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GOWERITE, $CaB_5O_8(OH) \cdot B(OH)_3 \cdot 3H_2O$: CRYSTAL STRUCTURE AND COMPARISON WITH RELATED BORATES[1]

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ABSTRACT

Using a combination of Fourier and direct phase-determining methods for about 1000 data collected by 2θ-scans with Mo X-radiation and a scintillation counter, the structure of gowerite, $CaO \cdot 3B_2O_3 \cdot 5H_2O$, has been solved and refined by least-squares methods to a residual of 0.09. Gowerite is monoclinic, $P2_1/a$, $a = 12.882 \pm 0.004$, $b = 16.360 \pm 0.007$, $c = 6.558 \pm 0.004$ Å, $\beta = 121.62 \pm 0.05°$, $Z = 4$, density (calc.) 2.003 g/cm^3, obs. specific gravity 2.00 ± 0.01. The structural formula is $CaB_5O_8(OH) \cdot B(OH)_3 \cdot 3H_2O$. Polyanions similar to the pentaborate polyanion are cross-linked in two directions to form $[B_5O_8(OH)]^{2-}$ sheets parallel to (010). Calcium cations fit into spaces within the polyanion sheets, each coordinated by six oxygen anions plus a water molecule on one side of a sheet and two hydroxyl ions of one of the isolated $B(OH)_3$ groups on the opposite side of the sheet. Two other crystallographically distinct water molecules are located between the polyanion sheets. Adjacent sheets are related by the 2_1 axes and are held together by hydrogen bonds only. Four hydrogen bonds averaging 2.68 Å are between atoms of adjacent sheets; five involving interstitial water molecules average 2.82 Å. The structural role of the water molecules agrees well with previously reported thermal analyses.

Gowerite provides the third example of a borate structure containing isolated $B(OH)_3$ groups in the presence of larger polyanions, the other two being the dimorphic pair, veatchite and *p*-veatchite, $Sr_2[B_5O_8(OH)]_2 \cdot B(OH)_3 \cdot H_2O$, recently solved, respectively, by Clark and Christ and by Rumanova and Gandymov. The structure of a synthetic compound, $K_2B_5O_8(OH) \cdot 2H_2O$, solved by Marezio, has polyanion sheets similar to those of gowerite. Comparison of the sheets in all four structures shows remarkable similarities; in particular, the same six oxygen anions of the sheet coordinate the cation in the different structures, with average *M*–O distances 2.57 Å (Ca), 2.69 Å (Sr), and 2.782 Å (K). In all cases the sheets are linked by hydrogen bonding, which may be entirely direct from one sheet to the next as in the veatchites, or partly direct and partly through interstitial water molecules as in gowerite. In the synthetic potassium polyborate the sheets are linked in both these ways and also by bonding to interstitial potassium cations. These recent studies show that a fifth principle can be added to the four established for formation of complex borate polyanions by C. L. Christ, as follows: the boric acid group, $B(OH)_3$, may exist in isolated form in the presence of more complex polyanions, or such insular groups may themselves polymerize and attach as side chains to more complex polyanions.

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[1] Studies of borate minerals (XVII). Publication authorized by the Director, U. S. Geological Survey.

INTRODUCTION

The mineral gowerite, $CaO \cdot 3B_2O_3 \cdot 5H_2O$, was discovered in 1955 in the Furnace Creek area of Death Valley National Monument, California. The occurrence and the chemical and physical properties of the new mineral were described by Erd *et al.* (1959). X-ray crystallographic data for gowerite were given by Christ and Clark (1960), who also proposed some possible structural formulas, although not the one now discovered.

Study of the crystal structures of the series $MO \cdot 3B_2O_3 \cdot xH_2O$ was initiated by Clark (1964) with tunellite, $SrO \cdot 3B_2O_3 \cdot 4H_2O$. The mineral was found to contain sheets based on a new polyanion, $[B_6O_7(OH)_6]^{2-}$. This polyanion was later found to exist in isolated form in macallisterite, $MgO \cdot 3B_2O_3 \cdot 7.5H_2O$ (Dal Negro *et al.*, 1969), and in aksaite, $MgO \cdot 3B_2O_3 \cdot 5H_2O$ (Dal Negro *et al.*, 1971). The consequent structural formulas are: tunellite $Sr[B_6O_9(OH)_2] \cdot 3H_2O$, macallisterite $Mg_2[B_6O_7(OH_6]_2 \cdot 9H_2O$, and aksaite $Mg[B_6O_7(OH)_6] \cdot 2H_2O$. Gowerite is the Ca analogue of aksaite, both minerals having $x = 5$ in the oxide formula, and by analogy the structural formula of gowerite might be expected to be similar to the one found for aksaite. However, Lehmann and Kessler (1967) observed from study of the infrared spectra of gowerite and aksaite that the two compounds "could not contain the same anion." The solution of the gowerite structure reveals that its structural formula is $CaB_5O_8(OH) \cdot B(OH)_3 \cdot 3H_2O$, comparable to veatchite (Clark and Christ, 1968, 1971) and *p*-veatchite (Gandymov *et al.*, 1968; Rumanova and Gandymov, 1971), both of which have the structural formula $Sr_2[B_5O_8(OH)]_2 \cdot B(OH)_3 \cdot H_2O$, corresponding to the oxide formula $4SrO \cdot 11B_2O_3 \cdot 7H_2O$. In this paper we describe the gowerite structure and its determination and compare it with related borate structures.

