

## Crystal structure of fabianite, $\text{CaB}_3\text{O}_5(\text{OH})$ , and comparison with the structure of its synthetic dimorph\*

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### Auszug

Die Kristallstruktur von Fabianit,  $\text{CaB}_3\text{O}_5(\text{OH})$ , von der Lagerstätte bei Diepholz in Niedersachsen wurde durch Patterson- und Elektronendichte-Synthesen aus 1300 ( $hkl$ )-Interferenzen bestimmt und bis  $R = 0,075$  verfeinert. Fabianit hat die Raumgruppe  $P2_1/a$ , die Gitterkonstanten  $a = 6,593 \text{ \AA}$ ,  $b = 10,488 \text{ \AA}$ ,  $c = 6,365 \text{ \AA}$ ,  $\beta = 113,38^\circ$  und bei  $Z = 4$  die berechnete Dichte  $2,788 \text{ g/cm}^3$ . Die Struktur enthält endlose Schichten von der Zusammensetzung  $[\text{B}_3\text{O}_5(\text{OH})]_n^{2n-}$  gleich den schon früher bei der synthetischen rhombischen Modifikation gefundenen. Die Schichten setzen sich wie beim Colemanit aus kreuzweis verbundenen Ketten zusammen. Im Fabianit sind dem Ca zwei OH und sechs O koordiniert; die Polyeder sind durch gemeinsame Kanten zu endlosen Ketten parallel zu  $a$  verknüpft, die ihrerseits die Schichten verbinden. In der synthetischen Verbindung sind dem Ca außer den zwei OH nur fünf O koordiniert; die Polyeder haben nur gemeinsame Ecken. Daher ist – obwohl die Ca–O-Bindungen in beiden Strukturen die aufeinanderfolgenden Schichten zusammenhalten – das Mineral viel dichter gepackt. Beide Strukturen haben wahrscheinlich Wasserstoffbindungen von einem OH der einen Schicht zu einem O der benachbarten, aber beim Mineral ist die Bindung bei  $2,76 \text{ \AA}$  viel stärker als bei der synthetischen Verbindung mit  $2,94 \text{ \AA}$ .

### Abstract

The crystal structure of fabianite,  $\text{CaB}_3\text{O}_5(\text{OH})$ , from salt deposits near Diepholz, Germany, has been solved by Patterson and electron-density syntheses using about 1300 reflections. Least-squares refinement reduced the residual to 0.075. Fabianite is monoclinic,  $P2_1/a$ ,  $a = 6.593$ ,  $b = 10.488$ ,  $c = 6.365 \text{ \AA}$ ,  $\beta = 113.38^\circ$ ,  $Z = 4$ , density (calc.)  $2.788 \text{ g/cm}^3$ . The structure contains infinite sheets of composition  $[\text{B}_3\text{O}_5(\text{OH})]_n^{2n-}$ , similar to those previously found in the synthetic orthorhombic dimorph. The sheets are formed by cross-linking colemanite-like chains. In fabianite Ca is coordinated by two hydroxyl ions and six oxygen atoms; the polyhedra share edges to form infinite chains along  $a$  that

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link polyanion sheets together. In synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$ , Ca is coordinated by two hydroxyl ions and only five oxygen atoms; the polyhedra form chains by corner-sharing only. Hence, although the Ca—O bonding holds adjacent sheets together in each structure, the packing is much more compact in the mineral. Both structures have probable hydrogen bonds from a hydroxyl ion of one sheet to an oxygen ion of an adjacent sheet, but the 2.76 Å bond in the mineral is obviously stronger than the longer 2.94 Å bond in the synthetic dimorph.

### Introduction

Synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$ , a member of the series  $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  with  $x = 1$ , was produced from inyoite crystals treated hydrothermally at 400°C and 2000 bars<sup>1</sup>. The compound was characterized by solution of its crystal structure (CLARK, CHRIST and APPLEMAN, 1962); its symmetry is orthorhombic, and its cell dimensions are given in Table 1. About the same time the crystal structure was published, GAERTNER, ROESE and KÜHN (1962) discovered a new mineral, fabianite, in the salt deposits near Diepholz, Germany, which also had the composition  $\text{CaB}_3\text{O}_5(\text{OH})$  but which had monoclinic symmetry. A more complete description of this new mineral was given by KÜHN, ROESE and GAERTNER (1962). Studies of infrared spectra of fabianite by KÜHN and MOENKE (1963) indicated that the structure had boron in both tetrahedral and triangular coordination with oxygen, that there were no water molecules, and that there was hydrogen bonding present. The cell constants of fabianite were determined by ERD, EBERLEIN and CHRIST (1969) and bear no obvious relationship to those of the synthetic dimorph (Table 1).

