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The crystal structure of wroewolfeite, a mineral with $[Cu_4(OH)_6(SO_4)(H_2O)]$ sheets

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Abstract

The crystal structure of wroewolfeite, $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, monoclinic, $a = 6.045(1)$, $b = 5.646(1)$, $c = 14.337(2)$Å, $\beta = 93.39(1)°$, $V = 488.5(1)Å^3$, space group *Pc*, has been solved by direct methods and refined by full-matrix least-squares to an *R* index of 6.7% using 711 observed ($I > 2.5\sigma$) reflections measured on a twinned crystal. The fundamental building block of the wroewolfeite structure is a $[Cu_4(SO_4)(OH)_{15}]^{9-}$ hetropolyhedral cluster that polymerizes in two dimensions by edge-sharing between octahedra to form the structure module, a $[Cu_4(SO_4)(OH)_6(H_2O)]^\circ$ sheet that is parallel to {001}. These sheets are linked solely by hydrogen bonding, involving an additional (H_2O) anion that is not directly bonded to a cation.

This $[Cu_4(SO_4)(OH)_6(H_2O)]^\circ$ sheet is also found in posnjakite and may also occur in langite. This and other related sheets may be described by the general formula $[M_4X_n\phi_{8-n}]$, in which M = octahedrally coordinated cation, X = complex anion, ϕ = simple anion (e.g. O^{2-}, $(OH)^-$, $(H_2O)^\circ$). The following structures are included: n = 0, botallackite; n = 1, wroewolfeite, langite, posnjakite; n = 2, ktenasite, serpierite, devillite. The intra-module linkages and hydration states in these minerals may be interpreted in terms of the Lewis basicity/acidity of structural fragments.

Introduction

Wroewolfeite is a monoclinic hydrated copper hydroxyl sulphate $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, first described by Dunn and Rouse (1975) from the Loudville lead mine, Loudville, Massachusetts. They assigned it to the same group as posnjakite, $Cu_4(SO_4)(OH)_6 \cdot H_2O$, and langite, $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, and it is presumably dimorphous with langite.

Experimental

The material used in this study is from the Loudville lead mine, Loudville, Massachusetts, and was obtained from the Department of Mineralogy and Geology, Royal Ontario Museum, collection number M37058. Single-crystal X-ray precession photographs indicate monoclinic symmetry, with systematic absences *h0l*; $l = 2n + 1$, consistent with space groups *P2/c* and *Pc*. The observed cell dimensions are in good agreement with the values reported by Dunn and Rouse (1975). The crystals are twinned by reflection on {001}, leading to overlap on reflections of the type $4h \cdot k \cdot l$. This overlap is not merohedral; there is a distinct misregistry of the reflections. This twin-law was reported by Dunn and Rouse (1975). However, there is additional twinning evident in the (*h0l*) zero-level photograph, namely twinning by reflection on {100}. Note that this twinning occurs for each member of the {001} twin, resulting in four individual twin components. The relative amounts of the twin components were estimated as approximately 70:25:4:1 for the crystal used in the collection of the X-ray intensity data.

The crystal was mounted on a Nicolet *R3m* automated four-circle diffractometer equipped with a molybdenum-target X-ray tube and a highly oriented graphite crystal monochromator mounted with equatorial geometry. A random orientation photograph showed many of the reflections to occur as pairs with an intensity ratio of ~3:1. Twenty-five reflections were centered, and the correct unit cell was selected from an array of real space vectors corresponding to potential unit cell axes. Twenty-three of the twenty-five reflections had integral indices; the remaining reflections were discarded as being from an alternate twin component. Additional reflections were centered and indexed, until the twenty-five reflections were all from the same twin component. Least-squares refinement of these reflections produced the monoclinically constrained cell dimensions given in Table 1, together with the orientation matrix relating the crystal axes to the diffractometer axes.

