by Pasava et al. (1986b), who obtained the formula $(Mg_{0.48}Fe^{2+}_{0.32}Fe^{3+}_{0.07}Mn_{0.21}Al_{0.02})_{\Sigma 1.00}SO_4 \cdot 6.66H_2O$.

Synthetic bieberite (Rohmer 1939, Aslanian et al. 1972) incorporates up to 50 mol % Mg (Fig. 1d), up to 54 mol % Zn (Fig. 1e), and up to 30 mol % Ni (Fig. 1f); solid solution between Co and Fe is complete. Substitution of Co by Mn seems to be limited to about 18 mol % at 20°C (Balarew et al. 1984), and incorporation of up to 32 mol % Cu at 25°C was reported by Crockford and Brawley (1932). Few analyses of natural bieberite are available, and these show little range in solid solution. Some of the few available analyses of mallardite, $MnSO_4 \cdot 7H_2O$, are near the end-member (Palache et al. 1951, Nambu et al. 1979), but Pasava et al. (1986a) obtained an analysis corresponding to $(Mn_{0.48}Fe^{2+}_{0.26}Mg_{0.24})_{\Sigma 0.98}SO_4 \cdot 6.52H_2O$, and another analysis has $Mn:Mg:Fe^{3+} = 50:47:2$ (Pasava et al. 1986b).

Most analyses of boothite (Palache et al. 1951) are near that of the end-member. Skounakis and Economou (1983) described an occurrence of boothite with compositions ranging to cuprian melanterite, but analytical results were not reported. Although morphological data seem to indicate that boothite and cuprian melanterite are isostructural, the two minerals are reportedly separated by a miscibility gap (Palache et al. 1951). Cuprian melanterite was previously known as 'pisanite,' a name no longer in good standing. Keating and Berry (1953) described melanterite with Fe:Cu:Zn = 100:80:3, thus corresponding to $(Fe_{0.53}Cu_{0.44}Zn_{0.02})SO_4 \cdot 7H_2O$, and a slightly more Cu-rich analysis was given by Palache et al. (1951). A Cu-Zn-rich melanterite with cation ratios $Fe_{0.40}Cu_{0.34}Zn_{0.26}$ was reported by Dristas (1979). The most Cu-rich analysis (18.81 wt % CuO) given by Palache et al. (1951) for 'melanterite' corresponds to $(Cu_{0.68}Fe_{0.34})_{\Sigma 1.02}SO_4 \cdot 7.12H_2O$, which is ferroan boothite rather than melanterite. Collins (1923) synthesized the Fe-Cu series at room temperature and concluded that the maximum Cu uptake is to $(Cu_{0.66}Fe_{0.34})SO_4 \cdot 7H_2O$, which is almost identical to the composition of the above-mentioned ferroan boothite. The range in compositions suggests that, if there is a solid-solution gap in the melanterite-boothite series, it must be rather narrow and it may be in the Cu-dominant part of the series. It has yet to be demonstrated unequivocally that boothite is isostructural with the other members of the melanterite group. However, comparison of the cell dimensions of the various members shows that the length of the *b* axis is almost constant; thus, cell parameters for boothite on the basis of its morphological axial ratios can be calculated to be a = 13.89, b = 6.50, c = 10.64 Å, β = 105.60° assuming isomorphism with melanterite. Cell parameters for other members of the melanterite group, and most other sulfate minerals mentioned in this chapter, are given by Hawthorne et al. (this volume).

Epsomite group The heptahydrates of the epsomite group are orthorhombic, in contrast to those of the melanterite group, which are monoclinic (Table 1). As in the monoclinic melanterite group (Baur 1964a, Kellersohn et al. 1991), one of the water molecules in the orthorhombic epsomite-group structures is not bonded to a metal ion and is readily lost (Beevers and Schwartz 1935, Baur 1964b, Ferraris et al. 1973).

The three minerals in the epsomite group (Table 1) are defined by their predominance of Mg (epsomite), Zn (goslarite), and Ni (morenosite). In the synthetic system, near room temperature, solid solutions of Zn-Ni (Aslanian et al. 1972), Zn-Mg (Balarew et al. 1973), and Ni-Mg (Soboleva 1958, 1960) are apparently complete. Presumably, therefore, the Zn-Ni-Mg ternary system does not contain a miscibility gap.

Substitution of Fe for Mg in epsomite in the synthetic system (Balarew et al. 1973, Siebke et al. 1983) is to a maximum of only 10 mol % (Fig. 1c), but older results (Palache et al. 1951) indicated that Mg:Fe ~5:1 was achievable (Fig. 2). In natural material, the most Fe-rich analysis listed by Palache et al. (7.77 wt % FeO) corresponds to $(Mg_{0.72}Fe_{0.28})_{\Sigma 1.00}SO_4 \cdot 6.99H_2O$, which is considerably beyond the limit indicated by syntheses.

Substitution of Mg in epsomite by elements such as Co, Cu, and Mn is possible. For the Mg-Co binary, the limit is 30 mol % Co (Fig. 1d). Solid-solution of Cu in the Mg-Cu binary is apparently limited to a few mol %, beyond which a monoclinic heptahydrate is formed (Balarew and Karaivanova 1975). Neither Co nor Cu seems to have been detected in appreciable quantities in natural epsomite. The extent of substitution of Mg by Mn in natural epsomite is probably large, but supporting data are poor; in synthetic material the reported limit is Mg:Mn ~5:2 (Palache et al. 1951).

For the Zn member, goslarite, solid solutions with Mg and with Ni are complete. Substitution of Zn by Fe can extend to 37 mol % Fe (Fig. 1b), and of Zn by Co can extend to 27 mol % Co (Fig. 1e). Analyses of natural goslarite also indicate that substantial substitution by Cu (up to 15 mol %; Milton and Johnston 1938) and Mn may occur, but the limits are not well-defined.

Few analyses of the Ni member, morenosite, are available because of uncertainties about the identification and homogeneity of the older samples. More recent analyses (e.g. King and Evans 1964, Otto and Schuerenberg 1974, Boscardin and Colmelet 1977) show that substitution of Ni is mainly by Mg, or (Mg+Fe), in agreement with the older analyses. In the synthetic system, substitution of Ni by Fe in the binary system is limited to 19 mol % Fe (Fig. 1a), but Co in the Ni-Co series can exceed Ni and still maintain the orthorhombic structure (Fig. 1f). At 25 °C, substitution of Ni by Cu is limited to about 18 mol % Cu (Jangg and Gregori 1967).

Hexahydrite group The hexahydrite group consists of monoclinic sulfates of the type $M^{2+}SO_4 \cdot 6H_2O$. The 'hexa' in the name alludes to the water content, and coincidentally, there are six minerals in the group (Table 1). Except for hexahydrite, $MgSO_4 \cdot 6H_2O$, which is known to precipitate in diverse settings such as saline lakes, soils, and weathered mine wastes, the minerals of the group occur sparingly and are mainly found as the oxidation products of sulfide deposits. An indication of the relative sparseness of the group is that only two of the minerals (hexahydrite and bianchite) were discovered prior to the 1960s.

Although little is known about the limits of solid solution in the hexahydrates, the similarity in crystal structure with that of the heptahydrates suggests that comparable levels of substitution can be accommodated. Synthetic bianchite, $ZnSO_4 \cdot 6H_2O$ apparently can contain Fe in solid solution up to Zn:Fe ~2:1, and an analysis of natural material (in Palache et al. 1951) corresponds to $(Zn_{0.65}Fe_{0.33})_{\Sigma 0.98}SO_4 \cdot 5.89H_2O$. Semi-quantitative analysis of bianchite from the Sterling mine, New Jersey, gave Zn:Fe:Mn = 55:45:5, with no Mg or Cu detected (Jenkins and Misiur 1994). A cupriferous variety with Zn:Fe:Cu = 64:21:15 has been reported from Bulgaria (Zidarov 1970). Compositions of natural metal-sulfate hexahydrates in the Fe–Cu–(Zn+Mg) system are shown in Figure 3.

Analysis of chvaleticeite, the Mn member so far known only from the type locality

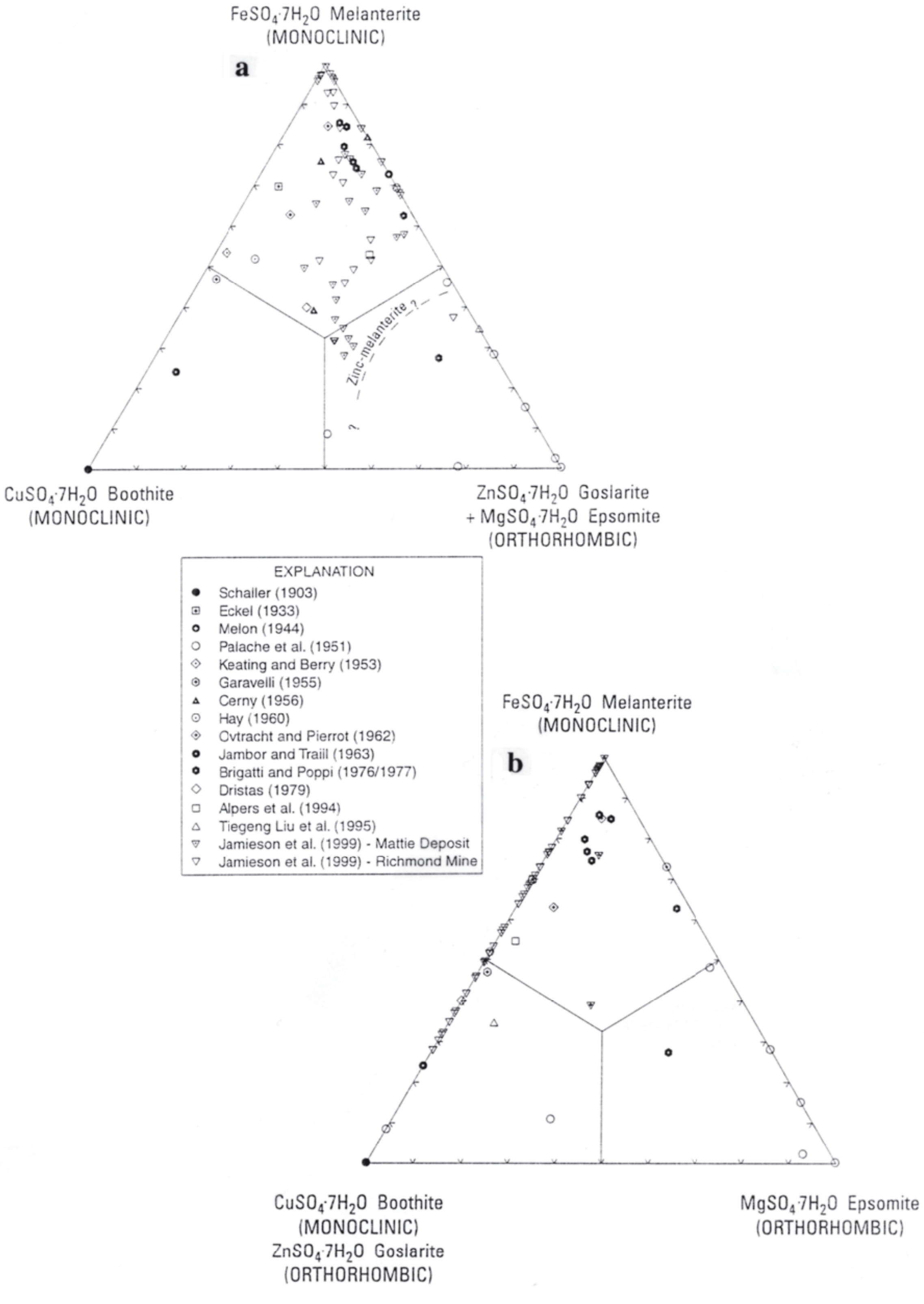


Figure 2. Ternary diagrams showing compositions of natural metal-sulfate heptahydrates: (a) $FeSO_4{\cdot}7H_2O$–$CuSO_4{\cdot}7H_2O$–$(Zn,Mg)SO_4{\cdot}7H_2O$; dashed line indicates possible compositional limit of zinc-melanterite (monoclinic); (b) $FeSO_4{\cdot}7H_2O$–$(Cu,Zn)SO_4{\cdot}7H_2O$–$MgSO_4{\cdot}7H_2O$, symbols are for both (a) and (b).

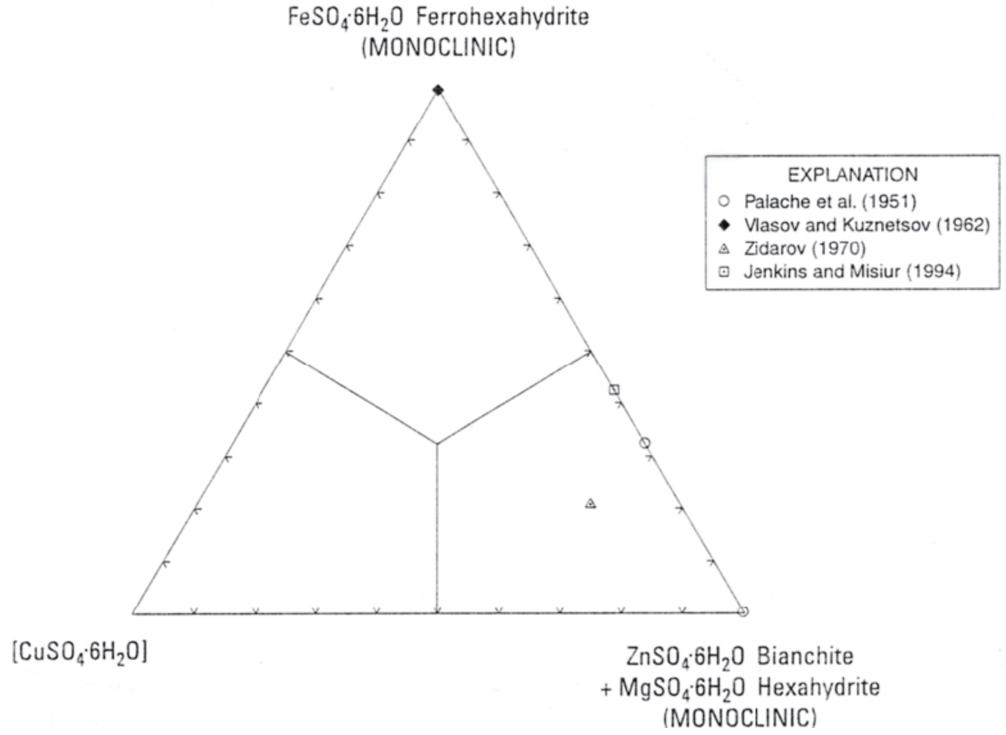


Figure 3. Ternary diagram showing compositions of natural metal-sulfate hexahydrate minerals: $FeSO_4 \cdot 6H_2O$–$CuSO_4 \cdot 6H_2O$–$(Zn,Mg)SO_4 \cdot 6H_2O$; note that $CuSO_4 \cdot 6H_2O$ is not a known mineral species.

(Pasava et al. 1986a), gave $(Mn_{0.57}Mg_{0.40})_{\Sigma 0.97}SO_4 \cdot 6.4H_2O$. For ferrohexahydrite, the original analysis showed Fe^{2+} but no Mg or Zn (Vlasov and Kuznetsov 1962). Although several occurrences of the mineral have since been reported, quantitative compositional data are sparse. The original analyses of nickelhexahydrite (Oleinikov et al. 1965) correspond to $(Ni_{0.78}Mg_{0.16}Fe_{0.10})_{\Sigma 1.04}SO_4 \cdot 5.90H_2O$ and $(Ni_{0.49}Mg_{0.28}Fe_{0.23}Cu_{0.01})_{\Sigma 1.01}SO_4 \cdot 6.04H_2O$. Analyses of the mineral from other occurrences (Karup-Møller 1973, Nawaz 1973, Otto and Scheurenberg 1974) show additional small amounts of Mn, Zn, and Co, but do not extend the range for Ni-Mg-Fe solid solution. For hexahydrite, which is the Mg-dominant member, Ni substitution to Mg:Ni = 73:27 has been found (Janjic et al. 1980). The Co-dominant member of the group, moorhouseite, is known only from a single locality. Analysis of the type material (Jambor and Boyle 1965) gave cation ratios of Co:Ni:Mn:Cu:Fe:Zn = 55:25:12:5:3:1. In the synthetic system, Co-Ni solid solution is complete at 61 °C, but mixed phases appear at lower temperatures (Rohmer 1939). At 50°C, the limit of Fe substitution is about 27 mol % (Balarew and Karaivanova 1976b).

Retgersite. Retgersite, $NiSO_4 \cdot 6H_2O$ is tetragonal, dimorphous with nickel-hexahydrite (Angel and Finger 1988; Table 1). The limits of solid solution are not known, and in natural occurrences (e.g. Frondel and Palache 1949, Fedotova 1967, Sejkora and Rídkosil 1993) only small amounts of substituting elements, especially Fe and Mg, have been detected. A mineral with Ni:Mg:Fe:Zn:Co = 65:19:13:2:1 described by Eliseev and Smirnova (1958) has since been determined to be nickelhexahydrite (Oleinikov et al. 1965), possibly with admixed morenosite (Sejkora and Rídkosil 1993).

Chalcanthite group The chalcanthite group consists of triclinic pentahydrates of Cu, Mg, Mn, and Fe (Table 1, Fig. 4). The Cu member, chalcanthite, is of common occurrence whereas the Mn member, jôkokuite, is known only from two localities.

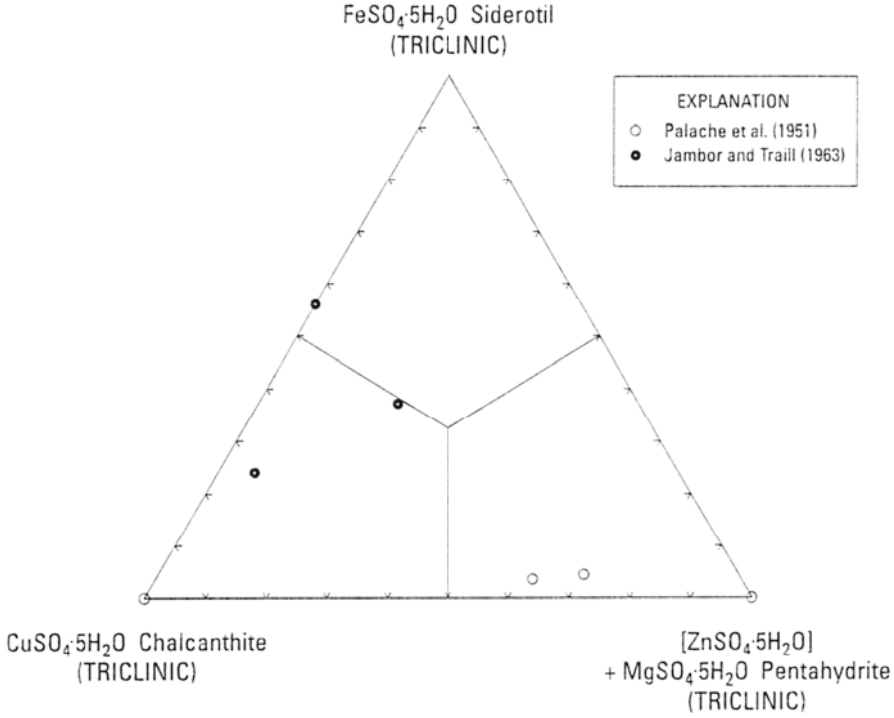


Figure 4. Ternary diagram showing compositions of natural metal-sulfate pentahydrate minerals: $FeSO_4 \cdot 5H_2O$–$CuSO_4 \cdot 5H_2O$–$(Zn,Mg)SO_4 \cdot 5H_2O$; note that $ZnSO_4 \cdot 5H_2O$ is not a known mineral species.

The composition of type jôkokuite (Nambu et al. 1978) corresponds to $(Mn_{0.94}Fe_{0.04}Zn_{0.03})_{\Sigma 1.01}SO_4 \cdot 5.07H_2O$, and material from Chvaletice, Czech Republic (Pasava et al. 1986b) has the composition $(Mn_{0.63}Mg_{0.31}Fe^{3+}_{0.02})_{\Sigma 0.96}SO_4 \cdot 5.33H_2O$. Although only small amounts of Mn have been reported as substituting in natural occurrences of the other members of the group, in the synthetic system at 21°C the Mn-Cu solid solution is evidently complete (Mellor 1932).

In synthetic chalcanthite at 25°C, up to 20 mol % Ni substitution for Cu was obtained by Jangg and Gregori (1967). The isomorphous pentahydrates of Ni and Co are known as synthetic products (Hammel 1939, Rohmer 1939) but have not yet been described as minerals. Substitution of 5 mol % Co for Cu in chancanthite was obtained by Crockford and Brawley (1932), and this increased to only 16 mol % Co at 60°C (Balarew and Karaivanova 1976a,c). Solid-solution incorporation of Mg or Zn in chalcanthite at 25°C was ≤6 mol % in the experiments by Balarew and Karaivanova (1975), but up to 19 mol % Zn was incorporated at 40°C (Balarew and Karaivanova 1976a). Mutual Cu-Fe substitution (chalcanthite-siderotil) is extensive in natural and synthetic material, and compositions extending to Cu:Fe near 1:1 have been reported for both minerals (Jambor and Traill 1963).

Relatively few analyses of the Mg member, pentahydrite, are available, and their low Fe and Zn contents of a percent or two are unlikely to reflect the solid-solution limits in natural material. The highest amounts of substitution for Mg are by Cu and Zn (Palache et al. 1951), with one analysis corresponding to $(Mg_{0.63}Cu_{0.35}Fe_{0.03}Mn_{0.01})_{\Sigma 1.02}SO_4 \cdot 4.78H_2O$, and another to $(Mg_{0.53}Cu_{0.26}Zn_{0.16}Fe_{0.04}Mn_{0.01})_{\Sigma 1.00}SO_4 \cdot 4.95H_2O$ (Fig. 4). These results suggest that the extent of mutual substitutions among Cu-Mg-Mn-Fe in the natural pentahydrates may be much larger than has yet been observed.

Rozenite group The rozenite group consists of five minerals (Table 1), with the Mn member, ilesite, the only species known prior to 1960. Nevertheless, the two minerals that occur the most abundantly and which have the widest distribution are rozenite, $FeSO_4{\cdot}4H_2O$, and starkeyite, $MgSO_4{\cdot}4H_2O$. Ilesite (Mn), aplowite (Co), and boyleite (Zn) are known from only a few localities.

All of the members of the group are readily synthesized, but solid-solution limits, if present, have not been established. In natural occurrences, some analyses of the Mg and Fe members show small amounts of solid solution (e.g. Kubisz 1960a, Brousse et al. 1966, Snetsinger 1973, Baltatzis et al. 1986). Pasava et al. (1986b) reported a manganiferous variety with the composition $(Fe_{0.78}Mn_{0.11}Mg_{0.09})_{\Sigma 0.98}SO_4{\cdot}3.85H_2O$. An analysis of ilesite (Palache et al. 1951) corresponds to $(Mn_{0.70}Zn_{0.16}Fe_{0.13})_{\Sigma 0.99}SO_4{\cdot}3.89H_2O$, and a magnesian variety reported by Pasava et al. (1986b) has the composition $(Mn_{0.62}Mg_{0.40})_{\Sigma 1.02}SO_4{\cdot}4.2H_2O$. A Zn-rich variety devoid of Fe and coexisting with the monohydrate was mentioned by Jambor and Boyle (1962), but no analyses were given. For the Co member, aplowite, cation ratios are Co:Mn:Ni:Cu:Fe:Zn = 50:25:22:1:1:1 (Jambor and Boyle 1965), thus indicating that extensive substitution by Mn and Ni is possible. The amount of Cu in the analysis is small, and the corresponding Cu tetrahydrate is not known in either natural or synthetic material; dehydration of $CuSO_4{\cdot}5H_2O$ leads directly to the trihydrate or, depending on conditions, to the monohydrate. For the Zn member of the group, boyleite, analysis of the type material gave Zn:Mg = 84:16 (Walenta 1978).

Bonattite. Bonattite, $CuSO_4{\cdot}3H_2O$, is the only trihydrate among the $MSO_4{\cdot}nH_2O$ minerals (Table 1). The compound crystallizes from solution (Posnjak and Tunell 1929), and forms by dehydration of the pentahydrate, chalcanthite, at elevated temperatures (Hammel 1939, Guenot and Manoli 1969). The mineral is extremely rare in ore deposits, probably in part because it may hydrate to chalcanthite at normal atmospheric humidity. Compositions of the mineral are close to that of the end-member (Garavelli 1957, Jambor 1962). Bonattite has also been observed as an atmospheric weathering product of sculptures (Zachmann 1999) and as a corrosion product of buried bronze artifacts (Nord et al. 1998). The synthetic analog was among several compounds that formed on artificially patinated layers on artistic bronze exposed to laboratory SO_2 contamination (Bastidas et al. 1997).

