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Studies of Borate Minerals. IV. The Crystal Structure of Inyoite, $CaB_3O_3(OH)_5.4H_2O$*

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Inyoite, $CaB_3O_3(OH)_5.4\,H_2O$, is monoclinic, $P2_1/a$, $a=10{\cdot}63$, $b=12{\cdot}06$, $c=8{\cdot}405$ Å (all $\pm0{\cdot}020$ Å), $\beta = 114°\ 02'\pm5'$, $Z = 4$. The calcium location was obtained from identification of Ca–Ca vector peaks on the sharpened Harker section ($v = \frac{1}{2}$) and on the three sharpened Patterson projections. Positions for the remaining 15 atoms of the asymmetric unit were found by application of various 'heavy-atom' techniques combined with known chemical and spatial requirements. Refinement was carried out from electron-density projections and difference syntheses. A 0·15 residual was obtained for each of the three principal zones. Inyoite contains the same isolated $[B_3O_3(OH)_5]^{-2}$ polyions that were found in meyerhofferite, $CaB_3O_3(OH)_5.H_2O$, and in the synthetic, $CaB_3O_3(OH)_5.2\,H_2O$. Such a polyion is formed by two BO_4 tetrahedra sharing a corner and one BO_3 triangle linking the two tetrahedra. Polyions of inyoite are connected to one another and to neighboring water molecules by bonding through calcium ions and by hydrogen bonds. Continuous polyion–calcium–water columns, oriented along lines parallel to [100], are thus formed. Adjacent columns are cross-linked chiefly by hydrogen bonding through water molecules. The observed cleavages, parallel to (001) and (010), break bonds only between columns.

Introduction

Study of the crystal structure of inyoite was undertaken as part of an investigation of the calcium borate series, $2\,CaO.3\,B_2O_3.xH_2O$. This series includes the minerals colemanite, meyerhofferite, and inyoite, with x equal respectively to 5, 7 and 13; for $x = 9$ a synthetic compound is obtained which has not yet been found in nature. There are no other known members of the series. The crystal structure of colemanite has been described in detail (Christ, Clark & Evans, 1958) and preliminary accounts have been given for the crystal structures of meyerhofferite (Christ & Clark, 1956) and of the synthetic compound (Clark & Christ, 1957).

Inyoite was first described by Schaller (1916) from an occurrence in Inyo County, California, where it was found in close association with meyerhofferite and colemanite. It was noted then that meyerhofferite appeared as a pseudomorph of inyoite. Description of excellent crystals found in New Brunswick, Canada, was given by Poitevin & Ellsworth (1921). These authors confirmed and added to the data on crystallography, optics and chemistry previously given by Schaller. Other reported occurrences of inyoite and a summary of physical and chemical data are given in Palache, Berman & Frondel (1951).

Experimental work

Crystal description, space group and cell dimensions

Crystals of artificial inyoite used for the structure study were prepared by W. T. Schaller by mixing 4 l. of a saturated solution of gypsum, $Ca_2SO_4.2\,H_2O$, with 0·25 l. of a saturated solution of borax, $Na_2B_4O_7.10\,H_2O$, and allowing the mixture to stand about nine months at room temperature. The space group, cell dimensions and X-ray powder data for inyoite were reported by Christ (1953); the space group and cell dimensions are repeated here.

Monoclinic; space group $P2_1/a$–C^5_{2h} (No. 14).
$a = 10{\cdot}63$, $b = 12{\cdot}06$, $c = 8{\cdot}405$ (all $\pm0{\cdot}020$ Å).
$\beta = 114°\ 02'\pm5'$ (Mo λ: $K\alpha = 0{\cdot}7107$ Å; $K\alpha_1 = 0{\cdot}70926$ Å).
Cell contents: $4[CaB_3O_3(OH)_5.4\,H_2O]$.
Density (g.cm.$^{-3}$): calc. = 1·873, obs. (Schaller, 1916) = 1·875.

The crystals are colorless, transparent, and of the general habit illustrated in Fig. 2 of Poitevin & Ellsworth (1921), i.e. tabular on {001}. While numerous forms have been observed on natural crystals, the synthetic crystals, measuring a few tenths millimeter per edge, exhibit only the following forms: dominant {001} and {110}, small {010}, occasional {111}.

Intensity measurements

X-ray equi-inclination Weissenberg patterns were taken with zirconium-filtered Mo radiation for seven-

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teen layers about [010] and for seven layers about [100]. For each exposure three films were interleaved with Ni foil 0·0005 in. thick in order to cut down the intensity from film to film. Exposures of about 72 hours at 50 kV. and 20 mA. were taken for each level; short exposures of about 2 hours each were also taken, when needed, to reduce the intensity of strong reflections to optimum reading range. Cu $K\alpha$ radiation was used for recording low-angle reflections. All intensities were estimated visually by comparison with a standard spot strip. The n spots for the reference intensities on the standard strip were made from a given reflection of the inyoite crystal following the relation, $I_n = I_0(2)^{n/2}$, where I_0 corresponded to a very faint blackening of the film. Excluding the space group absences, there are 5937 reflections contained in the sphere of radius $s = (\sin\theta)/\lambda = 0{\cdot}9$ Å^{-1}. Of these, 3632 had $I > 0$, 2195 had I below the threshold of observation, and no observation was made for 110. Estimated intensities were converted to F^2_{hkl} values by correcting for Lorentz and polarization factors, which were determined for each reciprocal lattice point as a function of cylindrical coordinates. Both IBM methods and the chart of Cochran (1948) were used to obtain the $1/Lp$. No attempt was made to correct for variations in intensity readings due to shape effects on reflections occurring in upper-level Weissenberg films. Because the crystals were small no correction was made for absorption effects which were assumed negligible.

The intensities of the various levels were brought to the same relative scale by the use of appropriate film factors, based on comparison of intensity readings from different films for equivalent reflections. A range in scaled F^2_{hkl} of one to 3000 was obtained. In order to arrive at a preliminary estimate of the temperature factor and of the factor required to convert the relative F^2_{hkl} to an absolute scale, the $K(s)$ curve described by Karle & Hauptman (1953) was constructed for inyoite. A set of absolute F^2_{hkl} was obtained by multiplying the factor, $K(0)$, into the relative F^2_{hkl} values.

