

# Henmilite, $\text{Ca}_2\text{Cu}(\text{OH})_4[\text{B}(\text{OH})_4]_2$ , a new mineral from Fuka, Okayama Prefecture, Japan.

## I. Occurrence and description

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### ABSTRACT

Henmilite,  $\text{Ca}_2\text{Cu}(\text{OH})_4[\text{B}(\text{OH})_4]_2$ , has been found in borate veins cutting marble exposed at the Fuka mine, Fuka, Okayama. It is triclinic, space group  $P\bar{1}$ ,  $a = 5.7617(5)$ ,  $b = 7.9774(6)$ ,  $c = 5.6488(4)$  Å,  $\alpha = 109.611(6)$ ,  $\beta = 91.473(7)$ ,  $\gamma = 83.686(7)^\circ$ ,  $Z = 1$ . The strongest lines in the Gandolfi camera diffraction pattern are  $5.25(\text{vs})(001, 0\bar{1}1)$ ,  $4.35(\text{s})(\bar{1}10)$ ,  $3.931(\text{m})(101)$ ,  $3.709(\text{s})(1\bar{1}1, 0\bar{2}1)$ ,  $3.302(\text{s})(120)$ ,  $2.494(\text{s, broad})(1\bar{1}2, 030, \bar{1}\bar{3}1)$ ,  $2.427(\text{s, broad})(2\bar{1}1, 102)$ ,  $2.346(\text{s})(\bar{1}21)$ . Henmilite is bluish violet, transparent with a vitreous luster, and a very pale violet to nearly white streak.  $D_{\text{calc}} = 2.523$  g/cm<sup>3</sup>. Henmilite is optically biaxial, negative,  $2V_{\text{meas}} = 58^\circ$ , with  $\alpha = 1.585(2)$ ,  $\beta_{\text{calc}} = 1.608$ ,  $\gamma = 1.615(2)$ ; extinction oblique, pleochroism strong, axial colors:  $X =$  pale pink,  $Y =$  pale purple,  $Z =$  very pale blue.

The crystal structure was refined to  $R = 0.026$  using 2430 observed reflections. B forms isolated  $\text{B}(\text{OH})_4$  groups and Cu exhibits a square planar coordination by hydroxyl ions. Ca is surrounded by eight hydroxyls. Two Ca polyhedra share an edge to form dimers, which are connected to each other through  $\text{B}(\text{OH})_4$  tetrahedra to form chains parallel to the  $c$  axis. The chains are linked through square planar  $\text{Cu}(\text{OH})_4$  groups into a three-dimensional structure.

### INTRODUCTION

During a survey of the borate veins at Fuka mine, Fuka, Okayama Prefecture, Japan, some small blue-violet crystals closely associated with pentahydroborite (Fujiwara et al., 1982)<sup>1</sup> were observed. Subsequent study has shown the mineral to be a new species, the first example of a borate containing both Ca and Cu.

We have named the new mineral henmilite for Prof. Kitinosuke Henmi and his daughter Dr. Chiyoiko Henmi, Department of Earth Science, Okayama University, in recognition of their work on skarn minerals from Fuka, including the discovery of three new species, bicchulite (Henmi et al., 1973), fukalite (Henmi et al., 1977), and ôyelite (Kusachi et al., 1980). The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. Type material

has been deposited in the Department of Geology, National Science Museum, Tokyo.

### OCCURRENCE

Henmilite was found at the Fuka mine, a marble quarry, operated by Ootori Seiko Co. at Bicchukogyosho, Fuka. The Fuka mine is approximately 40 km northeast of Okayama city. This area is famous for the occurrence of many skarn minerals, e.g., bicchulite, fukalite, ôyelite, spurrite, gehlenite, rankinite, etc. Most of these are hydrated silicates of Ca, which are produced by high-temperature metamorphism and metasomatism of limestone followed by hydration reactions.