Sanderite. Sanderite, $MgSO_4{\cdot}2H_2O$, is poorly described but is nonetheless a mineral in good standing. It occurs with hexahydrite, pentahydrite, and starkeyite in marine salt deposits (Berdesinki 1952), and as an efflorescence on Neogene rocks in Greece (Schnitzer 1977), and is a well-defined synthetic phase.

Kieserite group The kieserite group of monohydrate sulfates is made up of five members (Table 1). The cell volumes of these sulfates, and those of the analogous selenates, have been shown by Le Fur et al. (1966), Giester (1988), Wildner and Giester (1991), and Giester and Wildner (1992) to increase in accordance with the size of the predominant M^{2+} cation (Fig. 5). The most abundant and widely occurring members of the group are kieserite (Mg) and szomolnokite (Fe), with szmikite (Mn) much less common. Gunningite (Zn) is thought to be relatively rare, but reports of new occurrences seem to be increasing rapidly (e.g. Grybeck 1976, Sabina 1977, 1978; Jambor 1981, Avdonin 1984, Perroud et al. 1987, Avdonin et al. 1988, Yakhontova et al. 1988). Dwornkite, the Ni member, is known only from its type locality, Minasragra, Peru (Milton et al. 1982).

Analyses of kieserite, the Mg member, generally give compositions near that of the end-member, to the extent that kieserite is one of the few minerals for which analytical results are not listed in Palache et al. (1951). The stoichiometric compositions probably reflect occurrences in marine salt deposits, wherein high-purity, abundant material is available. Compositions of szomolnokite, the Fe member, are also commonly near that of

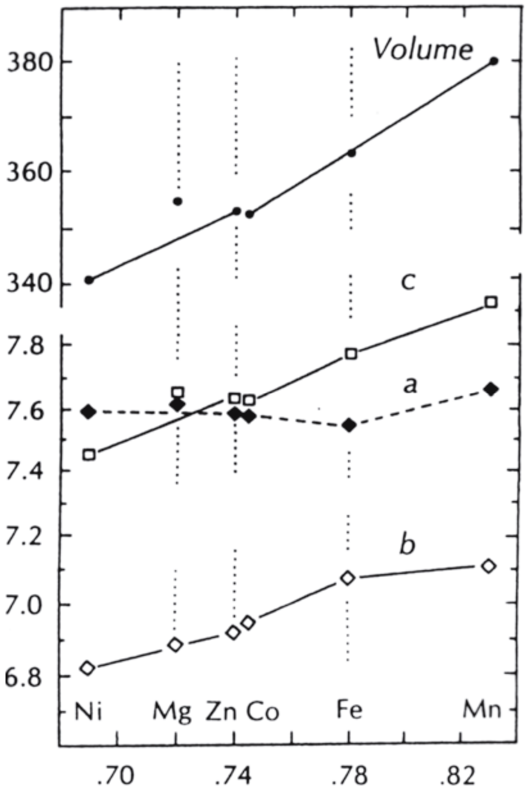


Figure 5. Dependency of cell volume (Å^3) and cell-dimensions *a*, *b*, *c* (Å) on ionic radii of the M^{2+} cations in the minerals of the kieserite group. Redrawn from Wildner and Giester (1991).

the end-member, but Kubisz (1960b) analyzed a magnesian variety corresponding to $(Fe_{0.59}Mg_{0.41})SO_4{\cdot}H_2O$, and Jamieson et al. (1999) reported szomolnokite compositions with up to 16 wt % Zn (corresponding to 39 mol % Zn) from Iron Mountain, California (Fig. 6). The few quantitative analyses for the Mn member, szmikite, show little substitution other than 1-2 wt % FeO (Palache et al. 1951, Matsubara et al. 1973). Although Jambor and Boyle (1962) reported the occurrence of a Zn-rich variety of szmikite, no analyses were given. In dwornikite, the Ni member, about 10 mol % of the Ni is substituted by Fe (Milton et al. 1982). The compositions of gunningite were found to range from the Zn end-member to Zn:Mn:Cd:Fe = 89:8:1:1 (Jambor and Boyle 1962).

In synthetic products (Jambor and Boyle 1962), up to 39 mol % Mn was substituted in gunningite, and indications were that the Zn-Fe series may be complete. These results must be treated with caution, however, because it is difficult to distinguish by X-ray powder-diffraction patterns the monoclinic $MSO_4{\cdot}H_2O$ members from those

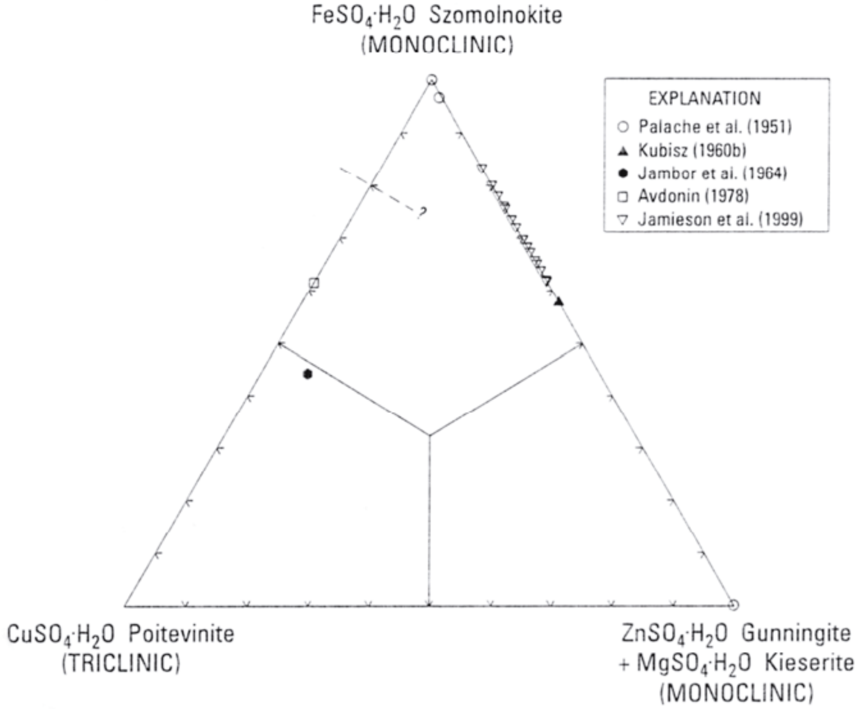


Figure 6. Ternary diagram showing composition of natural metal-sulfate monohydrates: $FeSO_4{\cdot}H_2O$–$CuSO_4{\cdot}H_2O$–$(Zn,Mg)SO_4{\cdot}H_2O$. The dashed line represents possible compositional limit of triclinic and monoclinic phases.

that are triclinic. For example, solid solution between Cu and Fe is limited to 20 mol % Cu, whereupon a triclinic phase (poitevinite) is formed (Giester et al. 1994). Similarly in the Mg-Cu series, a triclinic phase analogous structurally to poitevinite is formed when Cu equals or exceeds 20 mol % (Lengauer and Giester 1995). The situation arises because the M^{2+} cations are distributed into two sites, one of which is more distorted than the other, and Cu is preferentially accommodated within the distorted site; above 20 mol % Cu, this ordering becomes increasingly evident, and at >60 mol % Cu the more distorted site is occupied entirely by Cu (Lengauer and Giester 1995). It is likely that the relatively restricted range of solid solution for most ions in natural occurrences of the kieserite-group minerals (Fig. 6) reflects the small number of quantitative analyses rather than limits imposed by crystal-structure considerations.

Poitevinite. Poitevinite, $(Cu,Fe)SO_4 \cdot H_2O$, has triclinic symmetry, as noted above, thereby distinguishing it from the kieserite group, which is monoclinic. Analysis of the type material corresponds to $(Cu_{0.50}Fe_{0.46}Zn_{0.08})_{\Sigma 1.04}SO_4 \cdot 1.2H_2O$ (Jambor et al. 1964). Avdonin (1978) obtained $(Fe_{0.61}Cu_{0.38})SO_4 \cdot 1.2H_2O$ for a second occurrence, and the mineral has since been reported in association with siderotil, bianchite, apjohnite, and other supergene minerals in the Deputatsk tin deposit, Yakutia, Russia (Zhdanov and Solov'ev 1998). The analysis of poitevinite reported by Avdonin (1978), however, has Fe > Cu and is therefore neither poitevinite nor cuprian szomolnokite, but is instead apparently the unnamed Fe-dominant analog of poitevinite (Fig. 6). The situation arises because of Cu-Fe immiscibility in the monohydrate series, with Cu substitution in szomolnokite limited to 20 mol %. Thus, the remainder is a triclinic series extending from $(Fe_{0.80}Cu_{0.20})SO_4 \cdot H_2O$ to $CuSO_4 \cdot H_2O$, wherein the mineral with Fe > Cu is unnamed, and that with Cu > Fe is poitevinite.

Table 2. Simple hydrated sulfate salts of the trivalent ions.

Mineral	*Formula*	*Symmetry*	*Reference*
lausenite	$Fe_2(SO_4)_3 \cdot 6H_2O$	monoclinic	Posnjak and Merwin (1922)
kornelite	$Fe_2(SO_4)_3 \cdot 7H_2O$	monoclinic, $P2_1/n$	Robinson and Fang (1973)
coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	hexagonal, $P\bar{3}c$	Fang et al. (1970)
"paracoquimbite"	$Fe_2(SO_4)_3 \cdot 9H_2O$	rhombohedral, $R\bar{3}$	Robinson and Fang (1971)
quenstedtite	$Fe_2(SO_4)_3 \cdot 11H_2O$	triclinic, $P\bar{1}$	Thomas et al. (1974)
alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$	triclinic, $P\bar{1}$	Fang and Robinson (1976)
meta-alunogen	$Al_4(SO_4)_6 \cdot 27H_2O$	orthorhombic	Naray-Szabo (1969)

"Paracoquimbite", although still a mineral in good standing, has been shown by Fang and Robinson (1974) to be a polytype of coquimbite.

Trivalent cations

The minerals of this type are characterized by the general formula $A_2(SO_4)_3 \cdot nH_2O$, where A is Fe^{3+} or Al, and n ranges from 6 to 17 (Table 2). The anhydrous compounds occur naturally as mikasaite, $(Fe,Al)_2(SO_4)_3$, and millosevichite $(Al,Fe)_2(SO_4)_3$. Both minerals form in fumarolic conditions and are hygroscopic. In mikasaite, Fe:Al is 1.56:0.44 (Miura et al. 1994), and in millosevichite, Al:Fe extends to 1.58:0.42 (Srebrodol'skiy 1974c). The monohydrate $Fe_2(SO_4)_3 \cdot H_2O$ is known as a synthetic product, and an apparently natural occurrence in association with rozenite was noted by Omori and Kerr (1963). Coquimbite and alunogen are by far the most commonly occurring, whereas lausenite is known from only the type locality (Palache et al. 1951) and from a burning coal dump in the Ukraine (Srebrodol'skiy 1974a). The latter has

Fe:Al almost 1:1, but total cations are in considerable excess of the formula requirements. Kornelite, quenstedtite, and meta-alunogen, although not abundant, have been reported from several localities (e.g. Palache et al. 1951, Pemberton 1983, Gaines et al. 1997, Nordstrom and Alpers 1999a). In natural settings, the Fe^{3+} minerals represent a more advanced stage in the oxidation sequence insofar as the Fe^{2+} sulfates are the ones that are generally proximal to Fe sulfides.

Table 2 shows that the hydrated Fe^{3+} sulfates span a range of water contents, reaching a maximum of $11H_2O$ in quenstedtite. A higher hydrate, corresponding to $Fe_{3\text{-}x}(SO_4)_2{\cdot}14H_2O$ was described by Wang and Lee (1988), but the cell dimensions and matching triclinic symmetry and space group indicate that the mineral is likely lishizhenite, $ZnFe^{3+}{}_2(SO_4)_4{\cdot}14H_2O$ (Table 3).

Table 3. Mixed divalent – trivalent hydrated sulfate minerals

Mineral	*Formula*	*Symmetry*	*Reference*
ransomite	$Cu(Fe,Al)_2(SO_4)_4{\cdot}6H_2O$	monoclinic, $P2_1/c$	Wood (1970)
römerite	$Fe^{2+}Fe^{3+}_2(SO_4)_4{\cdot}14H_2O$	triclinic, $P\bar{1}$	Fanfani et al. (1970)
lishizhenite	$Zn\,Fe^{3+}_2(SO_4)_4{\cdot}14H_2O$	triclinic, $P\bar{1}$	Li and Chen (1990)
Halotrichite Group		monoclinic, $P2_1/c$	Menchetti and Sabelli (1976); Lovas (1986)
pickeringite	$MgAl_2(SO_4)_4{\cdot}22H_2O$		
halotrichite	$Fe^{2+}Al_2(SO_4)_4{\cdot}22H_2O$		
apjohnite	$Mn^{2+}Al_2(SO_4)_4{\cdot}22H_2O$		
wupatkiite	$Co^{2+}Al_2(SO_4)_4{\cdot}22H_2O$		
dietrichite	$ZnAl_2(SO_4)_4{\cdot}22H_2O$		
bilinite	$Fe^{2+}Fe^{3+}_2(SO_4)_4{\cdot}22H_2O$		
redingtonite	$Fe^{2+}(Cr,Al)_2(SO_4)_4{\cdot}22H_2O$		
Copiapite Group (OH-bearing)		triclinic, $P\bar{1}$	Süsse (1972); Fanfani et al. (1973); Bayliss and Atencio (1985)
aluminocopiapite	$Al_{2/3}\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
magnesiocopiapite	$Mg\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
calciocopiapite	$Ca\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
copiapite	$Fe^{2+}\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
ferricopiapite	$Fe^{3+}_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
cuprocopiapite	$Cu\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		
zincocopiapite	$Zn\,Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$		

Substitution of Fe^{3+} by Al is possible in this group of minerals, but analyses generally show no more than 1-3 wt % Al_2O_3 and lower levels of other metals. However, in coquimbite, $Fe_2(SO_4)_3{\cdot}9H_2O$, higher Al contents have been reported, with formula Fe:Al extending to 58:42 mol % (Palache et al. 1951, Fang and Robinson 1970).

The Al-sulfate salts are represented by alunogen and meta-alunogen; the latter is a lower hydrate per mole of aluminum (Table 2) and is inadequately described, although occurrences have been reported from several localities. The maximum H_2O content of alunogen was determined by Fang and Robinson (1976) to be 17 molecules; however, loss of water can occur without structure breakdown, and the variation is from 17 to 16 H_2O (Taylor and Bassett 1952). For meta-alunogen, the formula in Table 2 is from Mandarino (1999), reflecting the original analysis in which the water content was determined to be 13.5 H_2O. On the basis of the crystal structure of alunogen, Fang and Robinson (1976) concluded that the minimum water content to sustain the structure of alunogen would be 13.5 H_2O per formula unit. In the Powder Diffraction File, however, synthetic meta-alunogen is assigned the formulas $Al_2(SO_4)_3{\cdot}12H_2O$ and $Al_2(SO_4)_3{\cdot}14H_2O$, and the two XRD patterns have distinct differences from one another, and with that of alunogen. It is evident that meta-alunogen, if it is to be retained as a mineral name, is in need of a formal redefinition.

Mixed divalent–trivalent salts

Many of the mixed divalent–trivalent sulfate salts have the general formula $AR_2(SO_4)_2 \cdot nH_2O$, where *A* is Mg, Fe^{2+}, Mn^{2+}, Co^{2+}, or Zn, and *R* is Al, Fe^{3+}, or Cr^{3+} (Table 3). The minerals described in the previous sections can be considered as "simple" salts, on the basis that sulfate is the only anion and that formula OH is absent. In the discussion of the divalent–trivalent category, however, the OH-bearing copiapite group, generally $AR_4(SO_4)_6(OH)_2 \cdot 20H_2O$, is included because its minerals meet the divalent-trivalent criterion and they are among the most commonly observed metal-bearing soluble salts derived from the oxidation of mineral deposits rich in Fe sulfides.

Ransomite, $Cu(Fe,Al)_2(SO_4)_4 \cdot 6H_2O$, is known from only one locality, at which it formed as a result of a fire in a mine. Compounds that form under such conditions are no longer accepted as new minerals (Nickel 1995). In lishizhenite, which is also known only from a single locality, the *A* position has Zn:Mn:Fe:Mg = 86:9:1:1, and *R* has Fe^{3+}:Al = 1.96:0.06 (Li and Chen 1990). Compositions of römerite (Palache et al. 1951; also summarized by Van Loan and Nuffield 1959) show formula Fe:Zn:Mg up to 65:30:5, suggesting that a series may extend to lishizhenite. Appreciable substitution of Al for Fe^{3+} in römerite is generally not present, and the maximum that has been observed is Fe:Al = 84:16.

Halotrichite group In contrast to the preceding minerals, extensive solid solution occurs in the minerals of the halotrichite group. Intermediate compositions in the Mg-Fe^{2+} solid-solution series on the *A* site (pickeringite-halotrichite) are known (Fe:Mg = 51:49, Martin et al. 1999; Fe:Mg = 63:37, Cody and Grammer 1979), and solid solution seems likely to be complete (Bandy 1938, Palache et al. 1951). For apjohnite ($A = Mn^{2+}$), compositions extend from near the Mn end-member, to Mn^{2+}:Mg:Zn:Fe^{2+} = 64:28:6:2 (Menchetti and Sabelli 1976) and to Mn:Mg:Fe = 58:31:11 (Paulis 1991); Mn-rich halotrichite with Fe^{2+}:Mn^{2+} = 62:38 is also known, and it is likely that ternary Fe^{2+}-Mg-Mn^{2+} solid solution on the *A* site is complete (Palache et al. 1951).

Each of dietrichite (*A* = Zn, *R* = Al), redingtonite ($A = Fe^{2+}$, *R* = Cr,Al), and wupatkiite (*A* = Co, *R* = Al) is known from single or no more than two or three localities, and compositional data are accordingly sparse. For dietrichite, reported Zn:Fe^{2+}:Mn^{2+} = 42:33:25, and the Zn end-member apparently has been synthesized (Palache et al. 1951). Wupatkiite, known only from a single locality, has Co:Mg:Ni:Mn:Fe:Ca:Cu = 40:36:6:2:2:2:1 (Williams and Cesbron 1995). Bilinite ($A = Fe^{2+}$, $R = Fe^{3+}$) is known from several localities (Palache et al. 1951, Bolshakov and Ptushko 1967, Srebrodol'skiy 1977, Keith and Runnells 1998). Data for redingtonite are incomplete and the mineral has not been described adequately. The extent of substitution in R^{3+} within the mineral group is not well known, but an analysis of halotrichite with Al:Fe^{3+} = 62:38 is recorded in Palache et al. (1951), and Srebrodol'skiy (1974b) gave an analysis with Mg:Fe^{2+} = 85:17 and Al:Fe^{3+} = 120:76.

Thus, some of the sulfate minerals in the divalent–trivalent category are rather rare with regard to data and number of reported occurrences. Halotrichite is the most abundant and widely distributed, followed by pickeringite and römerite. In some cases the distinction between halotrichite and pickeringite is not made, but both are appreciably more abundant than römerite. Römerite has been observed in sulfate deposits and as an oxidation product of coals and massive sulfides. Römerite occurred at the Alcaparrosa sulfate deposit in Chile in sufficient abundance to be mined and processed as an acid source (Bandy 1938) and is locally abundant in the Richmond mine at Iron Mountain (Nordstrom and Alpers 1999a), but most occurrences are in oxidized sulfide deposits in which only minute quantities of the mineral are present.

Copiapite group The general formula of the copiapite group is $A^{2+}R^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$, wherein *R* is dominated by Fe^{3+} in all members. The seven minerals of the copiapite group are listed in Table 3, wherein all of the members are assigned 20 formula H_2O in accordance with the conclusions of Bayliss and Atencio (1985). Substitution of Al and Fe^{3+} in the A^{2+} position leads to the peculiarity that the aluminocopiapite and ferricopiapite end-members are trivalent rather than mixed divalent-trivalent salts. Substitution of trivalent ions in *A* leads to excess positive charge that is accommodated by vacancies, hence the formula is written with $Al_{2/3}$ for aluminocopiapite, and $Fe^{3+}_{2/3}$ for ferricopiapite (see also the discussion by Hawthorne et al., this volume). Because the *A*-site cations form such a small proportion of the total formula mass, small changes in analytical wt % have a pronounced effect on the mol % of the *A*-site cations. For example, end-member magnesiocopiapite contains 3.31 wt % MgO, and end-member copiapite contains 5.75 wt % FeO. Small amounts of contamination, or analytical errors, may therefore have a significant effect on the apparent range of solid solution.

With regard to *A*-site solid solution in the copiapite group, the 42 analyses listed by Berry (1947), and other analyses reported or discussed by Palache et al. (1951), Jolly and Foster (1967), Fanfani et al. (1973), Zodrow (1980), Bayliss and Atencio (1985), and Robinson (1999) strongly suggest that mutual substitution among Mg-Fe^{2+}-Fe^{3+}-Al is complete. Significant amounts of Na and Ca may be present in *A*, and only 4.54 wt % CaO is required for end-member calciocopiapite. For calciocopiapite, however, occurrences other than that of the type locality (Fleischer 1962) have not been documented.

The range in Cu contents found within the copiapite group (Palache et al. 1951, Escobar and Gifford 1961) is large, and includes compositions near that of cuprocopiapite, the Cu end-member. Type zincocopiapite (in Fleischer 1964) has $(Zn_{0.75}Fe^{2+}_{0.07}Mn^{2+}_{0.06}Ca_{0.04}K_{0.04}Na_{0.01})_{\Sigma 0.97}$ for the *A* site, and an analysis of the naturally occurring pure end-member is given by Perroud et al. (1987). Manganese contents within the copiapite group are generally <1 wt % MnO, but Pasava et al. (1986b) obtained an unusual composition for magnesiocopiapite that corresponds to $(Mg_{0.93}Mn_{0.07})_{\Sigma 1.00}(Fe^{3+}_{3.50}Fe^{2+}_{0.43}Mn_{0.17})_{\Sigma 4.10}(SO_4)_6(OH)_2{\cdot}19.9H_2O$. Copiapite-group minerals from the Richmond mine at Iron Mountain have two distinct textures and compositions (Fig. 7). The larger platy minerals, 10-50 μm in diameter, are magnesio-

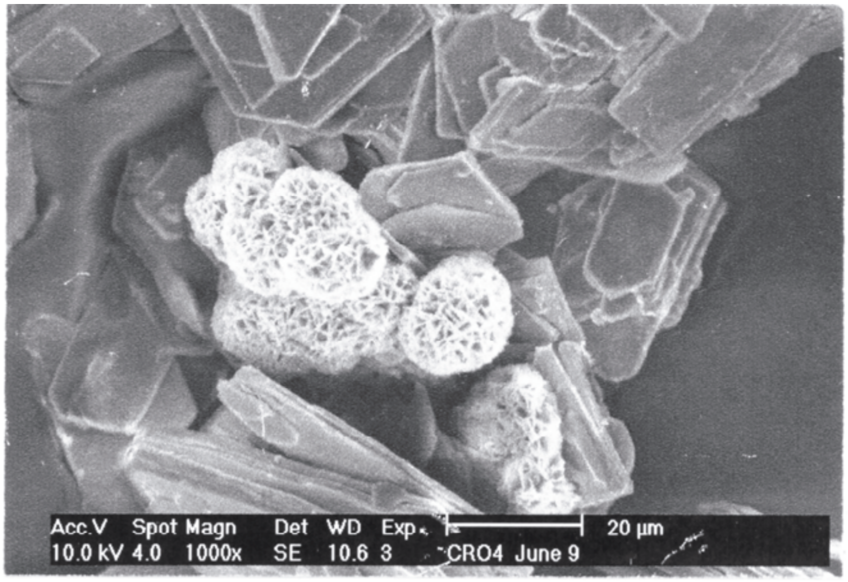


Figure 7. Scanning electron micrograph showing magnesiocopiapite (plates 10-50 μm in diameter) and Al-bearing ferricopiapite (spheroidal rosettes). Reproduced with permission from Robinson (1999).

copiapite, whereas the spheroidal aggregates are Al-bearing ferricopiapite, which may have formed by evaporation of pore waters after sample collection (Robinson 1999, Robinson et al. 2000a). Partial Al-for-Fe^{3+} substitution in R^{3+} has been demonstrated by Berry (1947), but the extent of possible accommodation of divalent metals in the R^{3+} position is not known. The synthesis of all of the minerals in the copiapite group, including calciocopiapite, was reported by Atencio et al. (1996), who also obtained the Mn, Ni, and Co analogs not yet known as minerals.

