

Acquisition and evaluation of thermodynamic data for bieberite-moorhouseite equilibria at 0.1 MPa

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ABSTRACT

Published estimates for the equilibrium relative humidity (RH) at 25 °C for the reaction: bieberite ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) = moorhouseite ($\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$) + H_2O , range from 69.8 to 74.5%. To evaluate these data, the humidity-buffer technique was used to determine equilibrium constants for this reaction between 14 and 43 °C at 0.1 MPa. Reversals along five humidity-buffer curves yield $\ln K = 18.03 - 6509.43/T$, where K is the equilibrium constant, and T is temperature in K. The derived standard Gibbs free energy of reaction is 9.43 kJ/mol, which agrees well with several previously reported values based on vapor-pressure measurements. It also agrees well with values calculated from the data derived mostly from calorimetric measurements. Previous studies indicated that the temperature of the invariant point for the assemblage bieberite-moorhouseite-aqueous solution-vapor is near 44.7 °C, and our extrapolated data predict 91.1% RH at this temperature; the predicted position for the invariant point is in excellent agreement with those reported previously.

INTRODUCTION

Secondary metal-sulfate salts can be important components of the hydrochemical cycles of metals, sulfur, and acidity at active and abandoned mine sites. Sulfate salts of Fe, which form from the oxidative weathering of pyrite or pyrrhotite, typically are the most common at these sites (Jambor et al. 2000). Salts of common base metals such as Cu, Zn, Ni, and Co, which result from the weathering of sulfide minerals of these metals, also can be found locally at these sites. Acid generated from the oxidation of pyrite or pyrrhotite can attack carbonate and silicate minerals in the country rock to contribute Ca, Mg, Mn, and Al, and yield salts of these elements.

Despite the occurrence of Cu-, Zn-, Ni-, and Co-sulfate salts in nature, these metals more commonly occur as solid solutions in more common sulfate salts such as melanterite [$\text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$]. Copper and Zn show extensive solid solution in the melanterite structure, both exceeding 50 mol% and both with possible miscibility gaps (Jambor et al. 2000; Peterson 2002). Solid solution of Ni in the melanterite structure approaches 20 mol%, whereas that for Co is complete (Jambor et al. 2000).

Metals present as major or minor constituents in sulfate salts can have significant impacts on aquatic ecosystems because the salts provide a means of storing metals and subsequently releasing them due to the high solubilities of the salts. Uncertainties in the thermodynamic properties of these salts, especially the Gibbs free energy of formation and the enthalpy of formation, severely limit the ability to model the behavior of these salts in natural and laboratory settings. The uncertainties also hinder the ability to model solid-solution effects in these minerals and the aqueous speciation of high ionic strength solutions in these systems. The humidity-buffer technique was developed recently to resolve discrepancies in the location of dehydration

reactions at near-ambient conditions (Chou et al. 2002). To date, the technique has been used to investigate dehydration equilibria of end-member system including those of Fe^{2+} sulfates (Chou et al. 2002), Cu sulfates (Chou et al. 2002), Zn sulfates (Chou and Seal 2005), Mg sulfates (Chou and Seal 2003a), and Ni sulfates (Chou and Seal 2003b). This paper extends our understanding to Co sulfates.

Mineralogy of cobalt sulfates

Bieberite is a member of melanterite group, which consists of monoclinic ($P2_1/c$) sulfate heptahydrate minerals of the type $\text{M}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$, where M represents Fe (melanterite), Cu (boothite), Co (bieberite), Mn (mallardite), and (Zn, Cu) (zinc-melanterite). In contrast, the common Mg sulfate heptahydrate, epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$], is orthorhombic and belongs to the epsomite group, wherein morenosite [$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$] and goslarite [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] are additional members (Jambor et al. 2000). Bieberite and mallardite are well known as synthetic compounds, and are more common in nature than boothite and Zn-melanterite, which have been found only at a few localities (Jambor et al. 2000). Bieberite forms a complete solid solution with other members of melanterite group, but miscibility gaps exist in synthetic metal-sulfate heptahydrates precipitated at room temperature for the binary systems of bieberite-epsomite, bieberite-goslarite, and bieberite-morenosite (Aslanian et al. 1972; Balarew et al. 1973; Siebke et al. 1983).

