The crystal structure of mawbyite, $PbFe_2(AsO_4)_2(OH)_2$

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Abstract

The crystal structure of mawbyite, $PbFe_2(AsO_4)_2(OH)_2$ has been refined. The mineral is monoclinic, $C2/m$ with $a = 9.066(4)$, $b = 6.286(3)$ $c = 7.564(3)$ Å, $\beta = 114.857(5)°$, $Z = 2$; the structure has been refined to a conventional $R = 4.3\%$ using 361 observed reflections [$I > 3\sigma(I)$]. The structure contains chains of edge-sharing $Fe(O,OH)_6$ octahedra which are linked by AsO_4 tetrahedra and Pb atoms in distorted square antiprismatic co-ordination. The hydrogen bonding network in the structure has been modelled using bond valence calculations. Mawbyite is confirmed to be isostructural with tsumcorite and dimorphous with carminite and the relationship between these two structures is discussed.

KEYWORDS: mawbyite, crystal structure, Broken Hill, New South Wales, arsenate.

Introduction

MAWBYITE, ideally $PbFe_2(AsO_4)_2(OH)_2$, was described by Pring et al. (1989) from the Kintore opencut, Broken Hill, New South Wales, where the mineral occurs with segnitite, duftite, mimetite and other arsenates. Mawbyite is the ferric analogue of tsumcorite and is also dimorphous with carminite.

The crystal structure of carminite was determined by Finney (1963) and has recently been refined by Kharisun et al. (1996) and also by Olmi and Sabelli (1995). The crystal structure of tsumcorite was determined by Tillmanns and Gebert (1973). At the time of the description of mawbyite, Pring et al. (1989) were unable to locate a suitable crystal for structure determination and thus they were only able to discuss, in general terms, the topological relationships between the structures of carminite, tsumcorite and mawbyite. As part of a more detailed crystal chemistry study of carminite, mawbyite and other transition metal arsenates of lead we have undertaken a refinement of the mawbyite structure by single crystal X-ray diffraction methods.

Experimental

A number of mawbyite crystals from Broken Hill, New South Wales were taken from the type specimen (SAM G16062) for use in crystal structure determination. The average composition of these crystals as reported by Pring et al. (1989) was $Pb_{1.11}(Fe_{1.94}Zn_{0.07})(AsO_4)_2(OH,O)_2$. Most of the crystals were very small and not suitable for single crystal structure determination; however, several of the 'larger' crystals were examined under the polarizing microscope and a number were mounted for single crystal X-ray photography. Laue symmetry

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and the systematic absences suggested the space group could be either $C2/m$ or $P2_1/m$ or subgroups thereof.

Data were collected on a Siemens Smart CCD detector system at Madison, Wisconsin, USA, using graphite monochromated Mo-$K\alpha$ radiation. The data were collected for one hemisphere and absorption corrected. In addition to the set of reflections expected for the space group $C2/m$ ($C2$, Cm) there was a group of very weak reflections for $h+k$ odd, l odd (but not $h+k$ odd, l even). The sum of the intensity of all these reflections was less than 3% of the total and had the data been collected on a conventional diffractometer they would not have been observed. A major advantage of the CCD detector system is that the backgrounds are well determined, and weak reflections which would not be normally statistically significant are measurable.

The data, including the very weak reflections, appeared to indicate the space group $P2_1/m$ (or $P2_1$ or Pm) related to a parent structure (based on the strong reflections) of $C2/m$ (or $C2$ or Cm). A possible modulation of $C2/m$ to produce $P2_1/m$ would imply the destruction of the inversion at the origin of $C2/m$ while the inversion at 1/4,1/4,0 is retained. However, refinement of the structure in the space group $P2_1/m$ would not proceed satisfactorily, the lowest residual R for this space group being 0.16. Several models where proposed and tested to account for the weak additional reflections.

These models included: (1) a 1/2**c** stacking fault of layers perpendicular to **a***. (2) orientational disorder since the angle between **c** and 2**a** + **c** is 89.98°. (3) a generalized disorder model where disorder effects the relative scales of the classes of reflection data.