Other minerals

Two complex, hydrated sulfate salts, fibroferrite, $Fe^{3+}(SO_4)(OH)\cdot5H_2O$, and botryogen $MgFe^{3+}(SO_4)_2(OH)\cdot7H_2O$, particularly the former, are commonly associated with $M^{2+}SO_4\cdot nH_2O$ assemblages. The dimorphs butlerite and parabutlerite have the composition $Fe^{3+}(SO_4)(OH)\cdot2H_2O$; one would expect them to form as dehydration products of fibroferrite, but the authors are not aware of this having been documented.

Among the numerous other sulfates commonly associated with the preceding soluble sulfates in acidic environments, gypsum, $CaSO_4\cdot2H_2O$, occurs almost universally. With the availability of alkalis, as is typical in saline soils, the variety of salts can increase considerably. Alkali sulfates are not discussed in detail in this chapter (see Spencer, this volume, for end-member compositions and paragenetic relations among evaporite minerals).

It is appropriate to mention two K-bearing metal sulfates that form in association with the metal salts described previously: rhomboclase and voltaite. The formula of rhomboclase is variously written as $HFe^{3+}(SO_4)_2\cdot4H_2O$, $(H_3O)Fe^{3+}(SO_4)_2\cdot3H_2O$, or $(H_5O_2)Fe^{3+}(SO_4)\cdot2H_2O$, with the last formula from the crystal-structure determination by Mereiter (1974). A phase related in composition to rhomboclase is goldichite, $KFe^{3+}(SO_4)_2\cdot4H_2O$, which has K instead of H, and which is not isostructural with rhomboclase (Hawthorne et al., this volume). Unlike hydronium jarosite, which has a comparatively low solubility, dissolution of rhomboclase is fairly rapid, and the mineral can be an efficient, albeit temporary, storage place for sulfuric acid because of the extra H^+ in the formula. Several localities for rhomboclase are known, typically for occurrences in oxidized sulfide deposits. Nordstrom and Alpers (1999a) described the formation of rhomboclase stalagmites at Iron Mountain in association with water of pH = -3.6, the lowest value recorded in a field setting (Nordstrom et al. 2000).

Voltaite, $K_2Fe^{2+}{}_5Fe^{3+}{}_4(SO_4)_{12}\cdot18H_2O$, occurs in oxidized sulfide deposits and in fumarolic deposits. One of the analyses included for voltaite by Palache et al. (1951) corresponds to that of an unnamed Mg analog ($Mg > Fe^{2+}$). In the Zn analog, zincovoltaite, which is known only from an oxidized sphalerite-galena-pyrite deposit in China, the divalent Fe site is occupied by $(Zn_{3.69}Fe^{2+}{}_{0.91}Mn_{0.35})_{\Sigma4.95}$ (Li et al. 1987). Zoned crystals of voltaite, intergrown with szomolnokite, were determined to vary systematically in Zn-for-Fe substitution for samples collected from Iron Mountain, California (Jamieson and Przybylowicz 1997, Jamieson et al. 1999).

PROCESSES OF FORMATION, TRANSFORMATION, AND DISSOLUTION

Pyrite oxidation

The oxidation of pyrite to form sulfate involves a series of reactions, reviewed by Nordstrom (1982a), Lowson (1982), Nordstrom and Southam (1997), and Nordstrom and Alpers (1999b). The overall process is most commonly reported by the following reaction:

$$FeS_{2(s)} + 15/4\ O_{2(aq)} + 7/2\ H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\ H_2SO_{4(aq)} \qquad (1)$$

where $Fe(OH)_3$ is generally regarded to be a surrogate for ferrihydrite, a Fe^{3+} oxyhydroxide whose formula is contentious (see Bigham and Nordstrom, this volume). Other oxyhydroxides, such as goethite, α-FeOOH, and (rarely) lepidocrocite, γ-FeOOH, also form as insoluble precipitates. Reaction (1) forms sulfuric acid, and in acidic conditions ferrous iron can be generated

$$FeS_{2(s)} + 14\ Fe^{3+}_{(aq)} + 8\ H_2O_{(l)} \rightarrow 15\ Fe^{2+}_{(aq)} + 2\ SO_4{}^{2-}_{(aq)} + 16\ H^{+}_{(aq)} \qquad (2)$$

Indeed, soluble ferric iron and pyrite cannot coexist for any significant length of time because pyrite rapidly reduces $Fe^{3+}_{(aq)}$. This observation begs the question: how do goethite pseudomorphs after pyrite form? Such pseudomorphs are common for single pyrite crystals of generally large crystal size (≥1 mm), relatively discrete occurrence of pyrite, and within rock that contains sufficient buffering capacity to keep the ground water near neutral (or even alkaline) in pH. Hence, the low surface area slows the reaction rate considerably, and the buffered water maintains low concentrations of $Fe^{3+}_{(aq)}$ in association with the formation of insoluble Fe^{3+}-bearing minerals. In this manner, conditions are optimized for direct transformation from pyrite to goethite without the formation of sulfate minerals. However, during formation of gossans, which commonly are the oxidized equivalent of massive sulfide deposits, there are large quantities of pyrite in contact with ground water in systems that do not have the buffering capacity to override the acid production from pyrite oxidation.

In the initial stage of gossan development, oxidation of sulfides leads to the formation of Fe oxyhydroxides and soluble Fe sulfates. The soluble sulfates form in the upper parts of the vadose zone as the acid waters evaporate and dry out. These waters may have extremely low pH values (e.g. Nordstrom and Alpers 1999a,b; Nordstrom et al. 2000). The soluble sulfates, if detectable, initially form within the oxidized rims of the sulfide minerals, with melanterite usually the first to appear (Nordstrom 1982a, Nordstrom and Alpers 1999b). In the pH range of 2.5 to 8 typical of the saturated zone at and below the water table, Fe oxyhydroxides form. By far the most abundant of the oxyhydroxide products is goethite, with smaller amounts of ferrihydrite and possibly the sulfate-bearing oxyhydroxide schwertmannite (see Bigham and Nordstrom, this volume). The Fe oxyhydroxides are fine-grained, and in mineral deposits they may contain large amounts (commonly low percentages) of sorbed elements, including those of the heavy metals, as well as sulfate. Ferrihydrite and schwertmannite are metastable with respect to goethite, and thus goethite attains overwhelming predominance both by direct precipitation and by conversion of metastable Fe phases. As oxidation progresses and an overall acidic domain is established, the initial oxidation scenario moves downward, in concert with the evolving low-pH front. In the zone nearer surface, however, the Fe oxyhydroxide assemblage seems to undergo a recycling, which is probably recrystallization and the concomitant development of a coarser grain size; the attendant effect is that sorption capacity decreases, and thus the bulk of the sorbed elements is lost and moves downward. The near-surface product is a purer oxyhydroxide, most commonly goethite. Over time, the goethite may convert to hematite; there may also be pathways directly from ferrihydrite to hematite, depending on pH and the presence of trace elements (e.g. Alpers and Brimhall 1989; and references therein). The soluble sulfates are dissolved and the low-pH, sulfate-rich pore waters may precipitate jarosite, generally of composition $(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6$ (see Dutrizac and Jambor, this volume; Stoffregen et al., this volume). In sialic rocks lacking carbonates, even minor dissolution of aluminosilicates typically occurs only after acidic conditions have already been established. Among the common rock-forming minerals that are potential sources of the K that is incorporated in jarosite, the trioctahedral micas (e.g. biotite) have been observed to be the most susceptible to alteration (Jambor and Blowes 1998, Malström and Banwart 1997).

With the maturation of a gossan, the near-surface sulfides are depleted and the aluminosilicate minerals are leached, leaving a goethite-rich, siliceous residue (Blanchard 1967, Blain and Andrew 1977). Relatively insoluble sulfate minerals may accumulate at depth, and soluble sulfates and other metal oxides may precipitate at lateral seeps if climatic conditions are appropriate.

In mine settings, contemporary precipitates of soluble sulfates are generally most noticeable on the older walls of open pits and underground mine workings, and at the exposed surfaces of accumulated mine wastes, such as undisturbed tailings impoundments. The walls of open-pit mines that exploit porphyry copper deposits commonly display blue to pale green stains that consist predominantly of chalcanthite and melanterite. Such efflorescent blooms are generally temporary because of the high solubility of the salts and their susceptibility to dissolution by rain or snowmelt. Underground mines not only provide a more sheltered environment for the preservation of water-soluble minerals, but such mines also have yielded a wider spectrum of oxidation minerals because the ore types are commonly more diverse than those extracted by open-pit methods.

Field studies

Metal-sulfide depsits. Metal-sulfate salts occur most commonly in association with the oxidation of metal-sulfide mineral deposits. Many of the most famous deposits of the world (Rio Tinto, Spain; Rammelsberg, Germany; Chuquicamata, Chile; Bingham, USA; Butte, USA; Cornwall, UK; Sain Bel, France; Falun, Sweden) have efflorescent metal-sulfate salts of various types in mine workings, in open pits, and on waste rock and tailings piles. The classic paper on this subject is the work of Bandy (1938), who described in considerable detail the mineralogy of salts at Chuquicamata, Quetena, and Alcaparrosa, Chile.

Numerous efflorescent sulfate minerals have been reported from the Rio Tinto mines in Spain. Among those listed by García García (1996) are chalcanthite, copiapite, coquimbite, botroygen, epsomite, fibroferrite, gypsum, goslarite, halotrichite, mallardite, melanterite, and römerite. At the Nikitov mercury deposits, Donet'sk, Ukraine, oxidation of melanterite was concluded by Bolshakov and Ptushko (1971) to have produced rhomboclase, römerite, bilinite, copiapite, and voltaite. Numerous reports of similar assemblages are available in the Russian literature. Among the many examples, Velizade et al. (1976) identified chalcanthite, melanterite, siderotil, halotrichite, jarosite, alunogen, and slavikite $NaMg_2Fe^{3+}_5(SO_4)_7(OH)_6\cdot33H_2O$ in the oxidation zone of the Datsdag deposit, and Kravtsov (1971, 1974) reported jarosite, copiapite, römerite, and quenstedtite from cassiterite–sulfide deposits at Sakha, Azerbaijan. The processes of sulfide oxidation and sulfate formation in cryogenic zones have been discussed by Kravtsov (1974), Chernikov et al. (1994), Yurgenson (1997), and others. Permafrost conditions generally limit the availability of aqueous solutions, thereby simulating, in some respects, arid conditions.

Many examples of occurrences of soluble metal salts in the United States could be cited. Milton and Johnston (1938) photographically documented extensive blooms of epsomite and pickeringite associated with gypsum, melanterite, goslarite, pentahydrite, copiapite, voltaite, and rhomboclase at the Comstock Lode, Nevada. At the Dexter Number 7 mine, Utah, chalcanthite, melanterite, copiapite, coquimbite, römerite, fibroferrite, halotrichite, alunogen, voltaite, butlerite, parabutlerite, goldichite, and other minerals cement a talus breccia (Rozenzweig and Gross 1955). Stalactitic material at the San Manuel mine, Pinal County, Arizona, contained the first occurrence of jurbanite, $AlSO_4OH\cdot5H_2O$, which was associated with epsomite, hexahydrite, starkeyite, pickeringite, and lonecreekite, $(NH)_4Fe(SO_4)_2\cdot12H_2O$. At the Leviathan mine, California, chalcopyrite and cryptocrystalline pyrite (Pabst 1940) oxidized and produced chalcanthite, halotrichite, melanterite, and römerite (Gary 1939). Nordstrom (1982a) demonstrated, with a color photograph, the conversion of melanterite to rozenite and to copiapite from an efflorescence taken from the face of the Brick Flat massive sulfide at Iron Mountain, California. Nordstrom and Alpers (1999a) observed massive quantities of melanterite, rhomboclase, voltaite, coquimbite, copiapite, halotrichite, and römerite in underground workings of the Richmond Cu-Zn-pyrite mine at Iron Mountain. Acid waters that seemed to be in equilibrium with many of these minerals had, in several instances, negative pH values (Nordstrom et al. 2000). Solubility studies that examined Cu-Zn partitioning in melanterite from Iron Mountain showed a greater incorporation of Cu over Zn during precipitation relative to the starting solutions. These results help to explain the variations in Zn/Cu ratios of the effluent water during the annual wet-dry cycle (Alpers et al. 1994).

Tailings impundments. The surfaces, channels, and vadose zones in tailings impoundments in arid climates have yielded a rich array of soluble salts. Agnew (1998), for example, reported the presence of several Fe and Mg salts of the type $M^{2+}SO_4{\cdot}nH_2O$ at impoundments in Australia. At some sites these were accompanied by rare or unusual minerals such as: blödite $Na_2Mg(SO_4)_2{\cdot}4H_2O$, hydrobasaluminite $Al_4(SO_4)(OH)_{10}{\cdot}12\text{-}36H_2O$, hemimorphite $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, a mineral in the picromerite group $A_2Mg(SO_4)_2{\cdot}6H_2O$, and possibly wattevillite $Na_2Ca(SO_4)_2{\cdot}4H_2O$(?). The latter two are from the Ranger uranium mine, at which sulfuric acid used in mineral processing apparently accounts for the acid source. The association between arid climate and elevated temperatures is common but, as has been noted, the metal salts also form in cryogenic (permafrost) zones, as in the Antarctic (Keys and Williams 1981).

Mineralogical studies of tailings impoundments have revealed the presence of many of the sulfate minerals of the types listed in Tables 1, 2, and 3 (Jambor 1994, Jambor and Blowes 1998). Most weathered sulfide-rich impoundment surfaces contain blooms of the $FeSO_4{\cdot}nH_2O$ minerals. Blowes et al. (1991) observed that near-surface melanterite was sufficiently abundant to form a hardpan layer at the Heath Steele tailings impoundment in New Brunswick, Canada. In various impoundments, the simple hydrated sulfates (e.g. Tables 1 and 2) are commonly accompanied by those of more complex formulation, such as rhomboclase, copiapite, fibroferrite, and halotrichite (Shcherbakova and Korablev 1998, Jambor et al. 2000). Dagenhart (1980) noted that, during dry-weather conditions, melanterite, rozenite, magnesiocopiapite, aluminocopiapite, halotrichite, pickeringite, and gypsum were abundant on tailings and related wastes at the Sulfur, Boyd Smith, and Arminius Cu-Zn mines along Contrary Creek, Virginia. He also identified lesser amounts of alunogen, ferricopiapite, chalcanthite, ferrohexahydrite, siderotil, szomolnokite, gunningite, bianchite, epsomite, hexahydrite, pentahydrite, rhomboclase, fibroferrite, coquimbite, paracoquimbite, jarosite, the Cu minerals antlerite $Cu_3SO_4(OH)_4$, brochantite $Cu_4(SO_4)(OH)_6$, and serpierite $Ca(Cu,Zn)_4(SO_4)_2(OH)_6{\cdot}3H_2O$, and the Pb minerals anglesite $PbSO_4$ and linarite $PbCu(SO_4)(OH)_2$.

Although the sulfate minerals in tailings impoundments are typically Fe-dominant, the Mg-dominant sulfates have been noted to form abundantly where the gangue minerals contain dolomite. As well, the identification of Zn-dominant minerals such as gunningite, boyleite, and goslarite in mine wastes (Avdonin et al. 1988) serves to emphasize that, although the sulfates are overwhelmingly those of Fe, the compositions of the sulfate salts will reflect those of the oxidizing source materials.

Coal depsits. Soluble metal-sulfate salts commonly occur in coal or form by the oxidation of pyrite and marcasite in coal wastes (Gruner and Hood 1971, Taylor and Hardy 1974, Wagner et al. 1982, Baltatzis et al. 1986, Foscolos et al. 1989, Ward 1991). Sulfate efflorescences in coal deposits commonly contain melanterite (± rozenite and szomolnokite), copiapite, and the pickeringite-halotrichite series (McCaughey 1918, Nuhfer 1967, Young and Nancarrow 1988, Cravotta 1994, Rose and Cravotta 1998, Querol et al. 1999). Cravotta (1994) observed römerite, copiapite, and coquimbite on mine spoils, coal outcrops, and overburden at the bituminous coalfields of western Pennsylvania. Wiese et al. (1987) showed that melanterite and rozenite were the earliest Fe-sulfate hydrates to form from the oxidation of pyrite and marcasite in Utah and Ohio coalfields; also noted was that szomolnokite and halotrichite appeared to be the most stable phases.

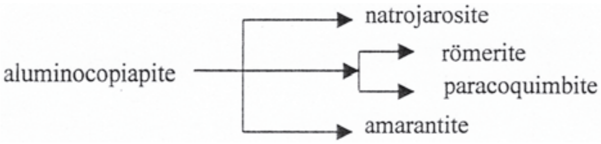
McCaughey (1918) observed the common occurrence of melanterite in bituminous coal mines and described one specimen that formed a 14 kg (30 lb) mass. After storage for a year, the mineral was noted to be transforming to copiapite (and possibly some rozenite-szomolnokite). Similar transformations have been noted for other melanterite specimens stored in museums (Nordstrom, unpublished data). The dehydration of melanterite to rozenite has been observed frequently, beginning with the reports of Kubisz (1960a) and Kossenberg and Cook (1961).

Nuhfer (1967, 1972) studied the occurrence of efflorescent sulfates in the bituminous coal deposits near Morgantown, West Virginia. Melanterite, szomolnokite, pickeringite, copiapite, gypsum, and hexahydrite were observed to be common; thenardite, Na_2SO_4, and possible boothite were uncommon, and the thenardite may have had an anthropogenic source. The following is a summary of Nuhfer's observations and inferences:

1. Melanterite and szomolnokite were the first to form as a result of pyrite oxidation.
2. Copiapite was abundant and likely included significant quantities of ferricopiapite and minor magnesiocopiapite.
3. Epsomite was known to occur in the area, but he detected only hexahydrite.
4. Halotrichite-pickeringite and copiapite occur in sheltered areas in close proximity to pyrite.
5. Sulfate efflorescences reflect the composition of the waters from which they form.
6. Sulfate efflorescences are easily dissolved by rainwater, and the sulfate-rich solutions move into adjacent streams.
7. Formation of hydrated sulfate minerals contributed to fracturing and spallation of rock faces.

The presence of hydrated iron sulfates in the Sydney coalfield of Cape Breton, Nova Scotia, was observed by Zodrow and colleagues (Zodrow and McCandlish 1978, Zodrow et al. 1979, Zodrow 1980), who identified melanterite (as the first mineral formed), rozenite, epsomite, pickeringite, halotrichite, aluminocopiapite, fibroferrite, rhomboclase, thenardite, sideronatrite $Na_2Fe^{3+}(SO_4)_2(OH)_3\cdot 3H_2O$, and metasideronatrite $Na_2Fe^{3+}(SO_4)_2(OH)\cdot H_2O$. Zodrow et al. (1979) noted that the sulfate efflorescences induced mechanical stress and rock erosion; thus, the buildup of salts in fractures, with consequent heaving and slippage, was at least partly responsible for some of the pillar collapses in the coal mines. Oxidation of pyrite-bearing shales and mudrocks is a common geotechnical problem because of the ensuing heaving and cracking of many types of structures (Hawkins and Pinches 1997, Cripps and Edwards 1997, Hawkins and Higgins 1997), and because of the rapid erosion of highway material (Byerly 1996).

Zodrow (1980) demonstrated a wide range of substitutions by Al, Mg, Na, Cu, Ni, and Zn in copiapite, and complex transformations of aluminocopiapite on storage:



(The formula of amarantite is $Fe^{3+}_2(SO_4)_2O{\cdot}7H_2O$; Mandarino 1999).

Other occurrences. Metal-sulfate salts can form in diverse environments other than weathering zones of coal and metallic deposits. Hexahydrite has been identified in human concretions (Gibson 1974), and the Mg salts are common in evaporites. For example, kieserite occurs widely in marine evaporite deposits in Germany and several other countries, among which in the United States are the Permian salt deposits of Texas and New Mexico (Palache et al. 1951). Epsomite occurs similarly, and both it and hexahydrite form as precipitates in saline lakes. Both minerals are also present in some soils and their efflorescences (Doner and Lynn 1977, Skarie et al. 1986, Timpson et al. 1986, Ducloux et al. 1994), and these minerals may have formed evaporite deposits on the surface of Europa, one of the satellites of Jupiter (McCord et al. 1998). Melanterite, rozenite, and copiapite have been reported commonly to form at or near the surfaces of active acid sulfate soils (Van Breemen 1982, Wagner et al. 1982, Fanning et al. 1993, Montoroi 1995).

Metal-sulfate salts are common around active crater lakes, fumaroles, and acid hot springs. In these environments, H2S oxidizes to elemental sulfur, which accumulates and is further oxidized by microbial activity to form sulfuric acid. The acid reacts with the surrounding silicate bedrock and, upon evaporation, can form a variety of metal-sulfate salts. In deposits of native sulphur in the Ukraine, Srebrodol'skiy (1977) determined that alteration of melanterite resulted in two different assemblages. One of the paragenetic associations consisted of ferrohexahydrite, siderotil, rozenite, and szomolnokite, i.e. the 7-, 6-, 5-, 4-, and 1-hydrates of FeSO4. The other association consisted of melanterite, römerite, bilinite, copiapite, and Fe oxyhydroxides. The formation of soluble sulfates in other sulfur deposits and in aluminite deposits has been reported in numerous papers (e.g. Srebrodol'sky 1971, Smirnova 1971, Vdovichenko et al. 1974, Sokolov et al. 1985, Lizalek et al. 1989, Zavalía and Galliski 1995). Among the minerals most commonly observed are melanterite, siderotil, rozenite, szomolnokite, epsomite, basaluminite (felsöbányaite), halotrichite, pickeringite, copiapite, fibroferrite, and voltaite. Charles et al. (1986) included szomolnokite, rozenite, halotrichite, and alunogen in the vapor-produced alteration assemblage in the Sulphur Springs hydrothermal system at Valles Caldera, New Mexico. Delines (1975) observed chalcanthite among the sublimates at Nyamuragira Volcano, Zaire, and Africano and Bernard (2000) reported alunite, schlossmacherite (hydronium-dominant alunite), anhydrite/gypsum, and an Fe-Mg sulfate close to magnesiocopiapite in composition in the fumarolic environment of Usu Volcano, Japan.

There are a number of localities that use the name of Alum Creek or Alum Rock. One striking example is the deposit of alum rock next to the Gila River in Grant County, New Mexico, where an andesitic breccia is highly altered and contains aluminum sulfate salts in addition to large quantities of kaolinite (Hayes 1906). Alunogen and halotrichite are present, and one incrustation of alunogen was described as being more than a meter thick. The weathering of fine-grained pyrite and acid hydrothermal alteration seem to have been responsible for the occurrence of metal-sulfate salts rich in aluminum.

Stoiber and Rose (1974) identified 29 metal-sulfate salts at 14 Central American volcanoes; most of the salts were soluble hydrated minerals and are the same as those at metal-sulfide mines and mineral deposits. In fumarolic incrustations at Mount St. Helens, Washington, Keith et al. (1981) observed that halotrichite and gypsum are common, and also present are anhydrite, melanterite, alunite, thenardite, sal ammoniac NH_4Cl, and glauberite $Na_2Ca(SO_4)_2$. Melanterite and other salts occur as volcanic sublimates in Japan (Ossaka 1965) and Kamchatka, Russia (Vergasova 1983), as authigenic minerals from volcanic emanations in Greece (Stamatakis et al. 1987, Kyriakopoulos et al. 1990), and as pseudofumarolic deposits in burning coal dumps (Lazarenko et al. 1973, Novikov and Suprychev 1986). Martin et al. (1999) found alunogen, meta-alunogen, halotrichite, melanterite, potash alum, mirabilite $Na_2SO_4{\cdot}10H_2O$, and tschermigite $(NH_4)Al(SO_4)_2{\cdot}12H_2O$ as products of the sulfuric-acid alteration of ignimbrite at Te Kopia geothermal field in New Zealand. Gypsum, alunite, jarosite, halite NaCl, kalinite $KAl(SO_4)_2{\cdot}11H_2O$, and tamarugite $NaAl(SO_4)_2{\cdot}6H_2O$ also occur in the field (Rodgers et al. 2000). Diverse assemblages that include water-soluble simple sulfates such as rozenite, coquimbite, halotrichite, and alunogen have been observed in other geothermal fields (Zhu and Tong 1987). Among the minerals identified by Minakawa and Noto (1994) as occurring in a tufa deposit at the Myoban hot spring, Oita Prefecture, Japan, are melanterite, halotrichite, copiapite, alunogen, tamarugite, voltaite, and metavoltine $K_2Na_6Fe^{2+}Fe^{3+}{}_6(SO_4)_{12}O_2{\cdot}18H_2O$.