Henmilite occurs in small cavities in pentahydroborite veins at the marble quarry, where contact-metamorphosed limestone is being mined. Henmilite occurs as anhedral masses and rarely as euhedral crystals up to 0.2 mm growing on the surface of pentahydroborite. Since euhedral crystals of henmilite were also observed intergrown with pentahydroborite, the formation period of this

\* Deceased, January 6, 1985.

<sup>1</sup> References are listed after part II of this paper.

mineral is after or the same as that of pentahydroborite. Other associated minerals are calcite, minor brucite, and an unidentified borate mineral.

### CHEMISTRY

The sample was chemically analyzed using an electron microprobe with an operating voltage of 15 kV and a beam current of 0.15  $\mu$ A. A wavelength scan disclosed the presence of Ca and Cu in major amounts and no other elements of atomic number greater than 9. The standards used for quantitative analysis were cuprite for Cu and pentahydroborite for Ca. It must be noted here that microprobe analysis is not really suitable for henmilite, since the mineral easily decomposes under the electron beam. The data were corrected using the MAGIC-4 computer program. Inductively coupled plasma (ICP)-atomic emission spectroscopic analysis showed the presence of B, Ca, Cu, and minor Mg, but the presence of Mg in the mineral is uncertain because of the contamination of the sample by intimately associated minerals. Quantitative analysis of B was made by the ICP analysis. An IR spectrum clearly showed absorption by hydroxyl ion (Fig. 1), but water could not be directly determined owing to the limited amount of the sample available. Water content has there-

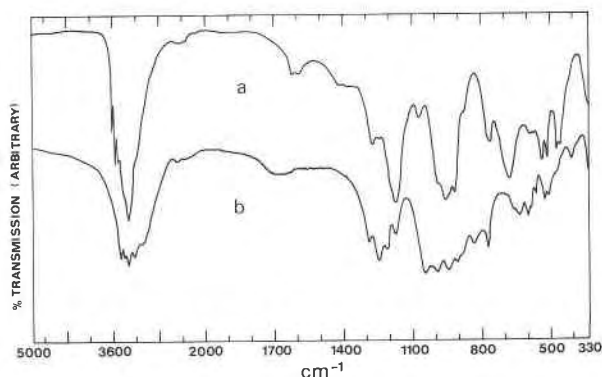


Fig. 1. Infrared spectra for (a) henmilite and (b) pentahydroborite from Fuka, Okayama Prefecture, Japan.

fore been calculated by difference. The result of the analyses gives CaO 31.7%, CuO 23.7%, B<sub>2</sub>O<sub>3</sub> 21.4%, H<sub>2</sub>O (by difference) 23.2%, and total 100.0%. The empirical formula calculated on the basis of O = 6 in the anhydrous part is Ca<sub>1.90</sub>Cu<sub>1.00</sub>B<sub>2.07</sub>O<sub>6</sub>·4.33H<sub>2</sub>O. The extremely limited availability of the sample together with the difficulty in accurately analyzing B and H<sub>2</sub>O precluded obtaining a reliable chemical formula. The chemical formula has been

