Bleasdaleite

$(Ca,Fe^{3+})_2Cu_5(Bi,Cu)(PO_4)_4(H_2O,OH,Cl)_{13}$ A New Mineral from Lake Boga, Victoria, Australia

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Abstract

Bleasdaleite is a new calcium copper bismuth phosphate from a granite quarry near the town of Lake Boga, in northwestern Victoria, Australia. The mineral occurs as minute tabular crystals, up to about 20 µm across but less than 1 µm thick. These form scaly crusts and hemispheres up to about 0.1 mm across, in cavities in etched chalcocite patches in a pegmatite boulder. Accompanying minerals include malachite, pseudomalachite, chalcosiderite/turquoise, ulrichite, torbernite, libethenite and iodargyrite. Bleasdaleite aggregates are dark brown, with a resinous lustre on broken surfaces. The streak is pale brown, Mohs hardness is estimated to be about 2, and crystals show a well-developed (001) cleavage in thin-section. Bleasdaleite is biaxial negative, with refractive indices of α = 1.718, β = 1.748, γ = 1.748. The 2V$_u$ (calculated) is close to 0°, and the optical orientation is X = c, Y/Z = a/b. Pleochroism is medium strong, X = pale yellow-brown, Y = Z = dark yellow-brown. Chemical analysis gave (wt. %) CaO 7.59, CuO 34.79, Bi$_2$O$_3$ 15.53, Fe$_2$O$_3$ 3.04, Al$_2$O$_3$ 0.13, P$_2$O$_5$ 21.70, As$_2$O$_5$ 0.34, Cl 1.01, H$_2$O by difference 16.10, less O $\equiv$ Cl 0.23, total 100.00. The simplified formula is $(Ca,Fe^{3+})_2Cu_5(Bi,Cu)(PO_4)_4(H_2O,OH,Cl)_{13}$. Bleasdaleite is monoclinic (pseudotetragonal) with unit cell parameters a = 14.200(7), b = 13.832(7), c = 14.971(10) Å, β = 102.08(8)°, V = 2875(2) Å³. With Z= 4, the calculated density is 2.77 gcm⁻³. The strongest lines in the X-ray powder diffraction pattern are [d$_{obs}$ (Å), I$_{obs}$, hkl] 14.57 (100) 001; 6.95 (40) 200; 6.28 (40) -112, 021; 3.469 (30) 312, 400; 3.104 (40) 402; 2.816 (40) 043. The crystal structure has not been solved due to the small size of the crystals. However, bleasdaleite is very similar stoichiometrically and optically to richelsdorfite, Ca$_2$Cu$_5$Sb[Cl(OH)$_6$(AsO$_4$)$_4$].6H$_2$O, suggesting very similar structures. The [Sb(OH)$_6$.6H$_2$O]⁻ layer of richelsdorfite is probably replaced by a [Bi(OH)$_4$.8H$_2$O]⁺ layer in bleasdaleite, with the change in valency from 5+ to 3+ brought about by the replacement of Sb by Bi probably being compensated by protonation of two OH groups to form H$_2$O molecules. Bleasdaleite formed by a series of alteration reactions involving chalcocite and aqueous phosphate and chlorine-bearing solutions. The mineral is named after Reverend John Ignatius Bleasdale (1822-1884).

INTRODUCTION

An outcrop of Devonian granite, 10 km SSW of the township of Lake Boga (lat. 35° 28' S, long. 143° 38' E) in northern Victoria, Australia (Figure 6), has yielded a suite of secondary copper and/or uranium phosphate minerals, including at least one new species, ulrichite (Birch, 1993; Birch *et al.*, 1988). The granite is extensively quarried (Figure 1) and is visited regularly by mineral collectors. In April 1995, Gordon and Robin Sharp broke open a boulder of pegmatite in the quarry, exposing copper mineralisa-

tion consisting of massive supergene chalcocite partially altered to a suite of secondary copper and silver minerals, including one containing Ca, Cu, Bi, P and Cl (Birch, 1996). This mineral has now been shown to be a new species which appears to be closely related to richelsdorfite, Ca$_2$Cu$_5$Sb[Cl(OH)$_6$(AsO$_4$)$_4$].6H$_2$O (Süsse and Schnorrer-Köhler, 1983).

