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Determination of goslarite–bianchite equilibria by the humidity-buffer technique at 0.1 MPa

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Abstract

Goslarite–bianchite equilibria were determined along four humidity-buffer curves at 0.1 MPa and between 27 and 36 °C. Results, based on tight reversals along each humidity buffer, can be represented by $\ln K (\pm 0.005) = 19.643 - 7015.38/T$, where K is the equilibrium constant and T is temperature in K. Our data are in excellent agreement with several previous vapor-pressure measurements and are consistent with the solubility data reported in the literature. Thermodynamic analysis of these data yields $9.634 (\pm 0.056) \text{ kJ mol}^{-1}$ for the standard Gibbs free energy of reaction, which is in good agreement with the value of $9.658 \text{ kJ mol}^{-1}$ calculated from the thermodynamic data compiled and evaluated by Wagman et al. [Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttal, R.L., 1982. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C₁ and C₂ organic substances in SI units. J. Phys. Chem. Ref. Data 11, Suppl. 2]. Published by Elsevier B.V.

Keywords: Hydrated zinc sulfates; Humidity; Experimental; Goslarite; Bianchite

1. Introduction

Metal-sulfate salts are highly soluble and commonly form as efflorescences on waste rocks, on tailings and on mine workings. The salts store acidity and metals for subsequent release during rain events or spring snow-melt. At abandoned metal mines, metal-sulfate salts sequester a variety of metals, especially Fe, Al, Cu and

Zn, and form a variety of minerals (Alpers et al., 1994a; Jambor et al., 2000; Hammarstrom et al., 2005). Common alteration minerals at abandoned metal mines include melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$], rozenite [$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$], copiapite [$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$], alunogen [$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$], halotrichite [$\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$], chalcantite [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] and goslarite [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]. The role of these minerals in metal cycling is further complicated by extensive solid solutions. Alpers et al. (1994b) proposed that seasonal variations in the Zn/Cu ratio of effluent from the Richmond adit at Iron Mountain, California were the result of precipitation and dissolution of Cu-rich

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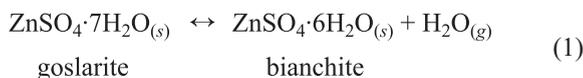
melanterite in the mine workings. The ability model to quantitatively the behavior of the minerals is hindered by limited phase-equilibria and thermodynamic data for these compounds. A better understanding of end-member systems is necessary before solid-solution effects can be addressed. Recent refinements in experimental techniques for investigating dehydration equilibria among the salts have improved our understanding of the $\text{FeSO}_4\text{-H}_2\text{O}$ and $\text{CuSO}_4\text{-H}_2\text{O}$ systems (Chou et al., 2002), and also the $\text{NiSO}_4\text{-H}_2\text{O}$ (Chou and Seal, 2003a), $\text{CoSO}_4\text{-H}_2\text{O}$ (Chou and Seal, 2003b) and $\text{MgSO}_4\text{-H}_2\text{O}$ (Chou and Seal, 2003c) systems. The present study continues this research into the $\text{ZnSO}_4\text{-H}_2\text{O}$ system by investigating the dehydration equilibrium between goslarite [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] and bianchite [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$]. The tetrahydrate, boyleite, and the monohydrate, gunningite, are also known as minerals (Jambor et al., 2000) but are not dealt with in our study.

Goslarite is a member of the epsomite group, which consists of orthorhombic ($P2_12_12_1$) sulfate minerals of the type $M^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$, wherein M stands for Mg (epsomite), Ni (morenosite) and Zn (goslarite). Goslarite forms complete solid solutions with the Mg and Ni end-members, and the substitution of Zn by Fe, Co and Cu can extend to 37, 27 and 15 mol%, respectively; substitution of Zn by Mn may also occur, but the limits are not well defined (Jambor et al., 2000).

Bianchite is one of the six members of the hexahydrate group, which are monoclinic ($C2/c$) sulfate minerals of the type $M^{2+}\text{SO}_4 \cdot 6\text{H}_2\text{O}$, wherein M is Mg (hexahydrate), Mn (chvaleticeite), Fe (ferrohexahydrate), Ni (nickelhexahydrate), Co (moothouseite) and Zn (bianchite). Even though little is known about the limits of solid solution in these hexahydrates, significant replacement of Zn in natural bianchite by Fe (up to 45 mol%), Mn (5 mol%) and Cu (15 mol%) has been reported (Jambor et al., 2000).

