Description and crystal structure of bobkingite, $Cu_5^{2+}Cl_2(OH)_8(H_2O)_2$, a new mineral from New Cliffe Hill Quarry, Stanton-under-Bardon, Leicestershire, UK

F. C. Hawthorne[1,*], M. A. Cooper[1], J. D. Grice[2], A. C. Roberts[3] and N. Hubbard[4]

[1] Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2
[2] Research Division, Canadian Museum of Nature, P.O. Box 3443, Station 'D', Ottawa, Ontario, Canada K1P 6P4
[3] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8
[4] 30 Thirlmere Road, Barrow-upon-Soar, Leicestershire, LE12 8QQ, UK

ABSTRACT

Bobkingite, ideally $Cu_5^{2+}Cl_2(OH)_8(H_2O)_2$, is a new mineral from the New Cliffe Hill Quarry, Stanton-under-Bardon, Leicestershire, England. It occurs as very thin ($\leqslant 5$ μm) transparent plates up to 0.2 mm across, perched on a compact fibrous crust of malachite and crystalline azurite attached to massive cuprite. Crystals are tabular on {001} with dominant {001} and minor {100} and {110}. Bobkingite is a soft pale blue colour with a pale-blue streak, vitreous lustre and no observable fluorescence under ultraviolet light. It has perfect {001} and fair {100} cleavages, no observable parting, conchoidal fracture, and is brittle. Its Mohs' hardness is 3 and the calculated density is 3.254 g/cm^3. Bobkingite is biaxial negative with $\alpha = 1.724(2)$, $\beta = 1.745(2)$, $\gamma = 1.750(2)$, $2V_{\gamma meas} = 33(6)°$, $2V_{calc} = 52°$, pleochroism distinct, X = very pale blue, Z = pale greenish blue, $X \wedge a = 22°$ (in β obtuse), $Y = c$, $Z = b$. Bobkingite is monoclinic, space group $C2/m$, unit-cell parameters (refined from powder data): $a = 10.301(8)$, $b = 6.758(3)$, $c = 8.835(7)$ Å, $\beta = 111.53(6)°$, $V = 572.1(7)$ Å^3, $Z = 2$. The seven strongest lines in the X-ray powder-diffraction pattern are [d (Å), I, (hkl)]: 8.199, 100, (001); 5.502, 100, (110); 5.029, 40, ($\bar{2}$01); 2.883, 80, (310); 2.693, 40, ($\bar{1}$13); 2.263, 40, (113), ($\bar{4}$03); 2.188, 50, ($\bar{2}$23). Chemical analysis by electron microprobe and crystal-structure solution and refinement gave CuO 70.46, Cl 12.71, H$_2$O 19.19, O $\equiv$ Cl -2.87, sum 99.49 wt.%, where the amount of H$_2$O was determined by crystal-structure analysis. The resulting empirical formula on the basis of 12 anions (including 8 (OH) and 2H$_2$O) is Cu$_{4.99}$Cl$_{2.02}$O$_{10}$H$_{12}$. The crystal structure was solved by direct methods and refined to an R index of 2.6% for 638 observed reflections measured with X-rays on a single crystal. Three distinct (Cuϕ_6) (ϕ = unspecified anion) octahedra share edges to form a framework that is related to the structures of paratacamite and the Cu$_2$(OH)$_3$Cl polymorphs, atacamite and clinoatacamite. The mineral is named for Robert King, formerly of the Department of Geology, Leicester University, prominent mineral collector and founding member of the Russell Society. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Introduction

THE new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The mineral is named after Robert King (1923–), mineralogist at the Department of Geology, Leicester University (UK), now retired, a prominent mineral collector and founding member of the Russell Society. The holotype specimen of bobkingite is stored in the collection of the Canadian Museum of Nature, Ottawa,

* E-mail: frank_hawthorne@umanitoba.ca

Ontario, Canada (CMNNG 83270: crystal used for optical determinations) and in the X-ray powder-mount reference collection in the X-ray diffraction laboratory at the Geological Survey of Canada, Ottawa, Ontario, Canada.

Occurrence

Bobkingite was found at New Cliffe Hill Quarry, Stanton-under-Bardon, Leicestershire, England, grid reference SK 462 107. New Cliffe Hill quarry was started in 1990, producing aggregate and processing road metal. The quarry is currently working, but is expected to close next year, when the neighbouring Cliffe Hill quarry will be re-activated. Both quarries work a diorite (Snowball, 1952) from one of a series of dioritic laccoliths, the South Charnwood diorites, near the junction of the Maplewell and Brand members of the (Precambrian) Charnian Series of pyroclastic and epiclastic rocks (Sylvester-Bradley and Ford, 1968). The South Charnwood diorites crop out in an arc between Brodgate Park and Stanton-under-Bardon, and probably form part of a single intrusion (Hill and Bonney, 1978; Worrsam and Old, 1988). The diorite consists of primary calcic amphibole, calcic plagioclase and quartz that has altered to epidote, carbonate white mica and chlorite.

"A couple of hundred tons" of vein copper minerals were discovered in 1990/1991, but most of it was buried in the dumps. The rock containing bobkingite was collected from the dump in August 1992. The pieces recovered consist primarily of native copper and cuprite with malachite, azurite and a large suite of secondary copper-oxysalt minerals (Hubbard, in prep). Bobkingite occurs as parallel growths of thin platy crystals, up to 0.2 mm across, on a compact fibrous crust of malachite and crystalline azurite on massive cuprite. The malachite and azurite fill pore spaces in the cuprite, and both the carbonate minerals and bobkingite have formed by alteration of cuprite.

