Mawbyite, a new arsenate of lead and iron related to tsumcorite and carminite, from Broken Hill, New South Wales

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Abstract

Mawbyite is a new lead iron zinc arsenate, the Fe analogue of tsumcorite, from the Kintore Opencut, Broken Hill, New South Wales, Australia. The new mineral forms drusy crusts on fractures and in small cavities in spessartine- and quartz-rich host rocks. Associated minerals include beudantite-corkite, adamite-olivenite, mimetite, bayldonite, duftite, hidalgoite, and pharmacosiderite. Mawbyite has formed from the oxidation of primary sulfides and arsenides under less acidic pH conditions compared to its apparent dimorph carminite.

Mawbyite crystals are usually "dogtooth" to prismatic, more rarely tabular, up to 0.2 mm long, and dominated by forms {110}, {$\bar{1}$01}, and {001}. The color ranges from orange-brown (for compositions with Fe:Zn ≈ 1:1) to bright reddish brown (for compositions close to the pure Fe end-member). The crystals are transparent to translucent, with adamantine luster and orange-yellow streak, are nonfluorescent, and have an estimated Mohs hardness of 4. There is a prominent cleavage on {001}; fracture is conchoidal.

A range in composition was detected by electron microprobe, from zincian mawbyite (with Fe:Zn ≈ 1:1) to close to the Fe end-member (Fe:Zn = 1.94:0.06). The general formula is $Pb(Fe_{2-x},Zn_x)(AsO_4)_2(OH)_{2-x}(H_2O)_x$, with $0 < x < 1$, based on 10 oxygen atoms and with all Fe assumed to be trivalent. The type material has a composition CuO 0.23, ZnO 6.74, Fe_2O_3 18.18, Al_2O_3 0.13, CaO 0.13, PbO 35.77, P_2O_5 0.16, As_2O_5 35.07, H_2O (by difference) 3.59, total 100.00 wt%. The simplified formula is close to $Pb(Fe_{1.5}Zn_{0.5})(AsO_4)_2(OH)_{1.5}(H_2O)_{0.5}$.

The strongest lines in the X-ray powder-diffraction pattern for the type composition are {d_{obs}, I_{obs}, hkl} 4.647 (100) ($\bar{1}$11); 4.458 (30) ($\bar{2}$01); 3.245 (100) ($\bar{1}$12); 3.136 (20) (020); 2.860 (40) (021); 2.724 (70) ($\bar{3}$11); and 2.546 (60) ($\bar{3}$12), (112). The X-ray data were indexed on a monoclinic cell with $a = 9.052(5)$, $b = 6.277(4)$, $c = 7.580(3)$ Å, $\beta = 114°34'(2)$, $V = 391.6(4)$ Å³, and $Z = 2$. The probable space group is $C2/m$. The calculated density is 5.53(2) g/cm³ for the type composition.

Mawbyite is chemically and structurally related to tsumcorite and the pure ferric end-member appears to be dimorphous with carminite. The unit cells of monoclinic mawbyite and orthorhombic carminite are related by $a_{maw}\sin\beta = \frac{1}{2}a_{carm}$; $b_{maw} = \frac{1}{2}c_{carm}$; $c_{maw} = b_{carm}$. Optical properties for mawbyite could not be measured in full; the refractive indices for the type material range from ~1.94 to >2. Crystals are length-fast, and pleochroism is faint from brown to reddish brown. The name is for Sir Maurice Mawby (1904–1977).

Introduction

Tsumcorite was originally described by Geier et al. (1971) from Tsumeb, Namibia; it has subsequently been found in several other localities including the Beltana zinc-lead deposit, Puttapa, South Australia (Elliot et al., 1988). Geier et al. (1971) gave the formula of tsumcorite as $PbZnFe(AsO_4)_2 \cdot H_2O$. However, the crystal-structure determination of Tillmanns and Gebert (1973) showed that Zn and Fe occupy the same crystallographic site and that the formula is $Pb(Zn,Fe)_2(AsO_4)_2(H_2O,OH)_2$. The analysis of tsumcorite from Tsumeb showed Zn to be dominant, and the Puttapa material is also Zn-dominant.