Published experimental data for the equilibrium relative humidity (RH) associated with goslarite and bianchite at 25 °C span a range from approximately 55% to 65% (Frowein, 1887; Lescoeur, 1889; Foote and Scholes, 1911; Schumb, 1923; Ishikawa and Murooka, 1933; Bonnell and Burridge, 1935; Bell, 1940). Estimates of RH calculated from published thermodynamic data range from approximately 65% to 80% (Wagman et al., 1982; DeKock, 1982).

The present study uses a humidity-buffer technique (Polyanskii et al., 1976; Malinin et al., 1977; Chou et al., 2002) to resolve inconsistencies in the phase equilibria and thermodynamics of the $\text{ZnSO}_4\text{-H}_2\text{O}$ system. The equilibrium RH and refined thermodynamic relations between goslarite and bianchite at temperatures ranging from 27 to 36 °C at 0.1 MPa were determined for the reaction:



where s and g are solid and gas, respectively. For the reaction,

$$\begin{aligned} \Delta G_r^\circ &= -RT \ln(K) = -RT \ln(f\text{H}_2\text{O}) \\ &= -RT \ln[(f^*\text{H}_2\text{O})(\%RH)/100], \end{aligned} \quad (2)$$

where ΔG_r° is the standard Gibbs free energy of reaction, K equilibrium constant, R gas constant, T absolute temperature, $f\text{H}_2\text{O}$ equilibrium H_2O fugacity and $f^*\text{H}_2\text{O}$ fugacity of pure H_2O .

2. Previous work

All previously published data for goslarite–bianchite equilibrium in terms of temperature and relative humidity are summarized in Fig. 1. Vapor-pressure measurements were made at 0.1 MPa and 25 °C by Frowein (1887), Lescoeur (1889), Foote and Scholes (1911), Schumb (1923) and Ishikawa and Murooka (1933), between 10 and 25 °C by Bonnell and Burridge (1935), between 21.5 and 39 °C by Copeland and Short (1940), and between 25 and 35 °C by Bell (1940). Thermodynamic data derived from calorimetric and vapor-pressure measurements for goslarite and bianchite were evaluated and compiled by Wagman et al. (1982) and DeKock (1982), and the goslarite–bianchite phase boundaries based on these data are shown in Fig. 1 as dotted and dashed lines, respectively. The location of point A, a quadruple invariant point (Fig. 1), is uncertain and other reported positions are shown in Fig. 1. According to the data of Wagman et al. (1982), reaction curves for the phase boundaries for $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}\text{-ZnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}\text{-ZnSO}_4 \cdot \text{H}_2\text{O}$ radiate from point A (Fig. 1). For clarity, phase boundaries reported by