EXPERIMENTAL WORK

Crystal Description, Unit Cell, Symmetry, and Density

The crystal used for the structural study was a slender needle, elongation direction [001], slightly flattened on (010), about 0.08 × 0.05 × 0.62 mm in size. It was selected from a sample of crystals obtained by R. C. Erd, U. S. Geological Survey, at the Furnace Creek area of Death Valley National Monument, California. The cell parameters measured from precession photographs corrected for film shrinkage are: $a = 12.882 \pm 0.004$, $b = 16.360 \pm 0.007$, $c = 6.558 \pm 0.004$ Å, β 121.62 ± 0.05°, for space group $P2_1/a$ (unique axis taken as b). The values are in good agreement with those reported by Christ and Clark (1960). The calculated density is 2.003 g/cm^3 for cell contents $4[CaO \cdot 3B_2O_3 \cdot 5H_2O]$; the specific gravity observed by Erd *et al.* (1959), 2.00 ± 0.01, is in excellent agreement.

Collection and Processing of Data.

About 2700 reflections were collected with Zr-filtered Mo X radiation on a Picker automatic diffractometer equipped with a scintillation counter. The 2θ-scan method was used with a scan range calculated as suggested by Alexander and Smith (1964). Twenty-second background counts were made at the beginning and end points of the scan range for each reflection. The crystal was mounted with $[\bar{2}01]^*$ parallel to the ϕ-axis, and the $\bar{4}52$ reflection was monitored as a standard after every 30 reflections measured. Some equivalent reflections were also checked.

Computer programs written by C. T. Prewitt, SUNY, Stony Brook, and modified for the IBM 360/65 by D. E. Appleman, U. S. Geological Survey, were used to obtain diffractometer settings and to reduce the raw data. Corrections were made for the total background count, for Lorentz and polarization factors, for absorption ($\mu = 6.1\ \text{cm}^{-1}$), and for secondary extinction. No primary extinction effects were observed. For 1667 reflections, $|F_o|$ was less than four times the standard deviation of $|F_o|$ as determined by the counting statistics; such data were coded as "less-thans" and omitted in the refinement which used 1018 nonequivalent reflections.

Refinement of Data.

Computer programs from *X-Ray 67, Program System for X-ray Crystallography,* by J. M. Stewart, University of Maryland, adapted for the IBM 360/65 by D. E. Appleman, U. S. Geological Survey, were used during the structural determination, with scattering factors for Ca^{2+} and neutral oxygen and boron (Cromer and Waber, 1965). Refinement of the structural parameters, as well as calculations of bond distances and angles, and thermal ellipsoids, was carried out with programs written by L. W. Finger, Geophysical Laboratory, Washington, D. C. Anomalous dispersion corrections were included in the refinement; scattering factors for Ca^{2+}, O^{1-}, and neutral boron were taken from the tables given by Cromer and Mann (1968). Unit weights were used throughout the refinements.

DETERMINATION OF THE STRUCTURE

The structural problem consisted of locating one calcium, fifteen oxygen, and six boron atoms, each in the general fourfold position 4*e* of space group $P2_1/a$. A Patterson synthesis indicated that the calcium atom, and probably quite a bit more of the scattering matter, lay either on or quite close to the glide plane at $y = 1/4$, but x- and z-coordinates could not be readily determined. Therefore, the symbolic addition method for centrosymmetric structures, developed by Karle and Karle (1966) was used. The normalized structure factors E_{hkl} were obtained and the origin was fixed by assigning positive signs to three reflections: 214; $\bar{7}.12.1$; and $\overline{10}.3.1$, following the procedures described by Hauptman and Karle (1953). The statistical averages for the data confirmed the presence of a center of symmetry. About 100 phases were calculated by hand methods, and these 100 data were used in the PHASE subroutine of the *X-Ray 67* program system to obtain 331 phases which were used in calculation of an E-map.

This map indicated the position of the calcium atom quite clearly, but there appeared to be a pseudo mirror plane at $y = \frac{1}{4}$, all of the strongest peaks not due to Ca appearing both above and below this plane, though not always with equal heights. Most of the *hkl* reflections with high *E*-values had even values of *h*, so initial study of the *E*-map concentrated on the area around $x = \frac{1}{2}$, as well as on a projection along *b* of the region around the glide plane at $y = \frac{1}{4}$. A partial structure was chosen which contained nine oxygen and five boron atoms in addition to the calcium atom. Study of a difference electron-density map indicated that for one of the nine oxygen atoms the wrong "mirror image" had been chosen, but positions could be assigned to four more oxygen atoms and to the remaining boron atom. At this point the conventional residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 0.40. Two cycles of least-squares refinement for these atomic coordinates reduced *R* to 0.17. A final difference Fourier revealed the locations of the remaining two oxygen atoms. Following three cycles of isotropic, least-squares refinement for all atoms, the *R* value for the 1018 reflections with $|F_o| > 4$ standard deviations dropped to 0.10. Further refinement including the extinction coefficient and anisotropic thermal parameters for the calcium atom did not decrease *R*; two cycles of refinement including anisotropic thermal parameters for all atoms decreased *R* only slightly to 0.09. The final positional and isotropic thermal parameters are given in Table 1, and the observed and calculated structure factors are compared in Table 2[1].