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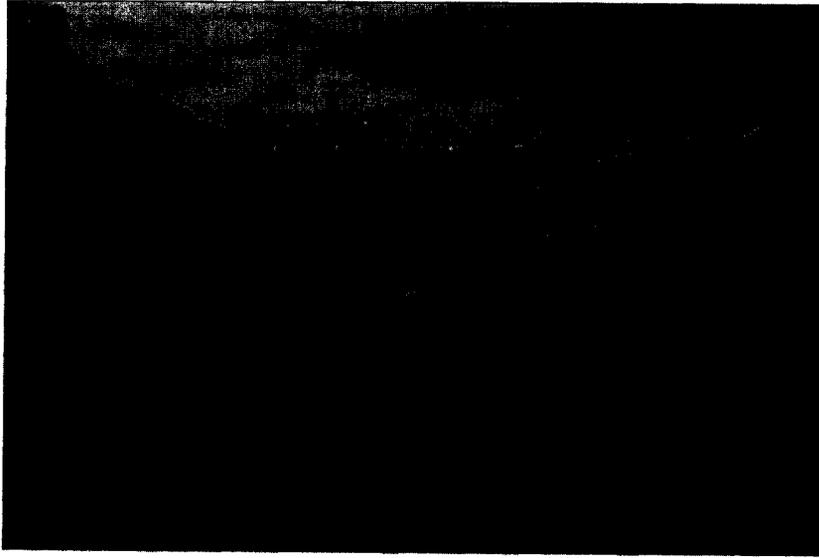
Figure 1: View of the Lake Boga quarry. Photo: W. Birch.

The new mineral, with a suggested chemical formula $(Ca,Fe^{3+})_2Cu_5(Bi,Cu)(PO_4)_4(H_2O,OH,Cl)_{13}$, has been named bleasdaleite, after the Reverend John Ignatius Bleasdale (1822-1884) (Figure 2), an enthusiastic proponent of Victorian minerals, especially gemstones, during the 1860s. The data and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. The type specimen of bleasdaleite is lodged in the Museum Victoria collection (M44699), with co-type material in the South Australian Museum collection. Several small specimens remain in the collection of the discoverers.
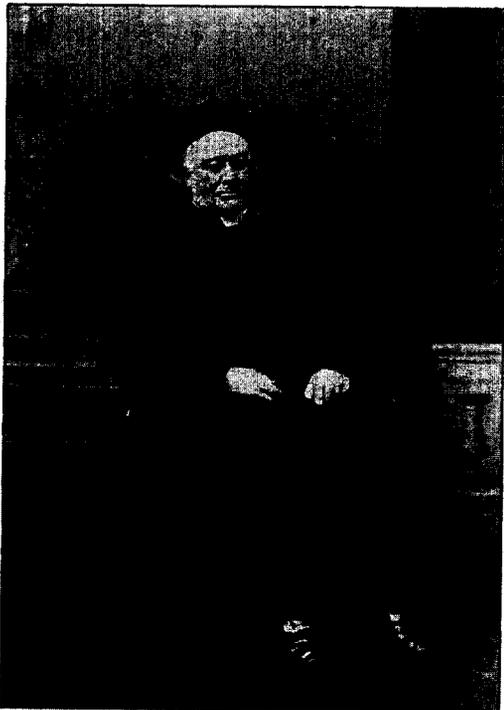
Figure 2: John Ignatius Bleasdale (1822-1884)

Figure 4: Thin section showing platy bleasdaleite crystals. Cluster is about 25 µm across. Photo: W. Birch.
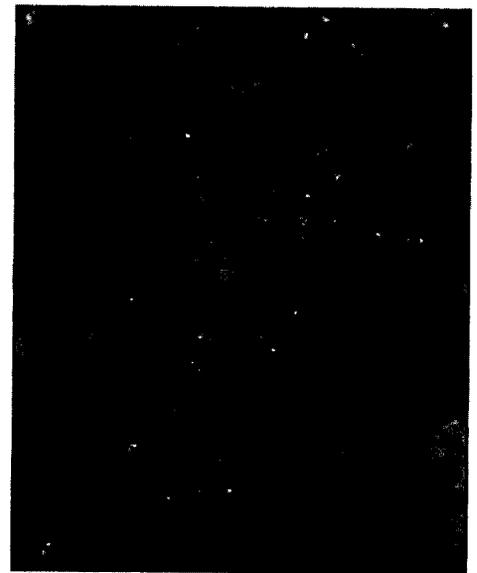
Figure 3: Brownish hemispheres of bleasdaleite scattered over chalcocite with malachite (green). Field of view is about 3 mm across. Photo: W. Birch. Specimen: R. and G. Sharp Collection.