Table 1. Observed and calculated X-ray powder-diffraction data for henmilite

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>*</sup>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub> <sup>**</sup>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>*</sup>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub> <sup>**</sup>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>*</sup>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub> <sup>**</sup>
010	7.47	<1	7.50	w	112	2.148	4			213	1.557	3	1.557	w
100	5.73	45	5.71	vw	112	2.085	17	2.090	m	143	1.552	5		
001	5.32	33			231	2.044	15	2.045	m	302	1.542	3	1.541	w
011	5.24	100	5.25	vs	212	2.039	8			233	1.536	3		
110	4.80	2	4.81	w	031	2.012	8	2.013	w	203	1.516	1	1.518	vw
110	4.33	29	4.35	s	222	1.998	13			312	1.495	2		
101	3.921	22	3.931	m	212	1.983	11	1.987	m	321	1.495	2	1.496	m
101	3.875	15			041	1.982	5			050	1.494	2		
111	3.750	36			202	1.961	3			331	1.469	5	1.473	w
021	3.694	33	3.709	s	131	1.955	3			312	1.433	2		
120	3.295	80	3.302	s	300	1.909	9			400	1.432	4	1.433	wb
111	3.248	4			310	1.899	7	1.894	wb	342	1.398	5		
111	3.066	22	3.070	m	022	1.889	10			250	1.387	1		
120	2.985	6	2.993	m	222	1.875	9			153	1.386	1	1.384	w
121	2.974	3			042	1.847	12	1.845	w	034	1.381	1		
021	2.666	3			131	1.846	13			153	1.329	1	1.329	w
002	2.660	6			231	1.836	6			134	1.328	3		
031	2.617	3			311	1.832	3			161	1.313	2	1.313	w
211	2.583	28	2.587	m	122	1.828	6			062	1.309	4		
210	2.582	3			301	1.790	4			422	1.292	1		
201	2.509	6			113	1.787	25	1.786	m	412	1.291	1	1.295	vw
112	2.504	13			320	1.779	5			142	1.275	2	1.279	vw
030	2.490	24	2.494	sb	113	1.772	4			402	1.267	1		
131	2.483	53			311	1.748	17	1.752	m	342	1.267	2	1.270	vw
211	2.448	27	2.427	sb	033	1.747	6			151	1.266	2		
102	2.424	34			231	1.722	11	1.727	w	422	1.224	1	1.224	vw
102	2.402	24			142	1.710	5	1.706	vw	244	1.222	2		
130	2.379	16	2.394	vw	320	1.630	5	1.630	m	204	1.212	2	1.214	vw
221	2.379	5			331	1.627	3			313	1.210	1		
121	2.344	19	2.346	s	222	1.624	6							
122	2.328	11			321	1.617	3							
131	2.289	12	2.294	m	013	1.609	4	1.610	w					
032	2.228	6	2.230	m	041	1.603	3							
211	2.216	6			223	1.591	3							
220	2.163	8			051	1.583	4	1.584	w					
221	2.163	17	2.166	m										

\* Intensities calculated by RIETAN (Izumi, 1985). The calculated pattern has 399 reflections within  $2\theta \leq 90^\circ$  (CuK $\alpha_1$ ). Reflections with calculated intensities (*I*/*I*<sub>0</sub>) > 3 are listed.

\*\* Intensities visually estimated (s, strong; m, medium; w, weak; v, very; b, broad).

determined by crystal-structure analysis to be  $\text{Ca}_2\text{Cu}(\text{OH})_4[\text{B}(\text{OH})_4]_2$  (see Part II of this paper). Henmilite is easily soluble in (1:2) HCl and (1:2)  $\text{HNO}_3$ .

### CRYSTALLOGRAPHY

Single crystals were studied using the precession and Weissenberg methods. The diffraction photographs showed that henmilite is triclinic with possible space groups  $P1$  or  $P\bar{1}$ ; the latter has been established as correct by the crystal-structure analysis. Unit-cell dimensions, determined by a least-squares refinement of 25 high-angle reflections measured on an automated four-circle diffractometer, are  $a = 5.7617(5)$ ,  $b = 7.9774(6)$ ,  $c = 5.6488(4)$  Å,  $\alpha = 109.611(6)$ ,  $\beta = 91.473(7)$ , and  $\gamma = 83.686(7)^\circ$ . The euhedral crystals exhibit well developed  $\{100\}$  and  $\{010\}$  pinacoids.

X-ray powder-diffraction data were obtained with a Gandolfi camera of 114.6-mm diameter using Ni-filtered  $\text{CuK}\alpha$  radiation. The data are listed in Table 1, which also includes calculated powder-diffraction data obtained from the crystal structure using the program RIETAN (Izumi, 1985). The agreement of the two patterns is quite satisfactory.

### PHYSICAL AND OPTICAL PROPERTIES

Henmilite is transparent and bluish violet in color. It has a vitreous luster and a very pale violet to nearly white streak. The mineral is soft and fragile. Hardness could not be determined but is lower than that of the associated

pentahydroborite, which has a Mohs' hardness of  $2\frac{1}{2}$ . The density calculated from the ideal formula is  $2.523 \text{ g/cm}^3$ .

