

## THE ATOMIC STRUCTURE OF SIDEROTIL, (Fe,Cu)SO<sub>4</sub>•5H<sub>2</sub>O

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### ABSTRACT

Light-blue crystals of siderotil from the B drift in the Richmond Cu–Zn–pyrite mine, Iron Mountain, California, occur with coquimbite, römerite, halotrichite, copiapite and voltaite. The average result of electron-microprobe analyses of small crystals gave (Fe<sub>0.55</sub>Cu<sub>0.28</sub>Mg<sub>0.09</sub>Zn<sub>0.08</sub>)<sub>Σ1</sub>SO<sub>4</sub>•5H<sub>2</sub>O as the empirical formula. The atomic structure of siderotil has been determined by least-squares refinement of single-crystal X-ray-diffraction data; *wR* = 5.7% for 1633 reflections, *P* $\bar{1}$ , *a* 6.292(5), *b* 10.632(8), *c* 6.072(5) Å,  $\alpha$  82.63(1),  $\beta$  110.02(1),  $\gamma$  105.19(1)°. Siderotil is isostructural with chalcantite CuSO<sub>4</sub>•5H<sub>2</sub>O. Bond-lengths and angles are similar to those of chalcantite except that the long apical bonds of the octahedral sites in chalcantite, which are the result of a square-planar distortion by Cu, are considerably shorter in siderotil because of the dominance of Fe at that site. The relative amount of Cu at the *M1* and *M2* sites can be inferred from the octahedral distortion that occurs as the result of substitution of Cu for Fe. Copper occupies only one of the metal sites (*M1*) in siderotil, and the composition is estimated to be (Fe,Zn,Mg)<sub>0.73</sub>Cu<sub>0.27</sub>SO<sub>4</sub>•5H<sub>2</sub>O on the basis of degree of site distortion.

*Keywords:* siderotil, sulfate minerals, crystal structure, mine waste, melanterite, rozenite.

### SOMMAIRE

On trouve des cristaux bleu pâle de sidérotil le long de la galerie B de la mine Richmond (minerai de Cu–Zn–pyrite) à Iron Mountain, en Californie, en présence de coquimbite, römerite, halotrichite, copiapite et voltaïte. Les résultats d'analyses à la microsonde électronique ont donné, comme formule empirique moyenne, (Fe<sub>0.55</sub>Cu<sub>0.28</sub>Mg<sub>0.09</sub>Zn<sub>0.08</sub>)<sub>Σ1</sub>SO<sub>4</sub>•5H<sub>2</sub>O. La structure atomique de ce matériau a été déterminé par affinement par moindres carrés de données en diffraction X prélevées sur cristal unique, menant à un résidu *wR* de 5.7% pour 1633 réflexions, *P* $\bar{1}$ , *a* 6.292(5), *b* 10.632(8), *c* 6.072(5) Å,  $\alpha$  82.63(1),  $\beta$  110.02(1),  $\gamma$  105.19(1)°. Le sidérotil possède la même structure que la chalcantite, CuSO<sub>4</sub>•5H<sub>2</sub>O. Les longueurs et les angles des liaisons ressemblent à ceux de la chalcantite sauf que les longues liaisons apicales des sites octaédriques dans la chalcantite, qui résultent de l'octaèdre difforme autour du Cu, dû à une coördinance en plan carré, sont considérablement raccourcies dans le sidérotil à cause de la dominance du Fe à ce site. On peut évaluer la proportion de Cu aux sites *M1* et *M2* selon le degré de distorsion attribuable au Cu. Le cuivre n'occupe qu'un seul des sites dans le sidérotil, *M1*, et la composition devrait être (Fe,Zn,Mg)<sub>0.73</sub>Cu<sub>0.27</sub>SO<sub>4</sub>•5H<sub>2</sub>O pour rendre compte de la distorsion du site.