Physical properties

Bobkingite occurs as very thin ($\leqslant 5$ μm) transparent plates (Fig. 1). Crystals are tabular on {001} with dominant {001} pinacoid, minor {100} pinacoid and {110} prism. The crystals contain abundant randomly-oriented inclusions of malachite and (possibly) paratacamite. The streak is pale blue, the lustre vitreous. There is a perfect

{001} cleavage and a fair {100} cleavage; no parting was observed. The Mohs' hardness is 3. The density could not be measured due to the very small volume of individual crystals and the presence of inclusions; the calculated density is 3.254 g/cm^3.

Optical properties were measured (on the crystal used for collection of the X-ray intensity data) with a Bloss spindle stage for the wavelength 590 nm, using a gel filter. The indices of refraction are α = 1.724(2), β = 1.745(2), γ = 1.750(2), the calculated birefringence ($\gamma-\alpha$) is 0.026, 2V$_{\gamma meas}$ 33(6)°, 2V$_{calc}$ 52°. Bobkingite has distinct pleochroism, X = very pale blue, Z = pale greenish blue, orientation $X^\wedge a$ = 22° (in β obtuse), $Y = c$, $Z = b$.

Chemical composition

Crystals were analysed using a Cameca SX-50 electron microprobe operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 20 μm. The following standards were used: cuprite (Cu) and tugtupite (Cl). The data were reduced and corrected by the 'PAP' method of Pouchou and Pichoir (1984, 1985). The presence and quantity of (OH) and (H$_2$O) groups were established by crystal-structure solution and refinement (Hawthorne and Grice, 1990). The resultant chemical composition is given in Table 1, together with the formula unit based on 12 anions [including 8 (OH) and 2 (H$_2$O) groups] p.f.u. (per formula unit).

X-ray powder diffraction

The powder-diffraction pattern was recorded with a 114.6 mm Debye-Scherrer powder camera

TABLE 1. Chemical composition (wt.%)* and unit formula** (a.p.f.u.) for bobkingite.

CuO	70.46	Cu	4.99
Cl	12.71		
*H$_2$O	19.19	Cl	2.02
O≡Cl	−2.87		
Sum	99.49	OH	8
		H$_2$O	2

* average of five determinations
** the unit formula was calculated on the basis of 12 anions with (OH) = 8 and (H$_2$O) = 2 p.f.u.
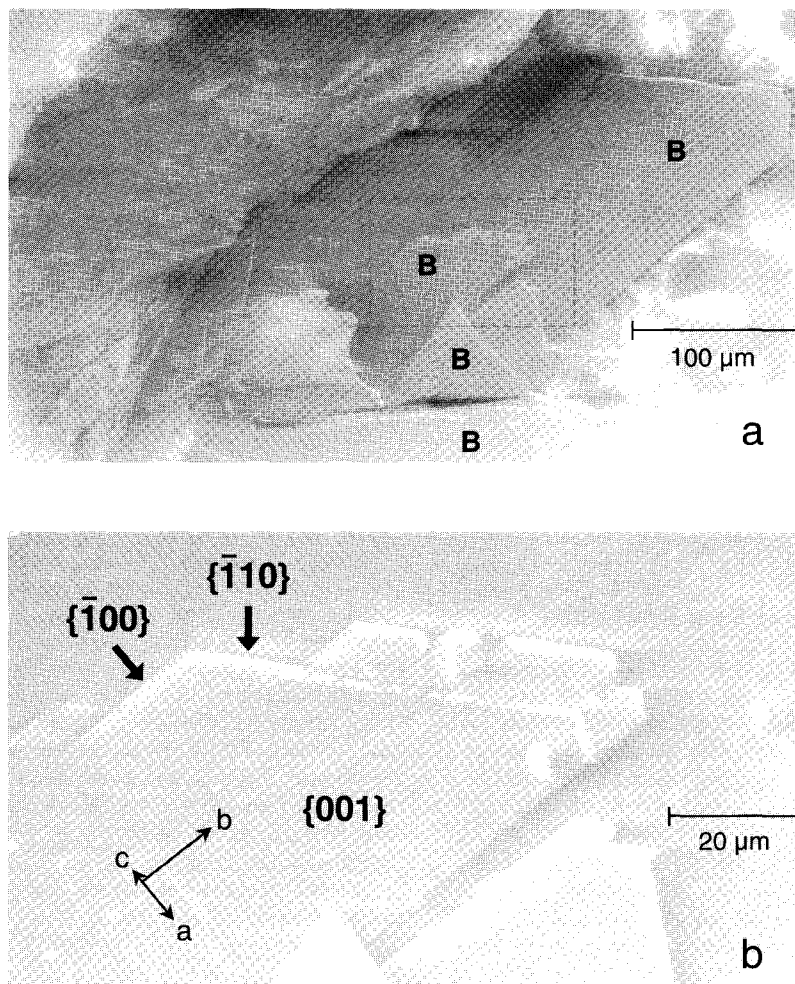
302

FIG. 1. Scanning electron micrographs of bobkingite. (*a*) Thin plates of bobkingite "B"; (*b*) magnified central portion of (*a*) with crystallographic labelling.

using Ni-filtered Cu-$K\alpha$ X-radiation. Table 2 shows the X-ray powder-diffraction data for bobkingite, together with the refined unit-cell dimensions.