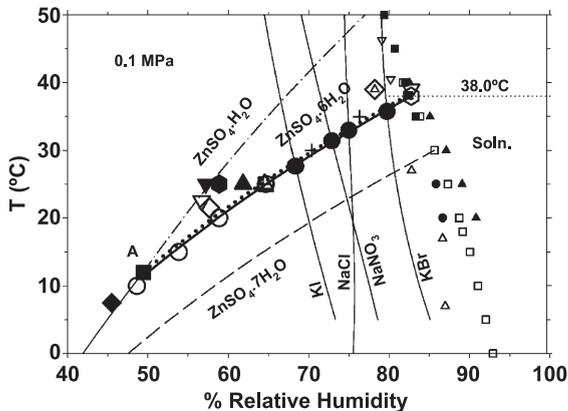


Fig. 1. Experimental results for the goslarite–bianchite equilibria at 0.1 MPa and phase relations in the binary system $\text{ZnSO}_4\text{--H}_2\text{O}$. For the goslarite–bianchite reaction, current results listed in Table 2 are shown by large dots along four humidity-buffer curves (thin near-vertical solid lines) and the thick solid line represents the least-squares fit of the data. The inclined dotted line and dashed line are the goslarite–bianchite phase boundary based on the data of Wagman et al. (1982) and DeKock (1982), respectively. The solid square at 12 °C and 49.4% RH, point A, is the quadruple invariant point for the assemblage ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{ZnSO}_4 \cdot \text{H}_2\text{O} + \text{vapor}$) as derived from Wagman et al. (1982), and the dashed-dot line and thin solid line radiating from point A are phase boundaries for $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O} - \text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} - \text{ZnSO}_4 \cdot \text{H}_2\text{O}$, respectively. Other reported locations for this invariant point include the solid diamond at 7.5 °C and 45.5% RH (Bonnell and Burridge, 1935), the open diamond at 21.5 °C and 51.6% RH (Copeland and Short, 1940), and the open triangle with the apex pointing down at 22.5 °C and 56.7% RH (D'Ans et al., 1957). The goslarite–bianchite equilibria data obtained from vapor-pressure measurements at 25 °C are shown by the filled large triangle with the apex pointing up (Frowein, 1887), the filled hexagon (Lescoeur, 1889), the filled triangle with the apex pointing down (Foote and Scholes, 1911), the open large triangle with the apex pointing up (Schumb, 1923) and the open square (Ishikawa and Murooka, 1933). Those between 10 and 25 °C are shown by the open circles (Bonnell and Burridge, 1935), those at 21.5 and 39 °C by the open diamonds (Copeland and Short, 1940), and those between 25 and 35 °C by the plus signs (Bell, 1940). The goslarite–aqueous-solution phase boundary obtained by vapor-pressure measurements is indicated by small filled triangles (Ishikawa and Murooka, 1933), small dots (Diesnis, 1935) and small open triangles with the apex pointing up (Copeland and Short, 1940). This phase boundary was also determined by Giauque et al. (1950) by e.m.f. measurements in a Clark cell and their results are shown by small open squares. The bianchite–aqueous-solution phase boundary obtained by Copeland and Short (1940) and by Giauque et al. (1950) is indicated by small triangles with the apex pointing down and by filled small squares, respectively. The quadruple invariant point for the assemblage ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{aqueous solution} + \text{vapor}$) is marked by the open diamond at 39 °C and 78.2% RH (Copeland and Short, 1940), the open large triangle with the apex pointing down at 39 °C and 82.7% RH (D'Ans et al., 1957), and the open hexagon at 38.0 °C and 82.7% RH (this study; see text for discussion).

Copeland and Short (1940) and D'Ans et al. (1957) are not shown.

In a P – T phase diagram in the binary system $\text{ZnSO}_4\text{--H}_2\text{O}$, Copeland and Short (1940) presented their data points for reaction (1) together with those for four additional univariant assemblages: ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{ZnSO}_4 \cdot \text{H}_2\text{O} + \text{vapor}$), ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{ZnSO}_4 \cdot \text{H}_2\text{O} + \text{vapor}$), ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{aqueous solution} + \text{vapor}$) and ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{aqueous solution} + \text{vapor}$). Unfortunately, their experimental values were not given. The open diamond symbol shown in Fig. 1 at 39 °C and 78.2% RH represents their quadruple invariant point for the assemblage ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{aqueous solution} + \text{vapor}$). However, this invariant point was located by Giauque et al. (1950) at 38.12 °C and 82.49% RH, and by D'Ans et al. (1957) at 39 °C and 82.7% RH, and, on the basis of the vapor-pressure measurements of Ishikawa and Murooka (1933) for goslarite–saturated solution, at 38.0 °C and 83.5% RH. The temperature of 38.0 °C is the average from the previously reported temperatures of 37.9 °C (Gmelins Handbuch, 1956; Linke and Seidell, 1965) and 38.12 °C (Barieau and Giauque, 1950). The vapor-pressure measurements of Copeland and Short (1940) and Diesnis (1935) define lower humidities than those reported by Ishikawa and Murooka (1933) for the phase boundary between goslarite and solution.

Because of large uncertainties associated with the previously reported RH values for the goslarite–bianchite equilibrium at 0.1 MPa, ranging from 57.2% to 78.0% (Fig. 1), experiments were performed to evaluate the existing data. Once reliable and internally consistent thermodynamic data have been obtained for reaction (1) for the pure Zn end-member, the effects of solid solutions on this reaction can be studied.