(Traduit par la Rédaction)

*Mots-clés:* sidérotil, minéraux sulfatés, structure cristalline, déchets miniers, mélanterite, rozenite.

### INTRODUCTION

Hydrous metal sulfates are commonly found in mine waste and are intimately involved with the retention and release of metals to the effluent that flows from the waste (Jambor 1994, Alpers *et al.* 1994). If we are to understand the mechanisms that operate in these sys-

tems, we must understand the details of the atomic structure and the phase relationships of these minerals. Siderotil commonly occurs as a result of the dehydration of melanterite in mine waste. The atomic structure is related to that of chalcantite. The ability of siderotil to incorporate metals other than Fe may be explained by distortions induced in the atomic structure by the incorporation of Cu.

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## PREVIOUS WORK

The melanterite group of minerals commonly occurs in oxidized, sulfide-rich mine waters; natural and synthetic materials have been investigated recently (Peterson 2003, Anderson 2002). Melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) dehydrates to rozenite ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ) or siderotil [ $(\text{Fe,Cu})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ ], depending on the copper content (Jambor & Traill 1963) and may also dehydrate to szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). Jambor & Traill (1963) described a sample of rozenite found in Manitoba that had dehydrated from melanterite and the naturally occurring "pentahydrate" (siderotil) from Yerington, Nevada. The reader is referred to Jambor & Traill (1963) for a summary of the work done on these mineral species prior to 1963. Melanterite constitutes a cement in some hardpan layers that form in mine tailings (Blowes *et al.* 1992). This hardpan layer may form an impediment to downward movement of dissolved constituents. As humidity conditions change and the groundwater table adjusts to seasonal variations, the melanterite may dehydrate to siderotil, which will affect the ability of this hardpan layer to cap the mine waste.

Chou *et al.* (2002) have delimited the fields of stability of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  as a function of temperature and relative humidity, as well as the fields of stability of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . Chou *et al.* worked in the Fe-only or Cu-only systems and did not observe siderotil or boothite,  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ . The fields of stability of these two phases remain uncertain, but both likely require the incorporation of more than one type of cation to be stable.

Siderotil is isostructural with chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Jambor & Traill (1963) determined the unit cell of siderotil using a combination of single-crystal and powder-diffraction data. In the present study, we confirm this unit cell; however, the setting of Bacon & Titterton (1975) is used throughout (Table 1) to permit detailed comparison of the two structures.

Work in progress on the natural occurrence and dehydration behavior of sulfates with the formula  $\text{MSO}_4 \cdot 5\text{H}_2\text{O}$  indicates that the dehydration to lower

hydrates is very dependent on the composition. For some compositions, the pentahydrate does not dehydrate, even under conditions of very low humidity (Peterson *et al.*, in prep.). In this study, we provide an atomic structure basis on which to interpret the stability relationships among the different minerals in the group.

## OCCURRENCE

The siderotil crystals were collected in 1998 in the B drift of the Richmond Cu–Zn–pyrite mine, Iron Mountain, California. The reader is referred to Peterson (2003, and references therein) for a description of the deposit as well as the unusual acidity of the associated mine-waters. The small masses (<5 mm) of siderotil are light blue and occur in a complex mixture of coquimbite, r merite, halotrichite, copiapite and voltaite (Fig. 1). The <1 mm crystals include many very fine needles of halotrichite. Melanterite, with colors ranging from green to blue to yellow, is common in the underground environment of the Richmond mine (Peterson 2003). The siderotil is similar in appearance to some blue samples of melanterite, and other occurrences of siderotil in the Richmond mine may have been overlooked because of this similarity.

Upon collection, the sample was immediately submerged in mineral oil and remained in the oil until studied in February of 2002. This procedure has been effective in not allowing the melanterite and other hydrous minerals to dehydrate. It is very unlikely that the siderotil described here formed after collection, as it is unlikely that a dehydration product would have the observed high degree of crystallinity required for studies using single-crystal diffraction.