Shales commonly contain fine-grained pyrite that forms salt efflorescences upon weathering. Badak (1959) and Kubisz and Michalek (1959) detected melanterite and epsomite in weathered oil shales, and Ievlev (1988) reported the occurrence of melanterite, rozenite, halotrichite, copiapite, and coquimbite that formed from the weathering of shale in permafrost conditions. Development of efflorescences is typical during dry periods when evaporation takes place, which may occur in a variety of climates. However, the salts tend to persist for longer periods of time in regions with prolonged dry seasons, i.e. hyper-arid, arid, and semi-arid climates. In the Upper Colorado River Basin, for example, Whittig et al. (1982) observed gypsum, epsomite, hexahydrite, pentahydrite, starkeyite, kieserite, thenardite, mirabilite $Na_2SO_4{\cdot}10H_2O$, löweite $Na_{12}Mg_7(SO_4)_{13}{\cdot}15H_2O$, and blödite $Na_2Mg(SO_4)_2{\cdot}4H_2O$ as efflorescences on the Mancos Shale. Their dissolution was determined to be responsible for the high contents of dissolved salts in some of the streams draining into the Upper Colorado River.

As has been emphasized, the compositions of soluble metal-sulfate minerals reflect the compositions of the solutions from which the minerals precipitate. In supergene zones, therefore, these sulfates are closely linked to the compositions of the sulfide minerals that have been oxidized, as well as to the composition of the surrounding minerals that have been susceptible to dissolution by the ensuing low-pH solutions.

Dissolution during rainfall events

Dissolution of Fe sulfates during storm runoff (Dagenhart 1980, Olyphant et al. 1991, Bayless and Olyphant 1993) or after reclamation efforts (Cravotta 1994) can acidify streams, can rapidly increase metal loading to surface waters, and can lead to the development of acidic groundwaters. Such dissolution can also lead to deleterious consequences for remediation efforts that involve the flooding of mine voids by plugging of mine openings (e.g. Cravotta 1994, Nordstrom and Alpers 1999a).

Dissolution of metal-sulfate salts during storm runoff events has been found to cause a spiked increase in the concentrations of dissolved metals and sulfate even as the stream discharge increased (Dagenhart 1980). Figure 8 shows spiked increases in Fe, Cu, and Zn during the rising limb of the discharge in Contrary Creek, Virginia, for a rainstorm event of June 19, 1978. Careful mineralogical examination showed that the spiked increases in solute concentrations were related to the dissolution of efflorescent salts on mine tailings.

Keith and Runnells (1998) and Keith et al. (1999) noted that the dissolution of sulfates, accumulated at base-metal waste sites during the dry season, gave a pronounced hydrogeochemical response following the first storm of the wet season. Rapid response to local climatic conditions has also been noted by Alpers et al. (1994), who observed that dissolution of melanterite, in which solid solutions of other metals were present, led to seasonal variations of Zn/Cu in acidic effluents at Iron Mountain, California. Cyclical changes in metal and sulfate concentrations through storm events (Dagenhart 1980) and cyclical changes in Zn/Cu ratios through seasonal wet-dry cycles (Alpers et al. 1992, 1994)

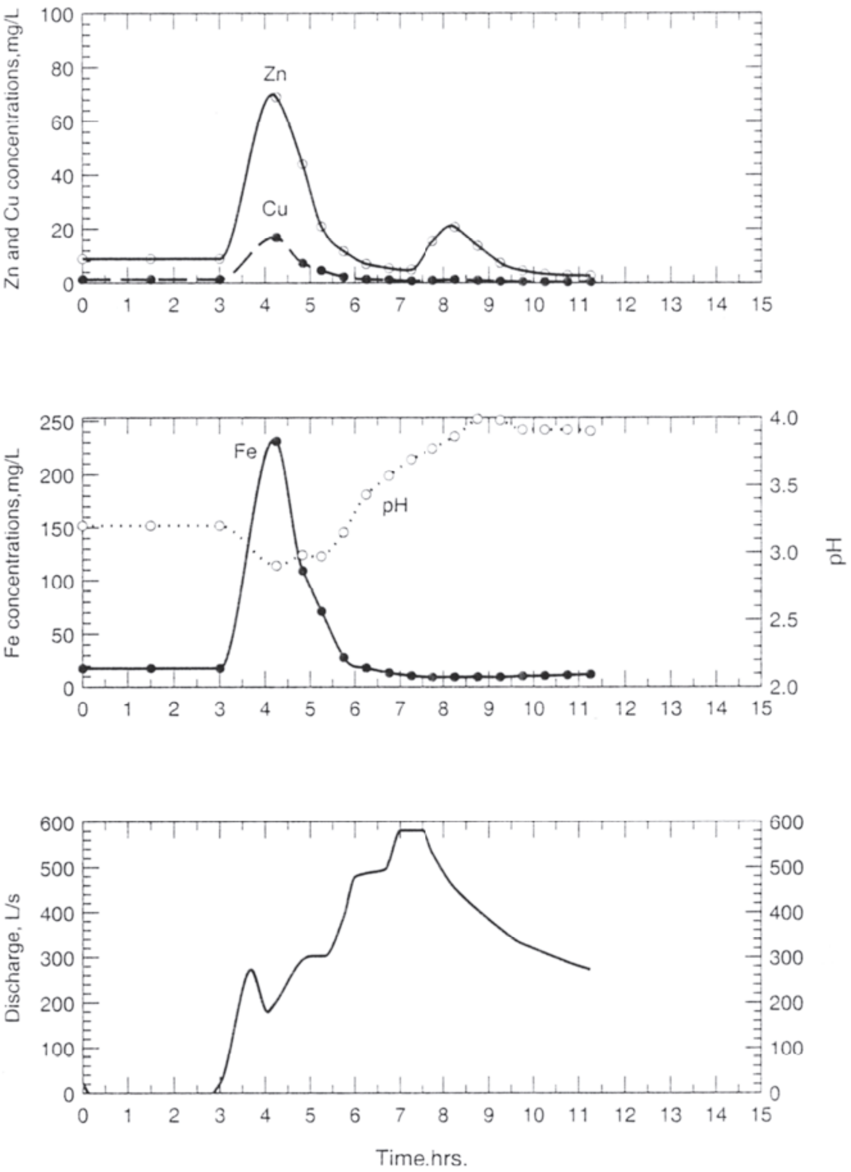


Figure 8. Variations in Zn, Cu, and Fe, and decrease in pH in relation to stream discharge after a rainstorm at Contrary Creek, Virginia (after Dagenhart 1980).

can be attributed to dissolution and reprecipitation of soluble metal-sulfate salts.

One of the environmental consequences of metal concentrations increasing during the rising limb of a stream discharge during storm events is that downstream aquatic life receives a much greater loading of metals than if the rainstorm simply diluted the existing water quality. Indeed, fish kills are commonly associated with some of the early rainstorm events of the wet season in areas with a periodically dry climate.

Plugging of mine adits and the consequent rise in underground water levels can cause the dissolution of soluble salts that have accumulated in the mine workings. For the Richmond mine at Iron Mountain, California, it was estimated by Nordstrom and Alpers (1999a) that about 600,000 m^3 of highly acidic water ($pH < 1$) containing many grams per liter of dissolved heavy metals could accumulate underground as a result of proposed (and later rejected) plans for remediation by mine plugging. Figure 9 shows the anticipated drop in pH with increasing dissolution of soluble salts that was computed on the basis of the

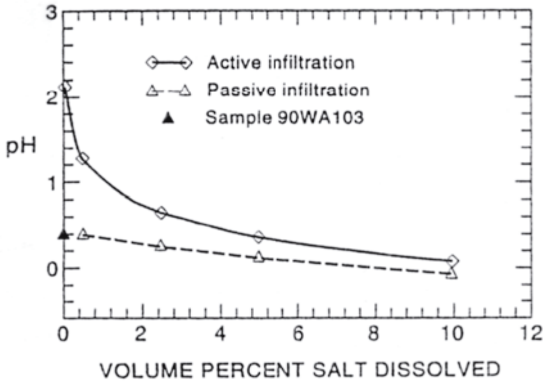


Figure 9. Calculated decrease in pH related to the potential volume of metal-sulfate salts dissolved at Iron Mountain, California (from Nordstrom and Alpers 1999a).

observed mineralogy and composition of salts found underground at Iron Mountain. A plot similar to Figure 9 was produced by Keith et al. (1999) to show the effect on predicted pH by the dissolution of different mass amounts of specific salts.

Laboratory studies

One of the more accessible examples of the development of soluble sulfate minerals is their presence, as a result of spontaneous growth, on laboratory and museum specimens (Workman and Rader 1961, Buurman 1975, Wiese et al. 1987). Such sulfates formed so readily on samples of cored pyritiferous mine tailings that the minerals were included in Jambor's (1994) classification as 'quaternary' minerals to distinguish them from 'tertiary' sulfates that had crystallized from pore waters during drying of the cores. In a study of museum and collectors' specimens of pyrite and marcasite, Blount (1993) identified ten Fe-sulfate minerals, and two other sulfates that were concluded to have formed as alteration products as a result of humidity variations during storage of pyrite and marcasite specimens. Luzgin (1990) noted that, in addition to szomolnokite and chalcanthite, the Co arsenate mineral erythrite had formed during long-term storage of collected specimens. Grybeck (1976) observed that specimens of sphalerite continued to form coatings of gunningite even after repeated washings had cleansed the sphalerite surfaces.

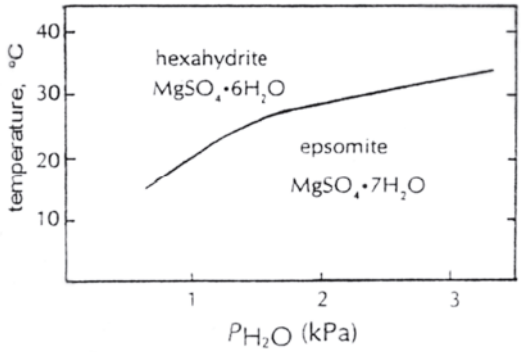


Figure 10. Stability of the simple sulfates of Mg as a function of temperature and water (modified from Keller et al. 1986a).

Many of the simple salts are extremely sensitive to atmospheric conditions and will change their hydration state, in some cases reversibly, in response to the local temperature and humidity conditions (Fig. 10; Keller et al. 1986a,b; Waller 1992, Chou et al. 2000). Preservation of samples in their original, as-collected state is thus a common problem for mineralogical studies. Waller (1992) compiled data on humidity-controlled reactions among hydrous minerals (Table 4) and discussed various strategies for sample conservation.

Solubilities and stability relationships

Ferrous sulfate hydrates. Pure, synthetic forms of three of the naturally occurring ferrous sulfate minerals, melanterite, rozenite, and szomolnokite, have been the subject of

Table 4. Sulfate minerals subject to humidity-related phase transitions. Modified from Waller (1992).

Species	*Formula*[a]	*Reaction*[b]	*%RH*[c]	*T*[d]	*Reference*[e]
aluminite	$Al_2(SO_4)(OH)_4{\cdot}7H_2O$	$-nH_2O$			Waller 1992
alunogen	$Al_2(SO_4)_3{\cdot}17H_2O$	deliquesce	88	20	Waller 1992
		$-nH_2O$			
bianchite	$(Zn,Fe^{2+})SO_4{\cdot}6H_2O$	$+1H_2O \rightarrow 7$	59	20	Bonnell and Burridge 1935
		$-1H_2O \rightarrow 6$	56	20	
bieberite	$CoSO_4{\cdot}7H_2O$	deliquesce	94	20	Waller 1992
		$-1H_2O \rightarrow 6$	70	20	Waller 1992
bonattite	$CuSO_4{\cdot}3H_2O$	$+2H_2O \rightarrow 5$	33	20	Collins and Menzies 1936
		$-2H_2O \rightarrow 1$	22	25	Collins and Menzies 1936
boothite	$CuSO_4{\cdot}7H_2O$	$-nH_2O$			Parsons 1922
boussingaultite	$(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$	deliquesce	96	25	Waller 1992
		$-2H_2O \rightarrow 4$	20	25	Caven and Ferguson 1924
boyleite	$(Zn,Mg)SO_4{\cdot}4H_2O$	$-nH_2O$			Bari et al. 1982
chalcanthite	$CuSO_4{\cdot}5H_2O$	deliquesce	97	25	Collins and Menzies 1936
		$-2H_2O \rightarrow 3$	33	25	Collins and Menzies 1936
chalcocyanite	$CuSO_4$	$+1H_2O \rightarrow 1$	3	25	Foote and Scholes 1911
coquimbite	$Fe^{3+}{}_2(SO_4)_3{\cdot}9H_2O$	deliquesce	~73	20	Waller 1992
		$-nH_2O$			Bannister 1937
cyanochroite	$K_2Cu(SO_4){\cdot}6H_2O$	$-2H_2O \rightarrow 4$	36	25	Caven and Ferguson 1922
darapskite	$Na_3(SO_4)(NO_3){\cdot}H_2O$	deliquesce			Parsons 1922
epsomite	$MgSO_4{\cdot}7H_2O$	deliquesce	91	20	Waller 1992
		$-H_2O \rightarrow 6$	83	20	Randall 1930
ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$	$-nH_2O$			Palache et al. 1951
ferrinatrite	$Na_3Fe^{3+}(SO_4)_3{\cdot}3H_2O$	deliquesce			Palache et al. 1951
ferrohexahydrite	$Fe^{2+}SO_4{\cdot}6H_2O$	$+1H_2O \rightarrow 7$	61	25	Bonnell and Burridge 1935
fibroferrite	$Fe^{3+}(SO_4)(OH){\cdot}5H_2O$				Palache et al. 1951
goslarite	$ZnSO_4{\cdot}7H_2O$	deliquesce	89	25	O'Brien 1948
		$-nH_2O$			Palache et al. 1951
gunningite	$(Zn,Mn^{2+})SO_4{\cdot}H_2O$	$+5H_2O \rightarrow 6$	54	25	Foote and Scholes 1911
		$-1H_2O \rightarrow 0$	4	25	Foote and Scholes 1911
halotrichite	$Fe^{2+}Al_2(SO_4)_4{\cdot}22H_2O$	$-nH_2O$			Bannister 1937
hanksite	$KNa_{22}(SO_4)_9(CO_3)_2Cl$	deliquesce	~75	RT	Waller 1992
hexahydrite	$MgSO_4{\cdot}6H_2O$	$+1H_2O \rightarrow 7$	51	25	Bonnell and Burridge 1935
		$-1H_2O \rightarrow 5$	41	25	Foote and Scholes 1911
hydrobasaluminite	$Al_4(SO_4)(OH)_{10}{\cdot}15H_2O$ [a]	$-nH_2O \rightarrow 5$			Sunderman and Beck 1969
jôkokuite	$Mn^{2+}SO_4{\cdot}5H_2O$	$+2H_2O \rightarrow 7$	84	15	Randall 1930
		$-4H_2O \rightarrow 1$	74	20	Randall 1930
kainite	$MgSO_4{\cdot}KCl{\cdot}3H_2O$	deliquesce			
		$-3H_2O \rightarrow 0$	3	32	Randall 1930
kieserite	$MgSO_4{\cdot}H_2O$	$+3H_2O \rightarrow 4$	21	25	Foote and Scholes 1911
		$-1H_2O \rightarrow 0$	4	25	Foote and Scholes 1911

Table 4, continued

konyaite	$Na_2Mg(SO_4)_2\cdot 5H_2O$	$-1H_2O \rightarrow 4$			van Doesburg et al. 1982
langbeinite	$K_2Mg_2(SO_4)_3$	deliquesce			Bannister 1937
leonite	$K_2Mg(SO_4)_2\cdot 4H_2O$	$+2H_2O \rightarrow 6$			Palache et al. 1951
löweite	$Na_{12}Mg_7(SO_4)_{13}\cdot 15H_2O$	deliquesce			Palache et al. 1951
mallardite	$Mn^{2+}SO_4\cdot 7H_2O$	$-2H_2O \rightarrow 5$		<9	Linke 1965
mascagnite	$(NH_4)_2SO_4$	deliquesce	81	20	Wexler and Hasegawa 1954
matteuccite	$NaHSO_4\cdot H_2O$	deliquesce	52	20	O'Brien 1948
		$-1H_2O \rightarrow 0$	16	20	Heitmankova and Cerny 1974
melanterite	$Fe^{2+}SO_4\cdot 7H_2O$	deliquesce	95	20	Waller 1992
		$-6H_2O \rightarrow 1$	57	20	Waller 1992
mendozite	$NaAl(SO_4)_2\cdot 11H_2O$	$-5H_2O \rightarrow 6$			Palache et al. 1951
mercallite	$KHSO_4$	deliquesce	86	20	O'Brien 1948
mirabilite	$Na_2SO_4\cdot 10H_2O$	deliquesce	93	RT	O'Brien 1948
moorhouseite	$(Co,Ni,Mn^{2+})SO_4\cdot 6H_2O$	$+1H_2O \rightarrow 7$	70	20	Schumb 1923
morenosite	$NiSO_4\cdot 7H_2O$	deliquesce	93	25	Waller 1992
pentahydrite	$MgSO_4\cdot 5H_2O$	$+1H_2O \rightarrow 6$	41	25	Randall 1930
		$-1H_2O \rightarrow 4$	37	25	Randall 1930
poitevinite	$(Cu,Fe^{2+},Zn)SO_4\cdot H_2O$	$+2H_2O \rightarrow 3$	22	25	Collins and Menzies 1936
		$-1H_2O \rightarrow 0$	3	25	Foote and Scholes 1911
quenstedtite	$Fe^{3+}{}_2(SO_4)_3\cdot 10H_2O$	$-1H_2O \rightarrow 9$			Bandy 1938
retgersite	$NiSO_4\cdot 6H_2O$	$+1H_2O \rightarrow 7$	84	20	Bonnell and Burridge 1935
rhomboclase	$(H_5O_2)^+Fe^{3+}(SO_4)_2\cdot 2H_2O$	$-nH_2O$			Bannister 1937
sanderite	$MgSO_4\cdot 2H_2O$	$+2H_2O \rightarrow 4$	22	31	Randall 1930
sideronatrite	$Na_2Fe^{3+}(SO_4)_2(OH)\cdot 3H_2O$	$-nH_2O$			Zodrow et al. 1979
sodium alum	$NaAl(SO_4)_2\cdot 12H_2O$	$-6H_2O \rightarrow 6$	86	20	Hepburn and Phillips 1952
starkeyite	$MgSO_4\cdot 4H_2O$	$+1H_2O \rightarrow 5$	37	25	Foote and Scholes 1911
szmikite	$Mn^{2+}(SO_4)\cdot H_2O$	$+4H_2O \rightarrow 5$	83	25	Carpenter and Jette 1923
		$-1H_2O \rightarrow 0$	17	20	Randall 1930
szomolnokite	$Fe^{2+}SO_4\cdot H_2O$	$-1H_2O \rightarrow 0$	11	20	Waller 1992
		$+6H_2O \rightarrow 7$	57		
tamarugite	$NaAl(SO_4)_2\cdot 6H_2O$	$+6H_2O \rightarrow 12$	86	20	Hepburn and Phillips 1952
thenardite	Na_2SO_4	$+10H_2O \rightarrow 10$	81	25	Wilson 1921
tschermigite	$(NH_4)Al(SO_4)_2\cdot 12H_2O$	$-6H_2O \rightarrow 6$	7	25	Hepburn and Phillips 1952
uranopilite	$(UO_2)_6(SO_4)(OH)_{10}\cdot 12H_2O$	$-nH_2O$			Palache et al. 1951
voltaite	$K_2Fe^{2+}{}_5Fe^{3+}{}_4(SO_4)_{12}\cdot 18H_2O$	$-nH_2O$			Bannister 1937
zaherite	$Al_{12}(SO_4)_5(OH)_{26}\cdot 20H_2O$	$-nH_2O$			Ruotsala and Babcock 1977
zinc-melanterite	$(Zn,Cu,Fe^{2+})SO_4\cdot 7H_2O$	deliquesce	89	25	O'Brien 1948
		$-1H_2O \rightarrow 6$	65	25	Bonnell and Burridge 1935

[a] Formulas from Waller (1992) or Mandarino (1999) except for hydrobasaluminite (Bigham and Nordstrom, this vol.)

[b] The number of water molecules specified as being gained or lost in a reaction is for the reaction as written with the formula given. If the reaction is deliquescence, then decomposition, oxidation, or hydrolysis may also occur.

[c] The relative humidity at which a reaction occurs is dependent on temperature. The relative humidity given in column 4 applies at the temperature given in column 5. See Waller (1992) for methods of calculation.

[d] Temperatures are given in degrees Celsius. RT = room temperature (normally ~ 22°C).

[e] References as cited by Waller (1992).

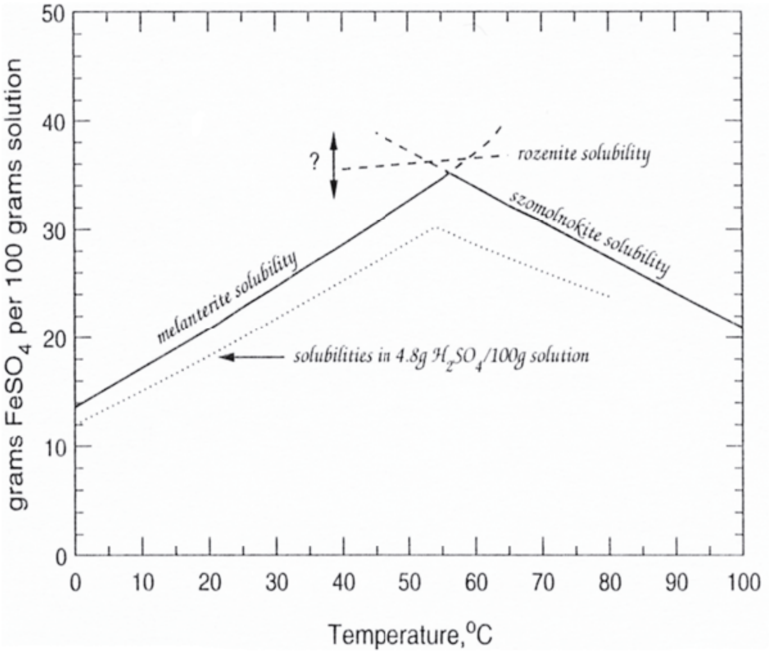


Figure 11. Solubility data for melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), and szomolnokite ($FeSO_4 \cdot H_2O$); data of Bullough et al. (1952) and Reardon and Beckie (1987).

numerous laboratory studies of solubility. These studies help to define the range of environmental stability for each mineral. Early data have been compiled by Mellor (1923), International Critical Tables (1927), Gmelins Handbuch (1932), and Linke and Seidell (1958). Phase equilibria and electrolyte properties in the $FeSO_4$–H_2SO_4–H_2O system have been studied more recently by Bullough et al. (1952) and Reardon and Beckie (1987). In anoxic systems the solubility equilibria for the three hydrate minerals are shown in Figure 11. Rozenite appears to be a metastable phase in aqueous solutions according to the carefully reversed solubility measurements of Bullough et al. (1952) and as discussed by Reardon and Beckie (1987). Bursa and Stanisz-Lewicka (1982) found rozenite to be a metastable intermediate during the recrystallization of melanterite with increasing sulfuric acid concentrations at temperatures of 45, 55, and 60° C. Rozenite formed first and then slowly recrystallized to szomolnokite. Hence, the solubility curve of rozenite is estimated to be slightly above the point of intersection of the solubilities for melanterite and szomolnokite. A conclusion to be drawn from these data is that the occurrence of rozenite would require dehydration of melanterite (or rehydration of szomolnokite) in the absence of a solution phase. Rozenite must form by dehydration at <100% relative humidity. For example, Mitchell (1984) determined that melanterite dehydrated to rozenite when the relative humidity is less than 65%. Parkinson and Day (1981) measured an equilibrium relative humidity of 55.8% at 20° C.

The dotted line in Figure 11 shows the effective lowering of the solubilities by the additional of 4.8 wt % sulfuric acid. This concentration of acid is close to the maximum concentration of sulfuric acid commonly observed for acid mine waters, and it would be equivalent to a pH range of 0 to 1. The presence of sulfuric acid produced by pyrite oxidation can be seen to enhance the formation of melanterite and szomolnokite by decreasing their solubility through the common-ion effect. Melanterite commonly contains some divalent metals in solid solution (Fig. 2), which further decreases its solubility (Mellor 1923) and increases its stability (see Glynn, this volume).