Other considerations

Throughout the analysis the observed and calculated structure factors were compared by using a scaling constant k, where $k\Sigma|F_o| = \Sigma|F_c| \exp[-Bs^2]$. The method of Wilson (1942) was applied to determine the values of the average isotropic temperature factor, B. In the early stages of the calculations, atomic scattering curves for the neutral atoms, Ca and O, were taken from Viervoll & Ögrim (1949); for the final calculations, the values given by Berghuis *et al.* (1955) were used. The atomic scattering factors taken for boron were those of Ibers (1957). At the present stage of refinement ionization states have not been taken into account. Maxima on the electron-density projections were calculated by the method of Booth (1948) for all resolved atoms.

Derivation and refinement of structure

The structural problem was to determine the coordinates for one calcium, twelve oxygen and three boron atoms, all in positions 4(e) of space group $P2_1/a$ (*International Tables*, 1952). Although preliminary processing of three-dimensional data had been handled by IBM methods, machine facilities were not available either for three-dimensional series calculations or for Hauptman–Karle sign determination procedures. Therefore the structure derivation was begun by study of a Harker section, taken at $v = \frac{1}{2}$, and of three Patterson projections, each taken on a plane normal to a crystallographic axis. Each Fourier series was sharpened by taking coefficients, p_{hkl}, formed from the observed relative F^2_{hkl} by correcting for both atomic form factor and thermal motion, as follows:

$$p_{hkl} = [K(s)F^2_{hkl}]/(\hat{f})^2, \quad \text{where } \hat{f} = \sum_{j=1}^{N} f_j \Big/ \sum_{j=1}^{N} Z_j .$$

The sharpened Harker section for inyoite is shown in Fig. 1. Each of the sixteen atoms in the asymmetric unit is expected to give rise to two Harker peaks on this section, one at $u = \frac{1}{2}-2x$, $w = -2z$, and the other at $u = \frac{1}{2}+2x$, $w = 2z$. Each Ca–Ca Harker peak is expected to be about six times as large as an O–O Harker peak and about 2·5 times as large as any 'non-Harker' Ca–O peak. Fig. 1 shows that the two largest peaks, labelled A and B respectively, actually have a ratio of about 2:1. By comparing each of these peaks, with respect to both location and size, to peaks occurring on each of the three Patterson projections, selection of A as the Ca–Ca interaction was confirmed. Peak B was later found to be the result of three 'non-Harker' superpositions, i.e. two Ca–O vectors, one with $v = \frac{1}{2}$ and one with $v \approx \frac{1}{2}$, and one O–O vector with $v \approx \frac{1}{2}$.

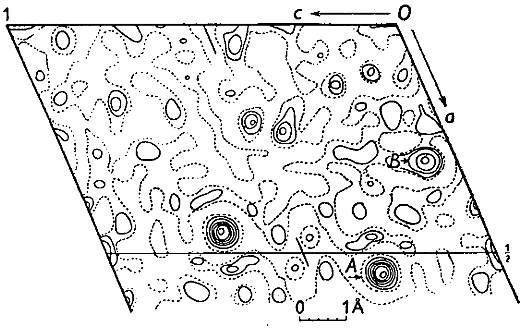

Fig. 1. Sharpened Harker section, $P(u, \frac{1}{2}, w)$. Contours at arbitrary levels, the dashed line at the lowest level and others at intervals of 200, except around A and B where the intervals become 400. A designates the Ca–Ca Harker peak; B is a peak caused by superposition of three 'non-Harker' interactions.

The x, y, z coordinates for calcium given in Table 1 were established from calculations of peak maxima on the Harker section and on each Patterson projec-

Table 1. *Calcium coordinates from Patterson functions*

Parameter	Harker section	$P_w(u, v)$	$P_v(u, w)$	$P_u(v, w)$	Average
x	0·022	0·021	0·023	—	0·022
y	—	0·130	—	0·130	0·130
z	0·161	—	0·160	0·156	0·159

tion. Structure factors based on the calcium contribution only were calculated for the three zones and gave the following residuals: $R(hk0)$, 0·55; $R(h0l)$, 0·50; $R(0kl)$, 0·54. The first electron-density projections were prepared using as coefficients those terms which could reasonably be considered fixed in sign according to these structure factors. The series for $\varrho_y(x, z)$ included about two-thirds of the possible 149 terms. However, the calculations for each of the other two projections included only about one-third of the possible 180 terms, since many $hk0$ and $0kl$ structure factors received only a small contribution from the calcium atom as a result of its having an x-coordinate of nearly zero and a y-coordinate of about one-eighth.

Application of a superposition method appeared to be a useful supplementary approach to the problem of locating oxygen atoms. Accordingly the minimum-function technique, described by Buerger (1951), was applied in turn to each Patterson projection, the known Ca–Ca inversion peaks being used as a basis for a first superposition, and the glide plane symmetry used for a second superposition to produce the three approximate electron-density maps. Each of these maps was similar in detail to the corresponding first electron-density projection described above. Study of all the maps showed that there must be many overlapping atoms in the structure viewed along [100], so principal attention was directed to the other two projections.

The coordinates for selected peaks from each projection were assigned the oxygen scattering factor and their total contribution was added to the calcium contribution for calculation of both $hk0$ and $h0l$ structure factors (S.F.). The residuals for both zones remained persistently higher than those obtained for calcium alone. Examination of individual atomic contributions to the F_{h0l} revealed that subtraction of the contribution of one 'atom' led ultimately to an R of 0·34 for a set of S.F. containing calcium and twelve oxygens. The $\varrho_y(x, z)$ based on that set of S.F. included 120 terms and showed no trace of the original false peak. Consideration of the oxygen coordination that could reasonably be expected about the calcium atom led to selection of x- and y-coordinates for six oxygen atoms; the calculated F_{hk0} based on these six oxygens and the calcium gave an R of 0·45. The ensuing $\varrho_z(x, y)$ contained 128 terms, and study of this analysis, taken together with the last $\varrho_y(x, z)$ and a ball model, revealed the structure. The atomic coordinates assigned for the next S.F. calculation are listed in Table 2, column 1. The oxygen O_{12} of one water molecule was omitted from this calculation but its position