In order to find out whether the two structures contained different kinds of borate polyanions or whether there merely existed differing arrangements of the same kind of polyanions (as proved to be the case), we solved the structure of fabianite. We present here the complete information about the structural determination, and compare the structural details for fabianite and the synthetic dimorph; a preliminary report was given by CLARK, KONNERT and CHRIST (1969). Contrary to a suggestion made by TENNYSON (1963), there is no obvious resemblance between the structures of searlesite (KRAVCHENKO, 1964) and the synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$ , as ERD, EBERLEIN and CHRIST (1969) previously pointed out. Neither is there any resemblance between the searlesite and fabianite structures.

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<sup>1</sup> Hydrothermal studies by Prof. BRIAN J. SKINNER, now at Yale University, New Haven, Conn.

## Experimental work

The crystal used for the structural study was a chunky trapezoid flattened on (100), about  $0.40 \times 0.40 \times 0.18$  mm. The cell parameters were taken from ERD, EBERLEIN and CHRIST (1969), and are compared in Table 1 with those of the synthetic dimorph.

About 1450 reflections were collected with Zr-filtered Mo radiation on a Picker automatic diffractometer with a scintillation counter using the  $2\theta$ -scan method with a range calculated as suggested by ALEXANDER and SMITH (1964). Background counts of 20 seconds duration were made for each reflection at the beginning and end of the scan range. The crystal was mounted with  $c^*$  parallel to the  $\Phi$  axis, and the  $(\bar{3}1\bar{3})$  reflection was monitored as a standard after each 30 reflections measured; some equivalent reflections were also checked.

Table 1. *Crystallographic data for fabianite and synthetic CaB<sub>3</sub>O<sub>5</sub>(OH)*

	Fabianite ERD, EBERLEIN and CHRIST (1969)	Synthetic CaB <sub>3</sub> O <sub>5</sub> (OH) CLARK, CHRIST and APPLE- MAN (1962)
Symmetry	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$Pbn2_1$
<i>a</i>	$6.593 \pm 0.001 \text{ \AA}$	$6.972 \pm 0.021 \text{ \AA}$
<i>b</i>	$10.488 \pm 0.002$	$13.47 \pm 0.04$
<i>c</i>	$6.365 \pm 0.001$	$4.391 \pm 0.013$
$\beta$	$113.38 \pm 0.02^\circ$	(90°)
<i>V</i>	$401.1 \pm 0.1 \text{ \AA}^3$	$412.4 \text{ \AA}^3$
<i>Z</i>	4	4
Density		
calculated	2.788 g/cm <sup>3</sup>	2.72 <sub>9</sub> g/cm <sup>3</sup>
observed	$2.77 \pm 0.01$	$2.72 \pm 0.01$

Computer programs written by Prof. C. T. PREWITT, State University of New York, Stony Brook, and modified for the IBM 360/65 by D. E. APPELMAN, U. S. Geological Survey, were used to obtain the diffractometer settings and to reduce the raw data, including corrections for the total background count and for Lorentz and polarization factors. No corrections were made for absorption ( $\mu = 14.3 \text{ cm}^{-1}$ ) or for extinction. For 149 reflections  $|F_o|$  was less than four times the standard deviation of  $|F_o|$  as determined by the counting statistics; these data were coded "less-thans" and omitted in the refinement, which used 1309 nonequivalent reflections.

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 throughout the structure determination and refinement. Scatter-

Table 2. *Atomic parameters for fabianite*

Atom	Parameters*			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ca	0.3041 (2)	0.4371 (2)	0.6372 (2)	0.91 (3) Å <sup>2</sup>
OH(1)	0.4243 (6)	0.1284 (4)	0.5278 (6)	1.03 (6)
O(2)	0.3930 (6)	0.2387 (4)	0.8489 (6)	0.99 (6)
O(3)	0.2161 (6)	0.0325 (3)	0.7225 (6)	0.91 (6)
O(4)	0.6207 (6)	0.0502 (3)	0.8902 (6)	0.88 (6)
O(5)	0.6739 (6)	0.1892 (3)	1.2175 (6)	1.03 (6)
O(6)	0.9845 (6)	0.1131 (4)	1.1527 (6)	1.10 (6)
B(1)	0.4139 (9)	0.1124 (5)	0.7556 (9)	0.95 (7)
B(2)	0.7562 (10)	0.0765 (5)	1.1259 (9)	0.97 (8)
B(3)	0.5174 (9)	0.2690 (5)	1.0739 (9)	0.93 (7)

\* Errors in parentheses are for one standard deviation: for 0.3041 (2), read  $0.3041 \pm 0.0002$ , etc. Equivalent isotropic *B* calculated from the anisotropic thermal parameters (see Table 3).

