

Barlowite, $\text{Cu}_4\text{FBr}(\text{OH})_6$, a new mineral isostructural with claringbullite: description and crystal structure

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ABSTRACT

The new mineral species barlowite, ideally $\text{Cu}_4\text{FBr}(\text{OH})_6$, has been found at the Great Australia mine, Cloncurry, Queensland, Australia. It is the Br and F analogue of claringbullite. Barlowite forms thin blue, platy, hexagonal crystals up to 0.5 mm wide in a cuprite-quartz-goethite matrix associated with gerhardtite and brochantite. Crystals are transparent to translucent with a vitreous lustre. The streak is sky blue. The Mohs hardness is 2–2.5. The tenacity is brittle, the fracture is irregular and there is one perfect cleavage on {001}. Density could not be measured; the mineral sinks in the heaviest liquid available, diluted Clerici solution ($D \approx 3.8 \text{ g/cm}^3$). The density calculated from the empirical formula is 4.21 g/cm^3 . Crystals are readily soluble in cold dilute HCl. The mineral is optically non-pleochroic and uniaxial (–). The following optical constants measured in white light vary slightly suggesting a small variation in the proportions of F, Cl and Br: ω 1.840(4)–1.845(4) and ϵ 1.833(4)–1.840(4). The empirical formula, calculated on the basis of 18 oxygen atoms and H_2O calculated to achieve 8 anions and charge balance, is $\text{Cu}_{4.00}\text{F}_{1.11}\text{Br}_{0.95}\text{Cl}_{0.09}(\text{OH})_{5.85}$. Barlowite is hexagonal, space group $P6_3/mmc$, $a = 6.6786(2)$, $c = 9.2744(3)$ Å, $V = 358.251(19)$ Å³, $Z = 2$. The five strongest lines in the powder X-ray diffraction pattern are [$d(\text{Å})(I)(hkl)$]: 5.790(100)(010); 2.889(40)(020); 2.707(55)(112); 2.452(40)(022); 1.668(30)(220).

KEYWORDS: barlowite, new mineral species, copper bromide fluoride, crystal structure, Great Australia mine.

Introduction

DURING the late 1980s and the 1990s, specimens containing a suite of unusual Cu minerals, including buttgenbachite, claringbullite, connellite, cornetite, gerhardtite and nantokite (Wallace and Pring, 1990; Day and Beyer, 1995; Sharpe and Williams 1999; Hibbs *et al.*, 2003) were collected from the dumps of the Great Australia mine, located 2 km south of Cloncurry, northwest Queensland, Australia. Barlowite has been identified on several specimens collected in the late 1980s by Ron and Betty Wallace, who

donated the type specimen to the South Australian Museum in 1990. Barlowite is isostructural with claringbullite (Fejer *et al.*, 1977; Burns *et al.*, 1995b) and is the second new species described from the deposit after cloncurryite (Colchester *et al.*, 2007). The Great Australia mine, is one of several hundred mines within the mineral-rich, 60,000 square kilometre Mt. Isa–Cloncurry province. Major copper and lead-zinc-silver, and smaller gold, uranium and cobalt mineralization is hosted in Early-to-Middle Proterozoic rocks. It was the first of several copper deposits discovered in north western Queensland in the late 1860s by Ernest Henry, a pastoralist who travelled to the region in search of land suitable for cattle production

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(Hardy, 1984). The mine was worked intermittently until closure in 1919, producing 100,000 tonnes of ore (Carter *et al.*, 1961). It was reopened and worked by open pit mining between 1995 and 1999 by the Cloncurry Mining Company NL. Barlowite is named in honour of William Barlow (1845–1934), English amateur geologist and crystallographer. Barlow was one of three workers who independently enumerated the 230 space groups in 3 dimensions, the other two being E.S. Fedorov and A.M. Schönflies. Barlow also proposed several crystal structures in the 1880s, that were later validated by X-ray crystallography, including the sodium chloride, cesium chloride, nickel arsenide, sphalerite and wurtzite structures (Pope, 1935; Pauling, 1994). The type specimen of barlowite is lodged in the collection of South Australian Museum (registration number G17449).

