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THE CRYSTAL STRUCTURE OF WHERRYITE, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, A MIXED SULFATE–SILICATE WITH $[^{[6]}M(TO_4)_2\phi]$ CHAINS

MARK COOPER AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of wherryite, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, monoclinic, *a* 20.789(4), *b* 5.787(1), *c* 9.142(3) Å, β 91.24(2)°, *V* 1099.5(6) Å^3, space group *C2/m*, Z = 2, was solved by direct methods and refined to an *R* index of 5.6% for 1203 reflections measured with Mo*K*α X-radiation. There are four independent Pb^{2+} positions, with coordination numbers [7], [8], [9] and [10]. In the larger coordination-polyhedra ([9] and [10]), there are two subsets of bond lengths, one short (~2.46 Å) and one long (~3.05 Å); the short bonds all occur to one side of the central Pb^{2+} cation, indicative of a stereoactive lone-pair of electrons. In the smaller coordination-polyhedra ([7] and [8]), there is no obvious one-sided nature to the disposition of short bonds, suggesting that the lone-pair of electrons is not stereoactive in either of these coordination polyhedra. This suggests that the presence or absence of stereoactive lone-pair behavior is to a large extent dictated by the local stereochemistry (*i.e.*, bond-valence requirements) of the surrounding anions. There is one $(Cu\phi_6)$ octahedron that shows the usual [4+2] elongation associated with Jahn–Teller relaxation around the central Cu^{2+} cation. The structural unit of wherryite is a $[Cu(SO_4)(SiO_4)OH]$ chain of general stoichiometry $[^{[6]}M(TO_4)_2\phi]$; parallel chains are linked by interstitial Pb^{2+} cations, and there is an additional (SO_4) group bonded only to H and Pb^{2+} cations. The $[M(TO_4)_2\phi]$ chain is a common constituent of oxysalt minerals, being found in the brackebuschite, fornacite and vauquelinite groups. The above formula of wherryite is different from previous proposals. Cell dimension, space group and powder patterns indicate that wherryite and macquartite are isostructural.

Keywords: wherryite, crystal structure, lead, stereoactive lone-pair.

SOMMAIRE

Nous avons résolu la structure cristalline de la wherryite, $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, monoclinique, *a* 20.789(4), *b* 5.787(1), *c* 9.142(3) Å, β 91.24(2)°, *V* 1099.5(6) Å^3, groupe spatial *C2/m*, *Z* = 2, par méthodes directes, et porté l'affinement jusqu'à un résidu *R* de 5.6% en utilisant 1203 réflexions mesurées avec rayonnement Mo*K*α. La structure contient quatre positions indépendantes occupées par des atomes de Pb^{2+}, ayant une coordinence de [7], [8], [9] et [10], respectivement. Dans le cas des polyèdres où la coordinence est [9] ou [10], plus volumineux, il y a deux ensembles de longueurs de liaison, un où elles sont plus courtes (~2.46 Å), et un où elles sont plus longues (~3.05 Å); les liaisons plus courtes se trouvent toutes sur un côté du cation central, indication d'une paire d'électrons isolés stéréoactive. Dans les polyèdres plus petits, à coordinence [7] et [8], une telle asymétrie dans la disposition des liaisons n'est pas évidente, ce qui fait penser que dans ces polyèdres, la paire d'électrons isolés n'est pas stéréoactive. D'après cette observation, il semble que la présence ou l'absence d'une paire stéréoactive d'électrons est en grande partie décidée par les effets stéréochimiques locaux, c'est-à-dire, les exigeances des valences de liaisons des anions voisins. La structure contient un octaèdre $(Cu\phi_6)$ qui montre l'allongement [4 + 2] typique d'une décontraction due à l'effet de Jahn–Teller autour du cation de Cu^{2+} central. La trame structurale de la wherryite est une chaîne $[Cu(SO_4)(SiO_4)OH]$ ayant une stoechiométrie généralisée $[^{[6]}M(TO_4)_2\phi]$; de telles chaînes parallèles sont liées par des cations Pb^{2+} interstitiels; en plus, la structure contient un groupe (SO_4), lié à H et Pb^{2+} seulement. La chaîne $[M(TO_4)_2\phi]$ est présente dans plusieurs oxysels, par exemple dans les groupes de la brackebuschite, fornacite et vauquelinite. La formule chimique de la wherryite citée ici diffère des versions antérieures. D'après les dimensions de la maille, le groupe spatial et les clichés de diffraction X, la wherryite et la macquartite seraient isostructurales.