Henmilite is optically biaxial negative, with refractive indices  $\alpha = 1.585(2)$ ,  $\beta_{\text{calc}} = 1.608$ , and  $\gamma = 1.615(2)$ . The value of  $2V_x$ , measured with an universal stage, is about  $58^\circ$ . Pleochroism is strong, with  $X =$  pale pink,  $Y =$  pale purple, and  $Z =$  very pale blue. The crystals show inclined extinction. Calculation of the Gladstone-Dale relationship, using the constants of Mandarino (1981), yields values of  $K_C = 0.240$  and  $K_P = 0.239$ . The compatibility index of Mandarino (1979),  $1 - (K_P/K_C)$ , is 0.004, indicating superior internal consistency of the data.

### IR SPECTRUM

IR spectra were measured by the conventional KBr method for the region  $5000$  to  $330 \text{ cm}^{-1}$ . Figure 1 shows the spectrum of henmilite and that of pentahydroborite for comparison. The strong absorption bands at about  $3400 \text{ cm}^{-1}$  are attributed to the OH stretching vibration and the weak bands at about  $1650 \text{ cm}^{-1}$  to the OH bending vibration. Numerous bands below  $1400 \text{ cm}^{-1}$  are characteristic of the borate ion (Takéuchi, 1958). Henmilite contains the  $\text{B}(\text{OH})_4$  group, and all the O atoms are in the form of hydroxyl ions, while pentahydroborite contains the  $\text{B}_2\text{O}(\text{OH})_6$  group and free  $\text{H}_2\text{O}$  molecules in its structure (Egorov-Tismenko et al., 1973). These structural differences are reflected in the differences between the two spectra.

## Henmilite, $\text{Ca}_2\text{Cu}(\text{OH})_4[\text{B}(\text{OH})_4]_2$ , a new mineral from Fuka, Okayama Prefecture, Japan. II. Crystal structure

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### INTRODUCTION

Study of the bonding of the Cu atom as well as the coordination geometry of B in the structure of henmilite is interesting, because copper borates are rare in nature. Bandyte is the first naturally occurring copper borate, henmilite being the second. Synthetic copper borates whose crystal structures have been reported are the anhydrous copper borates  $\text{Cu}_3[(\text{B}_3\text{O}_6)_2]$  (Martinez-Ripoll et al., 1971) and  $\text{Cu}_{15}\text{O}_2[(\text{B}_2\text{O}_3)_2(\text{BO}_3)_6]$  (Behm, 1982) and the hydrated copper borates  $\text{Cu}_2(\text{OH})_3[\text{BO}(\text{OH})_2]$  (Behm and Baerlocher, 1985) and  $\text{Na}_6\text{Cu}_2[\text{B}_{16}\text{O}_{24}(\text{OH})_{10}] \cdot 12\text{H}_2\text{O}$  (Behm, 1983). To the knowledge of the author, no synthetic hydrated calcium copper borates are known to date. The present structural study was undertaken to establish the chemical formula of the new calcium copper borate and to contribute to the crystal chemistry of borate minerals.

### STRUCTURE DETERMINATION

A small euhedral crystal of henmilite,  $0.2 \times 0.1 \times 0.05$  mm in size, was used for the crystal-structure determination. The intensity data were collected by the  $2\theta-\omega$  scan method on a Rigaku AFC-5 four-circle automated diffractometer equipped with Rotaflex RU-200 X-ray generator (operating conditions: 50 kV, 160 mA), using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å), and scan rate of  $2^\circ/\text{min}$ . The intensity measurements were repeated up to three times for each reflection unless  $\sigma_{|F_o|}/|F_o|$  was less than 0.05. Three standard reflections, 400, 050, 013, were monitored every 50 reflections; the maximum intensity variation was 1.7%. A total of 3043 independent reflections were measured within the limit of  $2\theta \leq 95^\circ$ , out of which 2430 reflections with  $|F_o| \geq 3\sigma_{|F_o|}$  were regarded as observed and were used in the