Occurrence

The geological province known as the Mt Isa inlier comprises a north-northwesterly trending belt of Precambrian rocks, ~500 km long and with an average width of 120 km (Blake, 1987). It consists of Proterozoic sediments and igneous rocks associated with multiple rifting and granite emplacement events between 1900 and 1600 Ma. The host rocks for the Great Australia lode are Lower Proterozoic basaltic meta-andesites, dolerites and interbedded metasediments of the Toole Creek Volcanics. Vein-replacement style mineralization occurs within a major splay of the N–S trending Cloncurry fault and is considered to be of magmatic origin, related to the intrusion of the Williams/Naraku batholith (Cannell and Davidson, 1998). Primary mineralization comprises Co-bearing pyrite and chalcopyrite within a gangue mineral assemblage of dolomite-calcite-quartz-actinolite-albite-magnetite. A zone of supergene enrichment is dominated by abundant malachite, chrysocolla, cuprite, chalcocite and native copper. The assemblage of secondary copper minerals, which are mostly found lining cavities in cuprite-rich rocks, have formed by oxidation of primary Cu mineralization (copper, chalcopyrite, cuprite) under low-temperature conditions. The overall sequence of crystallization probably represents a change from acid to more alkaline conditions, with claringbullite and barlowite being among the last minerals to form (Williams, 1990; Day and Beyer 1995).

Physical and optical properties

Barlowite occurs in cavities in a cuprite-quartz-goethite matrix as thin, blue, hexagonal crystals, flattened on {001} and as aggregates of platy crystals up to 3 mm across. Individual crystals are up to 0.5 mm across and 0.3 mm thick. The only form observed is {0001}. Associated minerals are crystals of blue gerhardtite and greenish-blue brochantite. The streak is sky blue. Crystals are transparent to translucent with a vitreous lustre. The Mohs hardness is 2–2.5. The tenacity is brittle, the fracture is irregular and there is one perfect cleavage on {001}. Density could not be measured; the mineral sinks in the heaviest liquid available, diluted Clerici solution ($D \approx 3.8 \text{ g/cm}^3$). The density calculated from the empirical formula is 4.21 g/cm^3 . Crystals are readily soluble in cold dilute HCl. The mineral is optically non-pleochroic and uniaxial (–). The refractive indices measured in white light vary slightly suggesting a small variation in the proportions of F, Cl and Br: ω 1.840(4)–1.845(4) and ϵ 1.833(4)–1.840(4). The range in the observed refractive indices is consistent with the range in content of Br, F and Cl from the microprobe analysis of two grains of the mineral. A Gladstone-Dale calculation, using an n_{mean} value of 1.839 from the measured range of refractive indices and the calculated density from the empirical formula, gives a compatibility index of 0.001, which is regarded as superior (Mandarino, 1981).

TABLE 1. Compositional data for barlowite.

Constituent	Wt.%	Range	Standard deviation
CuO	70.08	68.65–70.93	0.78
F	4.64	3.96–5.03	0.25
Cl	0.73	0.59–1.04	0.12
Br	16.79	16.1–17.43	0.39
H ₂ O*	11.59		
O=F	–1.95		
O=Cl	–0.16		
O=Br	–1.68		
Total	100.04		

Number of analysis = 20.

* Calculated to obtain charge balance.

