

Combined neutron powder and X-ray single-crystal diffraction refinement of the atomic structure and hydrogen bonding of goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)

J. L. ANDERSON^{1,*}, R. C. PETERSON¹ AND I. P. SWAINSON²

¹ Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

² Neutron Program for Materials Research, National Research Laboratory, Chalk River, Ontario, Canada K0J 1J0

ABSTRACT

The atomic structure of synthetic, deuterated goslarite ($\text{ZnSO}_4 \cdot 7\text{D}_2\text{O}$), $a = 11.8176(6)$ Å, $b = 12.0755(7)$ Å, $c = 6.8270(4)$ Å, space group $P2_12_12_1$, $Z = 4$, has been refined in a combined neutron powder diffraction and X-ray single-crystal data refinement to wRp 1.92%, R_p 1.45% and $R(F^2)$ 12.66% for the neutron powder data contribution and $R(F^2)$ 8.72% for the X-ray single-crystal data contribution. Both data sets were necessary to achieve the best overall fit agreement in the Rietveld refinement and reasonable geometry within structural units. The results of this study confirm that the H-bonding scheme for goslarite is the same as that of the other epsomite group minerals. Small but significant variations of the Zn–O bond lengths can be attributed to details of the H bonds to the O atoms of the Zn octahedra. This investigation of the atomic structure and hydrogen bonding of goslarite is groundwork for future studies into phase relationships and the mechanisms of hydration and dehydration in the ZnSO_4 – H_2O system.

KEYWORDS: goslarite, hydrogen bonding, mine waste, sulphate minerals, crystal structure, neutron diffraction.

Introduction

HYDROUS metal sulphates are commonly observed in areas of acid mine drainage. These minerals undergo a cycle of dehydration, hydration, dissolution and recrystallization as the system changes with seasonal variations in temperature and rainfall. As the sulphate minerals precipitate and dissolve in response to changing conditions, they contribute to the retention and release of metals to the environment (Jambor, 1994; Alpers *et al.*, 1994). A thorough understanding of the atomic structure and phase relationships of sulphate minerals is essential to understand properly the mineral stabilities and limits to chemical substitution in these dynamic systems. The focus of this study is the mineral goslarite, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, which has been observed as a

sphalerite oxidation byproduct and is known to dehydrate to bianchite ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$), boyleite ($\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$) and gunningite ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) (Fig. 1). Minerals of the general formula $M\text{SO}_4 \cdot 7\text{H}_2\text{O}$ fall into either the epsomite group ($M = \text{Mg}, \text{Zn}, \text{Ni}$) (Fig. 2) or melanterite ($M = \text{Fe}, \text{Cu}, \text{Co}, \text{Mn}$) (Fig. 3) group. The melanterite structure is known to accommodate significant amounts of Zn (Peterson, 2003a; Jambor *et al.*, 2000) and Mg (Peterson *et al.*, 2003). Although goslarite and epsomite are orthorhombic and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is monoclinic, all three phases dehydrate to isostructural phases (Fig. 4). Ferroxahydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$), a phase that is rarely observed in nature (Vlasov and Kuznetsov, 1962), is isostructural with bianchite ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$) (Spiess and Gruehn, 1979). Rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) is isostructural with boyleite ($\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$) (Walenta, 1978) and szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) is isostructural with gunningite ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) (Hawthorne *et al.*, 1987).

* E-mail: anderson@students.geol.queensu.ca
DOI: 10.1180/0026461056930249

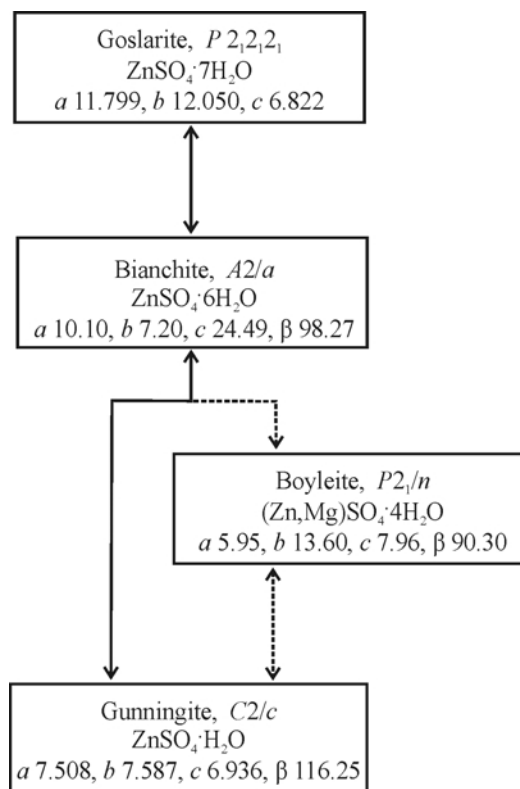


FIG. 1. Schematic diagram showing reversible hydration/dehydration phase changes that occur in the $\text{ZnSO}_4\text{--H}_2\text{O}$ system. Zn end-member boyleite, without metal substitution, does not have a defined stability field in the $\text{ZnSO}_4\text{--H}_2\text{O}$ equilibrium phase diagram (Chou *et al.*, 2002). Unit-cell dimensions are from Gaines *et al.* (1997).

This investigation of the atomic structure and hydrogen bonding of goslarite is the basis for future studies into the different dehydration behaviour and transformation mechanisms in the $\text{ZnSO}_4\text{--H}_2\text{O}$ and $(\text{Fe,Cu})\text{SO}_4\text{--H}_2\text{O}$ systems. The structure and hydrogen bonding of phases in the $(\text{Fe,Cu})\text{SO}_4\text{--H}_2\text{O}$ system have been reported previously (Anderson *et al.*, 2002). Phase-equilibria boundaries between goslarite-bianchite (Chou and Seal, 2001) and melanterite-rozenite (Chou *et al.*, 2002) have been determined experimentally. Work in progress involves X-ray diffraction (XRD) studies of these hydrous phases as they dehydrate and re-hydrate in a relative-humidity and temperature-controlled environment (Peterson, 2003b).

Previous X-ray single-crystal diffraction studies on isostructural minerals include the

structure and calculated H positions of morenosite ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) (Beevers and Schwartz, 1935) and epsomite (Baur, 1964). In the present study both neutron powder and X-ray single-crystal diffraction data were necessary to obtain an accurate refinement of the crystal structure of goslarite. The refinement with X-ray single-crystal diffraction data yielded accurate atomic coordinates for the Zn, S and O atoms. Hydrogen positions by X-ray methods were less accurate than those obtained by neutron diffraction. X-ray scattering occurs primarily by interaction with the electrons that surround an atom and in the case of an atom such as H, the scattering is weak. It became clear that a successful refinement of this complex material would require a combined X-ray and neutron diffraction study.