Final  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.075$ ;  $R_{wt} = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.089$ , where  $w = 1$ .

Table 3. *Anisotropic temperature factor tensor values and thermal ellipsoids for fabianite\**

Tensor values

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ca	7.0 (2)	2.4 (1)	4.4 (5)	- 0.1 (1)	1.9 (2)	0.3 (1)
OH(1)	9.0 (9)	2.6 (3)	4.4 (9)	- 0.3 (4)	2.2 (7)	0.2 (4)
O(2)	8.3 (9)	2.1 (3)	4.7 (9)	0.3 (4)	0.9 (7)	- 0.1 (4)
O(3)	5.9 (8)	2.5 (3)	4.9 (9)	0.1 (4)	1.2 (6)	0.5 (4)
O(4)	7.2 (8)	2.3 (3)	3.6 (9)	- 0.4 (4)	1.4 (6)	- 0.1 (4)
O(5)	8.9 (9)	2.2 (3)	4.6 (9)	- 0.4 (4)	1.1 (7)	0.4 (4)
O(6)	7.6 (8)	2.6 (3)	6.7 (9)	- 0.1 (4)	1.7 (7)	- 1.1 (4)
B(1)	9.0 (12)	2.3 (4)	3.8 (11)	0.0 (6)	2.5 (9)	0.1 (5)
B(2)	10.0 (13)	2.2 (4)	3.4 (12)	- 0.2 (6)	2.8 (9)	0.3 (5)
B(3)	7.1 (12)	2.2 (4)	5.6 (12)	- 0.3 (6)	2.3 (9)	0.1 (5)

\*  $\beta_{ij} \times 10^3$ ; temperature factor form  $\exp \left( - \sum_{i=1}^3 \sum_{j=1}^3 \mathbf{h}_i \mathbf{h}_j \beta_{ij} \right)$

Errors in parentheses are for one standard deviation; for 7.0 (2) read  $0.0070 \pm 0.0002$ , etc.

Table 3. (Continued)

## Thermal ellipsoids

Atom	<i>i</i> of ellipsoid axes $r_i$	Root mean square amplitude	Angle of $r_i$ with		
			<i>a</i>	<i>b</i>	<i>c</i>
Ca	1	0.086 (5) Å	95 (3)°	100 (3)°	21 (3)°
	2	0.114 (2)	134 (15)	134 (15)	84 (6)
	3	0.119 (2)	45 (15)	135 (15)	110 (4)
OH(1)	1	0.086 (9)	97 (7)	97 (10)	18 (7)
	2	0.117 (7)	106 (18)	161 (17)	92 (11)
	3	0.134 (6)	18 (17)	107 (18)	108 (6)
O(2)	1	0.088 (9)	81 (7)	86 (19)	33 (7)
	2	0.106 (7)	100 (10)	10 (12)	88 (18)
	3	0.137 (6)	167 (8)	99 (9)	57 (7)
O(3)	1	0.087 (8)	72 (13)	107 (10)	45 (13)
	2	0.113 (7)	32 (37)	110 (42)	135 (13)
	3	0.120 (7)	65 (42)	27 (35)	92 (32)
O(4)	1	0.078 (9)	90 (8)	88 (10)	24 (8)
	2	0.110 (7)	66 (22)	24 (22)	101 (13)
	3	0.123 (6)	24 (22)	114 (22)	111 (8)
O(5)	1	0.087 (9)	86 (7)	103 (16)	30 (6)
	2	0.108 (7)	106 (9)	160 (13)	94 (15)
	3	0.141 (6)	164 (9)	75 (9)	60 (6)
O(6)	1	0.096 (8)	84 (11)	59 (11)	43 (9)
	2	0.120 (7)	138 (20)	53 (17)	87 (17)
	3	0.134 (6)	131 (20)	127 (16)	47 (9)
B(1)	1	0.079 (13)	101 (8)	92 (14)	13 (9)
	2	0.112 (10)	89 (23)	178 (16)	92 (15)
	3	0.131 (9)	11 (9)	89 (23)	103 (9)
B(2)	1	0.071 (15)	103 (7)	98 (13)	13 (9)
	2	0.112 (10)	96 (16)	169 (14)	96 (13)
	3	0.139 (9)	15 (9)	98 (16)	101 (7)
B(3)	1	0.098 (11)	98 (28)	99 (40)	18 (20)
	2	0.108 (10)	121 (36)	147 (37)	89 (44)
	3	0.120 (9)	32 (36)	122 (36)	108 (20)