The question mark in Figure 11 suggests that there are several inadequacies in the solubility data. Solubility data for rozenite are not well-established, and no data seem to exist for ferrohexahydrite or siderotil to confirm their metastability. The solubility data between 50 and 65° C are in need of detailedstudy because that is the temperature range in which ferrohexahydrie and siderotil would form, and the existing measurements contain inconsistencies. The data of Reardon and Beckie (1987) produce a melanterite-szomolnokite transition temperature of about 65° C instead of the 56.7° C measured by Bullough et al. (1952), but it is likely that the data cannot be fit much better at this time. Mitchell (1984) was able to prepare rozenite both by recrystallization from solution at 60° C and by hydration of an X-ray amophous monohydrate in the relative humidity range of >0 to 65%. Above 65% the heptahydrate formed. A dihydrate salt reported rarely in lab studies requires verification and has not been reported to occur in nature.

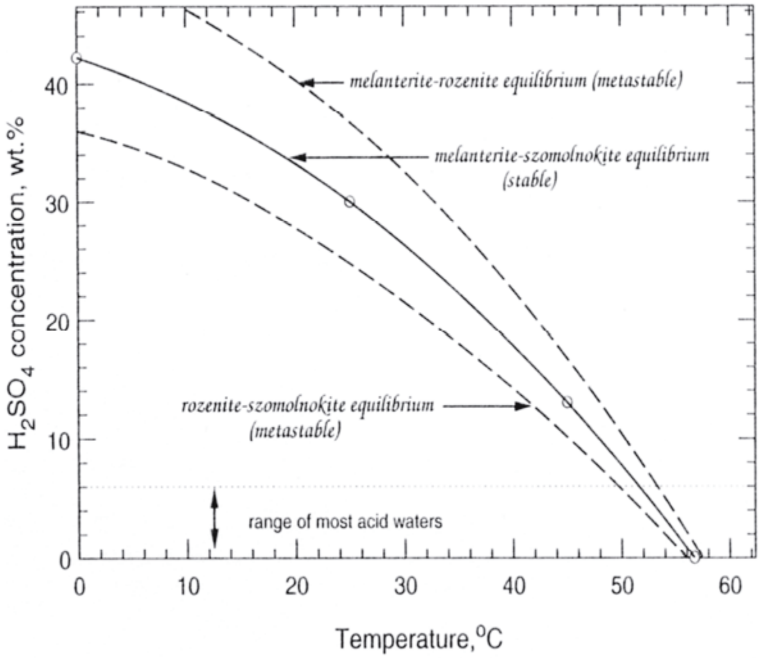


Figure 12. Univariant equilibria for the coexistence of melanterite and szomolnokite as a function of temperature and concentration of H_2SO_4; data sources as in Figure 11.

A number of solubility studies over a range of sulfuric acid concentrations help to define the stability relationships and provide convincing evidence that only melanterite and szomolnokite are stable in contact with saturated solutions. Figure 12 shows the variation in the stable univariant equilibrium for the coexistence of melanterite and szomolnokite as a function of temperature and sulfuric acid concentration. Estimated curves for the metastable extensions of the melanterite-rozenite and rozenite-szomolnokite equilibria in the presence of water (100% relative humidity) are shown as dashed lines in Figure 12. The metastable equilibria intersect the stable equilibrium line at <100% relative humidity. Both the concentrations of sulfuric acid and the relative humidity are independent measurements of the activity of water and can be used to confirm the consistency and accuracy of the stability relations and to recover thermodynamic properties.

Zinc sulfate hydrates. Solubility data for the zinc sulfate hydrates, goslarite ($7H_2O$), bianchite ($6H_2O$), and gunningite ($1H_2O$) are based on the best fits by Linke and Seidell (1958) and the data shown in Figure 166 of Gmelins Handbuch (1956). The solubility curves (Fig. 13) are similar to the ferrous sulfate data except that bianchite, the hexahydrate, is the stable intermediate hydrate between 37.9 and 48.8° C. The enthalpy of

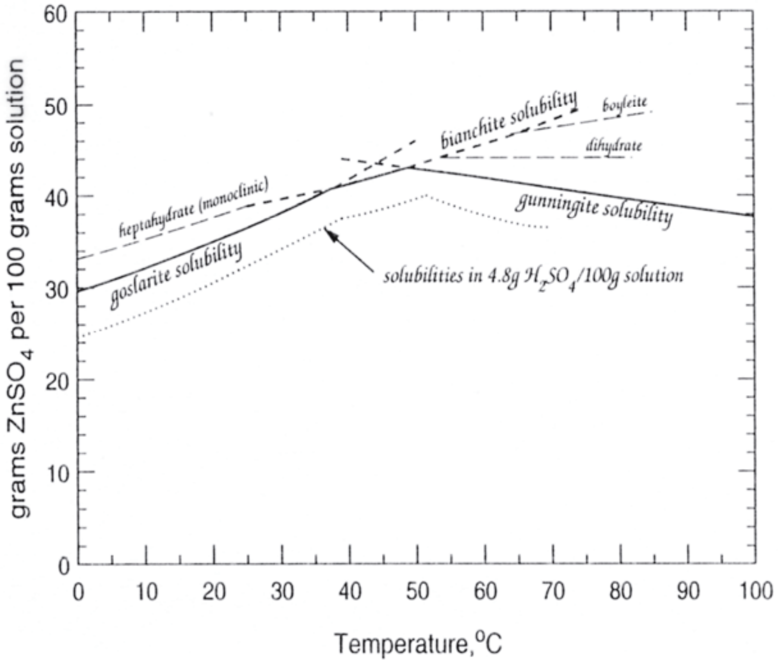


Figure 13. Solubility data for the $ZnSO_4$–H_2O system, from Gmelins Handbuch (1956) and Linke and Seidell (1958).

transition for the reaction goslarite to bianchite plus water in aqueous solution was determined by Grønvold and Meisingset (1982) to be 16.5 kJ mol^{-1} at 38° C. The tetrahydrate, boyleite, and the dihydrate are metastable in aqueous solutions. The hemiheptahydrate, the trihydrate, and the pentahydrate have been reported from lab studies but these are not confirmed as metastable phases from the solubility studies. The dashed lines in Figure 13 show the metastable extensions of each solubility, and the dotted line shows the lowering of the solubility of the stable phases with the addition of 4.8 wt % sulfuric acid. Impurities of divalent metal also lower the solubility of the zinc sulfate hydrates (Mellor 1923, Petlicka 1971).

Solubility data for the zinc sulfate system in sulfuric acid are sufficient to plot the univariant equilibria as a function of temperature (Fig. 14). The quadruple point for the coexistence of goslarite, bianchite, gunningite, and solution does occur for saturated solution conditions (at 21.5° C) although it is outside the acid range of most acid mine waters. These equilibria demonstrate that all three zinc hydrates can form directly from solution and that the temperature and sulfuric acid concentrations for their stability range fall within well-defined limits. Furthermore, boyleite (like rozenite) is metastable and must form by dehydration of bianchite or goslarite (or hydration of gunningite). The solubility studies also predict the metastability of a zinc sulfate dihydrate phase that has not yet been identified as a mineral. There are several examples of synthetic compounds that were later identified as minerals. For example, the solubility of boyleite was known from the 1930s, but the compound was not identified as a mineral until 1962 (Jambor and Boyle 1962, Walenta 1978).

Inconsistencies occur in the phase-equilibria data for the aqueous zinc sulfate system. For example, the equilibrium for the coexistence of bianchite and gunningite has been determined by more than one investigator and, in the absence of sulfuric acid, it occurs at 48.8° C. However, carefully measured solubilities over a range of sulfuric acid concentrations extrapolate to about 56° C at zero sulfuric acid concentration (Fig. 14). This difference is greater than the error of the measurements.

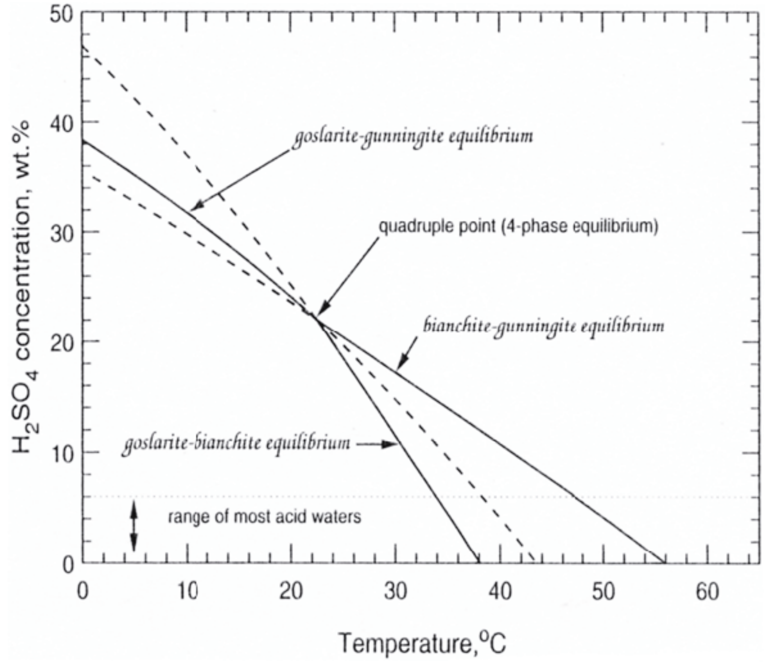


Figure 14. Univariant equilibria for the $ZnSO_4$ system; sources of data as in Figure 13.

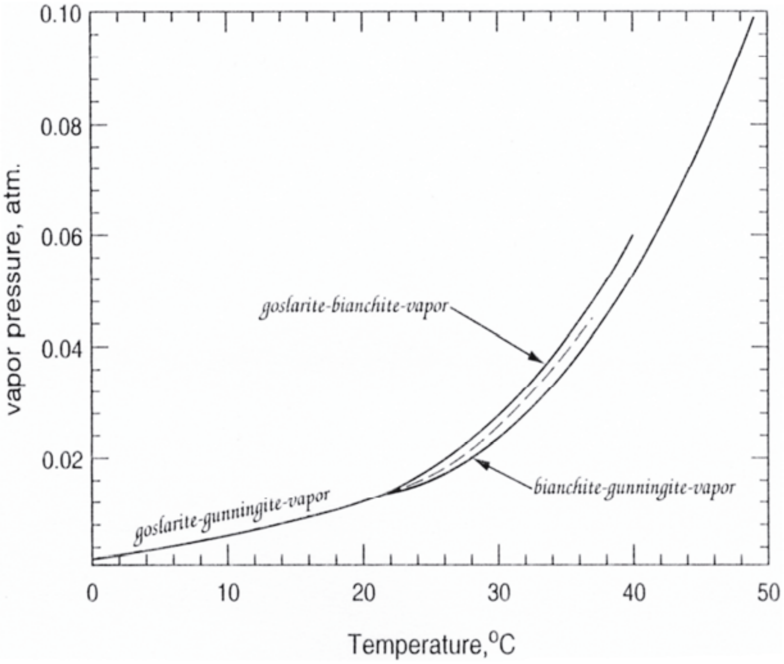


Figure 15. Vapor-pressure equilibria for zinc sulfate hydrates; data from Gmelins Handbuch (1956).

Considerable data on equilibrium vapor-pressure studies exist for the zinc sulfate hydrate thermal transitions. These data are summarized in Gmelins Handbuch (1956) and are plotted here in Figure 15. As in Figure 14, the stable three-phase univariant equilibria are shown by solid lines and the metastable extension for the goslarite-gunningite-vapor line is dashed. The invariant quadruple point (coexisting goslarite, bianchite, gunningite, and water vapor) is located in Figure 15 at 21.5°C, consistent with the solubility diagram (Fig. 14). The vapor-pressure data demonstrate the range of stability for goslarite, bianchite, and gunningite, with boyleite an unmeasured metastable phase.

Copr sulfate hydrates . Solubility and other phase-equilibria studies summarized by Mellor (1923) and in the Gmelins Handbuch (1958) indicate that only the penta-, the tri-, and the monohydrate (chalcanthite, bonattite, and poitevinite, respectively) are stable phases in the $CuSO_4–H_2O$ system. Experimental work has demonstrated that pure boothite is very unstable but there are indications that it can be made more stable with the substitution of divalent cations. For example, de Boisbadran (cited in Mellor 1923) was able to synthesize boothite by adding a seed crystal of melanterite to a supersaturated solution of copper sulfate. This observation, combined with the difficulty in sythesizing pure boothite in solubility studies and its rare occurrence in nature, indicates that boothite is unlikely to be found as end-member, monoclinic $CuSO_4 \cdot 7H_2O$.

The transition from chalcanthite to bonattite occurs at 95.9° C (Collins and Menzies 1936) which helps to explain the rare occurrence of bonattite and its tendency to hydrate to chalcanthite under most environmental conditions. The pure copper sulfate monohydrate has an even higher transition temperature of 116.6° C (Collins and Menzies 1936).

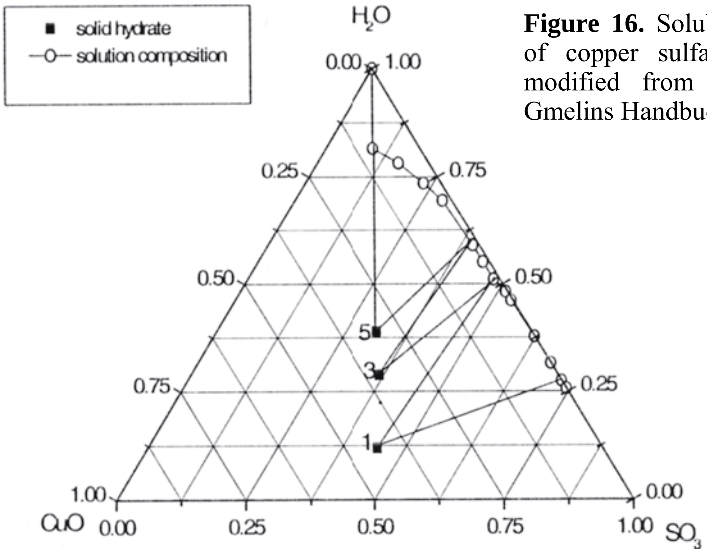


Figure 16. Solubility of the hydrates of copper sulfate in sulfuric acid; modified from Mellor (1923) and Gmelins Handbuch (1958).

The ternary phase diagram for the solubility of copper sulfate hydrates in sulfuric acid solutions is shown in Figure 16. Note that chalcanthite covers a large field of stability which also accounts for the rare occurrence of bonattite and boothite. Recent evaluations of aqueous copper-sulfate electrolyte systems using the Pitzer approach have made refinements on the solubility of chalcanthite for systems involving sulfuric acid (Baes et al. 1993) and copper chloride and sodium sulfate (Christov 2000).

Nickel sulfate hydrates. The relatively evenly spaced solubilities of morenosite ($7H_2O$, orthorhombic), retgersite ($6H_2O$, tetragonal), and nickelhexahydrite ($6H_2O$, monoclinic) as a function of temperature are shown in Figure 17. Dwornikite, the monohydrate, is not stable until the temperature is above 84° C. The solubilities for the first three minerals also have nearly congruent slopes because morenosite and retgersite differ by only one water molecule of hydration, and retgersite and nickelhexahydrite are dimorphs. Four metastable hydrates have been measured at temperatures above 90° C: the di-, tri-, tetra-, and pentahydrate. Reardon (1989) has applied the Pitzer model to the solubilities of morenosite, retgersite, and nickelhexahydrite in water and in sulfuric acid for temperatures of 0 to 70° C.

Cobalt sulfate hydrates. The solubilities of the cobalt sulfate hydrates (Fig. 18)

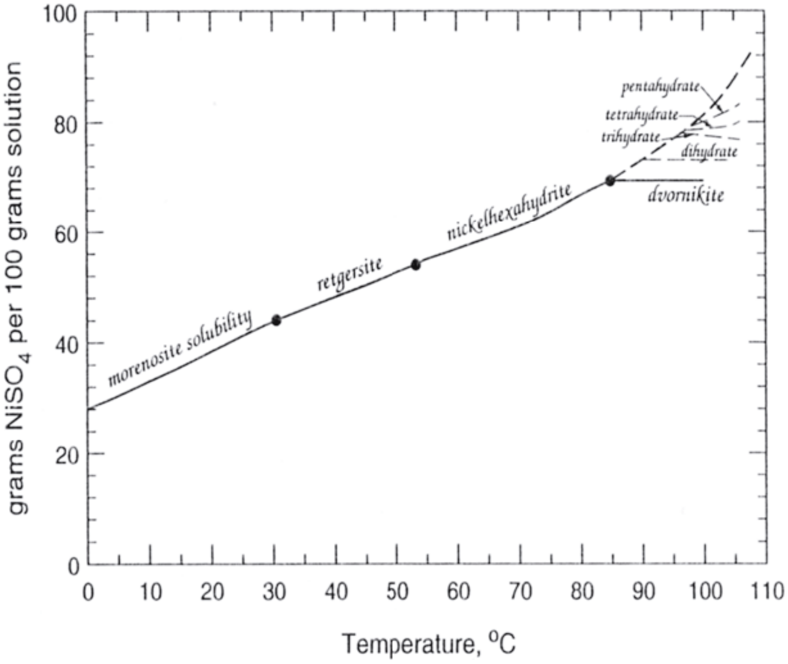


Figure 17. Solubility of the hydrates of nickel sulfate; data from Gmelins Handbuch (1966) and Reardon (1989).

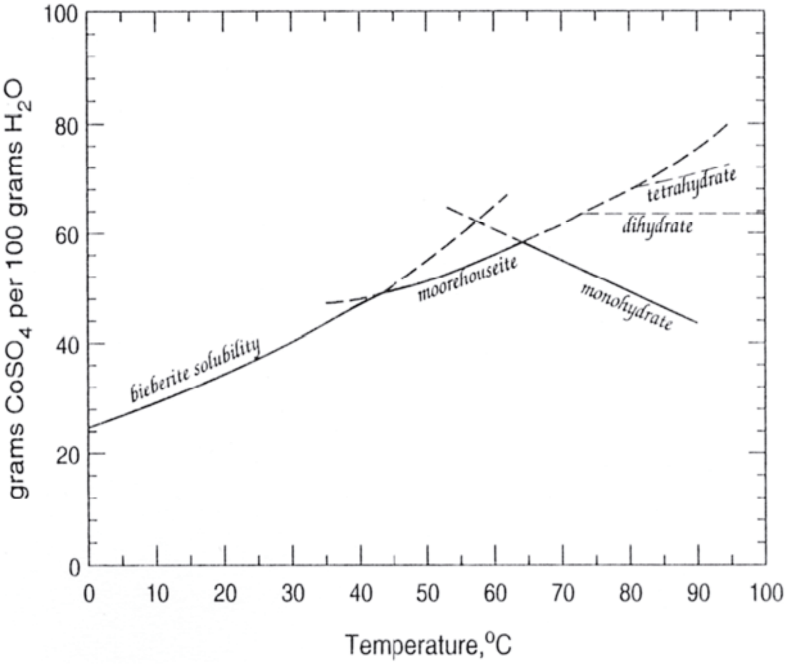


Figure 18. Solubility of the hydrates of cobalt sulfate; data from Gmelins Handbuch (1961).

are similar to, but have a larger range than, those of the zinc sulfate hydrates. The monohydrate is stable at temperatures above 62° C, and the dihydrate and tetrahydrate form two metastable phases.

Magnesium sulfate hydrates. The pattern of solubility for the magnesium sulfate hydrates (Fig. 19) is similar to that for iron, zinc, nickel, and cobalt in that the heptahydrate (epsomite) covers the largest temperature range of stability. With increasing temperature,

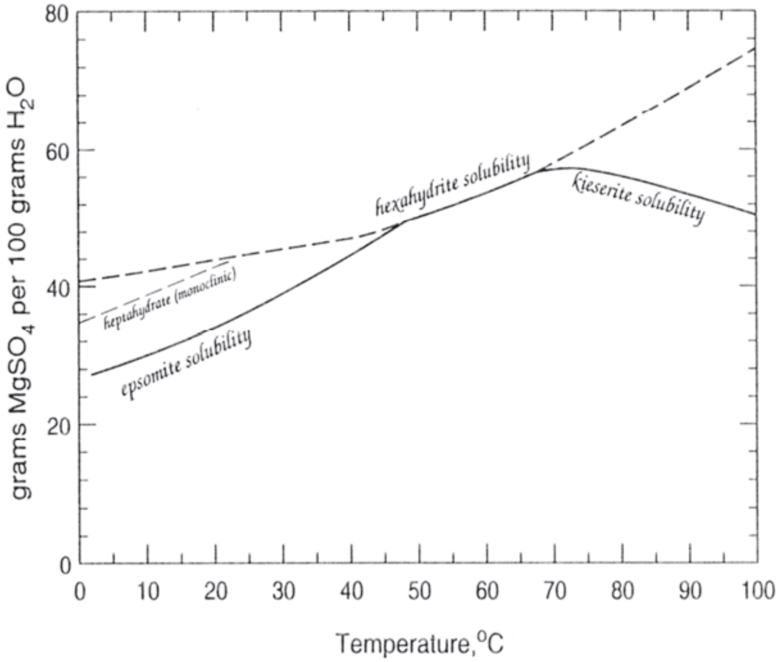


Figure 19. Solubility of the hydrates of magnesium sulfate; data from Gmelins Handbuch (1939).

the heptahydrate transforms to the hexahydrate mineral (hexahydrite), and then to the monohydrate (kieserite). No stability fields are present at 100% relative humidity for the pentahydrate (pentahydrite), the tetrahydrate (starkeyite), or the dihydrate (sanderite), and no metastable solubility data are reported. It is unusual that hexahydrite solubility can be measured far into its temperature range of metastability on both the high-temperature end and the low-temperature end. Isopiestic measurements and a thermodynamic evaluation of the $MgSO_4$–H_2O system by Archer and Rard (1998) includes a measurement of epsomite solubility at 25° C.

Aluminum sulfate hydrates. The dissolution of aluminum sulfate in water causes considerable hydrolysis to occur. Solubilities of aluminum sulfate hydrates can only be measured in sulfuric acid solutions. Hence, we have reproduced in Figure 20 the more

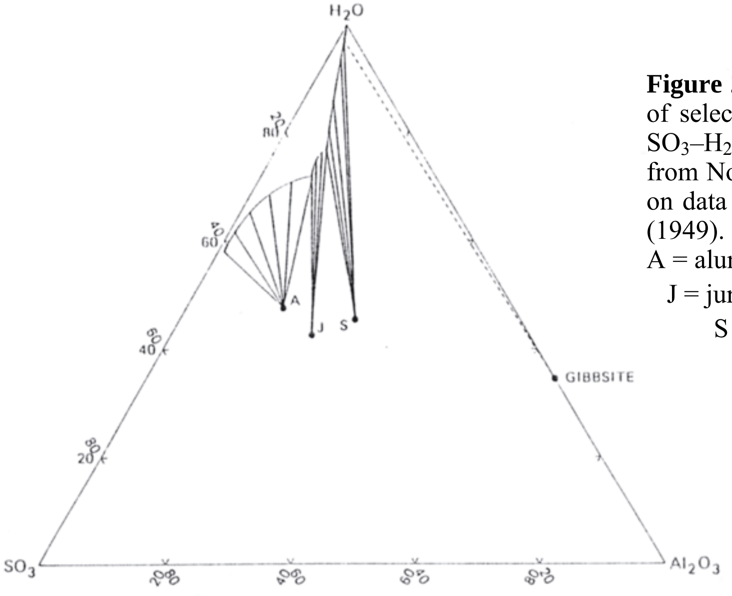


Figure 20. Solubility relation-ships of selected minerals in the Al_2O_3–SO_3–H_2O system at 25° C, modified from Nordstrom (1982b) and based on data from Bassett and Goodwin (1949).
A = alunogen $Al_2(SO_4)_3 \cdot 17H_2O$;
J = jurbanite $Al(SO_4)(OH) \cdot 5H_2O$;
S = synthetic phase, $Al_{10}(SO_4)_6(OH)_{18} \cdot 37H_2O$;
gibbsite = $Al(OH)_3$.

soluble portion of the ternary system Al_2O_3–SO_3–H_2O (or Al_2SO_4–H_2SO_4–H_2O) from Nordstrom (1982b), which is based on the work of Bassett and Goodwin (1949). On this diagram there are three phases, A (alunogen), J (jurbanite), and S (synthetic compound $Al_{10}(SO_4)_6(OH)_{18}{\cdot}37H_2O$) that appear at 25° C. The phase at S, which has not been identified as a mineral, has a composition similar to that of alunite, but with a much higher water content. Several other relatively insoluble minerals of aluminum sulfate are known and are discussed by Bigham and Nordstrom (this volume). Reardon (1988) applied the Pitzer approach to the aqueous aluminum-sulfate system and established mixing parameters for sulfate solutions of Cu, Ni, Fe(II), and Mg (see Ptacek and Blowes, this volume). The work included refinements of the solubility for alunogen, halotrichite, and pickeringite. The solubility of potassium alum was evaluated with the Pitzer model by Reardon and Stevens (1991).