DESCRIPTION OF THE STRUCTURE

The gowerite structure is illustrated in the stereoscopic-pair views of Figures 1 and 2. The primary framework (Fig. 1) consists of a basic $[B_5O_8(OH)]^{2-}$ unit, polymerized into thick sheets parallel to (010); these sheets have spaces which accommodate the calcium cations. The sheets stack along the *b*-axis (Fig. 2), and the spaces between them are occupied by $B(OH)_3$ groups and water molecules.

The $[B_5O_8(OH)]^{2-}$ group is composed of two six-membered boron-oxygen rings joined through a tetrahedral boron common to both rings. The configuration is similar to that of the pentaborate polyanion $[B_5O_6(OH)_4]^{1-}$ discovered by Zachariasen (1937) in $KB_5O_8 \cdot 4H_2O$; the structure was later refined by Zachariasen and Plettinger (1963). The polyanion in gowerite has one ring with two triangular boron atoms in addition to the central tetrahedral one; the other ring is formed with one tetrahedral and one triangular boron atom in addition to the central tetrahedron. These fundamental units polymerize into sheets (Fig. 1), linking into chains along *a* through O(1) oxygen atoms related by the *a*-glide, and into sheets parallel to (010) through O(7) oxygen atoms related by a cell translation along *c*.

The boron-oxygen distances in the gowerite polyanion and in the

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[1] To obtain a copy of Table 2, order NAPS Document #01708 from National Auxiliary Publications Service, c/o CCM Information Corporation, 866 Third Avenue, New York, N. Y. 10022, remitting in advance $2.00 for microfiche or $7.10 for photocopies, payable to CCMIC-NAPS.

Table 1. Atomic Parameters for Gowerite

Atom	Parameter[a/] x	y	z	B (Å^2)
Ca	0.1908(3)	0.2521(3)	0.0879(5)	1.46(5)
B(1)	0.631(1)	0.239(1)	0.577(3)	1.8(3)
B(2)	0.440(2)	0.309(1)	0.492(3)	2.0(3)
B(3)	0.477(1)	0.274(1)	0.172(3)	1.9(3)
B(4)	0.345(2)	0.313(1)	0.731(3)	2.0(3)
B(5)	0.418(2)	0.439(1)	0.647(3)	2.0(3)
B(6)	0.232(2)	0.071(1)	0.061(4)	3.2(4)
O(1)	0.238(1)	0.293(1)	0.741(2)	2.4(2)
O(2)	0.554(1)	0.262(1)	0.650(2)	2.2(2)
O(3)	0.595(1)	0.251(1)	0.341(2)	2.5(2)
O(4)	0.400(1)	0.295(1)	0.240(2)	2.5(2)
O(5)	0.468(1)	0.397(1)	0.548(2)	2.5(2)
O(6)	0.342(1)	0.282(1)	0.523(2)	2.1(2)
O(7)	0.455(1)	0.279(1)	-0.051(2)	2.5(2)
O(8)	0.356(1)	0.403(1)	0.742(2)	2.6(2)
OH(9)	0.429(1)	0.524(1)	0.665(2)	3.6(2)
OH(10)	0.183(1)	0.109(1)	0.171(2)	3.5(2)
OH(11)	0.288(1)	0.127(1)	-0.015(2)	4.0(3)
OH(12)	0.229(1)	-0.010(1)	0.021(2)	4.2(3)
$H_2O(1)$	0.131(1)	0.390(1)	0.062(2)	4.0(3)
$H_2O(2)$	0.087(2)	0.453(1)	0.418(4)	8.8(5)
$H_2O(3)$	0.384(1)	0.109(1)	0.711(3)	5.3(3)

[a/] Errors in parenthesis are for one standard deviation, e.g., 0.1908(3) means 0.1908±0.0003.

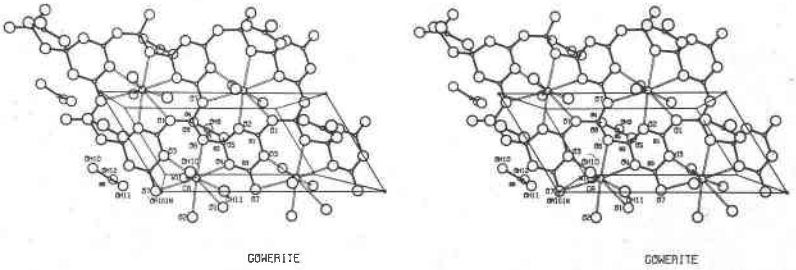

FIG. 1. Stereoscopic-pair view along *b* of one polyanion sheet, $[B_5O_8(OH)]^{2-}$, in gowerite. The outline of one unit cell is shown with *a* horizontal. Ca coordination is indicated by double lines. W1 designates a water molecule.