Table 2. Atomic positional parameters and temperature factors

Atom	x	y	z	$B_{eq}^*$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ca	0.50791(6)	0.24095(4)	0.22595(6)	0.80	0.00579(8)	0.00331(4)	0.00747(9)	-0.00038(4)	0.00008(6)	0.00133(5)
Cu	0	0	0	0.89	0.00588(7)	0.00366(4)	0.00933(9)	-0.00051(4)	0.00094(6)	0.00169(5)
B	0.2790(3)	0.4068(2)	0.7480(4)	0.78	0.0059(4)	0.0034(2)	0.0074(5)	-0.0004(2)	-0.0001(3)	0.0019(3)
O(1)	0.3061(2)	-0.0192(2)	0.1455(3)	1.03	0.0067(3)	0.0041(2)	0.0108(4)	-0.0009(2)	0.0004(3)	0.0016(2)
O(2)	0.8404(2)	0.0684(2)	0.3239(3)	1.18	0.0081(3)	0.0059(2)	0.0102(4)	0.0007(2)	0.0010(3)	0.0028(2)
O(3)	0.2467(2)	0.2907(2)	0.8972(3)	1.06	0.0097(3)	0.0038(2)	0.0104(4)	-0.0005(2)	0.0006(3)	0.0033(2)
O(4)	0.1523(2)	0.3538(2)	0.5106(3)	1.18	0.0084(3)	0.0055(2)	0.0090(4)	-0.0010(2)	-0.0027(3)	0.0008(2)
O(5)	0.7879(2)	0.4055(2)	0.0978(3)	0.98	0.0080(3)	0.0029(2)	0.0099(4)	-0.0005(2)	0.0004(3)	0.0009(2)
O(6)	0.5261(2)	0.3983(2)	0.6742(3)	1.08	0.0060(3)	0.0069(2)	0.0082(3)	-0.0006(2)	0.0001(2)	0.0027(2)
H(1)	0.705(5)	0.040(4)	0.735(5)	0.5(5)						
H(2)	0.923	0.065	0.427	2.0						
H(3)	0.226(6)	0.194(5)	0.828(7)	3.4(9)						
H(4)	0.043	0.418	0.526	2.0						
H(5)	0.904	0.385	0.058	2.0						
H(6)	0.619(5)	0.387(4)	0.768(6)	1.5(6)						

Note: The anisotropic-temperature-factor form is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

\* For non-H atoms  $B_{eq}$  values are calculated from  $4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab \cos \gamma + 2\beta_{13}ac \cos \beta + 2\beta_{23}bc \cos \alpha)$ .

structure determination. The data were corrected for Lorentz and polarization factors; no corrections were made for absorption ( $\mu_1 = 33.40 \text{ cm}^{-1}$ ).

An interpretation of the three-dimensional Patterson map indicated the positions of the Ca and Cu atoms. Subsequent Fourier and difference syntheses revealed the positions of the B and O atoms and led to a cell content of  $\text{H}_{12}\text{Ca}_2\text{CuB}_2\text{O}_{12}$ . A full-matrix isotropic refinement using *RFINE2* (Finger, 1969) resulted in a conventional *R* factor of 0.046, and anisotropic refinement reduced *R* to 0.029. The maximum shift/error in the last cycle was less than 0.01. A difference synthesis revealed the positions of the six H atoms, but three of these could not be refined in the subsequent least-squares refinement and were included in the calculation with fixed positions and isotropic thermal parameters of  $2.0 \text{ \AA}^3$ . Further refinement in which positional parameters and isotropic thermal parameters of three H atoms were allowed to vary, while the positional and anisotropic thermal parameters of the non-H atoms were fixed at their refined values, yielded a final *R* of 0.026 and  $R_w$  of 0.034 ( $w = 1/\sigma_{F_o}^2$ ).

The final atomic parameters are given in Table 2 together with the standard deviation of each parameter. The final observed and calculated structure factors are compared in Table 3.<sup>2</sup> Bond distance and angles are listed in Table 4. The atomic scattering factors for neutral atoms were taken from Cromer and Mann (1968) and the anomalous dispersion factors from *International Tables for X-ray Crystallography* (1974). The calculations were carried out at the Science Information Processing Center of the University of Tsukuba.