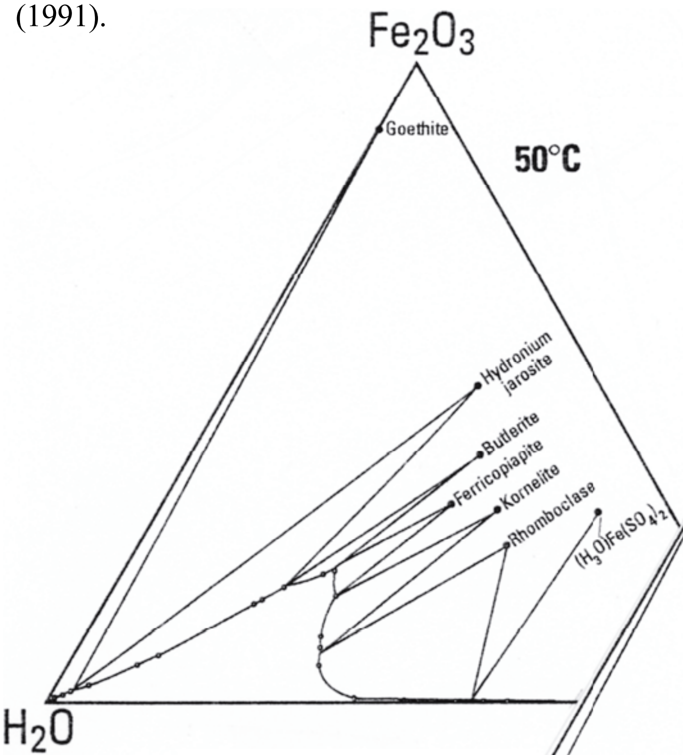


Figure 21. Solubility relationships of minerals in the Fe_2O_3–SO_3–H_2O system at 50° C, modified from Posnjak and Merwin (1922).

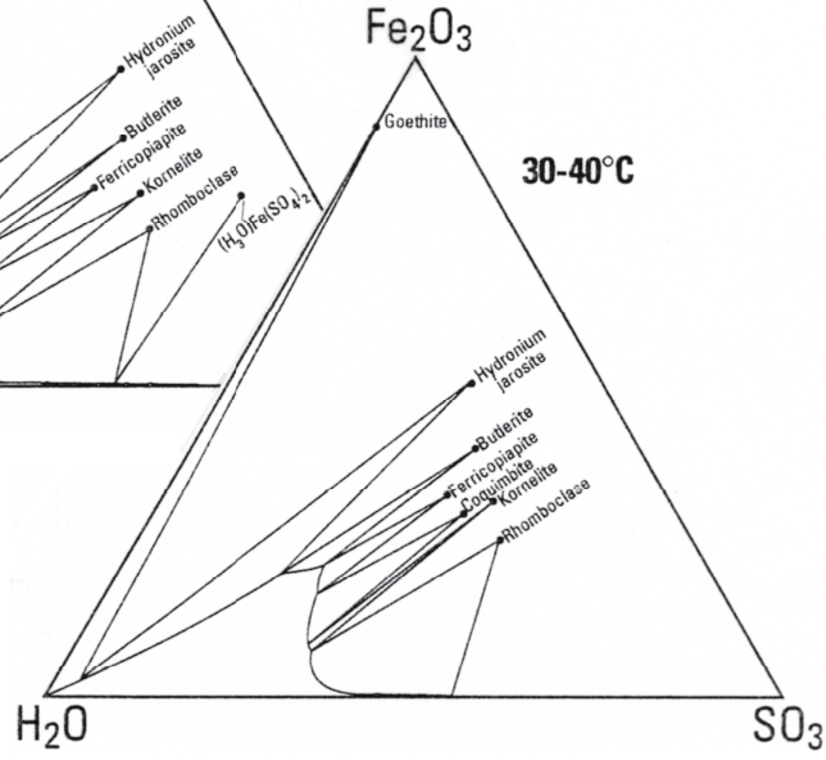


Figure 22. Solubility relationships of minerals in the Fe_2O_3–SO_3–H_2O system at 30 to 40° C, modified from Merwin and Posnjak (1937).

Ferric sulfate hydrates. The most extensive work on the ferric sulfate solubilities was from Posnjak and Merwin (1922); their ternary system solubilities for Fe_2O_3–SO_3–H_2O for 50° C is shown in Figure 21, and a similar diagramestimated for 30-40° C is shown in Figure 22 (Merwin and Posnjak 1937). The only significant difference between Figures 21 and 22 is the appearance of a stability field for coquimbite, replacing part of the kornelite field. The sequence of mineral formation from hydronium jarosite → butlerite → ferricopiapite → coquimbite → kornelite → rhomboclase describes

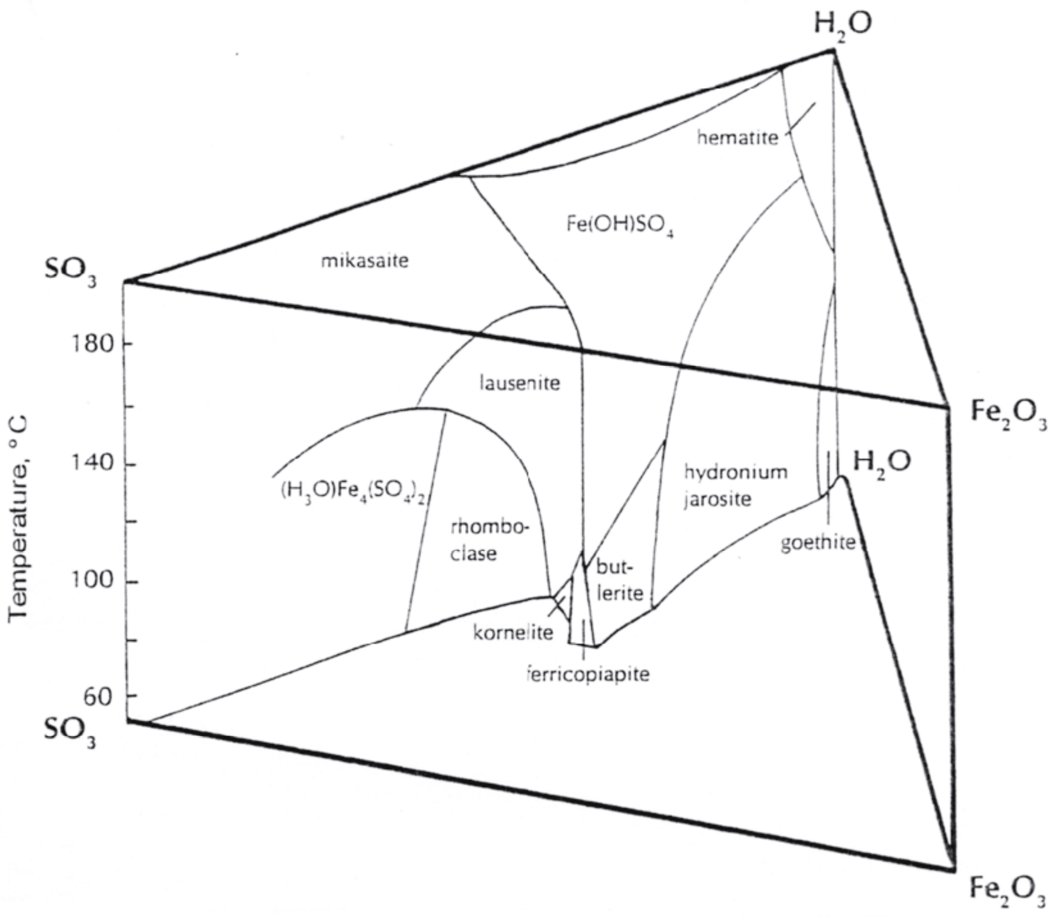


Figure 23. Phase diagram for the system Fe_2O_3–SO_3–H_2O as a function of temperature (redrawn from Atencio and Hypolito 1992, 1992/1993). Sulfate-mineral equivalents are

mikasaite = $Fe_2^{3+}(SO_4)_3$, lausenite = $Fe_2^{3+}(SO_4)_3 \cdot 6H_2O$,
rhomboclase = $(H_3O)Fe^{3+}(SO_4)_2{\cdot}3H_2O$, kornelite = $Fe_2^{3+}(SO_4)_3 \cdot 7H_2O$,
ferricopiapite = $Fe_{2/3}^{3+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$, butlerite = $Fe^{3+}(SO_4)(OH){\cdot}2H_2O$,
hydronium jarosite = $(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6$, goethite = FeOOH, and hematite = Fe_2O_3.

solution conditions in which the pH continually decreases and the solution SO_4/Fe ratio increases. This observation is consistent with field pH measurements of mine waters that have been found in equilibrium with jarosite (pH = 1 to 2.35), copiapite (pH = -1), and rhomboclase (pH = -2.5 to -3.6) from Iron Mountain, California (Alpers et al. 1989, Nordstrom and Alpers 1999a,b; Robinson 1999, Robinson et al. 2000a,b). A phase diagram for the ferric sulfate hydrate solubilities as a function of temperature from 50 to 200° C is shown in Figure 23.

Sideronatrite and ferrinatrite. Sideronatrite $Na_2Fe^{3+}(OH)(SO_4)_2{\cdot}3H_2O$ and ferrinatrite $Na_3Fe^{3+}(SO_4)_3{\cdot}3H_2O$ are minerals of moderately high solubility. Ferrinatrite is trigonal and transforms to sideronatrite, which is orthorhombic, in moist air. Solubilities of these two minerals were determined by Linke and Seidell (1958) and by Flynn and Eisele (1987).

Ferrous-ferric sulfate hydrates. There are only limited solubility data for mixed divalent–trivalent Fe sulfate salts, including römerite and bilinite (Gmelins Handbuch 1932). There has been no systematic effort to describe phase stability relations in the $FeSO_4$–$Fe_2(SO_4)_3$–H_2O system. The lack of an aqueous model that can account for mineral precipitation from Fe^{3+}-sulfate or Fe^{2+}–Fe^{3+}-sulfate solutions at high concentrations makes it difficult to obtain a complete picture of phase relations in acid mine waters and other settings where the solubility of Fe and other metals may be controlled by the formation of sulfate minerals. Ptacek and Blowes (this volume) discuss the available aqueous models for predicting sulfate-mineral solubilities in concentrated solutions.

PARAGENESIS

Paragenesis in this context refers to the sequence of mineral formation and alteration that occurs as metal-sulfate minerals form and continue to evolve with time. It was mentioned previously that the general sequence observed, both at the mineral-deposit scale and on a microscopic scale, is from initial $Fe^{2+}SO_4 \cdot nH_2O$ salts to those of Fe^{3+}, and thence to jarosite and ultimately to Fe oxyhydroxides.

Within the $Fe^{2+}SO_4 \cdot nH_2O$ minerals, the sequence melanterite (n = 7) → siderotil (n = 5) → rozenite (n = 4) → szomolnokite (n = 1) can reflect decreasing local moisture contents or increasing temperature; reversibility of hydration states among the tetrahydrate–pentahydrate–heptahydrate is easy, but the monohydrate is relatively more stable. The sequence from the heptahydrate to the monohydrate is also known to be favored as liquor acidity increases.

The sequences melanterite → fibroferrite → aluminocopiapite, or melanterite → fibroferrite → jarosite → ‘limonite’ (goethite), or melanterite → halotrichite → botryogen have been observed in various oxidized deposits (Cherkasov 1975, Zodrow et al. 1979, Kravtsov 1984, Minakawa and Noto 1994). Bolshakov and Ptushko (1967) noted a sequence in which melanterite altered to siderotil, szomolnokite, and copiapite, and subsequent decomposition of these products led to the formation of rhomboclase, römerite, voltaite, and bilinite. A similar sequence (Fig. 24) at another oxidized deposit was observed by Bolshakov and Ptushko (1971). The preservation of these types of sequences seems to be best in cryogenic or arid regions, wherein the sulfates can evolve with minimal climatic perturbation. In the cold, dry climate of northern Greenland, Jacobsen (1989) observed that in fault zones, römerite, melanterite, and rozenite occurred at depth, followed upward by fibroferrite, and then by surface crusts of copiapite.

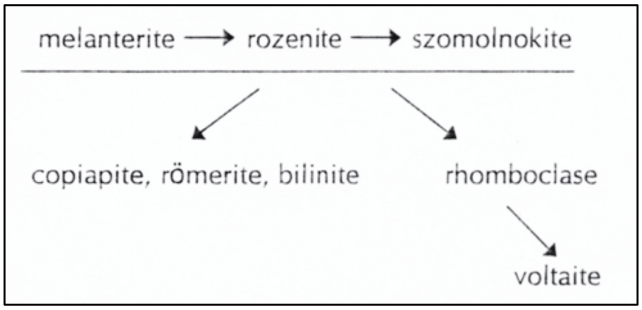
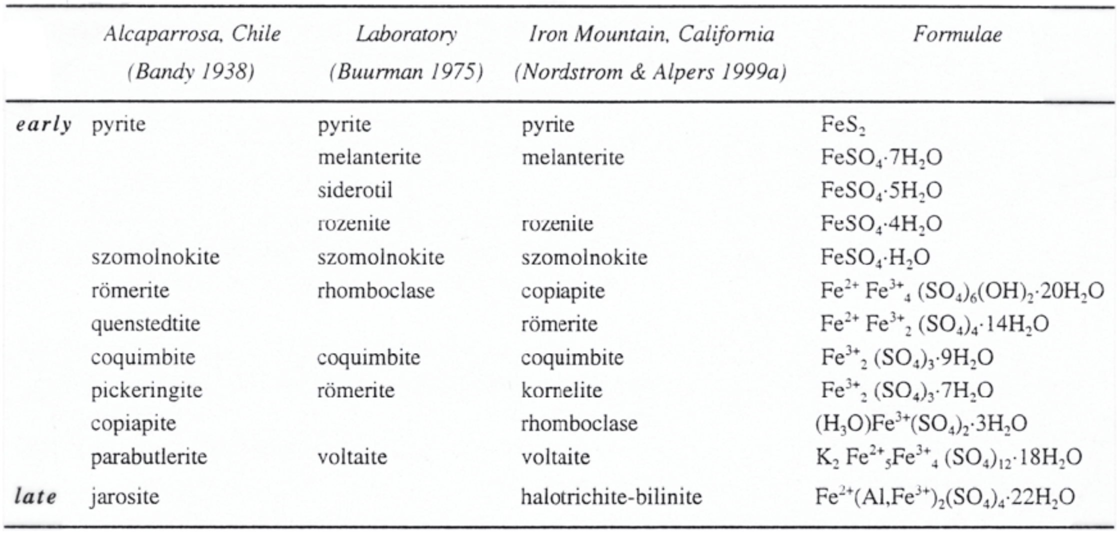


Figure 24. Natural dehydration and decomposition products of melanterite, as observed by Bolshakov and Ptushko (1971).

In his classical study of the sulfate deposits of Chile, Bandy (1938) observed the following (abridged) sequence at Alcaparrosa: pyrite → szomolnokite → römerite → quenstedtite → coquimbite → pickeringite → copiapite → parabutlerite → jarosite. Thus the trend is from the divalent to the mixed divalent–trivalent, and thence from the trivalent to the basic sulfates. In oxidized deposits in Kazakhstan, under arid conditions similar to those of northern Chile, Chukhrov (1953) observed the following trend downward from surface: ‘limonite’ (goethite) → jarosite → parabutlerite → Fe^{3+} sulfate hydrates (copiapite, metavoltine, ferrinatrite, quenstedtite, coquimbite, römerite) → divalent salts (halotrichite, szomolnokite). This general pattern was also observed to be present in oxidized ore deposits in the arid climate of northwestern China, where Tu and Li (1963) noted that the zonation was from 'limonite'-hematite at the surface, downward to Fe^{3+} sulfates (copiapite, sideronatrite, fibroferrite, römerite), and thence to gypsum, sulfur, melanterite, and

Table 5. Paragenetic sequences of Fe-sulfate minerals from pyrite oxidation.



	Alcaparrosa, Chile (Bandy 1938)	*Laboratory (Buurman 1975)*	*Iron Mountain, California (Nordstrom & Alpers 1999a)*	*Formulae*
early	pyrite	pyrite	pyrite	FeS_2
		melanterite	melanterite	$FeSO_4 \cdot 7H_2O$
		siderotil		$FeSO_4 \cdot 5H_2O$
		rozenite	rozenite	$FeSO_4 \cdot 4H_2O$
	szomolnokite	szomolnokite	szomolnokite	$FeSO_4 \cdot H_2O$
	römerite	rhomboclase	copiapite	$Fe^{2+} Fe^{3+}{}_4 (SO_4)_6(OH)_2 \cdot 20H_2O$
	quenstedtite		römerite	$Fe^{2+} Fe^{3+}{}_2 (SO_4)_4 \cdot 14H_2O$
	coquimbite	coquimbite	coquimbite	$Fe^{3+}{}_2 (SO_4)_3 \cdot 9H_2O$
	pickeringite	römerite	kornelite	$Fe^{3+}{}_2 (SO_4)_3 \cdot 7H_2O$
	copiapite		rhomboclase	$(H_3O)Fe^{3+}(SO_4)_2 \cdot 3H_2O$
	parabutlerite	voltaite	voltaite	$K_2 Fe^{2+}{}_5 Fe^{3+}{}_4 (SO_4)_{12} \cdot 18H_2O$
late	jarosite		halotrichite-bilinite	$Fe^{2+}(Al,Fe^{3+})_2(SO_4)_4 \cdot 22H_2O$

halotrichite at depth. These weathering profiles are consistent with the paragenetic sequences noted above, in that the deepest minerals correspond to the most recently formed, as the oxidation front descends in response to erosion and landscape evolution.

Buurman (1975) immersed pyritiferous concretions in distilled water at 25° C for one week, filtered the resulting solution, and determined the sequence of crystallization that evolved as the solution slowly evaporated. The results, summarized in Table 5, show a remarkable correlation with the approximate sequence of deposition that has been established to date for secondary minerals in the underground workings at the Iron Mountain massive sulfide deposits in California (Nordstrom and Alpers 1999a). Although there are some variations in the order of precipitation, Table 5 illustrates well the general sequential crystallization of the soluble metal salts.

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REFERENCES

Africano F, Bernard A (2000) Acid alteration in the fumarolic environment of Usu volcano, Hokkaido, Japan. *In* Varekamp JC, Rowe GL Jr (eds) Crater Lakes. J Volcanol Geotherm Res 97:475-495

Agnew M (1998) The formation of hardpans within tailings as possible inhibitors of acid mine drainage, contaminant release and dusting. PhD thesis, University of Adelaide, Adelaide, Australia

Agricola G (1546) De Natura Fossilium (Textbook of Mineralogy). Translated by Bandy MC, Bandy JA (1955) Geol Soc Am Spec Paper 63

Agricola, G (1556) De Re Metallica (On Metallic Substances). Translated by Hoover HC, Hoover LH (1950) Dover Publications, New York

Alpers CN, Brimhall GH (1989) Paleohydrologic evolution and geochemical dynamics of cumulative supergene metal enrichment at La Escondida, Atacama Desert, northern Chile. Econ Geol 84:229-255

Alpers CN, Nordstrom DK, Ball JW (1989) Solubility of jarosite solid solutions precipitated from acid mine waters, Iron Mountain, California, U.S.A. Sci Géol Bull 42:281-298

Alpers CN, Nordstrom DK, Burchard JM (1992) Compilation and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California, 1940-91. US Geol Survey Water-Resources Invest Rept 91-4160

Alpers CN, Nordstrom DK, Thompson JM (1994) Seasonal variations of Zn/Cn ratios in acid mine water from Iron Mountain, California. *In* Alpers CN, Blowes DW (eds) Environmental Geochemistry of Sulfide Oxidation. Am Chem Soc Symp Series 550:324-344

Angel RJ, Finger LW (1988) Polymorphism of nickel sulfate hexahydrate. Acta Crystallogr C44:1869-1873

Archer DG, Rard JA (1998) Isopiestic investigation of the osmotic and activity coefficients of aqueous $MgSO_4$ and the solubility of $MgSO_4 \cdot 7H_2O$(cr) at 298.15 K: Thermodynamic properties of the $MgSO_4 + H_2O$ system to 440 K. J Chem Eng Data 43:791-806

Aslanian S, Balarew C (1977) On the crystal-structure differences of the $MeSO_4 \cdot nH_2O$ salt-types. Kristall Technik 12:435-446 (in German)

Aslanian S, Balarew C, Oikova T (1972) Isomorphic relations between $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7H_2O$. Kristall Technik 7:525-531 (in German)

Atencio D, Hypolito R (1992) The system $Fe_2O_3–SO_3–H_2O$: Mineralogical aspects. Anais Assoc Brasil Quím 41-42(1-4):32-38 (in Portugese)

Atencio D, Hypolito R (1992/1993) Minerals and synthetic equivalents in the system $Fe_2O_3–SO_3–H_2O$. Bol IG-USP Sér Cient 24:67-75

Atencio D, Carvalho FMS, Hypolito R (1996) Synthesis and X-ray ray powder diffraction data for Mg-, Al- and Ni- end-members of the copiapite group. Anais Assoc Brasil Quím 45:66-72

Avdonin VN (1978) Poitevinite from the Gai deposit as the first discovery in the USSR. Mineral Petrogr Urala 1:71-76 (Chem Abstr 92:61932b)

Avdonin VN (1984) Gunningite from the industrially induced oxidation zone of the Uchaly deposit. Chem Abstr 102:188215a

Avdonin VN, Maloshag VP, Federova TV (1988) Zinc sulfates (goslarite, boyleite, and gunningite) in the technology generated oxidation zone of the Degtyarsk deposit. Chem Abstr 110:216425e

Bacon GE, Titterton DH (1975) Neutron-diffraction studies of $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5D_2O$. Z Kristallogr 141:330-341

Badak J (1959) Occurrence of secondary minerals in the oxidized zone of the menilite beds in the Carpathians. Bull Acad Polon Sci Ser Sci Chim Geol Geogr 7:759-763

Baes CF Jr, Reardon EJ, Moyer BA (1993) Ion interaction model applied to the $CuSO_4–H_2SO_4–H_2O$ system at 25°C. J Phys Chem 97:12343-112348

Balarew C, Karaivanova V (1975) Change in the crystal structure of zinc sulphate heptahydrate and magnesium (II) sulphate heptahydrate due to isodimorphous substitution by copper (II), iron (II), and cobalt (II) ions. Kristall Technik 10:1101-1110

Balarew C, Karaivanova V (1976a) Preparation of pure crystal hydrates of the type $M^{II}SO_4 \cdot nH_2O$ free of isodimorphous admixtures. Z anorg allg Chem 422:173-178 (in German)

Balarew C, Karaivanova V (1976b) Isodimorphous cocrystallization in sulfate systems as a possibility of predicting the existence of crystal hydrates of the type $MSO_4 \cdot nH_2O$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$). Z anorg allg Chem 422:283-288 (in German)

Balarew C, Karaivanova V (1976c) Effect of isodimorphously included Co(II), Fe(II) and Cu(II) ions on the crystal structures of $ZnSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$. *In* Mullin JW (ed) Industrial Crystallization 6th Proc 1975. Plenum, New York, p 239-243

Balarew C, Karaivanova V, Aslanian S (1973) Isomorphic relations among the heptahydrate sulfates of single divalent metals ($Mg^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}$). Kristall Technik 8:115-125 (in German)

Balarew C, Karaivanova V, Stefanov I (1984) Effect of isodimorphic guest component on the host crystal structures and habits. *In* Jancic SJ, de Jong EJ (eds) Industrial Crystallization '84. Elsevier Science, Amsterdam, The Netherlands, p 335-338

Baltatzis E, Stamatakis MG, Kyriakopoulos KG (1986) Rozenite and melanterite in lignitic layers from the Voras mountain, western Macedonia, Greece. Mineral Mag 50:737-739

Bandy MC (1938) Mineralogy of three sulphate deposits of northern Chile. Am Mineral 23:669-760

Bannister FA (1937) The preservation of minerals and meteorites. Museums J 36:465-476