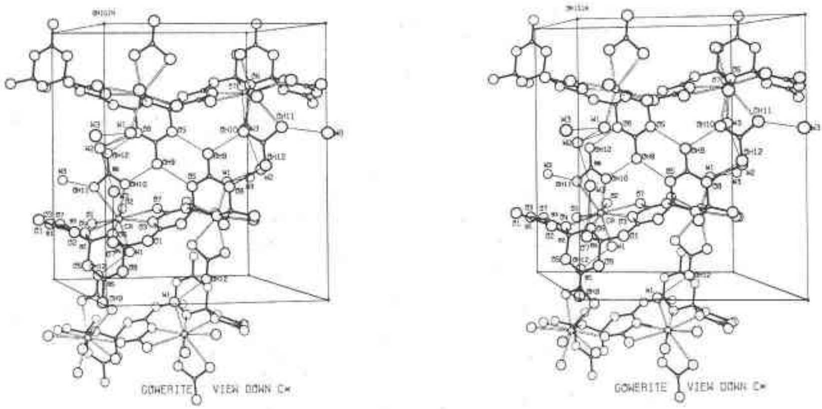

FIG. 2. Stereoscopic-pair view of a part of the gowerite structure along c^* to show the stacking of sheets and the intersheet linkages. The outline of one unit cell is shown with *a* horizontal. W designates the water molecules; hydrogen bonds are drawn with light, thin lines.

$B(OH)_3$ group are given in Table 3 and are in good agreement with those found in other borate structures. The average values are 1.47 Å for the tetrahedra and 1.36 Å for the triangles. The O–B–O and B–O–B angles in gowerite also fall within expected values (Tables 3, 4).

As can be seen in Figure 1, the calcium cations fit snugly into spaces in the sheet. Each cation is coordinated by six oxygen anions from within the sheet. The coordination sphere is brought to a total of nine atoms by a water molecule on one side of the sheet and two hydroxyl ions from the $B(OH)_3$ group on the other side of the sheet. The polyhedra are isolated from one another in the structure. The nine Ca–O distances range from 2.36 to 2.73 Å, with an average distance of 2.54 Å (Table 5).

The unit cell contains two polyanion sheets stacked along *b* and related by the twofold screw axis. The view in Figure 2 shows the sheets edge-on to illustrate the linkage between sheets in the *b* direction, which is by hydrogen bonding only. These bonds can be divided into two groups (Table 6), those that go directly from one sheet to another, and those that do not. In the first group there are four bonds averaging 2.68 Å, and in the second group, five averaging 2.82 Å. Most of the proton donors can be unambiguously identified by chemical considerations.

In addition to the $[B_5O_8(OH)]^{2-}$ polyanion sheets, isolated $B(OH)_3$ groups fit between the layers, held in place by coordination of two of the hydroxyl ions to the calcium cation, as mentioned above. There are three water molecules in the structure; the one labelled W1 in Figure 2 is part of the calcium coordination sphere, but the other two are held in place only by hydrogen bonds. The environments of the three water molecules are reasonable for this kind of structure. Each one apparently forms two donor hydrogen bonds, provided that $H_2O(3)$ is considered the donor to hydroxyl ion OH(11). However, OH(11) would then be retaining its own proton and the charge balance sums produce a surplus of positive charge for OH(11). Because water molecules do not always use both protons to form hydrogen bonds, it is probably more reasonable to follow the dictates of the

Table 3. Distances and Angles for Boron and Oxygen Atoms in Gowerite Compared With Those in $K_2B_5O_8(OH)\cdot 2H_2O$

		Bond distance (Å)			Bond angle (°)	
Boron atom no.	Oxygen atom no.	Gowerite This study[a]	$K_2B_5O_8(OH)\cdot 2H_2O$ Marezio (1969)[b]	Oxygen atoms of O-B-O angle	Gowerite This study[a]	$K_2B_5O_8(OH)\cdot 2H_2O$ Marezio (1969)[b]
1	1	1.33	1.346(5)	1, 2	117.	126.
	2	1.36	1.353(6)	1, 3	124.	113.
	3	1.37	1.412(6)	2, 3	119.	120.
	ave.	1.35	1.370	Σ	360.	359.
3	3	1.39	1.390(6)	3, 4	120.	120.
	4	1.33	1.359(6)	3, 7	114.	121.
	7	1.34	1.363(5)	4, 7	126.	119.
	ave.	1.35	1.371	Σ	360.	360.
5	5	1.32	1.365(5)	5, 8	124.	123.
	8	1.37	1.362(6)	5, 9	120.	121.
	OH(9)	1.40	1.379(6)	8, 9	116.	116.
	ave.	1.36	1.369	Σ	360.	360.
2	2	1.50	1.485(5)	2, 4	109.	110.
	4	1.47	1.496(5)	2, 5	108.	107.
	5	1.48	1.494(6)	2, 6	110.	110.
	6	1.45	1.454(5)	4, 5	110.	105.
	ave.	1.48	1.482	4, 6	107.	113.
				5, 6	113.	111.
				ave.	110.	109.
4	1	1.45	1.496(5)	1, 6	114.	109.
	6	1.44	1.454(6)	1, 7	108.	105.
	7	1.50	1.485(5)	1, 8	107.	110.
	8	1.48	1.496(6)	6, 7	108.	113.
	ave.	1.47	1.483	6, 8	111.	111.
				7, 8	108.	108.
				ave.	109.	109.