## CHEMICAL ANALYSIS

The chemical composition of the siderotil was determined from energy-dispersion spectra collected using an ARL–SEM electron microprobe. A proper surface for microprobe analysis could not be polished because of the small size of the crystals and the tendency for this material to dehydrate. Instead, five individual grains were quickly cleaned with alcohol and acetone and then placed on a carbon disk and coated with carbon to improve conductivity. The electron beam (beam current ~20 nA at 15 kV) was rastered over an area  $0.1 \times 0.1$  mm to minimize sample damage over the 200 seconds of collection time. The lack of a flat surface and the fragility of the siderotil under the beam resulted in low analytical totals. A minor Al peak observed in the energy-dispersion scan can be attributed to the very fine needles of halotrichite that are intergrown with the siderotil. We used the following standards: NBS 470K12 glass for Al and Mg, S–371 pyrite for Fe and S, S–376 chalcocopyrite for Cu, and S–49 zinc metal for Zn. Table 2 presents values of the metal ratios that were obtained after a ZAF matrix cor-

TABLE 1. UNIT-CELL DIMENSIONS OF SIDEROTIL, COMPARED TO THOSE OF CHALCANTHITE

	Siderotil Iron Mountain	Siderotil ICPDS 22–357	Chalcantite B & T (1975)
$a$ (Å)	6.292(5)	6.25	6.141
$b$	10.632(8)	10.63	10.736
$c$	6.072(5)	6.06	5.986
$\alpha$ (°)	82.63(1)	82.75	82.26
$\beta$	110.02(1)	109.67	107.43
$\gamma$	105.19(1)	105.0	102.66

rection. The values are similar for all of the grains analyzed, and the metal/sulfur ratio is close to one, as is expected.

### X-RAY DIFFRACTION

A small chip (0.25 mm) of light blue siderotil was mounted in mineral oil in a 0.3 mm glass capillary to retard dehydration of the crystal. X-ray-diffraction data were collected using a Bruker AXS diffractometer equipped with a CCD detector. The 2467 reflections were sorted to 1633 unique reflections with an agreement factor  $R$  of 0.07. Initial atomic positions for non-hydrogen atoms were taken from the structure of chalcantite (Bacon & Titterton 1975). The atomic structure was refined with the program SHELXL-97

(Sheldrick 1997) to a final agreement factor of  $wR = 0.057 = [\sum w(|F_o| - |F_c|)^2 / (\sum w|F_o|^2)]^{1/2}$ . Scattering curves for neutral atoms were taken from Hahn (1987). Table 3 gives the resulting coordinates and thermal displacement parameters of the atoms. Calculated and observed structure-factors are available from the Depository of Unpublished Data CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

### DISCUSSION

The crystal structure of siderotil is closely related to that of chalcantite. The atomic structure consists of chains of corner-sharing sulfate tetrahedra and octahedrally coordinated metal sites. These chains are held together by hydrogen bonding (Fig. 2). In Table 4, we compare the bond lengths and angles for siderotil, as acquired in the present study, to those obtained by Bacon & Titterton (1975) for chalcantite. Both octahedra have similar average bond-lengths, but the variance of the bond-lengths shows that the octahedra are considerably more distorted in chalcantite. In siderotil, the  $M1-O1$  bonds are longer than the other bonds in the octahedra. This square-planar distortion is a result of the  $d^9$  configuration of Cu. The Jahn-Teller distortion of the octahedra causes the polyhedra to spontaneously distort to lower the free energy of the polyhedron (Strens 1966). In chalcantite, both metal sites contain only Cu, and this distortion attains its maximum extent. In this sample of siderotil, only 27.5% of the metal atoms are Cu (Table 2) and therefore Cu may occupy  $M1$  or  $M2$  or be disordered over both octahedrally coordinated sites. It is clear from Table 4 that the  $M1$  site, with a bond-length variance of 0.012, is more distorted, in a square-planar fashion, than  $M2$ , with a bond-length variance of 0.001, because of the long  $M1-O1$  bond. Figure 3 is a plot of