None of the above models would refine satisfactorily. However, it was eventually shown that the additional weak reflections were due to twinning. It is possible to twin about the (100) plane so that $\mathbf{a}' = -(\mathbf{a} + \mathbf{c})$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = \mathbf{c}$, [2$\mathbf{a}'$ + $\mathbf{c}'$ = $-(2\mathbf{a} + \mathbf{c})$]. We note that only when l is even do the reflections include intensity from both twin components. The weak $h+k$ odd, l odd reflections are twin related to $h+k$ even, l odd reflections allowing $C2/m$ to be the symmetry of a single twin component.

A twin parameter of $\alpha = 0.109(2)$ was obtained for the structural model $(1-\alpha)|F(hkl)|^2 + \alpha |F(-h-1,-k,l)|^2$ and the twin structure model was refined using the program RAELS92 (A.D. Rae, Australian National University, 1992). The AsO$_4$ group was refined using a TLX rigid body thermal parameter model constrained to 10 variables by site symmetry (Rae, 1975). A total of 552 independent reflections were collected of which 361 reflections, with I>3σ(I), were used in the refinement of the twin structure. The final residual was R = 0.043. The detailed value for subsets of data were:

127 $h+k$ even, l even reflections	R = 0.0349
132 $h+k$ even, l odd reflections	R = 0.0375
103 $h+k$ odd, l odd reflections	R = 0.0907

The remaining 191 reflections included all those 132 reflections with $h+k$ odd, l even that have zero intensity in the twin model. Crystal data are listed in Table 1.

The hydrogen atom of the hydroxide group could not be located in the difference Fourier maps but it was placed in a calculated position (see below) and its parameters not refined. Twinning of the mawbyite structure on (100) creates a tetrahedral cation site, on the twin composition plane, which is then occupied by Zn rather than Fe. We assume O(1)–H is eliminated or replaced by a water molecule at a longer distance.

TABLE 1. Crystal data and results of crystal structure refinement for mawbyite

Crystal data:	
Formula	[Pb(Fe$_{1.94}$Zn$_{0.07}$)(AsO$_4$)2(OH,H$_2$O]
Crystal system	Monoclinic
Space group	$C2/m$
a (Å)	9.066(4)
b (Å)	6.286(3)
c (Å)	7.564(3)
β	114.857(5)°
V (Å^3)	391.1(3)
D$_c$ (g cm^{-3})	5.365
Z	2
μ (mm^{-1})	35.50
λ (Mo-K$_\alpha$) (Å)	0.71073
Crystal dimension (mm)	0.01 × 0.01 × 0.05
Data Collection:	
Diffractometer	Siemens CCD system
θ_{max} (°)	30
h	$-9 \to 9$
k	$-3 \to 6$
l	$-8 \to 7$
Total reflections	665
Number after averaging	552
R for averaging	0.040
Refinement:	
Refinement on	F
R	0.043
Reflection used in refinement	(I > 3σ(I)) 361
Number of parameters refined	51
Goodness of fit S	1.1
$(\Delta/\sigma)_{max}$	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	± 3.0 e

TABLE 2. Fractional atomic coordinates and equivalent isotropic displacement parameters of mawbyite

Atom	X	Y	Z	Ueq*/Uiso ($\mathring{A}^2$)
Pb	0	0	0	0.025(1)
Fe(Zn)	0.25	0.25	0.50	0.013(1)
As	0.9176(3)	0.50	0.2131(3)	0.016(16)
O(1)	0.3421(18)	0.50	0.4101(19)	0.014(3)
O(2)	0.3103(15)	0	0.3553(21)	0.018(13)
O(3)	0.0370(11)	0.2826(17)	0.2701(13)	0.018(14)
O(4)	0.2197(17)	0.50	0.0127(20)	0.028(26)
H	0.2973	0.50	0.2646	

H coordinates were calculated (see text).

The final atomic coordinates and isotropic equivalent displacement parameters are summarized in Table 2 and anisotropic displacement parameters are given in Table 3. The selected bond length and angles are presented in Table 4. A summary of the bond valences of the atoms is given in Table 5. A full list of observed and calculated structure factors for the final refinement are given in Table 6*.