OCCURRENCE, PHYSICAL AND OPTICAL PROPERTIES

The chalcocite in the bleasdaleite-bearing boulder forms massive patches up to about 5 cm across, occupying space between large orthoclase crystals. The rock around these patches is stained green, possibly due to malachite. Thin sections show that much of the chalcocite has been corroded and altered to veinlets of covellite. Secondary minerals have precipitated on the corroded surface of the chalcocite-covellite. Pseudomalachite and chalcosiderite/turquoise form globules and crusts, while rare ulrichite, libethenite, torbernite and iodargyrite are present as scattered crystals with dimensions less than 1 mm. Bleasdaleite itself occurs as thin, dark brown scaly crusts and hemispherical clusters up to about 0.1 mm across (Figures 3 and 5).

Scanning electron microscopy reveals delicate tabular crystals forming open rosette-like clusters and linings (Figure
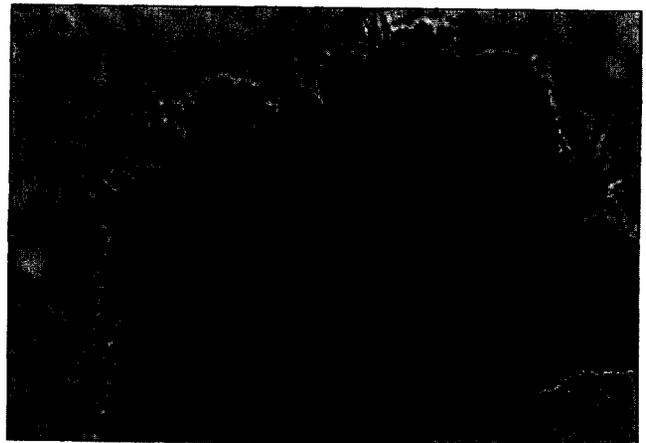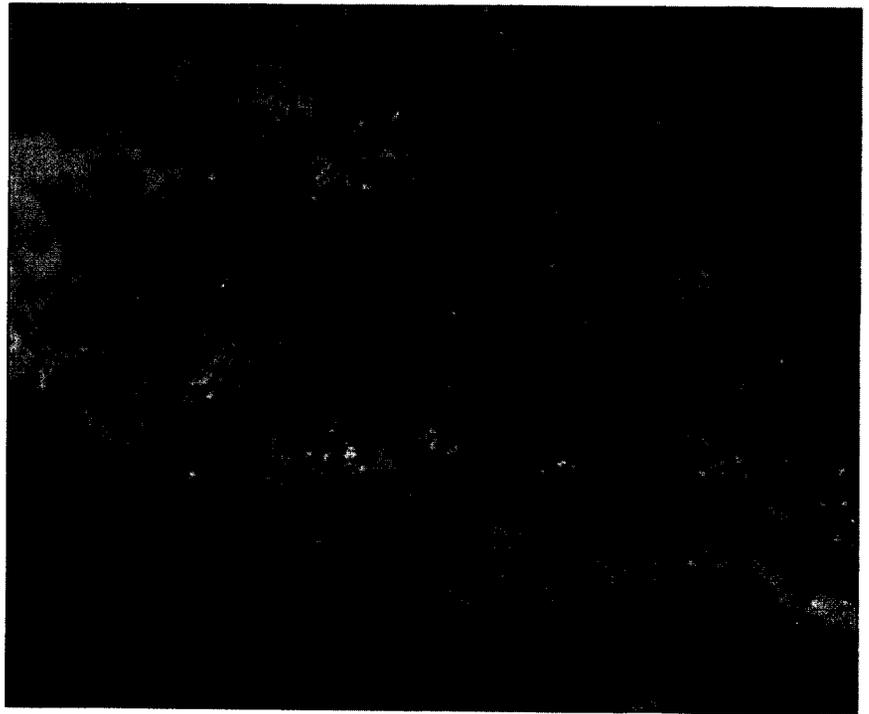
Figure 5: Brownish crusts of bleasdaleite on chalcocite (dark grey), with clay mineral (yellowish) and torbernite (green). Field of view is 3 mm across. Photo: F. Coffa. Specimen: Museum Victoria collection, M44699 (type specimen).