Experimental

The crystal of bobkingite used for the collection of the single-crystal X-ray intensity data is an ultra-thin plate that was mounted on a Bruker four-circle diffractometer equipped with a CCD detector and Mo-$K\alpha$ X-radiation. A sphere of intensity data was collected to $60°2\theta$ according to the procedure of Cooper and Hawthorne (2001)

using a frame width of $0.2°$ and a frame time of 120 s. The final cell parameters (Table 3) are based on least-squares refinement of 1399 reflections ($>10\sigma I$). An empirical absorption correction was used in which the crystal was modelled as a (001) thin plate, and reflections within a $5°$ glancing angle of the plate were removed. Of 876 unique reflections remaining, 638 were considered as observed ($F_o > 5\sigma F$).

All calculations were done with the SHELXTL PC (PLUS) system of programs; R indices are of the form given in Table 3. The structure was solved by direct methods and refined to convergence; three of the five H-atom sites were then

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

I_{est}	d_{meas} (Å)	d_{calc} (Å)	hkl		I_{est}	d_{meas} (Å)	d_{calc} (Å)	hkl
100	8.199	8.218	001		3	2.204	2.204	$4\bar{2}$
100	5.502	5.523	110	*	50	2.188	2.190	$23\bar{2}$
5	5.123	5.112	$11\bar{1}$	*	5	2.128	2.128	23
40	5.029	5.017	$\bar{2}01$	*	15	2.102	2.102	401
3	4.813	4.791	200		3	2.076	2.076	131
* 20	4.190	4.192	111		"	"	2.074	$14\bar{1}$
* 20	4.113	4.109	002		"	"	2.073	203
5	3.895	3.907	$\bar{2}02$	*	10	2.059	2.055	4
* 15	3.607	3.604	201	*	10	2.049	2.044	$21\bar{4}$
* 15	3.376	3.379	020		3	2.006	2.006	$32\bar{1}$
* 20	3.129	3.125	021	*	15	1.958	1.960	$12\bar{5}$
* 15	3.064	3.061	$\bar{3}11$		5	1.893	1.883	$31\bar{3}$
3	3.006	3.006	112	*	10	1.878	1.879	$23\bar{4}$
* 80	2.883	2.888	310	*	10	1.864	1.865	$13\bar{5}$
3	2.840	2.849	$\bar{3}12$		15	1.842	1.846	$24\bar{2}$
20	2.795	2.803	$\bar{2}21$		"	"	1.841	330
* 20	2.766	2.761	220	*	30	1.786	1.787	$33\bar{1}$
* 30	2.741	2.740	003	*	40	1.767	1.767	223
* 40	2.693	2.691	$\bar{1}13$		10	1.723	1.723	313
* 20	2.606	2.610	022		"	"	1.720	331
* 30	2.559	2.559	$\bar{2}22$	*	20	1.707	1.704	$33\bar{3}$
* 10	2.510	2.509	$\bar{4}02$	*	20	1.690	1.690	40
3	2.480	2.479	311	*	10	1.671	1.671	$5\bar{4}$
* 5	2.461	2.465	221		3	1.654	1.655	41
3	2.432	2.431	$\bar{3}13$	*	10	1.643	1.646	133
* 30	2.397	2.396	400					
40	2.263	2.270	113					
"	"	2.261	$\bar{4}03$					

114.6 mm Debye-Scherrer powder camera
Cu radiation, Ni filter (λ Cu-$K\alpha$ = 1.54178 Å)
Intensities estimated visually
Corrected for shrinkage and no internal standard
* = lines used for unit-cell refinement
Indexed with a = 10.301(8), b = 6.758(3), c = 8.835(7) Å, β = 111.53(6)
Calculated powder pattern from single-crystal structure used to aid indexing

found on difference-Fourier maps. All non-H atoms were represented with anisotropic displacements, the isotropic displacements for the H atoms were fixed (Table 4), the O—H distances were subject to the soft constraint that O—H ≈ 0.98 Å, and the structure was refined until convergence at an R index of 2.6%. Final positions and displacement parameters are listed in Table 4, selected interatomic distances and angles are given in Table 5, and a bond-valence table is given as Table 6. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Discussion

Cation and anion coordination

There are three symmetrically distinct Cu sites in the structure of bobkingite. The Cu(1) site is surrounded by six (OH) groups in an octahedral arrangement with a <Cu–OH> distance of 2.100 Å; this distance is in accord with the observed degree of octahedral distortion according to the relation of Burns and Hawthorne (1996). The longer axial bonds (Table 5) indicate significant Jahn-Teller distortion associated with the degenerate ground-state of a d^9 metal (Cu^{2+}) in a holosymmetric

TABLE 3. Miscellaneous information for crystal-structure analysis of bobkingite.

a (Å)	10.3113(9)	Crystal size (mm)	$0.004 \times 0.10 \times 0.14$
b	6.7606(5)	Radiation	Mo $K\alpha$/graphite
c	8.8386(8)	No. of reflections	3342
β ($^\circ$)	111.468(5)	No. after glancing angle correction	2992
V (Å^3)	573.4(1)		
Sp. Gr.	$C2/m$	No. in Ewald sphere	2406
Z	2	No. unique reflections	876
		No. $F_o > 5\sigma F$	638
		R_{merge} %	2.8
		R_{obs} %	2.6
		wR_{obs} %	2.8
Cell content	$2[Cu_5Cl_2(OH)_8(H_2O)_2]$		

