The crystal structure of carminite: refinement and bond valence calculations

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Abstract

The crystal structure of carminite, $PbFe_2(AsO_4)_2(OH)_2$ has been refined. The mineral is orthorhombic, *Cccm* with $a = 16.591(2)$, $b = 7.580(1)$, $c = 12.285(1)$ Å, $Z = 8$; the structure has been refined to a conventional R = 3.3% using 913 observed reflections [$I > 2\sigma(I)$]. The structure contains stepped chains of edge-sharing pairs of $Fe(O,OH)_6$ octahedra; these chains 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.

KEYWORDS: carminite, crystal structure refinement, hydrogen bonding network.

Introduction

CARMINITE is a lead ferric hydroxy-arsenate which occurs with other lead arsenate minerals and is formed as an oxidation product of sulphide and arsenide ores. It was originally described by Sandberger in 1850 from the Louise Mine, Horhausen, Westerwald, Germany (Palache *et al.*, 1951), but has also been reported from a number of other localities including Tsumeb, Namibia (Gebhard, 1991), Mapimi, Mexico (Foshag, 1937) and Broken Hill, N.S.W. (Birch and van der Hayden, 1988). Foshag (1937) showed that the mineral was orthorhombic and determined the formula to be $PbFe_2(AsO_4)_2(OH)_2$. The crystal structure was determined by Finney (1963) but several aspects of the structure and crystal chemistry were left unclear; in particular, it was not possible to distinguish between the two possible space groups, centric *Cccm* or non-centric *Ccc2*.

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Pring *et al.* (1989) described mawbyite as a monoclinic dimorph of carminite and established, in general terms, the topological relationship between the two structures. 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 carminite structure by single crystal X-ray diffraction methods. We have also explored the hydrogen bonding network in carminite with the aid of the bond valence approach of Brown (1981) using the EUTAX program of O'Keeffe (1991). This program also proved to be a convenient method of readily establishing the crystal chemical reliability of the structure refinement.

Experimental

A number of carminite specimens from Broken Hill, N.S.W and Mapimi, Mexico were examined from the collections of the South Australian Museum. Several suitable single crystals were selected under the optical microscope from a specimen from Broken Hill, N.S.W. (SAM G18020). The orthorhombic symmetry of the mineral was confirmed by

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precession photography, and the systematic absences indicated that the space group was either $Cccm$ or

TABLE 1. Crystal data, data collection information, and refinement detail for carminite

Crystal data:

Formula	$PbFe_2(AsO_4)_2(OH)_2$
M_r	630.734
Orthorhombic	
Space Group	$Cccm$
a (Å)	16.591(2)
b (Å)	7.580(1)
c (Å)	12.285(1)
V (Å^3)	1545.0(3)
Z	8
D_{calc} (g cm^{-3})	5.405
μ (cm^{-1})	341.91
λ (Mo Kα) (Å)	0.71073
Crystal dimension (mm)	$0.15 \times 0.10 \times 0.03$
Shape	tabular
Colour	brownish red

Data collection:

Diffractometer	Enraf-Nonius CAD4 Turbo
θ_{max} (°)	30
h	$0 \rightarrow -23$
k	$10 \rightarrow -10$
l	$17 \rightarrow -17$
Total reflection measured	4324
Number after averaging	1175
R for averaging (F^2)	0.055

Absorption correction analytical	(Meulenaer and Tompa, 1965)
Transmission factors:	
min	0.03
max	0.26

Refinement:

Refinement on	F
Weight	$1/\sigma^2(F)$
R	0.033
R_w	0.037
Reflections used in refinement (I>2σ(I))	913
Number of parameters refined	52
H atoms not located	
Goodness of fit S	1.88(5)
$(\Delta/\sigma)_{max}$	0.0005
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	$-3.62, 3.51$

