

DETERMINATION OF THE CRYSTAL STRUCTURE OF PROBERTITE $\text{CaNa}[\text{B}_5\text{O}_7(\text{OH})_4] \cdot 3\text{H}_2\text{O}$

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The hydrated (Ca, Na)-borate known as probertite, $\text{CaNaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$, crystallizes in the monoclinic system. The lattice parameters are $a = 13.38 \pm 0.03$, $b = 12.54 \pm 0.03$, $c = 6.59 \pm 0.02$ Å, and $\beta = 100^\circ 15'$; the Fedorov group $\text{C}_{2h}^5 = \text{P}2_1/a$, $Z = 4$. The motif of the structure was found by statistically determining the signs of the structure factors. The coordinates of the atoms were refined by a sequence of phase, ordinary, and weighted zonal projections of electron density. Probertite contains a new type of borate chains $[\text{B}_5\text{O}_7(\text{OH})_4]_n^{-3n}$; an individual link of the chain is made up of three borate tetrahedra and two triangles connected by common O vertices. The Ca cations are disposed inside oxygen nonahedra and the Na in severely-deformed octahedra. The Ca and Na polyhedra are connected by common edges into discrete groups of two Ca and two Na polyhedra. These cation quartets are linked into a single structure by borate chains and also hydrogen bonds.

First mention of probertite, a colorless borate of Ca and Na discovered in California, was made in 1929 [1]. In 1949, the unit-cell parameters and space group of the mineral were published: $a = 13.88$, $b = 12.56$, $c = 6.609$ Å, $\beta = 107^\circ 40'$, and $\text{C}_{2h}^5 = \text{P}2_1/n$ [2]. For the chemical formula $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ and density $d = 2.141$ g/cm³ [3], the number of units per cell is $Z = 4$. Clark and Christ carefully repeated the parameter determination and gave the results in a different form: $a' = 13.43 \pm 0.04$, $b = 12.57 \pm 0.04$, $c = 6.589 \pm 0.02$ Å, $\beta = 100^\circ 15' \pm 5'$, $d_{\text{calc}} = 2.134$ g/cm³ [4] (according to [2] $d_{\text{calc}} = 2.126$ g/cm³), and $\text{C}_{2h}^5 = \text{P}2_1/a$. A preliminary communication regarding the structure of probertite was published in 1963 by ourselves [5].

For examination we took fine crystals from the Widow Mine, Ryan District, Inyo County (California) kept in the Mineralogical Museum of the Academy of Sciences of the USSR. The parameters of the monoclinic cell of probertite, determined by the RKV camera in Cu K α radiation, $a = 13.38 \pm 0.03$, $b = 12.54 \pm 0.03$, $c = 6.59 \pm 0.02$ Å, $\beta = 100^\circ 15'$, and $d_{\text{calc}} = 2.144$ g/cm³, agreed with the earlier results [2, 4]. Layer lines of order 0, 1, 2, and 3 were obtained in the Weissenberg x-ray

goniometer (Mo K α radiation) for rotation around the c axis, as well as those for $0kL$, $1kL$, $2kL$, and $h0L$. Reflections at low angles φ were obtained in Ni radiation. The intensities of the reflections were estimated visually on a blackening scale with a $\sqrt{2}$ step taken from x-ray photographs with multiple exposures. Absorption and extinctions were not considered. In all we fixed over two thousand nonzero reflections: 175 F_{hk0} , 441 F_{hk1} , 453 F_{hk2} , 483 F_{hk3} , 85 F_{0kL} , 170 F_{1kL} , 170 F_{2kL} , and 136 F_{h0L} , with maximum $\sin \varphi/\lambda$ between 0.8 and 0.9₅ Å⁻¹. From analysis of the extinctions the Fedorov group was determined unequivocally as $\text{C}_{2h}^5 = \text{P}2_1/a$.

