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Studies of Borate Minerals (X): The Crystal Structure of $CaB_3O_5(OH)$.*

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One of two orthorhombic products formed when inyoite, $CaB_3O_3(OH)_5.4H_2O$, is heated for several days at 400 °C. and 2000 bars H_2O pressure has been shown by crystal-structure analysis to be $CaB_3O_5(OH)$. The crystals are piezoelectric, $Pbn2_1$, $a=6{\cdot}97_2$, $b=13{\cdot}47$, $c=4{\cdot}39_1$ Å (all $\pm 0{\cdot}3\%$); density (g.cm.$^{-3}$) $2{\cdot}72 \pm 0{\cdot}01$ obs., $2{\cdot}72_9$ calc., cell contents $4[CaB_3O_5(OH)]$. Infinite sheets of composition $[B_3O_5(OH)]_n^{-2n}$ are formed by cross-linking of colemanite-like chains. The sheets are held together through Ca–O bonding.

Introduction

As a part of a continuing study of borate minerals, we have determined the crystal structures of the several members of the colemanite series of calcium borate hydrates, which have the general oxide formula $2\,CaO.3\,B_2O_3.xH_2O$. The presently known members of this series are listed in Table 1, together with their structural formulas and references to the crystal structure determinations.

Table 1. *The calcium borate hydrates,* $2\,CaO.3\,B_2O_3.xH_2O$

x	Mineral	Structural formula	Structure reference
1	Synthetic	$CaB_3O_5(OH)$	This paper
5	Colemanite	$CaB_3O_4(OH)_3.H_2O$	Christ, Clark & Evans (1958)
7	Meyerhofferite	$CaB_3O_3(OH)_5.H_2O$	Christ & Clark (1960)
9	Synthetic	$CaB_3O_3(OH)_5.2H_2O$	Clark & Christ (1959)
13	Inyoite	$CaB_3O_3(OH)_5.4H_2O$	Clark (1959)

The present paper describes the crystal structure of a previously unknown member of this series, for which $x=1$. This compound was discovered during a preliminary reconnaissance of the system $CaO–B_2O_3–H_2O$ at elevated temperatures and pressures, carried out by our colleague Brian J. Skinner. The structural formula of this compound is shown to be $CaB_3O_5(OH)$; it is formed when inyoite ($x=13$) is heated at 400 °C. and 2000 bars H_2O pressure for several days. A second compound is also formed under these conditions; it is characterized at present only by crystallographic data (Clark & Christ, 1960) and is currently under further study.

Experimental work

Crystal description, cell dimensions, space group, and powder data

Only three crystals of size suitable for single-crystal X-ray studies have been synthesized. The dimensions of each of these three crystals is about 1·5 mm. long, and about 0·3 by 0·2 mm. in cross-section. Assignment of the chemical formula has been made solely on the basis of the crystal structure analysis. Crystallographic and optical data for $CaB_3O_5(OH)$ are given in Table 2. The cell dimensions were obtained from measurements of X-ray precession photographs made on quartz-calibrated precession cameras with Zr-filtered Mo radiation (Mo $K\alpha$, $\lambda=0{\cdot}7107$ Å). Indices of refraction were measured in white light at room temperature (~ 25 °C.), and an Abbé refractometer was used to check the indices of the standard index liquids. Optical orientation was correlated to axial directions determined from X-ray precession examination.

Table 2. *Crystallographic and optical data for* $CaB_3O_5(OH)$

Orthorhombic, space group $Pbn2_1$, $Z=4[CaB_3O_5(OH)]$

Cell dimensions (all $\pm 0{\cdot}3\%$)

a	$6{\cdot}97_2$ Å
b	$13{\cdot}47$
c	$4{\cdot}39_1$
Volume	$412{\cdot}_4$ Å^3
Density (calc.)	$2{\cdot}72_9$ g.cm.$^{-3}$
Density (obs.)	$2{\cdot}72 \pm 0{\cdot}01$ (by flotation)

Indices of refraction and optical orientation

Biaxial negative

α (not measured)	$X=b$
β $1{\cdot}608 \pm 0{\cdot}002$	$Y=c$
γ $1{\cdot}638 \pm 0{\cdot}005$	$Z=a$

The $CaB_3O_5(OH)$ crystals are of sword-like habit, elongated [001], with terminal {111} and prism forms {110}, {120} and {010}. Tests for piezoelectricity on an apparatus of the Giebe–Scheibe type are positive, confirming assignment of the acentric space group $Pbn2_1$. No ready cleavage or fracture has been observed during handling of the few available crystals.

An X-ray powder pattern was prepared from a spindle made of carefully selected minute crystals. A 114·59 mm. diameter powder camera was used with

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Table 3. *X-ray powder data for* $CaB_3O_5(OH)$

Orthorhombic: $Pbn2_1$,
$a=6\cdot97_2$, $b=13\cdot47$, $c=4\cdot39_1$ Å (all ±0·3%)

Calculated*		Measured†	
hkl	d_{hkl}	d_{hkl}	*I*
020	$6\cdot73_5$	6·73	25
110	$6\cdot19_2$	6·19	10
120	$4\cdot84_4$	4·84	5
130	$3\cdot77_5$	3·78	5
101	3·716		
021	3·678	3·69	100
111	3·582	3·58	35
200	3·486	3·48	50
210	3·375	3·37	50
040	3·368		
121	3·253	3·25	35
220	3·096	$3\cdot09_5$	40
140	3·032	$3\cdot03_6$	10
131	2·862	2·859	35
230	2·754	2·752	5
211	2·676	2·672	100
041	2·672		
221	2·530	2·531	20
150	2·513		
141	2·495	2·494	25
240	2·422		
231	2·333	2·354	25
310	2·290	2·285	5
060	2·245	2·242	20
320	2·197	2·189	70
002	2·196		
151	2·181		
160	2·137		
250	2·132		
241	2·121	2·116	25
022	2·087	2·083	5
112	2·069		
330	2·064		
301	2·054	2·047	50
311	2·031	2·024	25
122	2·000	1·998	40
061	1·999		
321	1·965		
		1·919	35
		1·885	35
		1·862	10
		1·835	10
		1·787	20
		1·775	20
		1·758	20
		1·712	10
		plus additional lines, all with $I \leq 20$	

* All calculated *d*-spacings listed for $d \geq 1\cdot950$ Å.