[a] One standard deviation, B-O distances ±0.01 Å, angles ±1°.

[b] One standard deviation in parentheses; for 1.346(5) read 1.346±0.005 Å. Atoms renumbered to correspond to those in gowerite as follows: B(1), M = B(4); B(2), M = B(2); B(3), M = B(5); B(4), M = B(3); B(5), M = B(1); O(1),M = O(8); O(2), M = O(7); O(3), M = O(4); O(4), M = O(5); O(5), M = O(6); O(6), M = O(1); O(7), M = O(2); O(8), M = OH(9); O(9), M = O(3). Values not given in reference were calculated during this study from the given coordinates.

Table 4. Boron-Boron Distances and Boron-Oxygen-Boron Angles Compared for the Rings in Gowerite and Synthetic $K_2B_5O_8(OH)\cdot 2H_2O$

Boron atom nos.		B-B distance (Å)	
		Gowerite This study[a]	$K_2B_5O_8(OH)\cdot 2H_2O$ Marezio (1969)[b]
1	2	2.50	2.500
	3	2.41	2.411
	4	2.54	2.586
2	3	2.46	2.520
	4	2.44	2.531
	5	2.43	2.496
4	5	2.43	2.479
Atoms of B-O-B angle		**Angle (°)**	
B(1)-O(2)-B(2)		122.	123.6
B(1)-O(3)-B(3)		121.	118.7
B(1)-O(1)-B(4)		131.	130.9
B(2)-O(4)-B(3)		123.	124.0
B(2)-O(6)-B(4)		115.	121.0
B(2)-O(5)-B(5)		120.	121.5
B(4)-O(8)-B(5)		117.	120.3

[a] One standard deviation, B-B distances ±0.02 Å, angles ±1°

[b] Atoms renumbered as given in Table 3, footnote b. Values were calculated during this study using coordinates from the reference.

Table 5. Calcium Coordination in Gowerite

Oxygen atom no.	Coordinates of oxygen atom[a] x	y	z	Ca-O distance (Å) (±0.01 Å)
1	0.238	0.293	-0.259	2.73
2	0.054	0.238	-0.350	2.47
3	0.095	0.249	0.341	2.53
4	0.400	0.295	0.240	2.44
6	0.342	0.282	0.523	2.52
7	-0.045	0.221	-0.051	2.72
OH(10)	0.183	0.109	0.171	2.42
OH(11)	0.288	0.127	-0.015	2.66
$H_2O(1)$	0.131	0.390	0.062	2.36
			ave.	2.54

[a] Ca at x, y, z in Table 1.

charge balance considerations and to assume that OH(11) is in fact the proton donor to $H_2O(3)$. On this basis the electron balance for OH(11) is exact.

Clearly $H_2O(1)$ is the most tightly held water molecule in the structure, as it receives a proton from $H_2O(2)$ and also coordinates the calcium cation in addition to forming two donor hydrogen bonds (Fig. 2). Apparently $H_2O(2)$ must be considered the most loosely held water molecule, as it is retained in place only by its two donor hydrogen bonds which merely go to other water molecules and so are not particularly important structurally (Fig. 2, labelled W2). In view of the OH(12)–O(8) hydrogen bond, a 3.08 Å distance between $H_2O(2)$ and O(8) is considered to be a van der Waals contact only. Thus all the evidence, including the observed temperature factors (Table 1), suggests that $H_2O(2)$ is the water molecule first lost from the structure on heating, $H_2O(3)$ follows, and $H_2O(1)$ is retained as long as possible. This arrangement accords well with the thermal-

Table 6. Hydrogen Bonds and Water-Molecule Environment in Gowerite[a]

(see Fig. 2)