Diffraction experiments and Rietveld refinement

Synthesis

Colourless goslarite crystals were synthesized at room temperature with 10 g of reagent-grade ZnSO_4 (Fisher Z234Z) and 15 ml of 0.1 M D_2SO_4 prepared from D_2O (AECL ZX098) and D_2SO_4 (C/D/N Isotopes Inc. D-39). The large incoherent scattering cross-section of H causes severe background problems for neutron powder diffraction. The use of D, the coherent scattering of which is 6.67 fm, is used instead. The infrared (IR) spectra of the synthetic sample were obtained using the Nicolet Avatar 320 Fourier Transform Infrared Spectrometer and a Golden Gate diamond ATR. The spectra of the synthesized sample display peaks corresponding to the stretching and bending vibrations of both D_2O and H_2O . The final D:H ratio of the powder was measured quantitatively by including, in the least squares refinement of the diffraction data, refinement of the average overall D site occupancy factor. The solution was heated to 50°C and the reagent was allowed to dissolve completely. The solution was left to cool and the crystals of goslarite grew after some evaporation of the solution at room temperature (22°C). The crystals that precipitated were 2–3 cm long and displayed both a silky fibrous habit of multiple crystals and a long acicular habit of single crystals. Crystals intended for the neutron experiment were powdered in contact with the reaction solution to avoid dehydration. The powder was sealed in a vanadium sample canister

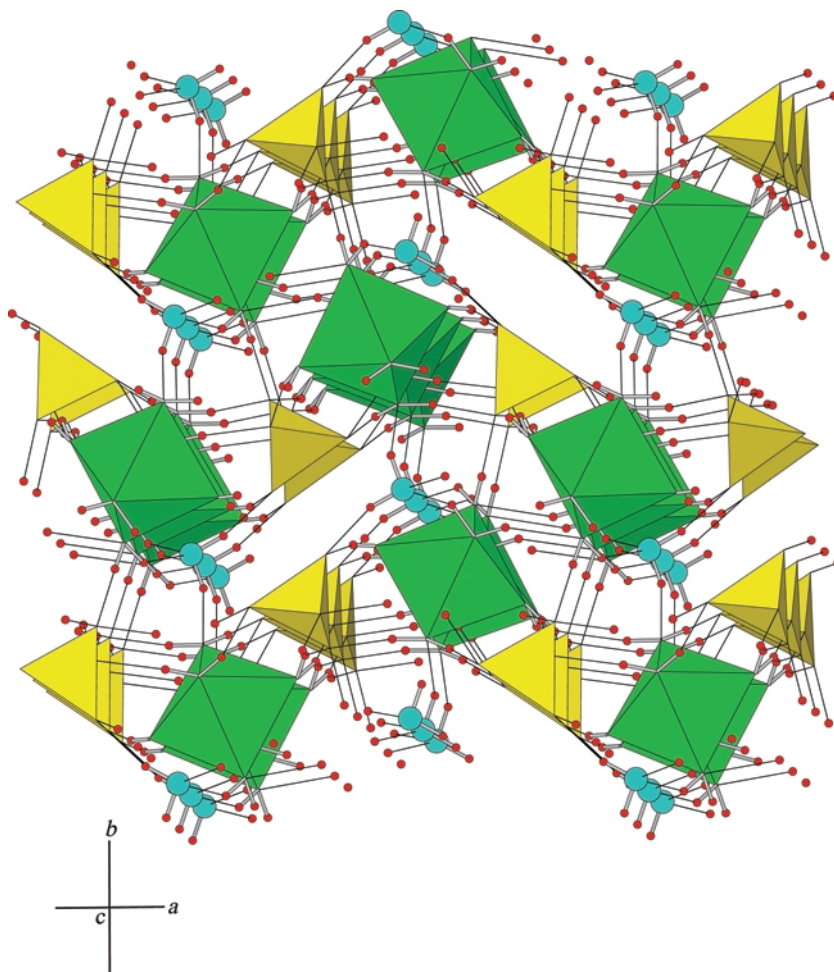


FIG. 2. The atomic structure and topology of goslarite, $P2_12_12_1$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (ATOMS 6.0, Dowty 2003). H atoms are indicated in red. The goslarite structure contains linear arrays of sulphate tetrahedra (yellow) linked via H bonds to linear arrays of Zn octahedra (green) in a corrugated layer parallel to the perfect cleavage (010). The interstitial water molecule, Ow7 (bright blue), bridges these layers. The H-bond network of the goslarite structure produces a void space in the mineral, in the form of a channel parallel to the c axis.

with a soft malleable indium wire to prevent dehydration to one of the lower hydrates of the $\text{ZnSO}_4\text{--H}_2\text{O}$ system during data collection.

At the time of the neutron experiment the entire deuterated sample was powdered, therefore new crystals were required for the X-ray experiment when the neutron refinement failed to converge. Non-deuterated crystals of goslarite were synthesized by the same method as above (0.1 M H_2SO_4 instead of 0.1 M D_2SO_4) for the data collection by X-ray single-crystal diffraction. A fragment of an acicular goslarite crystal with an approximate

radius of 0.15 mm was broken to ~ 0.15 mm long and mounted in a 0.3 mm glass capillary. The capillary was filled with mineral oil (CAS# 8012-95-1) to prevent dehydration of the crystal during data collection.

Experimental setup

Neutron-powder-diffraction data for goslarite were collected at room temperature over a 6 h period on the Dualspec C2 high-resolution constant-wavelength powder diffractometer of

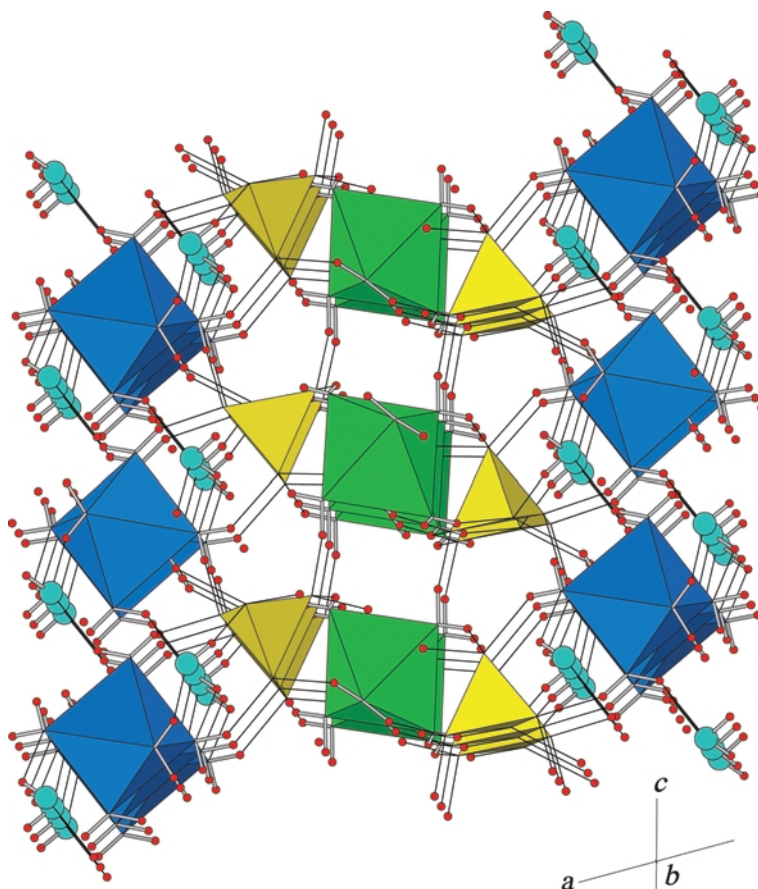


FIG. 3. The structure and topology of zinc-melanterite, $P2_1/c$, $(\text{Zn,Fe,Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (ATOMS 6.0, Dowty, 2003). The colour scheme is the same as that of goslarite (Fig. 2). The $M1$ and $M2$ octahedra are designated as green and blue, respectively. The melanterite structure consists of linearly arranged polyhedra linked via H bonds in a corrugated, repeating layer of $M1\text{-SO}_4\text{-}M2\text{-SO}_4$ polyhedra. This corrugated layer is parallel to the perfect cleavage (001) and unlike the similar (010) layer in goslarite (Fig. 2), the interstitial water molecule, Ow7, is H bonded within the layer. H bonds associated with the Ow7 water molecule link the linear arrays of $M2$ -octahedra to the linear arrays of sulphate tetrahedra.