TABLE 2. ATOMIC PROPORTIONS IN SIDEROTIL, AS CALCULATED FROM THE RESULTS OF ELECTRON-MICROPROBE ANALYSES

	Fe	Cu	Zn	Mg	S
	0.54	0.30	0.07	0.09	1.084
	0.55	0.29	0.07	0.09	1.069
	0.57	0.27	0.07	0.09	1.004
	0.56	0.30	0.06	0.09	0.936
	0.58	0.27	0.07	0.09	1.163
	0.56	0.26	0.09	0.09	1.019
	0.56	0.25	0.09	0.09	1.022
	0.55	0.28	0.08	0.09	1.112
average	0.55	0.275	0.08	0.09	1.051
standard deviation	0.01	0.015	0.011		

Calculated assuming Fe + Cu + Zn + Mg = 1 apfu. The magnesium concentration was calculated from the average of the three analyses with the highest counts and then applied to all calculations. Proportions are quoted in atoms per formula unit (apfu).

TABLE 3. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN SIDEROTIL

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{eq}$
$M1$	0	0	0	0.0275(5)	0.0297(5)	0.0233(4)	0.0073(3)	0.0072(3)	-0.0006(3)	0.0270(3)
$M2$	½	½	0	0.0205(5)	0.0255(5)	0.0183(5)	0.0066(3)	0.0063(3)	0.0015(3)	0.0214(3)
S	0.0301(2)	0.2886(1)	0.6519(2)	0.0177(5)	0.0254(6)	0.0168(5)	0.0052(4)	0.0046(4)	0.0008(4)	0.0204(3)
O1	0.9256(6)	0.1519(3)	0.7050(6)	0.028(2)	0.030(2)	0.032(2)	0.000(1)	0.008(1)	0.002(1)	0.0323(8)
O2	0.2628(6)	0.3269(3)	0.8290(6)	0.024(2)	0.031(2)	0.027(2)	0.005(1)	-0.001(1)	0.001(1)	0.0300(7)
O3	0.8838(6)	0.3748(4)	0.6554(6)	0.025(2)	0.041(2)	0.026(2)	0.015(1)	0.006(1)	-0.003(1)	0.0295(7)
O4	0.0581(6)	0.2988(6)	0.4177(5)	0.034(2)	0.041(2)	0.021(2)	0.012(1)	0.012(1)	0.001(1)	0.0303(7)
OW5	0.8283(7)	0.0750(4)	0.1585(6)	0.039(2)	0.035(2)	0.035(2)	0.006(2)	0.018(2)	-0.004(2)	0.0349(8)
OW6	0.3097(7)	0.1173(4)	0.1807(6)	0.034(2)	0.028(2)	0.034(2)	0.002(1)	0.011(1)	-0.002(1)	0.0327(8)
OW7	0.4765(6)	0.4040(4)	0.3171(5)	0.030(2)	0.043(2)	0.021(2)	0.009(1)	0.009(1)	0.006(1)	0.0316(8)
OW8	0.7603(6)	0.4061(4)	0.0277(6)	0.029(2)	0.047(2)	0.028(2)	0.020(1)	0.009(1)	-0.000(1)	0.0328(5)
OW9	0.4476(6)	0.1302(4)	0.6631(7)	0.027(2)	0.043(2)	0.037(2)	0.008(2)	0.008(2)	0.007(2)	0.0373(9)

$$\text{displacement parameter} = \exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$$