Table 4. (Continued)

h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	h	$ F_o $	$F_c$	
(h 0 -8)			8	68	62	0	276	-274	4	83	75	h -6 -8	5	136	-127	2	66	69	2	125	-132
4	126	136	h -2 -8	1	114	-117	5	82	-87	h -6 -8	6	38	-35	3	72	-78	3	62	61		
6	320	-314	-1	114	110	2	106	-106	6	31	-33	0	169	-166	4	67	-74	4	8*	-9	
8	72	-65	0	211	207	4	171	176	1	162	-164	h -8 -8	5	122	-127	5	63	65			
h -1 -8			1	139	-152	5	75	78	h -5 -8	2	98	101	2	201	202	6	32	-35	6	2*	5
-1	151	136	2	142	-155	6	198	-195	0	2*	-1	3	92	97	h -2 -9	h	-4	-9			
0	8*	-4	3	165	185	7	100	-90	4	56	-59	4	256	-252	1	113	-120	2	7*	-2	
1	141	-154	4	125	139	8	122	116	5	16*	5	5	52	46	2	130	139	3	172	-179	
2	100	-113	5	163	-169	h -4 -8			6	114	107	h 0 -9	3	96	-105	4	54	-58			
3	14*	-16	6	38	-41	4	170	170	h -7 -8	2	158	168	4	183	-194	5	117	120			
4	16*	-20	7	107	-97	-1	195	194	5	174	-170	4	189	-198	5	186	191	h -5 -9			
5	235	246	8	77	65	0	69	-65	6	263	-247	1	92	87	6	84	79	6	93	95	
6	59	-55	h -3 -8			1	195	-206	7	98	91	3	159	158	h -3 -9	h	-3	-9	3	113	116
7	158	-152	-1	179	172	2	48	57	4	167	164	1	14*	20	1	89	93	4	81	78	
			3	81	88										5	19*	19				

\* Reflections have  $|F_o| < 4$  standard deviations in counting statistics and were not used in refinements

ing factors for neutral atoms were used, taken from the tables in MACGILLAVRY and RIECK (1962). Bond distances, angles and thermal ellipsoids were calculated using program BADTEA written by L. W. FINGER, Geophysical Laboratory, Washington, D. C.

### Determination of the structure

The structural problem consisted of locating the single Ca, six oxygen and three boron atoms in the general fourfold positions  $4e$  of space group  $P2_1/a$ . The Ca position was assigned after study of a three-dimensional Patterson synthesis. A difference Fourier synthesis, using calculated structure factors for the Ca only, indicated the three boron and six oxygen positions among the dozen strongest peaks.

The conventional residual  $R$  for the 1309 reflections with  $|F_o| > 4$  standard deviations was initially 0.28 and dropped to 0.083 following two cycles of least-squares refinement of positional parameters and individual isotropic temperature factors. One further cycle of refinement for positional parameters and individual anisotropic temperature factors brought the final  $R$  to 0.075. A final difference Fourier was essentially featureless. The final parameters are given in Table 2, and the anisotropic thermal parameters and ellipsoids are given in Table 3. Observed and calculated structure factors are compared in Table 4.