† Film no. 14494; measurements uncorrected for film shrinkage. Camera diameter, 114·59 mm.; radiation Cu/Ni, Cu $K\alpha$, $\lambda=1\cdot5418$ Å. Lower limit of 2θ measurable, approximately 7° (13 Å).

Ni-filtered radiation (Cu $K\alpha$, $\lambda=1\cdot5418$ Å); film measurements are uncorrected for film shrinkage. All observed lines on the powder pattern are satisfactorily indexed on the basis of *d*-spacings calculated from the single-crystal data. Observed and calculated *d*-spacings for the powder pattern are compared in Table 3.

Intensity measurements

Intensities were estimated visually from X-ray Weissenberg patterns of the *hk*0 and 0*kl* zones. The experimental techniques used were the same as those described for $CaB_3O_3(OH)_5.2H_2O$ (Clark & Christ, 1959). Intensities greater than zero were found for 399 *hk*0 reflections and for 169 0*kl* reflections. The estimated intensities were converted to F^2_{hkl} values by correcting for Lorentz and polarization factors. No corrections were made for absorption effects. A range in F^2_{hkl} of approximately 1 to 2000 was obtained.

Other considerations

Atomic scattering factors were used as follows: for boron, the zero-valence values of Ibers (1957); for all oxygen atoms, the zero-valence values of Berghuis *et al.* (1955); and for calcium, a curve constructed by plotting the Berghuis values for zero-valence Ca in the range $(\sin\theta)/\lambda \geq 0\cdot3$ Å^{-1} and smoothing in to $f=18$ at $(\sin\theta)/\lambda=0$. Peak positions on the electron-density projections were evaluated by the method of Booth (1948).

Least-squares refinement of the data was carried out on a Burroughs 220 computer, using a program developed by our colleague, J. Marsheck, and one of us (D. E. A.). Using this program, the following parameters may be refined: atomic coordinates, temperature coefficients (overall isotropic, individual isotropic or anisotropic), and scaling constants *k* relating calculated and observed structure amplitudes. The program uses the full matrix of the normal equations. In carrying out the refinement, preliminary cycles were computed with an overall isotropic temperature factor, and the later cycles with refined isotropic temperature coefficients for each atom.

Determination of structure

Preliminary considerations

Chemical analysis of this compound was infeasible because of the sparsity of material. Hence the structure determination was started with the assumption that, due to the conditions of the synthesis, the compound was a hydrated calcium borate, probably having a somewhat higher density than that of colemanite. These considerations combined with the crystallographic requirements indicated a probable total of 24 oxygen atoms per cell.

In previous studies of hydrated calcium borates (references, Table 1) the separation of two oxygen atoms bound to the same boron atom, in either tetrahedral or triangular coordination, has been found to be approximately 2·4 Å. The *c*-axis length of 4·39 Å in this crystal therefore suggested to us the possibility that the crystal contained infinite chains of linked boron–oxygen tetrahedra, $[BO(OH)_2]_n^{-n}$, running nearly parallel to the *c*-axis. The cell contents in this case would be $4\,Ca[BO(OH)_2]_2$, and the calculated density would be 2·68 g.cm.$^{-3}$. This assumption was strengthened by the marked similarity in cell constants (Table 4) between the present compound and calcium metaborate, $Ca(BO_2)_2$, in which there are infinite chains of linked boron–oxygen triangles running parallel to the *c*-axis (Zachariasen & Ziegler, 1932).

Table 4. *Comparison of crystallographic data for calcium metaborate*, $Ca(BO_2)_2$, *and* $CaB_3O_5(OH)$

	$Ca(BO_2)_2$ Zachariasen & Ziegler (1932)	$CaB_3O_5(OH)$ Present study
Symmetry	Orthorhombic	Orthorhombic
Space group	*Pnca*	$Pbn2_1$
a	6·20 Å	6·97$_2$ Å
b	11·62	13·47
c	4·29	4·39$_1$
V	309·1 Å^3	412·4 Å^3
Formula units/cell	4	4
Density (calc.)	2·70 g.cm.$^{-3}$	2·72$_9$ g.cm.$^{-3}$
Density (obs.)	2·65	2·72 ± 0·01

Structure analysis

With the above ideas in mind, the Patterson projection on (001) was prepared, and the Ca–Ca vectors identified, *x*- and *y*-coordinates being assigned to the calcium atom. An electron-density projection on (001) was calculated, using those terms for which signs were presumably determined by the contribution of calcium to the structure factors. This electron-density map was readily interpreted in terms of the postulated $[BO(OH)_2]_n^{-n}$ chains, and *x*- and *y*-coordinates were assigned to six oxygen and two boron atoms. Structure factors, F_c, calculated from this model, when compared with the observed structure factors, F_o, yield a residual factor,

$$R = \Sigma\big||F_o| - |F_c|\big| / \Sigma|F_o| \;,$$

of 0·27 (terms with $F_o = 0$ omitted).

A second electron-density projection on (001) was then prepared. Although it was a cleaner and sharper version of the first map, a region of density where no atom had been assigned recurred with a peak height appropriate to a boron atom. Study of the model revealed that association of a boron with this peak position was structurally feasible, leading to the formula $CaB_3O_5(OH)$. Subsequent refinement of the structure showed beyond any doubt that this is the correct formula.