the NRU reactor at Chalk River Laboratories (Neutron Program for Materials Research (NPMR), Chalk River, Ontario, Canada). As a consequence of the low symmetry and relatively large unit-cell volume of goslarite, $974.24(7) \text{ \AA}^3$, there is a large number of peaks in the diffraction data set. The ability to resolve these peaks approaches the resolution of the instrument and compromises the success of the refinement. A neutron wavelength of $2.3734 \text{ \AA}$ was selected to reduce the overlap problem that would result if a refinement were to be attempted with neutrons of a shorter wavelength. The inclusion of X-ray single-crystal data out to higher $\sin \theta/\lambda$ helps to

compensate for the high $\sin \theta/\lambda$ diffraction data that were sacrificed by using a longer neutron wavelength.

Neutron powder diffraction data were collected over a scattering range of 10 to $90^\circ 2\theta$ with a pyrolytic graphite filter and monochromator of Si (311) crystal at $92.7^\circ 2\theta$. The wavelength of $2.3734 \text{ \AA}$ was calibrated with the external standard NIST Si 640b.

A crystal of goslarite (colourless, prism-shaped, size $0.3 \times 0.04 \times 0.04 \text{ mm}$) sealed with mineral oil in a glass capillary was mounted for X-ray single-crystal diffraction. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffract-

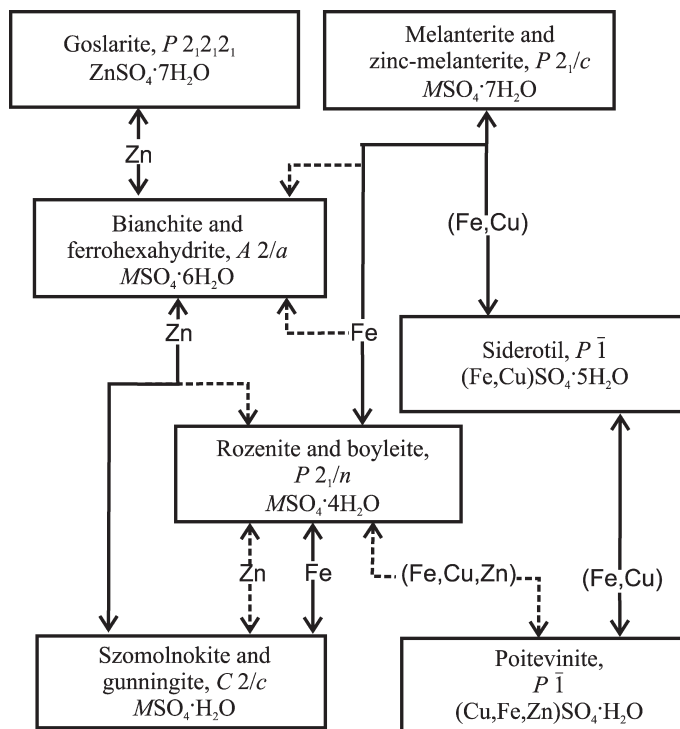


FIG. 4. Hydration/dehydration behaviour in the $\text{ZnSO}_4\text{-H}_2\text{O}$ and $(\text{Fe,Cu})\text{SO}_4\text{-H}_2\text{O}$ systems. Solid arrows represent well documented phase changes and dashed lines indicate phase changes that may only occur in metal-substituted material or produce metastable phases.

ometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), operating at 50 kV and 35 mA at 25°C over a 2θ range of 4.86 to ~ 56.50 (Department of Chemistry, Queen's University). No significant decay of standard intensity was observed during the data collection.

Data were processed using the Bruker AXS Windows NT software package (version 5.10). The single-crystal unit-cell parameters were obtained using *SMART* software and refined with *SAINT-Plus* software, using all of the observed reflections. The raw intensity data were converted (including corrections for background, Lorentz and polarization effects) to structure amplitudes and their esd values using the program *SAINT-Plus*. Empirical absorption corrections were applied using the program *SADABS*.

The X-ray single-crystal diffraction data set includes 6891 reflections sorted to 2269 unique reflections with an agreement factor for merging of symmetry equivalents of $R_{\text{(int)}} = 3.29\%$.

Refinement of structure

The structure and D/H positions of goslarite were refined by least-squares refinement of single-crystal data and by Rietveld analysis of powder diffraction data using *General Structure Analysis Software* (GSAS) (Larson and Von Dreele, 1994). In the first attempt to find all 14 D positions for goslarite, from the neutron data, unit-cell parameters and Zn, S and O positions were refined. The intention was to use this model to calculate a Fourier difference map and find all D positions. However, the refinement failed to converge when D was omitted from the model. In terms of coherent scattering cross sections, D contributes 56% of the neutron scattering power of goslarite and this exclusion represents a significant omission. Consequently, the starting parameters used were the Zn, S and O positions determined by the XRD experiment and the H positions reported for epsomite (Baur, 1964).

The refinement was performed in three steps in order to achieve convergence. In the first stage of

the refinement the unit-cell dimensions, atomic coordinates and hydrogen positions for goslarite based on the X-ray data were used as the starting model and only the neutron-diffraction data set was refined. Bond lengths were restrained for the sulphate tetrahedron (S—O; 1.47 ± 0.03 Å) and water molecules (H—Ow; 0.96 ± 0.05 Å) based upon a previous neutron diffraction study of another hydrated sulphate mineral starkeyite $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (Baur, 1962). These restraints were heavily weighted for the initial stages of the refinement. Each of the following was allowed to refine in the following order: scale factor, background, zero position, lattice parameters, Gaussian peak shape (Gw) and atomic coordinates. As the D:H ratio was unknown its value was determined by refinement of the effective scattering length of the D site. *GSAS* does not allow refinement of the atomic scattering length directly, and so in order to minimize the number of constraints that would be necessary to do this, we refined the average site occupancy instead. The site occupancy can be related to the D:H ratio by multiplying it by the nominal scattering length to determine the effective scattering length. Site occupancies and isotropic thermal parameters for D sites were refined and constrained to be equal.