In the independent quarter of the probertite cell, in the absence of a heavy atom, one medium-weight cation (Ca) is associated with 20 light atoms: 1 Na, 14 O, and 5 B (not counting H). Hence, the structure may be interpreted by the direct determination of F_{hkL} signs [6-9]; this has proved especially effective in determining the structures of more complex borates [9-13]. The signs were found in two stages: first, the signs of the "key" reflections were established by the comparison method [6, 7], and then, the statistical relation of Sayre and Zachariasen [8, 9] was used to determine

the rest of the signs from the key group. According to [6], for monoclinic crystals with a special b direction the sign-comparison method is most effective for reflections obtained from rotation photographs taken around the c (or a) axis when the indices of the comparison pair, $aS_{h_A}S_{k_A}l$ and $S_{h_B}k_B l$

are related by $h_A = h_B$, $|k_A| \neq |k_B|$ (and correspondingly for comparing $S_{h_A}k_A l$ and $S_{h_B}k_B l$ by relations $|k_A| \neq |k_B|$, $l_A = l_B$). As regards the $h0l$ reflections (and equally other sets of $F_{hk}l$ obtained from rotation photographs around b), the signs of these cannot be compared with one another, but only with reflections belonging to other b layer lines which are analogous to the former in respect of h and l.

It was therefore natural to begin the sign determination with rotation photographs based on the short axis c (these containing the largest number of reflections) and first of all with the $hk0$ and $hk1$. Some 30% of the $hk0$ and $hk1$ reflections with the largest unitary amplitudes $|U|$ were taken into the key group. In order to increase the number of determining pairs [6], some 30% of the $hk2$ and $hk3$ reflections were taken in, and altogether 533 $S_{hk}l$ were used. The comparison S_{hk0} and equally the S_{hk1} were chosen in accordance with the conditions mentioned earlier, the determining products for S_{hk0} having the form $S_{h_1k_1}l \cdot S_{h_2k_2}l$ and for S_{hk1} the form $S_{h_1k_1}l \cdot S_{h_2k_2}l_{+1}$.

Since the symmetry of the xy projection of the probertite structure is described by the pgg group, the indices h and k in the F_{hk0} formula are equally valid. Hence, in the particular case of comparing $S_{h_A}k_A0$ and $S_{h_B}k_B0$, when the determining products are $S_{h_1k_1}0 \cdot S_{h_2k_2}0$, we may also compare pairs with indices linked by the relations $|h_A| \neq |h_B|$, $|k_A| = |k_B|$; analogously, when comparing $S_{h_A}k_A1$ and $S_{h_B}k_B1$ by means of the products $S_{h_1k_1}0 \cdot S_{h_2k_2}1$, pairs for which $h_A \neq h_B$, $|k_A| = |k_B|$ are effective as well as those indicated.

As a result of using the comparison process, we were able to establish 67 relationships between the signs S_{hk0} and 279 between S_{hk1} . The comparison signs were regarded as identical or opposite if, when the number of determining pairs was ≤ 4 , the probability w that a fixed (\pm) sign should occur equalled unity ($w = 1$), or for $n > 4$ if $w \geq \frac{2}{3}$. By means of the 45 S_{hk0} and 95 S_{hk1} common to different pairs it was possible to link up 16 and 15 sign

chains, respectively. In each of these the signs were denoted by means of a letter. In order to establish connections between the 16 S_{hk0} chains, for each of the 45 S_{hk0} we wrote down the statistical equations [8, 9]

$$S_{hk0} = S(\overline{S_{h_1k_1,0} \cdot S_{h_2k_2,0}}), \quad (1')$$

which on careful analysis made it possible to connect individual letters (S_{hk0}) with the products of two others, and equally the products of different letters with each other. In all, the number of letters was reduced to two: $S_{h=2n+1, k=2m, 0 = \pm q}$, $S_{h=2n, k=2m+1, 0 = \pm r}$. After applying relation (1') to the key reflections which did not fall into the chains, it was possible to broaden the key group to 55 S_{hk0} . These two letters were then arbitrarily given plus signs, so fixing the origin of the cell projection in one of the four centers of symmetry. In order to reduce the number of S_{hk1} chains, we used the equation