the observed distortions of the octahedra in melanterite as a function of Cu content, as observed by Peterson (2003) for melanterite from Iron Mountain, as well as the distortion observed in chalcantite. The distortions in siderotil are consistent with the *M1* site being occupied by 54% Cu and the *M2* site having no Cu. This occupancy closely matches the measured chemical composition of 27.5% Cu, which translates into 55% Cu at the *M1* site if no Cu is located at the *M2* site. This analysis neglects the effects of the different radii of the minor Zn and Mg, which also occupy the octahedral sites, but these cations would not induce a square-planar distortion. These observations indicate that there is a structural limit of 50% substitution of Cu into the siderotil structure, but natural material approaching this limit has not been observed. A related species,  $\text{Mg}_{0.5}\text{Cu}_{0.5}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , arises in the Mg–Cu– $\text{SO}_4$ – $\text{H}_2\text{O}$  system (Peterson *et al.* 2001).

Work is currently in progress to outline the liquid-absent fields of stability of these minerals by *in situ* diffraction experiments at controlled temperatures and relative humidity. A series of siderotil compositions with varying amounts of Cu, Mg and Fe has been synthesized, and the dehydration temperatures at various relative humidities are being measured.

#### ACKNOWLEDGEMENTS

We thank J.L. Jambor and A.M. McDonald for careful reviews, which improved the manuscript, and Mati Raudsepp and Robert F. Martin for editorial assistance. The research was supported by a grant from the Natural Sciences and Engineering Research Council of Canada to RCP.