### DESCRIPTION OF THE STRUCTURE

The empirical bond-valence sums for henmilite were calculated using the method of Donnay and Allmann (1970) and the values of the bond lengths and coordina-

tion numbers in Table 4. The bond-valence sums  $\Sigma c_v$  for O(1), O(2), O(4), O(5), and O(6) are 1.06, 0.78, 1.00, 0.99, 1.01, and 1.17, respectively. From these values it is readily apparent that all the O atoms belong to hydroxyl groups,

Table 4. Interatomic distances and bond angles for henmilite

Cu(OH) <sub>4</sub> square			
Cu-O distances (Å)		O-Cu-O angles (°)	
Cu-O(1) <sup>(o,i)</sup>	1.939(1) × 2	O(1)-O(2) <sup>(iv)</sup>	93.04(6)
-O(2) <sup>(iii,v)</sup>	1.949(2) × 2	-O(2) <sup>(iv)</sup>	86.96(6)
Mean	1.944		90.00
Ca(OH) <sub>6</sub> polyhedron			
Ca-O distances (Å)		O-H distances (Å)	
Ca-O(1)	2.395(2)	O(1)-H(1)	0.75(3)
-O(1) <sup>(iv)</sup>	2.426(1)		
-O(2)	2.398(2)	O(2)-H(2)	0.75
-O(3) <sup>(iv)</sup>	2.468(2)	O(3)-H(3)	0.76(3)
-O(4)	2.527(1)	O(4)-H(4)	0.75
-O(5)	2.452(2)	O(5)-H(5)	0.70
-O(6)	2.425(1)	O(6)-H(6)	0.76(3)
-O(6) <sup>(iv)</sup>	2.726(1)		
Mean	2.477		0.75
B(OH) <sub>4</sub> tetrahedron			
B-O distances (Å)		O-B-O angles (°)	
B-O(3)	1.474(3)	O(3)-O(4)	112.0(2)
-O(4)	1.466(2)	-O(5) <sup>(iv)</sup>	109.2(2)
-O(5) <sup>(iv)</sup>	1.471(2)	-O(6)	112.6(2)
-O(6)	1.482(2)	O(4)-O(5) <sup>(iv)</sup>	112.4(2)
Mean	1.473	-O(6)	105.0(2)
O-O distances (Å)		O(5) <sup>(iv)</sup> -O(6)	
O(3)-O(4)	2.437(2)		105.5(1)
-O(5) <sup>(iv)</sup>	2.400(2)		
-O(6)	2.460(2)		
O(4)-O(5) <sup>(iv)</sup>	2.440(2)		
-O(6)	2.338(2)		
O(5) <sup>(iv)</sup> -O(6)	2.351(2)		
Mean	2.404		109.5

Note: The equivalent positions (refer to Table 2) are designated as superscripts and are (o) = *x, y, z*; (i) =  $-x, -y, -z$ ; (ii) =  $1-x, 1-y, 1-z$ ; (iii) =  $x-1, y, z$ ; (iv) =  $1-x, -y, -z$ ; (v) =  $x, y, z-1$ ; (o) is designated only if necessary. Estimated standard errors refer to the last digit.

<sup>2</sup> To obtain a copy of Table 3, order Document AM-86-314 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