Description of the Structure

In general terms the mawbyite structure consists of infinite chains of edge-sharing $Fe(O,OH)_6$ octahedra parallel to b which are linked via AsO_4 tetrahedra to form layers of composition $[Fe(O,OH)_6AsO_4)]$ parallel to the a—b plane (Fig. 1). Within the chains, the FeO_6 octahedra share an edge along mirror planes at y = 0 and 0.5. Figure 2, a projection down the b axis, shows the connection between parallel chains of octahedra. Two vertices of the AsO_4 tetrahedron share O atoms with the FeO_6 octahedra and another vertex shares an O atom with

that of an FeO_6 octahedron in the next chain. The remaining vertex, O(4), is bonded only to Pb and As. In Fig. 1 the arsenate groups appear to sit atop one another, however they are not in contact as is clearly shown in Fig. 2. The distance between the two vertices (O(1)—O(1)) of overlying As tetrahedra is 3.17 $\mathring{A}$. The structure of tsumcorite, the Zn analogue, is very similar to that of mawbyite; all coordinates are within 0.039 $\mathring{A}$ when the two sets of atomic parameters are compared. The largest difference is in the z coordinate of O(2), which is 0.039 $\mathring{A}$. The structure therefore confirms the topology determined for tsumcorite by Tillmanns and Gebert (1973) and the isostructural relationship between mawbyite and tsumcorite.

Calculation of the bond valences for the structure suggests that the O(1) atom is the OH group as it has the lowest bond valence of all the oxygen atoms. This assignment is confirmed by stereochemical considerations as O(1) is the only oxygen atom coordinated to only Fe and not As or Pb. The OH group hydrogen bonds with O(4). The calculated H position gives an

TABLE 3. Anisotropic atomic displacement parameters of mawbyite

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.024(1)	0.022(1)	0.028(1)	0.00	−0.003(1)	0.00
Fe(Zn)	0.012(2)	0.008(2)	0.017(2)	0.001(1)	−0.002(1)	−0.013(1)
As	0.011(11)	0.016(31)	0.021(7)	0.000	0.001(8)	0.000
O(1)	0.003(6)	0.023(10)	0.015(8)	0.00	−0.004(1)	0.00
O(2)	0.005(13)	0.021(21)	0.028(7)	0.00	0.000(7)	0.00
O(3)	0.016(7)	0.014(31)	0.024(9)	0.004(3)	−0.001(4)	−0.008(3)
O(4)	0.024(20)	0.037(10)	0.023(8)	0.00	−0.004(13)	0.00

U_{ij} values defined relative to orthonormal axes parallel to a,b,c* so that the isotropic equivalent is given by $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

*A copy of this table may be obtained, on request, from the Editor.

TABLE 4. Selected bondlengths and angles for mawbyite

Pb—O(3) ×4	2.620(9)			
—O(4) ×2	2.583(14)			
—O(2) ×2	2.963(13)			
mean	2.697			
Fe—O(1)×2	2.027(9)		As—O(2)	1.727(14)
—O(2)×2	2.114(10)		—O(3) ×2	1.683(10)
—O(3)×2	1.993(9)		—O(4)	1.637(10)
mean	2.045		mean	1.685
FeO$_6$ octahedra			AsO$_4$ tetrahedra	
O(1)—Fe—(3) ×2	89.3(5)		O(4)—As—O(3) ×2	113.1(4)
O(2)—Fe—(3) ×2	90.5(4)		O(4)—As—O(2)	105.6(7)
O(2)—Fe—(3) ×2	89.5(4)		O(2)—As—O(3) ×2	108.1(4)
O(1)—Fe—(3) ×2	90.7(5)		O(3)—As—O(3)	108.6(7)
O(1)—Fe—(2) ×2	80.2(4)			
O(1)—Fe—(2) ×2	99.8(5)			

O(1) —H contact of 1.00 Å and O(4)....H contact of 1.73 Å (see Brown and Altermatt, 1985). This hydrogen bonding scheme is in accord with that reported for tsumcorite by Tillmanns and Gebert (1973). The bond valence sum for Fe^{3+}, which occupies the octahedral site, is low and this indicates that most of the Zn^{2+} shown in the chemical analysis also occupies this site. Twinning about the (100) plane leads to the formation of a tetrahedral site on the twin plane (Fig. 3). Using apparent valence arguments, there is reason to believe that the four coordinate site on the twin plane is occupied by Zn^{2+} atoms rather than Fe^{3+}. We assume that O(1)—H is eliminated or replaced by a water at a longer distance. However some zinc must also occupy the octahedral sites, as the density of twin planes in the mawbyite crystal is low. The result of the analysis of the bond valence are presented in Table 5.