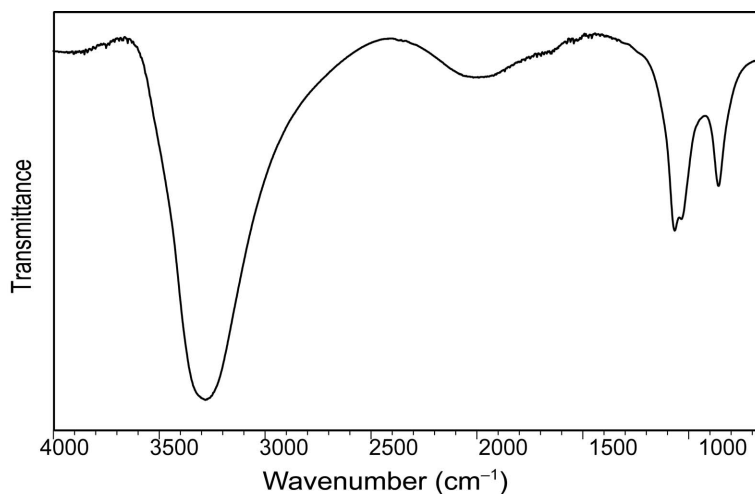


FIG. 1. Fourier transform IR spectrum of powdered barlowite.

Chemical analysis

Chemical analyses (Table 1) were performed in wavelength-dispersive spectroscopic (WDS) mode on a Cameca SX51 electron microprobe. Data reduction was performed using the $\phi(\rho Z)$ method of Pouchou and Pichoir (1985). The operating voltage was 20 kV, the beam current was 20 nA and the beam size 5 μm . The following standards were used: $\text{CuK}\alpha$ (chalcopyrite), $\text{FK}\alpha$ (fluorite), $\text{ClK}\alpha$ (tugtupite), $\text{BrK}\alpha$ (thallium bromide). An energy-dispersion spectrum indicated the absence of elements with an atomic number greater than 8 other than those reported here. The empirical formula, calculated on the basis of 18 oxygen atoms and H_2O calculated to achieve 8 anions and charge balance, is $\text{Cu}_{4.00}\text{F}_{1.11}\text{Br}_{0.95}\text{Cl}_{0.09}(\text{OH})_{5.85}$.

Infrared spectroscopy

An infrared (IR) absorption spectrum of barlowite was obtained using a Nicolet 5700 FTIR spectrometer equipped with a Nicolet Continuum IR microscope and a diamond anvil cell. A crystal aggregate was crushed in the diamond cell and a spectrum recorded in the range 4000 to 650 cm^{-1} (Fig. 1). The spectrum shows a broad band at ~ 3595 to ~ 2540 cm^{-1} , centred on 3275 cm^{-1} , due to OH-stretching vibrations. There is no band present in the region expected for H–O–H bending of H_2O groups, indicating that molecular water is not present.

Powder X-ray diffraction data

Powder X-ray diffraction data (Table 2) were obtained with a 100 mm Guinier-Hägg camera

TABLE 2. Powder X-ray diffraction data for barlowite.

I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)	h	k	l
100	5.790	100	5.786	0	1	0
5	4.915	5	4.909	0	1	1
		2	3.618	0	1	2
15	3.338	13	3.340	1	1	0
40	2.889	46	2.893	0	2	0
15	2.759	19	2.762	0	2	1
		2	2.726	0	1	3
55	2.707	62	2.710	1	1	2
40	2.452	49	2.454	0	2	2
5	2.316	8	2.318	0	0	4
5	2.184	12	2.187	1	2	0
5	2.148	10	2.152	0	1	4
		9	2.128	1	2	1
		5	2.112	0	2	3
		1	1.978	1	2	2
		1	1.929	0	3	0
		7	1.905	1	1	4
		8	1.888	0	3	1
10	1.807	11	1.809	0	2	4
5	1.787	3	1.785	1	2	3
20	1.778	30	1.781	0	3	2
		7	1.766	0	1	5
30	1.668	37	1.670	2	2	0
		1	1.636	0	3	3

using CrK α radiation ($\lambda = 2.28970 \text{ \AA}$) and silicon (NBS SRM 640a) as an internal standard. Intensities were estimated visually and the calculated intensities were obtained from the structural model. The Guinier-Hägg film was scanned using an Epson film scanner, the powder-diffraction profile over the 2θ range 10 to 90° was extracted. The unit-cell parameters refined from the powder data using the Le Bail profile-fitting method (Le Bail *et al.*, 1988; Hunter, 1998) are $a = 6.681(1)$, $c = 9.274(1) \text{ \AA}$, $V = 358.43(6) \text{ \AA}^3$, and are close to those refined using single-crystal methods.