3. Experimental method and results

The humidity-buffer technique used in this study was described by Chou et al. (2002). Starting materials were either reagent-grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (ACROS, Lot no. A012317801) or mixtures of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and its dehydration product, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$. A weighed amount of the starting material, typically 400–700 mg, was loaded into a plastic sample container (8 mm ID, 20 mm tall), which was partly immersed in a humidity-buffer

Table 1
Experimental results at 0.1 MPa

Humidity buffer	Run no.	T (°C) ^a	Mass of initial sample (mg) ^b	Duration (h)	Mass change (mg)
KI	1	(26.85)	412.12	182	+7.0
	2	27.46	659.24	141	0.00
	3	27.46	613.97	141	+0.01
	4	27.93	659.24	120	-0.19
	5	(28.42)	659.05	144	-0.74
	6	(28.42)	614.11	144	-0.74
NaNO ₃	1	30.08	590.37	144	+2.37
	2	30.08	493.48	144	+2.49
	3	(30.92)	592.74	120	+0.46
	4	(30.92)	495.42	120	+0.36
	5	(31.88)	591.84	144	-1.53
	6	(31.88)	494.76	144	-1.28
NaCl	1	(31.86)	658.29	120	+1.13
	2	(31.86)	663.66	120	+1.16
	3	33.08	658.31	144	-0.02
	4	(34.08)	542.32	120	-4.65
	5	(34.08)	(696.95)	120	-3.34
KBr	1	(35.21)	653.93	120	+0.52
	2	(35.21)	529.06	120	+1.00
	3	(36.27)	656.46	144	-2.05
	4	(36.27)	530.66	144	-3.68

^a Values in parentheses were used to bracket the reaction.

^b Starting material consisted of a mixture of ZnSO₄·7H₂O and ZnSO₄·6H₂O, except the one in parentheses, which contained ZnSO₄·7H₂O only.

solution in a glass container (17.5 mm ID, 40 mm tall) sealed by a rubber stopper. The four humidity-buffer solutions used, each of which is a saturated solution that has well-characterized humidity variations with temperature (Greenspan, 1977; Chou et al., 2002), were KI, NaNO₃, NaCl and KBr (Fig. 1). The whole assembly was then immersed in a water

Table 2
Derived equilibrium constants at 0.1 MPa

Humidity buffer	T (°C) ^a	$f^*\text{H}_2\text{O}$ (MPa) ^b	% RH ^c	$\ln K$
KI	27.64±0.79	0.0037045	68.35±0.24	-3.676±0.041
NaNO ₃	31.40±0.48	0.0046003	72.84±0.32	-3.396±0.022
NaCl	32.97±1.11	0.0050252	74.96±0.11	-3.279±0.060
KBr	35.74±0.53	0.0058625	79.73±0.22	-3.063±0.026

^a Equilibrium T ; mean of the two values used to bracket equilibrium (see Table 1).

^b Calculated from Haar et al. (1984).

^c Calculated from Greenspan (1977).

bath whose temperature was controlled to ±0.03 °C and was measured by a Pt resistance probe accurate to ±0.02 °C. Small holes through the cap of the sample chamber allowed the vapor phase of the sample to equilibrate with that of the buffer system at the fixed temperature. The direction of reaction was determined by the mass change of the sample (precise to ±0.05 mg). Both the starting material and experimental products were examined by X-ray diffraction and optical methods, and no unexpected phases were identified. Experimental results are listed in Tables 1 and 2, and are plotted in Fig. 1.

4. Thermodynamic analysis

Equilibrium constants and ΔG_r° values for reaction (1) were obtained from our experimental data using Eq. (2) and are listed in Table 2 and 3 respectively. Fig. 2 shows the relation between $\ln K$ and $1/T$ for reaction (1); our reversal data can be represented by $\ln K (\pm 0.005) = 19.643 - 7015.38/T$. The standard

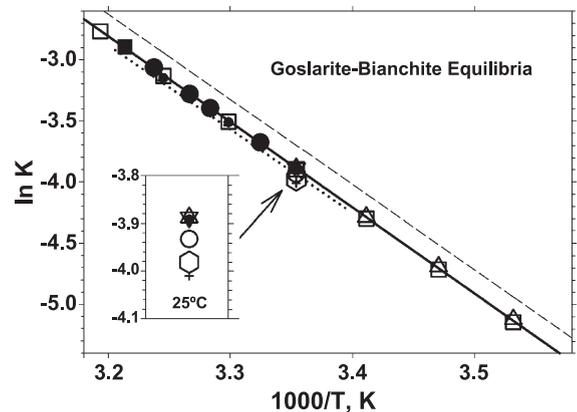


Fig. 2. Plot of $\ln K$ vs. $1/T$ for the goslarite-bianchite equilibria. Large dots are current data from Table 2 and the solid line is a least-squares regression of the data. Previous data are shown by the open squares (Wagman et al., 1982), dashed line (DeKock, 1982), small dots (Bell, 1940), open triangles with the apices pointing up (Bonnell and Burridge, 1935) and dotted line (Copeland and Short, 1940). Data at 25 °C (insert) are from Frowein (1887, open circle), Lescoeur (1889, diamond), Foote and Scholes (1911, plus sign) and Ishikawa and Murooka (1933, open triangle with the apex pointing down). The solid square is the quadruple invariant point at 38.0 °C and 82.7% RH for the assemblage (ZnSO₄·7H₂O+ZnSO₄·6H₂O+aqueous solution+vapor); for detail, see Fig. 1 and text.