$Ccc2$. Crystal data and details of the data collection are given in Table 1. The XTAL 3.2 program system (Hall et al. 1992) was used for all crystallographic calculations, with CRYLSQ (Olthof-Hazekamp, 1992) being used for the refinement. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). Anomalous dispersion corrections were applied. The atomic coordinates from Finney's determination in the centric space group $Cccm$ were used as a starting model for the structure. The initial cycle of refinement gave R = 0.28 which reduced to R = 0.09 after further cycles of least squares refinement with isotropic displacement parameters. The final refinement with anisotropic displacement parameters for the heavy atoms and isotropic displacement parameters for the oxygen atoms yielded R = 0.033 and R_w = 0.037. It was not possible to locate the hydrogen atoms of the hydroxide groups in the refinement. The matter of whether the space group was $Cccm$ or $Ccc2$ was carefully considered. The starting model was refined in $Ccc2$ using data averaged in the point group $mm2$ and including an absolute structure parameter (Flack, 1983). The refinement of 88 variables converged with R = 0.037, R_w = 0.041, S = 2.41 and with a Flack parameter not significantly different from 0.5. We concluded, therefore, that the structure is centrosymmetric and that the correct space group is $Cccm$. Further details of the final refinement in $Cccm$ are given in Table 1.

Description of the structure and bonding.

The final atomic coordinates and displacement parameters for the refinement in $Cccm$ are summarized in Table 2 and selected bond length and angles are presented in Table 3. The final list of observed and calculated structure factor amplitudes is given in Table 4[1].

The refinement confirmed the basic topology of the structure as reported by Finney (1963); however significant differences in positional parameters for a number of atoms were found. The largest differences were associated with the positions of the OH groups; O(6) is shifted 0.16 Å along b and O(7) 0.14 Å along a. Differences in the positions of Fe, As and other O atoms were all less than 0.06 Å. In general terms the structure consists of chains of $Fe(O,OH)_6$ octahedra which are linked via AsO_4 tetrahedra and PbO_8 square antiprisms. The $Fe(O,OH)_6$ octahedra form edge-shared pairs, the common edge being on a mirror plane, and these pairs are linked to others via corner-sharing, giving two-up-two-down chains

[1] A copy of this table is available upon request from the editor.

TABLE 2. Final atomic coordinates for carminite

Positional parameters for the atoms

	x/a	y/b	z/c	Ueq./Uiso (Å^2)
Pb(1)	0	0	0.250	0.0145(2)
Pb(2)	0.25	0.75	0	0.0115(2)
Fe	0.37751(7)	0.1300(1)	0.13516(8)	0.0088(2)
As(1)	0.04286(6)	0.7384(1)	0	0.0070(3)
As(2)	0.21189(6)	0	0.25	0.0054(2)
O(1)	0.0172(3)	0.2469(6)	0.1114(5)	0.009(1)
O(2)	0.0923(4)	0.5401(9)	0	0.011(1)
O(3)	0.1121(4)	−0.1041(9)	0	0.013(1)
O(4)	0.1512(3)	0.1758(6)	0.2415(5)	0.013(1)
O(5)	0.2723(3)	−0.0034(6)	0.1390(4)	0.0087(9)
O(6)	0.1690(4)	0.2387(8)	0	0.006(1)
O(7)	0.4222(4)	0	0.25	0.011(1)

running parallel to c (Fig. 1). The two AsO_4 tetrahedra are crystallographically distinct, As(1) is linked through all 4 vertices to the $Fe(O,OH)_6$ octahedra while As(2) shares only three of its four oxygens with the octahedra, while O(3) is bonded only to As(2) and Pb.

The bond length-bond valence method (Brown, 1981; O'Keeffe, 1991) has been used to analyse the crystal chemistry of the structure. Bond valence calculations provide a simple way of monitoring the quality of the refinement and also provide an insight into the nature of distortions from ideal coordination. The atomic bond valence sums calculated from Finney's (1963) coordinates and this refinement are summarized in Table 5. The detailed bond valence analysis of the refined structure is presented in Table 6. It is clear from Table 5 that the bond valence sums for the current refinement are much closer to their ideal values than those from the refinement by Finney (1963). This is particularly so for the AsO_4 tetrahedra; Finney's refinement found that for As(1) the mean As—O distance was 1.74 Å and for As(2), 1.64 Å while the current refinement shows that the two AsO_4 tetrahedra are very similar with mean As—O distances of 1.69 and 1.68 Å, though to be fair to Finney he noted that because of the experimental uncertainty in his As–O distances the differences were not significant. The abnormal bond valence sums for As atoms calculated from Finney's coordinates reflect the uncertainty in the As–O distance therein.