A third electron-density projection yielded *x*- and *y*-coordinates which were refined by least-squares techniques, described above. Four cycles were calculated, refining an average isotropic temperature factor, and three cycles, refining individual isotropic temperature factors. The residual factor at this stage is 0·087.

Determination of the *z*-coordinates for all atoms was started by calculation of 0*kl* structure factors using the *y*-coordinates from refinement of the *hk*0 data, and *z*-coordinates estimated from a ball model of the crystal structure. In the acentric space group $Pbn2_1$, the origin is chosen by fixing the *z*-coordinate of one atom. The *z* of calcium was therefore selected for convenience as zero. Phases from this first set of structure factors were used to calculate an electron-density projection on (100), and the peak positions of this projection were evaluated to obtain a new set of *z*-coordinates.

Least-squares refinement of 0*kl* data was then started, and the observed structure factors were given weights $w^{\frac{1}{2}}$ as follows: $w^{\frac{1}{2}} = |F_o/4F_{\text{min.}}|$ for observed $|F_{0kl}|$ smaller than four times the minimum observed $|F_{0kl}|$; $w^{\frac{1}{2}} = |4F_{\text{min.}}/F_o|$ for $|F_o| > |4F_{\text{min.}}|$. Five cycles of refinement with an average isotropic temperature coefficient and three cycles with individual isotropic temperature coefficients were calculated. At this stage the residual for this zone has the satisfactory value of 0·125.

The *hk*0 and 0*kl* data were then combined and refined by five cycles of least-squares analysis, in order to obtain the final *x*, *y*, and *z*-coordinates, and the standard errors associated with the atomic parameters. The results of this refinement are given in Table 5 and the equations used for computation of the standard errors are described in the Appendix. For the final refinement, the *hk*0 observations were given a uniform weight of 1·0; the 0*kl* observations were given

Table 5. *Final atomic parameters and standard errors for* $CaB_3O_5(OH)$

					Standard errors			
	Coordinates (cycles)			Isotropic temperature factor (Å^2)	Coordinates (cycles)			Temperature factor (Å^2)
Atom	*x*	*y*	*z*	B	ε_x	ε_y	ε_z	ε_B
Ca	0·2044	0·0951	0*	0·467	0·0003	0·0001	—	0·016
O_1	0·1539	0·5325	0·4606	0·519	0·0012	0·0004	0·0046	0·066
O_2	0·0478	0·3579	0·4763	0·527		(same for all oxygens)		
O_3	0·2572	0·4306	0·8597	0·594				
O_4	0·3831	0·4027	0·3500	0·683				
O_5	0·2226	0·2672	0·0999	0·597				
O_6	0·0289	0·1774	0·4246	0·548				
B_1	0·2155	0·4265	0·5384	0·548	0·0020	0·0007	0·0069	0·098
B_2	0·3469	0·3553	0·0584	0·516		(same for all borons)		
B_3	0·0935	0·2693	0·3374	0·476				

* Chosen as zero to fix origin in $Pbn2_1$.

Table 6. *Comparison of observed and calculated structure factors for hk*0 *and* 0*kl zones of* $CaB_3O_5(OH)$*