Bari H, Catti M, Ferraris G, Ivaldi G, Permingeat F (1982) Phaunouxite, $Ca_3(AsO_4)_2 \cdot 11H_2O$, a new mineral strictly associated with rauenthalite. Bull Soc franc Minéral Cristallogr 105:327-332 [as cited in Am Mineral 68:850 (1983)]

Bassett H, Goodwin TH (1949) The basic aluminum sulphates. J Chem Soc 2239-2279

Bastidas JM, Lopez-Delgado A, Lopez FA, Alonso MP (1997) Characterization of artificially patinated layers on artistic bronze exposed to laboratory SO_2 contamination. J Mater Sci 32(1):129-133

Baur WH (1962) On the crystal chemistry of salt hydrates: Crystal structure of $MgSO_4 \cdot 4H_2O$ (leonhardtite) and $FeSO_4 \cdot 4H_2O$ (rozenite). Acta Crystallogr 15:815-826 (in German)

Baur WH (1964a) On the crystal chemistry of salt hydrates: III. The determination of the crystal structure of $FeSO_4 \cdot 7H_2O$ (melanterite). Acta Crystallogr 17:1167-1174

Baur WH (1964b) On the crystal chemistry of salt hydrates: IV. The refinement of the crystal structure of $MgSO_4 \cdot 7H_2O$ (epsomite). Acta Crystallogr 17:1361-1369

Baur WH (1964c) On the crystal chemistry of salt hydrates: II. A neutron diffraction study of $MgSO_4 \cdot 4H_2O$. Acta Crystallogr 17:863-869

Baur WH, Rolin JL (1972) Salt hydrates: IX. The comparison of the crystal structure of magnesium sulfate pentahydrate with copper sulfate pentahydrate and magnesium chromate pentahydrate. Acta Crystallogr B28:1448-1455

Bayless ER, Olyphant GA (1993) Acid-generating salts and their relationship to the chemistry of groundwater and storm runoff at an abandoned mine site in southwestern Indiana, U.S.A. J Contam Hydrol 12:313-328

Bayliss P, Atencio D (1985) X-ray powder-diffraction data and cell parameters for copiapite-group minerals. Can Mineral 23:53-56

Beevers CA, Lipson H (1932) The crystal structure of nickel sulphate hexahydrate, $NiSO_4 \cdot 6H_2O$. Z Kristallogr 83:123-135

Beevers CA, Schwartz CM (1935) The crystal structure of nickel sulfate heptahydrate, $NiSO_4 \cdot 7H_2O$. Z Kristallogr 91:157-169

Berdesinki W (1952) Sanderite, leonhardtite, allenite and hexahydrite, new minerals of marine salt deposits. Neues Jahrb Mineral Monatsh 28-29 (in German)

Berry LG (1947) Composition and optics of copiapite. Univ Toronto Studies Contrib Can Mineral 51: 21-34

Blain CF, Andrew RL (1977) Sulfide weathering and the evaluation of gossans in mineral exploration. Minerals Sci Eng 9:119-149

Blanchard R (1967) Interpretation of leached outcrops. Nevada Bur Mines Bull 66:1-196

Blount AM (1993) Nature of the alterations which form on pyrite and marcasite during collection storage. Collection Forum 9:1-16

Blowes DW, Reardon EJ, Jambor JL, Cherry JA (1991) The formation and potential importance of cemented layers in inactive sulfide mine tailings. Geochim Cosmochim Acta 55:965-978

Bolshakov AP, Ptushko LI (1967) New supergene iron sulfates from the Mikitivka mercury deposit. Akad Nauk Ukr RSR Dopov Seriya B 29:696-699 (in Ukrainian)

Bolshakov AP, Ptushko LI (1971) Alteration products of melanterite from the Nikitov mercury ore deposits. Internat Geol Rev 13:849-854

Bonnell DFR, Burridge LW (1935) The dissociation pressures of some salt hydrates. Farad Soc Trans 31:473-478

Boscardin M, Colmelet G (1977) Morenosite of the Val d'Ayas, Aosta. Riv Mineral Ital 8:31-32 (in Italian)

Brigatti MF, Poppi L (1976/1977) Crystallochemical study and thermal behavior of natural heptahydrate sulfates: I. Research on some terms of the melanterite series. Mineral Petrogr Acta 21:157-164 (in Italian)

Brousse R, Gasse-Fournier R, Lebouteiller F (1966) Rozenite and melanterite crystals at the La Bade (Cantal) diatomite mine. Bull Soc franc Minéral Cristallogr 89:348-352 (in French)

Bullough W, Canning TA, Strawbridge MI (1952) The solubility of ferrous sulphate in aqueous solutions of sulphuric acid. J Appl Chem 2:703-707

Bursa S, Stanisz-Lewicka (1982) Solubility isotherms of the iron (II) sulfate–sulfuric acid–water system at 318, 328, and 333 K. Pol Pr Nauk Politech Szczecin 183:27-37

Buurman P (1975) In vitro weathering products of pyrite. Geol Mijnbouw 54:101-105

Byerly DW (1996) Handling acid-producing material during construction. Environ Eng Geosci II:49-57

Carpenter CE, Jette ER (1923) The vapor pressure of certain hydrated metal sulfates. J Am Chem Soc 45: 578-590

Caven RM, Ferguson J (1922) The dissociation pressures of hydrated double sulphates: Part I. Hydrated cupric alkalki sulfates. J Chem Soc London 121:1406-1414

Caven RM, Ferguson J (1924) The dissociation pressures of hydrated double sulphates: Part II. Various double sulphates of the type $M^{++}SO_4$, $M^{+}{}_2SO_4 \cdot 6H_2O$. J Chem Soc London 125:1307-1312

Cerny P (1956) Contribution to the mineralogy of the sulfates of Smolnik. Spisy pírodovdecké fakulty Masarykovy Univ 376:1-26 (Mineral Abstr 14:226)

Charles RW, Vidale Buden RJ, Goff F (1986) An interpretation of the alteration assemblages at Sulphur Spring, Valles Caldera, New Mexico. J Geophys Res 91:1887-1898

Cherkasov GN (1975) Sulfuric acid weathering crusts of western Yakutia as a possible source of aluminum oxide. Trudy Sibirsky Nauchno-Issled Inst Geol Geofiz Mineral Syr'ya 189:33-43 (Chem Abstr 86:58164y)

Chernikov AA, Dorfman MD, Dvurechenskaya SS (1994) Genesis of mineral associations of cryogenic and deep supergene zones. Dokl Akad Nauk 335:485-488 (in Russian)

Chou I-M, Seal RR II, Hemingway BS (2000) Low-temperature thermodynamic properties of hydrated ferrous sulfates: Experimental results and evaluation of published data. Abstracts with programs, Geol Soc Am 32(7):A-108

Christov C (2000) Thermodynamic study of the Na–Cu–Cl–SO_4–H_2O system at the temperature 298.15 K. J Chem Thermodyn 32:285-295

Chukhrov FV (1953) Sequence of the formations in oxidation zones in ore deposits of the Kazakhstan steppe. Voprosy Petrog Mineral Akad Nauk SSSR 2:93-99 (in Russian)

Cody AD, Grammer TR (1979) Magnesian halotrichite from White Island. NZ Geol Geophys 22:495-498

Collins EM, Menzies AWC (1936) A comparative method for measuring aqueous vapor and dissociation pressures, with some of its applications. J Phys Chem 40:379-397

Collins HF (1923) On some crystallized sulphates from the province of Huelva, Spain. Mineral Mag 20:32-38

Cravotta CA III (1994) Secondary iron-sulfate minerals as sources of sulfate and acidity: Geochemical evaluation of acidic groundwater at a reclaimed surface coal mine in Pennsylvania. *In* Alpers CN, Blowes DW (eds) Environmental Geochemistry of Sulfide Oxidation. Am Chem Soc Symp Series 550:345-364

Cripps JC, Edwards RL (1997) Some geotechnical problems associated with pyrite bearing mudrocks. *In* Hawkins AB (ed) Ground Chemistry: Implications for Construction. Proc internat conf implications ground chem microbiol construction, Bristol, UK, 1992. AA Balkema, Rotterdam, The Netherlands, p 77-88

Crockford HD, Brawley DJ (1932) The system $CuSO_4$–$CoSO_4$–H_2O. J Phys Chem 36:1594-1596

Dagenhart TV Jr (1980) The acid mine drainage of Contrary Creek, Louisa County, Virginia: Factors causing variations in stream water chemistry. MSc thesis, Univ Virginia, Charlottesville, Virginia

Delines M (1975) Volcanic sublimates of Rugarama, Kiva region, Republic of Zaire. Bull Surv Geol (Rwanda) 8:1-11 (Chem Abstr 86:58182)

Doner HE, Lynn WC (1977) Carbonate, halide, sulfate, and sulfide minerals. *In* Dixon JB, Weed SB (eds) Minerals in Soil Environments. Soil Sci Soc Am Spec Publ 75-98

Dristas JA (1979) Zincian pisanite in the Las Picazas mine, San Rafael department, Mendoza province, Argentina. Assoc Geol Argent Rev 34:108-112 (Chem Abstr 93:10826h)

Ducloux J, Guero Y, Fallavier P, Valet S (1994) Mineralogy of salt efflorescences in paddy field soils of Kollo, southern Niger. Geoderma 64:57-71

Eckel EB (1933) Stability relations of a Colorado pisanite (cuprian melanterite). Am Mineral 18:449-454

Elerman Y (1988) Refinement of the crystal structure of $CoSO_4\cdot 6H_2O$. Acta Crystallogr C44:599-601

Eliseev EN, Smirnova SI (1958) Iron- and magnesium-bearing retgersite. Zap Vses Mineral Obshch 87:3-13 (in Russian)

Escobar C, Gifford G (1961) Some new powder X-ray diffraction diagrams of copper ores from Chile. Bol Acad Nacional Ciencias 42:245-256

Fanfani L, Nunzi A, Zanazzi PF (1970) The crystal structure of roemerite. Am Mineral 55:78-89

Fanfani L, Nunzi A, Zanazzi PF, Anzari AR (1973) The copiapite problem: The crystal structure of a ferrian copiapite. Am Mineral 58:314-322

Fang JH, Robinson PD (1970) Crystal structures and mineral chemistry of hydrated ferric sulphates: I. The crystal structure of coquimbite. Am Mineral 55:1534-1540

Fang JH, Robinson PD (1974) Polytypism in coquimbite and paracoquimbite. Neues Jahrb Mineral Monatsh 89-91

Fang JH, Robinson PD (1976) Alunogen, $Al_2(H_2O)_{12}(SO_4)_3\cdot 5H_2O$: Its atomic arrangement and water content. Am Mineral 61:311-317

Fanning DS, Rabenhorst MC, Bigham JM (1993) Colors of acid sulfate soils. *In* Bigham JM, Ciolkosz EJ (eds) Soil Color. Soil Sci Soc Am Spec Publ 31:91-108

Fedotova MG (1967) Retgersite of the Allarechensk deposit. Mater Mineral Kol'sk Poluostrova Akad Nauk SSSR Kol'sk Filial 5:70-73 (Chem Abstr 69:53489x)

Ferraris G, Jones DW, Yerkess J (1973) Refinement of the crystal structure of magnesium sulphate heptahydrate (epsomite) by neutron diffraction. J Chem Soc (Dalton Trans) 1973:816-821

Fleischer M (1962) New mineral names. Am Mineral 47:805-810

Fleischer M (1964) New mineral names. Am Mineral 49:1774-1778

Flynn CM Jr, Eisele JA (1987) Solubilities of sideronatrite and ferrinatrite in the system Na_2SO_4–Fe_2O_3–H_2SO_4–H_2O. US Bur Mines Report Invest RI-9100:1-17

Foote HW, Scholes SR (1911) The vapour pressure of hydrates, determined from their equilibria with aqueous alcohol. J Am Chem Soc 33:1309-1326

Foscolos AE, Goodarzi F, Koukouzas CN, Hatziyannis G (1989) Reconnaissance study of mineral matter and trace elements in Greek lignites. Chem Geol 76:107-130

Frondel C, Palache C (1949) Retgersite $NiSO_4 \cdot 6H_2O$, a new mineral. Am Mineral 34:188-194

Gaines RV, Skinner HCW, Foord EE, Mason B, Rosenzweig A (1997) Dana's New Mineralogy. John Wiley & Sons, New York

Garavelli C (1955) Some sulfates of the iron deposit of Terranera (Elba Island, Italy). Rend Soc Mineral Ital 11:100-146 (in Italian)

Garavelli CL (1957) Bonattite: A new mineral in the Elban deposit at Cape Calamita. Lincei–Rend Sc Fis Mat Nat 22:318-327 (in Italian)

García García G (1996) The Rio Tinto mines, Huelva, Spain. Mineral Record 27:275-285

Gary GL (1939) Sulphate minerals at the Leviathan sulphur mine, Alpine County, California. Calif J Mines Geol 35:488-489

Gerkin RE, Reppart WJ (1988) Structure of monoclinic nickel(II) sulfate hexahydrate. Acta Crystallogr C44:1486-1488

Gibson RI (1974) Descriptive human pathological mineralogy. Am Mineral 59:1177-1182

Giester G (1988) The crystal structures of copper(II) sulfate monohydrate and copper(II) selenate monohydrate, and their relationships to kieserite. Mineral Petrol 38:277-284

Giester G, Wildner M (1992) The crystal structures of kieserite-type compounds: II. Crystal structures of $Me(II)SeO_4 \cdot H_2O$ (Me = Mg,Mn,Co,Ni,Zn). Neues Jahrb Mineral Monatsh 135-144

Giester G, Lengauer CL, Redhammer G (1994) Characterization of the $FeSO_4 \cdot H_2O$–$CuSO_4 \cdot H_2O$ solid-solution series, and the nature of poitevinite, $(Cu,Fe)SO_4 \cdot H_2O$. Can Mineral 32:873-884

Gmelins Handbuch der Anorganischen Chemie (1932) Eisen: System-Nummer 59. Verlag Chemie, Berlin

Gmelins Handbuch der Anorganischen Chemie (1939) Magnesium: System-Nummer 27. Verlag Chemie, Berlin

Gmelins Handbuch der Anorganischen Chemie (1956) Zink: System-Nummer 32. Verlag Chemie, Weinheim

Gmelins Handbuch der Anorganischen Chemie (1958) Kupfer: System-Nummer 60. Verlag Chemie, Weinheim

Gmelins Handbuch der Anorganischen Chemie (1961) Kobalt: System-Nummer 58. Verlag Chemie, Weinheim

Gmelins Handbuch der Anorganischen Chemie (1966) Nickel: System-Nummer 57. Verlag Chemie, Weinheim

Grønvold F, Meisingset KK (1982) Thermodynamic properties and phase relations of salt hydrates between 270 and 400 K. I. Ammonium aluminum sulfate, potassium aluminum sulfate, aluminum sulfate, zinc sulfate, sodium sulfate, and sodium thiosulfate hydrates. J Chem Thermodyn 14:1083-1098

Gruner D, Hood WC (1971) Three iron sulfate minerals from coal mine refuse dumps in Perry County, Illinois. Trans Ill State Acad Sci 64:156-158

Grybeck D (1976) Some additions to the ore mineralogy of Colorado. Mineral Record 7:274-276

Guenot J, Manoli J-M (1969) Thermogravimetry of solid–gas systems: III. Thermogravimetry of the hydrate salts: Influence of low pressure. Bull Soc Chim France (8):2663-2665 (in French)

Hammel F (1939) Contribution to the study of the sulfates of the magnesium series. Ann Chim 11:247-358 (in French)

Hawkins AB, Higgins MD (1997) The generation of sulphates in the proximity of cast in situ piles. *In* Hawkins AB (ed) Ground Chemistry: Implications for Construction. Proc internat conf implications ground chem microbiol construction, Bristol, UK, 1992. AA Balkema, Rotterdam, The Netherlands, p 101-110

Hawkins AB, Pinches GM (1997) Understanding sulphate generated heave resulting from pyrite degradation. *In* Hawkins AB (ed) Ground Chemistry: Implications for Construction. Proc internat conf implications ground chem microbiol construction, Bristol, UK, 1992. AA Balkema, Rotterdam, The Netherlands, p 51-76

Hawthorne FC, Groat LA, Raudsepp M (1987) Kieserite, $Mg(SO_4)(H_2O)$, a titanite-group mineral. Neues Jahrb Mineral Abh 157:121-132

Hay RF (1960) The geology of Mangakahia subdivision. NZ Geol Survey Bull 61:1-109

Hayes CW (1906) The Gila River alum deposits. US Geol Survey Bull 315:215-223

Heitmankova J, Cerny C (1974) Solid–gas equilibrium in the binary system sodium hydrogen suphate – water. Coll Czech Chem Comm 39:1787-1793

Hepburn JRL, Phillips RF (1952) The alums: Part I. A study of the alums by measurement of their aqueous dissociation pressures. J Chem Soc London 2569-78 (as cited by Waller 1992)

Ievlev AA (1988) Mineralogy and formation of weathering zones in phosphorite-bearing shales of Pai Khoi. Sov Geol (10):81-93 (Chem Abstr 110:157951y)

International Critical Tables (1926-30) Vol I to VI. McGraw-Hill, New York

Jacobsen UH (1989) Hydrated iron sulfate occurrences at Navarana Fjord, central North Greenland. Bull Geol Soc Denmark 37:175-180

Jambor JL (1962) Second occurrence of bonattite. Can Mineral 7:245-252

Jambor JL (1981) Mineralogy of the Caribou massive sulphide deposit, Bathurst area, New Brunswick. CANMET Nat Res Can Rept 81-8E

Jambor JL (1994) Mineralogy of sulfide-rich tailings and their oxidation products. *In* Jambor JL, Blowes DW (eds) Environmental Geochemistry of Sulfide Mine-Wastes. Mineral Assoc Can Short Course 22:59-102

Jambor JL, Blowes DW (1998) Theory and applications of mineralogy in environmental studies of sulfide-bearing mine wastes. *In* Cabri LJ, Vaughan DJ (eds) Modern Approaches to Ore and Environmental Mineralogy. Mineral Assoc Can Short Course 27:367-401

Jambor JL, Boyle RW (1962) Gunningite, a new zinc sulphate from the Keno Hill – Galena Hill area, Yukon. Can Mineral 7:209-218

Jambor JL, Boyle RW (1965) Moorhouseite and aplowite, new cobalt minerals from Walton, Nova Scotia. Can Mineral 8:166-171

Jambor JL, Traill RJ (1963) On rozenite and siderotil. Can Mineral 7:751-763

Jambor JL, Lachance GR, Courville S (1964) Poitevinite, a new mineral. Can Mineral 8:109-11

Jambor JL, Blowes DW, Ptacek CJ (2000) Mineralogy of mine wastes and strategies for remediation. *In* Vaughan DJ, Wogelius RA (eds) Environmental Mineralogy. EMU Notes Mineral 2:255-290

Jamieson HE, Przybylowicz WJ (1997) The incorporation of toxic elements in iron sulfates precipitated from acid mine waters. Geol Assoc Can – Mineral Assoc Can Program Abstr 22:A73

Jamieson HE, Alpers CN, Nordstrom DK, Peterson RC (1999) Substitution of zinc and other metals in iron-sulfate minerals at Iron Mountain, California. *In* Goldsack D, Belzile N, Yearwood P, Hall G (eds) Conference Proc, Sudbury '99: Mining and the Environment II, September 12-16, 1999, Sudbury, Ontario, Canada. 1:231-241

Jangg G, Gregori H (1967) Crystallization equilibria in the system $CuSO_4$–$NiSO_4$–H_2O, $CuSO_4$–$ZnSO_4$–H_2O, $NiSO_4$–$ZnSO_4$–H_2O. Z anorg allg Chem 351:81-99 (in German)

Janjic S, Gakovic M, Dordevic D, Bugarski P (1980) Nickeloan hexahydrite from Droskovac near Vares, Bosnia, Yugoslavia. Glas Prir Muz Beogradu Ser A, 34:5-11 (Chem Abstr 95:46247a)

Jenkins RE II, Misiur SC (1994) A complex base-metal assemblage from the Sterling mine, New Jersey. Mineral Record 25:95-104

Jolly JH, Foster HL (1967) X-ray diffraction data of aluminocopiapite. Am Mineral 52:1220-1223

Karup-Møller S (1973) Nickelhexahydrite from Finland. Bull Geol Soc Finl 45(2):155-158

Keating LF, Berry LG (1953) Pisanite from Flin Flon, Manitoba. Am Mineral 38:501-505

Keith DC, Runnells DD (1998) Chemistry, mineralogy, and effects of efflorescent sulfate salts in acid mine drainage areas. Abstracts with programs, Geol Soc Am 30:254

Keith DC, Runnells DD, Esposito KJ, Chermak JA, Hannula SR (1999) Efflorescent sulfate salts: Chemistry, mineralogy, and effects on ARD streams. *In* Tailings Mine Waste '99, Proc 6th internat conference. Balkema, Rotterdam, The Netherlands, p 573-579

Keith TEC, Casadevall TJ, Johnston DA (1981) Fumarole encrustations: Occurrence, mineralogy, and chemistry. US Geol Survey Prof Paper 1250:239-250

Keller LP, McCarthy GJ, Richardson JL (1986a) Mineralogy and stability of soil evaporites in North Dakota. Soil Sci Soc Am J 50:1069-1071

Keller LP, McCarthy GJ, Richardson JL (1986b) Laboratory modeling of northern Great Plains salt efflorescence mineralogy. Soil Sci Soc Am J 50:1363-1367

Kellersohn T (1992) Structure of cobalt sulfate tetrahydrate. Acta Crystallogr C48:776-779

Kellersohn T, Delaplane RG, Olovsson I (1991) Disorder of a trigonally planar coordinated water molecule in cobalt sulfate heptahydrate, $CoSO_4 \cdot 7D_2O$ (bieberite). Z Naturforsch 46b:1635-1640

Keys JR, Williams K (1981) Origin of crystalline, cold desert salts in the McMurdo region, Antarctica. Geochim Cosmochim Acta 45:2299-2309

King RJ, Evans AM (1964) An occurrence of morenosite in Ireland. Mineral Mag 33:1110-1113

Kossenberg M, Cook AC (1961) Weathering of sulphide minerals in coal; production of ferrous sulphate heptahydrate. Mineral Mag 32:829-830

Kravtsov ED (1971) Minerals from the permafrost oxidation zone of the D'yakhtardakh deposit. Zap Vses Mineral Obshch 100:282-290 (in Russian)

Kravtsov ED (1974) Cryogenic oxidation zone of cassiterite – sulfide deposits in the northeastern Yakutsk ASSR. Probl. Kriolitologii 4:165-174 (Chem Abstr 83:196339y)

Kravtsov ED (1984) Characteristics of sulfate metasomatism of sulfide ores in a cryogenic zone. Metasomatizm Rudoebraz (5th Mater–Vses Konf 1982) 189-198 (Chem Abstr 101:94744z)

Kubisz J (1960a) Rozenite, $FeSO_4 \cdot 4H_2O$, a new mineral. Bull Acad Polon Sci, Ser Sci Geol Geogr 8:107-113

Kubisz J (1960b) Magnesium szomolnokite, $(Fe,Mg)SO_4 \cdot H_2O$. Bull Acad Polon Sci, Ser Sci Geol Geogr 8:101-105

Kubisz J, Michalek Z (1959) Minerals of the oxidized zone of the menilite beds in the Carpathians. Bull Acad Polon Sci, Ser Sci Chim Geol Geogr 7:765-771

Kyriakopoulos KG, Kanaris-Sotiriou R, Stamatakis MG (1990) The authigenic minerals formed from volcanic emanations at Soussaki, west Attica Peninsula, Greece. Can Mineral 28:363-368

Lazarenko EK, Orlov OM, Panov BS (1973) Recent mineral formation in the Donets Basin. Mineral Sbornik (Lvov) 27:254-257 (in Russian)

Le Fur Y, Coing-Boyat J, Bassi G (1966) Structure of the monoclinic monohydrate sulfates of the transition metals, MSO_4, H_2O (M = Mn, Fe, Co, Ni and Zn). C R Acad Sci Paris Ser C 262:632-635 (in French)

Lengauer CL, Giester G (1995) Rietveld refinement of the solid-solution series: $(Cu, Mg)SO_4 \cdot H_2O$. Powder Diffraction 10:189-194

Li Wanmao, Chen Guoying (1990) Lishizhenite: A new zinc sulfate mineral. Acta Mineral Sinica 10:299-305 (in Chinese; Am Mineral 76:2022)

Li Wanmao, Chen Guoying, Sun Shurong (1987) Zincovoltaite: A new sulfate mineral. Acta Mineral Sinica 7:309-312 (in Chinese; Am Mineral 75:244-245)

Linke WF (1965) Solubilities of Inorganic and Metal Organic Compounds, Vol. II. Am Chem Soc, Washington, DC

Linke WF, Seidell A (1958) Solubility of Inorganic and Organic Compounds, Vol. I. Am Chem Soc, Washington, DC

Lizalek NA, Ivlev NF, Madaras A, Speshilova MA (1989) The Namana occurrence of secondary sulfates in Yakutia. Sov Geol (9):46-52 (Chem Abstr 113:155920a)

Lovas GA (1986) Structural study of halotrichite from Recsk (Matra Mts., N-Hungary). Acta Geol Hung 29:389-398

Lowson RT (1982) Aqueous oxidation of pyrite by molecular oxygen. Chem Rev 82:461-497

Luzgin BN (1990) Mineralogy of cryogenic oxidation zones in ore deposits of southeastern Gorny Altai. Zap Vses Mineral Obshch 119(6):100-106 (in Russian)

Magnus A (1205-1280) Book of Minerals. Translated by Wyckoff D (1967). Clarenden Press, Oxford, UK

MalstrⅡm M, Banwart S (1997) Biotite dissolution at 25°C: The pH dependence of dissolution rate and stoichiometry. Geochim Cosmochim Acta 61:2779-2799

Mandarino JA (1999) Fleischer's Glossary of Mineral Species. Mineralogical Record, Tucson, Arizona

Martin R, Rodgers KA, Browne PRL (1999) The nature and significance of sulphate-rich aluminous efflorescences from the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand. Mineral Mag 63:413-419.