The bond valence calculations provide a numerical method of establishing the location of the hydroxide groups and hydrogen bonding networks within the structure, as it was not possible to locate the H atoms directly in the structure refinement (Brown, 1992; Brown and Altermatt, 1985). There are three O atoms

TABLE 3. Selected bond lengths (Å) and angles (deg) for carminite

Pb (1) – O		
	– O(1) × 4	2.547(5)
	– O(4) × 4	2.842(5)
mean		2.695
Pb(2) – O		
	– O(3) × 2	2.540(7)
	– O(5) × 4	2.558(5)
	– O(2) × 2	3.063(7)
mean		2.680
Fe – O		
	– OH(7)	1.874(3)
	– O(1)	2.001(5)
	– O(5)	2.018(5)
	– O(4)	2.025(6)
	– OH(6)	2.084(4)
	– O(2)	2.161(4)
mean		2.027
As(1) – O		
	– O(3)	1.657(7)
	– O(1) × 2	1.697(6)
	– O(2)	1.713(7)
mean		1.691
As(2) – O		
	– O(4) × 2	1.673(5)
	– O(5) × 2	1.693(5)
mean		1.683

Bond angles

O(1) – As(1) – O(1)	107.51(26)
O(1) – As(1) – O(2) × 2	109.79(20)
O(3) – As(1) – O(1) × 2	111.14(20)
O(3) – As(1) – O(2)	107.48(35)
O(4) – As(2) – O(4)	106.0(26)
O(4) – As(2) – O(5) × 2	108.53(26)
O(4) – As(2) – O(5) × 2	113.23(25)
O(5) – As(2) – O(5)	107.43(26)
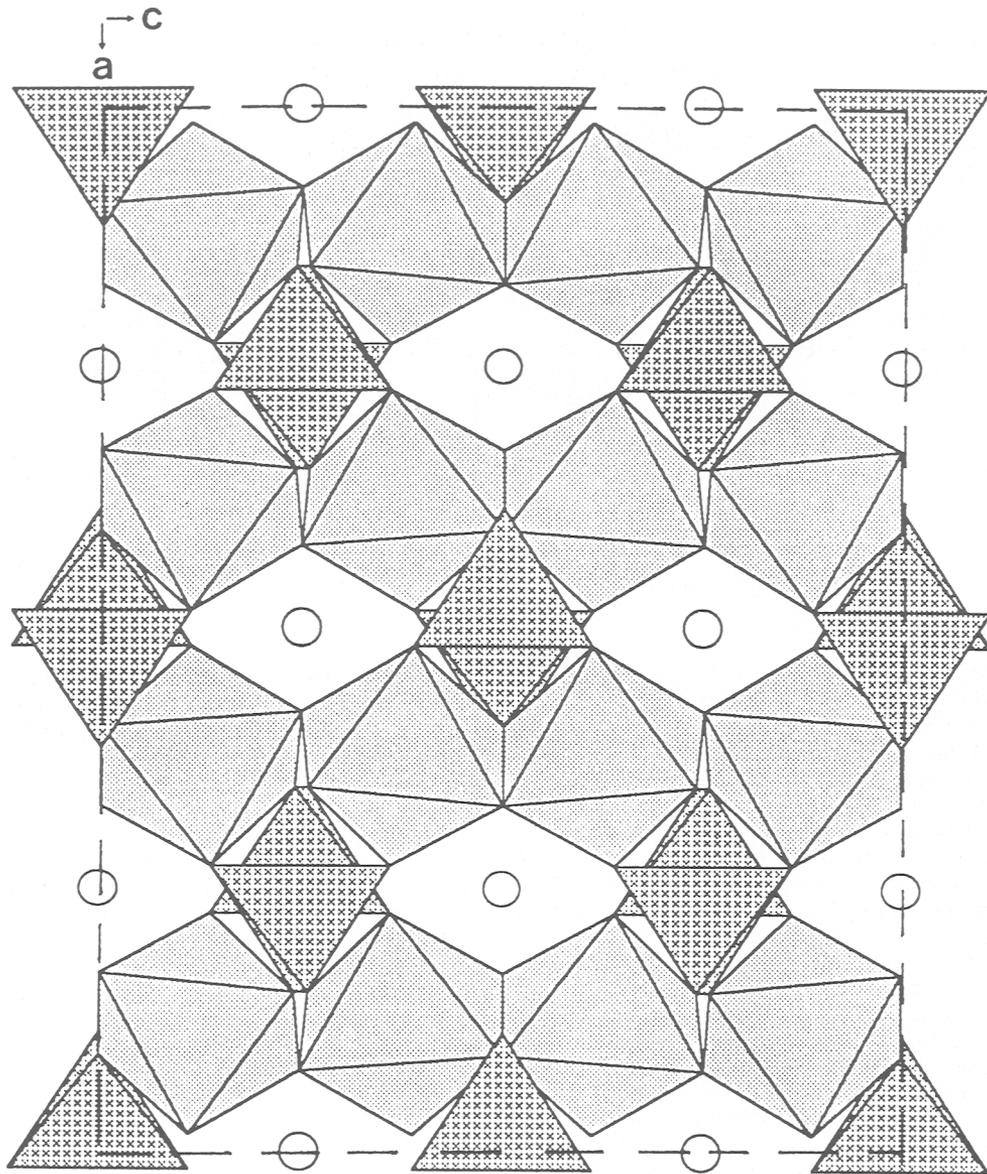
FIG. 1. Schematic view of the carminite structure down [010] showing the polyhedral linkages. The Pb atoms are shown as open circles.