7). The crystals reach up to about 20 μm across but are less than 1 μm thick. The lustre on broken surfaces is resinous, streak pale brown, and estimated Mohs hardness (by comparison with richelsdorfite) about 2. The crystals are too small to enable density to be measured but the calculated density is 2.77 g/cm^3.

Thin sections show bleasdaleite crystals are transparent and also reveal a well-developed (001) cleavage (Figure 4). Platy crystal fragments, assumed to be {001}, show sharp rectangular outlines, very slight anisotropism and straight extinction, suggesting (pseudo)orthorhombic or pseudotetragonal symmetry. Fragments lying edge-on show maximum birefringence and pleochroism, have positive elongation and straight or very slightly inclined extinction. These observations indicate bleasdaleite is biaxial (pseudo-uniaxial). The refractive indices, measured in white light, are α = 1.718(4), β = 1.748(3), γ = 1.748(3). The optical sign is negative and 2Vα(calculated) is close to 0°. The optical orientation is X = c, Y/Z = a/b; pleochroism is medium strong, X = pale yellow-brown, Y = Z = dark yellow-brown; absorption is X < Y = Z.
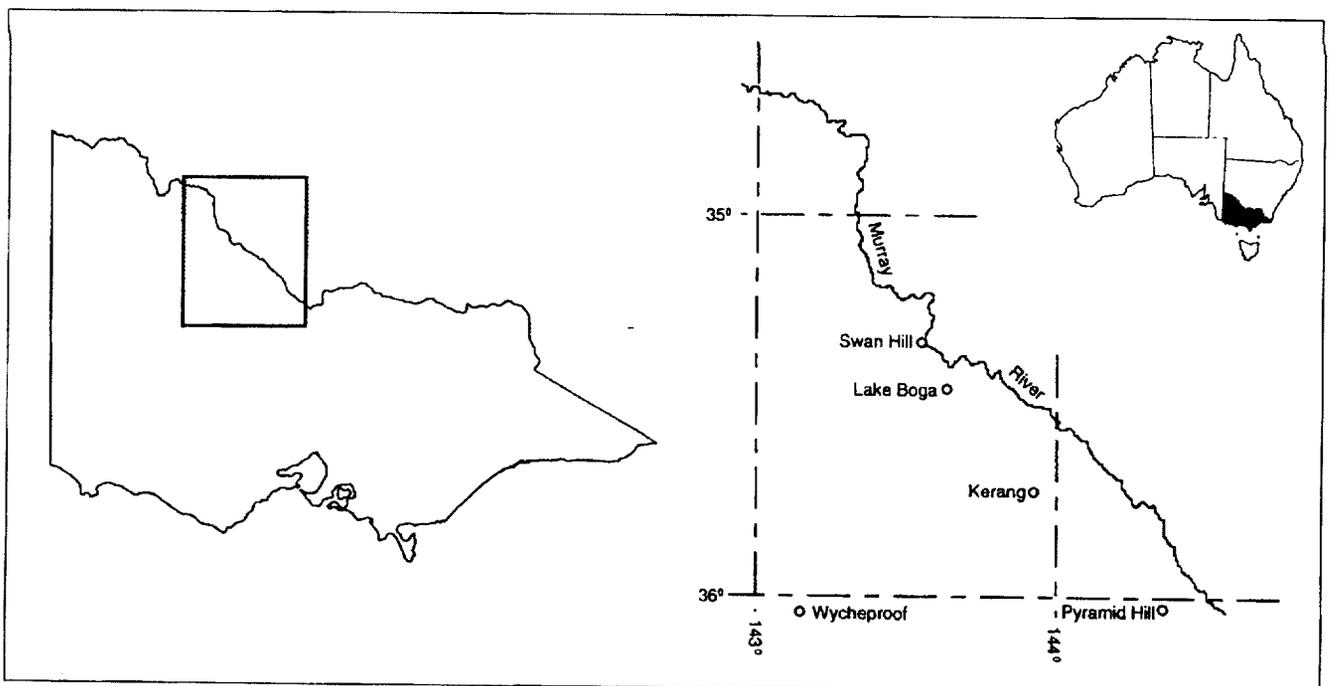
Figure 6: Locality map.
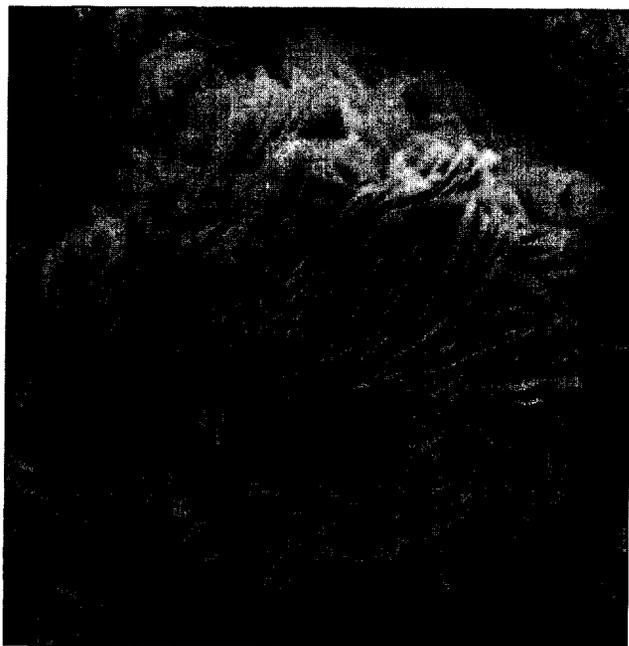
Figure 7: Scanning electron micrograph showing cluster of platy bleasdaleite crystals about 50 μm across.