The Pb^{2+} in mawbyite/tsumcorite is a matter of some interest. It is coordinated by eight oxygen atoms arranged at the corners of a distorted square antiprism with average Pb—O bond lengths of 2.70 Å. The Pb co-ordination in mawbyite is more symmetrical than it is in most Pb-oxysalts (Kharisun, 1996). In the majority of Pb oxysalts the stereo-chemical activity of the Pb^{2+} lone pair leads to distorted co-ordination, with the Pb—O distances one side being longer than the other.

As noted above, there is a close topological relationship between the structures of carminite and mawbyite/tsumcorite. In general the frameworks of both structures are similar, in that they are built up by the chains of octahedra which are linked by the AsO$_4$ tetrahedra to form layers of FeO$_6$ octahedra—AsO$_4$

tetrahedra. The layers of octahedra-tetrahedra are connected by PbO$_8$ distorted square antiprisms and H bonding to form a three dimensional network.

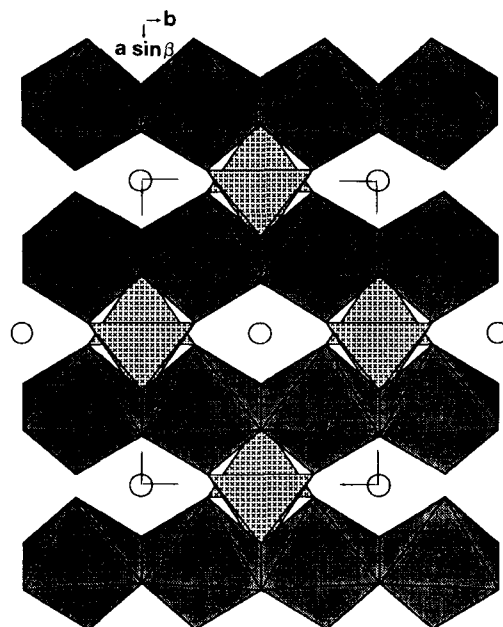

FIG. 1. Schematic diagram of the mawbyite structure down [001] showing the polyhedral likages. The Pb atoms are shown as open circles.

TABLE 5. Empirical bond-valence for mawbyite

	Pb	Fe	As	H	Sum
O(1)	—	0.49(× 2) (× 2)	—	0.87	1.85
O(2)	0.10 (× 2)	0.39(× 2) (× 2)	1.11	—	1.99
O(3)	0.25 (× 4)	0.53 (× 2)	1.25 (× 2)	—	2.03
O(4)	0.28 (× 2)	—	1.42	0.12	1.82
Sum	1.76	2.82	5.03	0.99	