$l = 0$

h	k	|Fo|	Fc
00	02	25	16
00	04	66	-60
00	06	68	-70
00	08	-	-1
00	10	18	15
00	12	37	35
00	14	8	-8
00	16	32	-33
00	18	17	-14
00	20	6	6
00	22	24	26
00	24	19	-20
00	26	10	-12
00	28	5	5
00	30	17	17
00	32	5	4
00	34	8	8
00	36	10	-12
01	01	14	14
01	02	10	12
01	03	31	-26
01	04	30	-23
01	05	28	-24
01	06	18	16
01	07	20	-16
01	08	3	3
01	09	-	0
01	10	3	3
01	11	42	43
01	12	53	-58
01	13	8	-8
01	14	14	-11
01	15	10	-10
01	16	9	9
01	17	-	1
01	18	34	34
01	19	7	8
01	20	9	10
01	21	6	4
01	22	-	1
01	23	7	8
01	24	17	-20
01	25	8	-9
01	26	7	-7
01	27	7	-7
01	28	10	10
01	29	-	1
01	30	12	12
01	31	-	0
01	32	-	3
01	33	6	5
01	34	9	-9
01	35	5	-4
01	36	-	-2
01	37	4	-5
02	00	54	-73
02	01	33	-30
02	02	49	-47
02	03	24	20
02	04	2	-1
02	05	8	6
02	06	82	88
02	07	29	26
02	08	4	4
02	09	21	17
02	10	25	-23
02	11	11	10
02	12	22	-20
02	13	8	-8
02	14	-	-1
02	15	4	-3
02	16	22	19
02	17	3	3
02	18	6	4
02	19	-	-2
02	20	7	-8
02	21	5	4
02	22	-	-2
02	23	13	-13
02	24	6	5
02	25	6	-5
02	26	-	2
02	27	-	-3
02	28	9	8
02	29	6	5
02	30	12	-14
02	31	-	-1
02	32	9	-10
02	33	-	1
02	34	-	3
02	35	3	-3
02	36	8	8
02	37	-	2
03	01	29	-25
03	02	36	32
03	03	29	26
03	04	10	8
03	05	66	70
03	06	50	-48
03	07	3	-1
03	08	24	-23
03	09	25	-24
03	10	11	11
03	11	22	-20
03	12	20	20
03	13	10	-10
03	14	18	18
03	15	4	4
03	16	-	-1
03	17	25	25
03	18	31	-32
03	19	18	-17
03	20	13	-13
03	21	23	-24
03	22	15	16
03	23	-	-2
03	24	17	20
03	25	12	14
03	26	-	4
03	27	10	11
03	28	6	-7
03	29	-	2
03	30	9	-9
03	31	6	-6
03	32	-	0
03	33	-	-2
03	34	-	3
03	35	3	4
03	36	3	2
03	37	-	4
04	00	34	31
04	01	4	3
04	02	10	-10
04	03	30	29
04	04	10	-11
04	05	27	26
04	06	20	-18
04	07	50	-49
04	08	20	-18
04	09	43	-41
04	10	5	4
04	11	7	8
04	12	19	19
04	13	26	27
04	14	6	6
04	15	7	8
04	16	10	8
04	17	12	-14
04	18	-	2
04	19	10	-11
04	20	6	-6
04	21	5	5
04	22	-	2
04	23	9	9
04	24	4	-2
04	25	11	12
04	26	4	-4
04	27	-	3
04	28	-	1
04	29	15	-15
04	30	-	3
04	31	-	3
04	32	-	2
04	33	9	9
04	34	-	0
04	35	4	4
04	36	6	-6
05	01	25	22
05	02	4	6
05	03	17	-14
05	04	17	18
05	05	24	-20
05	06	19	18
05	07	10	-9
05	08	8	7
05	09	13	10
05	10	12	13
05	11	26	25
05	12	20	-20
05	13	-	-1
05	14	-	0
05	15	20	-19
05	16	9	7
05	17	11	-10
05	18	9	9
05	19	6	6
05	20	-	-2
05	21	17	15
05	22	5	-4
05	23	9	9
05	24	15	-14
05	25	12	-12
05	26	4	-5
05	27	9	-10
05	28	-	0
05	29	-	-1
05	30	-	2
05	31	6	6
05	32	5	5
05	33	6	6
05	34	-	-1
05	35	-	-2
05	36	-	1
06	00	4	-4
06	01	49	-51
06	02	10	9
06	03	44	-45
06	04	6	-6
06	05	-	1
06	06	23	22
06	07	28	26
06	08	-	0
06	09	19	18
06	10	4	3
06	11	-	-2
06	12	7	-6
06	13	28	-29
06	14	12	-12
06	15	14	-14
06	16	9	-8
06	17	13	12
06	18	8	-7
06	19	19	22
06	20	6	6
06	21	7	7
06	22	6	3
06	23	21	-21
06	24	-	4
06	25	6	-6
06	26	7	-6
06	27	11	11
06	28	-	4
06	29	9	9
06	30	4	-3
06	31	-	-1
06	32	6	4
06	33	-	-2
06	34	3	3
06	35	9	-9
07	01	16	-16
07	02	25	-24
07	03	15	-14
07	04	17	-16
07	05	21	22
07	06	13	-12
07	07	10	9
07	08	24	24
07	09	9	-8
07	10	11	10
07	11	25	-26
07	12	14	-14
07	13	14	16
07	14	18	-17
07	15	18	17
07	16	14	13
07	17	16	17
07	18	-	-2
07	19	10	-10
07	20	7	4
07	21	6	-6
07	22	-	0
07	23	8	-7
07	24	5	-4
07	25	-	5
07	26	-	2
07	27	11	10
07	28	8	7
07	29	-	0
07	30	4	4
07	31	10	-11
07	32	4	-4
07	33	7	-7
07	34	6	-6
07	35	-	5
08	00	9	-7
08	01	19	18
08	02	-	-1
08	03	15	14
08	04	13	12
08	05	22	23