$$S_{hk1} = S(\overline{S_{h_1k_1,0} \cdot S_{h_2k_2,1}}). \quad (1'')$$

Since 55 key signs S_{hk0} were already known, it was possible, by choosing the frequently-recurring relationships between individual letters S_{hk1} and $S_{h+h_1, k+k_1, 1}$, to reduce all the surviving letters to one. Assigning the latter a minus sign, we finally fixed the origin of coordinates in one of two remaining possible centers of symmetry, $c/2$ apart. The key group of signs from the 95 S_{hk1} was also broadened by means of relation (1'') to 132 S_{hk1} . The signs of the remaining reflections were found from (1') and (1'') on the basis of the key S_{hk0} and S_{hk1} . In all, 121 S_{hk0} and 350 S_{hk1} were determined. The 121 F_{hk0} and 350 F_{hk1} provided by the statistical signs were used to construct electron-density projections $\sigma(x, y)$ and a pair of conjugate weighted projections $C_1(x, y) = \int_0^1 \rho(x, y, z) \cos 2\pi z dz$ and $S_1(x, y) = \int_0^1 \rho(x, y, z) \sin 2\pi z dz$ (Fig. 1a). In analyzing the pictures obtained, peaks (or depression) on these with similar (x, y) coordinates and with the greatest moduli were compared; the z coordinates of the peaks were approximately determined from the formula

$$\frac{2\pi z_n}{c} = \arctan \frac{S_1(x_n, y_n)}{C_1(x_n, y_n)}.$$

If a peak with a large modulus was present on only one of the projections or contradicted the steric