See Brown and Altermatt (1985).
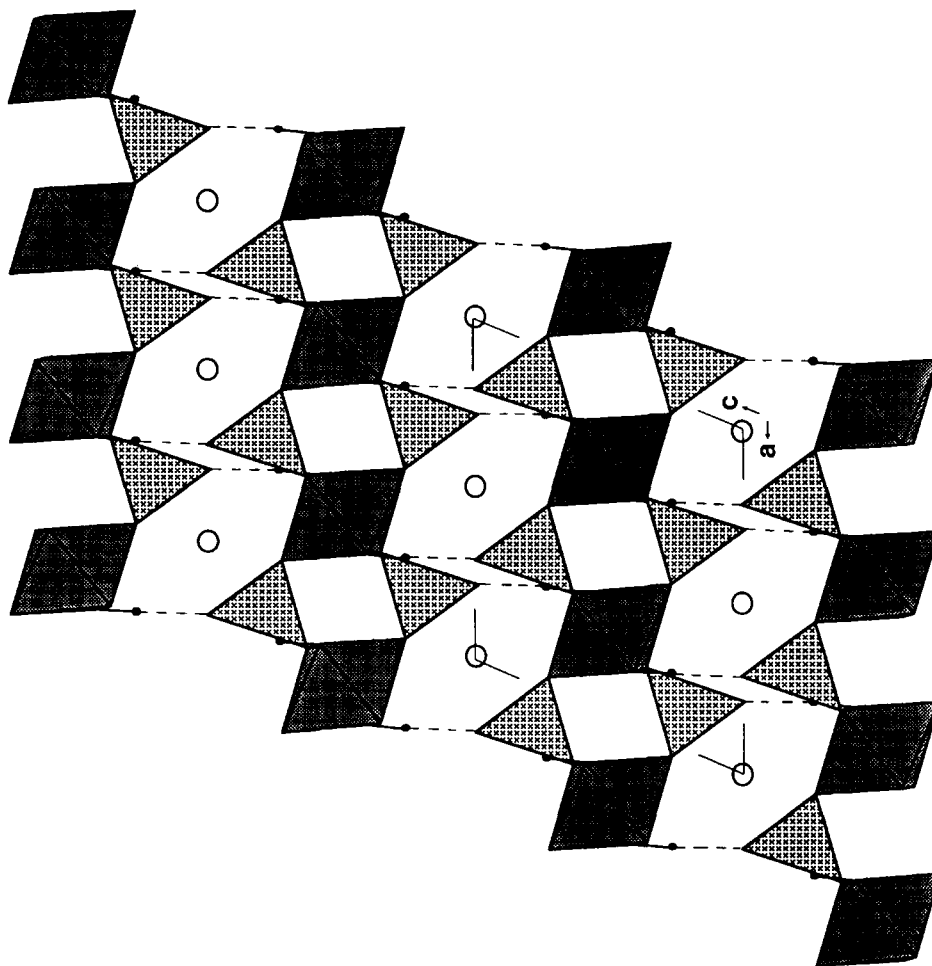
FIG. 2. Schematic diagram of the mawbyite structure down [010] showing the polyhedral likages and the proposed hydrogen bonding network. The Pb atoms are shown as open circles.
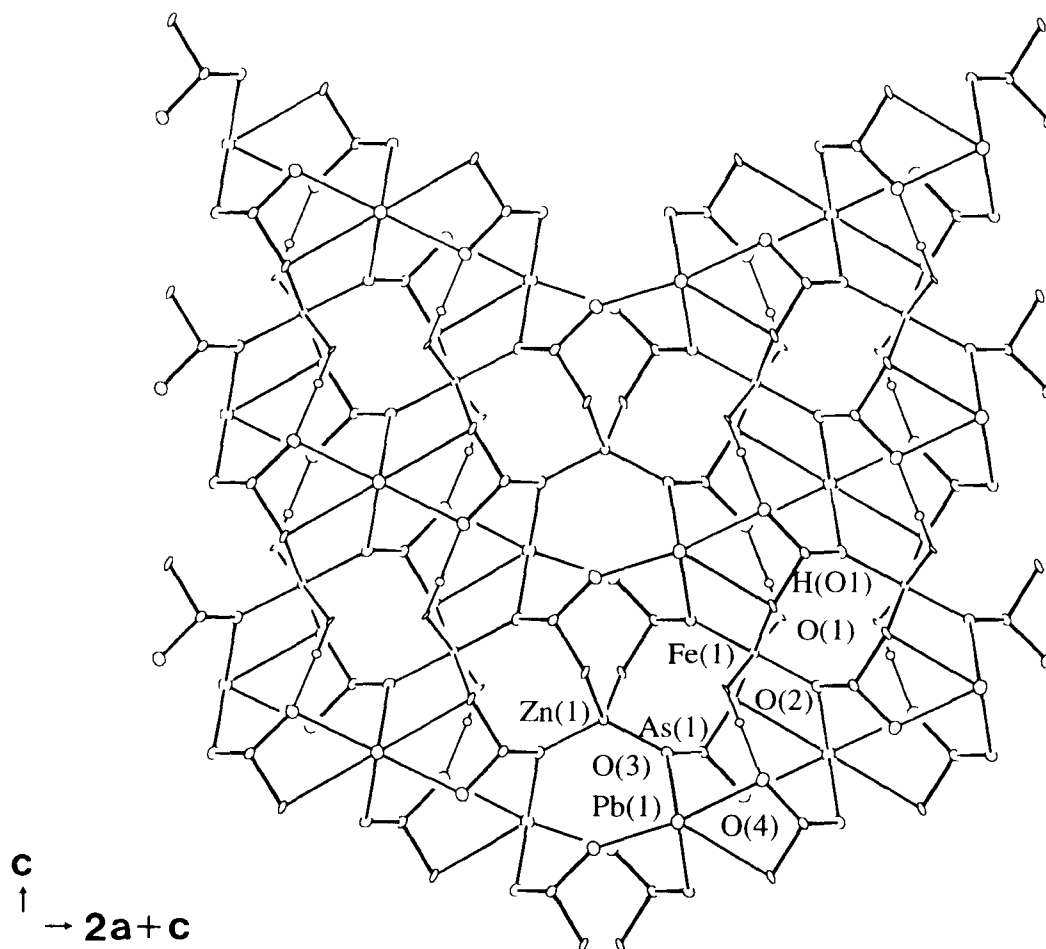
FIG. 3. Schematic diagram of twinning on the (100) plane showing the tetrahedral Zn^{2+} sites.