Intensity data were collected in the θ–2θ scan mode, using 96 steps with a scan range from $[2\theta(MoK\alpha_1) - 1]°$ to $[2\theta(MoK\alpha_2) + 1]°$ and a variable scan rate between 4.0 and 29.3°/min depending on the intensity of an initial one second count at the center of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. Two standard reflections were monitored every 48 measurements to check for stability and constancy of crystal alignment. A total of 2588 reflections were measured over two asymmetric units out to a maximum 2θ of 55°. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of Ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0–350°. These data were used to calculate a thin plate empirical absorption correction, the *R* (symmetric) index being reduced from 10.0% to 2.2% for the azimuthal data. This correction was then applied to the whole data set, minimum and maximum transmission being 0.374 and 0.728 resepectively and the merging *R* (symmetric) being 2.3%. The data were also corrected for Lo-

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Table 1. Miscellaneous information concerning wroewolfeite

a	6.045(1)Å	Crystal size(mm)	0.03x0.12x0.16
b	5.646(1)	Rad|Mono	Mo|Gr
c	14.337(2)	Total $\|F_o\|$	1104
β	93.39(1)°	$\|F_o\| > 4\sigma$	1008
V	488.5(1)Å^3	Non-overlapped $\|F_o\|$	711
Space Group	Pc	Final R (obs)	6.7%
		Final R_w (obs)	6.2%

Unit cell contents: $2[Cu_4(SO_4)(OH)_6 \cdot 2H_2O]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, w=1

rentz, polarization and background effects, averaged and reduced to structure factors. Of the 1104 unique reflections, 1008 were classed as observed ($|F_o| < 4\sigma$).

Solution and refinement

Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer and Mann (1968) and Cromer and Liberman (1970). *R* indices are of the form given in Table 1 and are expressed as percentages.

In the first stage of structure solution, the overlap due to twinning was disregarded. The structure was solved by direct methods. The distribution of *E*-values were characteristic of a non-centrosymmetric space group, and thus the space group *Pc* was adopted. The phase set with the highest combined figure of merit gave a solution which eventually refined to an *R* index of ~13%. The stereochemistry of this model was rather nonsensical, and inspection of a difference Fourier map indicated the presence of a twinned structure component. At this stage, reflections of the type $4h \cdot k \cdot l$ were removed from the data set. A difference Fourier located the remaining anions, and subsequent refinement converged to an *R* index of 6.7% for an isotropic thermal model. The diffraction data still contained a small contribution from the {001} twin, leading to overlap on *hk*0; however, removal of these data did not significantly affect the refinement results. Because of the incomplete data set (due to removal of partially overlapped reflections) and residual effects from other twin components, an anisotropic thermal model or refinement of H atom positions was not attempted. Final parameters are given in Table 2, observed and calculated structure factors are listed in Table 3[1] and interatomic distances and angles are given in Table 4. An empirical bond-valence analysis is given in Table 5.

Structural description

There is one unique S position in wroewolfeite; the S is coordinated by four O^{2-} anions, the resulting tetrahedron showing a typical range of bond lengths and bond angles. There are three long S–O bonds, ⟨S–O⟩ = 1.49Å, and one short S–O bond, S–O = 1.43Å; this correlates well with the local bond-valence requirements according to the hydrogen bonding scheme proposed later. There are four unique Cu positions, each Cu being coordinated by six anions in distorted octahedral arrangements. Cu(1) is coordinated by one O^{2-} and five $(OH)^{1-}$ anions, with four short meridional bonds and two longer axial bonds to one $(OH)^{1-}$ and one O^{2-}. Cu(2) is coordinated by five $(OH)^-$ anions and one $(H_2O)^\circ$ molecule, with four short meridional bonds and two longer axial bonds to an $(OH)^-$ and the $(H_2O)^\circ$ molecule. Cu(3) and Cu(4) are both bonded to one O^{2-} anion and five $(OH)^{1-}$ anions, again with similar distributions of bond lengths. Thus each of the $Cu\phi_6$ octahedra (where $\phi = O^{2-}$, OH^-, H_2O) show typical Jahn–Teller distortions involving strong extension of the axial Cu-ϕ bonds.

The structure of wroewolfeite is illustrated in Figures 1 and 2. The fundamental building block (FBB) of the structure (Hawthorne, 1985a) is the $[Cu_4(SO_4)(OH)_{15}]^{9-}$ heteropolyhedral cluster that is repeated by simple translation along *a* and *b*. This links, by octahedral edge-sharing in both directions to form the structure module pictured in Figure 1, an infinite sheet of edge-sharing $Cu\phi_6$ octahedra with projecting (SO_4) tetrahedra; this has the formula $[Cu_4(SO_4)(OH)_6(H_2O)]^\circ$. The structure module is electrostatically neutral, and adjacent sheets are linked solely by hydrogen bonding, the proposed arrangement being shown in Figure 2. There is one unique (H_2O) molecule in the structure that is not directly bonded to a cation. How-