Table 2. *Refinement of atomic coordinates (cycles)*

Atom	Parameter	Stage of refinement 1	2	3	4
Ca	x	0·020	0·020	0·020	0·022
	y	0·131	0·130	0·130	0·129
	z	0·156	0·158	0·160	0·160
O_1*	x	0·044	0·043	0·041	0·043
	y	0·200	0·204	0·205	0·208
	z	0·915	0·919	0·913	0·912
O_2*	x	0·137	0·140	0·138	0·137
	y	0·483	0·482	0·483	0·486
	z	0·782	0·786	0·786	0·787
O_3	x	0·172	0·180	0·175	0·174
	y	0·134	0·133	0·131	0·131
	z	0·752	0·750	0·750	0·752
O_4†	x	0·041	0·040	0·040	0·040
	y	0·331	0·334	0·334	0·334
	z	0·217	0·212	0·216	0·216
O_5	x	0·167	0·168	0·166	0·164
	y	0·467	0·481	0·490	0·490
	z	0·083	0·080	0·081	0·081
O_6*	x	0·127	0·128	0·125	0·123
	y	0·603	0·600	0·600	0·601
	z	0·292	0·290	0·291	0·290
O_7	x	0·140	0·136	0·138	0·139
	y	0·032	0·032	0·032	0·032
	z	0·991	0·980	0·980	0·982
O_8†	x	0·066	0·061	0·057	0·057
	y	0·863	0·856	0·854	0·851
	z	0·613	0·631	0·612	0·615
O_9†	x	0·234	0·238	0·236	0·236
	y	0·652	0·652	0·650	0·650
	z	0·649	0·632	0·641	0·644
O_{10}*	x	0·226	0·221	0·221	0·220
	y	0·854	0·848	0·848	0·848
	z	0·011	0·012	0·010	0·010
O_{11}*	x	0·044	0·044	0·048	0·048
	y	0·936	0·938	0·938	0·940
	z	0·299	0·295	0·295	0·296
O_{12}†	x	—	0·186	0·188	0·188
	y	—	0·332	0·331	0·331
	z	—	0·579	0·586	0·586
B_1	x	0·100	0·095	0·077	0·073
	y	0·100	0·105	0·104	0·108
	z	0·817	0·830	0·831	0·835
B_2	x	0·228	0·229	0·232	0·232
	y	0·463	0·463	0·467	0·467
	z	0·975	0·980	0·980	0·976
B_3	x	0·192	0·200	0·206	0·206
	y	0·577	0·580	0·580	0·578
	z	0·175	0·197	0·213	0·211
R	$hk0$	0·32	0·21	0·17	0·15
	$h0l$	0·32	0·24	0·17	0·15
	$0kl$	0·33	0·20	0·16	0·14
B	$hk0$	0·9	1·15	1·09	0·94
	$h0l$	1·2	1·36	1·30	1·07
	$0kl$	1·2	1·42	1·20	1·09
k	$hk0$	3·1	3·0	3·1	3·2
	$h0l$	2·3	2·3	2·3	2·5
	$0kl$	2·8	2·7	2·9	2·9

$R = \Sigma|\Delta F|/\Sigma|F_o|$, ΔF omitted if $F_o = 0$.
B = average isotropic temperature factor (Å^2).
k = scaling factor (see text).

* Hydroxyl oxygen.
† Water oxygen.

was immediately evident on the next electron-density projections, which gave coordinates for all atoms as shown in Table 2, column 2.

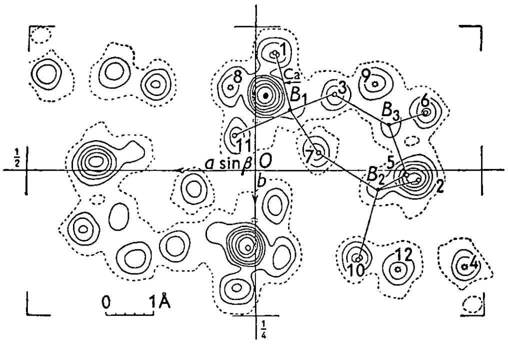

Fig. 2. Final $\varrho_z(x, y)$. Contours at intervals of 4 e.Å^{-2} except around Ca where intervals become 10 e.Å^{-2} after the 20 e.Å^{-2} contour. Dashed contour at 4 e.Å^{-2}. Orientation of the $[B_3O_3(OH)_5]^{-2}$ polyion is shown. Atomic sites are marked: open circles for oxygens or hydroxyl oxygens; spoked circles for water oxygens. Tables 5 and 6 list bond distances and angles within the polyion.

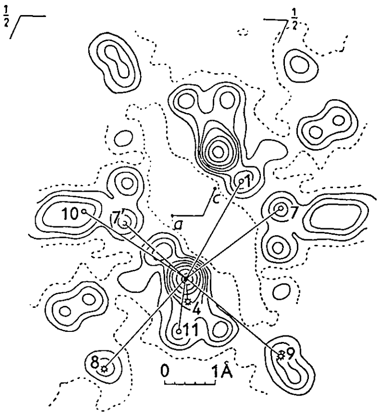

Fig. 3. Final $\varrho_y(x, z)$. Contours at intervals of 4 e.Å^{-2} except around Ca where intervals become 10 e.Å^{-2} after the 20 e.Å^{-2} contour. Dashed contour at 4 e.Å^{-2}. Oxygen coordination around one Ca ion is shown; open circles are at sites of oxygens or hydroxyl oxygens, and spoked circles are at sites of water oxygens. Table 8 lists Ca–O bond distances.

A final set of electron-density projections was then prepared, each series containing 99% of all possible terms. Any omitted term had a very small $|F_o|$. The final $\varrho_z(x, y)$ and $\varrho_y(x, z)$, which are on an absolute scale, are shown in Figs. 2 and 3 and the atomic coordinates taken from all three projections are given in Table 2, column 3. Difference syntheses, $D_z(x, y)$ and $D_y(x, z)$, were calculated and the indicated shifts in atomic positions yielded the coordinates listed in Table 2, column 4. Comparison of F_o with the F_c based on this last set of coordinates is shown in Table 3; the R value for each of the three zones is 0·15. Further refinement of the structure from the three-dimensional data is planned, and a detailed analysis of the accuracy of the structure parameters and of the bond distances has therefore been postponed. For the colemanite structure (Christ, Clark & Evans, 1958) standard errors in bond distances were calculated following least-squares refinement of atomic coordinates. Because the inyoite structure is directly comparable to colemanite and both structures are at a similar stage of refinement, standard errors for bond distances in inyoite may reasonably be expected to be the same as for colemanite. On this basis the limits assigned to bond distances in inyoite are as follows: Ca–O, ±0·02; O–O, ±0·03; B–O, ±0·04 (Å).