08	06	-	3
08	07	22	-21
08	08	6	-7
08	09	-	-1
08	10	7	-8
08	11	5	4
08	12	-	-4
08	13	13	12
08	14	-	3
08	15	11	13
08	16	11	11
08	17	10	-11
08	18	5	5
08	19	11	-12
08	20	10	-10
08	21	4	-5
08	22	10	-9
08	23	7	7
08	24	-	1
08	25	5	-4
08	26	8	7
08	27	4	3
08	28	-	3
08	29	12	-12
08	30	-	0
08	31	-	1
08	32	-	-3
08	33	4	4
09	01	18	19
09	02	23	22
09	03	-	0
09	04	20	20
09	05	17	-19
09	06	20	-19
09	07	-	2
09	08	21	-20
09	09	5	4
09	10	8	-7
09	11	15	15
09	12	7	5
09	13	9	-9
09	14	12	9
09	15	9	-9
09	16	8	8
09	17	17	-17
09	18	17	-17
09	19	7	7
09	20	6	-4
09	21	8	8
09	22	10	12
09	23	6	5
09	24	9	9
09	25	10	-8
09	26	-	1
09	27	4	-5
09	28	7	-6
09	29	4	3
09	30	-	-5
09	31	6	5
09	32	3	3
09	33	4	5
10	00	9	9
10	01	10	-10
10	02	-	1
10	03	-	0
10	04	7	-8
10	05	-	0
10	06	26	-30
10	07	-	-2
10	08	-	2
10	09	-	1
10	10	27	28
10	11	-	3
10	12	14	16
10	13	6	-5
10	14	11	-12
10	15	-	0
10	16	12	-14
10	17	-	0
10	18	8	5
10	19	-	0
10	20	9	9
10	21	6	6
10	22	11	11
10	23	4	-3
10	24	-	0
10	25	-	0
10	26	7	-8
10	27	-	1
10	28	12	-12
10	29	-	0
10	30	4	4
10	31	-	-1
10	32	5	6
11	01	-	1
11	02	16	-20
11	03	-	0
11	04	6	-4
11	05	-	-1
11	06	12	11
11	07	-	3
11	08	10	12
11	09	-	0
11	10	13	12
11	11	7	-5
11	12	8	-7
11	13	4	2
11	14	9	-8
11	15	4	2
11	16	-	-1
11	17	4	-4
11	18	9	8
11	19	4	-3
11	20	5	4
11	21	4	2
11	22	6	-7
11	23	-	-2
11	24	13	-13
11	25	-	1
11	26	-	0
11	27	-	1
11	28	5	5
11	29	-	1
11	30	-	2
11	31	-	-1
12	00	21	-21
12	01	5	-4
12	02	-	-3
12	03	5	-5
12	04	20	20
12	05	-	0
12	06	14	14
12	07	6	-5
12	08	-	-2
12	09	-	1
12	10	17	-17
12	11	-	-2
12	12	13	-12
12	13	-	-5
12	14	7	6
12	15	-	0
12	16	12	12
12	17	-	2
12	18	-	4
12	19	-	2
12	20	11	-10
12	21	4	3
12	22	12	-11
12	23	-	0
12	24	3	3
12	25	-	-1
12	26	10	10
12	27	3	4
12	28	3	3
12	29	-	0
13	01	11	-11
13	02	6	7
13	03	-	-2
13	04	10	12
13	05	5	5
13	06	-	-3
13	07	10	12
13	08	15	-15
13	09	8	-8
13	10	-	-2
13	11	12	-11
13	12	7	8
13	13	-	4
13	14	9	8
13	15	17	17
13	16	-	-2
13	17	-	1
13	18	8	-9
13	19	-	1
13	20	-	-2
13	21	5	-4
13	22	-	4
13	23	4	-3
13	24	4	4
13	25	-	2
13	26	3	2
13	27	5	4
13	28	-	-4
14	00	7	6
14	01	-	4
14	02	-	4
14	03	16	17
14	04	-	-2
14	05	-	-3
14	06	9	9
14	07	-	-3
14	08	4	3
14	09	-	-1
14	10	5	5
14	11	-	2
14	12	-	2
14	13	-	2
14	14	-	-3
14	15	8	7
14	16	8	-8
14	17	-	-1
14	18	3	-3
14	19	10	-11
14	20	4	3
14	21	-	1
14	22	3	2
14	23	-	2
14	24	-	0
14	25	-	2
14	26	-	0
15	01	8	8
15	02	11	-11
15	03	-	-1
15	04	7	-7
15	05	10	-10
15	06	-	4
15	07	7	-6
15	08	-	1
15	09	12	11
15	10	-	2
15	11	5	4
15	12	9	-8
15	13	-	2
15	14	4	-2
15	15	11	-10
15	16	-	-1
15	17	6	-7
15	18	7	7
15	19	-	2
15	20	4	3
15	21	9	8
15	22	-	1
15	23	-	1
15	24	-	-4
16	00	9	-9
16	01	4	-4
16	02	-	3
16	03	13	-12
16	04	4	-3
16	05	5	-5
16	06	-	-1
16	07	8	9
16	08	-	-1
16	09	14	14
16	10	-	3
16	11	4	-3
16	12	-	-1
16	13	10	-11
16	14	3	2
16	15	-	-2
16	16	-	2
16	17	5	6
16	18	-	1
16	19	3	4
16	20	3	4
16	21	-	-1
17	01	4	-5
17	02	4	-5
17	03	6	7
17	04	-	3
17	05	4	6
17	06	-	4
17	07	-	-1
17	08	-	2
17	09	-	-2
17	10	-	-2
17	11	6	-7
17	12	5	4
17	13	-	-1
17	14	3	-3
17	15	3	4
17	16	-	1
17	17	4	3
17	18	-	0
18	00	-	-1
18	01	7	7
18	02	-	-1
18	03	8	8
18	04	-	1
18	05	-	1
18	06	-	1
18	07	9	-9
18	08	-	3
18	09	9	-7
18	10	4	-3
18	11	-	-1
18	12	3	-2
18	13	4	5
18	14	-	3
19	01	-	0
19	02	4	4
19	03	-	0
19	04	3	5
19	05	5	-6
19	06	-	-1
19	07	-	-2
19	08	-	-6