### Description of the structure

The principal features of the fabianite structure are illustrated in Figs. 1, 2 and 3. As in the synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$  dimorph (CLARK, CHRIST and APPLEMAN, 1962), the basic polyanion unit consists of a six-membered boron-oxygen ring formed by two boron-oxygen tetrahedra sharing a corner and a boron-oxygen triangle linking the two tetrahedra at corners. As Fig. 1 shows, in fabianite these rings are polymerized, through O(6) oxygen atoms related by the  $a$ -glide symmetry



operation, into colemanite-like chains (CHRIST, CLARK and EVANS, 1958) zig-zagging along in the  $a$  direction. The chains are cross-linked into sheets approximately parallel to  $(01\bar{1})$  through tetrahedral O(3) oxygen atoms of rings related by centers of symmetry, as shown in Fig. 3. This arrangement differs from that found in the synthetic dimorph, where relatively straight colemanite-like chains along  $[101]$  are formed by linking rings related by the  $n$ -glide symmetry plane, and sheets parallel to  $(010)$  are created by linking chains related by a cell translation along  $c$  (Fig. 4). Fabianite has only one sheet to a cell; syn-

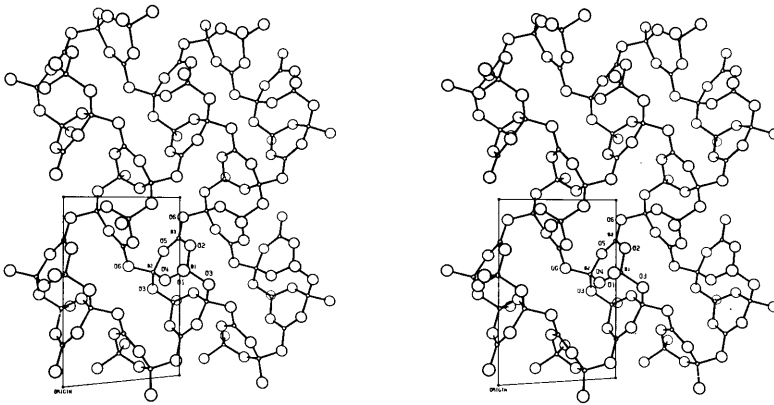


Fig. 1. Stereoscopic-pair view of a polyanion sheet in fabianite looking along  $-c^*$ . The outline of the  $(001)$  plane is shown with the origin at the lower left,  $a$  horizontal. O(1) is the hydroxyl ion. Drawing produced with ORTEP (JOHNSON, 1965)

thetic  $\text{CaB}_3\text{O}_5(\text{OH})$  has two sheets in each cell, related by a twofold screw axis.

As the densities indicate (Table 1), the mineral is slightly more compact than its synthetic dimorph. In fabianite the calcium is 8-coordinated; each Ca ion is surrounded by six oxygen atoms and two hydroxyl ions with distances ranging from 2.37 Å to 2.79 Å, the average distance being 2.49 Å (Table 5). Each calcium polyhedron shares edges with adjacent polyhedra related by the  $a$ -glide planes to form chains along  $a$  (Fig. 2). These polyhedral chains fit between the polyanion sheets and hold them together in stacks along  $c$  (Fig. 3) by using in each polyhedron four oxygen atoms and one hydroxyl ion from one layer, and two oxygen atoms and one hydroxyl ion from the next layer. A hydrogen bond of  $2.76 \pm 0.01$  Å from OH(1) in one layer to tetra-

Table 5  
*Comparison of calcium coordination in fabianite and synthetic CaB<sub>3</sub>O<sub>5</sub>(OH)*

Oxygen atom of Ca—O	Fabianite*			Distance	Synthetic CaB <sub>3</sub> O <sub>5</sub> (OH) CLARK, CHRIST and APPELMAN (1962) Distance**
	This study				
	Coordinates				
	<i>x</i>	<i>y</i>	<i>z</i>		
OH(1)	-0.0757	0.3716	0.5278	2.417 (4) Å	2.40 Å
OH(1)	0.0757	0.6284	0.4722	2.478 (4)	2.70
O(2)	0.3930	0.2387	0.8489	2.421 (4)	2.48
O(3)	0.7161	0.4675	0.7225	2.570 (4)	—
O(3)	0.2839	0.5325	0.2775	2.453 (4)	2.32
O(4)	0.1207	0.4498	0.8902	2.370 (4)	2.34
O(5)	0.1739	0.3108	0.2175	2.794 (4)	2.36
O(6)	0.5155	0.6132	0.8473	2.379 (4)	2.49
Average				2.485	2.44

\* Ca at *x*, *y*, *z* (Table 2). Errors in parentheses are for one standard deviation: for 2.417 (4) read  $2.417 \pm 0.004$  Å.

\*\* Distances all  $\pm 0.023$  Å.

hedral O(5) in the next layer also is a factor in holding the layers together.