Hydrogen donor	Receptor atom	Bond distance (Å)	Coordinates of receptor atom x	y	z	Atoms	Bond angle (°)
OH(9)	O(5)	2.71	0.532	0.603	0.452	O(5)-OH(9)-OH(10)	119.
OH(10)	OH(9)	2.60	0.071	0.024	0.335	O(8)-OH(12)-$H_2O(1)$	108.
OH(12)	O(8)	2.71	0.144	-0.097	0.258		
$H_2O(1)$	OH(12)	2.70	0.271	0.490	-0.021		
Interlayer	average	2.68					
OH(11)	$H_2O(3)$	2.67	0.384	0.109	-0.289		
$H_2O(1)$	$H_2O(3)$	2.78	-0.116	0.391	-0.289		
$H_2O(2)$	$H_2O(1)$	2.87	0.131	0.390	0.062		
$H_2O(2)$	$H_2O(3)$	2.79	0.116	0.609	0.289		
$H_2O(3)$	O(6)	3.01	0.342	0.282	0.523		
	Average	2.82					
Water molecule no.	Neighbor atom		Coordinates of neighbor atom x	y	z	Atoms of O-H_2O-O angle	
1 H to	OH(12)	2.70	0.271	0.490	-0.021	OH(12), $H_2O(3)$	115.
H to	$H_2O(3)$	2.78	-0.116	0.391	-0.289	OH(12), $H_2O(2)$	113.
H from	$H_2O(2)$	2.87	0.087	0.453	0.418	OH(12), Ca	111.
	Ca	2.36	0.191	0.252	0.088	$H_2O(3)$, $H_2O(2)$	92.
						$H_2O(3)$, Ca	105.
						$H_2O(2)$, Ca	119.
2 H to	$H_2O(1)$	2.87	0.131	0.390	0.062	$H_2O(1)$, $H_2O(3)$	88.
H to	$H_2O(3)$	2.79	0.116	0.609	0.289		
3 H to	O(6)	3.01	0.342	0.282	0.523	O(6), OH(11)	97.
H from	OH(11)	2.67	0.288	0.127	0.985	O(6), $H_2O(1)$	103.
H from	$H_2O(1)$	2.78	0.631	0.110	1.062	O(6), $H_2O(2)$	139.
H from	$H_2O(2)$	2.79	0.413	-0.047	0.582	OH(11), $H_2O(1)$	100.
						OH(11), $H_2O(2)$	119.
						$H_2O(1)$, $H_2O(2)$	89.

[a] One standard deviation, distances ±0.01 Å, angles ±1°. Donor atoms and water molecules taken at x, y, z in Table 1.

analysis data obtained by Gode (1949) and confirmed by Erd *et al.* (1959), who observed that the first mole of water is lost at 85°C, the second, between 85° and 110°C, and no further water is driven off until 230°C and above. However, for gowerite, this interpretation of weight loss upon heating could be complicated by possible loss of some of the molecular $B(OH)_3$ contained in the crystal.

COMPARISON OF GOWERITE WITH RELATED STRUCTURES

The structures of veatchite, $Sr_2[B_5O_8(OH)]_2 \cdot B(OH)_3 \cdot H_2O$ (Clark and Christ, 1968, 1971), and of its dimorph *p*-veatchite (Gandymov *et al.*, 1968; Rumanova and Gandymov, 1971), as well as that of a synthetic potassium polyborate, $K_2[B_5O_8(OH)] \cdot 2H_2O$ (Marezio, 1969), all contain sheets of polymerized $[B_5O_8(OH)]^{2-}$ groups similar to those found in gowerite. The sheets in gowerite are built up of chains formed by connecting groups related by an *a*-glide, whereas in the synthetic potassium borate, the chains are formed by linking groups related by an *n*-glide. In these two structures, therefore, the rings that are approximately perpendicular to the main network are alternately first on one side of the sheet and then on the other (Figs. 2, 3). In veatchite the chains are formed by linking groups related by the *A* face-centering, and in *p*-veatchite, by linking groups related by a cell translation in *a*. In these two structures the perpendicular rings thus all extend on one side of the sheet. A view of the veatchite that illustrates this point is shown in Figure 4. In every case the sheets are formed by linking chains related by a cell translation along the short axis, about 6.5 Å.

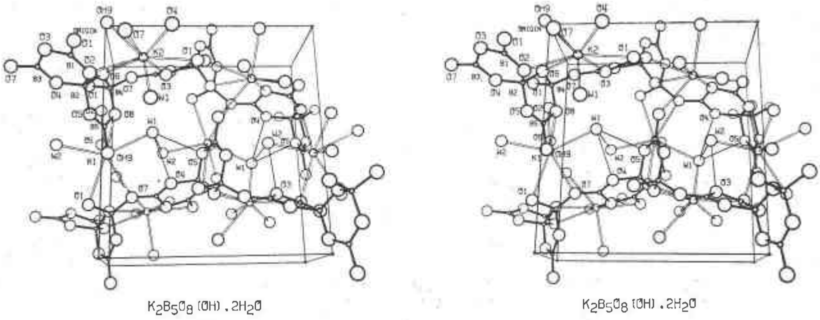

FIG. 3. Stereoscopic-pair view along *b* of a part of the synthetic $K_2B_5O_8(OH) \cdot 2H_2O$ structure to illustrate the intersheet linkages; data from Marezio (1969). The outline of one unit cell is shown with *c* horizontal; a rotation of 20° around *c* was made for clarity. W designates the water molecules; hydrogen bonds are drawn by light, thin lines.