Crystal structure

A single crystal ($80 \mu\text{m} \times 60 \mu\text{m} \times 10 \mu\text{m}$) of barlowite was mounted on a Bruker D8 three-circle diffractometer equipped with a rotating anode generator (MoK α X-radiation), multi-layer optics and an APEX-II CCD detector. The intensities of 12,878 reflections were collected to $60^\circ 2\theta$ using 30 s per 0.2° frame with a crystal-to-detector distance of 5 cm. Empirical absorption corrections (*SADABS*: Sheldrick, 1998) were applied and identical data merged to give 3909 reflections covering the entire Ewald sphere. The

TABLE 3. Crystal data, data collection and refinement details for barlowite.

Crystal data	
Formula	Cu _{4.00} F _{1.11} Br _{0.95} Cl _{0.09} (OH) _{5.85}
Space group	<i>P</i> 6 ₃ / <i>mmc</i>
a , c (Å)	6.6786(2), 9.2744(3)
V (Å ³), Z	358.251(19), 2
$F(000)$	428
μ (mm ⁻¹)	17.3
Absorption correction	empirical
Crystal dimensions (μm)	80 \times 60 \times 10
Data collection	
Diffractometer	Bruker D8
Temperature (K)	293
Radiation	MoK α , $\lambda = 0.71073 \text{ \AA}$
Crystal-to-detector distance (mm)	50
Rotation axes, width ($^\circ$)	ϕ , ω ; 0.2
Total no. of frames	10000
Collection time per frame (s)	30
θ range ($^\circ$)	3.52–30.07
h, k, l ranges	$-9 \rightarrow 9$, $-9 \rightarrow 9$, $-12 \rightarrow 12$
Total reflections measured	12,878
Data completeness (%)	100
Unique reflections	231 ($R_{\text{int}} = 0.016$)
Refinement	
Refinement on	F^2
$R1^*$ for $F_o > 4\sigma(F_o)$	1.45%
$wR2^\dagger$ for all F_o^2	4.05%
Reflections used $F_o > 4\sigma(F_o)$	231
Number of parameters refined	25
Extinction factor	0.0037(9)
$(\Delta/\sigma)_{\text{max}}$	0.082
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e/Å ³)	0.502, -0.275
Gof	1.261

* $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

† $wR2 = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w |F_o|^2$; $w = 1/[\sigma^2(F_o) + (0.0172 P)^2 + 0.5324 P]$;
 $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_o^2) / 3$

unit-cell parameters were obtained by least-squares refinement of 9178 reflections ($I > 10\sigma I$), and are given in Table 3 along with other pertinent crystallographic details. The crystal structure was solved by direct methods and refined with the Bruker *SHELXTL* Version 5.1 system of programs (Sheldrick, 1997). The position of the H atom was identified in a difference Fourier map and was inserted into the refinement and constrained to be 0.98 Å from the donor O(1) anion. The final R_1 index was 1.45% using a fully anisotropic model for all non-hydrogen sites. Fractional atomic coordinates and anisotropic displacement parameters are given in Table 4, selected bond distances in Table 5 and bond valences in Table 6.

Barlowite is isostructural with claringbullite (Burns *et al.* 1995*b*). Each $\text{Cu}(1)\phi_6$ (ϕ : O, Br) [4+2] distorted octahedron shares four edges with adjacent octahedra to form a sheet in the (0001) plane (Fig. 2). The sheets are a variant of an $[\text{M}\phi_2]_N$ sheet of edge-sharing octahedra (brucite-type sheets), a common stoichiometry for polyhedral sheets in mineral structures. Sheets in which $M = (\text{Cu}^{2+}, \text{Zn})$ are the basis for the structures of many hydroxy-(hydrated) Cu^{2+} oxysalt minerals, in particular Cu^{2+} and Zn sulfates (Eby and Hawthorne, 1993; Hawthorne and Schindler, 2000). There is one vacancy for each four Cu(1) cations in the sheet. Sheets of [4 + 2]-distorted octahedra which contain vacancies or regular (i.e. non-Jahn-Teller distorted) octahedra have been termed interrupted sheets by Hawthorne and Schindler (2000). Interrupted sheets are also found in the structures of bechererite, chalcophanite, chalcophyllite, cianciullite, gordaite, namuwite, ramsbeckite and simonkolleite (Hawthorne and Sokolova, 2002).

