

Refinement of the crystal structure of botallackite

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ABSTRACT. The crystal structure of botallackite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, monoclinic, $a = 5.717(1)$, $b = 6.126(1)$, $c = 5.636(1)$ Å, $\beta = 93.07(1)^\circ$, $V = 197.06(5)$ Å³, space group $P2_1/m$, $Z = 1$, has been refined to an R index of 3.8% for 350 observed (4σ) reflections, measured with Mo- $K\alpha$ X-radiation on an automatic four-circle diffractometer. The structure consists of sheets of edge-sharing $\text{Cu}\phi_6$ (ϕ = unspecified anion) octahedra of composition $\text{Cu}_2(\text{OH})_3\text{Cl}$; these sheets are // $\{100\}$, and are joined by hydrogen bonding between oxygen and chlorine anions, thus accounting for the perfect $\{100\}$ cleavage and the platy habit of botallackite.

KEYWORDS: crystal structure, botallackite, Botallack Mine, Cornwall.

BOTALLACKITE is a copper hydroxy-chloride, $\text{Cu}_2\text{Cl}(\text{OH})_3$, found associated with atacamite and paratacamite at the Botallack Mine, Cornwall. The crystal structure of botallackite was solved by Voronova and Vainshtein (1958) using electron diffraction data. Botallackite is trimorphous with atacamite and paratacamite, the structures of which were reported by Wells (1949) and Fleet (1975) respectively.

Experimental. The crystals used in this study were obtained from the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, catalogue number M37011; the original locality is the Botallack Mine, Cornwall. The crystal used for the intensity data collection was mounted on a Nicolet R3m automatic four-circle diffractometer, and twenty-five strong reflections were automatically aligned. Least-squares refinement of the setting angles produced the (monoclinically constrained) cell dimensions given in Table I, together with the orientation matrix relating the crystal axes to the diffractometer axes.

Intensity data were collected in the θ - 2θ scan mode with the scan rate variable between 4.0 and 29.3°/min depending on the intensity of an initial 1 s count at the centre of the scan range. Two standard reflections were monitored every forty-eight measurements to check for power stability and constancy of crystal alignment. A total of 762 reflections were measured over two asymmetric units out to a maximum 2θ of 60°. Ten strong

Table I. Miscellaneous information: botallackite

a	5.717(1)Å	Crystal size (mm):	0.03x0.12x0.18
b	6.126(1)	Rad/Mono	Mo/Gr.
c	5.636(1)	Total # of $ F_o $	379
β	93.07(1)°	$ F_o > 4\sigma$	350
V	197.06(5)Å ³	Final R (obs.)	3.8%
Space Group	$P2_1/m$	Final R_w (obs.)	4.2%
Unit cell contents: $[\text{Cu}_2(\text{OH})_3\text{Cl}]$			
$R = \sum (F_o - F_c) / \sum F_o $			
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$, $w = 1$			

reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0-350°. These were then used to calculate an empirical absorption correction, modelling the crystal as a thin plate. The minimum and maximum transmissions calculated were 0.276 and 0.727 respectively. The data were corrected for Lorentz, polarization, and background effects, and reduced to structure factors; of the 379 unique reflections, 358 were classed as observed [$I > 2.5\sigma(I)$].

Systematic absences confirmed the space group $P2_1/m$ assigned by Voronova and Vainshtein (1958). Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer and Mann (1968) and Cromer and

Table II. Positional parameters for botallackite

	x	y	z	$U_{\text{equiv.}}^{\dagger}$
Cu(1)	0.4914(3)	1/4	-0.0053(2)	0.87(4)
Cu(2)	1/2	0	1/2	0.92(4)
Cl	0.1339(5)	1/4	0.2974(5)	1.59(8)
O(1)	0.6686(16)	1/4	0.6249(15)	1.3(3)
O(2)	0.6415(9)	0.0076(11)	0.1832(11)	1.3(2)
H(1)	0.776(24)	1/4	0.533(24)	0.5*
H(2)	0.734(15)	0.042(16)	0.169(16)	0.5

$^{\dagger}U_{\text{equiv.}} = U_{\text{equiv.}} \times 10^2$; *fixed during refinement

Table III. Anisotropic temperature factor coefficients for botallackite

	U_{11}^*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	154(7)	45(7)	58(6)	0	-19(5)	0
Cu(2)	169(7)	57(7)	53(6)	-20(6)	16(5)	-12(5)
Cl	103(13)	166(14)	209(15)	0	22(11)	0
O(1)	196(47)	86(40)	99(42)	0	24(34)	0
O(2)	141(29)	100(29)	149(28)	-26(25)	34(24)	12(25)

* $U_{ij}^* = U_{ij} \times 10^4$

Lieberman (1970) respectively. The structure proposed by Voronova and Vainshtein (1958) refined rapidly to an R index of 5.5% for an isotropic thermal model. Insertion of hydrogen atoms and conversion of all non-hydrogen atom temperature factors to anisotropic resulted in convergence at an R index of 3.8% and a weighted R index of 4.2% for observed data. Final parameters are given in Tables II and III, and observed and calculated structure factors are given in Table IV.* Bond distances and angles are listed in Table V, and a bond-valence analysis is given in Table VI.