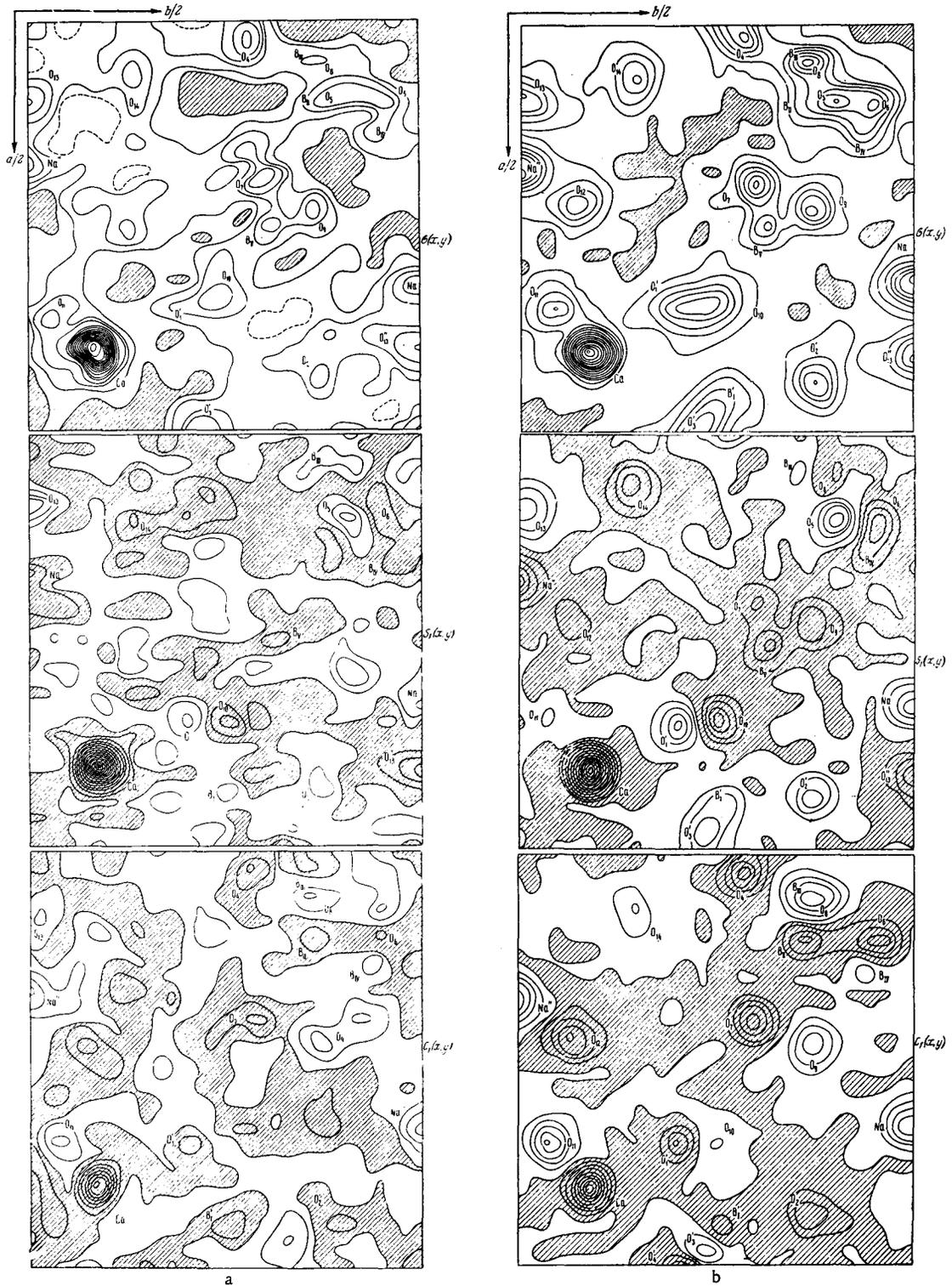


Fig. 1. Electron-density projections of probertite on the xy plane: a) Syntheses calculated from F_{hk0} and F_{hkl} with statistical signs; b) final syntheses. The lines of equal density are drawn every 3 electrons/ \AA^2 , the regions of negative sign are shaded, and depressions are shown by broken lines. A single prime indicates atoms connected with the basal glide plane; two primes indicate a screw axis.

laws, it was rejected as false. This analysis enabled us to establish the positions of most atoms in the structure, except for the two oxygens not belonging to the borate radical. From the fixed x, y coordinates of the 19 basic atoms we calculated a further Fourier synthesis $\sigma(x, y)$; on this the maximum of the established atoms stood out far more clearly, the false peaks receded, and there were also two new maxima identifiable with the two missing oxygen atoms (O_{12} and O_{14}). Owing to the considerable overlapping of the groups (O_3, B_1 and $O_4, B_{III}, O_8, B_{II}, O_5, O_6$ and B_{IV}, O_1 and O_{10}) in the xy projection, the xy coordinates of the atoms, and more particularly the z , must be regarded as very approximate. For determining the latter, the $\sigma(y, z)$, $C_1(y, z)$, and $S_1(y, z)$ syntheses were especially important. The signs S_{0kl} and S_{1kl} required for their construction were determined statistically. For this purpose a key group S_{hk0} was set up, the signs for this being calculated from the xy coordinates already found. By means of the new "fundamental" key group, using statistical Eq. (1"), we again created an S_{hk1} key group, somewhat altered as a result of the addition, elimination, and also alteration of certain S_{hk1} . Starting from the new key S_{hk0} and S_{hk1} , we determined the key signs S_{hk2} and S_{hk3} . From the whole set of key S_{hk0} to S_{hk3} we analyzed the signs of reflections $0k0 - 0k6, 1k0 - 1k6$, and then from the key S_{0k0} to S_{0k6} and

S_{1k0} to S_{1k6} respectively found the remaining signs in the S_{0kl} and S_{1kl} sets. In this way we were able in all to determine 67 S_{0kl} and 127 S_{1kl} , and these signs were used to calculate the Fourier projection $\sigma(y, z)$ and pair of conjugate weighted electron-density projections $C_1(y, z)$ and $S_1(y, z)$. Peaks confirming the earlier-found structural motif were seen clearly on these syntheses. The coordinates of the atoms were then refined by a cycle of $\sigma(x, y)$, $\sigma(y, z)$, $C_1(x, y)$, $S_1(x, y)$, $C_1(y, z)$, and $S_1(y, z)$ syntheses.