These optical characteristics are comparable to those of richelsdorfite (Sarp *et al.*, 1994). They yield a Gladstone-Dale (G-D) compatibility of -0.288; this poor figure is associated with uncertainties about the G-D constant for Bi_2O_3, a major constituent of bleasdaleite. Poor G-D compatibilities are shared by most new Bi-bearing species (Mandarino, 1989).

CHEMICAL ANALYSIS

Bleasdaleite crystals were analysed using a Cameca SX50 electron microprobe, at 15 kV and specimen current of about 0.2 μA. Standards used were wollastonite (Ca), Cu metal, Bi metal, hematite (Fe), corundum (Al), fluorapatite (P), arsenopyrite (As) and halite (Cl). A fragment of natural mrazekite, $Cu_3Bi_2(PO_4)_2O_2(OH)_2.2H_2O$, was used as a secondary standard. There was insufficient material to determine water directly, so H_2O was calculated by difference. Twenty-four analyses were obtained from multiple crystals, with the calculated oxide averages and ranges shown in Table 1. An empirical formula was calculated on the basis of 29 (O, OH, Cl), by analogy with the stoichimetry of richelsdorfite. There appears to be more water in bleasdaleite, but this is probably due to analytical difficulties. The small size of the crystals and their reaction to the microprobe beam resulted in slightly low totals for the measured elements (in particular for P), hence slightly enhanced 'water by difference'. The Cl contents of bleasdaleite reach only about 50 atom % of the amount present in richelsdorfite, and are presumably offset by additional hydroxyl. A Cl-free richelsdorfite has been described from a German locality (Walenta and Dunn, 1988).

A feature of all the analyses is a small but consistent amount of iron, which is assumed to be trivalent; micro-

Table 1: Chemical analysis of bleasdaleite

Oxide	Wt.%	Range
CaO	7.59	7.13 - 8.33
CuO	34.79	31.85 - 37.01
Bi_2O_3	15.53	12.83 - 18.63
Fe_2O_3	3.04	1.13 - 4.53
Al_2O_3	0.13	0.02 - 0.57
P_2O_5	21.70	20.30 - 23.92
As_2O_5	0.34	0.11 - 0.53
Cl	1.01	0.36 - 1.41
H_2O^*	16.10	
Less O⇨Cl	0.23	
Total	100.00	

* H_2O by difference

EMPIRICAL FORMULA: (based on 29 (O, OH, Cl))