Table 2. Atomic parameters for wroewolfeite

Atom	x	y	z	$U^*_{iso.}$
Cu(1)	0	0.3311(4)	1/4	0.91(5)
Cu(2)	0.5020(5)	0.3212(4)	0.2501(2)	1.01(5)
Cu(3)	-0.2476(5)	-0.1682(4)	0.2428(2)	1.02(5)
Cu(4)	0.2474(5)	0.1734(4)	-0.2572(2)	1.08(5)
S	-0.0798(11)	0.0358(9)	0.0352(4)	1.43(8)
O(1)	-0.0261(21)	0.0098(27)	0.1376(9)	1.4(3)
O(2)	0.1279(25)	0.0012(30)	-0.0132(11)	2.5(3)
O(3)	-0.1607(24)	0.2811(27)	0.0154(9)	1.8(3)
O(4)	-0.2443(27)	-0.1331(33)	0.0052(11)	2.9(4)
O(5)†	0.2525(19)	0.4991(22)	0.1932(9)	0.8(2)
O(6)†	0.2523(20)	0.1401(23)	0.3052(8)	0.9(2)
O(7)†	0.0063(21)	-0.2845(23)	0.3153(9)	0.9(2)
O(8)†	0.7406(19)	0.5073(21)	0.1894(9)	0.6(2)
O(9)†	0.7577(20)	0.1470(24)	0.3076(9)	1.1(2)
O(10)†	0.4891(18)	-0.0581(21)	0.1753(8)	0.6(2)
O(11)††	0.5101(25)	0.6230(28)	0.3738(11)	2.1(3)
O(12)††	0.2240(27)	0.4638(30)	-0.4964(11)	2.4(3)

$^*U_{iso.} = U_{iso.} \times 10^2$

†Indicates hydroxyl oxygens

††Indicates water oxygens

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[1] To receive a copy of Table 3, order Document AM-85-273 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfich.