(Traduit par la Rédaction)

Mots-clés: wherryite, structure cristalline, plomb, paire d'électrons isolés stéréoactive.

INTRODUCTION

Wherryite is a lead–copper oxysalt mineral first described by Fahey *et al.* (1950) from the Mammoth mine, Arizona. They gave the formula of wherryite as $Pb_4Cu(CO_3)(SO_4)(OH,Cl)_2O$ with $Z = 4$. Strunz (1966) questioned the validity of wherryite as a mineral species, but McLean (1970) determined the powder pattern and cell dimensions of three separate samples of wherryite, firmly establishing it as a distinct species. McLean (1970) also noted a dimensional similarity between the cell parameters of wherryite and leadhillite $[Pb_4(CO_3)_2(SO_4)(OH)_2]$, with $a_w \approx a_L$, $2b_w \approx b_L$, $c_w \approx c_L$, leadhillite having space-group symmetry $P2_1/c$. As part of a general study of Cu^{2+} oxysalt minerals (Eby & Hawthorne 1993), the structure of wherryite has been solved and refined; the results are reported here.

EXPERIMENTAL

X-ray data collection

The material used for this work is from the Mammoth mine, Arizona; it was obtained from the Royal Ontario Museum, sample number M23619. The wherryite crystals are light green, anhedral, and occur together with diaboléite, minor chrysocolla and various lead carbonates and oxychloride minerals. The appearance, locality and paragenesis closely match those reported by Fahey *et al.* (1950). The crystal used for measurement of the cell dimensions and collection of the reflection intensities is a plate; it was mounted on a Nicolet *R*3*m* automated four-circle diffractometer, and the cell dimensions and orientation matrix were derived by least-squares methods from the setting angles of 25 aligned reflections. Intensity data were collected according to the method of Hawthorne & Groat (1985). A total of 1802 intensities was collected over the range $3 \leq 2\theta \leq 60°$. The data were corrected for absorption (psi-scan method), Lorentz, polarization and background effects, and reduced to structure factors; of the 1802 reflections measured, 1203 were classed as observed ($|F_o| > 5\sigma$). Experimental details are listed in Table 1; the cell dimensions closely match those reported for wherryite by McLean (1970).

TABLE 1. MISCELLANEOUS EXPERIMENTAL INFORMATION FOR WHERRYITE

a(Å)	20.789(4)	Crystal Size (mm)	0.11 x 0.11 x 0.06
b	5.787(1)	Radiation	Mo*K*α/Gr
c	9.142(3)	No. of intensities	1802
β(°)	91.24(2)	No. of $\lvert F_o\rvert > 5\sigma$	1203
V(Å³)	1099.5(6)	*R*(azimuthal) %	15.5 → 4.6
Sp. Gr.	*C*2/*m*	*R*(obs) %	5.6
μ(cm⁻¹)	551.6	*wR*(obs) %	6.4

Cell content: $2[Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{½}$, $w = 1$

Structure solution and refinement

Structure solution and refinement were done with the program system SHELXTL PC. The data gave an $|E^2-1|$ value of 0.925, compared with the ideal values of 0.968 and 0.736 for centrosymmetry and non-centrosymmetry, respectively; hence the space group *C*2/*m* was used in the structure solution. The structure