$(Ca_{1.63}Fe^{3+}_{0.46})_{\Sigma2.09}Cu_5(Bi_{0.80}Cu_{0.25})_{\Sigma1.05}[(PO_4)_{3.67}(AsO_4)_{0.04}]_{\Sigma3.71}[Cl_{0.34}(OH)_{6.15}].7.7H_2O$

SIMPLIFIED FORMULA:
$(Ca,Fe^{3+})_2Cu_5(Bi,Cu)(PO_4)_4(H_2O,OH,Cl)_{13}$

chemical tests gave a positive, albeit weak reaction for trivalent iron. In calculating the empirical formula for bleasdaleite, this Fe^{3+} has been assumed to offset a deficiency in Ca, amounting to about 25% of the site occupancy. A deficiency in Bi is probably offset by a small amount of excess Cu, above the 5 formula units in richelsdorfite. As these substitutions contribute to charge imbalances between sites, it is difficult to present a simplified formula which is 'balanced'. This problem has been overcome by combining H_2O, OH and Cl in the formula, assigning them a total of 13 formula units. In this way, substitutions in the cation positions can be balanced by equivalent changes in the ratio of $OH:H_2O$. The simplified formula for bleasdaleite is best expressed as $(Ca,Fe^{3+})_2Cu_5(Bi,Cu)(PO_4)_4(H_2O,OH,Cl)_{13}$.

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction data for bleasdaleite were recorded using a 100 mm Guinier Hägg camera with Cr Kα radiation and with Si as an internal standard. An additional pattern was recorded using a 114.6 mm diameter Gandolfi camera with Co Kα radiation (exposure time 60 hours). The two patterns were very similar, differing only in the relative intensity of some of the lines. The d-spacings in the pattern given in Table 2 are based on a 32-hour Guinier-Hägg exposure recorded under vacuum, with the intensities based on the Gandolfi film. Although the bleasdaleite diffraction pattern is similar to that of richelsdorfite, the differences in composition suggest that the cells do not necessarily have the same symmetry.

In addition, the fact that the three cell repeats of richelsdorfite are all about 14 Å meant that the pattern was very difficult to index. Electron diffraction studies revealed a pseudotetragonal net down [001] for bleasdaleite
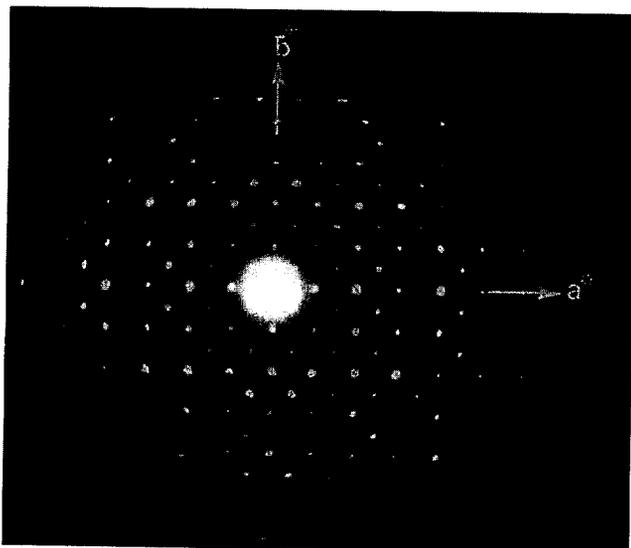
Figure 8: Electron diffraction pattern of bleasdaleite taken down [001] showing the pseudotetragonal 9.4 x 9.4 Å net.

(Figure 8), with $a_{tetr} \approx 9.4$ Å, corresponding to a C-centred monoclinic cell similar to richelsdorfite (Sarp *et al.* (1994). The cell parameters were refined by least squares methods to give $a = 14.200(7)$, $b = 13.832(7)$, $c = 14.971(10)$ Å, $\beta = 102.08(8)°$, $V = 2875(2)$ Å³. On the basis of this cell, the empirical formula and with $Z = 4$, the calculated density is 2.77 gcm⁻³, considerably lower than that of richelsdorfite (3.2 gcm⁻³; Sarp *et al.*, 1994).