In the second stage of the refinement the structural model was taken from the preliminary neutron powder refinement of the first stage and only the X-ray single-crystal data set was included. The only bond-length restraint that was necessary was 0.96 ± 0.05 Å for H—O distances. The restraints were heavily weighted in the beginning of the refinement and progressively made smaller as the model improved. The scale, atomic coordinates and isotropic thermal parameters of the sulphate tetrahedron and Zn octahedron were refined. The H positions were not allowed to refine during this stage of the refinement. Although the H positions were not refined it was necessary to have the H—O restraints in the model at this stage of the refinement. The restraint on H—O bond length limits the displacement of the O atoms and keeps the refinement from diverging.

In the third stage of the refinement the two data sets were combined. The neutron powder diffraction data was included with the X-ray single-crystal data in the refinement. The scale factor, background, zero position, lattice parameters and Gaussian peak shape (Gw) relating to the powder histogram were refined. All atomic coordinates, isotropic thermal parameters and constrained D

site occupancies were allowed to refine. The weight of bond-length restraints was successively lowered and the final contribution to the refinement from bond-length restraints was 1.52%, which was calculated using the formula:

$$[\chi^2_{(\text{res})}/\#\text{Obs}_{(\text{res})}]/[\chi^2_{(\text{tot})}/\#\text{Obs}_{(\text{tot})}]$$

The final refined site occupancy for all D positions is 0.71(2), assuming there is only D in the site. Assuming this site is fully occupied with a D/H mixture and given the coherent neutron scattering lengths of D (6.67 fm) and H (−3.74 fm) (Lander, 1992), the fractional occupancy may be recalculated to give $\text{D}_{0.82}\text{H}_{0.18}$ for all proton positions. This ratio was constrained to be equal for all sites.

The final least-squares cycle yielded a final *wRp* of 1.92%, *Rp* 1.45% and $R(F^2)$ of 12.66% for the neutron powder histogram and an $R(F^2)$ of 8.72% for the single-crystal data (Table 1, Fig. 6). The atomic coordinates as determined by this method are listed in Table 2.

Discussion

Goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), a member of the epsomite group, is orthorhombic and crystallizes in the space group $P2_12_12_1$, with a 11.8176(6) Å, b 12.0755(7) Å, c 6.8270(4) Å, $Z = 4$. Atomic coordinates are given in Table 2. From earlier work (Beevers and Schwartz, 1935; Baur, 1964) we know that minerals of the epsomite group ($M = \text{Mg}, \text{Ni}, \text{Zn}$) consist of a sulphate tetrahedron, six water molecules forming octahedral coordination about the M atom and one interstitial water molecule that is not coordinated to the M atom. Polyhedra of the goslarite structure are arranged in linear arrays of sulphate tetrahedra linked via H bonds to linear arrays of Zn octahedra in a corrugated layer parallel to the perfect cleavage (010). The interstitial water molecule, Ow7, bridges these layers (Fig. 2).

Cell parameters obtained from the single-crystal and combined studies are significantly different: $\Delta a = 0.09$ Å, $\Delta b = 0.1$ Å, $\Delta c = 0.05$ Å, $\Delta V = 23.4$ Å³ (Table 1). These differences are reflected in the different bond lengths obtained for the two datasets, which can amount to 0.03–0.06 Å for the Zn—O bonds (Table 3). This difference results from the uncertainty of the neutron wavelength calibration. The difference in size of the unit cell determined based on the neutron and XRD experiments may also be due in part to the difference in deuteration of the

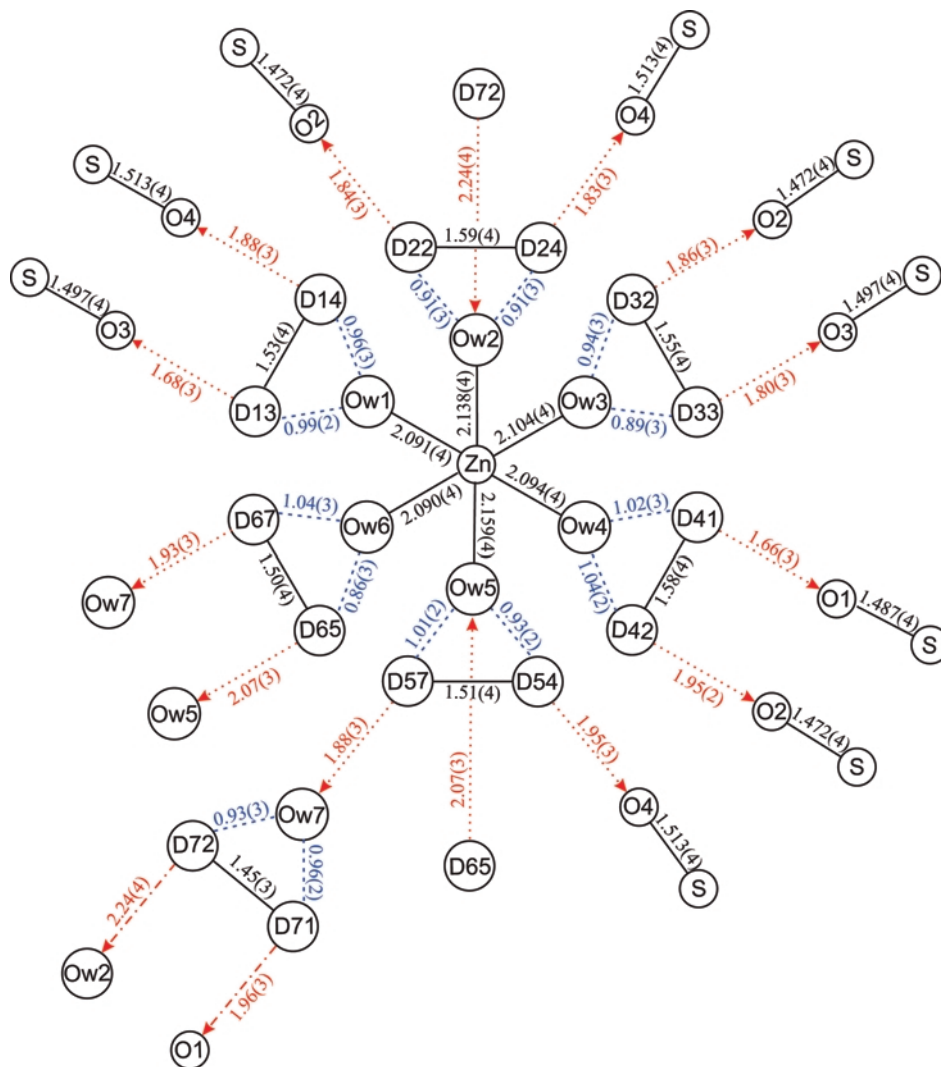


FIG. 5. Bonding scheme for goslarite as determined by the combined X-ray single-crystal and neutron powder diffraction refinement. O–H distances of the water molecules are indicated by the dashed blue lines. Dotted red lines represent H bonds. This diagram is not to scale and only represents the atomic linkages present in the structure. The apical water molecules Ow2 and Ow5 are the only two water molecules of the Zn octahedra to receive additional H bonds from neighbouring H atoms. The Zn–Ow2 and Zn–Ow5 bonds lengthen to compensate for the reduced bond valence due to these additional H-bond interactions.

materials studied. A deuterated sample was powdered for the neutron experiment and a new non-deuterated single crystal was prepared for the XRD experiment, at a later date.