* Calculated structure factors based on parameters of Table 5.

a uniform weight of 0·5 to allow for the poorer quality of the 0*kl* data. The final value of *R* for the 568 combined *hk*0 and 0*kl* terms with $|F_o| > 0$ is 0·114. Observed and calculated structure factors for the *hk*0 and 0*kl* zones are compared in Table 6.

Interatomic distances (Tables 7–9) have been calculated from the coordinates of Table 5. The standard errors in the distances are as follows: Ca–O, $\pm 0{\cdot}02_3$; O–O, $\pm 0{\cdot}03_2$; B–O, $\pm 0{\cdot}04_2$; B–B, $\pm 0{\cdot}04_9$; and Ca–Ca, $\pm 0{\cdot}006$ Å. These values were obtained using equations described in the Appendix.

Description and discussion of the structure

The principal structural features of $CaB_3O_5(OH)$ are illustrated in Figs. 1 and 2. The crystal contains six-

Table 6 (*cont.*)

h = 0

k	l	|Fo|	|Fc|	k	l	|Fo|	|Fc|	k	l	|Fo|	|Fc|	k	l	|Fo|	|Fc|	k	l	|Fo|	|Fc|	k	l	|Fo|	|Fc|
02	01	48	49	22	02	19	18	06	04	27	26	30	05	6	5	20	07	11	11	18	09	9	9
04	01	46	47	24	02	9	7	08	04	7	7	32	05	-	2	22	07	9	9	20	09	-	4
06	01	72	69	26	02	14	13	10	04	16	15	34	05	-	5	24	07	13	12	22	09	4	4
08	01	75	65	28	02	9	7	12	04	10	9	00	06	26	25	26	07	-	0	24	09	7	7
10	01	27	27	30	02	8	7	14	04	15	15	02	06	16	15	28	07	5	5	00	10	-	2
12	01	24	20	32	02	7	6	16	04	18	20	04	06	21	20	30	07	4	4	02	10	4	4
14	01	32	26	34	02	6	6	18	04	11	14	06	06	29	29	00	08	17	18	04	10	-	2
16	01	14	11	36	06	5	6	20	04	17	16	08	06	9	7	02	08	7	7	06	10	-	4
18	01	33	31	02	03	37	39	22	04	10	10	10	06	17	17	04	08	9	10	08	10	4	3
20	01	14	12	04	03	31	30	24	04	5	5	12	06	14	13	06	08	18	18	10	10	5	6
22	01	23	20	06	03	29	25	26	04	13	12	14	06	10	10	08	08	7	6	12	10	4	4
24	01	23	21	08	03	30	30	28	04	7	6	16	06	15	16	10	08	10	11	14	10	4	4
26	01	9	8	10	03	29	30	30	04	-	2	18	06	5	5	12	08	8	7	16	10	3	2
28	01	10	9	12	03	15	15	32	04	8	7	20	06	11	10	14	08	-	1	18	10	-	3
30	01	10	11	14	03	12	11	34	04	-	4	22	06	7	8	16	08	9	8	20	10	5	4
32	01	5	4	16	03	12	11	02	05	35	31	24	06	3	4	18	08	-	2	02	11	5	5
34	01	8	6	18	03	11	11	04	05	11	12	26	06	6	6	20	08	7	6	04	11	7	7
36	01	2	1	20	03	7	6	06	05	14	13	28	06	3	3	22	08	3	4	06	11	-	1
00	02	75	113	22	03	17	15	08	05	26	29	30	06	6	6	24	08	5	5	08	11	3	3
02	02	34	25	24	03	10	10	10	05	8	8	32	06	6	5	26	08	4	5	10	11	-	2
04	02	45	50	26	03	4	4	12	05	15	16	02	07	24	24	28	08	3	3	12	11	-	2
06	02	15	16	28	03	12	7	14	05	21	22	04	07	9	7	02	09	9	9	14	11	3	2
08	02	20	19	30	03	-	3	16	05	12	14	06	07	14	13	04	09	11	9	16	11	3	2
10	02	16	16	32	03	4	3	18	05	6	5	08	07	14	14	06	09	10	9	00	12	6	6
12	02	16	18	34	03	8	7	20	05	13	10	10	07	-	1	08	09	-	2	02	12	2	3
14	02	13	9	36	03	-	1	22	05	12	10	12	07	13	12	10	09	5	4	04	12	2	2
16	02	28	26	00	04	20	19	24	05	11	10	14	07	16	16	12	09	8	9	06	12	9	6
18	02	19	17	02	04	21	20	26	05	3	1	16	07	6	7	14	09	-	2	08	12	-	2
20	02	15	13	04	04	28	28	28	05	8	7	18	07	12	12	16	09	4	3				

membered boron–oxygen rings formed from two boron–oxygen tetrahedra sharing a corner and one boron–oxygen triangle linking the two tetrahedra. These rings are polymerized into infinite chains as in colemanite (Christ *et al.*, 1958), and the chains are further cross-linked by polymerization into infinite sheets having the composition $[B_3O_5(OH)]_n^{-2n}$. The chemical formula of this compound is therefore $CaB_3O_5(OH)$; in oxide form the formula for

$$2\,[CaB_3O_5(OH)]$$

becomes $2\,CaO.3\,B_2O_3.H_2O$, so that the compound is an $x=1$ member of the series listed in Table 1.

The $[B_3O_5(OH)]_n^{-2n}$ sheets existing in this crystal are shown in Fig. 1 as projected on (010). The rings are linked into colemanite-like chains through O_6; these chains run approximately along $[\bar{2}12]$. Cross-linking of the chains into $[B_3O_5(OH)]_n^{-2n}$ sheets is made through O_3, and tetrahedral chains running approximately along [001] are thus formed. The $[B_3O_5(OH)]_n^{-2n}$ sheets are tightly joined together by the calcium–oxygen bonding illustrated in Fig. 2. Each calcium ion is surrounded by an irregular octahedral array of five oxygens and one hydroxyl oxygen at an average distance of 2·40 Å; three longer contacts are also found (Table 7). The compact structure is in accord with the observation that no easy cleavage or fracture occurs in handling the crystals.

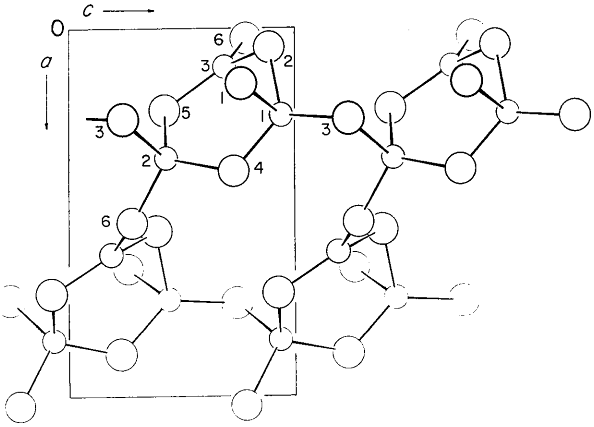

Fig. 1. Projection on (010) of the cell contents lying between $y=0$ and $y=\frac{1}{2}$ of $CaB_3O_5(OH)$. Ca atoms are not shown. The larger open circles represent oxygen atoms and the smaller ones, boron atoms; the atoms of one ring are numbered. The origin of this figure should be moved in the [001] direction $+0{\cdot}285c$ to agree with the coordinates of Table 5.