The principal difference between the two structures lies in the configuration of the FeO_6 octahedral chains, in mawbyite/tsumcorite they are continuous edge sharing chains while in carminite the octahedra share alternately edges and corners forming stepped two up two down chains. (see Fig. 4) Observations of local mineral associations for carminite and mawbyite specimens suggests that carminite is formed under strongly acidic conditions (pH 3), while mawbyite appears to form in a less acidic environment (pH 5), (Pring *et. al.*, 1989). It seems possible that the topological differences of the FeO_6 chains are related to the pH of the crystallizing solution.

There are two crystallographically distinct $Pb-O_8$ co-ordination polyhedra in carminite, one is more symmetrical than the Pb site in mawbyite while the

other (Pb—O(2) of Kharisun *et al.*, 1996) is very similar both in geometry and bond lengths to the Pb in mawbyite.

A number of other minerals appear to be structurally related to mawbyite, even though there are differences in the unit cells; helmutwinklerite $PbZn_2(AsO_4)_2 \cdot 2H_2O$ (Süsse and Schnorrer, 1980), thometzekite $Pb(Cu,Zn)_2(AsO_4)_2 \cdot 2H_2O$ (Schmetzer *et al.*, 1985) and gartrellite $Pb(Cu,Zn)_2(AsO_4)_2 \cdot 2H_2O$ (Nickel *et al.*, 1989). Nickel *et. al.* (1989) suggested that gartrellite, thometzekite, helmutwinklerite and tsumcorite have a common triclinic subcell. However no full crystal-structure analyses have been reported of gartrellite, thometzekite or helmutwinklerite so the relationship between these structures still remains unclear.
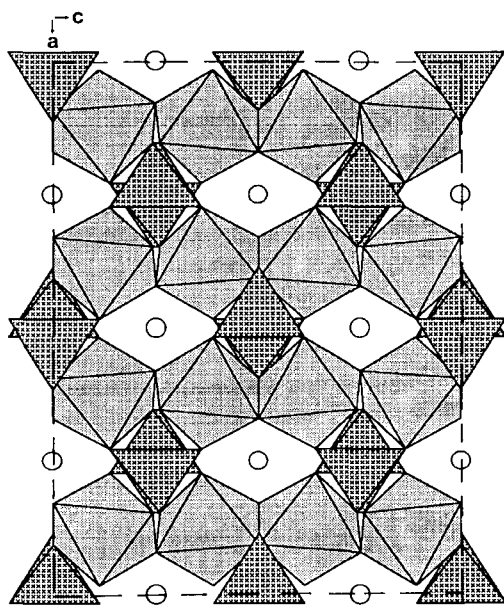
FIG. 4. Schematic diagram of the carminite structure down [010] showing the polyhedral likages. The Pb atoms are shown as open circles (After Kharisun et al., 1996).

Acknowledgements

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