We notice that on the syntheses constructed from the statistical signs the Ca peaks appeared rather large while the oxygen atoms were far too weak. This is due partly to waves of errors arising from the absence of 20 to 30% of the reflections from the synthesis (the signs of these not being determined), and partly from errors in the S_{hk0} and S_{hk1} found. In fact, after checking at the end of the investigation, it was found that 10 S_{hk0} out of 121 and 37 S_{hk1} out of 350 were wrong, of which 9 S_{hk0} and 32 S_{hk1} coincided with the contributions of the Ca atoms to the corresponding F_{hk0} and F_{hk1} . Of the total number of nonzero F_{hk0} and F_{hk1} , however,

the signs of the Ca contributions coincided with the signs of $\sim 83\%$ of the structure factors. In the majority of cases where the contribution of the Ca to F_{hk0} was considerable, the sign of the F_{hk0} was fixed statistically almost without contradiction from a large number of determining pairs. For small Ca contributions, the probability of determination (and correspondingly the number of determining pairs) fell substantially; this indicates the strong influence of the Ca cation on the course of the statistical determination of signs.

Finally, we once more calculated the signs of $F_{hk0} - F_{hk3}$, $F_{0kl} - F_{2kl}$, F_{h0l} , and from these constructed ordinary and weighted Fourier projections $\sigma(y, z)$, $\sigma(z, x)$, $\sigma(x, y)$, $C_l(x, y)$, $S_l(x, y)$ for $l = 1, 2, 3$ (see Fig. 1b) and $C_h(y, z)$, $S_h(y, z)$ for $h = 1, 2$. The coordinates of the atoms were refined by means of ordinary and "phase" projections [15]; the latter were made up from the synthesized weighted projections. The coordinates of the non-overlapping atoms were refined from the ordinary and phase projections $C_l(x, y, Z_j)$ or $C_h(X_j, y, z)$; the coordinates of overlapping atoms were determined from phase projections $S_l(x, y, Z_j)$ and $S_h(X_j, y, z)$. For cases where the phase projections proved ineffective,¹ several zonal weighted projections were combined [16].

Thus, in the xy projection the O'_1 and O_{10} atoms, for which the difference $zO'_1/c - zO_{10}/c = 0.463$, i.e., ~ 0.5 , overlap. In order to refine the (x, y) coordinates of O'_1 we set up a $S_{2/3}^{[0, 3c/4]}(x, y)$ projection, which most clearly distinguished the atom situated in the center of the interval $[0, 3c/4]$ but not fixing atoms with z coordinates outside this interval [16]. The O'_1 atom with $z/c = 0.332$ appeared sharply on the projection, while the O_{10} with $z/c = 0.794$ was absent. In order to locate O_{10} we set up the function

$$C_{2/3}^{[3c/8, 9c/8]}(x, y) = \int_{3c/8}^{9c/8} \rho(x, y, z) \cos \frac{4\pi z}{3c} dz \\ = \frac{1.7}{\pi} \left[-\frac{\sigma(x, y)}{1.13} + S_1(x, y) + \frac{S_3(x, y)}{15.4} - \frac{C_4(x, y)}{19.8} + \dots \right],$$

on which an atom with $z/c = 3/4$ should be most clearly discernible. Since the value of zO_{10} was close to $3c/4$, the O_{10} atom was well "formed" on this projection, while the O'_1 did not fall within the projection interval ($zO'_1 \leq 3c/8$). In setting up

¹For the overlapping of a pair of atoms for which the difference $z_1/c - z_2/c \sim 0.5$, and also for the overlapping of more than two atoms [16].