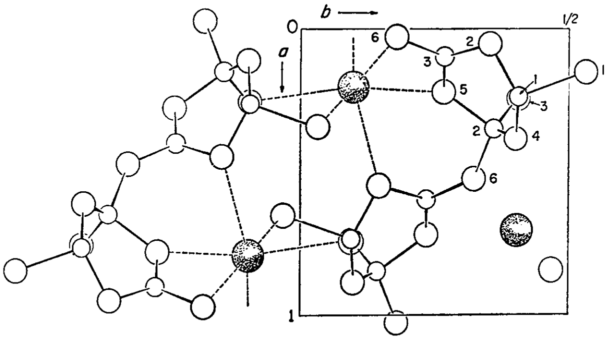

Fig. 2. Projection on (001) of $CaB_3O_5(OH)$. The larger open circles represent oxygen atoms, the smaller open circles, boron atoms, and the stippled circles, calcium atoms. The dashed lines show the Ca–O coordination; the atoms of one ring are numbered (Table 5).

Within the $[B_3O_5(OH)]_n^{-2n}$ sheets, average boron–oxygen distances (Table 8) are comparable to those found in numerous other borates (references, Table 1; Zachariasen, 1952; Morimoto, 1956; Krogh-Moe, 1960): tetrahedral boron to oxygen, 1·47 Å; triangular boron to oxygen, 1·38 Å. Average oxygen–oxygen distances between oxygens bonded to the same boron (Table 9) are also comparable to those previously found: 2·41 Å (tetrahedra); 2·38 Å (triangle). The difference in these two average distances is believed to be real and to stem from the difference to be expected between edges of a regular tetrahedron with average center-to-apices distance 1·47 Å and of a triangle with average center-to-apices distance 1·38 Å (Christ & Clark, 1960). The oxygen–boron–oxygen angles are reasonable, the averages for the two tetrahedra being 109·5° and 109·4°, respectively. As in other members of this series, the triangularly coordinated boron has been found to lie in the plane of the triangle oxygens. The variation in individual bond lengths and angles within the tetrahedra and triangle are believed to be real, the variations representing accommodation of the $[B_3O_5(OH)]^{-2}$ unit to its surroundings in the crystal.

The six-membered boron–oxygen ring (Fig. 1) is made up of the successively linked atoms B_1, O_4, B_2, O_5, B_3, O_2. The plane defined by the three oxygen atoms obeys the equation (in perpendicular form):

$$0{\cdot}3293x-0{\cdot}6268y+0{\cdot}7062z=-1{\cdot}4351\ .$$

Boron B_1 lies almost exactly in this plane, boron B_2 is 0·59 Å above the plane, and boron B_3 is 0·42 Å below the plane. These departures from planarity are

Table 7. *Calcium–oxygen bond lengths, calcium–calcium and boron–boron interatomic distances in* $CaB_3O_5(OH)$

(See Fig. 2)

Ca–O bonds (Å)	
$Ca–O_3$	2·32
$Ca–O_1$	2·34 (3·07)
$Ca–O_5$	2·36
$Ca–O_1$*	2·40 (2·70)
$Ca–O_2$	2·48
$Ca–O_6$	2·49 (3·02)
Average of six shortest	2·40

(All Ca–O bonds $\pm 0{\cdot}02_3$ Å)

Ca–Ca distances (Å)	
Ca–Ca ($z=0{\cdot}500$ cycles)	4·42
Ca–Ca ($z=1{\cdot}000$ cycles)	4·39

(Ca–Ca distances $\pm 0{\cdot}006$ Å)

B–B distances (Å)

Between borons in the ring	
$B_1–B_2$	2·49
$B_1–B_3$	2·45
$B_2–B_3$	2·44
Average	2·46
Between borons linked by O_6 to form colemanite-like chains	
$B_2–B_3'$	2·59
Between borons linked by O_3 to joint adjacent colemanite-like chains	
$B_1–B_2$ ($z=1{\cdot}058_4$ cycles)	2·66

(B–B distances $\pm 0{\cdot}04_9$ Å)

* Hydroxyl oxygen.

Table 8. *Boron–oxygen bond lengths and bond angles for* $CaB_3O_5(OH)$

(See Fig. 1)

B–O bonds		Bond angles	
Tetrahedron around B_1			
$B_1–O_1$*	1·53 Å	O_1*$–B_1–O_2$	108·2°
$B_1–O_2$	1·52	O_1*$–B_1–O_3$	103·8
$B_1–O_3$	1·44	O_1*$–B_1–O_4$	107·6
$B_1–O_4$	1·47	$O_2–B_1–O_3$	110·8
Average	1·49 Å	$O_2–B_1–O_4$	112·3
		$O_3–B_1–O_4$	113·6
		Average	109·4°
Tetrahedron around B_2			
$B_2–O_3$	1·48 Å	$O_3–B_2–O_4$	108·0°
$B_2–O_4$	1·45	$O_3–B_2–O_5$	111·9
$B_2–O_5$	1·48	$O_3–B_2–O_6$	109·6
$B_2–O_6$	1·47	$O_4–B_2–O_5$	110·2
Average	1·47 Å	$O_4–B_2–O_6$	109·5
		$O_5–B_2–O_6$	108·3
		Average	109·6°
Triangle around B_3			
$B_3–O_2$	1·38 Å	$O_2–B_3–O_5$	120·2°
$B_3–O_5$	1·38	$O_3–B_3–O_6$	125·6
$B_3–O_6$	1·37	$O_5–B_3–O_6$	114·0
Average	1·38 Å	$\Sigma =$	359·8°
		$B_1–O_4–B_2$	117·0°
		$B_1–O_2–B_3$	115·4
		$B_2–O_5–B_3$	117·3
		$B_2–O_6–B_3'$	131·8
		$B_1–O_3–B_2'$	129·6

(B–O bonds all $\pm 0{\cdot}04_2$ Å) (All angles $\pm 1{\cdot}5°$)

* Hydroxyl oxygen.