Table 4. Interatomic distances (Å) and angles (°) in wroewolfeite

Cu(1)-0(1)	2.425(15)	Cu(2)-0(5)	1.950(12)
Cu(1)-0(5)	2.010(12)	Cu(2)-0(6)	2.022(13)
Cu(1)-0(6)	1.993(12)	Cu(2)-0(8)	2.023(12)
Cu(1)-0(7)a	2.363(13)	Cu(2)-0(9)	1.971(13)
Cu(1)-0(8)b	2.010(11)	Cu(2)-0(10)	2.394(12)
Cu(1)-0(9)b	2.013(13)	Cu(2)-0(11)	2.458(16)
<Cu(1)-0>	2.136	<Cu(2)-0>	2.136
Cu(3)-0(1)	2.306(14)	Cu(4)-0(1)d	2.405(13)
Cu(3)-0(7)	1.918(12)	Cu(4)-0(5)e	1.982(13)
Cu(3)-0(8)c	1.985(12)	Cu(4)-0(6)d	1.982(13)
Cu(3)-0(9)b	2.007(13)	Cu(4)-0(7)e	1.943(13)
Cu(3)-0(10)b	1.917(11)	Cu(4)-0(10)d	1.914(12)
Cu(3)-0(11)c	2.718(16)	Cu(4)-0(11)e	2.648(15)
<Cu(3)-0>	2.142	<Cu(4)-0>	2.146
S-0(1)	1.492(15)		
S-0(2)	1.483(17)		
S-0(3)	1.491(16)		
S-0(4)	1.426(18)		
<S-0>	1.473		
0(1)-0(5)	3.31(2)	0(1)-Cu(1)-0(5)	96.0(5)
0(1)-0(6)	2.94(2)	0(1)-Cu(1)-0(6)	83.0(5)
0(1)-0(8)b	3.25(2)	0(1)-Cu(1)-0(8)b	93.7(5)
0(1)-0(9)b	2.94(2)	0(1)-Cu(1)-0(9)b	84.7(4)
0(5)-0(6)	2.59(2)	0(5)-Cu(1)-0(6)	80.5(5)
0(5)-0(7)a	2.66(2)	0(5)-Cu(1)-0(7)a	74.5(5)
0(5)-0(8)b	3.09(2)	0(5)-Cu(1)-0(8)b	100.5(5)
0(6)-0(7)a	3.58(2)	0(6)-Cu(1)-0(7)a	110.2(5)
0(6)-0(9)b	2.99(2)	0(6)-Cu(1)-0(9)b	96.7(5)
0(7)a-0(8)b	2.62(2)	0(7)a-Cu(1)-0(8)b	73.2(5)
0(7)b-0(9)b	3.54(2)	0(7)a-Cu(1)-0(9)b	107.9(5)
0(8)b-0(9)b	2.65(2)	0(8)b-Cu(1)-0(9)b	82.2(5)
<0-0 Cu(1)>	3.01	<0-Cu(1)-0>	90.3
0(5)-0(6)	2.59(2)	0(5)-Cu(2)-0(6)	81.2(5)
0(5)-0(8)	2.96(2)	0(5)-Cu(2)-0(8)	96.1(5)
0(5)-0(10)	3.47(2)	0(5)-Cu(2)-0(10)	105.6(5)
0(5)-0(11)	3.02(2)	0(5)-Cu(2)-0(11)	85.8(5)
0(6)-0(9)	3.05(2)	0(6)-Cu(2)-0(9)	99.8(5)
0(6)-0(10)	2.66(2)	0(6)-Cu(2)-0(10)	73.6(5)
0(6)-0(11)	3.26(2)	0(6)-Cu(2)-0(11)	93.0(5)
0(8)-0(9)	2.65(2)	0(8)-Cu(2)-0(9)	83.0(5)
0(8)-0(10)	3.44(2)	0(8)-Cu(2)-0(10)	106.1(5)
0(8)-0(11)	3.13(2)	0(8)-Cu(2)-0(11)	88.0(5)
0(9)-0(10)	2.69(2)	0(9)-Cu(2)-0(10)	75.2(5)
0(9)-0(11)	3.25(2)	0(9)-Cu(2)-0(11)	93.6(5)
<0-0 Cu(2)>	3.01	<0-Cu(2)-0>	90.1
0(1)-0(7)	3.04(2)	0(1)-Cu(3)-0(7)	91.5(5)
0(1)-0(8)c	3.27(2)	0(1)-Cu(3)-0(8)c	99.2(5)
0(1)-0(9)b	2.94(2)	0(1)-Cu(3)-0(9)b	85.5(5)
0(1)-0(10)b	3.04(2)	0(1)-Cu(3)-0(10)b	91.5(5)
0(7)-0(8)c	2.62(2)	0(7)-Cu(3)-0(8)c	84.4(5)
0(7)-0(9)b	2.86(2)	0(7)-Cu(3)-0(9)b	93.6(5)
0(7)-0(11)c	3.20(2)	0(7)-Cu(3)-0(11)c	85.6(5)
0(8)c-0(10)b	2.95(2)	0(8)c-Cu(3)-0(10)b	95.4(5)
0(8)c-0(11)c	3.13(2)	0(8)c-Cu(3)-0(11)c	81.8(5)
0(9)b-0(10)b	2.68(2)	0(9)b-Cu(3)-0(10)b	86.3(5)
0(9)b-0(11)c	3.47(2)	0(9)b-Cu(3)-0(11)c	93.4(5)
0(10)b-0(11)c	3.36(2)	0(10)b-Cu(3)-0(11)c	91.4(5)
<0-0>Cu(3)	3.05	<0-Cu(3)-0>	90.2
0(1)d-0(5)e	3.41(2)	0(1)d-Cu(4)-0(5)e	101.6(5)
0(1)d-0(6)d	2.94(2)	0(1)d-Cu(4)-0(6)d	83.7(5)
0(1)d-0(7)e	3.04(2)	0(1)d-Cu(4)-0(7)e	88.0(5)
0(1)d-0(10)d	3.15(2)	0(1)d-Cu(4)-0(10)d	93.0(5)
0(5)e-0(7)e	2.66(2)	0(5)e-Cu(4)-0(7)e	85.4(5)
0(5)e-0(10)d	2.90(2)	0(5)e-Cu(4)-0(10)d	96.2(5)
0(5)e-0(11)e	2.53(1)	0(5)e-Cu(4)-0(11)e	80.1(5)
0(6)d-0(7)e	2.83(2)	0(6)d-Cu(4)-0(7)e	92.2(5)
0(6)d-0(10)d	2.66(2)	0(6)d-Cu(4)-0(10)d	86.1(5)
0(6)d-0(11)e	3.42(2)	0(6)d-Cu(4)-0(11)e	94.3(5)
0(7)e-0(11)e	3.15(2)	0(7)e-Cu(4)-0(11)e	85.3(5)
0(10)d-0(11)e	3.36(2)	0(10)d-Cu(4)-0(11)e	93.6(5)
<0-0>Cu(4)	3.01	<0-Cu(4)-0>	90.0
0(1)-0(2)	2.41(2)	0(1)-S-0(2)	107.9(9)
0(1)-0(3)	2.43(2)	0(1)-S-0(3)	109.2(9)
0(1)-0(4)	2.39(2)	0(1)-S-0(4)	109.8(9)
0(2)-0(3)	2.41(2)	0(2)-S-0(3)	108.1(9)
0(2)-0(4)	2.40(2)	0(2)-S-0(4)	111.4(9)
0(3)-0(4)	2.40(2)	0(3)-S-0(4)	110.4(9)
<0-0>S	2.41	<0-S-0>	109.5
Hydrogen bonds: donor-acceptor contacts			
0(5)-0(12)	2.72(2)	0(6)-0(1)	2.94(2)
		0(6)-0(2)	2.87(2)
0(7)-0(2)	2.99(2)		
		0(8)-0(3)	2.90(2)
0(9)-0(4)	2.83(2)		
		0(10)-0(1)	3.03(2)
0(11)-0(3)	2.81(2)	0(10)-0(4)	3.04(2)
0(11)-0(12)	2.77(2)		
		0(12)-0(2)	2.70(2)
		0(12)-0(3)	2.75(2)