Table 3
Derived thermodynamic data for the goslarite–bianchite dehydration reaction at 298.15 K and 0.1 MPa

ΔG_r° (kJ mol ⁻¹)	ΔH_r° (kJ mol ⁻¹)	ΔS_r° (J mol ⁻¹ K ⁻¹)	Reference
9.634±0.056	58.33±0.85	163.3±3.1	This study
9.748	n.d.	n.d.	Frowein (1887)
9.869	n.d.	n.d.	Lescoeur (1889)
9.941	n.d.	n.d.	Foote and Scholes (1911)
9.642	n.d.	n.d.	Schumb (1923)
9.636	n.d.	n.d.	Ishikawa and Murooka (1933)
9.636	57.64	161.0	Bonnell and Burridge (1935)
9.744	56.94	158.3	Copeland and Short (1940)
9.649	56.85	158.3	Bell (1940)
9.658	58.472	163.7	Wagman et al. (1982)
9.173	57.98	163.7	DeKock (1982)

n.d.=not determined.

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 calculated values of ΔH_r° for reaction (1) are listed in Table 3 together with the entropy of reaction, ΔS_r° , as calculated from the relation:

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

Although the ΔG_r° and ΔH_r° values obtained in this study are precise, the value for ΔS_r° involves large uncertainties because it was calculated from the difference of two large numbers for ΔG_r° and ΔH_r° .

Data from the present study are in excellent agreement with most of the previous vapor-pressure measurements (Ishikawa and Murooka, 1933; Bonnell and Burridge, 1935; Bell, 1940), as shown in Table 3 and Fig. 2. The results also agree well with the thermodynamic data evaluated and compiled by Wagman et al. (1982). Our ΔG_r° value is about 0.5 kJ mol⁻¹ higher than the value recommended by DeKock (1982), but is still within the uncertainty of her estimate, which is more than 1 kJ mol⁻¹. As shown in Fig. 1, our data are consistent with the position of the invariant point reported previously for the assemblage goslarite–bianchite–aqueous solution–

vapor. Extrapolating our goslarite–bianchite boundary shown in Fig. 1 to 38.0 °C, we predict 82.7% RH at this invariant point, which agrees well with those reported by Giauque et al. (1950) (38.12 °C and 82.49% RH) and D’Ans et al. (1957) (39 °C and 82.7% RH), and also agrees well with that extrapolated from the goslarite–aqueous solution boundary reported by Ishikawa and Murooka (1933) (38.0 °C and 83.5% RH).

5. Discussion

The results of this study and those of Chou et al. (2002) 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 -238.0 kJ mol⁻¹. The Gibbs free-energy contribution for each water of crystallization can be calculated from the experimental results of this study for goslarite–bianchite equilibrium by the equation:

$$\Delta G_{\text{xw},298\text{K}}^\circ = -(\Delta G_{\text{r},298\text{K}}^\circ - n\Delta G_{\text{fH}_2\text{O},298\text{K}}^\circ)/n \quad (5)$$

where $\Delta G_{\text{xw},298\text{K}}^\circ$ is the Gibbs free-energy contribution for each additional water of crystallization at 298.15 K, $\Delta G_{\text{r},298\text{K}}^\circ$ is the Gibbs free energy of the reaction at 298.15 K, $\Delta G_{\text{fH}_2\text{O},298\text{K}}^\circ$ is the Gibbs free energy of formation from elements for water vapor at 298.15 K (Cox et al., 1989), and n is the stoichiometric coefficient for water in the dehydration reaction. For reaction (1), $\Delta G_{\text{r},298\text{K}}^\circ$ is 9.634 kJ mol⁻¹, $\Delta G_{\text{fH}_2\text{O},298\text{K}}^\circ$ is -228.6 kJ mol⁻¹ and n is 1, which yields a $\Delta G_{\text{xw},298\text{K}}^\circ$ of -238.23 kJ mol⁻¹. For melanterite–rozenite and chalcantite–bonattite equilibria (Chou et al., 2002), calculated values for $\Delta G_{\text{xw},298\text{K}}^\circ$ are -238.34 and -239.90 kJ mol⁻¹, respectively. The value for morenosite–retgersite equilibria is -237.44 kJ mol⁻¹ (Chou and Seal, 2003a), for bieberite–moorhouseite equilibria is -238.03 kJ mol⁻¹ (Chou and Seal, 2003b), and for epsomite–hexahydrate equilibria is -238.73 kJ mol⁻¹ (Chou and Seal, 2003c). The improved understanding of the free-energy contribution of individual water molecules associated with hydration of efflorescent