Discussion of the structure

The crystal structure of inyoite contains isolated polyions, $[B_3O_3(OH)_5]^{-2}$, one of which is illustrated in Fig. 2 as it appears on $\varrho_z(x, y)$. Single polyions are connected to one another (Fig. 4) to form continuous polyion–calcium–water columns parallel to [100]. The polyions within one column are held together principally by bonding from calcium ions to oxygens and hydroxyls of adjacent polyions and to oxygens of water molecules. Some hydrogen bonds also link adjacent polyions to one another and to water molecules. Each calcium ion is coordinated by eight oxygens,

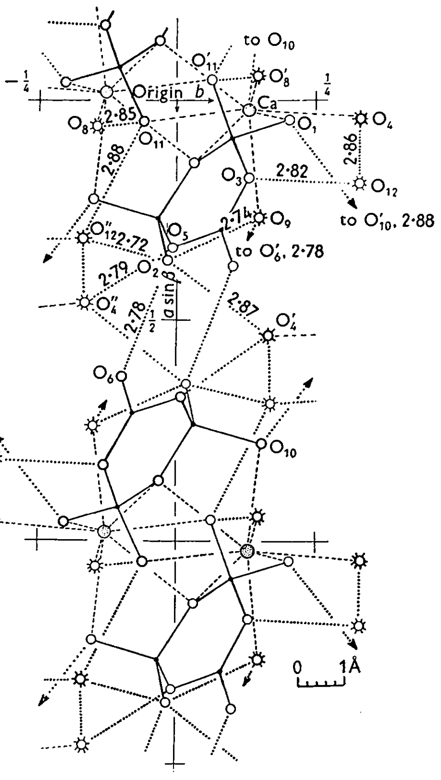

Fig. 4. View of the structure along [001] showing a polyion–calcium–water column. Dashed lines indicate Ca–O bonds; dotted lines represent hydrogen bonds (Table 9). Polyions are shown with solid lines.

Table 3. *Comparison of observed and calculated structure factors for the three zones*: *hk*0, *h*0*l*, 0*kl*

Calculated F_{hkl} are based on the atomic coordinates of Table 2, column 4

*hk*0	F_o	F_c	*hk*0	F_o	F_c	*hk*0	F_o	F_c	*hk*0	F_o	F_c
020	49	53	3,17,0	11	8	720	9	−2	11,5,0	10	−10
040	119	−111	3,18,0	9	4	730	11	−9	11,6,0	10	12
060	103	91	3,19,0	—	−2	740	—	0	11,7,0	10	12
080	56	52	3,20,0	—	4	750	10	−10	11,8,0	—	3
0,10,0	30	−25	3,21,0	—	−2	760	22	19	11,9,0	8	11
0,12,0	21	−14	400	54	42	770	—	1	11,10.0	14	−16
0,14,0	11	16	410	24	−18	780	9	15	11,11,0	—	4
0,16,0	—	−1	420	67	−63	790	8	−9	11,12,0	—	1
0,18,0	—	−4	430	12	16	7,10,0	32	−38	11,13,0	—	−2
0,20,0	7	−5	440	68	−73	7,11,0	15	−17	11.14 0	12	9
110	53	63	450	30	26	7,12,0	6	3	11,15,0	—	−3
120	33	−28	460	16	16	7,13,0	11	−12	11,16,0	8	−10
130	70	−68	470	31	28	7,14,0	25	28	12,0,0	24	−21
140	32	−28	480	—	2	7,15,0	—	2	12,1,0	26	−28
150	38	−44	490	12	13	7,16,0	15	−15	12,2,0	—	2
160	42	35	4,10,0	37	−37	800	—	−4	12,3,0	12	−11
170	11	11	4,11,0	—	−7	810	50	−50	12,4,0	—	3
180	42	38	4,12,0	17	17	820	22	20	12,5,0	28	40
190	15	14	4,13,0	12	10	830	20	−20	12,6,0	—	3
1,10,0	15	−13	4,14,0	16	19	840	—	6	12,7,0	9	8
1,11,0	55	−57	4,15,0	—	0	850	34	36	12,8,0	11	14
1,12,0	—	4	4,16,0	10	7	860	—	−2	12,9,0	14	−15
1,13,0	22	−20	4,17,0	—	2	870	—	0	12,10,0	—	2
1,14,0	16	17	4,18,0	—	−6	880	18	20	12,11,0	6	14
1,15,0	26	30	4,19,0	—	3	890	28	−27	12,12,0	—	−3
1,16,0	—	−3	4,20,0	—	−6	8,10,0	—	4	12,13,0	15	20
1,17,0	—	−2	4,21,0	—	3	8,11,0	8	−9	12,14,0	—	−1
1,18,0	9	4	510	17	16	8,12,0	10	−12	12,15,0	—	1
1,19,0	—	−11	520	8	12	8,13,0	12	10	13,1,0	—	−2
1,20,0	—	11	530	28	−29	8,14,0	7	−7	13,2,0	24	−24
1,21,0	—	−1	540	20	22	8,15,0	10	−11	13,3,0	8	−10
200	35	26	550	32	−34	8,16,0	—	−3	13,4,0	10	10
210	44	−36	560	15	12	910	10	−14	13,5,0	—	−8
220	38	−32	570	25	22	920	29	−28	13,6,0	23	26
230	7	4	580	17	20	930	—	4	13,7,0	—	0
240	37	−36	590	20	28	940	16	16	13,8,0	8	−15
250	—	1	5,10,0	20	−22	950	6	14	13,9,0	—	−6
260	26	−26	5,11,0	22	−24	960	25	21	13,10,0	8	−14
270	33	−32	5,12,0	—	−10	970	18	18	13,11,0	8	12
280	12	11	5,13,0	7	−10	980	—	−6	13,12,0	9	16
290	29	−33	5,14,0	7	8	990	—	0	13,13,0	—	1
2,10,0	6	5	5,15,0	19	21	9,10,0	16	−18	13,14,0	10	12
2,11,0	27	−32	5,16,0	15	−15	9,11,0	—	8	14,0,0	—	−7
2,12,0	25	−32	5,17,0	—	2	9,12,0	—	6	14,1,0	12	−9
2,13,0	6	−8	5,18,0	10	−14	9,13,0	7	4	14,2,0	—	12
2,14,0	—	5	5,19,0	7	−7	9,14.0	11	13	14,3,0	22	−22
2,15,0	—	0	5,20,0	—	−5	9,15,0	—	−1	14,4,0	8	10
2,16,0	17	21	600	38	37	9,16,0	4	−2	14,5,0	—	2
2,17,0	11	−11	610	32	−32	10,0,0	27	−29	14,6,0	—	−4
2,18,0	—	4	620	17	17	10,1,0	—	−2	14,7,0	10	14
2,19,0	7	−12	630	9	7	10,2,0	14	−10	14,8,0	—	0
2,20,0	7	−6	640	—	0	10,3,0	—	0	14,9,0	8	−10
2,21,0	—	6	650	33	36	10,4,0	20	−14	14,10,0	—	2
310	109	92	660	14	16	10,5,0	—	−3	14,11,0	—	−8
320	18	−13	670	28	28	10,6,0	10	−15	14,12,0	9	4
330	12	−13	680	24	27	10,7,0	—	−5	15,1,0	—	0
340	—	−1	690	6	7	10,8,0	—	0	15,2,0	12	−14
350	—	−2	6,10,0	—	8	10,9,0	14	−17	15,3,0	—	7
360	7	7	6,11,0	24	−24	10,10,0	4	4	15,4,0	7	−2
370	17	17	6,12,0	9	−10	10,11,0	11	−14	15,5,0	8	8
380	22	21	6,13,0	8	4	10,12,0	—	3	15,6,0	—	7
390	25	29	6,14,0	7	4	10,13,0	10	13	15,7,0	—	4
3,10,0	30	−29	6,15,0	13	18	10,14,0	—	−5	15,8,0	—	−7
3,11,0	—	1	6,16,0	17	20	10,15,0	—	5	15,9,0	—	−8
3,12,0	17	−22	6,17,0	—	3	10,16,0	6	6	15,10,0	—	−1
3,13,0	—	3	6,18,0	—	−3	11,1,0	—	1	15,11,0	—	1
3,14,0	9	10	6,19,0	—	−6	11,2,0	23	−19	16,0,0	—	−4
3,15,0	18	20	6,20,0	12	−16	11,3,0	—	1	16,1,0	—	−6
3,16,0	—	8	710	—	−3	11,4,0	13	−10	16,2,0	—	1