which have low bond valence sums: O(3), O(6) and O(7) (Table 5). Two of the oxygen atoms, O(6) and O(7), were identified by Finney (1963) as OH groups on the basis of their coordination; they are only coordinated to Fe and have the shortest metal–O distances. The bond valence sums for O(6) and O(7), without the contributions of H, are 0.84 and 1.46 *vu*

(valence units), respectively, while that of O(3) is 1.66 *vu*. The H bonds link pairs of O(7) atoms between the strings of Fe(O,OH)$_6$ octahedra. The O(7)–O(7) distance is 2.58 Å which is consistent with one H atom between the two O(7) atoms. If the H atom sits exactly midway between the two O(7) atoms it would occupy a 4(b) special position at 0.5,
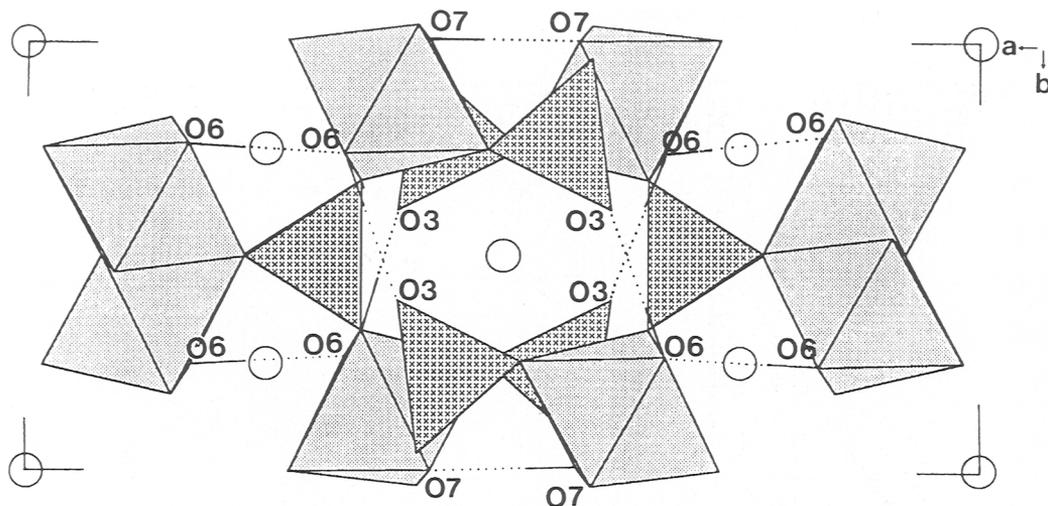
FIG. 2. Schematic view of the carminite structure down [001] showing the polyhedral linkages and the proposed hydrogen bonding network. The Pb atoms are shown as open circles.