Moorhouseite is one of the six members of the hexahydrate group, which are monoclinic ($C2/c$) sulfate minerals of the type $\text{M}^{2+}\text{SO}_4 \cdot 6\text{H}_2\text{O}$, where M represents Mg (hexahydrate), Mn (chvaleticeite), Fe (ferrohexahydrate), Ni (nickelhexahydrate), Co (moorhouseite), and Zn (bianchite). The minerals of the group, except hexahydrate, occur sparingly in nature, and mainly as the oxidation products of sulfide deposits. Moorhouseite has been reported from only two localities, and the cation ratios for the type material are Co:Ni:Mn:Cu:Fe:Zn = 55:25:12:5:3:1

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TABLE 1. Experimental results at 0.1 MPa

Humidity buffer	Run no.	T (°C)*	Mass of initial sample (mg)†	Duration (h)	Mass change (mg)
KNO ₃	1	41.40	452.57	93	+1.65
	2	41.40	546.84	93	+2.92
	3	(42.18)	545.03	96	+3.15
	4	(42.18)	451.45	96	+0.25
	5	(42.38)	546.58	73	-0.29
	6	(42.38)	450.80	73	-0.12
	7	42.65	451.70	94	-0.90
	8	42.65	548.18	94	-1.60
	9	43.16	454.22	118	-2.77
	10	43.16	549.56	118	-4.53
KBr	1	(34.07)	466.99	120	+0.16
	2	(34.07)	562.40	120	+0.28
	3	(34.56)	561.22	96	-0.33
	4	(34.56)	465.61	96	-0.14
	5	35.14	562.68	119	-1.46
	6	35.14	467.15	119	-1.54
NaNO ₃	1	(28.05)	562.70	65	+0.39
	2	(28.05)	467.10	65	+0.35
	3	(29.04)	563.09	95	-0.69
	4	(29.04)	467.45	95	-0.46
KI	1	17.01	438.09	95	+2.26
	2	17.01	382.82	95	+3.41
	3	17.97	379.61	65	+3.21
	4	17.97	435.60	65	+2.49
	5	20.16	440.35	120	+1.43
	6	20.16	386.23	120	+1.59
	7	21.19	441.78	119	+0.55
	8	21.19	387.82	119	+0.30
	9	(23.24)	442.17	72	+0.17
	10	(23.24)	387.94	72	+0.08
	11	24.04	388.12	96	+0.00
	12	24.04	442.33	96	-0.01
	13	(24.25)	442.34	96	-0.05
	14	(24.25)	388.02	96	-0.05
	15	25.06	388.06	95	-0.56
	16	25.06	442.29	95	-0.42
	17	25.90	437.26	73	-1.66
	18	25.90	381.34	73	-1.73
NaBr	1	8.81	415.67	68	+6.97
	2	8.81	420.71	68	+4.52
	3	14.06	419.15	96	+0.17
	4	14.06	416.20	96	+0.27
	5	14.06	442.18	96	+0.12
	6	(14.53)	441.87	93	+0.26
	7	(14.53)	387.50	93	+0.24
	8	(14.53)	415.20	93	+0.69
	9	(14.53)	418.93	93	+0.76
	10	(14.83)	417.13	46	-0.93
	11	(14.83)	419.95	46	-0.80
	12	(14.83)	442.50	46	-0.32
	13	15.42	387.70	42	-0.10
	14	15.43	422.41	52	-2.46
	15	15.43	442.84	52	-0.34
	16	16.17	437.59	73	-0.78
	17	16.17	441.63	73	-1.64
	18	17.01	438.88	95	-0.77
	19	17.01	435.64	95	-1.06
	20	17.97	439.99	65	-1.11
	21	17.97	436.81	65	-1.17

* Values in parentheses were used to bracket the reaction.