In the absence of other effects, the geometry of the Zn octahedron is expected to be ideal, as the electronic configuration of Zn ($d^{10}s^2$) is spherical and will not contribute to the distortion of the site.

However, the Zn octahedron of goslarite deviates from ideal octahedral symmetry. Octahedral distortion is common among hydrated sulphates and is attributed to neighbouring electrostatic effects communicated to the octahedra via H bonds (Baur, 1964; Peterson, 2003a). A Zn–O bond length of 2.11 Å is expected based on a mean of 103 Zn–O bond lengths from nine Zn–S-

TABLE 1. Crystallographic data and refinement results for goslarite by X-ray single crystal diffraction and the combined neutron powder-X-ray single-crystal refinement. Space group $P2_12_12_1$ and $Z = 4$.

Single crystal X-ray		Combined refinement	
a (Å)	11.728(4)	a (Å)	11.8176(6)
b (Å)	11.973(4)	b (Å)	12.0755(7)
c (Å)	6.772(2)	c (Å)	6.8270(4)
V (Å ³)	950.8(8)	V (Å ³)	974.24(7)
Radiation	Mo- $K\alpha$	Neutron wavelength	2.3734 Å
2θ range	4.86–56.5	2θ range	10–90
Total reflections	6891	$wRp_{(\text{neutron})}$ (%)	1.92
Unique reflections	2269	$Rp_{(\text{neutron})}$ (%)	1.45
$R_{(\text{int})}$ (%)	3.29	$R(F^2)_{(\text{neutron})}$ (%)	12.66
		$R(F^2)_{(\text{X-ray})}$ (%)	8.72
		Restraint contribution (%)	1.52

TABLE 2. Atomic coordinates ($\times 10^4$ for all non-H positions; $\times 10^3$ for all H positions) and equivalent isotropic-displacement parameters (Å² $\times 10^2$) for goslarite (ZnSO₄·7H₂O) by X-ray single-crystal diffraction and the combined neutron powder-X-ray single crystal refinement.

	X-ray single-crystal refinement				Combined refinement			
	x	y	z	U_{iso}	x	y	z	U_{iso}
Zn	4223(1)	1061(1)	399(1)	2.4(1)	4223(1)	1060(1)	0402(1)	1.9(2)
S	7266(1)	1830(1)	4908(1)	2.3(1)	7271(1)	1829(1)	4908(2)	2.0(1)
O1	6851(2)	0753(2)	4263(3)	4.2(1)	6844(4)	0734(3)	4241(5)	3.6(1)
O2	8511(1)	1860(2)	4829(3)	3.3(1)	8515(3)	1859(3)	4817(5)	2.9(1)
O3	6886(2)	2047(2)	6924(3)	3.7(1)	6900(4)	2070(4)	6960(6)	3.4(1)
O4	6803(2)	2713(2)	3631(3)	3.1(1)	6794(3)	2725(3)	3597(5)	2.3(1)
Ow1	2608(2)	1707(2)	0047(3)	3.3(1)	2609(3)	1739(3)	0027(5)	2.8(1)
Ow2	4712(2)	2515(2)	1939(3)	2.6(1)	4718(3)	2513(3)	1973(5)	2.0(1)
Ow3	4682(2)	1726(2)	7731(3)	3.4(1)	4690(3)	1736(3)	7681(6)	2.7(1)
Ow4	5853(2)	0488(2)	0737(3)	3.9(1)	5879(4)	0473(3)	0740(5)	3.1(1)
Ow5	3730(2)	9600(2)	8909(4)	3.2(1)	3742(3)	9564(3)	8883(5)	2.3(1)
Ow6	3642(3)	0360(3)	2968(4)	4.1(1)	3632(3)	0352(3)	3003(5)	3.1(1)
Ow7	5097(2)	9376(2)	5657(4)	3.8(1)	4890(3)	4389(3)	9346(6)	3.5(1)
H13	246(3)	229(3)	085(6)	07(1)	224(3)	211(3)	115(5)	10.8(8)
H14	246(3)	193(3)	908(5)	04(1)	241(3)	219(2)	893(4)	10.8(8)
H22	412(3)	276(3)	284(5)	07(1)	420(3)	274(2)	287(5)	10.8(8)
H24	536(3)	250(3)	246(5)	06(1)	547(3)	251(2)	224(6)	10.8(8)
H32	436(3)	214(3)	710(5)	05(1)	417(3)	212(3)	688(5)	10.8(8)
H33	542(4)	195(3)	738(5)	08(2)	542(2)	188(3)	746(6)	10.8(8)
H41	629(4)	068(4)	197(7)	13(2)	631(3)	048(3)	203(4)	10.8(8)
H42	615(3)	004(3)	026(5)	06(1)	611(3)	030(2)	021(5)	10.8(8)
H54	369(3)	903(3)	962(5)	07(1)	356(2)	899(3)	972(6)	10.8(8)
H57	415(3)	945(3)	824(5)	04(1)	413(3)	917(3)	777(4)	10.8(8)
H65	310(3)	035(3)	314(5)	04(1)	295(3)	017(3)	328(4)	10.8(8)
H67	404(4)	995(3)	378(6)	10(2)	411(3)	968(2)	349(4)	10.8(8)
H71	568(3)	975(3)	560(5)	06(1)	582(2)	977(2)	574(5)	10.8(8)
H72	518(3)	874(3)	515(6)	08(2)	537(3)	866(2)	560(6)	10.8(8)

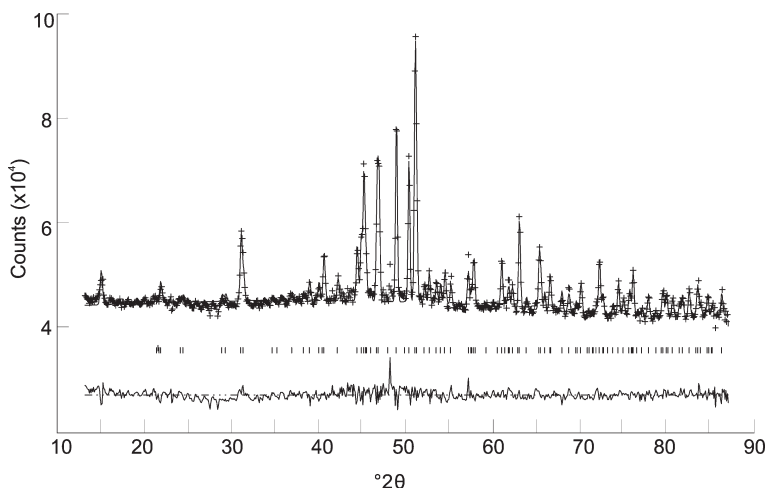


FIG. 6. The observed and difference profiles from the combined neutron powder-X-ray single-crystal refinement of the crystal structure of goslarite.