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR = [\Sigma w^2(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 1$

octahedral field (Jahn and Teller, 1937). The Cu(2) site is surrounded by four (OH) groups and one Cl anion in a square-pyramidal arrangement, with Cl occupying the apex of the pyramid and the (OH) groups occupying the corners of the base, with <Cu−OH> = 1.96 Å. There is an additional (H$_2$O) group (OW site) that is located in an extreme apical position on the other side of the square pyramid opposite the Cl position, and lying 3.276 Å from the Cu(2) site. Although the bond valence associated with this long Cu(2)−OW interaction is very weak (Table 6), we have chosen to include the (H$_2$O) group as a sixth ligand, and represent the Cu(2) polyhedron as an elongated octahedron (Table 5). The Cu(3) site is surrounded by four meridional (OH) groups at a mean distance of 1.982 Å and two apical Cl anions at a distance of 2.795 Å; these values are close to the average values for $[Cu^{2+}(OH)_4Cl_2]$ octahedra in minerals and are close to the optimum ranges given by Hartree-Fock calculations (Burns and Hawthorne, 1995).

The Cl$^-$ anion is surrounded by three Cu^{2+} cations, but all bonds show typical Jahn-Teller elongation, and the sum of the bond valences at Cl solely from the Cu^{2+} cations is only 0.38 value units (v.u.). Hence Cl must be a significant hydrogen-bond acceptor.

Hydrogen bonding

It is fairly straightforward to identify the type of anions in the bobkingite structure. The sum of the bond valences incident at the anions (exclusive of any hydrogen bonding) is shown in the central Σ column of Table 6. The sums are $\geqslant 1$ v.u. at OH(1), OH(2) and OH(3), and hence these anions

must be (OH); the sum at (H$_2$O) is 0 v.u., and hence this anion must be an (H$_2$O) group. The H-atom sites associated with the (OH) groups were found in the refinement of the structure, and these are labelled H(1), H(2) and H(3) (Tables 4, 5 and 6). The H-atom sites associated with the (H$_2$O) group were not found in the final difference-Fourier maps, and were assigned from the bond-valence arguments given above; these atoms are shown as H[4] and H[5] in Table 6.

The H(1) atom is part of the OH(1) group and hydrogen-bonds to the Cl$^-$ anion at a distance of 2.14 Å; note that Cl accepts two hydrogen-bonds from adjacent OH(1) anions (Table 6); these hydrogen bonds occur within the octahedral holes of the octahedral sheets (Figs 2a, 3a). The H(2) atom is part of the OH(2) group and hydrogen-bonds to the (H$_2$O) group at a distance of 1.77 Å; these hydrogen bonds are directed approximately along [001] from the octahedral sheet to the OW sites between the sheets (Figs 2e, 3a,b).

The H(3) atom is disordered off the 2-fold rotational axis that passes through the shared OH(3)−OH(3) edge of the Cu(2)−Cu(2) dimer along ½, y, ½ (Table 4); the hydrogen bond is directed toward the OW position of the (H$_2$O) group 1.84 Å away; this configuration gives a sensible OH(3)−H(3)...OW angle of 172° (Table 5, Fig. 3a).

The H[4] and H[5] atoms had somewhat nebulous signatures in difference-Fourier maps; however, unambiguous acceptor anions for the hydrogen bonds of the (H$_2$O) group can be recognized easily. After assignment of the hydrogen bonds associated with the H(1), H(2) and H(3) atoms, there are only two remaining

TABLE 4. Atom positions and displacement factors for bobkingite.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu(1)	1/2	1/2	0	0.0104(5)	0.0102(5)	0.0113(5)	0	0.0061(4)	0	0.0100(3)
Cu(2)	0.46706(8)	1/2	0.32367(9)	0.0175(4)	0.0127(4)	0.0097(3)	0	0.0043(3)	0	0.0135(2)
Cu(3)	1/4	1/4	0	0.0133(3)	0.0093(3)	0.0121(3)	0.0006(3)	0.0044(3)	−0.0013(3)	0.0116(2)
Cl	0.1835(2)	1/2	0.2129(2)	0.0138(6)	0.0173(7)	0.0192(7)	0	0.0078(6)	0	0.0163(5)
OH(1)	0.4469(3)	0.3104(5)	0.1456(4)	0.0146(13)	0.0124(14)	0.0143(14)	−0.0012(12)	0.0049(11)	0.0033(11)	0.0139(9)
OH(2)	0.2661(5)	1/2	−0.1032(5)	0.0339(27)	0.0108(21)	0.0084(20)	0	0.0073(19)	0	0.0178(16)
OH(3)	1/2	0.3127(8)	1/2	0.0345(27)	0.0173(23)	0.0135(21)	0	0.0066(20)	0	0.0224(16)
OW	0.1931(7)	1/2	0.5669(7)	0.0637(45)	0.0405(37)	0.0193(28)	0	0.0143(29)	0	0.0414(25)
H(1)	0.512(5)	0.199(6)	0.170(7)							0.0300 *
H(2)	0.254(9)	1/2	−0.219(3)							0.0300 *
H(3)	0.437(9)	0.199(10)	0.470(14)							0.0300 *

* fixed in refinement

TABLE 5. Selected interatomic distances (Å) and angles (°) in the crystal structure of bobkingite.