TABLE 2. FINAL PARAMETERS FOR WHERRYITE

Site	*x*	*y*	*z*	$^*U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.1434(1)	0	0.2632(2)	27(1)	29(1)	26(1)	26(1)	0	4(1)	0
Pb(2)	0.4739(1)	0	0.7061(2)	26(1)	28(1)	31(1)	21(1)	0	1(1)	0
Pb(3)	0.3419(1)	0	0.3212(2)	31(1)	28(1)	36(1)	28(1)	0	-1(1)	0
Pb(4)	0	0	0	32(1)	37(1)	28(1)	30(1)	0	-4(1)	0
Cu	1/4	1/4	0	23(1)	25(2)	21(2)	22(2)	0(2)	3(2)	2(2)
S(1)	0.2668(5)	0	0.6575(10)	21(3)	27(5)	19(5)	17(4)	0	4(3)	0
S(2)	0.4318(4)	1/2	0.3475(10)	21(3)	21(4)	21(5)	20(4)	0	3(3)	0
Si	0.3960(5)	0	-0.0089(11)	26(3)	28(5)	23(5)	26(5)	0	5(4)	0
O(1)	0.3192(13)	0	0.030(3)	27(8)	27(12)	17(13)	38(15)	0	9(11)	0
O(2)	0.3356(14)	0	0.615(3)	35(9)	41(16)	32(16)	32(15)	0	14(12)	0
O(3)	0.4173(8)	0.216(3)	-0.110(2)	24(5)	32(8)	25(9)	15(7)	0(7)	5(8)	5(7)
O(4)	0.2235(13)	0	0.531(3)	33(9)	33(14)	40(17)	25(13)	0	-9(11)	0
O(5)	0.3850(14)	1/2	0.222(3)	35(9)	36(15)	44(18)	24(13)	0	-5(11)	0
O(6)	0.4351(15)	0	0.148(3)	32(9)	43(18)	26(15)	26(13)	0	7(12)	0
O(7)	0.2576(9)	0.206(4)	-0.251(2)	31(6)	38(10)	36(11)	19(8)	-1(8)	7(7)	0(9)
O(8)	0.4236(10)	0.293(5)	0.438(2)	45(8)	40(11)	62(17)	33(10)	9(11)	-2(9)	-6(11)
O(9)	0.5036(13)	1/2	-0.285(4)	43(11)	19(13)	54(22)	56(20)	0	3(13)	0
O(10)	0.3091(12)	1/2	-0.029(3)	25(7)	25(12)	30(14)	21(12)	0	-5(10)	0

$^*U_{ij} = U_{ij} \times 10^3$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN WHERRYITE

Pb(1)-O(2)d	x2	3.13(1)	Pb(3)-O(1)		2.69(3)
Pb(1)-O(3)a	x2	2.49(2)	Pb(3)-O(2)		2.69(3)
Pb(1)-O(4)		2.93(3)	Pb(3)-O(4)		3.16(1)
Pb(1)-O(7)a	x2	2.67(2)	Pb(3)-O(5)e	x2	3.17(1)
Pb(1)-O(9)a		3.07(3)	Pb(3)-O(6)		2.53(3)
Pb1-O(10)a		2.36(3)	Pb(3)-O(7)a	x2	2.74(2)
			Pb(3)-O(8)	x2	2.61(2)
Pb(2)-O(2)		2.98(3)			
Pb(2)-O(3)b	x2	2.43(2)	Pb(4)-O(3)a	x4	2.56(2)
Pb(2)-O(6)c		2.29(3)	Pb(4)-O(5)f	x2	3.17(3)
Pb(2)-O(8)c	x2	3.05(2)	Pb(4)-O(9)f	x2	2.61(3)
Pb(2)-O(8)	x2	3.14(2)			
Pb(2)-O(9)b	x2	2.96(1)	Cu-O(1)	x2	2.06(2)
			Cu-O(10)	x2	1.92(2)
Si-O(1)		1.64(3)	Cu-O(7)	x2	2.32(2)
Si-O(3)	x2	1.62(2)			
Si-O(6)		1.64(3)	S(1)-O(2)		1.49(3)
<Si-O>		1.63	S(1)-O(4)		1.45(3)
			S(1)-O(7)	x2	1.47(2)
O(10)-O(5)		2.75(4)			1.47
O(10)-O(7)		3.17(4)			
			S(2)-O(5)		1.49(3)
			S(2)-O(8)	x2	1.47(3)
			S(2)-O(9)		1.47(3)
					1.48

Equivalent positions: a: ½-x, ½-y, -z; b: x, y, 1+z; c: 1-x, y, 1-z; d: ½-x, ½-y, 1-z; e: x, -y, z; f: -½+x, -½+y, z.

was solved by direct methods. The solution with the highest figure of merit gave the positions of the heavy cations, and the remaining cations and anions were located by difference-Fourier techniques. No carbonate group was found. An atomic position was found with a scattering power of approximately $Z = 13$ *e* and surrounded by a tetrahedron of oxygen atoms; the mean cation–anion distance is ~1.63 Å. These findings indicate that this cation position is occupied by Si. Consequently, the position was designated as Si and represented by the scattering factor for Si. The structure refined to an *R* index of 5.6% with an anisotropic displacement model and ionized scattering factors for all atoms. Statistical weighting schemes were tried, but led to no improvement in the refinement, and the unit-weight model was adopted. Final parameters are listed in Table 2, and selected interatomic distances are given in Table 3. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2. A bond-valence summation (Table 4) was calculated from the parameters of Brown (1981).