Table 3 (*cont.*)

*hk*0	F_o	F_c
16,3,0	7	−12
16,4,0	—	1
16,5,0	—	6
16,6,0	—	−4
16,7,0	—	4
16,8,0	—	−5
17,1,0	—	−6
17,2,0	15	−15
17,3,0	—	3
17,4,0	—	−6
17,5,0	—	2

*h*0*l*	F_o	F_c
001	73	110
002	73	−63
003	10	16
004	—	3
005	46	50
006	26	17
007	16	14
008	—	1
009	11	−12
0,0,10	6	8
0,0,11	6	8
0,0,12	10	11
0,0,13	14	19
200	27	26
201	26	20
202	88	−82
203	62	−55
204	69	−68
205	7	−7
206	44	45
207	8	3
208	13	−16
209	17	−17
2,0,10	—	3
2,0,11	—	0
2,0,12	8	6
2,0,13	19	23
$20\bar{1}$	11	8
$20\bar{2}$	57	−56
$20\bar{3}$	136	−122
$20\bar{4}$	22	−16
$20\bar{5}$	36	−49
$20\bar{6}$	16	−15
$20\bar{7}$	36	32
$20\bar{8}$	8	−16
$20\bar{9}$	41	−47
$2,0,\overline{10}$	21	−19
$2,0,\overline{11}$	—	0
$2,0,\overline{12}$	—	0
$2,0,\overline{13}$	11	8
$2,0,\overline{14}$	—	0
400	42	42
401	42	−37
402	19	14
403	20	20
404	14	−10
405	13	14
406	32	36
407	—	−2
408	14	−14
409	16	−15
4,0,10	17	−21
4,0,11	—	7
4,0,12	11	10
$40\bar{1}$	63	70
$40\bar{2}$	26	−19
$40\bar{3}$	106	−98
$40\bar{4}$	97	−89
$40\bar{5}$	26	26
$40\bar{6}$	36	31
$40\bar{7}$	27	23
$40\bar{8}$	24	28
$40\bar{9}$	—	0
$4,0,\overline{10}$	—	−7
$4,0,\overline{11}$	11	−4
$4,0,\overline{12}$	—	8
$4,0,\overline{13}$	—	6
$4,0,\overline{14}$	—	0
600	30	36
601	—	−1
602	49	−56
603	5	0
604	22	28
605	13	8
606	9	−16
607	15	−18
608	9	−9
609	6	−8
6,0,10	—	−12
6,0,11	—	−5
$60\bar{1}$	56	56
$60\bar{2}$	39	43
$60\bar{3}$	98	−102
$60\bar{4}$	39	−39
$60\bar{5}$	14	−7
$60\bar{6}$	—	−4
$60\bar{7}$	51	48
$60\bar{8}$	6	−3
$60\bar{9}$	—	1
$6,0,\overline{10}$	—	7
$6,0,\overline{11}$	—	−3
$6,0,\overline{12}$	8	10
$6,0,\overline{13}$	7	4
$6,0,\overline{14}$	11	10
$6,0,\overline{15}$	—	6
800	—	−4
801	13	−8
802	17	−16
803	7	−3
804	14	16
805	29	24
806	27	30
807	7	−7
808	12	−10
809	—	0
$80\bar{1}$	33	48
$80\bar{2}$	21	20
$80\bar{3}$	17	11
$80\bar{4}$	—	−4
$80\bar{5}$	36	−38
$80\bar{6}$	28	26
$80\bar{7}$	40	35
$80\bar{8}$	21	22
$80\bar{9}$	—	4
$8,0,\overline{10}$	27	−28
$8,0,\overline{11}$	22	−15
$8,0,\overline{12}$	14	−14
$8,0,\overline{13}$	—	−4
$8,0,\overline{14}$	18	16
$8,0,\overline{15}$	—	3
10,0,0	21	−28
10,0,1	36	−39
10,0,2	16	−10
10,0,3	—	−2
10,0,4	17	22
10,0,5	22	16
10,0,6	12	12
10,0,7	—	4
10,0,8	16	−20
$10,0,\bar{1}$	25	27
$10,0,\bar{2}$	17	15
$10,0,\bar{3}$	33	−35
$10,0,\bar{4}$	33	−37
$10,0,\bar{5}$	14	−21
$10,0,\bar{6}$	13	−10
$10,0,\bar{7}$	27	27
$10,0,\bar{8}$	32	36
$10,0,\bar{9}$	—	1
$10,0,\overline{10}$	25	−21
$10,0,\overline{11}$	22	−24
$10,0,\overline{12}$	7	−7
$10,0,\overline{13}$	—	0
$10,0,\overline{14}$	7	11
12,0,0	19	−20
12,0,1	21	−26
12,0,2	13	−10
12,0,3	8	−6
12,0,4	—	2
12,0,5	11	13
12,0,6	6	−8
$12,0,\bar{1}$	21	20
$12,0,\bar{2}$	28	30
$12,0,\bar{3}$	—	1
$12,0,\bar{4}$	26	−30
$12,0,\bar{5}$	32	−36
$12,0,\bar{6}$	5	10
$12,0,\bar{7}$	14	17
$12,0,\bar{8}$	23	20
$12,0,\bar{9}$	8	7
$12,0,\overline{10}$	32	−35
$12,0,\overline{11}$	—	−2
$12,0,\overline{12}$	14	14
$12,0,\overline{13}$	—	−3
$12,0,\overline{14}$	—	6
14,0,0	—	−6
14,0,1	—	0
14,0,2	9	−7
14,0,3	8	−10
14,0,4	16	17
$14,0,\bar{1}$	8	11
$14,0,\bar{2}$	31	29
$14,0,\bar{3}$	22	24
$14,0,\bar{4}$	6	−9
$14,0,\bar{5}$	—	1
$14,0,\bar{6}$	11	17
$14,0,\bar{7}$	—	1
$14,0,\bar{8}$	8	16
$14,0,\bar{9}$	7	5
$14,0,\overline{10}$	—	−3
$14,0,\overline{11}$	12	−14
$14,0,\overline{12}$	15	−16
$14,0,\overline{13}$	9	13
16,0,0	—	−4
16,0,1	12	−19
16,0,2	7	−5
$16,0,\bar{1}$	—	−9
$16,0,\bar{2}$	—	1
$16,0,\bar{3}$	16	16
$16,0,\bar{4}$	—	−7
$16,0,\bar{5}$	14	−13
$16,0,\bar{6}$	9	−9
$16,0,\bar{7}$	—	0
$16,0,\bar{8}$	7	5
$16,0,\bar{9}$	16	9
$16,0,\overline{10}$	—	−3
$16,0,\overline{11}$	15	−19
$16,0,\overline{12}$	11	−11