Cu(1)–OH(1)	×4	2.028(3)	Cu(3)–OH(1)	×2	2.008(3)
Cu(1)–OH(2)	×2	2.245(5)	Cu(3)–OH(2)	×2	1.956(3)
<Cu(1)–OH>		2.100	Cu(3)–Cl	×2	2.795(2)
			<Cu(3)–OH,Cl>		2.253
Cu(2)–OH(1)	×2	1.981(3)			
Cu(2)–OH(3)	×2	1.939(3)	OH(2)–H(2)		0.98(3)
Cu(2)–Cl		2.722(2)	H(2)–OW		1.77(2)
Cu(2)–OW		3.276(7)	OH(2)–H(2)–OW	168(8)	
<Cu(2)–OH,OW, Cl>		2.306	OH(2)OW		2.732(7)
OH(1)–H(1)		0.98(4)	OH(3)–H(3)		0.98(8)
H(1)–Cl		2.14(5)	H(3)–OW		1.84(8)
OH(1)–H(1)–Cl	168(4)		OH(3)–H(3)–OW	172(10)	
OH(1)Cl		3.107(3)	OH(3)OW		2.815(6)
			OWCl		3.094(7)
			OWOH(3)		2.815(6)
			Cl–OW–OH(3)		91.7(1)

anions that are underbonded [Cl = 0.78 v.u. and OH(3) = 1.80 v.u.]. We therefore assigned hydrogen bonds from the H[4] and H[5] atoms to the anions at the Cl and OH(3) sites, respectively; this assignment is supported by both geometrical and bond-valence considerations (Tables 5, 6). Because the O-atom at OH(3) acts as a hydrogen-bond acceptor and a hydrogen-bond donor, disorder of the H(3) atom must be coupled to disorder in the hydrogen-bond configuration associated with the (H$_2$O) group. We have depicted various local hydrogen-bond configurations associated with ordered H(3) sites in Fig. 3c. Note that a particular local hydrogen-bond configuration (circled in red) does not have any effect on neighbouring local configurations; hence, H is equally likely to occur locally at either site. We

tested the possibility of lower symmetry (Cm) that might be consistent with an ordered H(3) site; however, the disorder was still present in Cm, and hence we report the disordered C2/m model here. It should be noted that certain stereochemical arrangements of H(3) atoms will not occur. An example is given in Fig. 3d; the H$_2$O group cannot receive two H-bonds from two neighbouring H(3) atoms, as, although this arrangement satisfies the incident bond-valence requirements at OW', Cl', OH(3)' and OH(3)'', Cl'' and OW'' remain significantly underbonded.

Structure topology

The (Cuϕ$_6$) (ϕ = unspecified anion) octahedra link by sharing edges to form a framework structure that is strongly related to the structures

TABLE 6. Bond-valence (v.u.) table for bobkingite*.

	Cu(1)	Cu(2)	Cu(3)	Σ	H(1)	H(2)	H(3)	H[4]**	H[5]**	Σ
OH(1)	0.39×4↓	0.44×2↓	0.41×2↓	1.24	0.80					2.04
OH(2)	0.22×2↓		0.47×2↓→	1.16		0.80				1.96
OH(3)		0.50×2↓→		1			0.80		0.20	2.00
OW		0.01		0.01		0.20	0.20	0.80	0.80	2.01
Cl		0.14	0.12×2↓→	0.38	0.20×2→			0.20		0.98
Σ	2.00	2.03	2.00		1.00	1.00	1.00	1.00	1.00	

* from the curves of Brown and Altermatt (1985)
** not located in the refinement

BOBKINGITE   (001)
CLINOATACAMITE   (011)
PARATACAMITE   (20$\bar{1}$)

ATACAMITE   (101)

$\leftarrow$ $Cu(OH)_4Cl_2$ $\rightarrow$

$\leftarrow$ $Cu(OH)_6$ $Cu(OH)_5Cl$ $\rightarrow$

$\leftarrow$ $Cu(OH)_4Cl_2$ $\rightarrow$

a   **b**

CLINOATACAMITE [3$\bar{1}$1]
PARATACAMITE   [$\bar{2}$$\bar{1}$4]
$Cu(OH)_4Cl_2$ **c**