O-H bearing phases found in the inorganic crystal structure database (Bear *et al.*, 1986; Black *et al.*, 1975; Iitaka *et al.*, 1962; Kemnitz *et al.*, 1996; Nyberg, 1973; Quinones and Baggio, 1972; Spiess and Gruehn, 1979; Troyanov and Simonov, 1989; Wildner and Giester, 1991). Octahedral Zn–Ow bonds in goslarite range from 2.090(4) Å to 2.159(4) Å with a mean value of 2.113(4) Å (Table 3). The mean bond length of the four equatorial bonds is 2.095 Å, slightly less than the mean value calculated from the literature. The apical bonds Zn–Ow2 [2.138(4) Å] and Zn–Ow5 [2.159(4) Å] are the longest bonds of the Zn octahedron. The Ow2 and Ow5 water molecules are the only bonds of the Zn octahedron to receive additional H bonds from neighbouring H atoms. The Zn–Ow2 and Zn–Ow5 bonds lengthen to compensate for the reduced bond valence due to these additional hydrogen-bonded interactions. A schematic diagram of the bonding network for goslarite is presented in Fig. 5.

The geometry of water molecules within the goslarite structure (Table 3) is comparable to that observed in other crystalline hydrates (Ferraris and Marchini-Angelo, 1972) (Fig. 7). The mean H-bond length in goslarite is 1.90 Å. The longest H bonds of the goslarite structure (>1.90 Å) are those in which the H-bond acceptor atom is an O atom from a neighbouring water molecule. The shortest H bonds of the structure (<1.90 Å) have a sulphate O as the acceptor atom. There are a few exceptions to this observation. The first exception is the H71...O1 bond at 1.96(3) Å; this bond is

longer than the mean value of 1.90 Å and falls in the range of H bonds the O acceptor atom of which belongs to a water molecule; the acceptor atom in this case is an O of the sulphate group. H71 belongs to the interstitial water molecule; it is reasonable to expect the only water molecule not coordinated to the Zn atom to be the most loosely linked in the three dimensional H-bond network and, therefore, to be associated with long, weak H bonds. The only other exceptions to this classification of H bonds are the H42...O2 and H54...O4 bonds. These are the only two H bonds with acceptor O atoms from the sulphate group with bond lengths >1.90 Å (bond lengths are 1.95(2) and 1.95(3) Å, respectively). Both of these bonds and the H65...Ow5 and H72...Ow2 H bonds are broken as the mineral cleaves along (010), which is consistent with the long, weak H bonds observed across the perfect (010) cleavage.

The sulphate tetrahedron in hydrated sulphate minerals exhibits little polyhedral distortion. Any variations in the geometry of a sulphate tetrahedron may be related to the electrostatic sums received by the coordinated O atoms. The mean S–O bond length of goslarite falls within the range of expected S–O bond lengths (Hawthorne *et al.*, 2000).

Metal substitution in goslarite

The ability of a structure to incorporate different metals is related to its ability to distort the octahedra without disrupting the polyhedral connectivity. Minerals associated with mine-

TABLE 3. Selected bond lengths (Å) and angles (°) for goslarite by X-ray single-crystal diffraction and the combined neutron powder-X-ray single-crystal refinement.

	X-ray	Combined		X-ray	Combined
Zn—Ow1	2.059(2)	2.091(4)	S—O1	1.446(2)	1.487(4)
Zn—Ow2	2.109(2)	2.138(4)	S—O2	1.460(2)	1.472(4)
Zn—Ow3	2.047(2)	2.104(4)	S—O3	1.459(2)	1.497(4)
Zn—Ow4	2.045(2)	2.094(4)	S—O4	1.469(2)	1.513(4)
Zn—Ow5	2.100(2)	2.159(4)	<S—O>	1.458	1.492
Zn—Ow6	2.048(3)	2.090(4)			
<Zn—Ow>	2.07	2.11			
Ow1—Zn—Ow2	89.8(1)	89.4(2)	O1—S—O2	110.3(1)	110.4(2)
Ow1—Zn—Ow3	89.7(1)	88.8(2)	O1—S—O3	109.8(1)	111.1(2)
Ow1—Zn—Ow5	90.3(1)	91.7(2)	O1—S—O4	109.8(1)	109.2(2)
Ow1—Zn—Ow6	86.9(1)	87.7(2)	O2—S—O3	109.6(1)	109.1(2)
Ow2—Zn—Ow3	92.5(1)	93.0(2)	O2—S—O4	109.3(1)	109.2(2)
Ow2—Zn—Ow4	88.1(1)	88.1(1)	O3—S—O4	108.0(1)	107.8(2)
Ow2—Zn—Ow6	90.5(1)	90.0(2)	<O—S—O>	109.5	109.5
Ow3—Zn—Ow4	89.0(1)	89.0(2)			
Ow3—Zn—Ow5	88.4(1)	88.2(2)			
Ow4—Zn—Ow5	91.8(1)	90.9(1)			
Ow4—Zn—Ow6	94.5(1)	94.6(2)			
Ow5—Zn—Ow6	88.6(1)	88.8(2)			
<O—Zn—O>	90.0	90.0			

Single crystal X-ray	H—Ow	Ow—H	<i>O</i> …H	H… <i>O</i>	H—H	H—O—H
O3…H13—Ow1—H14…O4	0.90(4)	0.73(3)	1.84(4)	2.04(3)	1.27(5)	102(4)
O2…H22—Ow2—H24…O4	0.84(3)	0.97(4)	1.89(3)	1.79(3)	1.51(5)	113(4)
O2…H32—Ow3—H33…O3	0.94(4)	0.84(3)	2.03(3)	3.05(4)	1.28(6)	97(4)
O1…H41—Ow4—H42…O2	1.01(5)	0.72(3)	1.69(5)	2.33(3)	1.40(6)	107(8)
O4…H54—Ow5—H57…Ow7	0.83(4)	0.69(3)	2.06(4)	2.07(3)	1.19(5)	102(5)
Ow5…H65—Ow6—H67…Ow7	0.65(3)	0.87(4)	2.21(3)	1.90(4)	1.28(6)	114(1)
O1…H71—Ow7—H72…O2	0.82(4)	0.84(3)	2.04(4)	2.05(4)	1.38(5)	112(4)
<O…H—Ow—H…O>		0.83		2.07	1.33	107

Combined refinement	D—Ow	Ow—D	<i>O</i> …D	D… <i>O</i>	D—D	D—O—D
O3…D13—Ow1—D14…O4	0.99(2)	0.96(3)	1.68(3)	1.88(3)	1.53(4)	104(3)
O2…D22—Ow2—D24…O4	0.91(3)	0.91(3)	1.84(3)	1.83(3)	1.59(4)	122(4)
O2…D32—Ow3—D33…O3	0.94(3)	0.89(3)	1.86(3)	1.80(3)	1.55(4)	116(3)
O1…D41—Ow4—D42…O2	1.02(3)	1.04(2)	1.66(3)	1.95(2)	1.58(4)	100(3)
O4…D54—Ow5—D57…O7	0.93(2)	1.01(2)	1.95(3)	1.88(3)	1.51(4)	102(3)
Ow5…D65—Ow6—D67…Ow7	0.86(3)	1.04(3)	2.07(3)	1.93(3)	1.50(4)	104(2)
O1…D71—Ow7—D72…Ow2	0.96(2)	0.93(3)	1.96(3)	2.24(4)	1.45(3)	100(2)
<O…D—Ow—D…O>		0.96		1.90	1.53	107

waste occurrences, where solutions are rich in metals, and metal-bearing polyhedra are connected by weak H bonds, may be expected to substitute considerable amounts of different metals. However this is not the case with epsomite group minerals.