0*kl*	F_o	F_c
020	44	53
040	108	−110
060	93	90
080	50	51
0,10,0	27	−24
0,12,0	19	−13
0,14,0	10	15
0,16,0	—	−1
0,18,0	—	−3
0,20,0	6	−5
001	85	110
011	7	−4
021	65	54
031	34	35
041	35	39
051	84	84
061	16	17
071	—	−2
081	31	30
091	32	−39
0,10,1	8	12
0,11,1	10	12
0,12,1	25	−26
0,13,1	11	15
0,14,1	5	2
0,15,1	—	0
0,16,1	—	2
0,17,1	10	−6
0,18,1	8	−8
0,19,1	—	2
0,20,1	6	−7
0,21,1	9	8
002	85	−63
012	8	−4
022	21	−14
032	44	−36
042	73	70
052	20	16
062	33	28
072	20	16
082	21	−20
092	16	−10
0,10,2	4	−7
0,11,2	5	−5
0,12,2	3	0
0,13,2	8	4
0,14,2	5	−8
0,15,2	15	20
0,16,2	17	−20
0,17,2	14	−13
0,18,2	6	−4
0,19,2	9	−15
0,20,2	6	5
0,21,2	11	11
003	12	16
013	7	−3
023	20	−17
033	70	−66
043	30	24
053	—	−2
063	10	8
073	25	29
083	35	−34
093	22	−22
0,10,3	19	−23

Table 3 (*cont.*)

0*kl*	F_o	F_c	0*kl*	F_o	F_c	0*kl*	F_o	F_c	0*kl*	F_o	F_c
0,11,3	—	−4	0,12,5	8	8	0,15,7	7	7	0,5,10	5	−6
0,12,3	14	14	0,13,5	21	−23	0,16,7	5	6	0,6,10	—	2
0,13,3	6	7	0,14,5	—	−3	0,17,7	9	−11	0,7,10	8	9
0,14,3	8	−4	0,15,5	—	3	0,18,7	—	0	0,8,10	19	−20
0,15,3	—	−8	0,16,5	7	−10	008	—	1	0,9,10	16	22
0,16,3	23	−27	0,17,5	13	13	018	4	−1	0,10,10	—	4
0,17,3	12	−17	0,18,5	—	−7	028	9	−7	0,11,10	—	2
0,18,3	—	0	0,19,5	—	−4	038	—	4	0,12,10	14	16
0,19,3	—	−1	0,20,5	10	−9	048	8	−10	0,13,10	—	−1
0,20,3	16	16	006	30	17	058	11	8	0,14,10	—	−2
0,21,3	—	−4	016	14	−17	068	9	12	0,0,11	7	7
004	—	3	026	12	11	078	16	22	0,1,11	11	9
014	47	44	036	5	−1	088	5	5	0,2,11	—	−1
024	44	40	046	35	−35	098	5	−5	0,3,11	16	19
034	24	27	056	13	18	0,10,8	10	−17	0,4,11	—	−1
044	27	27	066	—	−8	0,11,8	8	−13	0,5,11	—	7
054	10	−12	076	—	3	0,12,8	5	−4	0,6,11	—	0
064	10	−10	086	19	22	0,13,8	20	24	0,7,11	—	0
074	8	−11	096	14	10	0,14,8	—	3	0,8,11	—	6
084	12	−17	0,10,6	16	−18	0,15,8	—	−1	0,9,11	12	12
094	11	12	0,11,6	14	17	0,16,8	7	−8	0,10,11	—	2
0,10,4	4	−2	0,12,6	17	−21	0,17,8	16	−20	0,11,11	8	8
0,11,4	10	7	0,13,6	—	2	009	13	−12	0,12,11	—	−6
0,12,4	6	8	0,14,6	—	−4	019	15	−15	0,13,11	8	−4
0,13,4	22	−26	0,15,6	—	2	029	—	2	0,0,12	11	11
0,14,4	10	−13	0,16,6	—	3	039	—	−3	0,1,12	7	8
0,15,4	12	−11	0,17,6	13	12	049	24	26	0,2,12	7	−7
0,16,4	9	−9	0,18,6	8	−8	059	7	8	0,3,12	5	5
0,17,4	—	0	0,19,6	—	2	069	8	10	0,4,12	10	−10
0,18,4	—	−1	007	18	14	079	5	6	0,5,12	—	−3
0,19,4	—	−5	017	15	−12	089	16	−18	0,6,12	—	8
0,20,4	—	−2	027	—	3	099	7	11	0,7,12	—	3
005	53	50	037	5	5	0,10,9	5	−1	0,8,12	11	14
015	60	60	047	30	−31	0,11,9	5	6	0,9,12	7	8
025	4	−3	057	26	23	0,12,9	12	15	0,10,12	—	1
035	40	40	067	12	−16	0,13,9	8	7	0,0,13	16	18
045	28	−30	077	18	16	0,14,9	—	0	0,1,13	—	5
055	38	−38	087	9	8	0,15,9	—	0	0,2,13	—	2
065	41	44	097	—	−2	0,16,9	11	−11	0,3,13	—	−5
075	4	−5	0,10,7	9	−10	0,0,10	7	8	0,4,13	9	−9
085	7	12	0,11,7	4	−6	0,1,10	10	10	0,5,13	—	−6
095	38	38	0,12,7	18	−20	0,2,10	7	7	0,6,13	—	3
0,10,5	21	−28	0,13,7	16	16	0,3,10	10	13	0,7,13	—	9
0,11,5	9	7	0,14,7	11	−13	0,4,10	20	19			