ATACAMITE [10$\bar{1}$]
$Cu(OH)_5Cl$ **d**

BOBKINGITE [$\bar{1}$00]
$Cu(OH)_4Cl(H_2O)$ **e**
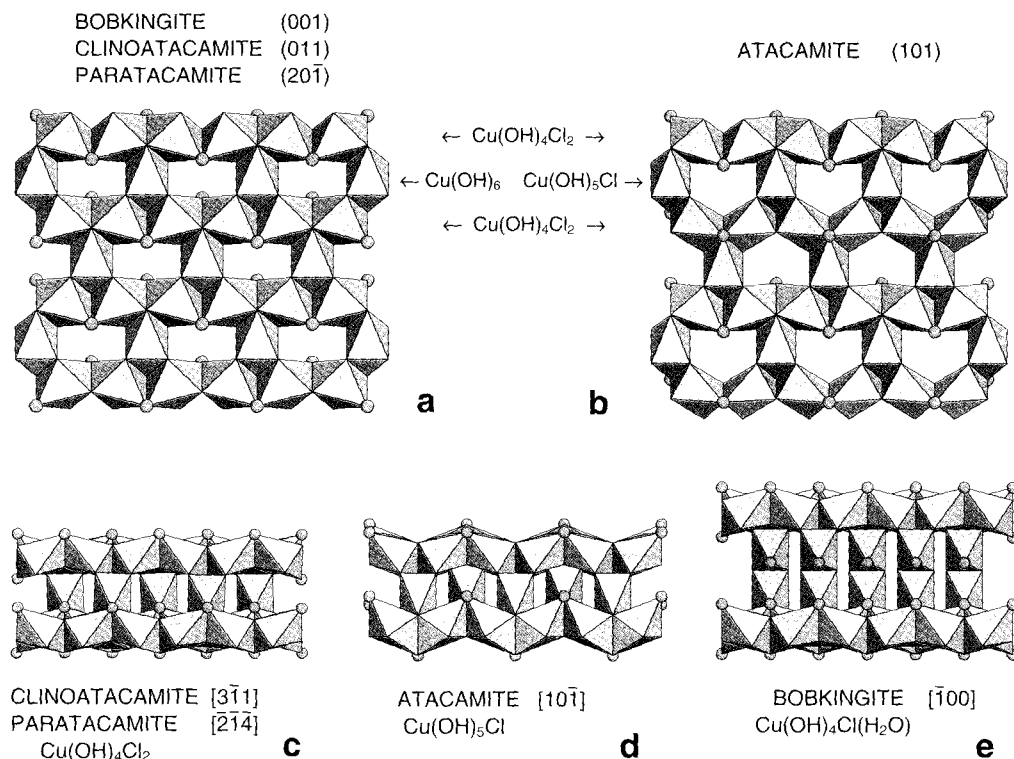
FIG. 2. The structure of bobkingite and structural relations in bobkingite, paratacamite and the $Cu_2(OH)_3Cl$ polymorphs atacamite and clinoatacamite; green circles, Cl; orange circles, H_2O.

of paratacamite (Fleet, 1975) and the $Cu_2(OH)_3Cl$ polymorphs, atacamite (Parise and Hyde, 1986) and clinoatacamite (Grice *et al.*, 1996); note that the captions to Fig. 3*a,b* of Grice *et al.* (1996) should read (a) (101) projection.... and (b) (010) projection... . A comparison of the $Cu_2(OH)_3Cl$ polymorphs (atacamite, clinoatacamite, botallackite) and the related paratacamite is given by Grice *et al.* (1996). Here, we have chosen different principal sheets to better facilitate comparison with the structure of bobkingite (Fig. 2). The atacamite, clinoatacamite, paratacamite and bobkingite structures are all framework structures based on edge-sharing of $(Cu\phi_6)$ octahedra (ϕ = unspecified anion); botallackite is a sheet structure (Hawthorne, 1985) and will not be discussed further.

A key unit in all four structures is the interrupted octahedral sheet shown in Fig. 2. Rutile-like chains of $(Cu\{OH\}_4Cl_2)$ octahedra are common to all four structures (extending horizontally across the page in Figs 2*a* and 2*b*),

and are linked into sheets by $(Cu\{OH\}_6)$ octahedra in bobkingite, clinoatacamite, and paratacamite, and by $(Cu\{OH\}_5Cl)$ octahedra in atacamite. These sheets are topologically identical in all four structures, but the difference in stereochemistry between atacamite and the other three minerals produces significant geometrical differences (Fig. 2*a,b*). In Fig. 2*a*, the vacant octahedra have the vertices $(OH)_4Cl_2$, whereas in Fig. 2*b*, the vacant octahedra have the vertices $(OH)_5Cl$. In Fig. 2*a*, each successive $[Cu(OH)_4Cl_2]$ chain is shifted laterally by one octahedron, whereas for atacamite (Fig. 2*b*) there is no relative shift in adjacent chains. As a result, $(Cu\phi_6)$ octahedra linking adjacent $[Cu(OH)_4Cl_2]$ chains have compositions $(Cu\{OH\}_6)$ and $(Cu\{OH\}_5Cl)$ in Figs 2*a* and 2*b*, respectively. This difference in offset of $[Cu(OH)_4Cl_2]$ chains can also be seen looking along the sheet in Figs 2*c* and 2*d*.