Figure 9: Schematic diagram of the richelsdorfite structure. View of the structure down [010]. The layers due to $[Ca_2Cu_5Cl(AsO_4)]^+$ clusters and the $[Sb(OH)_6.6H_2O]^-$ layers are indicated. Note that in bleasdaleite, the $[Sb(OH)_6.6H_2O]^-$ layer is replaced by a $[Bi(OH)_4.8H_2O]^-$ layer with the Bi probably in a more distorted coordination.

Table 2: Powder X-ray diffraction data for bleasdaleite.

I(rel)	d(meas)	d(calc)	hkl
100	14.57	14.64	001
40	6.95	6.94	200
40	6.28	6.33, 6.25	112, 021
20b	4.908	5.027, 4.900	022, 220
5	4.877	4.880	003
10	4.060	4.119	131
10	3.998	3.992	311
10	3.646	3.649, 3.643	203, 313
30b	3.469	3.473, 3.471	312, 400
20	3.427	3.427	402
15	3.366	3.370, 3.365	133, 041
5	3.263	3.267	330
10	3.228	3.230, 3.227	401, 223
30	3.104	3.102	402
5	2.968	2.972	241
40	2.816	2.821	043
5	2.704	2.698, 2.696	115, 025
20	2.617	2.617	513
30	2.507	2.511, 2.510	152, 243
30	2.452	2.450	440
10	2.414	2.414	153
10	2.359	2.360	335, 441
5	2.313	2.314	600
5b	2.285	2.284	603, 531
10b	2.191	2.191	352, 444, +
5b	2.098	2.098, 2.091	354, 007
5	2.052	2.053, 2.050	317, 353
20b	1.915	1.919, 1.913	553, 461
5	1.786	1.788, 1.786, 1.785	464, 371, 642
5b	1.771	1.773, 1.769	734, 028
10b	1.730	1.731, 1.729	372, 080, 138
5	1.719	1.720, 1.719	463, 822
5b	1.686	1.688, 1.685	518, 266
10b	1.587	1.592, 1.587, 1.582	644, 573, 448

Structure determination by single crystal methods was not achievable due to the small size of the fragments. However, some conclusions can be drawn about the structure of bleasdaleite from the structure of richelsdorfite as determined by Süsse and Tillmans (1987). The two minerals are very similar stoichiometrically and optically (Table 3) and it is very likely that the pseudotetragonal $[Ca_2Cu_5Cl(XO_4)_4]^+$ unit is common to both minerals ($X = P$ in bleasdaleite and As in richelsdorfite). Since pentavalent Bi does not occur in oxysalt minerals, the $[Sb(OH)_6.6H_2O]^-$ layer of richelsdorfite is probably replaced by a $[Bi(OH)_4.8H_2O]^-$ layer in ideal (unsubstituted) bleasdaleite (see Figure 9), with the change in valency from 5⁺ to 3⁺ brought about by the replacement of Sb by Bi probably being compensated by protonation of two OH groups to form H_2O molecules. It is very unlikely that Bi will have the same octahedral coordination as Sb; it is more likely to be in distorted trigonal prismatic coordination and be associated with the increase in the c parameter over that of richelsdorfite.

The well-developed (001) cleavage of bleasdaleite gives rise to plates that are so thin the electron diffraction spots are rods in reciprocal space. These persist in intersecting the Ewald sphere even when crystal fragments are tilted away from the [001] zone. In addition to the diffraction