† Starting material consisted of a mixture of CoSO₄·7H₂O and CoSO₄·6H₂O.

Figure 1. In Figure 1, the circles along each humidity-buffer curve represent reversal points, and the thick solid curve is the least-squares regression of these reversal points. Previous published results are also plotted for comparison.

Thermodynamic analysis

Equilibrium constants and ΔG_r° values for Reaction 1 were obtained from our experimental data using Equation 2 and these values are listed in Tables 2 and 3.

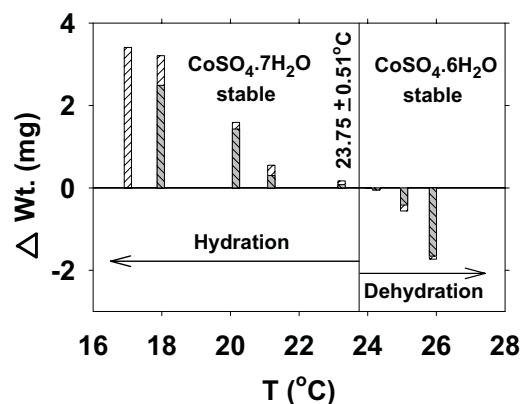


FIGURE 2. Experimental results showing weight changes of the bieberite-moorhouseite mixtures (381 to 442 mg) equilibrated with the KI-saturated buffer solution at fixed temperatures for 65 to 120 hours. Plotted are results listed in Table 1; two samples were run at each temperature and patterns indicate different samples. The equilibrium point was bracketed between 23.24 and 24.25 °C.

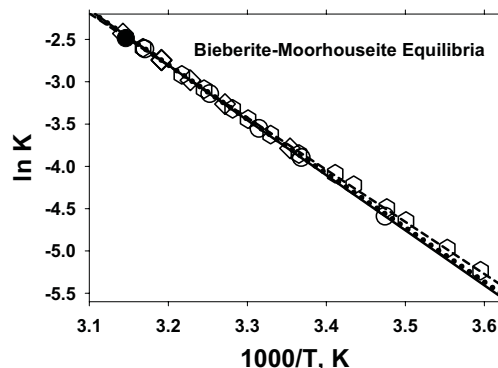


FIGURE 3. $\ln K$ vs. $1/T$ plot for the bieberite-moorhouseite equilibria at 0.1 MPa. Circles are current data from Table 2, and the solid line is a least-squares regression of the data. Data of Carpenter and Jette (1923) are shown by diamonds between 25 and 45.17 °C; the dotted line is a least-squares regression of the data. Data of Broers and Van Welie (1965) between 3 and 42.5 °C are shown by hexagons; the dashed line is a least-squares regression of the data. The large dot at the upper left corner is the invariant point at 44.7 °C for the assemblage bieberite + moorhouseite + aqueous solution + vapor (BMAV) reported by Broers and Van Welie (1965). For clarity, some previous data at 25 °C are not plotted. The regression lines based on the data of Wagman et al. (1982) and DeKock (1982) are very close to the solid line, and for clarity they are not shown.

Figure 3 shows the relation between $\ln K$ and $1/T$ for Reaction 1; our reversal data can be represented by $\ln K (\pm 0.013) = 18.03 - 6509.43/T$. The standard enthalpy of reaction, ΔH_r° , was calculated according to the relation:

$$\partial (\ln K) / \partial (1/T) = -\Delta H_r^\circ / R \quad (3)$$

The value of ΔH_r° for Reaction 1 is listed in Table 3, and the entropy of reaction, ΔS_r° , was calculated from the relation:

$$\Delta G_r^\circ = \Delta H_r^\circ - T \Delta S_r^\circ \quad (4)$$

and is also listed in Table 3. These derived thermodynamic data are compared with previous data in Table 3. Note that the uncertainties listed in Table 3 were derived from those associated with equilibrium temperatures and humidity buffers assuming