The occurrence at the Kintore Opencut, Broken Hill, New South Wales, is the first for the Fe-dominant end-member. The mineral has been named mawbyite in honor of Broken Hill–born Sir Maurice Mawby CBE (1904–1977), in recognition of his outstanding contribution to the Australian mining industry and to the preservation and general knowledge of the minerals of Broken Hill. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, In-

ternational Mineralogical Association. Type specimens are held in the collections of the South Australian Museum and the Museum of Victoria.

OCCURRENCE

Mawbyite occurs in the Kintore Opencut, a large mining development that straddles three of the original mining leases at Broken Hill, Blocks 9, 10, and 11. The opencut has been operated by Minerals, Mining and Metallurgy Ltd. since 1984 to recover ore remnants and stope-fill left behind by the underground mining operations of the late 1800s and early 1900s. The recent quarrying operations at Kintore have exposed more of the oxidized zone of the no. 2 and no. 3 lenses of the Broken Hill orebody. The complex secondary mineralogy has recently been discussed in detail by Birch and van der Heyden (1988).

The new mineral appears to be restricted to a small zone of several cubic meters at the southern end of the opencut, on the 250-m R.L. bench, about 35–40 m below the existing surface. South Mine grid coordinates for the occurrence are 225 m north and 120 m west. Mawbyite occurs in an As-rich reaction halo within the Main Shear. The principal rock type is a friable to compact granular metamorphic rock composed almost entirely of spessartine and quartz (the so-called "garnet sandstone" of the Broken Hill lode horizon). The mineral forms drusy pale orange-brown to reddish-brown crusts on fractures in the "garnet sandstone" and lines solution cavities in massive quartz. The most conspicuous mineral associated with mawbyite is a yellowish-green member of the corkite-beudantite series, forming a thin crust on which mawbyite crystals have grown. Other minerals observed either with or in close proximity to mawbyite include adamite-olivenite, duftite, mimetite, bayldonite, hidalgoite, pharmacosiderite, and an undescribed copper-iron-lead arsenate. Manganese oxides or goethite may form the substrate for mawbyite.

PHYSICAL AND OPTICAL PROPERTIES

Mawbyite ranges in color from pale brown through orange-brown to reddish brown, with a close correlation between color and composition. The pure Fe end-member is bright reddish brown, while the composition with the most Zn (Fe:Zn ≈ 1:1) is orange-brown. The streak is orange-yellow and does not appear to vary greatly with composition. The luster is adamantine, and crystals are transparent to translucent. No fluorescence was observed under either short- or long-wave ultraviolet light. Mawbyite exhibits a well-developed cleavage parallel to {001} and a conchoidal fracture. The Mohs hardness is about 4, and the calculated density, which varies slightly with composition, is 5.53(2) g/cm³ for the composition $Pb(Fe_{1.5}Zn_{0.5})(AsO_4)_2(OH)_{1.5}(H_2O)_{0.5}$.

Mawbyite occurs in a number of habits, the most common being "dogtooth" crystals, up to 0.15 mm long and dominated by the forms {$\bar{1}$01} and {1$\bar{1}$0}, with minor {001} (Fig. 1). The mineral also occurs as coatings and

scattered clusters of prismatic crystals up to 0.2 mm long (Fig. 2); as hemispherical, cylindrical, and sheaflike aggregates with a platy, spongy appearance (Fig. 3); and as tabular crystals forming V-shaped twins with composition plane (100). Thin compact crusts of mawbyite have also been observed.

The optical properties of mawbyite, like the color, vary considerably with composition; the refractive indices increase with increasing Fe content. All the refractive indices of the pure-Fe end-member are above 2.00. For the composition $Pb(Fe_{1.5}Zn_{0.5})(AsO_4)_2(OH,H_2O)_2$, the refractive indices range from ~1.94 to greater than 2.00. Because of the small crystal size, it was not possible to determine the $2V$ or the optical orientation; crystals are length-fast. Mawbyite exhibits faint pleochroism from brown to reddish brown, the slow ray having the reddish hue.