a: x, 1+y, z; b: x-1, y,z; c: x-1, y-1, z; d: x, -y, z-1/2; e: x, 1-y, z-1/2.

ever, the (H_2O) functions as an anion and plays an integral part in the proposed hydrogen bonding arrangement. As can be seen from the bond-valence table (Table 5), O(1–4) are O^{2-} anions, O(5–10) are $(OH)^{1-}$ anions and O(11–12) are $(H_2O)^{\circ}$ anions, and the hydrogen atom numbers indicate to which oxygen they are strongly bonded. H(5) and H(11)B hydrogen bond to O(12) which hydrogen bonds to O(2) and O(3), thus promoting inter-sheet linkage and contributing to the satisfaction of the O(1–4) bond-valence requirements. Note the approximately tetrahedral nature of the bonds about the O(12) oxygen, an arrangement that seems to be characteristic of this type of (H_2O) anion. The remaining hydrogen atoms (H(6–10) and H(11)A) hydrogen-bond to O^{2-} anions of the adjacent sheet, as shown in Figure 2.

This fairly weak linkage between the sheets accounts for the perfect cleavage on {001}; the reasons for the other two cleavages (on {100} and {010}) given by Dunn and Rouse (1975) are not clear. One might expect crystals to be platy on {001}; however, the crystal used in this study was platy on {010}. Again the reason for this is not at all clear. Conversely, it seems reasonable that the structure should twin on {001}, as the hydrogen bonds should easily adjust to an alternate arrangement of adjacent sheets at the twin plane. With regard to the twinning on {100}, this could be done by a 6° corrugation in the sheet, accompanied by a ∼30° rotation of the sulphate tetrahedra. It is notable that the three anions most affected by this (O(2–4)) have the highest temperature factors (except for the (H_2O) anions).

The Jahn–Teller distortions of the Cu octahedra were noted earlier. However, it is also interesting that these axial elongations of the $Cu\phi_6$ octahedra are also an integral part of the structural linkage. It is only for very weak M^{2+}–O bonds that an (SO_4) tetrahedron could link to three octahedrally coordinated divalent cations. This is in accord with the general observation that $(T^{6+}O_4)^{2-}$ groups only link to $(M\phi_2)$ sheets when $M = Cu^{2+}$.

Related structures

The $[Cu_4(SO_4)(OH)_6(H_2O)]^{\circ}$ sheet that is the structure module in wroewolfeite is also found in the structures of posnjakite and langite. Note that the structure module in this series of minerals is not topologically centrosymmetric, and these three minerals do have non-centrosymmetric space groups.