0,0, 0.25. This would give two O–H distances of 1.29 Å with a bond valence sum value of 0.4 *vu*, and would bring the bond valence sum for O(7) to 1.86 *vu*. Displacement of H from this special position is more likely. If it were displaced along *a* by 0.26 Å in a disordered manner, O–H distances of 1.03 Å and 1.55 Å would result with bond valence values of 0.82 and 0.18 *vu*, respectively, bringing the valence of H to 1 *vu* and the O valence on average to 1.97 *vu*. There are other hydrogen bonds: O(6)–H....O(3) and O(6)–H....O(6). Based on the linearity and length of the O–H...O linkage and by assuming an O(6)–H bond of 1.05 Å and O(3)...H contact of 1.75 Å, the bond valence contributions for O(6) and O(3) are 0.64 *vu* and 0.2 *vu*, respectively (Brown and Altermat, 1985). The O(6)–O(6) distance is 2.69 Å and with H–O distances of 1.03 Å and 1.66 Å, the bond valence values are 0.82 and 0.10 *vu*. From these simple calculations it is clear that the H atoms are associated with O(7), O(6) and O(3) but are disordered. The hydrogen bonding networks are shown in Fig. 2.

An unusual feature of the carminite structure is the symmetry of the Pb(1) coordination. The Pb(1)O$_8$ square antiprisms have four short contacts 2.547 Å and four long contacts 2.842 Å. In a survey of Pb coordination in some 60 Pb-oxysalt minerals, the coordination of Pb(1) in carminite was found to be the most regular and symmetric (Kharisun, unpublished results). The C-centred orthorhombic symmetry of the structure and the relatively high symmetry of the Pb co-ordination suggested the

possibility of morehedral twinning of a primitive monoclinic cell. The transformation from the C centred orthorhombic to monoclinic cell would be:

$$a_m = \tfrac{1}{2} a_o + \tfrac{1}{2} b_o$$
$$b_m = c_o$$
$$c_m = b_o$$

with the monoclinic cell parameters: $a = 9.120$, $b = 12.285$, $c = 7.580$ Å and $\beta = 114.56°$. Evidence of twinning was sought by electron diffraction and

TABLE 5. Summary of atomic bond valance sums for the carminite structure

	Finney	This work
Pb(1)	2.01	1.80
Pb(2)	2.03	1.98
Fe	2.97	3.01
As(1)	4.36	4.96
As(2)	5.59	5.04
O(1)	1.94	2.04
O(2)	1.73	1.95
O(3)	1.68*	1.66*
O(4)	2.02	1.93
O(5)	2.13	2.03
O(6)	1.03*	0.84*
O(7)	1.27*	1.46*

* without H bonding contribution

TABLE 6. Empirical bond valence sums for the atoms in the refinement of the carminite

	Pb(1)	Pb(2)	Fe	As(1)	As(2)	Sum
O(1)	0.31 (×4)		0.52 (×2)	1.21	–	2.04
O(2)	–	0.08 (×2)	0.34(×2)	1.19	–	1.95
O(3)	–	0.31 (×2)	–	1.35	–	1.66
O(4)	0.14 (×4)	–	0.49	–	1.30 (×2)	1.93
O(5)	–	0.30 (×4)	0.51	–	1.22 (×2)	2.03
O(6)	–	–	0.42(×2)	–	–	0.84
O(7)	–	–	0.73(×2)	–	–	1.46
Sum	1.80	1.98	3.01	4.96	5.04	

transmission electron microscope imaging, using both dark and bright field imaging but no evidence for structural twinning was found.

Finney (1963) was unable to establish whether the structure was centric (*Cccm*) or non-centric (*Ccc2*). He noted that in the event that carminite was non-centric, then neither O(2) nor O(3) would lie on a mirror plane and that both oxygens would be bonded to Fe and thus the two environments of the AsO$_4$ groups would be equivalent. Finney (1963) also noted that the temperature factors for the atoms lying on the mirror plane; As(1), O(2), O(3) and O(6), behaved erratically during refinement and suggested that the mirror may not be real. Although he was unable to find any evidence contrary to the existence of the mirror plane he concluded on the basis of uniformity of environment that the structure was slightly non-centric.

As noted above, this matter of whether the space group was centric or non-centric was considered in the refinement and we conclude on the basis of absolute structure parameter that the structure is centrosymmetric and that the correct space group is *Cccm*.

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