CHEMISTRY

Chemical analyses of mawbyite were obtained using a JEOL electron microprobe with an electron-beam accelerating voltage of 15 kV and a specimen current of 0.020 μA. The following standards were used: hematite (Fe), sphalerite (Zn), galena (Pb), arsenopyrite (As), fluorapatite (P), wollastonite (Ca), synthetic corundum (Al), and metallic copper (Cu). No other elements with an atomic number greater than 8 were detected. Water could not be determined owing to the small amount of material of any one composition available; therefore it was not possible to determine whether the end-member composition is anhydrous.

Representative analyses of mawbyite are presented in Table 1; they illustrate the range in Fe and Zn contents and show little other variation. The simplified general formula for mawbyite is $Pb(Fe_{2-x}Zn_x)(AsO_4)_2(OH)_{2-x}(H_2O)_x$ with $0 < x < 1$, calculated on the basis of 10 oxygen atoms and with all Fe assigned to the ferric oxidation state. This assumption is supported by the mineral's color, its association with minerals that contain only ferric iron, and by the crystal-structure study of tsumcorite by Tillmanns and Gebert (1973). Mawbyite is the Fe analogue of tsumcorite, $Pb(Zn_{2-x}Fe_x)(AsO_4)_2(H_2O)_{2-x}(OH)_x$ and the monoclinic dimorph of carminite, $PbFe_2(AsO_4)_2(OH)_2$. Although for practical purposes the term mawbyite applies to the end-member composition, $PbFe_2(AsO_4)_2(OH)_2$, the type material of mawbyite has the empirical formula

$$Pb_{1.03}(Fe^{3+}_{1.49}Zn_{0.53}Cu_{0.02}Al_{0.02})_{\Sigma2.06}(As_{1.95}P_{0.01})_{\Sigma1.96}H_{2.6}O_{10}$$
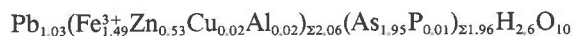
calculated on the basis of 10 oxygens. The simplified formula is $Pb(Fe_{1.5}Zn_{0.5})(AsO_4)_2(OH)_{1.5}(H_2O)_{0.5}$.

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction pattern of mawbyite was recorded using a 100-mm-diameter Guinier-Hägg camera, monochromated Cu$K\alpha$ radiation, and Si as an internal standard. The pattern, which is very similar to that of tsumcorite, was indexed with reference to the tsum-
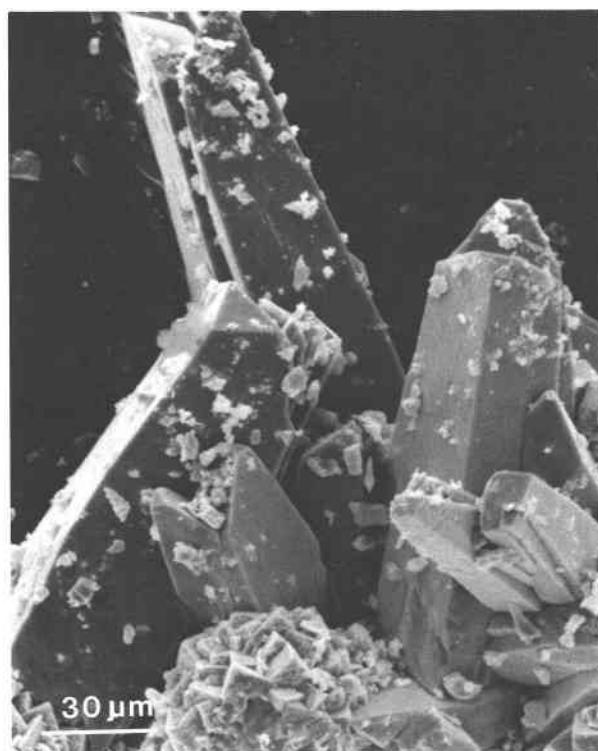
Fig. 2. Group of typical "dogtooth" mawbyite crystals. Largest crystal is 0.15 mm long.
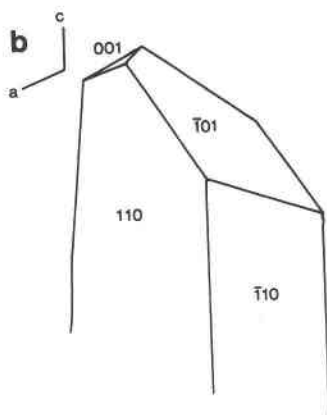