In synthetic CaB<sub>3</sub>O<sub>5</sub>(OH) the Ca ion is coordinated by six close oxygen atoms plus one somewhat further away (Table 5); the average

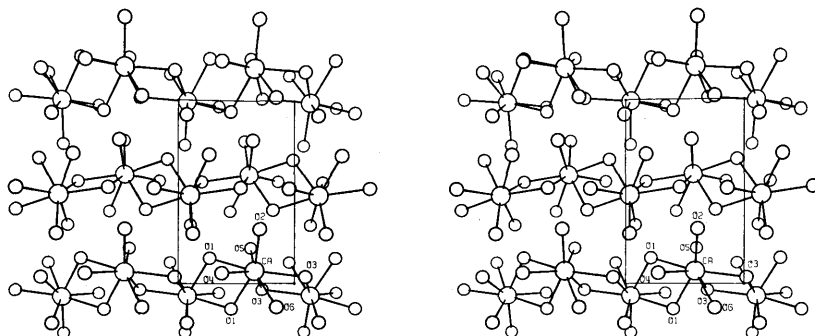


Fig. 2. Stereoscopic-pair view of the calcium-coordination polyhedral chains in fabianite. The orientation is the same as in Fig. 1, with the outline of the (001) plane shown, origin at lower left, *a* horizontal. O(1) is the hydroxyl ion. Drawing produced with ORTEP (JOHNSON, 1965)

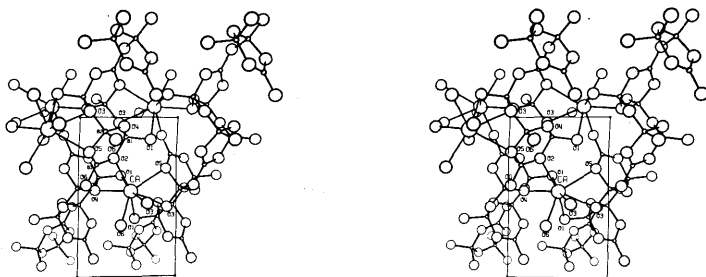


Fig. 3. Stereoscopic-pair view of the sheet linkage in fabianite looking along  $+a^*$ . The outline of the (100) plane is shown, the origin is at the lower left, and  $c$  is horizontal. O(1) is the hydroxyl ion; the hydrogen bond between O(1) and O(5) lies between the labelled atoms in the upper right of the plane outline. Drawing produced with ORTEP (JOHNSON, 1965)

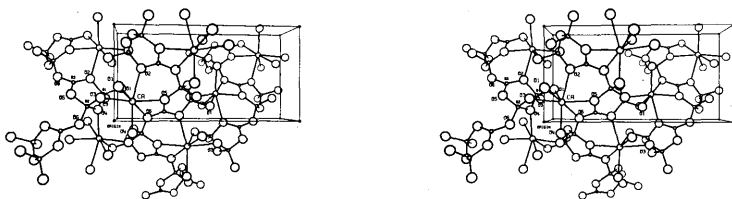


Fig. 4. Stereoscopic-pair view of the sheet linkage in synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$  looking along  $+c$ . The outline of the unit cell is shown;  $b$  is horizontal. The weak hydrogen bond is between the hydroxyl O(1) and oxygen O(3) labelled near  $b/2$ . Drawing produced with ORTEP (JOHNSON, 1965)

Ca—O distance for all seven is 2.44 Å. However, the polyhedra, instead of sharing edges as do those in the mineral structure, share only corners at OH(1) to create chains along  $c$ . These chains help hold adjacent layers together, because four oxygen atoms are from one layer, and one oxygen atom plus two hydroxyl ions are from the adjacent layer (Fig. 4). The possible hydrogen bonds in this compound were considered in detail by CLARK, APPLEMAN and CHRIST (1964), who overlooked a 2.94 Å distance discovered during the present study between OH(1) in one layer and O(3) of a triangle in an adjacent layer. By analogy to the fabianite structure, there is little doubt that this is a weak hydrogen bond.