The Cu(1) atom is coordinated by four OH groups and two Br atoms in a Jahn-Teller distorted octahedral arrangement (Jahn and Teller, 1937; Burns and Hawthorne, 1996). As is usual for mixed-ligand $\text{Cu}(1)\phi_6$ octahedra (ϕ = unspecified ligand), the Br ligands occur in the apical positions of the distorted octahedra (Burns and Hawthorne 1995*a*) with a Cu–Br distance of 3.0154 Å (Table 5). The bond distance of the four meridional (OH) groups is 1.9560(8) Å. The Cu(2) site, located on Wyckoff position $6h$, comprises three symmetrically equivalent positions, each 33% occupied, with separations of 0.756(2) Å. Each of the Cu(2) atoms is displaced away from the 2d position and adopts a [4+2] coordination resulting in a distorted trigonal

 TABLE 4. Fractional coordinates and displacement parameters (Å^2) for atoms for barlowite.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$	U^{11}	U^{22}	U^{33}	$U^{2,3}$	$U^{1,3}$	$U^{1,2}$
Cu(1)	0.5	0	0	0.01449(17)	0.01064(19)	0.0100(2)	0.0226(3)	-0.00382(14)	-0.00191(7)	0.00498(11)
Cu(2)	0.37107(10)	0.7421(2)	0.75	0.0123(3)	0.0113(4)	0.0179(5)	0.0098(4)	0	0	0.0090(3)
Br	0.6667	0.3333	0.75	0.0184(2)	0.0201(3)	0.0201(3)	0.0151(3)	0	0	0.01003(14)
F	0	0	0.75	0.0250(12)	0.0212(14)	0.0212(14)	0.033(2)	0	0	0.0106(7)
O(1)	0.20189(14)	0.79811(14)	0.90797(16)	0.0125(3)	0.0108(5)	0.0108(5)	0.0159(7)	0.0009(3)	-0.0009(3)	0.0054(6)
H(1)	0.1225(10)	0.8775(10)	0.871(3)	0.044(11)						

TABLE 5. Selected interatomic distances (Å), for barlowite.

Cu(1)–O(1) × 4	1.9560(8)	Cu(2)–O(1) × 4	1.9963(15)
Br × 2	<u>3.0154</u>	O(1) × 2	<u>2.4446(19)</u>
<Cu(1)–O>	2.309	<Cu(2)–O>	2.146

TABLE 6. Bond-valence analysis for barlowite.

	Cu(1)	Cu(2)	H(1)	Sum
O(1)	0.473 × 4 ↓ × 2 →	0.425 × 4 ↓ × 2/3 →	0.845	2.116
Br	0.126 × 2 ↓ × 1/3 →			0.378
F	0.063 × 2 ↓ × 6 →		0.155 × 6 →	0.930
Sum	2.018	1.952		

Note: Bond-valence values for the Br site were computed for an occupancy of Br_{0.92}Cl_{0.08}. Bond-valence parameters taken from Brese and O’Keeffe (1991) and Brown (2009).

prismatic arrangement with four short Cu(2)–O(1) bonds of 1.9963(15) Å, two long Cu(2)–O(1) bonds of 2.4446(19) Å and a <Cu(2)–O> bond length of 2.146 Å (Table 5).