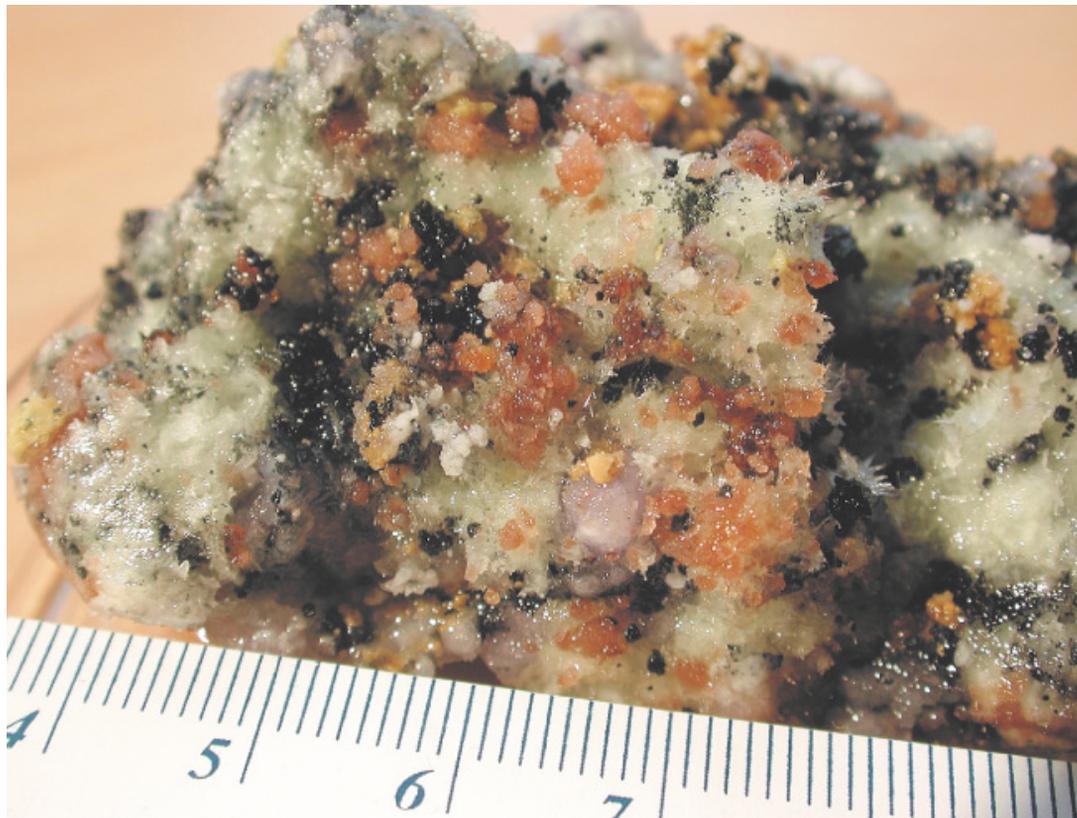


FIG. 1. The mineral associations in the Richmond mine are complex, with many different sulfates coexisting in the same sample. The sample from which the single crystal of siderotil was obtained contains voltaite,  $\text{K}_2\text{Fe}^{2+}_5\text{Fe}^{3+}_4(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$  (black), halotrichite,  $\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$  (white needles), coquimbite,  $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (violet), römerite  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$  (reddish brown), and copiapite,  $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  (light yellow). Each division on the scale is 1 mm.

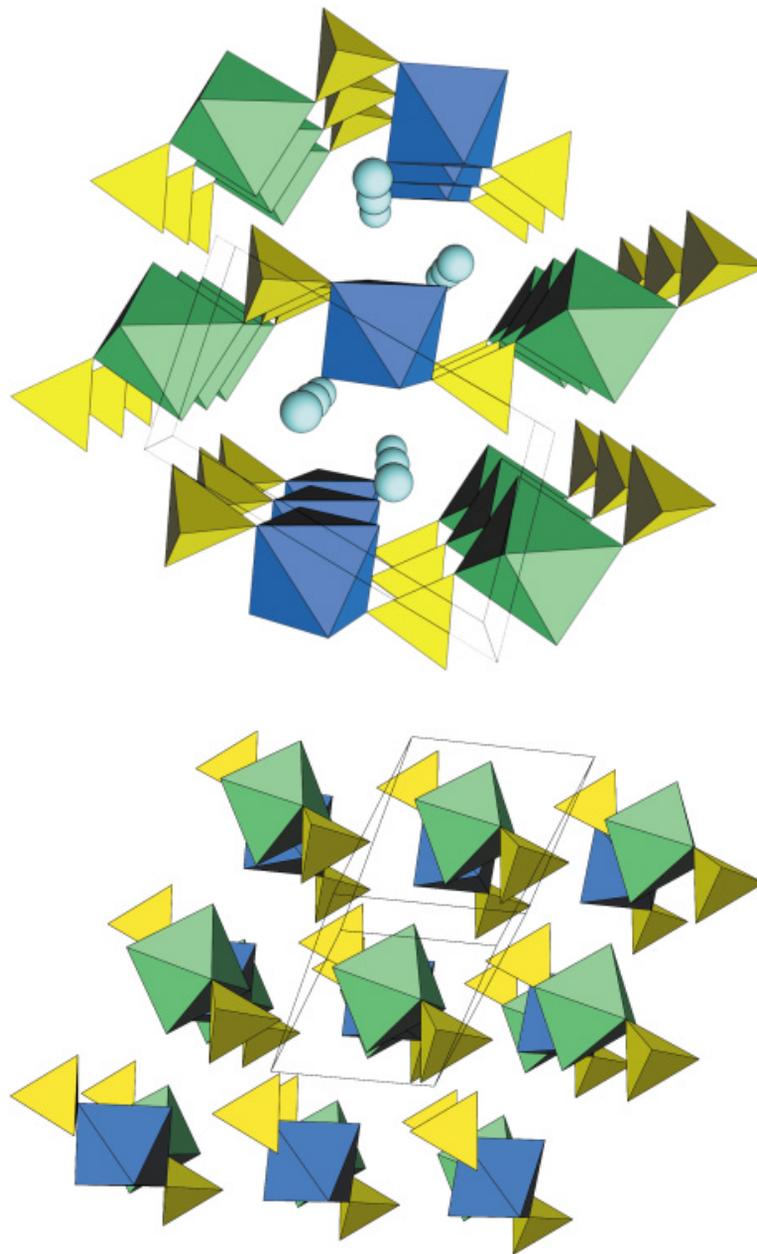


FIG. 2. (a) The atomic structure of siderotil viewed down the *c* axis. Chains consisting of corner-sharing sulfur-containing tetrahedra (yellow) and transition-metal-containing octahedra (*M1* blue and *M2* green) are aligned along the [110] direction. Also shown is OW9 (light blue spheres), which does not participate in the coordination of sulfur or the transition-metal sites. (b) The chains as viewed down the [110] direction (OW9 is not shown). Hydrogen positions were not determined.