DESCRIPTION OF THE STRUCTURE: COORDINATION OF CATIONS

S positions

There are two S positions, each coordinated by four oxygen atoms in distorted tetrahedral arrangements. There are significant differences between individual

TABLE 4. BOND-VALENCE* TABLE FOR WHERRYITE

	Pb(1)	Pb(2)	Pb(3)	Pb(4)	Cu	S(1)	S(2)	Si	H	Σ
O(1)			0.220		0.341$^{\times 2}$↓→			0.944		1.846
O(2)	0.096$^{\times 2}$↓→	0.126	0.220			1.435				1.973
O(3)	0.340$^{\times 2}$↓	0.391$^{\times 2}$↓		0.287$^{\times 4}$↓				1.003$^{\times 2}$↓		2.021
O(4)	0.137		0.092			1.627				1.856
O(5)			0.090$^{\times 2}$↓→	0.089$^{\times 2}$↓			1.452		0.46	2.18
O(6)		0.535	0.312					0.966		1.813
O(7)	0.228$^{\times 2}$↓		0.198$^{\times 2}$↓		0.167$^{\times 2}$↓	1.512$^{\times 2}$↓				2.105
O(8)		0.094$^{\times 2}$↓ 0.112$^{\times 2}$↓	0.260$^{\times 2}$↓				1.543$^{\times 2}$↓			2.009
O(9)	0.107	0.131$^{\times 2}$↓→		0.260$^{\times 2}$↓			1.530			2.159
O(10)	0.432				0.513$^{\times 2}$↓→				0.54	2.00
Σ	2.004	2.117	1.940	1.846	2.042	6.086	6.068	3.916		

* calculated with the curves of Brown (1981)

and mean S–O bond lengths, and although the standard deviations are large (arising from the presence of a large amount of very heavy scattering species in the crystal), the bond-valence arrangement in Table 4 does indicate that these (SO_4) distortions do occur as a result of local bond-valence requirements of the anions.

Si position

There is one *Si* position, surrounded by four oxygen atoms in a slightly distorted tetrahedral arrangement. The <*Si–O*> distance is 1.63 Å, in good agreement with the value expected (Brown & Gibbs 1969) for a (SiO_4) tetrahedron with a mean anion-coordination number of 3.75 (Table 4). The anisotropic displacement factors at the *Si* position are well behaved (*i.e.*, not excessively large or small, as would be the case if the scattering species at this site were wrongly identified).

Cu position

There is one *Cu* position, surrounded by six anions in a distorted octahedral arrangement; four of the anions are O^{2-}, and the other two anions are $(OH)^-$. The ($Cu\phi_6$) octahedron (ϕ: unspecified anion) shows strong elongation of one set of axial bonds, as is common for Cu^{2+} in octahedral coordination (Eby & Hawthorne 1993); as is well known, this is due to spontaneous relaxation associated with a partly occupied degenerate electronic state (the Jahn–Teller effect) of Cu^{2+} in holosymmetric octahedral coordination.

Pb positions

There are four distinct *Pb* positions in wherryite; the local coordinations are shown in Figure 1. All interatomic distances less than 3.2 Å are shown, and are given in Tables 3 and 4.