Figures 2*c*~*e* show how the layers are linked into frameworks in each of the structures. In
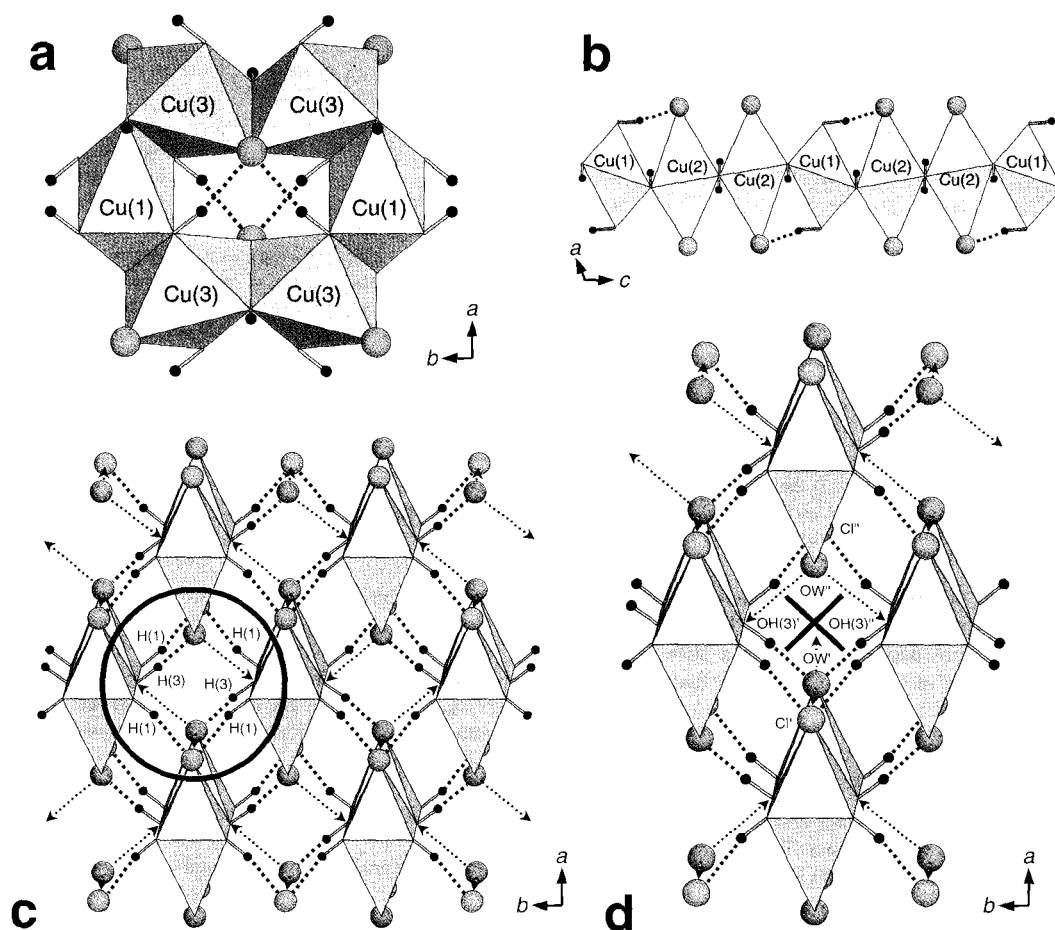
308

FIG. 3. H-bonding for bobkingite. Legend as in Fig. 2; small black spheres = H positions. (*a*) Dashed H-bonds directed from H(1) to Cl, projected onto (001); (*b*) dashed H-bonds directed from H(2) to OW, projected onto (010); (*c*) various H-bonding configurations involving disordered H(3) positions and OW acceptors (heavy dashes), H-bonds directed from H(1) to Cl (heavy dashes), and H-bonds from the H_2O group directed towards OH(3) and Cl acceptors (light dashes with arrows); projected down an axis 3° from **c***; (*d*) a forbidden H-bonding configuration involving disordered H(3) positions. Legend and orientation as in (*c*).

clinoatacamite and paratacamite, these sheets are linked by edge-sharing with $(Cu\{OH\}_4Cl_2)$ octahedra (Fig. 2*c*). In atacamite, the sheets are linked by $(Cu\{OH\}_5Cl)$ octahedra (Fig. 2*d*). Obviously, the linkage of sheets in bobkingite must be significantly different in order to account for the different chemical composition. In bobkingite, the sheets are linked by octahedral edge-sharing dimers of $[Cu(OH)_4Cl(H_2O)]$ octahedra (Fig. 2*e*).

Related minerals

Compositionally related Cu^{2+} and Zn hydroxy-(hydrated) chlorides are listed in Table 7, together with their symmetry and unit-cell dimensions. Most of these minerals are not hydrated, and hence do not fall in the family of decorated $[Cu^{2+}\phi_2]_N$ sheets discussed by Hawthorne and Schindler (2000). Both bobkingite and simonkolleite contain essential (H_2O), and at first sight,

TABLE 7. Selected Cu^{2+} and Zn hydroxy-(hydrated)-chloride minerals.

Mineral	Formula (a.p.f.u.)	a (Å)	b (Å)	c (Å)	β (°)	Space group	Ref.
Belloite	$CuCl(OH)$	5.552(3)	6.668(2)	6.124(2)	115.00(3)	$P2_1/a$	(1)
Atacamite	$Cu_2Cl(OH)_3$	6.030(2)	6.865(2)	9.120(2)	–	$Pnma$	(2)
Clinoatacamite	$Cu_2Cl(OH)_3$	6.805(1)	6.805(1)	9.112(1)	99.55(3)	$P2_1/n$	(3)
Paratacamite	$Cu_2Cl(OH)_3$	13.654(5)	a	14.041(6)	–	R	(4)
Botallackite	$Cu_2Cl(OH)_3$	5.717(1)	6.126(1)	5.636(1)	93.07(1)	$P2_1/m$	(5)
Simonkolleite	$Zn_5Cl_2(OH)_8(H_2O)$	6.3412(3)	a	23.646(1)	–	Rm	(6)
Bobkingite	$Cu_5Cl_2(OH)_8(H_2O)_2$	10.301(8)	6.758(3)	8.835(7)	111.53(6)	$C2/m$	(7)
Calumetite	$Cu(OH,Cl)_2(H_2O)_2$	–	–	–	–		(8)
Anthonyite	$Cu(OH,Cl)_2(H_2O)_3$	–	–	–	–		(8)
Claringbullite	$Cu_4Cl(Cl_{0.29}OH_{0.71})(OH)_6$	6.673(1)	–	9.185(1)	–	$P6_3/mmc$	(9)
Eriochalcite	$CuCl_2(H_2O)_2$	8.104(8)	3.757(4)	7.433(7)	–	$Pmna$	(10)