Fig. 1. (a) Group of prismatic mawbyite crystals showing the simple forms {001}, {110}, and {$\bar{1}$01}. Longest crystal is 0.2 mm. (b) Schematic diagram showing the principal forms of mawbyite.

corite data of Geier et al. (1971). Twenty-nine reflections with $2\theta < 60°$ were used to refine the unit-cell parameters by least-squares methods. The final monoclinic cell has $a = 9.052(5)$, $b = 6.277(4)$, $c = 7.580(3)$ Å, $\beta = 114°34'(2)$, and $V = 391.6(4)$ Å^3, which is slightly smaller than that of tsumcorite. Systematic absences in the powder data are similar to those of tsumcorite, and the space group $C2/m$ is therefore proposed. The full powder pattern of mawbyite is presented in Table 2. The axial ratio $a{:}b{:}c$ calculated from the unit-cell parameters is 1.442:1:1.208. No single-crystal X-ray diffraction studies on mawbyite

TABLE 1. Representative electron-microprobe analyses for mawbyite from the Kintore Opencut, Broken Hill

	1	2	3	4	5
CuO	0.08	0.45	0.23	0.76	—
ZnO	12.23	9.13	6.74	3.61	0.82
Fe$_2$O$_3$	12.52	14.75	18.18	21.15	23.66
Al$_2$O$_3$	0.34	0.68	0.13	0.26	0.02
CaO	—	—	0.13	—	—
PbO	38.18	37.75	35.77	36.36	37.91
P$_2$O$_5$	—	0.25	0.16	0.92	0.23
As$_2$O$_5$	34.04	34.56	35.07	34.32	34.90
H$_2$O (diff.)	2.61	2.43	3.59	2.62	2.46
Total	100.00	100.00	100.00	100.00	100.00
Formula based on 10 oxygens					
Cu	0.01	0.04	0.02	0.06	—
Zn	1.03	0.76	0.53	0.29	0.07
Fe^{3+}	1.08	1.25	1.46	1.71	1.94
Al	0.04	0.09	0.02	0.03	—
Ca	—	—	0.01	—	—
Pb	1.18	1.14	1.03	1.05	1.11
P	—	0.02	0.01	0.09	0.02
As	2.04	2.03	1.95	1.93	1.99
H	2.00	1.82	2.56	1.88	1.79
Fe^{3+}/Fe^{3+} + Zn	0.51	0.62	0.73	0.86	0.97

Note: Columns are (1) "dogtooth" crystals (Museum of Victoria M39065); (2) prismatic crystals (M39173); (3) prismatic crystals, globular crusts (type material) (M39178 and S.A.M. G16066); (4) hemispherical aggregates (M39068); (5) drusy "dogtooth" crystals (S.A.M. G16062). Analyst: W. Birch.
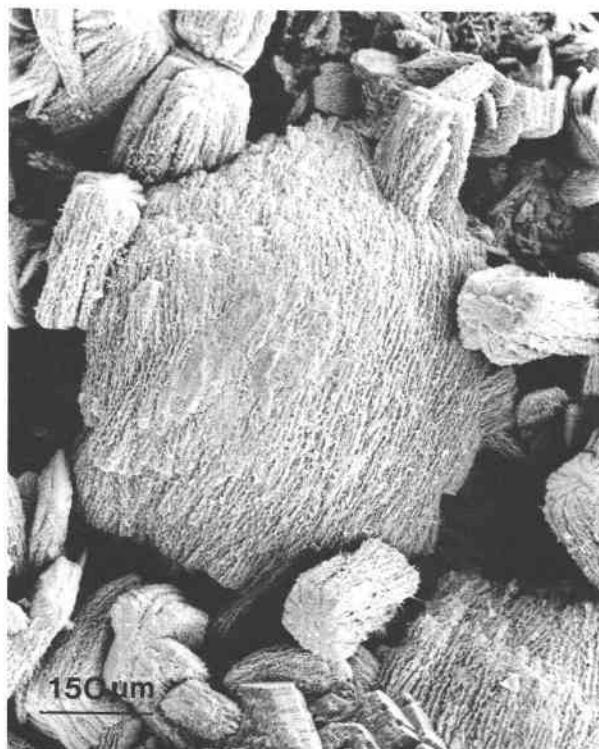
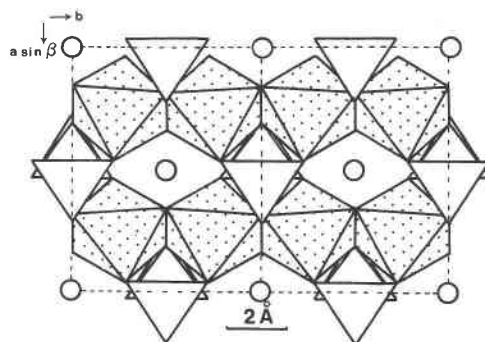Fig. 3.   Spongy hemispherical and cylindrical aggregates of mawbyite.