	bleasdaleite [1]	richelsdorfite [2]	richelsdorfite [3]	richelsdorfite [4]
Formula	$(Ca,Fe^{3+})_7Cu_5(Bi,Cu)$-$(PO_4)_4(H_2O,OH,Cl)_{13}$	$Ca_2Cu_5Sb[Cl/(OH)_6$-$(AsO_4)_4]\cdot6H_2O$	$Ca_2Cu_5Sb[Cl/(OH)_6$-$/(AsO_4)_4]\cdot6H_2O$	$Ca_2Cu_5Sb[Cl/(OH)_6$-$/(AsO_4)_4]\cdot6H_2O$
Symmetry	mon.	mon.	mon.	mon.
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$
a (Å)	14.200(7)	14.078(9)	14.17(6)	14.079
b (Å)	13.832(7)	14.207(8)	14.42(3)	14.203
c (Å)	14.971(10)	13.49(2)	13.57(5)	13.470
β (°)	102.08(8)	101.06(8)	102.0(2)	101.05
V (Å³)	2875(2)	2647(3)	2713	2643
Z	4	4	4	4
5 strongest lines in the powder pattern [d (I)]	14.57 (100), 6.95 (40), 6.28 (40), 2.816 (40), 3.469 (30b)	13.2 (100), 3.132 (90), 2.776 (35), 1.775 (35), 6.260 (30)	[very unreliable (strong preferred orientation)]	-
D(meas.), (calc.) [g/cm³]	-, 2.770	3.3, 3.33	3.20(3), 3.27	-, 3.2
Mohs Hardness	~2	~2	~2	-
α	1.718(4)	1.640(2)	[wrong (calc.)]	-
β	1.748(3)	1.692(2)	[wrong (calc.)]	-
γ	1.748(3)	1.694(2)	[wrong (calc.)]	-
birefringence	0.030	0.054	[wrong (calc.)]	-
Opt. character	biaxial negative (pseudo-uniaxial)	biaxial negative	biaxial negative	-
2V (meas.), (calc.) [°]	unmeasurable (probably ~0-20), ~0	10-15, 21.6	69(2), 68.7 [doubtful]	-
Dispersion	none observable (interference colours are normal)	r > v (medium strong)	r > v	-
Orientation	X ≅ c, Y/Z = a/b (pseudorthorhombic)	X ^ c (unmeasurable) Y = a, Z = b	X ∧ c, Y/Z = a/b	-
X (colour)	pale yellowish brown	colourless	pale blue	-
Y (colour)	dark yellowish brown	sky-blue	green-blue	-
Z (colour)	dark yellowish brown	sky-blue	pale green-blue	-
Absorption	X < Y = Z	X < Y = Z	not given	-
Twinning	none observed	none observed	none observed	-
Crystal shape	tabular on {001}, rectangular to pseudotetragonal	tabular on {001}, rectangular to pseudotetragonal	tabular on {001}, pseudotetragonal	-
Cleavage	{001}, perfect	{001}, perfect		-

1) This proposal; 2) Sarp et al. (1994); 3) Süsse & Schnorrer-Köhler (1983); 4) Süsse & Tillmann (1987) (Structure solution)

lines given in Table 2, there are two weak and diffuse lines in the pattern at d = 12.76 and 12.1 Å. These lines appear to be associated with the stacking disorder of $[Ca_2Cu_5Cl(XO_4)_4]^+$ units and $[Bi(OH)_4.8H_2O]^-$ layers. It is therefore possible that a number of polytypes of bleasdaleite may exist.

The richelsdorfite structure offers considerable scope for chemical substitution. Walenta and Dunn (1988) reported richelsdorfite-like minerals from the Clara Mine, Germany, which contain no Cl and in one case, no Sb. Drescher and Süsse (1997) reported a carbonate-rich richelsdorfite from Austria, their preliminary investigation suggesting that the CO_3^{2-} group replaced one of the AsO_4^{3-} groups in the $[Ca_2Cu_5Cl(XO_4)_4]^+$ unit. The full chemical flexibility of this structure type is yet to be established.

PARAGENESIS

Small amounts of primary and supergene copper sulphides (mainly chalcopyrite and chalcocite) are widespread in the Lake Boga granite. Trace amounts of silver must also be present to explain the occurrence of rare chlorargyrite and iodargyrite. While no primary bismuth sulphides have so far been detected, several Bi-bearing secondary minerals, other than bleasdaleite, have recently been collected, including two unknown green Cu-Bi phosphates. As well as small amounts of bismuth (up to 3.5 wt. %) in the chalcocite associated with bleasdaleite, zones with up to 3.6 wt. % Bi have been detected in chalcocite crystals found elsewhere in the granite.

It therefore appears that bleasdaleite is the product of a

series of alteration reactions, commencing with the formation of supergene chalcocite from chalcopyrite containing a primary Bi sulphide. This was followed by chalcocite alteration to covellite. Finally, the reaction between Ca- and P-bearing aqueous chloride solutions and the Bi-bearing supergene sulphides took place, giving rise to bleasdaleite and other secondary copper phosphates. The absolute timing of the stages in this sequence of reactions is unknown.

ACKNOWLEDGEMENTS

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