(1) Schlüter et al. (2000); (2) Parise and Hyde (1986); (3) Jambor et al. (1996); (4) Fleet (1975); (5) Hawthorne (1985); (6) Hawthorne and Sokolova (in press); (7) Hawthorne et al. (this work); (8) Williams (1963); (9) Burns et al. (1995); (10) Engberg (1970)

could possibly have a structure based on a decorated $[Cu^{2+}\phi_2]_N$ sheet. However, although bobkingite does contain such a sheet, there are additional non-sheet Cu^{2+} sites that result in a framework structure.

Acknowledgements

References

Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Crystallographica, B41, 244–247.

Burns, P.C. and Hawthorne, F.C. (1995) Mixed-ligand $Cu^{2+}\phi_6$ octahedra in minerals: Observed stereo-chemistry and Hartree-Fock calculations. The Canadian Mineralogist, 33, 1177–1188.

Burns, P.C. and Hawthorne, F.C. (1996) Static and dynamic Jahn-Teller effects in Cu^{2+} oxysalt minerals. The Canadian Mineralogist, 34, 1089–1105.

Burns, P.C., Cooper, M.A. and Hawthorne, F.C. (1995) Claringbullite: a Cu^{2+} oxysalt with Cu^{2+} in trigonal-prismatic coordination. The Canadian Mineralogist, 33, 633–639.

Cooper, M.A. and Hawthorne, F.C. (2001) Structure

topology and hydrogen bonding in marthozite, $Cu^{2+}[(UO_2)_3(SeO_3)_2O_2](H_2O)_6$, a comparison with guilleminite, $Ba[(UO_2)_3(SeO_3)_2O_2]$ $(H_2O)_3$. The Canadian Mineralogist, 39, 797–807,

Engberg, A. (1970) An X-ray refinement of the crystal structure of copper(II) chloride dihydrate. Acta Chemica Scandinavia, 24, 3510–3526.

Fleet, M.E. (1975) The crystal structure of paratacamite, $Cu_2(OH)_3Cl$. Acta Crystallographica, B31, 183–187.

Grice, J.D., Szymański, J.T. and Jambor, J.L. (1996) The crystal structure of clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$. The Canadian Mineralogist, 34, 73–78.

Hawthorne, F.C. (1985) Refinement of the crystal structure of botallackite. Mineralogical Magazine, 49, 87–89.

Hawthorne, F.C. and Grice, J.D. (1990) Crystal-structure analysis as a chemical analytical method: application to light elements. The Canadian Mineralogist, 28, 693–702.

Hawthorne, F.C. and Schindler, M.S. (2000) Topological enumeration of decorated $[Cu^{2+}\phi_2]_N$ sheets in hydroxy-hydrated copper-oxysalt minerals. The Canadian Mineralogist, 38, 751–761.

Hawthorne, F.C. and Sokolova, E.S. (2002) Simonkolleite, $Zn_5(OH)_8Cl_2(H_2O)$, a decorated interrupted-sheet structure of the form $[M\phi_2]_4$. The Canadian Mineralogist (in press).

Hill, E. and Bonney, T.G. (1978) The Precarboniferous rocks of Charnwood Forest. Quarterly Journal of Geological Society of London, 34, 199–239.

Jahn, H.A. and Teller, E. (1937) Stability of polyatomic molecules in degenerate electronic states.

Proceedings of the Royal Society, Series A, **161**, 220–236.

Jambor, J.L., Dutrizac, J.E., Roberts, A.C., Grice, J.D. and Szymañski, J.T. (1996) Clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$, and its relationship to paratacamite and 'anarakite'. *The Canadian Mineralogist*, **34**, 61–72.

Parise, J.B. and Hyde, B.G. (1986) The structure of atacamite and its relationship to spinel. *Acta Crystallographica*, **C42**, 1277–1280.

Pouchou, J.L. and Pichoir, F. (1984) A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aerospace*, **3**, 13–38.

Pouchou, J.L. and Pichoir, F. (1985) "PAP" $(\phi\rho\zeta)$ procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis, 1985*, San Francisco Press, San Francisco, California.

Schlüter, J., Klaska, K.-H. and Gebhard, G. (2000) Belloite, $Cu(OH)Cl$, a new mineral from Sierra Gorda, Antofagasta, Chile. *Neues Jahrbuch für Mineralogie Monatshefte*, 67–73.

Snowball, G.T. (1952) The Leicestershire intrusions. *Leicester Museum Art Gallery Bulletin*, third series, **1**, 2–7.

Sylvester-Bradley, P.C. and Ford, T.D. (1968) *The Geology of the East Midlands*. Leicester University Press.

Williams, S.A. (1963) Anthonyite and calumetite, two new minerals from the Michigan copper district. *American Mineralogist*, **48**, 614–619.

Worssam, B.C. and Old, R.A. (1988) Geology of the Country around Coalville. *British Geological Survey Memoir*. HMSO, London.