TABLE 2. Derived equilibrium constants for reaction 1 at 0.1 MPa

Humidity buffer	T (°C)†	$P_{\text{H}_2\text{O}}$ (MPa) ‡	% RH§	ln K
NaBr	14.68±0.15	0.0016714	60.78±0.05	-4.589±0.010
KI	23.75±0.51	0.0029414	69.12±0.11	-3.896±0.033
NaNO ₃	28.55±0.50	0.0039061	73.47±0.11	-3.549±0.031
KBr	34.32±0.25	0.0054201	79.85±0.03	-3.140±0.014
KNO ₃	42.28±0.10	0.0083289	88.15±0.04	-2.612±0.058

† Equilibrium T; mean of the two values used to bracket equilibrium (see Table 1). The uncertainty listed is half of the difference of the bracket values.

‡ Calculated from Haar et al. (1984).

§ Calculated from Greenspan (1977). Uncertainties are also based on Greenspan (1977).

TABLE 3. Derived thermodynamic data for Reaction 1 at 298.15K and 0.1 MPa

ΔG_r° (kJ/mol)	ΔH_r° (kJ/mol)	ΔS_r° [J/(mol·K)]	Reference
9.433 ± 0.008	54.12 ± 0.13	149.9 ± 0.5	This study
9.344	-	-	Wiedemann (1874)
9.450	-	-	Schumb (1923)
9.393	53.36	147.5	Carpenter and Jette (1923)
9.450	-	-	Diesnis (1935)
9.315	51.25	140.7	Broers and Van Welie (1965)
9.488	54.51	150.7	Wagman et al. (1982)
9.470	54.31	150.4	DeKock (1982)

no uncertainties for the vapor pressure of pure water.

As shown in Table 3 and Figures 1 and 3, our data are in excellent agreement with most of previous vapor-pressure measurements at and above 25 °C (Wiedemann 1874; Schumb 1923; Carpenter and Jette 1923; Diesnis 1935; Broers and Van Welie 1965). Our data for the bieberite-moorhouseite equilibria at lower temperatures are slightly lower in %RH than the values reported by Diesnis (1935) and Broers and Van Welie (1965), but are consistent with most of the high-temperature data, as demonstrated in Figures 1 and 3. Also, our data agree well with the thermodynamic data compiled by Wagman et al. (1982), and those compiled by DeKock (1982). Our value for ΔG_r° is 0.05 kJ/mol lower than the value reported by Wagman et al. (1982), and 0.04 kJ/mol lower than the value of DeKock (1982); these differences are well within the uncertainties of their estimates.

DISCUSSION

To verify our experimental results, we compared the invariant point for the assemblage bieberite + moorhouseite + aqueous solution + vapor (BMAV) derived from our results with that predicted by vapor-pressure measurements (Carpenter and Jette 1923; Broers and Van Welie 1965). The temperature of the invariant point for the assemblage BMAV is most likely near 44.7 °C (horizontal solid line in Fig. 1), as reported by Broers and Van Welie (1965); this temperature is between the values of 43.3 and 45.1 °C, reported by Rohmer (1939) and Carpenter and Jette (1923), respectively. Also shown in Figure 1 are the stability boundaries between bieberite and aqueous solution (Broers and Van Welie 1965) and between moorhouseite and aqueous solution (Carpenter and Jette 1923; Broers and Van Welie 1965). Extrapolation of the current bieberite-moorhouseite boundary to 44.7 °C yields 91.1% RH for the BMAV invariant point; this value agrees well with those reported by Carpenter and Jette (1923) and Broers and Van Welie (1965) at 91.4 and 89.9% RH (large open triangle at 44.7 °C shown in Fig. 1), respectively.