Mellini and Merlino (1979) also related posnjakite to the structures of ktenasite, serpierite and devillite (Table 6). These structures are based on the structure module

Table 5. Empirical bond-valence* table for wroewolfeite

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	S	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)†	H(11)A	H(11)B	H(12)A	H(12)B	
0(1)	0.126		0.171	0.133	1.431		0.105				(0.089)					1.966(2.055)
0(2)					1.469		0.105	0.142						0.205		1.921
0(3)					1.435				0.185			0.128			0.205	1.953
0(4)					1.738					0.218	(0.089)					1.956(2.045)
0(5)	0.390	0.468				0.718										2.0
0(6)	0.410	0.376					0.790									2.0
0(7)	0.148		0.516	0.424				0.858								2.0
0(8)	0.390	0.375	0.420	0.424					0.815							2.0
0(9)	0.386	0.439	0.393	0.478						0.782						2.0
0(10)		0.137	0.518	0.523							0.822					2.0
0(11)		0.117	0.064	0.075								0.872	0.872			2.0
0(12)						0.282							0.128	0.795	0.795	2.0
Σ	1.850	1.912	2.082	2.057	6.073	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

*Calculated from the curves of Brown (1981); †Values in parentheses have OH....O contacts >3.0Å.

$[Cu_4(SO_4)_2(OH)_6]^{2-}$, a corrugated octahedral edge-sharing sheet with (SO_4) tetrahedra attached to both sides of the sheet, rather than one side as in the wroewolfeite type structures. This module is centrosymmetric, and the structures based on it do have centrosymmetric space groups.

These sheets can be written in the general form $[M_4\phi_{8-n}X_n]$, where M represents a divalent cation, ϕ represents a simple anion (O^{2-}, $(OH)^-$, etc.) and X represents a complex anion ($(SO_4)^{2-}$, etc.). The ktenasite structures have n = 2, and the wroewolfeite structures have n = 1. The copper hydroxy-chloride botallackite (Hawthorne, 1985b) has n = 0, and the formula $Cu_2(OH)_3Cl$. The structure module can be written as $[Cu_4(OH)_6Cl_2]$, and the modules are linked by hydrogen bonding as in the sulphate structures.

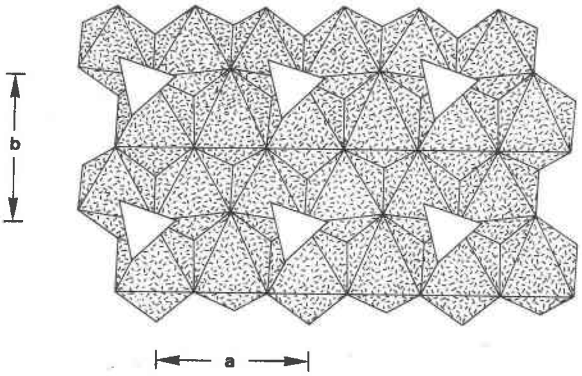

Fig. 1. The structure of wroewolfeite projected onto (001); octahedra are shaded, tetrahedra are not shaded.

Prediction of inter-module linkage

Certain aspects of these structures can be interpreted using the ideas of structural Lewis acidity/basicity relations described by Hawthorne (1985a). The structure module of the wroewolfeite structures is $[Cu_4(SO_4)(OH)_6(H_2O)]$. The bond-valence requirements of the (OH) and (H_2O) anions are more than satisfied, and thus one hydrogen bond should emanate from each (OH) and two hydrogen bonds from the (H_2O) anion. The O^{2-} anions are assumed to have a coordination number of [4]. With regard to the

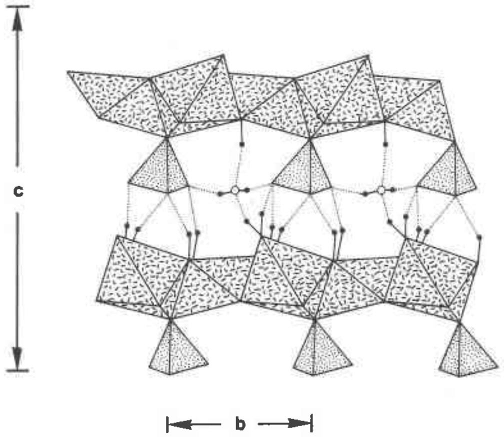

Fig. 2. The structure of wroewolfeite projected onto (100); octahedra are hatched, tetrahedra are dotted. Proposed hydrogen atoms are shown as small filled circles. Donor-hydrogen and hydrogen-acceptor bonds are shown by full and dotted lines respectively. The O(12) oxygen atoms are shown as unshaded large circles.