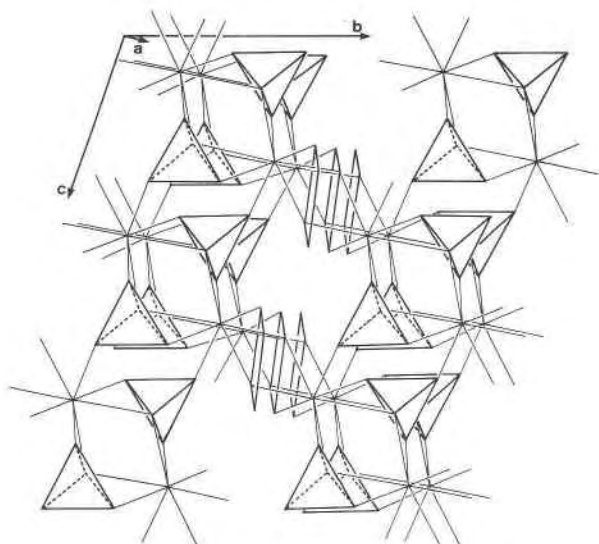


Fig. 2. Polyhedral diagram of the henmilite structure projected onto the (100) plane. The Ca–O bonds are drawn instead of the  $\text{Ca}(\text{OH})_8$  polyhedra.

confirming the H-atom positions located on the difference Fourier map. The chemical formula thus found is  $\text{Ca}_2\text{Cu}(\text{OH})_4[\text{B}(\text{OH})_4]_2$ .

The crystal structure of henmilite consists of isolated  $\text{B}(\text{OH})_4$  tetrahedra, planar  $\text{Cu}(\text{OH})_4$  groups and  $\text{Ca}(\text{OH})_8$  polyhedra. Figure 2 is drawn to exaggerate the linkages of the  $\text{B}(\text{OH})_4$  tetrahedra and  $\text{Cu}(\text{OH})_4$  squares; for simplicity the Ca–O bonds are drawn instead of the  $\text{Ca}(\text{OH})_8$  coordination polyhedra. The Ca polyhedra share edges to form dimers, the dimers being connected by square planar  $\text{Cu}(\text{OH})_4$  groups to form a sheet structure parallel to  $[01\bar{1}]$ . The sheets are then linked by  $\text{B}(\text{OH})_4$  tetrahedra into a three-dimensional structure. The henmilite structure can also be viewed as having dimers of Ca polyhedra connected to each other through two  $\text{B}(\text{OH})_4$  tetrahedra to form chains parallel to the c axis. The chains are, in turn connected through the square planar  $\text{Cu}(\text{OH})_4$  groups into a three-dimensional structure.

The B atom lies at the center of a nearly tetrahedral arrangement of hydroxyl ions. The mean B–O distance of 1.473 Å, O–O distance of 2.404 Å and O–B–O angle of  $109.5^\circ$  are typical for the borate tetrahedron (Clark et al., 1964). The isolated borate tetrahedron is relatively rare in borate structures (Christ and Clark, 1977). Examples are found in the structures of bandylite,  $\text{CuCl}[\text{B}(\text{OH})_4]$ , where the average B–O distance is 1.42 Å (Collin, 1951), seamanite,  $\text{Mn}_3(\text{OH})_2(\text{PO}_4)[\text{B}(\text{OH})_4]$ , average B–O = 1.466 Å (Moore and Ghose, 1971), cahnite,  $\text{Ca}_2(\text{AsO}_4)[\text{B}(\text{OH})_4]$ , average B–O = 1.47 Å (Prewitt and Buerger, 1961),  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$ , average B–O = 1.47 Å (Sedlacek and Dornberger-Schiff, 1971),  $\text{Na}[\text{B}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ , average B–O = 1.476 Å (Block and Perloff, 1963), and sinhalite,  $\text{AlMg}[\text{BO}_4]$ , average B–O = 1.49 Å (Fang and Newnham, 1965). The B–O distance in henmilite is very close to the values reported for the latter five borates.

The coordination about the Cu atom is a square coplanar arrangement of 2OH at 1.939 and 2OH at 1.949 Å. Similar coordinations are found in  $\text{Cu}_3[\text{B}_3\text{O}_6]_2$  (Martinez-Ripoll et al., 1971) and  $\text{Na}_6[\text{Cu}_2\text{B}_{16}\text{O}_{24}(\text{OH})_{10}] \cdot 12\text{H}_2\text{O}$  (Behm, 1983). Structural features of the Cu atom in borates are further discussed later.

The Ca atom exhibits the usual eightfold coordination by hydroxyl O at distances ranging from 2.395 to 2.726 with a mean of 2.477 Å. A similar  $\text{CaO}_8$  coordination is found in the structure of  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$ , where the mean Ca–O distance is 2.47 Å, very close to that in henmilite.