The results of the present study and those of Chou et al. (2002), Chou and Seal (2004), and Chou and Seal (2003a, 2003b) further confirm the conclusion of Hemingway et al. (2002) that the Gibbs free energy contribution for each water of crystallization in hydrated sulfate salts, except for the first water, is about -238.0 kJ/mol. The Gibbs free energy contribution for each water

of crystallization can be calculated from the experimental results of this study for Reaction 1 by the equation:

$$\Delta G_{\text{sw}, 298.15\text{K}}^\circ = -(G_{\text{r}, 298.15\text{K}}^\circ - nG_{\text{f}, \text{H}_2\text{O}, 298.15\text{K}}^\circ)/n \quad (5)$$

where $G_{\text{sw}, 298.15\text{K}}^\circ$ is the Gibbs free energy contribution for each additional water of crystallization at 298.15 K, $G_{\text{r}, 298\text{K}}^\circ$ is the Gibbs free energy of the reaction at 298.15 K, $G_{\text{f}, \text{H}_2\text{O}, 298.15\text{K}}^\circ$ is the Gibbs free energy of formation from elements for water at 298.15 K (Cox et al. 1989), and n is the stoichiometric coefficient for water in the dehydration reaction. For Reaction 1, $G_{\text{r}, 298.15\text{K}}^\circ$ is 9.433 kJ/mol, $G_{\text{f}, \text{H}_2\text{O}, 298.15\text{K}}^\circ$ is -228.6 kJ/mol (Cox et al. 1989), and n is 1, which yields a $G_{\text{sw}, 298.15\text{K}}^\circ$ of -238.03 kJ/mol. For melanterite-rozenite and chalcantite-bonattite equilibria (Chou et al. 2002), calculated values for $G_{\text{sw}, 298\text{K}}^\circ$ are -238.34 and -239.90 kJ/mol, respectively. The value for the goslarite-bianchite equilibria is -238.23 kJ/mol (Chou and Seal 2005), for epsomite-hexahydrate equilibria is -238.73 kJ/mol (Chou and Seal 2003a), and for morenosite-retgersite equilibria is -237.44 kJ/mol (Chou and Seal 2003b).

The scarcity of the Co-sulfate minerals bieberite, moorhouseite, and aplowite is due, in part, to the scarcity of primary Co-sulfide minerals in nature. Common Co-sulfide minerals include linnæite [Co₃S₄], carrollite [Cu(Co, Ni)₂S₄], cobaltite [CoAsS], and glaucodot [(Co, Fe)AsS]. These most commonly occur as accessory minerals in sulfide deposits primarily mined for Cu or Ni. The substitution of Co in pyrite and pyrrhotite is probably a more important precursor to Co-sulfate minerals. Experimental studies at 400 and 500 °C have demonstrated that the concentration of cobalt in pyrite is limited to less than 2 mol% CoS₂, whereas pyrrhotite shows complete solid solution with its Co counterpart (Wyszomirski 1980; Tauson and Akimov 1991). Nevertheless, the occurrence of Co-bearing sulfide minerals in nature is also limited by the low crustal abundance of Co (25 mg/kg; Craig et al. 1998). The scarcity can also be attributed to the fact that Co can readily substitute into other more-common simple sulfate minerals. The orthorhombic sulfates epsomite [MgSO₄·7H₂O], goslarite [ZnSO₄·7H₂O], and morenosite [NiSO₄·7H₂O] all can accept between 25 and 55 mol% Co (Jambor et al. 2000). Solid solution in the more common melanterite group, which is monoclinic and isostructural with bieberite, would be expected to be greater.

Reports of Co-sulfate minerals are not common. Bieberite is the most common, followed by moorhouseite and aplowite (Table 4). Invariably, all of the occurrences appear to be secondary alteration products of sulfide or arsenide minerals. Textural descriptions for all of the occurrences are insufficient to determine which minerals may be inferred to be in equilibrium. The presence of bieberite generally restricts the conditions at Leogang and the Rauris Valley (Austria), the Alfredo mine (Spain), the La Motte mine (USA), and Ticino (Switzerland) to humidities in excess of 60 percent assuming temperatures greater than 10 °C (Fig. 4). The presence of moorhouseite and aplowite at Walton (Canada) places this assemblage along the undetermined buffer curve corresponding to this assemblage, somewhere at lower humidities than the moorhouseite-bieberite curve. The mineral pairs from Saint Joachimsthal (Czech Republic) seem to record a range of disequilibrium humidities and temperatures,