The epsomite structure, which is isostructural with goslarite, is intolerant of metal substitution. From synthetic studies of the $\text{MgSO}_4\text{--CuSO}_4\text{--H}_2\text{O}$ system at 30°C (Minguzzi, 1948), epsomite, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ is known to substitute up to 4.7 mol.% Cu. Solids containing >4.7 mol.% Cu

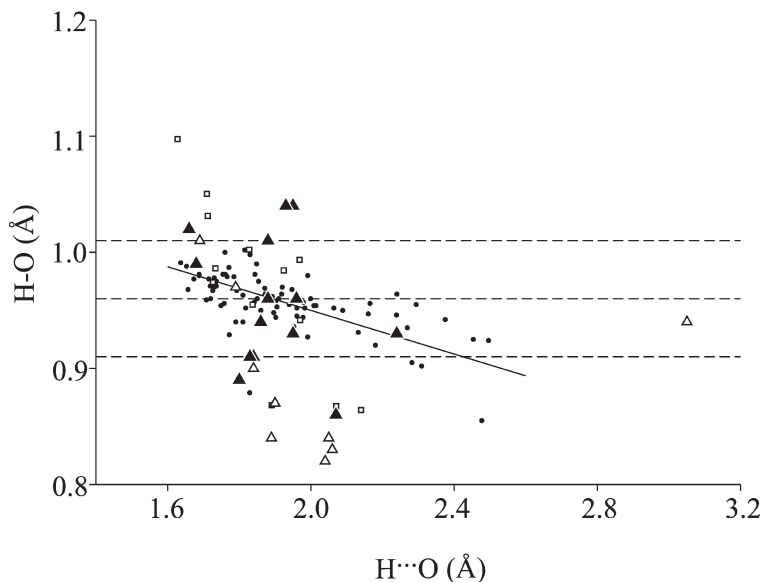


FIG. 7. Plot of water molecule H–O distances and H-bond distances. Small open circles and the least-squares line represent a compilation of 41 hydrated crystal structures (Ferraris and Marchini-Angelo, 1972). The results of the goslarite combined neutron powder and X-ray single-crystal refinement are plotted here as solid triangles. Dashed lines show the 0.96 ± 0.05 restraint values of the refinement. The results of the combined refinement fall much closer to the observed trends for hydrated structures than those determined by X-ray only, plotted here as open triangles. For comparison, data for the isostructural mineral epsomite (Baur, 1964) are plotted as open squares.

are mixtures of crystals with the orthorhombic epsomite structure and the monoclinic melanterite structure. The melanterite structure, which also contains metal-bearing polyhedra connected by weak H bonds, is able to substitute 28.3 to 38.9 mol.% Cu for Mg (Minguzzi, 1948).

Recently, a new (Mg,Cu)-sulphate heptahydrate mineral and member of the melanterite group, alpersite $(\text{Mg,Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$, has been recognized (Peterson *et al.*, 2003*a,b*). Considering the isostructural nature of epsomite and goslarite, it is reasonable to expect that the same phenomenon occurs in significantly Cu-substituted goslarite. The resulting phase would be the monoclinic (Zn,Cu)-sulphate heptahydrate and, indeed, this phase exists in nature as Zn-melanterite $((\text{Zn,Fe,Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O})$ (Tiegen and Lin, 1995).

A simple experiment was conducted to test the amount of Cu and Fe substitution possible into the goslarite structure. A series of beakers containing 0.1 M H_2SO_4 saturated solutions and a range of $\text{ZnSO}_4 \cdot \text{CuSO}_4$ and $\text{ZnSO}_4 \cdot \text{FeSO}_4$ mixtures between 1:0 and 1:1 were left out at room temperature (22°C) overnight to precipitate. The resulting precipitates were powdered and X-rayed

to identify mineral phases. Solutions with <0.005 mol.% Fe or Cu precipitated a mineral with the goslarite structure whereas solutions of 0.01 mol.% Fe or Cu, or greater, yielded coexisting epsomite and melanterite group phases. Due to the fine fibrous habit of these precipitates it was not possible to separate the two phases and partitioning of the metals between the reaction solution and the solid phase was not measured in the course of this experiment. The outcome of this experiment suggests metal substitution in the goslarite is very limited. Even small amounts of substitution in the octahedral sites cause distortions which make this orthorhombic mineral unstable relative to the lower symmetry, monoclinic structure of melanterite.

Dehydration behaviour

Metal substitution in the mineral structure will affect the integrity of the H-bonding network and result in changes to the dehydration path of the mineral. This phenomenon is observed in the dehydration behaviour of melanterite and Cu-substituted melanterite (Anderson *et al.*, 2002). Melanterite $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$ is known to dehydrate

to rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and Cu-substituted melanterite to siderotil ($\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$). Boyleite, a phase isostructural with rozenite and a dehydration product of goslarite, does not have a field of stability in the $\text{ZnSO}_4\text{--H}_2\text{O}$ equilibrium phase diagram (Chou and Seal, 2001; Walenta, 1978).

It is reasonable to expect H bonds interacting with the interstitial water molecule to be the longest, weakest H bonds in the structure and the interstitial water is most likely to be the first water molecule to be lost during dehydration. The long H bonds observed in this study associated with the interstitial water molecule support this reasoning. A closer look at the topology of goslarite and bianchite ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$) offers no evidence to the contrary, though at present there is no direct way to observe which of the seven water molecules is lost during dehydration. Ferroxahydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$) is isostructural with bianchite (Vlasov and Kuznetsov, 1962), although the field of stability for ferroxahydrate is not present in the $\text{FeSO}_4\text{--H}_2\text{O}$ equilibrium phase diagram (Chou *et al.*, 2002). Bianchite has a well documented stability field in the $\text{ZnSO}_4\text{--H}_2\text{O}$ phase diagram (Chou and Seal, 2001) and is frequently reported in the literature associated with mine waste (Jambor *et al.*, 2000).

While some sulphate minerals incorporate a wide variety of metals into their structures, others are quite intolerant of metal substitution. An understanding of why this is so and the limits of metal substitution within phases, will help us further understand how metals are retained and released from mine waste.

Acknowledgements

We gratefully acknowledge Alan Grant and Ruiyao Wang of Queen's University and the research staff at Chalk River Laboratories (NPMR) for their generous support on this project. We thank the editor and anonymous referee for constructive comments that led to significant improvements in the manuscript. An NSERC discovery grant to RCP funded the research.

References

- Alpers, C.N., Nordstrom, D.K. and Thompson J.M. (1994) Seasonal variations of Zn/Cu ratios in acid mine water from Iron Mountain, California. Pp. 247–270 in: *Environmental Geochemistry of Sulfide*

Mine-Wastes (J.L. Jambor and D.W. Blowes, editors). Short Course Handbook 22, Mineralogical Association of Canada, Ottawa, Ontario.