Table 6. The $[Cu_4(SO_4)_x(OH)_6(H_2O)_{2-x}](x = 1,2)$ minerals

Mineral	Formula	a(Å)	b(Å)	c(Å)	β(°)	Sp.Gr.	Ref.
Posnjakite	$[Cu_4(SO_4)(OH)_6(H_2O)]$	10.578(5)	6.345(3)	7.863(3)	117.98(5)	Pa	(1)
Langite	$[Cu_4(SO_4)(OH)_6(H_2O)](H_2O)$	$\underline{7.137(3)}$	6.031(5)	11.217(1)	90.00(1)	Pc	(2)
Wroewolfeite	$[Cu_4(SO_4)(OH)_6(H_2O)](H_2O)$	6.045(1)	5.646(1)	$\underline{14.337(2)}$	93.39(1)	Pc	(3)
Ktenasite	$Zn(H_2O)_6[(Cu,Zn)_4(SO_4)_2(OH)_6]$	5.589(1)	6.166(1)	$\underline{23.741(7)}$	95.55(1)	$P2_1/c$	(4)
Devillite	$Ca(H_2O)_3[Cu_4(SO_4)_2(OH)_6]$	$\underline{20.870(2)}$	6.135(2)	22.191(3)	102.73(2)	$P2_1/c$	(5)
Serpierite	$Ca(H_2O)_3[Cu_4(SO_4)_2(OH)_6]$	$\underline{22.186(2)}$	6.250(2)	21.853(2)	113.36(1)	C2/c	(6)

References: (1) Mellini and Merlino (1979); (2) Gentsch and Weber (1984); (3) This study; (4) Mellini and Merlino (1978); (5) Sabelli and Zanazzi (1972); (6) Sabelli and Zanazzi (1968).

*the cell dimension approximately orthogonal to the sheet is underlined

module cations, O(1) is coordinated by three Cu and one S, whereas O(2), O(3) and O(4) are coordinated by one S only. Thus the structure module requires 3 × 3 = 9 additional bonds to satisfy the [4] coordination requirements. The module is electrostatically neutral, having an ideal Lewis basicity of zero, and the additional required bonds must obviously come from the hydrogen bonding arrangement. The module ideally will provide $(6 \times 1) + (1 \times 2) = 8$ hydrogen bonds in posnjakite (six from the hydroxyls and two from the (H_2O) anion) and $(5 \times 1) + (1 \times 2) + 2 = 9$ hydrogen bonds in wroewolfeite (five from hydroxyls, two from the module (H_2O) anion and two from one hydroxyl the hydrogen bond of which is split by the transformer action of the non-module (H_2O) anion); these agree closely with the ideal number of [9] indicated above, and with the observed numbers of [7] (Mellini and Merlino, 1979) and [8] or [10] (Table 5) for posnjakite and wroewolfeite respectively.

The ktenasite structures are based on the $[Cu_4(SO_4)_2(OH)_6]^{2-}$ module, which has a Lewis basicity of $2/(6 \times 3 - 6) = 0.17$ v.u. (module charge/number of required bonds − number of module hydrogen bonds). According to the valence matching principle, the Lewis acidity of the extra-module cation should be approximately equal to the Lewis basicity of the structure module. The Lewis acidities of Ca^{2+} and Zn^{2+} are 0.29 and 0.36 v.u. respectively (Brown, 1981), significantly greater than the module basicity of 0.17 v.u.. However, the extra-module cations are partly to completely coordinated by (H_2O) anions, and the transformer action of (H_2O) (Hawthorne, 1985a) will considerably modify the actual cation acidity. For serpierite and devillite, the actual Lewis acidity of Ca is $2/(4 \times 1 + 3 \times 2) = 0.20$ v.u., in good agreement with the module basicity of 0.17 v.u. For ktenasite, the actual Lewis acidity of Zn is $2/(6 \times 2) = 0.17$ v.u., again matching the module basicity. These arguments thus account for the fact that the ktenasite group minerals are hydrated, and could be used to predict the relative degree of hydration in these structures.

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