TABLE 4. Selected mineralogy of cobalt-sulfate occurrences

Location	Cobalt sulfates	Other sulfates	Cobalt sulfides and arsenides	Other sulfides	Misc. minerals	References
Leogang, Austria	Bb			Py, Mc, Po	Lm, Gt, Er	Paar (1987)
Rauris Valley, Austria	Bb	Gyp		Py, Po	Lm, Gt	Schebesta (1984)
Walton, Nova Scotia, Canada	Mh, Ap			Py		Jambor and Boyle (1965)
St. Joachimsthal, Czech Republic	Bb, Mh	Mr, Rt, Nh, Rz, Me, Ha, Ma, Sz	Gl, Sk		Er	Hloušek and Tvrđý (2002)
Wildermann Mine, Germany	Bb	Ch, Rz, Sd, Rt, Mr	Sk, Sg	Py		Schnorrer et al. (2000)
Alfredo Mine, Rio Tinto, Spain	Bb	Me, Ch, Ma, Ha, Ep, Gy		Py		García-García (1992)
La Motte Mine, Missouri, U.S.A.	Bb					Kidwell (1946)
Ticino, Switzerland	Bb		Ln	Py	Ht, Lm	Schatz (1975)
Corinth Isthmus, Greece	Ap					Schnitzer (1976)

Notes: Abbreviations: Ap, aplowite [CoSO₄·4H₂O]; Bb, bieberite [CoSO₄·7H₂O]; Ch, chalcantinite [CuSO₄·5H₂O]; Ep, epsomite [MgSO₄·7H₂O]; Er, erythrite [Co₂(AsO₄)₂·8H₂O]; Gl, glaucodot [(Co,Fe)AsS]; Gt, goethite [Fe³⁺O(OH)]; Gy, gypsum [CaSO₄·2H₂O]; Ha, halotrichite [Fe²⁺Al₂(SO₄)₄·22H₂O]; Ht, heterogenite [Co³⁺O(OH)]; Lm, limonite [Fe³⁺O(OH)]; Ln, linnaeite [Co²⁺Co³⁺₂S₄]; Ma, mallardite [MnSO₄·7H₂O]; Mc, marcasite [FeS₂]; Me, melanterite [FeSO₄·7H₂O]; Mh, moorhouseite [CoSO₄·6H₂O]; Mr, morenosite [NiSO₄·7H₂O]; Nh, nickelhexahydrate [β-NiSO₄·6H₂O]; Py, pyrite [FeS₂]; Rt, retgersite [α-NiSO₄·6H₂O]; Rz, rozenite [FeSO₄·4H₂O]; Sd, siderotil [FeSO₄·5H₂O]; Sg, siegenite [(Ni,Co)₂S₃]; Sk, skutterudite (CoAs₃); Sz, szomolnokite [FeSO₄·H₂O].