Pb(1) lies on the mirror plane and is surrounded by nine anions between 2.38 and 3.13 Å. As shown in Table 4, all listed distances must be considered as bonds if the bond-valence requirements of the *Pb*(1) cation are to be satisfied. As can be seen from Figure 1, the five short *Pb*(1)–*O* bonds (mean = 2.54 Å) are all to one side of the cation. The remaining long bonds (mean = 3.07 Å) are on the side opposite from the short bonds, and also are arranged such that

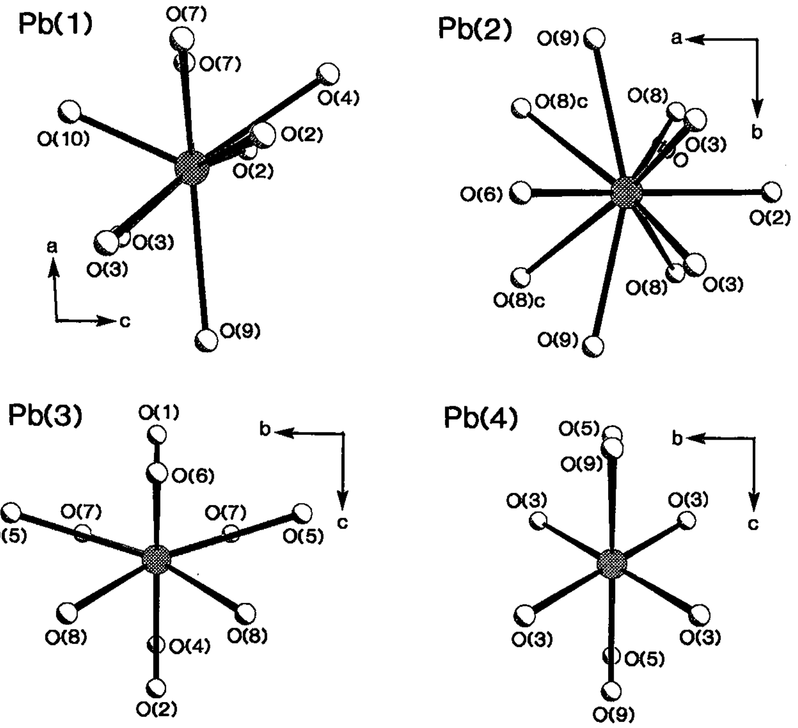

FIG. 1. The Pb coordinations in wherryite; Pb is the central cross-hatched atom, and the oxygen anions are the partly shaded circles.

there is a large solid angle not occupied by any anion (Fig. 1). This type of geometrical arrangement, typical of Pb^{2+} with a stereoactive lone-pair of electrons, suggests that the lone pair of the *Pb*(1) cation is stereoactive.

Pb(2) lies on the mirror plane and is surrounded by ten anions between 2.29 and 3.14 Å. The longest listed *Pb*(2)–*O* distance could be ignored without adversely affecting the bond-valence sum around the central cation [and there is a *Pb*(2)–*Si* contact of 3.10 Å], but as we will see later, such distances must be considered as bonds in the *Pb*(3) polyhedron. There are three short bonds (mean = 2.38 Å) and seven long bonds (mean = 3.04 Å). The three short bonds occur on one side of the cation (Fig. 1), and the seven long bonds occur on the opposite side. The general arrangement again suggests a stereoactive lone-pair of electrons; the space available for the lone pair is less than for *Pb*(1), but the lone pair presumably occurs between the four *Pb*(2)–*O*(8) bonds.

Pb(3) lies on the mirror plane and is surrounded by eight anions at distances from 2.53 to 3.17 Å. However, the distribution of distances is very different from the cases of *Pb*(1) and *Pb*(2). There are seven bonds with very similar *Pb*(3)–*O* distances (mean = 2.66 Å, range 2.53 – 2.74 Å) and three long bonds (mean = 3.17 Å). As can be seen from Figure 1, there is no obvious one-sided nature to the arrangement of anions around *Pb*(3); the seven short bonds are fairly isotropically disposed about the central cation, and the three long bonds occur at the vertices of a pseudo-equilateral triangle that is coplanar with the central cation. This suggests that the lone pair is *not* stereoactive in *Pb*(3). Are the long bonds significant? Omitting the long bonds gives a bond-valence of 1.668 v.u., compared to the ideal value of 2.0 v.u.; this indicates that these long contacts must be considered as bonds.

Pb(4) occurs at the junction of the mirror plane and the twofold screw axis at a center of symmetry. It is surrounded by eight anions, six of which occur at intermediate distances (mean = 2.58 Å, range 2.56 – 2.61 Å) and two of which occur at longer distances (mean = 3.17 Å). Again, the coordination is not one-sided (Fig. 1), suggesting that the lone pair is not stereoactive. It is possible that the central *Pb*(4) cation could be locally displaced off the center of symmetry to achieve a one-sided coordination; however, the anisotropic displacement factors show no evidence of such positional disorder, and we must conclude that the lone pair is not stereoactive in the *Pb*(4) cation. The bond-valence sum around *Pb*(4) is 1.846 v.u. (Table 4), a value that is already anomalously low; ignoring the two long contacts reduces this sum to 1.668 v.u., indicating that we must consider *Pb*(4) as [8]-coordinated.