three from water molecules and five from polyions within one column. This coordination is shown in Fig. 3 as it appears on $p_y(x, z)$. Two cleavages have been observed, one (Schaller, 1916) parallel to (001), the other (Bokiĭ, 1937) parallel to (010). Cleavage is easily produced in both directions, but the cleavage planes are not perfect. They lie between the columns and the bonds they break can be seen on Fig. 5, which shows the structure viewed along [100]. The (001) cleavage breaks only three hydrogen bonds, while the (010) cleavage breaks two hydrogen bonds and one Ca–H_2O bond.

The $[B_3O_3(OH)_5]^{-2}$ polyion is formed by two BO_4 tetrahedra sharing a corner and linked by a BO_3 triangle, which has one corner in common with each of the two tetrahedra. It was found first in meyerhofferite (Christ & Clark, 1956) and later in synthetic $2\,CaO.3\,B_2O_3.9\,H_2O$ (Clark & Christ, 1957). All the members of the series are listed in Table 4, together with their chemical formulas as determined from the crystal structures. Existence of the $[B_3O_3(OH)_5]^{-2}$ polyion was postulated from chemical evidence alone by Ingri, Lagerström, Frydman & Sillén (1957). The infinite boron–oxygen chains of colemanite may formally be derived from the isolated polyions by the condensation and dehydration reaction (Christ, Clark & Evans, 1958),

$$n[B_3O_3(OH)_5]^{-2} = [B_3O_4(OH)_3]_n^{-2n} + nH_2O\ .$$

The close structural relationship among the members of the series explains the occurrence in nature of colemanite and meyerhofferite pseudomorphs after inyoite (Palache, Berman & Frondel, 1951).

Table 4. *Series*, $2\,CaO.3\,B_2O_3.xH_2O$

x	Mineral	Formula
5	Colemanite	$CaB_3O_4(OH)_3.H_2O$
7	Meyerhofferite	$CaB_3O_3(OH)_5.H_2O$
9	(Synthetic)	$CaB_3O_3(OH)_5.2\,H_2O$
13	Inyoite	$CaB_3O_3(OH)_5.4\,H_2O$

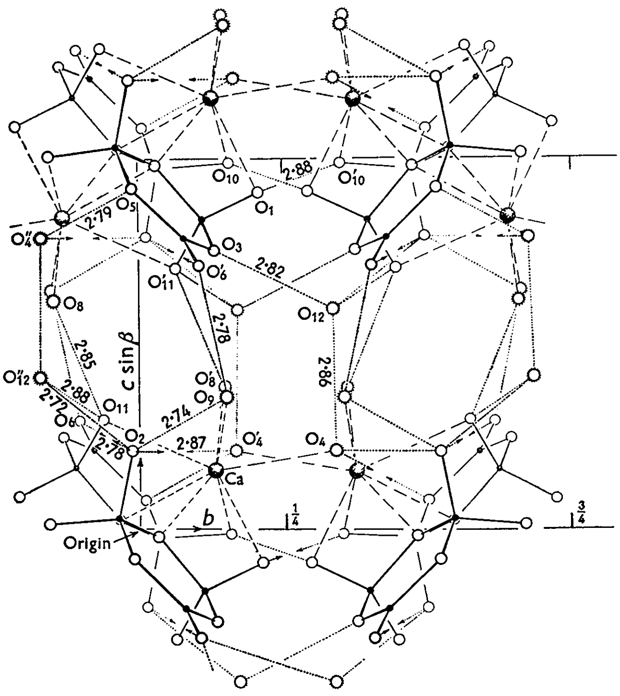

Fig. 5. View of the structure along [100] showing several columns and the inter-columnar bonds broken by the (001) and (010) cleavages. Dashed lines indicate Ca–O bonds; dotted lines represent hydrogen bonds (Table 9). Polyions are shown with solid lines.