$C_{2/3}^{[3c/8, 9c/8]}(x, y)$ we limited ourselves to the set F_{hk0} and F_{hk1} .

In the same xy projection the O_3 atom overlaps B_1 and O_4 , lying between these. In order to find the (x, y) coordinates we synthesized the function

$$C_{3/4}^{[-c/3, c/3]}(x, y) = \int_{-c/3}^{c/3} \rho(x, y, z) \cos \frac{3\pi z}{2c} dz$$

$$= \frac{1.715}{\pi} \left[\frac{\sigma(x, y)}{1.29} + C_1(x, y) + \frac{C_2(x, y)}{7.86} - \frac{C_3(x, y)}{9.65} \right.$$

$$\left. + \frac{C_4(x, y)}{35.3} + \dots + \frac{14 \cos \frac{2\pi l}{3}}{9 - 16l^2} C_l(x, y) + \dots \right],$$

compiling this from the F_{hk0} to F_{hk3} sets. Figure 2 shows part of the $C_{3/4}^{[-c/3, c/3]}(x, y)$ synthesis containing the O_3' together with the corresponding part of the $\sigma(x, y)$ for comparison. We see that the $B_1'(z/c = 0.340)$ and $O_4'(z/c = 0.513)$ atoms are in fact absent from the zonal projection.

In the yz projection the atoms Na' , O_{11} , and O_{13} overlap. In order to refine the z coordinates of the Na and O_{11} we made use of the zonal projections $C_{2/3}^{[3a/8, 9a/8]}(y, z)$, $S_1^{[a/2, a]}(y, z)$ and $S_{2/3}^{[0, 3a/4]}(y, z)$ [16], in whose construction only the F_{hk0} to F_{hk2} were required.

The coordinates of the basic atoms in the probertite structure, as determined from the various syntheses and averaged over the whole set of results, are set out in Table 1 together with the average arithmetical errors. In cases where the coordinates were determined from no more than two syntheses, the limits of accuracy are not given. All the atoms occupy general four-fold positions, and for the 21 basic atoms the centrosymmetric structure is characterized by 63 parameters.

From the coordinates finally accepted we estimated the divergence factors, calculated from all

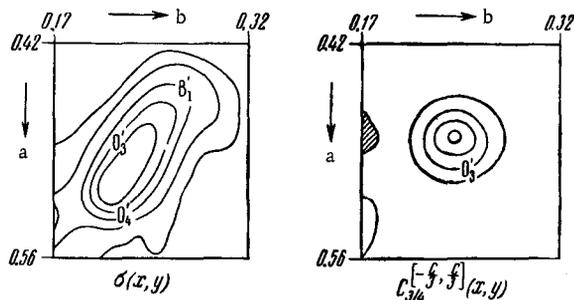


Fig. 2. Comparison between identical regions of the electron-density projection $\sigma(x, y)$ and the zonal weighted projection $C_{3/4}^{[-c/3, c/3]}(x, y)$. Contour lines every 3 electrons/ \AA^2 .