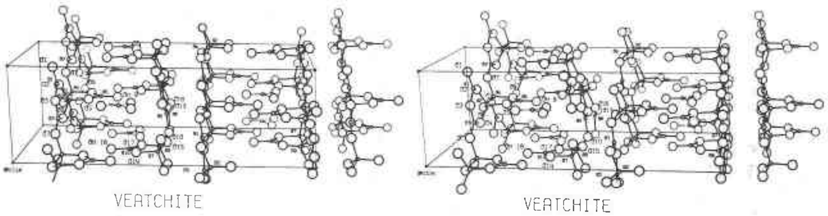

Fig. 4. Stereoscopic-pair view of the $[B_5O_8(OH)]^{2-}$ sheets in veatchite; data from Clark and Christ (1971). Outline of one unit cell is shown, with *a* horizontal, *b* into paper, and *c* vertical.

The similarities among the various sheets are indicated by the values in Table 7 which compare distances of the boron atoms from the planes of the three oxygen atoms in each of the six-membered rings, and angles between the planes for gowerite, veatchite, and the synthetic potassium polyborate.

In each of these compounds the cation fits into the space near the six oxygen atoms O(1), O(2), O(3), O(4), O(6), and O(7), as shown for gowerite in Figure 1 and for the potassium cation K(2) of the synthetic potassium polyborate in Figure 3; the Sr cations in the sheets of veatchite and *p*-veatchite are similarly coordinated. The average distances for these six coordinating oxygen atoms are as follows; gowerite, Ca–O 2.57 Å; veatchite, Sr–O 2.69 Å for each of the two polyanions; and the synthetic compound, K–O 2.782 Å. These values indicate the degree of flexibility offered by the polyanion sheet in accommodating cations of varying size and charge.

The linkage that holds adjacent sheets together is probably an important factor in determining whether sizable crystals can grow. The examples we are considering suggest several ways in which the intersheet bonding can be implemented. Hydrogen bonding is one of these means; it can occur either directly from one layer to the next, or indirectly, through interstitial water molecules. Veatchite and *p*-veatchite are in the first category, whereas gowerite combines both features. Another means of holding the sheets together is by bonding to interstitial cations, as in the synthetic potassium polyborate. Its interlayer bonding is worth some further consideration, including as it does both the hydrogen bonding, direct and indirect, and the bonding to interstitial potassium cations.

The synthetic potassium compound has only one crystallographically distinct sheet, containing potassium cation K(2) and water molecule $H_2O(1)$. Potassium cations K(1) and water molecules $H_2O(2)$ are located between the layers (Fig. 3). Four K(1)–O bonds are to oxygen

Table 7. Comparison of the Planarity of Rings and Triangles in Three Polyborates Having $[B_5O_8(OH)]^{2-}$ Sheets

Ring no.	Ring or triangle oxygen atoms		Associated atoms		Distance (Å) of associated atom from plane of given oxygen atoms			
					Synthetic[1]	Gowerite	Veatchite[2]	
					$K_2B_5O_8(OH)\cdot 2H_2O$	$CaB_5O_8(OH)\cdot B(OH)_3\cdot 3H_2O$	$Sr_2[B_5O_8(OH)]_2\cdot B(OH)_3\cdot H_2O$	
	I	II	I	II			I	II
1	2, 3, 4	11, 12, 13	ΔB(1)	ΔB(6)	-0.08	-0.07	0.1	0.0
			B(2)	B(7)	0.24	0.34	0.5	-0.3
			ΔB(3)	ΔB(8)	-0.14	-0.05	-0.1	0.1
			O(1)	O(10)	-0.25	-0.17	0.0	0.2
			O(7)	O(16)	-0.40	-0.04	-0.3	0.3
2	5, 6, 7	14, 15, 17	B(2)	B(7)	-0.24	-0.24	0.2	-0.3
			B(4)	B(9)	-0.36	-0.49	0.4	-0.4
			ΔB(5)	ΔB(10)	0.09	0.21	-0.2	0.2
			O(1)	O(10)	-1.83	-0.07	0.0	0.2
			O(7)	O(16)	0.28	-1.97	2.0	-1.8
			OH(9)	OH(18)	0.26	0.63	-0.5	0.4
			Angle between rings 1, 2		88.6°	83.0°	82°	81°
	1, 2, 3	10, 11, 12	Angle of Δ to ring plane 1		8.0°	4.8°	1.1°	4.7°
	3, 4, 7	12, 13, 16	Angle of Δ to ring plane 1		11.2°	1.0°	7.3°	8.6°
	5, 8, 9	14, 17, 18	Angle of Δ to ring plane 2		7.4°	18.0°	14.4°	12.1°

[1] Calculated from atomic coordinates given by Marezio (1969).

[2] Clark and Christ (1971); the two crystallographically distinct polyanion sheets are designated I and II.

atoms in the polyanions of one layer, two are to those in an adjacent layer, and one is to the water molecule H_2O (1) which is shared by the layer cation K(2). The eighth K(1)–O bond involves H_2O(2), so this bond is not part of the layer linkage. The oxygen polyhedron around K(1) shares the O(2)–H_2O(1) edge with the polyhedron of K(2) in one layer and the O(7)–OH(9) edge with the polyhedron of K(2) in an adjacent layer. Polyhedral chains parallel to *a* are thus created, and these chains are cross-linked along *c* by the corner-sharing of O(1) between K(1) and K(2) polyhedra. The cation coordination network thus holds the layers tightly together.