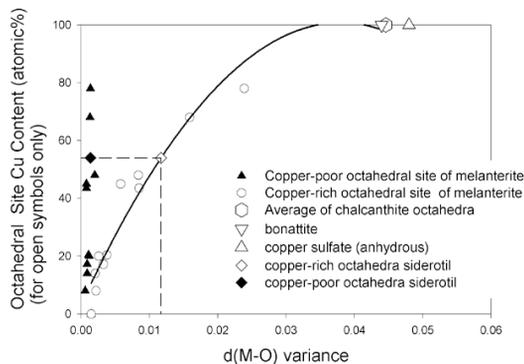


Fig. 3. The distortion exhibited by octahedra in siderotil, chalcantinite, bonattite and melanterite as a function of Cu content (Peterson 2003). The degree of distortion of Cu-rich octahedra in a variety of sulfates is plotted on the basis of site content; we assume that all the Cu determined by chemical analysis is at this site (open symbols). The corresponding Cu-poor or Cu-absent octahedra (relatively undistorted) for each sulfate whose structure is determined also is shown (solid symbols) for comparison of bond variance, but the Cu content of these sites is inferred to be zero. If we use the observed variance of 0.0117 for M1 of siderotil (Table 4) and the quadratic-function fit to data for the Cu-containing octahedra in melanterite (solid line), we predict that M1 in siderotil contains 54% Cu. This prediction matches well an occupancy of the M1 site of 55% Cu predicted using the chemical composition  $\text{Fe}_{0.55}\text{Cu}_{0.28}\text{Zn}_{0.08}\text{Mg}_{0.09}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , determined by electron-microprobe analysis.

TABLE 4. BOND LENGTHS (Å) AND ANGLES(°) IN SIDEROTIL

	siderotil	chalcantinite	siderotil	
M1-O1 (×2)	2.261(4)	2.386	OW5-Cu-OW6	91.1(2)
			OW6-Cu-O1	92.8(1)
M1-OW5 (×2)	2.022(4)	1.975	OW5-Cu-OW6	88.9(2)
			OW6-Cu-O1	87.2(1)
M1-OW6 (×2)	2.042(4)	1.977	OW5-Cu-O1	88.3(2)
			OW5-Cu-O1	91.7(2)
average	2.108	2.113		
variance	0.01172	0.03735		
M2-O2 (×2)	2.165(4)	2.440	OW8-Fe-OW7	87.9(1)
			OW7-Fe-O2	86.9(2)
M2-OW7 (×2)	2.093(3)	1.970	OW8-Fe-OW7	92.1(1)
			OW7-Fe-O2	93.1(2)
M2-OW8 (×2)	2.081(4)	1.945	OW8-Fe-O2	85.2(2)
			OW8-Fe-O2	94.8(2)
average	2.113	2.118		
variance	0.00141	0.05184		
S-O1	1.475(4)	1.482	O3-S-O1	111.0(2)
			O1-S-O4	109.2(2)
S-O2	1.479(3)	1.476	O3-S-O2	110.2(2)
			O2-S-O4	108.6(2)
S-O3	1.466(4)	1.469	O3-S-O4	109.5(3)
S-O4	1.479(3)	1.491	O1-S-O2	108.3(2)
average	1.475	1.479		

The chalcantinite data are taken from Bacon & Titterton (1975).

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Received July 14, 2002, revised manuscript accepted March 13, 2003.