Fig. 4.   Projection of the tsumcorite-mawbyite structure down [001]; the large open circles represent Pb atoms. Note the strips of edge-sharing $(Zn,Fe)O_6$ octahedra running parallel to b. (After Tillmanns and Gebert, 1973.)

have so far been undertaken owing to the lack of suitable crystals.

PARAGENESIS

Mawbyite appears to be a late-stage product of the oxidation of primary sulfide and arsenide minerals. The unoxidized spessartine-quartz sandstone contains galena, sphalerite, chalcopyrite, arsenopyrite, and loellingite (Birch et al., 1983). The close association of mawbyite with beudantite-corkite suggests an acidic ground-water environ-

TABLE 2.   X-ray powder-diffraction data for mawbyite

I_{obs}	d_{obs}	d_{cal}	hkl
10	6.919	6.894	001
5	4.991	4.991	110
100	4.647	4.636	$\bar{1}11$
30	4.458	4.439	$\bar{2}01$
25	4.120	4.116	200
5	3.629	3.631	111
10	3.439	3.439	$\bar{2}02$
100	3.245	3.241	$\bar{1}12$
30	3.136	3.138	020
40	2.860	2.856	021
70	2.724	2.719	$\bar{3}11$
50	2.546	{ 2.551 2.545	{ 112 $\bar{3}12$
20	2.514	2.514	310
30	2.498	2.496	$\bar{2}03$
30	2.317	2.318	$\bar{2}22$
10	2.225	2.226	202
25	2.175	2.177	221
10	2.057	2.058	400
10	2.006	2.002	$\bar{1}31$
10	1.831	1.832	$\bar{1}32$
10	1.813	1.812	$\bar{4}22$
10	1.721	1.721	420
10	1.712	1.710	$\bar{5}11$
15	1.693	1.687	$\bar{4}23$
20	1.622	1.622	$\bar{2}24$
10	1.606	1.604	$\bar{1}33$
10	1.592	1.592	510
10	1.573	1.569	040
20	1.547	1.548	421

Note: Unit cell $a = 9.052(5)$, $b = 6.277(4)$, $c = 7.580(3)$ Å, $\beta = 114°34'(2)$. Visually estimated intensities.
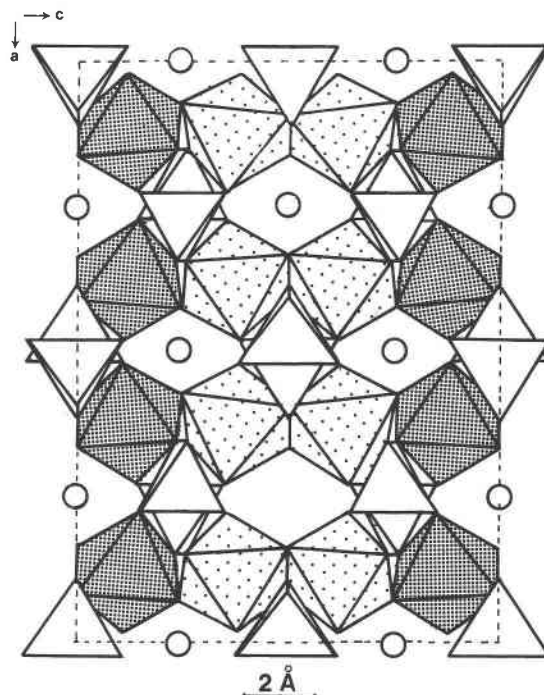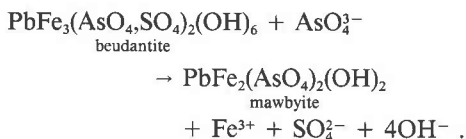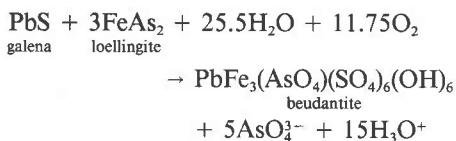