Pb coordination

We have argued, based on cation bond-valence requirements, that *Pb–O* contacts of up to 3.17 Å must be considered as significant bonds. If the bond-valence curve for Pb^{2+}–*O* were wrong, this would invalidate this particular argument, as having stronger shorter bonds and no long bonds also would lead to bond-valence satisfaction around the cations. However, the incident bond-valence requirements around the anions constrains this situation. In particular, consider the *O*(4) anion (Table 4). This is bonded to *S*(1) and *Pb*(1), and receives a bond-valence of 1.764 v.u. from these cations. The only other contact is a long (~3.17 Å) one with *Pb*(3), which brings the incident bond-valence sum at *O*(4) to 1.86 v.u., very low but much more reasonable than the value of 1.761 v.u. that would result if the *Pb*(3)–*O*(4) contact was not considered as a bond. Similar arguments can be made for some of the other anions, indicating that we must consider the long *Pb–O* contacts as bonds.

The hydrogen content of wherryite

We can write the general formula of wherryite as $Pb^{+}Cu^{+}(SO_4)_4(SiO_4)_2\phi_2$. The chemical analysis of Fahey *et al.* (1950) indicated the presence of hydrogen, and the above formula is neutral if ϕ = OH; ϕ was so assigned in this study.

The structure solution indicates that *O*(1) is the OH anion. However, the bond-valence sum to *O*(10) (neglecting H) is 1.46 v.u. (Table 4), indicating that there must be a very strong hydrogen-bond to other anions. Inspection of the short *O*(10)–*O* contacts (assuming that the donor and acceptor anions do not form an edge of a cation-coordination polyhedron) shows that only the *O*(5) and *O*(7) anions are within possible range of hydrogen bonding (Table 3). The short *O*(10)–*O*(5) distance, combined with the large bond-valence deficiency at *O*(5) (Table 4), suggest a very strong hydrogen-bond between *O*(10) and *O*(5).

DESCRIPTION OF THE STRUCTURE: POLYHEDRAL LINKAGES

The $(Cu\phi_6)$ octahedra link by sharing two *trans* edges to form a $[Cu\phi_6]$ linear chain (Fig. 2). The vertices of adjacent octahedra are linked *via* (SiO_4) groups that assume a staggered configuration along the length of the chain. The edge of the (SiO_4) tetrahedron is less than the separation of adjacent octahedral vertices for an $[M\phi_4]$ chain of maximal ribbon symmetry, and consequently there is a cooperative tilting of octahedra along the chain, promoting both the octahedron–tetrahedron [*i.e.*, $(Cu\phi_6)$ and (SiO_4)] linkage and the staggered arrangement of tetrahedra (Fig. 2). Sulfate tetrahedra link to one of the vertices of the edge shared between adjacent