Table 5. *Boron–oxygen bond lengths and bond angles for inyoite*

(See Fig. 2)

B–O bonds		Bond angles	
Triangle around B_3			
B_3–O_5	1·46 Å	O_5–B_3–O_6	117·5°
B_3–O_6^*	1·33	O_6–B_3–O_3	123·0
B_3–O_3	1·34	O_5–B_3–O_3	119·5
Average = 1·38 Å		Σ = 360·0°	
Tetrahedron around B_1			
B_1–O_1^*	1·46 Å	O_1–B_1–O_7	105·0°
B_1–O_7	1·47	O_1–B_1–O_3	111·9
B_1–O_3	1·52	O_1–B_1–O_{11}	112·6
B_1–O_{11}^*	1·43	O_7–B_1–O_3	108·3
Average = 1·47 Å		O_7–B_1–O_{11}	111·5
		O_3–B_1–O_{11}	107·5
		Average =	109·5°
Tetrahedron around B_2			
B_2–O_5	1·38 Å	O_5–B_2–O_2	110·0°
B_2–O_2^*	1·51	O_5–B_2–O_7	114·5
B_2–O_7	1·49	O_5–B_2–O_{10}	113·0
B_2–O_{10}^*	1·51	O_2–B_2–O_7	109·0
Average = 1·47 Å		O_2–B_2–O_{10}	106·6
		O_7–B_2–O_{10}	103·4
		Average =	109·4°

* Hydroxyl oxygens.

Bond lengths and angles as found for inyoite within the polyion are given in Tables 5 and 6, and the average values for boron–oxygen distances are compared in Table 7 with corresponding average values for some other borates. Individual variations within either tetrahedra or triangle of inyoite are not considered significant at present, but there is ample evidence from several borate structure determinations that a real difference exists between the B–O distance for tetrahedrally-coordinated boron and for triangularly-coordinated boron. This point has previously been discussed in detail (Christ, Clark & Evans, 1958).

Calcium–oxygen distances and some O–Ca–O angles

Table 6. *Oxygen–oxygen distances for inyoite within the* $[B_3O_3(OH)_5]^{-2}$ *polyion*

(See Fig. 2)

Triangle around B_3		Tetrahedron around B_1		Tetrahedron around B_2	
O_5–O_6^*	2·39 Å	O_7–O_3	2·43 Å	O_7–O_5	2·41 Å
O_3–O_6^*	2·35	O_7–O_1^*	2·32	O_7–O_2^*	2·44
O_3–O_5	2·42	O_7–O_{11}^*	2·40	O_7–O_{10}^*	2·38
Average = 2·39 Å		O_3–O_1^*	2·48	O_5–O_{10}^*	2·41
		O_3–O_{11}^*	2·38	O_5–O_2^*	2·37
		O_1^*–O_{11}^*	2·41	O_2^*–O_{10}^*	2·42
		Average = 2·40 Å		Average = 2·40 Å	

* Hydroxyl oxygen.

Table 7. *Comparison of average* B–O *bond lengths for inyoite and other borates*

Compound	Average B–O distance: Triangle	Average B–O distance: Tetrahedra	Reference
Colemanite	1·37 Å	1·48 Å	Christ, Clark & Evans, 1958
Meyerhofferite	1·38	1·49	Christ & Clark, 1956
$2\,CaO.3\,B_2O_3.9\,H_2O$	1·37	1·47	Clark & Christ, 1957
Borax	1·36	1·48	Morimoto, 1956
Metaboric acid	1·36	1·46	Zachariasen, 1952
Inyoite	1·38	1·47	Present study

Table 8. *Calcium–oxygen bond lengths and angles for inyoite*

(See Fig. 3)

Ca–O bonds		O–Ca–O angles	
Ca–O_1^*	2·38 Å	O_1–Ca–O_9	95·8°
Ca–O_{10}^*	2·40	O_9–Ca–O_8	94·0
Ca–O'_8†	2·37	O_8–Ca–O_{10}	81·0
Ca–O_9†	2·44	O_1–Ca–O_{10}	89·1
Average of 4 = 2·40 Å		Σ = 359·9°	
Ca–O_7	2·59 Å		
Ca–O'_7	2·54		
Ca–O_{11}^*	2·51		
Ca–O_4†	2·51		
Average of 4 = 2·54 Å			
Average of 8 = 2·47 Å			

* Hydroxyl oxygen. † Water oxygen.

are given in Table 8. Four of the eight oxygens coordinating calcium are contained with calcium in a plane nearly parallel to (010) and are arranged in an almost square array about calcium at an average distance of 2·40 Å. The other four coordinating oxygens are located irregularly about calcium at an average 2·54 Å distance. The closest Ca–Ca approach is 4·0 Å.

Hydrogen bonds have been identified on the basis of length, distances of 2·7 to 2·9 Å being considered indicative when at least one of the oxygens involved had been identified as belonging to hydroxyl ion or water molecule. Consideration of these bonds permits a tentative count of hydrogens and identification of their associated oxygens. The bond distances and contributor oxygens are given in Table 9, while the various bonds have been illustrated in Figs. 4 and 5. Of the thirteen hydrogens in each formula unit, only two presumably do not enter into hydrogen bonds. One of these two is associated with O_8 in a water molecule (although this one may be participating in a long bond listed in Table 9), while the other is associated with either O_1 or O_{10} in hydroxyl ion. No evidence was found for any disordering of hydrogens such as was discovered in colemanite (Christ, Clark & Evans, 1958), but the possibility cannot yet be entirely eliminated. The further refinement of the structure should resolve this question.

Table 9. *Oxygen–oxygen distances for postulated hydrogen bonds in inyoite*

(See Figs. 4 and 5)

O–O distance		Contributor oxygen
$O_2{}^*$–$O'_4{}^\dagger$	2·87 Å	$O'_4{}^\dagger$
O_5–$O''_4{}^\dagger$	2·79	$O''_4{}^\dagger$
$O_{11}{}^*$–$O_8{}^\dagger$	2·85	$O_8{}^\dagger$
$O_2{}^*$–$O_9{}^\dagger$	2·74	$O_9{}^\dagger$
$O'_6{}^*$–$O_9{}^*$	2·78	$O_9{}^\dagger$
O_3–$O_{12}{}^\dagger$	2·82	$O_{12}{}^\dagger$
$O_4{}^\dagger$–$O_{12}{}^\dagger$	2·86	$O_{12}{}^\dagger$
$O_2{}^*$–$O''_{12}{}^\dagger$	2·72	$O_2{}^*$
$O_{11}{}^*$–$O''_{12}{}^\dagger$	2·88	$O_{11}{}^*$
$O_6{}^*$–$O_2{}^*$	2·78	$O_6{}^*$
$O'_{10}{}^*$–$O_1{}^*$	2·88	either
($O'_{11}{}^*$–$O_8{}^\dagger$	2·97	$O_8{}^\dagger$)

* Hydroxyl oxygen. † Water oxygen.

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