Fig. 5.   Projection of the carminite structure down [010]; open circles represent Pb atoms. Note that the FeO_6 octahedra share edges to form pairs, and these pairs in turn share corners to form stepped two-up, two-down chains parallel to c. (After Finney, 1963.)

ment. The following paragenetic sequence is suggested for the Fe-rich end-member:

$$PbS + 3FeAs_2 + 25.5H_2O + 11.75O_2$$

galena   loellingite

$$\rightarrow PbFe_3(AsO_4)(SO_4)_6(OH)_6$$

beudantite

$$+ 5AsO_4^{3-} + 15H_3O^+$$

$$PbFe_3(AsO_4,SO_4)_2(OH)_6 + AsO_4^{3-}$$

beudantite

$$\rightarrow PbFe_2(AsO_4)_2(OH)_2$$

mawbyite

$$+ Fe^{3+} + SO_4^{2-} + 4OH^-.$$

This sequence is equally valid for the formation of carminite, a dimorph of mawbyite.

The paragenesis of tsumcorite and carminite has been studied at Tsumeb, Namibia, by Keller (1977), who suggested that carminite is derived from beudantite and that tsumcorite follows conichalcite in a much more complex paragenetic sequence. Carminite is formed under more acidic conditions (pH $\approx$ 3) and tsumcorite under less acidic conditions (pH $\approx$ 5). This dependence on pH provides a ready explanation for the occurrence of the two crystallographic forms of $PbFe_2(AsO_4)_2(OH)_2$ at Broken Hill.

RELATIONSHIP TO OTHER MINERALS

Mawbyite is both chemically and structurally related to tsumcorite, and the pure ferric end-member appears to be dimorphous with carminite. The relationship between the tsumcorite-mawbyite and carminite structures is quite clear. A solution of the mawbyite structure has yet to be undertaken, but the structure of tsumcorite was solved by Tillmanns and Gebert (1973). The tsumcorite structure consists of infinite chains of edge-sharing $(Zn,Fe)O_6$ octahedra, which are linked by AsO_4 tetrahedra, with the Pb atoms occupying large eightfold coordinated sites between the chains (Fig. 4). A similar arrangement also occurs in carminite (Finney, 1963); however, in this case the chains of FeO_6 octahedra form only edge-sharing pairs. The pairs are linked by corner-sharing to form stepped two-up, two-down chains (Fig. 5). The relationship between the monoclinic mawbyite and orthorhombic carminite cells is such that

$$a_{maw}\sin \beta = \tfrac{1}{2}a_{carm} = 8.3 \text{ Å}$$
$$b_{maw} = \tfrac{1}{2}c_{carm} = 6.3 \text{ Å}$$
$$c_{maw} = b_{carm} = 7.6 \text{ Å}.$$

Geier et al. (1971) noted the similarity of the tsumcorite cell to that of brackebuschite, $Pb_2(Mn,Fe)(VO_4)_2 \cdot H_2O$, and Finney (1963) discussed the relationship of brackebuschite to carminite. In brackebuschite the $(MnFe)O_6$ octahedra form infinite edge-sharing chains as in tsumcorite, but with only half the octahedral sites, because every second chain is omitted and replaced by Pb sites.

The relationship of mawbyite to helmutwinklerite $PbZn_2(AsO_4)_2 \cdot 2H_2O$ (Schnorrer-Köhler, 1980) is unclear. The crystallographic data of Schmetzer et al. (1985) suggest that helmutwinklerite and tsumcorite have a common triclinic subcell, but that helmutwinklerite has a complex triclinic supercell. A full crystal-structure analysis of helmutwinklerite is required before the relationship between the structures can be understood.

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