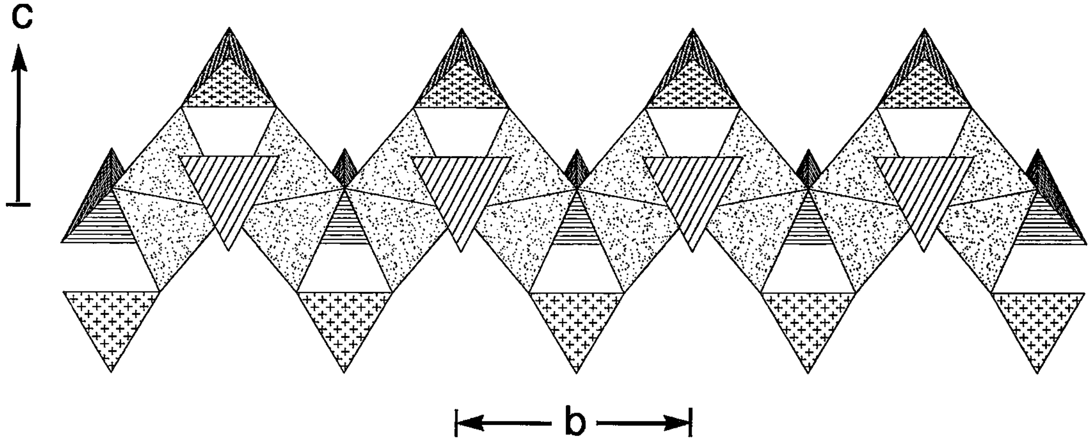

FIG. 2. The $[M(T\phi_4)_2\phi]$ chain in wherryite, viewed down [100]; $(Cu\phi_6)$ octahedra are random-dot-shaded, (SO_4) tetrahedra are cross-shaded, and (SiO_4) tetrahedra are line-shaded.

octahedra, and these tetrahedra also assume a staggered configuration along the chain. The resulting unit has the specific stoichiometry $[Cu\phi(SO_4)(SiO_4)]$, and the general stoichiometry $[M(T\phi_4)_2\phi]$.

Figure 3 shows the structure with these $[M(T\phi_4)_2\phi]$ chains viewed end-on. The chains are arranged in a square-lattice pattern, and are linked *via* the Pb cations. The other sulfate group [involving the *S*(2) cation] is "floating" in a sea of Pb cations, with no direct connection to the $[M(T\phi_4)_2\phi]$ chains.

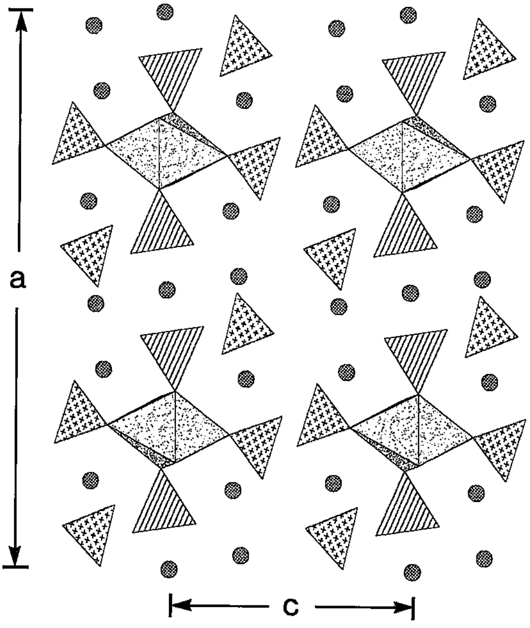

FIG. 3. The $[M(TO_4)_2\phi]$ chains in wherryite viewed end-on down [010]; shading as in Figures 1 and 2.

RELATION TO OTHER STRUCTURES

Hawthorne (1985) has described the structural hierarchy in minerals based on $[M(T\phi_4)_2\phi_n]$ structural units. There are three principal groups, the brackebuschite group, the fornacite group and the vauquelinite group (Table 5), based on an $[M(T\phi_4)\phi]$ chain of the type shown in Figure 2. This particular $[M(TO_4)_2\phi]$ chain shows very variable composition across the three groups, with M = Al, Cu, Fe^{2+} and Fe^{3+}, and T = P, As, V^{5+}, S, Cr^{6+} and Si. However, the interstitial cation is almost always Pb^{2+}, with Ba and Sr (and *REE* for the silicate) as less common constituents. This is also the case for wherryite (and macquartite), which have Pb^{2+} as the interstitial cation. Now Ca is a much more common divalent cation than Pb^{2+}, Sr or Ba. Why don't any of these minerals contain Ca as the interstitial cation? As discussed by Hawthorne (1990, 1992), this is due to the valence-matching principle, whereby the Lewis acidity of the interstitial cations(s) has to match the aggregate Lewis basicity of the structural unit. This is the case for Pb^{2+}, Ba and Sr (with Lewis acidities of ~0.22 v.u.), but is not so for Ca (with a Lewis acidity of ~0.28 v.u.).

The ideal repeat-distance of the $[M(TO)_4)_2\phi]$ chain is approximately 5.9 Å. This can be identified as the *b* axis in all minerals listed in Table 5, and in wherryite and macquartite. The chain has 2_1-screw symmetry along its length, and this finds expression in the space-group symmetries of the various structure-types: $P2_1/m$ and $C2/m$.