There are three hydrogen bonds linking one layer to the next: H_2O(1) to O(4) and to O(5) polyanion oxygen atoms, and OH(9) to O(6). The last bond is not drawn on Figure 3, but it occurs between the labelled atoms near the origin. Two other hydrogen bonds are not directly involved in the interlayer linkage; one is between the two water molecules, and the other is from H_2O(2) to polyanion oxygen O(3). In discussing the relationship of the thermal dehydration studies by Carpéni *et al.* (1960) to the structure, Marezio (1969) attributes the final irreversible reaction that destroys the structure to loss of the hydrogen bond, OH(9) to O(6). Actually it must be the final loss of hydroxyl ion itself that destroys the $[B_5O_8(OH)]^{2-}$ sheets and incidentally breaks the hydroxyl hydrogen bond. However, we agree with Marezio that the evidence supports the assignment of H_2O(2) as the water first lost from the structure, and then H_2O(1). As long as the $[B_5O_8(OH)]^{2-}$ sheets can remain intact the structure survives, in accord with the similar results for the gowerite structure.

CHARGE BALANCE CONSIDERATIONS

Following the ionic model originally suggested by Pauling (1929), assignment of bond strengths in these four structures is as follows: Ca–O, $2/9 = 0.22$ valence units; K–O, $1/8 = 0.125$ v.u.; Sr–O, $2/10 = 0.20$ v.u., and $2/11 = 0.18$ v.u.; ΔB–O, $3/3 = 1.00$ v.u.; tetrahedral B–O, $3/4 = 0.75$ v.u. For the hydrogen bonds, a strength of 0.75 v.u. can be assumed for the donor and 0.25 v.u. for the acceptor. Summing over each oxygen anion on this basis, we find the sums to be within the range 1.88 to 2.13 v.u. for all except O(3), and, in the veatchites, O(15). Interestingly enough, these are the oxygen atoms linking two boron-oxygen triangles which should therefore be fully satisfied by doing so according to this model. Instead, in each structure this atom also is part of the metal coordination polyhedron, and thus its summation is high by the amount of that contribution; *i.e.*, 2.125 v.u. for the K compound, 2.18 and 2.20 v.u. for the veatchites, and 2.22 v.u.

for gowerite. Longer B–O or *M*–O distances might therefore be expected, but there is only a slight tendency in this direction.

The empirical model proposed by Zachariasen (1963) for B–O and hydrogen bonds was also tried, and in the synthetic K compound, where the accuracy of the distances is high and the 0.125 v.u. assignment to each K–O bond appears satisfactory, the model does give sums closer to 2.00 v.u. than found by the simple ionic model. The problem atom O(3), for example, receives 1.96 v.u. using the empirical model; other oxygen atoms that have sums at the extremes of the given range in the simple model are similarly improved. For gowerite, however, the reverse is true (as it also is for the two veatchites, but their determinations are not sufficiently accurate to make comparison meaningful). In particular, the failure of the empirical model for oxygens of the $B(OH)_3$ group is worth mentioning. Whereas the simple ionic model is quite satisfactory for each hydroxyl ion of this group, application of the empirical curves produces sums as follows: OH(10), 1.98 v.u. (satisfactory), but OH(11), 1.83 v.u., assuming it to be the proton donor in the hydrogen bond with $H_2O(3)$, and OH(12), 2.07 v.u. Clearly the nature of the bonding in these borates requires further study.

CRYSTAL-CHEMICAL CONSIDERATIONS

During studies of quaternary ammonium polyborates, Petersen *et al.* (1959) suggested that some compounds classed as hexaborates might in fact be structurally pentaborates plus a boric acid molecule of crystallization. The solutions of the veatchite and *p*-veatchite structures first confirmed the actual presence of such $B(OH)_3$ groups together with the pentaborate sheets, but these two minerals are not hexaborates even though they were so classified for a number of years (*e.g.* Clark, 1964). The structure of gowerite, chemically a hexaborate, thus provides direct confirmation of the suggestion by Petersen *et al.* (1959).

The presence of the isolated $B(OH)_3$ groups takes on significance when considered in conjunction with the recent structural determinations for kaliborite, $HKMg_2[B_6O_8(OH)_5]_2 \cdot 4H_2O$ (Corazza and Sabelli, 1966) and strontioginorite, $SrCaB_{14}O_{20}(OH)_6 \cdot 5H_2O$ (Konnert *et al.*, 1970), a point discussed by Christ (1971). In both structures a small side chain is attached to a large polyanion; in kaliborite there is a single linked triangle, $[BO(OH)_2]^{1-}$, and in strontioginorite, a linked triangle pair, $[B_2O_2(OH)_3]^{1-}$. To the established set of four principles for the formation of fully hydrated borates (Christ, 1960), a fifth rule must therefore be added (Clark, 1971), as follows: the boric acid group, $B(OH)_3$, may exist in isolated form in the presence of more complex polyanions, or such insular groups may themselves polymerize and attach as side chains to more complex polyanions. The chemical conditions that govern the occurrence of such features are not understood at present and probably will not be revealed until systematic study correlated with the structural information is undertaken.

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