Table 9. *Oxygen–oxygen distances in* $CaB_3O_5(OH)$

(See Fig. 1 and 2)

Oxygens bonded to the same boron

Tetrahedron around B_1		Tetrahedron around B_2	
O_1*$–O_2$	2·47 Å	$O_3–O_4$	2·36 Å
O_1*$–O_3$	2·34	$O_3–O_5$	2·45
O_1*$–O_4$	2·42	$O_3–O_6$	2·40
$O_2–O_3$	2·43	$O_4–O_5$	2·41
$O_2–O_4$	2·48	$O_4–O_6$	2·38
$O_3–O_4$	2·43	$O_5–O_6$	2·39
Average	2·43 Å	Average	2·40 Å

Triangle around B_3	
$O_2–O_5$	2·39 Å
$O_2–O_6$	2·44
$O_5–O_6$	2·31
Average	2·38 Å

Oxygens not bonded to the same boron
(Only distances less than 3·2 Å listed)

O_1*$–O_2$	2·95, 3·05 Å
O_1*$–O_3$	3·06
O_1*$–O_1'$*	3·19

(All O–O bonds $\pm 0{\cdot}03_2$ Å)

* Hydroxyl oxygen.

possibly due to the distortions necessitated by the double polymerization. As might be expected from the presence of both tetrahedrally and triangularly coordinated boron in the same ring, there is considerable departure from the shape of a regular hexagon (see bond angles, Table 8).

The average distance between borons in the ring is 2·46 Å (Table 7). Between the two borons that are linked by O_6 to form the colemanite-like chains, the distance is slightly greater, 2·59 Å; and between the two borons linked by O_3 to join adjacent colemanite-like chains, the distance is 2·66 Å. The two shortest distances between calcium ions are 4·39 Å (the *c* repeat distance) and 4·42 Å (Table 7).

In crystals of hydrated borates, distances in the range 2·6 to 2·9 Å between hydroxyl oxygens not bonded to the same boron indicate hydrogen bonding. No distances within this range were found between hydroxyl oxygen O_1 and its neighboring oxygens in this crystal. Four distances lie between 2·95 and 3·19 Å (Table 9), and these are assumed to be van der Waals contacts.

APPENDIX

The standard errors ε_p in the atomic parameters p, which are refined by least-squares methods, are given by

$$\varepsilon_p = [d_{ii}]^{\frac{1}{2}} [\sum (w^{\frac{1}{2}} \Delta F)^2 - \sum_i \Delta p_i v_i]^{\frac{1}{2}} / [n-p]^{\frac{1}{2}}; \quad \varepsilon_p = (\varepsilon_x, \varepsilon_y, \varepsilon_z) \qquad (1)$$

where d_{ii} are the diagonal elements of the inverse matrix of the normal equations; w is the least-squares weight of an observation; $\Delta F = F_o - F_c$; Δp_i are the parameter changes; v_i are the elements of the vector v of the normal equations; n is the total number of observations for which $|F_o| > 0$; and p is the number of parameters being refined.

The standard errors ε_R in the interatomic distances R are given by

$$\varepsilon_R = [(\varepsilon'_R)^2 + (\varepsilon''_R)^2]^{\frac{1}{2}} \qquad (2)$$

where ε'_R is the approximate standard error in R due to errors in the atomic coordinates, and ε''_R is the standard error in R due to errors in the measurement of the cell dimensions, a, b, and c. For this crystal, ε'_R was computed from the formula

$$(\varepsilon'_{R(1,2)})^2 = (\varepsilon^2_{x(1,2)} + \varepsilon^2_{y(1,2)} + \varepsilon^2_{z(1,2)}) \qquad (3)$$

where $R(1, 2)$ is the distance in Å between atom 1 and atom 2, $\varepsilon_{x(1,2)} = a(\varepsilon^2_{x(1)} + \varepsilon^2_{x(2)})^{\frac{1}{2}}$, and $\varepsilon_{x(1)}$ is the standard error in the x-coordinate of atom 1, from formula (1). The average values obtained for ε'_R are: Ca–O, 0·023 Å; O–O, 0·032 Å; B–O, 0·041 Å; B–B, 0·049 Å; Ca–Ca 0·004 Å.

Values of ε''_R were computed from the estimated standard errors in the determination of the cell dimensions, using the formula

$$(\varepsilon''_R)^2 = \left(\frac{\partial R}{\partial a}\right)^2 \varepsilon^2_a + \left(\frac{\partial R}{\partial b}\right)^2 \varepsilon^2_b + \left(\frac{\partial R}{\partial c}\right)^2 \varepsilon^2_c, \qquad (4)$$

where ε_a is the estimated standard error in the cell edge a, etc. For this crystal,

$$\varepsilon_a = 0{\cdot}02,\ \varepsilon_b = 0{\cdot}04,\ \varepsilon_c = 0{\cdot}01_3\ \text{Å};$$

the average value of ε''_R for all interatomic distances is 0·005 Å. Average values of ε_R computed from equation (2) are: Ca–O, $0{\cdot}02_3$; O–O, $0{\cdot}03_2$; B–O, $0{\cdot}04_2$; B–B, $0{\cdot}04_9$; Ca–Ca, 0·006 Å.

We are indebted to a number of our colleagues for assistance in the course of this study. The crystals of $CaB_3O_5(OH)$ were synthesized by Brian J. Skinner; the density determination was carried out with the help and advice of Esper S. Larsen, 3*d*, and Nelson Hickling; the powder pattern was prepared by Mary E. Mrose.

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