The formulae of wherryite and macquartite

The formula of wherryite was reported as $PbCO_3 \cdot 2PbSO_4 \cdot Pb(Cl,OH)_2 \cdot CuO$ (Fahey *et al.* 1950), which can be rearranged to give $Pb_4Cu(CO_3)(SO_4)_2$

TABLE 5. MT$_2\varphi_n$ MINERALS BASED ON THE INFINITE [M(TO$_4$)$_2\varphi$] CHAIN

Mineral	Formula	a(Å)	b(Å)	c(Å)	β(°)	S.G.	Reference
Arsenbrackebuschite	$Pb_2[Fe^{2+}(AsO_4)_2(H_2O)]$	7.763(1)	6.046(1)	9.022(1)	112.5(1)	$P2_1/m$	(1)
Arsentsumebite	$Pb_2[Cu(SO_4)(AsO_4)(OH)]$	7.84	5.92	8.85	112.6	$P2_1/m$	–
*Brackebuschite	$Pb_2[Mn(VO_4)_2(H_2O)]$	7.68	6.18	8.88	111.8	$P2_1/m$	(2)
Gamagarite	$Ba_2[Fe^{3+},Mn)(VO_4)_2(OH)]$	7.88(1)	6.17(1)	9.15(1)	112.7(1)	$P2_1/m$	(3)
Goedkenite	$Sr_2[Al(PO_4)_2(OH)]$	7.26(2)	5.74(2)	8.45(2)	113.7(1)	$P2_1/m$	(4)
Tsumebite	$Pb_2[Cu(PO_4)(SO_4)(OH)]$	7.85	5.80	8.70	111.5	$P2_1/m$	(5)
*Fornacite	$Pb_2[Cu(AsO_4)(CrO_4)(OH)]$	8.101(7)	5.892(11)	17.547(9)	110.00(3)	$P2_1/c$	(6)
Molybdofornacite	$Pb_2[Cu(AsO_4)MoO_4)(OH)]$	8.100(5)	5.946(3)	17.65(1)	109.17(5)	$P2_1/c$	–
Törnebohmite	$(REE)_2[Al(SiO_4)_2(OH)]$	7.383(3)	5.673(3)	16.937(6)	112.04(2)	$P2_1/c$	(7)
Vauquelinite	$Pb_2[Cu(PO_4)(CrO_4)(OH)]$	13.754(5)	5.806(6)	9.563(3)	94.56(3)	$P2_1/n$	(8)

References: (1) Hofmeister & Tillmanns (1978). (2) Donaldson & Barnes (1955). (3) Basso *et al.* (1987). (4) Moore *et al.* (1975). (5) Nichols (1966). (6) Cocco *et al.* (1967). (7) Shen & Moore (1982). (8) Fanfani & Zanazzi (1968).

$(OH,Cl)_2O$ (McLean 1970). According to the structure determination and refinement, wherryite has the formula $Pb_7Cu_2(SO_4)_4(SiO_4)_2(OH)_2$, with both Pb and Cu in the divalent state as required for overall electroneutrality. The difference between this formula and the formula previously accepted for wherryite is the presence of $(SiO_4)^{4-}$ groups and the absence of $(CO_3)^{2-}$ groups. The appearance, locality of occurrence, paragenesis, cell dimensions and space group confirm the material examined by us as wherryite. As discussed above, the presence of Si and the absence of C are incontrovertibly demonstrated by the structure solution and refinement. In addition, neither the structural arrangement nor the stoichiometry of wherryite is consistent with the replacement of a (SiO_4) group by a (CO_3) group, as this would produce a very large bond-valence discrepancy at the *O*(1) or *O*(6) anions, and would lead to a non-neutral stoichiometry. Thus we suggest that the original chemical analysis was in error in this respect, and that wherryite is a sulfate–silicate mineral rather than a sulfate–carbonate mineral.

Macquartite (Williams & Duggan 1980) has similar cell dimensions (a 20.81, b 5.84, c 9.26 Å, β 91.8°) and the same space group as wherryite. The formula of macquartite was given as $Pb_3Cu(CrO_4)SiO_3(OH)_4{\cdot}2H_2O$. By analogy with the present results on wherryite, the formula for macquartite should probably be written as $Pb_7Cu_2(CrO_4)_4(SiO_4)_2(OH)_2$.

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