Table V. Interatomic distances (Å) and angles ($^\circ$) in botallackite

Cu(1)-O(1)	2.367(9)	Cu(2)-O(1)	1.920(5)x2
Cu(1)-O(2)	1.995(6)x2	Cu(2)-O(2)	2.001(6)x2
Cu(1)-O(2)'	1.998(6)x2	Cu(2)-Cl	2.789(2)x2
Cu(1)-Cl	2.732(3)		
O(1)-H(1)	0.8(1)		
H(1)-Cl	2.5(1)	O(1)-H(1)-Cl	116(3)
O(1)-Cl	3.318(9)		
O(2)-H(2)	0.6(1)		
H(2)-Cl	2.6(1)	O(2)-H(2)-Cl	132(15)
O(2)-Cl	3.214(6)		
O(1)-Cu(1)-O(2)	74.2(2)x2	O(1)-Cu(2)-O(2)	84.9(3)x2
O(1)-Cu(1)-O(2)'	106.1(2)x2	O(1)-Cu(2)-O(2)'	95.1(3)x2
O(2)-Cu(1)-O(2)'	79.7(2)x2	O(1)-Cu(2)-Cl	86.5(2)x2
O(2)-Cu(1)-O(2)''	96.3(3)	O(1)'-Cu(2)-Cl	93.5(2)x2
O(2)'-Cu(1)-O(2)''	104.2(3)	O(2)-Cu(2)-Cl	87.4(2)x2
O(2)-Cu(1)-Cl	89.1(2)x2	O(2)'-Cu(2)-Cl	92.6(2)x2
O(2)''-Cu(1)-Cl	92.0(2)x2		

Table VI. Bond-valence† table for botallackite

	Cu(1)	Cu(2)	H(1)	H(2)	Σ
O(1)	0.146	$0.513 \frac{x^2}{4}$	0.85		2.022
O(2)	$0.408 \frac{x^2}{2}$ $0.404 \frac{x^2}{4}$	$0.401 \frac{x^2}{4}$		0.85	2.063
Cl	0.190	$0.171 \frac{x^2}{4}$	0.15	$0.15 \frac{x^2}{2}$	0.982
Σ	1.960	2.170	1.0	1.0	

† calculated using the curves of Brown(1981)

* Copies of this structure factor table are available on request from the author. A copy has also been deposited in the Mineral Library, British Museum (Natural History).

Discussion. Cu(1) is octahedrally co-ordinated by five hydroxyls and one chlorine, whereas Cu(2) is octahedrally co-ordinated by four hydroxyls and two chlorines. Both polyhedra show strong Jahn-Teller distortion, with short equatorial bonds in a square-planar arrangement and elongated axial bonds involving chlorine and one hydroxyl. Each octahedron shares six edges with surrounding octahedra, forming a $[\text{Cu}_2(\text{OH})_3\text{Cl}]$ octahedral edge-sharing sheet parallel to $\{100\}$, as shown in fig. 1. These sheets are held together by hydrogen-bonding between the hydroxyl oxygens of one-sheet and the opposing chlorine atoms in the adjacent sheets (fig. 2), as proposed by Voronova and Vainshtein (1958) and Fleet (1975). The resulting weak bonding between the sheets accounts for the perfect $\{100\}$ cleavage and the typical platy habit of botallackite.

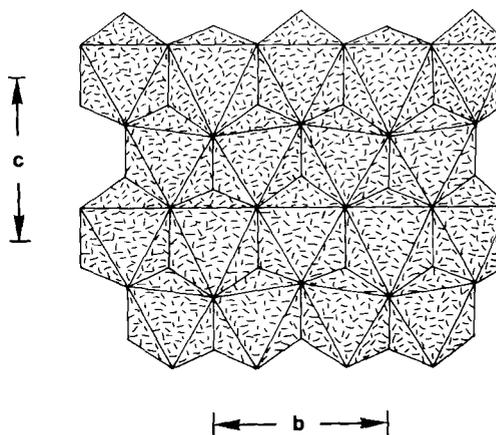


FIG. 1. The crystal structure of botallackite projected on to (100).

The empirical bond-valence table (Table VI) shows the relative strength of the equatorial and axial bonds of the $\text{Cu}\varphi_6$ (φ = unspecified anion) octahedra. The H-O bond-valences were arbitrary.

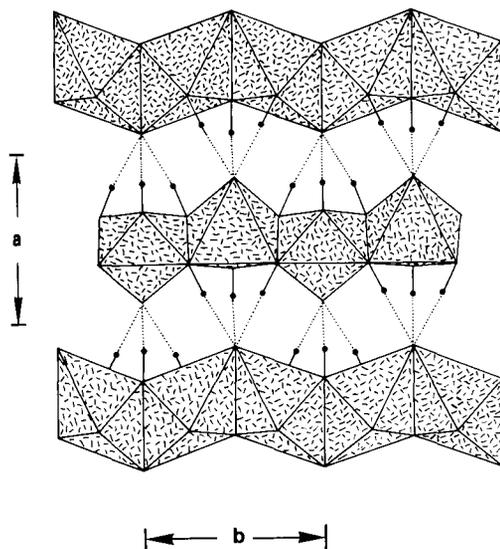


FIG. 2. The crystal structure of botallackite projected on to (001); hydrogen bonds are indicated by dotted lines.

rarily assigned as 0.85:0.15 v.u. for donor: acceptor bonds; the closeness of the anion bond-valence

sums to their ideal values suggests this assignment to be reasonable. It is interesting to note that the $\text{Cu}-\phi(\text{axial})$ bond-valences are approximately equal to the $\text{H}-\phi$ (acceptor) bond-valences.

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