### Comparison with related borates

As mentioned in the Part I of this paper, henmilite occurs in close association with pentahydroborite, whose crystal structure was reported by Egorov-Tismenko et al. (1973). No clear structural relationship can be found between henmilite and pentahydroborite. In the latter structure, B forms a  $\text{B}_2\text{O}(\text{OH})_6$  group, similar to the  $\text{Si}_2\text{O}_7$  group found in silicate structures, and the Ca atom is 7-coordinated by O.

Thus far only five structures of copper borates have been determined: bandylite (Collin, 1951),  $\text{Cu}_3[(\text{B}_3\text{O}_6)_2]$  (Martinez-Ripoll et al., 1971),  $\text{Cu}_{15}\text{O}_2[(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6]$  (Behm, 1982),  $\text{Cu}_2(\text{OH})_3[\text{BO}(\text{OH})_2]$  (Behm and Baerlocher, 1985), and  $\text{Na}_6\text{Cu}_2[\text{B}_{16}\text{O}_{24}(\text{OH})_{10}] \cdot 12\text{H}_2\text{O}$  (Behm, 1983). The overall structure of henmilite appears related to none of these reported structures.

Considering the geometry of the borate ion in these compounds, henmilite is comparable to bandylite, where isolated  $\text{B}(\text{OH})_4$  tetrahedra are also present (Collin, 1951). The tetrahedral borate ion also exists in the form of a  $(\text{B}_3\text{O}_6)^{3-}$  group in  $\text{Cu}_3[(\text{B}_3\text{O}_6)_2]$ . On the other hand,  $\text{Cu}_{15}\text{O}_2[(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6]$  and  $\text{Cu}_2(\text{OH})_3[\text{BO}(\text{OH})_2]$  contain triangular  $\text{BO}_3$  ions in the form of a planar  $\text{B}_2\text{O}_5$  group and an isolated  $\text{BO}_3$  group in the first compound and in the form of an isolated  $\text{BO}(\text{OH})_2$  group in the second compound. Complex polyborate rings composed of eight borate tetrahedra and eight borate triangles are observed in  $\text{Na}_6\text{Cu}_2[(\text{B}_{16}\text{O}_{24}(\text{OH})_{10})] \cdot 12\text{H}_2\text{O}$ .

There are three types of O coordination around the Cu atoms in these borate structures, i.e., square planar coordination,  $(4 + 1)$ -coordination (tetragonal pyramidal), and  $(4 + 2)$ -coordination (octahedral) showing Jahn-Teller distortion. The coordination in henmilite belongs to the first type, which is also found in  $\text{Cu}_3[(\text{B}_3\text{O}_6)_2]$ , with average Cu–O distances of 1.937 and 1.999 Å, and in  $\text{Na}_6\text{Cu}_2[\text{B}_{16}\text{O}_{24}(\text{OH})_{10}] \cdot 12\text{H}_2\text{O}$ , with an average Cu–O of 1.937 Å. The  $(4 + 2)$ -coordination occurs in bandylite, where the Cu atom is surrounded by a square of four hydroxyl groups at a distance of 1.98 Å, and two Cl atoms on a line at right angles to this plane with a Cu–Cl distance of 2.80 Å (Collin, 1951). A similar coordination is also observed in  $\text{Cu}_2(\text{OH})_3[\text{BO}(\text{OH})_2](\text{OH})$ , where the O atoms form a square with Cu–O bond distances from 1.91 to 1.98 Å, and two further O atoms are located at 2.64 and 2.73 Å. In the case of  $\text{Cu}_{15}\text{O}_2[(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6]$ , Behm (1982)

reported that Cu atoms exhibit a nearly quadratic planar coordination to four O atoms and that some of the Cu atoms seemed to have additional coordinations to one or two O atoms. Generally speaking, the (4 + 2)- or (4 + 1)-coordination types are more common in the stereochemistry of cupric compounds than the square planar type found in henmilite (Wells, 1975).

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