- Anderson, J.L., Peterson, R.C. and Swainson, I.P. (2002) A neutron diffraction study of the hydrogen bonding in Cu substituted melanterite. *18th general meeting of the IMA*. Programme with abstracts, September 2002, Edinburgh.
- Baur, W.H. (1962) Zur Kristallchemie der Salzhydrate. Die Kristallstrukturen von $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (Leonhardt) und $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (Rozenit). *Acta Crystallographica*, **15**, 815–826.
- Baur, W.H. (1964) On the crystal chemistry of salt hydrates. IV. The refinement of the crystal structure of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite). *Acta Crystallographica*, **17**, 1361–1369.
- Bear, I.J., Grey, I.E., Madsen, I.C., Newnham, I.E. and Rogers, L.J. (1986) Structures of the basic zinc sulfates $3\text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4 \cdot m\text{H}_2\text{O}$, $m=3$ and 5. *Acta Crystallographica*, **42**, 32–39.
- Beevers, C.A. and Schwartz, C.M. (1935) The crystal structure of nickel sulphate heptahydrate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. *Zeitschrift für Kristallographie*, **91**, 157–169.
- Black, W.H., Griffith, E.A.H. and Roberston, B.E. (1975) $\text{MS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ ($M=\text{Mg}, \text{Ni}, \text{Zn}$). *Acta Crystallographica*, **31**, 615–618.
- Bruker (1999) *Crystal Structure Analysis Package*, Version 5.10 (SMART NT (Version 5.053), SAINT-Plus (Version 6.01), SHELXTL (Version 5.1)); Bruker AXS Inc., Madison, Wisconsin.
- Chou, I.M. and Seal, R.R., II (2001) Determination of goslarite-bianchite equilibria by the humidity buffer technique at 0.1. *Eleventh Annual V.M. Goldschmidt Conference*.
- Chou, I.M., Seal, R.R., II and Hemmingway, B.S. (2002) Determination of melanterite-rozenite and chalcantite-bonattite equilibria by humidity measurements at 0.1 MPa. *American Mineralogist*, **87**, 108–114.
- Dowty, E. (2003) *ATOMS* version 6.0. Shape Software, 521 hidden Valley Road, Kingsport, Tennessee 37663, USA. <http://www.shapesoftware.com/>
- Ferraris, G. and Marchini-Angelo, M. (1972) Survey of the geometry and environment of water molecules in crystalline hydrates studied by neutron diffraction. *Acta crystallographica*, **28**, 3572–3583.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B. and Rosenzweig, A. (1997) *Dana's New Mineralogy* (eighth edition). John Wiley and Sons, New York.
- Hawthorne, F.C., Groat, L.A., Raudsepp, M. and Ercit, T.S. (1987) Kieserite, $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})$, a titanite group mineral. *Neues Jahrbuch für Mineralogie Abhandlungen*, **157**, 121–132.
- Hawthorne, F.C., Krivovichev, S.V. and Burns, P.C. (2000) The crystal chemistry of sulfate minerals. Pp.

- 1–112 in: *Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, **40**, Mineralogical Society of America, Washington, D.C.
- Iitaka, V.Y., Oswald, H.R. and Locchi, S. (1962) Die kristallstruktur von zink-hydroxidsulfat I, $\text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4$. *Acta Crystallographica*, **15**, 559–564.
- Jambor, J.L. (1994) Mineralogy of sulfide-rich tailings and their oxidation products. Pp. 59–102 in: *Environmental Geochemistry of Sulfide Mine-Wastes* (J.L. Jambor and D.W. Blowes, editors). Short Course Handbook, **22**, The Mineralogical Association of Canada, Ottawa, Ontario.
- Jambor, J.L., Nordstrom, D.K. and Alpers, C.N. (2000) Metal-sulfate salts from sulfide mineral oxidation. Pp. 303–350 in: *Sulfate minerals – Crystallography, Geochemistry, and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, **40**, The Mineralogical Society of America, and the Geochemical Society, Washington, D.C.
- Kemnitz, E., Werner, C., Stiewe, A., Worzala, H. and Troyanov, S.I. (1996) Synthese und struktur von $\text{Zn}(\text{HSO}_4)_2$ (H_2SO_4)₂ und $\text{Cd}(\text{HSO}_4)_2$. *Zeitschrift für Naturforschung, Teil B. Anorganisch Chemie, Organische Chemie*, **51**, 14–18.
- Lander, G. (editor) (1992) Neutron scattering lengths and cross sections. *Neutron News*, **3**(3) 29–37.
- Larson, A.C. and von Dreele, R.B. (1994) *General Structure Analysis System (GSAS)*, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Minguzzi, C. (1948) Contributi allo studio della geochimica del rame. L'isoterma a 30 deg. C del sistema $\text{CuSO}_4\text{--MgSO}_4\text{--H}_2\text{O}$. *Atti. Della Società Toscana di Scienze Naturali Residente in Pisa Memorie*, Serie A **55**, 26–48.
- Nyberg, B. (1973) The crystal structure of $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$. *Acta Chemica Scandinavica*, **27**, 1541–1551.
- Peterson, R.C. (2003a) The relationship between Cu content and distortion in the atomic structure of melanterite from the Richmond mine, Iron Mountain, California. *The Canadian Mineralogist*, **41**, 937–949.
- Peterson, R.C. (2003b) Dehydration of minerals in mine waste. The relationship among melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, siderotil $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, and rozenite $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$. *Geological Association of Canada – Mineralogical Association of Canada*. Program with Abstracts, **28**.
- Peterson, R.C., Hammarstrom, J.M. and Seal, R.R. II (2005) Alpersite (Mg,Cu) $\text{SO}_4 \cdot 7\text{H}_2\text{O}$ a new mineral of the melanterite group. Approved by the International Mineralogical Association commission on New Minerals as a new mineral species (#2003–040). *American Mineralogist* (in press).
- Quinones, H. and Baggio, S. (1972) The crystal structure of zinc sulphite dihydrate. *Journal of Inorganic and Nuclear Chemistry* **34**, 2153–2159.
- Spiess, M. and Gruehn, R. (1979) Zur thermischen Dehydratisierung des $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ und zum Hochtemperaturverhalten von wasserfreiem ZnSO_4 . *Zeitschrift für Anorganische und Allgemeine Chemie* **456**, 222–240.
- Tiegen, L. and Lin, Y. (1995) Discovery and investigation of zinc-melanterite in nature. *Kuang Wu Xue Bao (Acta Mineralogica Sinica)* **15**, 286–290.
- Troyanov, S.I. and Simonov, M.A. (1989) Crystal structure of $\text{Zn}(\text{H}_2\text{SO}_4)_2$. *Soviet Physics, Crystallography*, **34**, 233–234.
- Vlasov, V.V. and Kuznetsov, A.V. (1962) Melanterite and the products of its alteration. *Zapiski Vsesoiuznoe Mineralogicheskoe Obshchestvo*, **91**, 490–492.
- Walenta, K. (1978) Boyleite, a new sulfate mineral from Kropbach, southern Black Forest. *Chemie de Erde*, **37**, 73–79.
- Wildner, M. and Giester, G. (1991) The crystal structures of kieserite-type compounds. I. Crystal structures of $\text{Me(II)SO}_4 \cdot \text{H}_2\text{O}$ (Me = Mn, Fe, Co, Ni, Zn). *Neues Jahrbuch für Mineralogie, Monatshefte*, **7**, 296–306.

[Manuscript received 21 June 2004;
revised 28 February 2005]