Matsubara S, Kato A, Bunno M (1973) Occurrence of szmikite from the Toyoho mine, Hokkaido, Japan. Bull Nat Sci Museum Tokyo 16:561-570

McCaughey WJ (1918) Copiapite in coal. Am Mineral 3:162-163

McCord TB, Hansen GB, Fanale FP, Carlson RW, Matson DL, Johnson TV, Smyth WD, Crowley JK, Martin PD, Ocampo A, Hibbits CA, Granahan JC (1998) Salts on Europa's surface detected by Galileo's Near Infrared Mapping Spectrometer. Science 280:1242-1245

Mellor JW (1923) A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol 3. John Wiley, New York

Mellor JW (1932) A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol 12. John Wiley, New York

Melon J (1944) Epsomite and melanterite of Vedrin. Ann Soc Gé pl Belg Bull 67:B56-B59 (Mineral Abstr 10:116-117)

Menchetti S, Sabelli C (1976) The crystal structure of apjohnite. Mineral Mag 40:599-608

Mereiter K (1974) The crystal structure of rhomboclase $H_5O_2^+\{Fe[SO_4]_2 \cdot 2H_2O\}^-$. Tschermaks Mineral Petrog Mitt 21:216-232

Merwin HE, Posnjak E (1937) Sulphate incrustations in the Copper Queen Mine, Bisbee, Arizona. Am Mineral 22:567-571

Milton C, Johnston WD Jr (1938) Sulphate minerals of the Comstock Lode, Nevada. Econ Geol 33:749-771

Milton C, Evans HT Jr, Johnson RG (1982) Dwornikite, $(Ni,Fe)SO_4 \cdot H_2O$, a member of the kieserite group from Minasragra, Peru. Mineral Mag 46:351-353

Minakawa T, Noto S (1994) Botryogen from the Okuki mine, Ehime Prefecture, Japan. Chigaku Kenkyu 43:175-179 (Chem Abstr 123:61439e)

Mitchell AG (1984) The preparation and characterization of ferrous sulfate hydrates. J Pharm Pharmacol 36:506-510

Miura H, Niida K, Hirama T (1994) Mikasaite, $(Fe^{3+},Al)_2(SO_4)_3$, a new ferric sulphate mineral from Mikasa city, Hokkaido, Japan. Mineral Mag 58:649-653

Montoroi J-P (1995) Supply of an acid sulfate minerals sequence in a lower Casamance valley (Senegal). C R Acad Sci Paris Ser IIa 320:395-402 (in French)

Nambu M, Tanida K, Kitamura T, (1978) Jô kokuite, $MnSO_4 \cdot 5H_2O$, a new mineral from the Jô koku mine, Hiyama district, Hokkaido, Japan. Mineral J 9:28-38

Nambu M, Tanida K, Kitamura R, Kato E (1979) Mallardite from the Jô koku mine, Hokkaido, Japan. Ganseki Kobutso Kosho Gakkai-Shi [J Jap Assoc Mineral Petrol Econ Geol] 74:406-412

Naray-Szabo I (1969) Aluminum sulfate hydrates. Acta Chim 60:27-36

Nawaz R (1973) Nickel-hexahydrite from Tasmania, Australia. Mineral Mag 39:246-247

Nickel EH (1995) The definition of a mineral. Can Mineral 33:689-690

Nord AG, Mattsson E, Tronner K (1998) Mineral phases on corroded archaeological bronze artifacts excavated in Sweden. N Jahrb Mineral Monatsh 265-277

Nordstrom DK (1982a) Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. *In* Kittrick JA, Fanning DS, Hossner LR (eds) Acid Sulfate Weathering. Soil Sci Soc Am Spec Publ 10:37-56

Nordstrom DK (1982b) The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system Al_2O_3–SO_2–H_2O at 298 K. Geochim Cosmochim Acta 46:681-692

Nordstrom DK, Alpers CN (1999a) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc Natl Acad Sci USA 96:3455-3462

Nordstrom DK, Alpers CN (1999b) Geochemistry of acid mine waters. *In* Plumlee GS, Logsdon MJ (eds) The Environmental Geochemistry of Mineral Deposits: Part A. Processes, Methods, and Health Issues. Rev Econ Geol 6A:133-160

Nordstrom DK, Southam G (1997) Geomicrobiology of sulfide mineral oxidation. *In* Banfield JA, Nealson KH (eds) Geomicrobiology: Interactions between Microbes and Minerals. Rev Mineral 35:361-390

Nordstrom DK, Alpers CN, Ptacek CJ, Blowes DW (2000) Negative pH and extremely acidic mine waters from Iron Mountain, California. Environ Sci Technol 34:254-258

Novikov VP, Suprychev VV (1986) Conditions of recent mineral formation during the subsurface burning of coals in the Fan-Yagnovka deposit. Mineral Tadzh (7):91-104 (Chem Abstr 106:70434a)

Nuhfer EB (1967) Efflorescent minerals associated with coal. MSc thesis, West Virginia University, Morgantown, West Virginia

Nuhfer EB (1972) Coal blooms: Description of mineral efflorescences associated with coal. Earth Sci. (Sept-Oct), 237-241

O'Brien FEM (1948) The control of humidity by saturated salt solutions. J Sci Instr 25:73-76

Oleinikov BV, Shvartsev SL, Mandrikova NT, Oleinikova NN (1965) Nickelhexahydrite, a new mineral. Zap Vses Mineral Obshch 94:534-547 (in Russian)

Olyphant GA, Bayless ER, and Harper D (1991) Seasonal and weather-related controls on solute concentrations and acid drainage from a pyritic coal-refuse deposit in southwestern Indiana, U.S.A. J Contam Hydrol 7:219-236

Omori K, Kerr PF (1963) Infrared studies of saline sulfate minerals. Geol Soc Am Bull 74:709-734

Ossaka J (1965) Volcanic sublimates. Kazan 10:205-213 (Chem Abstr 67:4923j)

Otto J, Schuerenberg H (1974) New mineral finds in the southern Black Forest. Aufschluss 25:205-211 (in German)

Ovtracht A, Pierrot R (1962) Contributions to the mineralogy of Norway. No. 14. On the presence of melanterites at Lökken. Norsk Geol Tidssk 42:275-276

Pabst A (1940) Cryptocrystalline pyrite from Alpine County, California. Am Mineral 25:425-431

Palache C, Berman H, Frondel C (1951) The System of Mineralogy, Seventh Edn, Vol 2. John Wiley and Sons Inc, New York

Parkinson KJ, Day W (1981) Water vapour calibration using salt hydrate transitions. J Exp Bot 32:411-418

Parsons AL (1922) The preservation of mineral specimens. Am Mineral 7:59-63

Pasava J, Breiter K, Huka M, Korecky J (1986a) Chvaleticeite, $(Mn,Mg)SO_4 \cdot 6H_2O$, a new mineral. Neues Jahrb Mineral Monatsh (3):121-125

Pasava J, Breiter K, Huka M, Korecky J (1986b) Paragenesis of secondary ferrous, magnesium, and manganese sulphates from Chvaletice. Vestnik Ústredniko ústavu Geol 61:73-82 (in Czech)

Paulis P (1991) Magnesian apjohnite from Chvalitice in the Zelezne hory Mts. Vestnik Ústredniko ústavu Geol 66:245-246 (in Czech)

Pemberton HE (1983) Minerals of California. Van Nostrand Reinhold, New York

Perroud P, Meisser N, Sarp H (1987) Presence of zincocopiapite at Valais. Schweiz mineral petrogr Mitt 67:115-117 (in French)

Petlicka J (1971) Effect of impurities on the crystallization of zinc sulfate heptahydrate. Statni Vyzk Ustav Mater Rudny 19:22-25

Plumlee GS (1999) The environmental geology of mineral deposits. *In* Plumlee GS, Logsdon MJ (eds) The Environmental Geochemistry of Mineral Deposits. Rev Econ Geol 6A:71-116

Posnjak E, Merwin HE (1922) The system Fe_2O_3–SO_3–H_2O. J Am Chem Soc 44:1965-1994, 2629

Posnjak E, Tunell G (1929) The system, cupric oxide–sulphur trioxide–water. Am J Sci 18:1-34

Powder Diffraction File: International Centre for Diffraction Data, Swarthmore, Pennsylvania

Querol X, Alastuey A, Lopez-Soler A, Plana F, Zeng RS, Zhao J, Zhuang XU (1999) Geological controls on the quality of coals from the West Shandong mining district, Eastern China. Internat J Coal Geol 42:63-88

Randall M (1930) Free energy of chemical substances, activity coefficients, partial molal quantities, and related constants. *In* Washburn EW (ed) International Critical Tables. Vol VII. McGraw-Hill, New York, p 224-353

Reardon EJ (1988) Ion interaction parameters for $AlSO_4$ and application to the prediction of metal sulfate solubility in binary salt systems. J Phys Chem 92:6426-6431

Reardon EJ (1989) Ion interaction model applied to equilibria in the $NiSO_4$–H_2SO_4–H_2O system. J Phys Chem 93:4630-4636

Reardon EJ, Beckie RD (1987) Modelling chemical equilibria of acid mine-drainage: The $FeSO_4$–H_2SO_4–H_2O system. Geochim Cosmochim Acta 51:2355-2368

Reardon EJ, Stevens R(1991) Aluminum potassium sulfate dodecahydrate solubility in mixed K_2SO_4 + $Al_2(SO_4)_3$ solutions. J Chem Eng Data 36:422-424

Robinson, C (1999) The role of jarosite and copiapite in the chemical evolution of acid drainage waters, Richmond mine, Iron Mountain, California. MSc thesis, Queen's Univ, Kingston, Ontario, Canada

Robinson C, Jamieson HE, Peterson RC, Alpers CN, Nordstrom DK (2000a) Major and trace element composition of copiapite from Richmond mine, Iron Mountain, California. Abstracts with programs, Geol Soc Am 32(7):A-110

Robinson C, Jamieson HE, Alpers CN, Nordstrom DK (2000b) The composition of co-existing jarosite and water from the Richmond mine, Iron Mountain, CA. Abstracts with programs, Geol Soc Am 32(7):A-109

Robinson PD, Fang JH (1971) Crystal structures and mineral chemistry of hydrated ferric sulphates: II. The crystal structure of paracoquimbite. Am Mineral 56:1567-1572

Robinson PD, Fang JH (1973) Crystal structures and mineral chemistry of hydrated ferric sulphates: III. The crystal structure of kornelite. Am Mineral 58:535-539

Rodgers KA, Hamlin KA, Browne PRL, Campbell KA, Martin R (2000) The steam condensate alteration mineralogy of Ruatapu cave, Orakei Korako geothermal field, Taupo Volcanic Zone, New Zealand. Mineral Mag 64:125-142

Rohmer R (1939) Contribution to the study of nickel sulfate and cobalt sulfate. Ann Chim 12:611-725 (in French)

Rose AW and Cravotta CA III (1998) Geochemistry of coal mine drainage. *In* Brady KBC, Smith MW, Schueck J (eds) Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Dept Environ Protection 1:1-22

Rosenzweig A, Gross EB (1955) Goldichite, a new hydrous potassium ferric sulfate from the San Rafael Swell, Utah. Am Mineral 40:469-480

Ruotsala AP, Babcock LL (1977) Zaherite, a new hydrated aluminum sulfate. Am Mineral 62:1125-1128

Rutstein MS (1980) Nickeloan melanterite from Sudbury Basin. Am Mineral 65:968-969

Sabina AP (1977) New occurrences of minerals in parts of Ontario. Geol Survey Can Paper 77-1A:335-339

Sabina AP (1978) Some new mineral occurrences in Canada. Geol Survey Can Paper 78-1A:253-258

Schaller WT (1903) Minerals from Leona Heights, Alameda Co., California. Bull Dept Geol Univ California 3:191-217

Schnitzer WA (1977) An unusual efflorescence (aplowite) on Neogene rocks from the Ismuth of Corinth. Ann Geol Pays Hell 28:349-351 (Chem Abstr 91:24121v)

Schumb WC (1923) The dissociation pressures of certain salt hydrates by the gas-current saturation method. J Am Chem Soc 45:342-354

Sejkora J, Ridkosil T (1993) Retgersite from Jáchymov, Krusné hory Mountains, Czech Republic. Neues Jahrb Mineral Monatsh (9):393-400

Shcherbakova E, Korablev G (1998) Autoconservation of mining industry waste in the South Ural, Russia. Proc Latvian Acad Sci 52:286-288

Siebke W, Spiering H, Meissner E (1983) Cooperative pseudo-Jahn-Teller effect of the $Fe(H_2O)_6^{2+}$ complexes in the sulfate heptahydrates. Phys Rev B, 27:2730-2739

Skarie RL, Richardson JL, McCarthy GJ, Maianu A (1986) Evaporite mineralogy and groundwater chemistry associated with saline soils in eastern North Dakota. Soil Sci Soc Am J 51:1372-1377

Skounakis S, Economou M (1983) An occurrence of magnetite with network texture in serpentinites from Veria area, Greece. Neues Jahrb Mineral Monatsh (3):97-102

Smirnova SK (1971) Voltaite find in Uzbekistan. Dokl Akad Nauk Uzb SSR 28(2):92-93 (in Russian)

Snetsinger KG (1973) Ferroan starkeyite from Del Norte County, California. Can Mineral 12:229

Soboleva OS (1958) Equilibriums in the system $MgSO_4$–$NiSO_4$–H_2O: I. Solubility isotherms. Nauk Zap L'vivsk Derzhav Univ im I Franka 46, Ser Khim (5):91-106 (Chem Abs 55:24207)

Soboleva OS (1960) Equilibrium polytherm of the system $MgSO_4$–$NiSO_4$–H_2O system. Dokl Akad Nauk SSSR 135:91-93 (in Russian)

Sokolov PN, Korobov YuI, Kosukhina IG, Kolotova LV (1985) Mineralogy of water-soluble sulfates in the Namansk manifestation of aluminite (Yakutsk ASSR). *In* Kazanskii YuP, Korel VG (eds) Morfol genesis zakonomern razmeshchiniya mineral obraz Altae-Sayan skladchatoe obl Sib Platformy. Nauka Sib Otd, Novosibirsk, p 120-124 (Chem Abstr 104:21986g)

Srebrodol'skiy BI (1971) Zone of oxidized sulfur ores in the Vodinsk deposit. Geol Rudnyk Mestorozhd 13(3):106-114 (in Russian)

Srebrodol'skiy BI (1974a) First find of lausenite in the USSR. Dokl Akad Nauk SSSR 219:441-442 (in Russian)

Srebrodol'skiy BI (1974b) Sulfate from the halotrichite group. Akad Nauk Ukr RSR Dopov Seriya B 36:600-601 (in Ukrainian)

Srebrodol'skiy BI (1974c) An occurrence of millosevichite in the U.S.S.R. Dokl Akad Nauk SSSR 214:429-430 (in Russian)

Srebrodol'skiy BI (1977) Products of melanterite alteration. Akad Nauk Ukr RSR Dopov Seriya B 39:797-800 (in Ukrainian)

Stamatakis MG, Baltatzis EG, Skounakis SB (1987) Sulfate minerals from a mud volcano in the Katakolo area, western Peleponnesus, Greece. Am Mineral 72:839-841

Stoiber RE, Rose WI Jr (1974) Fumarole incrustations at active Central American volcanoes. Geochim Cosmochim Acta 38:495-516

Sunderman JA, Beck CW (1969) Hydrobasaluminite from Shoals, Indiana. Am Mineral 54:1363-1673

Süsse P (1972) Crystal structure and hydrogen bonding of copiapite. Z Kristallogr 135:34-55

Taylor D, Bassett H (1952) The system $Al_2(SO_4)_3$–H_2SO_4–H_2O. J Chem Soc 4431-4442

Taylor RK, Hardy RG (1974) Sulphate species in colliery spoil. Trans Inst Mining Metall 83A:123-126

Thomas JN, Robinson PD, Fang JH (1974) Crystal structures and mineral chemistry of hydrated ferric sulfates: IV. The crystal structure of quenstedtite. Am Mineral 59:582-586

Tiegeng Liu, Guolong Gong, Lin Ye (1995) Discovery and investigation of zinc-melanterite in nature. Acta Mineral Sinica 15:286-289 (in Chinese)

Timpson ME, Richardson JL, Keller LP, McCarthy GJ (1986) Evaporite mineralogy associated with saline seeps in southwestern North Dakota. Soil Sci Soc Am J 50:490-493

Tu Kwang-Chih, Li His-Lin (1963) Characteristic features of the oxidation zone of the sulfide deposits in arid to extremely arid regions (with special reference to observations obtained from five sulfide deposits in the Northwestern China. Ti Chih Hsueh Pao 43:361-377 (Chem Abstr 60:14263)

Van Breemen N (1982) Genesis, morphology, and classification of acid sulfate soils in coastal plains. *In* Kittrick JA, Fanning DS, Hossner LR (eds) Acid Sulfate Weathering. Soil Sci Soc Am Spec Publ 10:95-108

van Doesburg JDJ, Vergouwen L, van der Plas L (1982) Konyaite, $Na_2Mg(SO_4)_2\cdot 5H_2O$, a new mineral from the Great Konya Basin, Turkey. Am Mineral 67:1035-1038

Van Loan PR, Nuffield EW (1959) An X-ray study of roemerite. Can Mineral 6:348-356

Vdovichenko GM, Lazarev IS, Srebrodol'sky BI (1974) Geological-mineralogical characteristics and genesis of the oxidation zone at the Gaurdak sulfur deposit. *In* Sokolov AS (ed) Genezis mestorozhdenii samorodnoi sery perspekt. Ikh Poiskov Nauka, Moscow, p 106-119 (Chem Abstr 83:82739y)

Velizade SF, Efendieva EN, Aliev AA, Mustafazade BV, Pokidin AK (1976) Some minerals from the oxidized zone of the Katsdag deposit. Dokl Akad Nauk Az SSR 32(8):40-45 (in Russian)

Vergasova LP (1983) Fumarole incrustations of lava flows of the effusive-explosive period of the Great Tolbachik fissure eruption. Vulkanol Seismol (6):75-87 (in Russian)

Vergasova LP, Filatov SK, Serafimova EK, Starova GL (1982) Piypite $K_2Cu_2O(SO_4)_2$—a new mineral of volcanic sublimates. Dokl Akad Nauk SSSR 266:707-710 (in Russian)

Vlasov VV, Kuznetsov AV (1962) Melanterite and its oxidation products. Zap Vses Mineral Obshch 91:490-492 (in Russian)

Wagner DP, Fanning DS, Foss JE, Patterson MS, Snow PA (1982) Morphological and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland. *In* Kittrick JA, Fanning DS, Hossner LR (eds) Acid Sulfate Weathering. Soil Sci Soc Am Spec Publ 10:109-125

Walenta K (1978) Boyleite, a new sulfate mineral from Kropback, southern Black Forest. Chem Erde 37:73-79 (in German)

Waller R (1992) Temperature- and humidity-sensitive mineralogical and petrological specimens. *In* Howie FM (ed) The Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds. Butterworth-Heinemann, p 25-50

Wang Qiguang, Li Wanmao (1988) Crystal structure of a new ferric sulfate mineral. Kexue Tongbao 33:1783-1787 (in Chinese, English abstr)

Ward C (1991) Mineral matter in low-rank coals and associated strata of the Mae Moh basin, northern Thailand. Internat J Coal Geol 17:69-93

Wexler A, Hasegawa S (1954) Relative humidity–temperature relationships of some saturated salt solutions in the temperature range of 0 to 50°C. J Res Natl Bur Stds 53:19-26

Whittig LD, Deyo AE, and Tanji KK (1982) Evaporite mineral species in Mancos Shale and salt efflorescence, Upper Colorado River Basin. Soil Sci Soc Am J 46:645-651

Wiese RG Jr, Powell MA, Fyfe WS (1987) Spontaneous formation of hydrated iron sulfates on laboratory samples of pyrite- and marcasite-bearing coals. Chem Geol 63:29-38

Wildner M, Giester G (1991) The crystal structures of kieserite-type compounds: I. Crystal structures of $Me(II)SO_4\cdot H_2O$ (Me = Mn, Fe, Co, Ni, Zn). Neues Jahrb Mineral Monatsh (7):296-306

Williams SA, Cesbron FP (1995) Wupatkiite from the Cameron uranium district, Arizona, a new member of the halotrichite group. Mineral Mag 59:553-556

Wilson RE (1921) Some new methods for the determination of the vapor pressure of salt-hydrates. J Am Chem Soc 43:740-25 (as cited by Waller 1992).

Wood MM (1970) The crystal structure of ransomite. Am Mineral 55:729-734

Workman WF, Rader EK (1961) Comments on magnesium sulfate minerals formed in Brooks Museum on serpentine from Impruenta, Italy. Virginia J Sci 12:189

Yakhontova LK, Dvurechenskaya SS, Sandomirskaya SM, Sergeeva NE, Pal'chik NA (1988) Sulfates from the cryogenic supergene zone: First finds: Nomenclature problems. Mineral Zhurnal 10(4):3-15 (in Russian)

Young B, Nancarrow PHA (1988) Rozenite and other sulphate minerals from the Cumbrian coalfield. Mineral Mag 52:551-553

Yurgenson G (1997) Oxidized zones in permafrost rocks. Zap Vseross Mineral Obshch 126(5):15-27 (in Russian)

Zachmann DW (1999) The Brunswick Lion (Germany): Environment and corrosion. Mater Corros 50:17-26

Zahrobsky RF, Baur WH (1968) On the crystal chemistry of salt hydrates: V. The determination of the crystal structure of $CuSO_4\cdot 3H_2O$ (bonattite). Acta Crystallogr B24:508-513

Zalkin A, Ruben H, Templeton DH (1962) The crystal structure of cobalt sulfate hexahydrate. Acta Crystallogr 15:1219-1224

Zalkin A, Ruben H, Templeton DH (1964) The crystal structure and hydrogen bonding of magnesium sulfate hexahydrate. Acta Crystallogr 17:235-240

Zavalía MFM, Galliski MA (1995) Goldichite of fumarolic origin from the Santa Bárbara mine, Jujuy, northwestern Argentina. Can Mineral 33:1059-1062

Zhdanov YuYa, Solov'ev LI (1998) Geology and mineralogical composition of the oxidized zone in the Deputatsk tin ore deposit. Otechestvennaya Geol (6):77-79 (Chem Abstr 131:132401

Zhu Meixiang, Tong Wei (1987) Surface hydrothermal minerals and their distribution in the Tengchong geothermal area, China. Geothermics 16:181-195

Zidarov N (1970) Cupriferous bianchite from the Borieva mine, Madan mining region. Dokl Bolg Akad Nauk 23:1283-1286

Zodrow EL (1980) Hydrated sulfates from Sydney Coalfield, Cape Breton Island, Nova Scotia, Canada: The copiapite group. Am Mineral 65:961-967

Zodrow EL, McCandlish K (1978) Hydrated sulfates in the Sydney coalfield, Cape Breton, Nova Scotia. Can Mineral 16:17-22

Zodrow EL, Wiltshire J, McCandlish K (1979) Hydrated sulfates in the Sydney coalfield of Cape Breton, Nova Scotia: II. Pyrite and its alteration products. Can Mineral 17:63-70