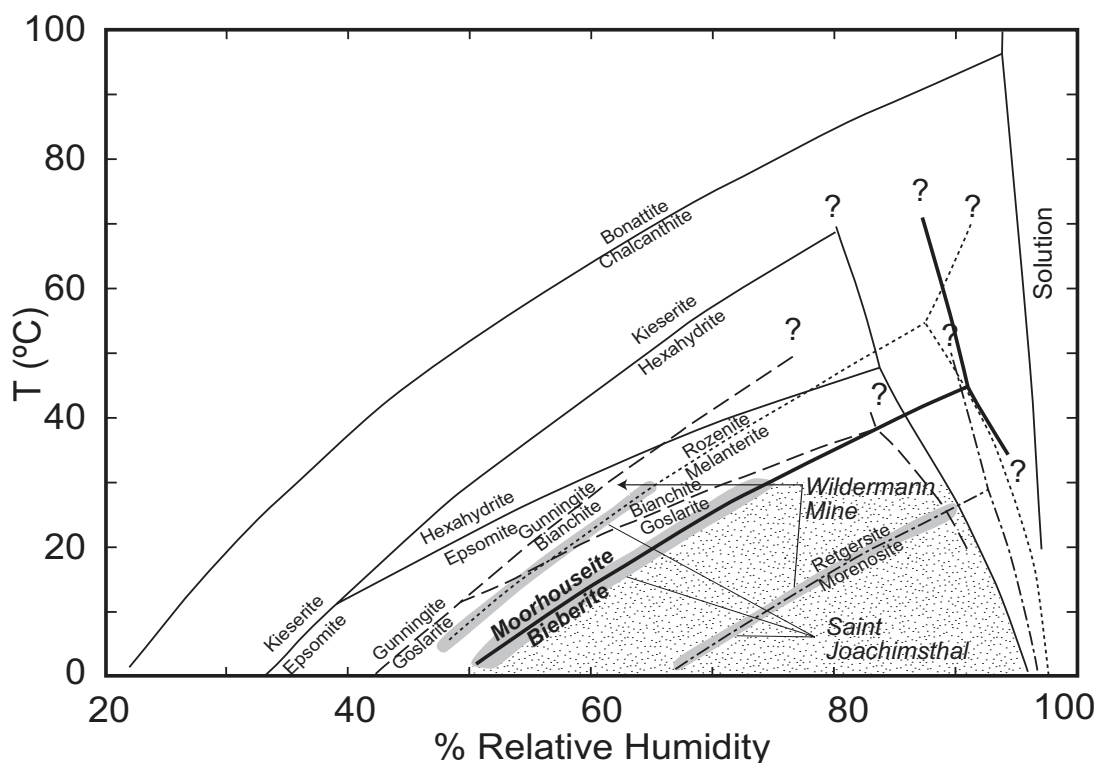


FIGURE 4. Hydrogenetic grid for selected hydrated metal-sulfate salts. Curves for bieberite and moorhouseite are from this study, those for melanterite and rozenite, and chalcantinite and bonattite are from Chou et al. (2002), those for goslarite, bianchite, and gunningite are from Chou and Seal (2005), those for epsomite, hexahydrate, and kieserite are from Chou and Seal (2003a), and those for morenosite and retgersite are from Chou and Seal (2003b). The stippled field indicates the stability of bieberite, the most common Co sulfate. The gray fields for various sites are derived from Table 4. Note the implied disequilibrium for St. Joachimsthal and the Wildermann mine. The arrow for the Wildermann mine indicates the approximate position for the siderotil-rozenite equilibrium position. For all sites, an annual temperature range from 0 to 30 °C was assumed.

although the effect of solid solutions is unknown (Hloušek and Tvrđý 2002). The lowest humidities or highest temperatures are recorded by the presence of rozenite and melanterite, followed in order of increasing humidity or decreasing temperature by moorhouseite and bieberite, and then by retgersite and morenosite (Fig. 4). At the Wildermann mine (Germany), the presence of retgersite and morenosite is consistent with the presence of bieberite as the only Co-sulfate mineral; however, the stability of siderotil with rozenite must lie at higher temperature or lower humidities than the moorhouseite-bieberite and the rozenite-melanterite curves (Fig. 4).

The addition of phase-equilibrium data for the system CoSO₄-H₂O improves the “hydrogenetic” grid that can be constructed for terrestrial ambient conditions by supplementing previous data (Fig. 4). The location of many of these dehydration reactions in the middle of the field of relative humidity and temperature conditions, and their rapid kinetics underscore the challenges of mineralogical characterization of samples as they relate to field conditions. The disequilibrium associations discussed above highlight the reality of these effects. The dissolution of these salts during summer storm events or spring-melt in snow-covered regions can significantly impact receiving watersheds. The

mineralogical controls on the partitioning of trace metals between dehydration products are poorly understood. Similarly, the role of differential partitioning of metals between sulfate salts and water in affecting surface runoff is inadequately known, although Alpers et al. (1994) demonstrated that preferential partitioning of Cu and Zn between melanterite and water can lead to seasonal variations in the Zn/Cu ratio of mine effluent at Iron Mountain, California. Ultimately, the greatest value from the present study may come from providing a sound thermodynamic basis from which to better understand solid-solution effects in multicomponent simple sulfate salts.

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