salts will improve the ability to estimate thermodynamic data for phases in the absence of experimentally determined values.

The results of this study and those of Chou et al. (2002) can be used to assess the secondary metal-sulfate salt assemblages to be expected at abandoned mine sites (Fig. 3). Metal-sulfate salts are most likely to form during dry periods in the summer in the eastern United States (Hammarstrom et al., 2005), where the average temperature typically ranges from ~10 to 40 °C and RH ranges from ~30% to 100%. Under these conditions, ferrous sulfates are expected to be dominated by either melanterite or rozenite, cupric sulfates are expected to be almost exclusively chalcantite, and zinc sulfates are expected to be goslarite, bianchite or gunningite. However, in multi-component systems, solid-solution effects can stabilize other minerals relative to the binary ones. Solid solution of Cu will establish for siderotil, the ferrous sulfate pentahydrate, a stable field between that of melanterite and rozenite (Jambor and Traill, 1963). Copper and Zn commonly occur in solid solution in minerals such as melanterite or siderotil but can locally form minerals such as chalcantite and goslarite (Jambor et al., 2000; Peterson et al., 2003; Peterson, 2003; Hammarstrom et al., this volume).

6. Summary

Equilibrium constants for reaction (1) were determined by measuring the equilibrium humidities using the humidity-buffer method at 0.1 MPa and between 27 and 36 °C. Mass changes of the solid equilibrium assemblage along four humidity buffers (Fig. 1) were measured at fixed P - T conditions and gave results in excellent agreement with several previous vapor-pressure measurements. Our data, which agree well with the thermodynamic data compiled and evaluated by Wagman et al. (1982), predict the position of the invariant point to be at 38.0 °C and 82.7% RH for the assemblage (goslarite–bianchite–aqueous solution–vapor). This predicted position agrees well with those reported previously.

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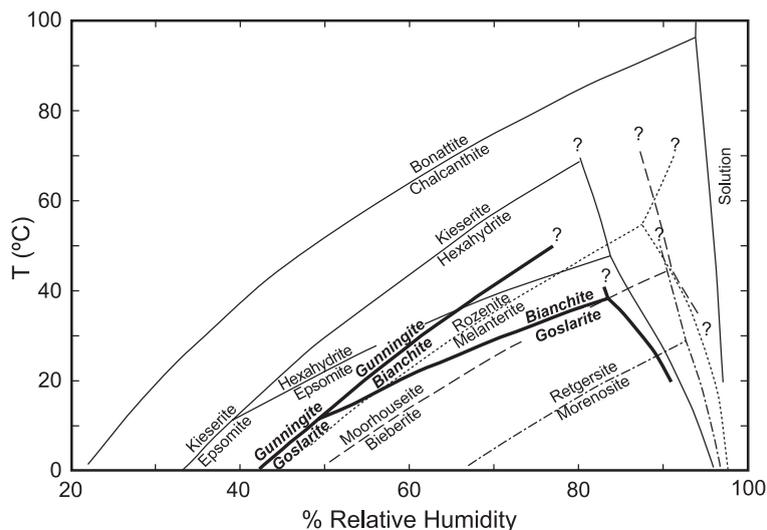


Fig. 3. Selected phase equilibria in terms of temperature and relative humidity in pure end-member systems. Phase boundaries in the FeSO_4 - H_2O system are shown as short-dashed (almost dotted) lines, in the CuSO_4 - H_2O (bonattite, chalcantite) and MgSO_4 - H_2O (epsomite, hexahydrate, kieserite) systems are shown as thin solid lines, in the CoSO_4 - H_2O system are shown as long-dashed lines, in the NiSO_4 - H_2O system are shown as dot-dashed lines, and in the ZnSO_4 - H_2O system are shown as thick solid lines.

only and does not constitute endorsement by the U.S. Government. [PD]

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