TABLE 1. Coordinates of the Basic Atoms in the Probertite Structure

Atoms	x/a	y/b	z/c
Ca	0.405 ± 0.0005	0.0885 ± 0.0005	0.654
Na	0.324 ± 0.001	0.494 ± 0.001	0.122 ± 0.001
O_1^*	-0.150 ± 0.001	0.295 ± 0.001	0.332 ± 0.001
O_2^*	-0.061 ± 0.001	0.125 ± 0.001	0.357
O_3	-0.015	0.262	0.142 ± 0.001
O_4	0.018	0.286 ± 0.001	0.513 ± 0.001
O_5	0.098	0.401 ± 0.001	0.287
O_6	0.100 ± 0.002	0.456 ± 0.001	0.629 ± 0.002
O_7	0.198 ± 0.001	0.297 ± 0.001	0.560 ± 0.003
O_8	0.048 ± 0.001	0.380 ± 0.001	0.923 ± 0.003
O_9	0.227 ± 0.001	0.375 ± 0.001	0.895 ± 0.002
O_{10}^*	0.342 ± 0.001	0.248	0.794 ± 0.002
O_{11}^*	0.348 ± 0.001	0.041 ± 0.001	0.040 ± 0.002
O_{12}^{**}	0.223 ± 0.001	0.071 ± 0.001	0.560 ± 0.004
O_{13}^{**}	0.091 ± 0.001	0.007 ± 0.001	0.22
O_{14}^{**}	0.063 ± 0.001	0.143 ± 0.001	0.822 ± 0.003
B_I	-0.051 ± 0.001	0.242 ± 0.001	0.340
B_{II}	0.103 ± 0.001	0.356 ± 0.002	0.506 ± 0.002
B_{III}	0.046	0.352 ± 0.004	0.120 ± 0.004
B_{IV}	0.136 ± 0.001	0.439 ± 0.001	0.856 ± 0.002
B_V	0.252 ± 0.001	0.311 ± 0.001	0.756 ± 0.001

O^* = O atom in OH group.

O^{**} = O atom in H_2O molecule.

the nonzero reflections, allowing for isotropic temperature corrections: $R_{hk0} = 12.8\%$, $R_{hk1} = 12.5\%$, $R_{hk2} = 13.7\%$, $R_{0kl} = 12.4\%$, $R_{1kl} = 11.1\%$, and $R_{2kl} = 11.5\%$. Table 2 compares the experimental and calculated values of F_{hk0} for the probertite structure.

Figures 3a and b show the structure of probertite and its detail in the yz projection. The most typical feature of the structure is the set of infinite $[B_5O_7(OH)_4]_n^{-3n}$ chains drawn out along the short axis ($c = 6.59$), the recurrent link in which consists of three B tetrahedra and two B triangles, interconnected by common vertices. In the link $[B_5O_8(OH)_4]^{-5}$ the two b triangles are connected by their vertices to the b tetrahedra but not connected with each other. This kind of chain was found for the first time in probertite. The $[B_5O_8(OH)_4]^{-5}$ radical on two-way condensation loses one O^{2-} , transforming into a chain "increment" $[B_5O_7(OH)_4]^{-3}$, which also figures in the formula of probertite. The negative valence of -3 balances the divalent Ca and monovalent Na. The former are disposed inside complex nonahedra (Fig. 4a) six vertices of which are formed by five triangular faces and three by four. The Na cations lie inside hexahedra which may be considered as distorted octahedra (Fig. 4b). The Na and Ca polyhedra are connected by common edges into discrete groups of two Na and two Ca polyhedra, the Na and Ca polyhedra having a common edge which links the hydroxyl group OH (O_{11})

TABLE 2. Experimental and Calculated Structure Factors F_{hk0} . The F_{calc} Contain Temperature Correction $\exp[-1.2 A^2 (\sin \theta/\lambda)^2]$. $R_{hk0} = 12.8\%$ from $F_{\text{exp}} \neq 0 (\sin \theta/\lambda \leq 0.82 \text{ \AA}^{-1})$