The Br anion is surrounded by six Cu²⁺ cations, and as all bonds are elongated due to the Jahn-Teller effect, the site has a very deficient bond-valence sum (Table 6). The structure refinement

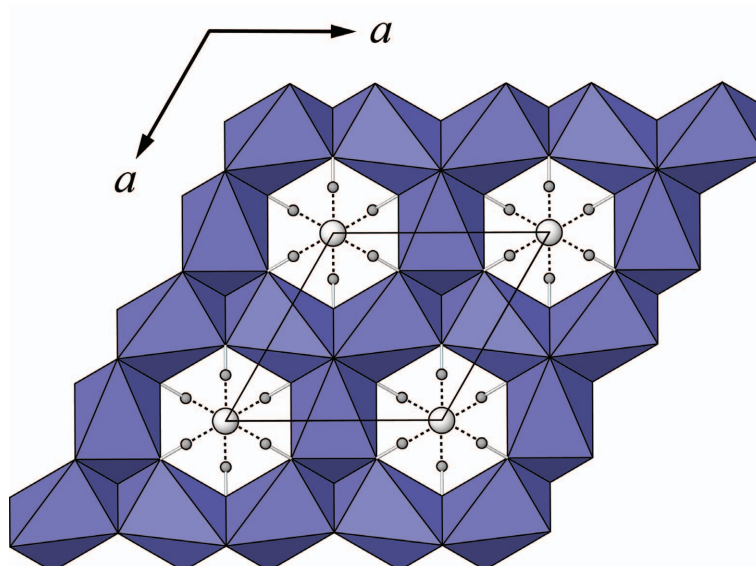


FIG. 2. The crystal structure of barlowite viewed along [001]; Cu(1)₆ polyhedra are blue; F atoms are white spheres; H atoms are small grey spheres. Hydrogen bonds are shown as dotted lines. The unit cell is outlined. All structure drawings were completed using *ATOMS* (Shape Software, 1997).

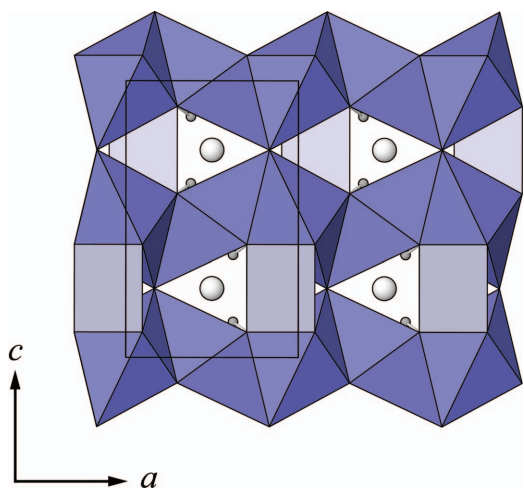


FIG. 3. The crystal structure of barlowite viewed along $[100]$. $\text{Cu}(2)\phi_6$ trigonal prisms are pale blue.

and chemical data show that the Br position is well ordered and nearly 100% occupied by Br. The equivalent site in the structure of claringbullite (Burns *et al.*, 1995b), which is 100% occupied by Cl, also has a low-incident valence sum (0.41 vu). The valence sum of the Cu(1) site is near its ideal value in both crystal structures. This suggests a low-valence sum at this anion site as a characteristic feature for this structure type.

Refined site-scattering located at the $2c$ ($2/3$ $1/3$ $3/4$) and $2b$ (0 0 $3/4$) anion sites, 32.17(13) and 9.57(16) electrons, respectively, is consistent with Br dominant at $2c$ and F dominant at $2b$ and is in agreement with the electron microprobe analysis which shows a near 1:1 ratio of Br:F with only minor Cl present.

Adjacent sheets link along $[0001]$ by sharing Br anions (Fig. 3). The $\text{Cu}_2(\text{OH})_6$ trigonal prism lies between adjacent sheets and shares three OH groups with each sheet. Channels in the structure run along $[001]$. The F anion is located in the centre of the channel at a point midway between adjacent sheets of octahedra. The H(1) atom hydrogen-bonds to the F anion at a distance of 1.807 Å. The F anion accepts six hydrogen bonds, three from donor anions in each adjacent sheet.

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