The boron-oxygen distances for fabianite are listed in Table 6; the averages for these distances, both tetrahedral (1.48 Å) and triangular (1.37 Å) are in good agreement with those found in other borate structures, and in particular are quite similar to those found in the synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$ . The oxygen-boron-oxygen angles are also reasonable

Table 6. *Distances and angles of polyanions in fabianite\**

Oxygen atoms of B—O	Distance	Oxygen atoms of O—B—O	Angle
Tetrahedron around B(1)			
OH(1)	1.488 (6) Å	OH(1), O(2)	109.7 (4)°
O(2)	1.481 (7)	OH(1), O(3)	107.6 (4)
O(3)	1.493 (7)	OH(1), O(4)	103.4 (4)
O(4)	1.446 (6)	O(2), O(3)	110.1 (4)
Average	1.477	O(2), O(4)	112.4 (4)
		O(3), O(4)	113.3 (4)
			Av. 109.4
Tetrahedron around B(2)			
O(3)	1.460 (6)	O(3), O(4)	113.7 (4)
O(4)	1.436 (6)	O(3), O(5)	109.1 (4)
O(5)	1.511 (7)	O(3), O(6)	105.7 (4)
O(6)	1.496 (7)	O(4), O(5)	112.6 (4)
Average	1.476	O(4), O(6)	110.4 (4)
		O(5), O(6)	104.7 (4)
			Av. 109.4
Triangle around B(3)			
O(2)	1.376 (6)	O(2), O(5)	122.5 (5)
O(5)	1.360 (6)	O(2), O(6)	118.0 (4)
O(6)	1.383 (7)	O(5), O(6)	119.5 (4)
Average	1.373		Σ 360.0
Within the ring			
B(1)—B(2)	2.563 (8)	B(1)—O(4)—B(2)	125.6 (4)
B(2)—B(3)	2.450 (8)	B(2)—O(5)—B(3)	121.0 (4)
B(1)—B(3)	2.484 (7)	B(1)—O(2)—B(3)	120.8 (4)
Linking adjacent rings			
B(1)—B(2)'	2.534 (8)	B(1)—O(3)—B(2)'	118.2 (4)
B(2)—B(3)'	2.381 (8)	B(2)—O(6)—B(3)'	118.9 (4)

\* Errors in parentheses are one standard deviation; for 1.488 (6) read  $1.488 \pm 0.006$  Å, etc.

(Table 6). The bond strengths, examined for each oxygen atom and the hydroxyl ion following the methods used by ZACHARIASEN (1963), are satisfactory when the hydrogen bond and the lengths of Ca—O bonds are taken into account.

As in the synthetic dimorph and in other members of this  $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  series, the triangularly coordinated boron lies in the plane of the triangle oxygen atoms. The angles within the six-membered ring, B(1)–O(4)–B(2)–O(5)–B(3)–O(2), show distortion from the regular hexagonal shape, as might be expected from the presence of both tetrahedrally and triangularly coordinated borons in the ring. The plane defined by the three ring oxygen atoms has the equation:  $8.048x + 8.630y - 4.975z = 1.0$ . Boron B(1) lies 0.30 Å below this plane; B(2) and B(3) are both located 0.10 Å above the plane. The plane defined by the triangle oxygen atoms makes an angle of  $9.4^\circ$  with the ring plane. The fabianite polyanion unit is more nearly planar than the basic unit of the synthetic  $\text{CaB}_3\text{O}_5(\text{OH})$ , in which B(1) lies in the plane of the ring oxygen, B(2) is 0.59 Å above the plane, B(3) is 0.42 Å below the plane, and the angle between the ring plane and the plane of the triangle is  $40.1^\circ$ .

The thermal ellipsoids of most of the fabianite atoms are very nearly oblate ellipsoids of revolution, although the triangular boron atom B(3) has approximately spherical thermal motion. Study of an ORTEP drawing the same as Fig. 3 except for the use of thermal ellipsoids shows that the maximum vibration occurs approximately normal to the layers. The hydroxyl OH(1), and the ring oxygen atoms O(2) and O(5) have the greatest degree of anisotropy (Table 3).

Following CHRIST's fourth rule (CHRIST, 1960), the polymerization reactions in this series of borate compounds can be expressed schematically (CLARK, APPLEMAN and CHRIST, 1964). To date the orthorhombic form of  $\text{CaB}_3\text{O}_5(\text{OH})$  is not known as a mineral. Fabianite has been reported only from the original locality, where it was found at a depth of about 2380 m (KÜHN, ROESE and GAERTNER, 1962). However, the depth at which the mineral was collected is not necessarily the depth at which it was formed. The more compact packing in the mineral structure is compatible with the assumption that the mineral formed under higher-pressure conditions than did the synthetic dimorph. However, the synthetic compound may not have formed under equilibrium conditions. Further studies of phase equilibria in the  $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  system would provide the necessary information for answering these questions.

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