$h \backslash k$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0	+712		25.4 +14.7	<4.3 +1.2		60.1 -54.7		40.5 +51.0		24.3 +25.8		<8.8 +7.5		17.5 +20.5		<10.6 +7.9		19.3 -16.3		16.3 +17.6	
1		74.0 -97.6	28.4 +33.1	62.5 +65.6	53.6 -51.8	43.7 +41.1	27.2 -26.5	89.1 +102	14.9 +17.7	<7.3 -5.8	29.4 +32.8	<8.3 +3.9	<8.8 +9.0	<9.3 +4.6	22.4 -21.8	17.0 +20.0	<10.6 -5.6	19.9 +23.6	<11.5 +7.5	<11.9 -2.8	<12.4 +7.4
2	51.2 +61.7	21.0 +13.2	42.3 -39.9	47.6 -44.7	37.7 -41.3	59.1 +60.4	33.2 -31.1	32.7 -33.6	36.6 -40.4	20.5 -19.5	14.5 -15.8	<8.3 -3.8	<8.8 +4.1	31.1 +33.8	<9.7 -2.2	<10.1 +6.1	15.4 -17.5	<11.1 -7.6	<11.5 -2.5	<11.9 -10.8	<12.4 +1.2
3		31.4 +24.4	<4.2 -2.5	42.6 -41.9	33.1 +25.3	26.4 -29.0	13.6 -10.3	29.5 -35.0	22.2 +23.3	24.8 +27.6	20.3 +15.8	12.7 -17.5	22.4 -22.1	23.6 -26.5	19.9 -21.1	<10.2 -3.1	21.1 -20.8	<11.2 -15.7	<11.6 +3.2	<12.0 -1.0	<16.9 +12.8
4	74.1 -69.9	17.8 -10.8	108 -102	16.5 +9.7	<5.4 -11.2	11.5 +13.6	18.1 +13.1	32.3 -38.6	11.8 +10.0	43.8 -52.0	<8.1 -12.9	<8.6 -12.9	19.1 -21.7	<9.5 +4.4	<10.0 +3.3	<10.4 -0.8	15.9 +17.2	<11.2 +6.8	<11.7 +5.7		
5		83.4 +79.6	64.1 +53.6	61.4 +55.0	36.3 +39.1	80.5 -81.4	<6.6 -5.6	28.0 -26.2	<7.4 -8.5	18.1 -21.7	31.4 +34.3	37.4 +40.6	12.3 -10.7	14.4 +17.1	20.4 -24.3	13.9 -14.0	<10.8 -9.8	13.3 -14.2	<11.8 -2.5		
6	61.4 -49.5	70.8 -59.8	77.8 -69.3	23.5 -22.0	126 +130	17.6 +15.9	28.2 +24.1	<7.2 +4.5	<7.6 +4.6	23.3 +24.0	12.4 -10.5	11.9 -12.5	10.7 -12.3	<9.8 +14.9	<10.1 +0.4	15.9 -14.4	<10.1 +9.7	<11.4 -1.9	13.9 +12.5		
7		23.8 -20.7	21.4 +23.1	8.9 -6.3	<6.6 +12.9	44.2 -43.8	<7.2 -6.0	<7.6 +9.5	32.0 -32.1	<8.3 +7.6	<8.7 -4.5	25.1 +27.5	<9.6 +10.4	<10.0 -7.0	23.0 +19.7	<10.8 -9.2	16.5 +20.9	<11.6 -10.1			
8	29.0 -25.7	43.7 +40.2	15.9 -12.9	23.3 -21.3	— +13.7	31.4 +36.7	30.1 -31.9	18.7 +18.2	38.4 -42.7	38.7 +45.2	<9.0 -7.0	<9.4 +5.7	<9.8 -2.4	13.7 -6.0	<10.5 -10.0	24.6 -20.5	<11.3 -7.6				
9		53.6 -48.8	21.2 +19.4	14.6 +13.2	17.0 +15.3	16.5 +14.8	21.1 -23.3	<8.2 -11.7	17.4 -14.2	23.4 -26.7	19.6 -21.3	<9.6 -4.2	<10.0 -0.3	<10.4 -12.7	14.5 +11.8	<11.1 +4.8	<11.5 +10.2				
10	21.8 +13.0	28.8 -23.5	39.7 +36.4	35.6 -31.6	<7.9 -1.0	<8.1 -11.8	28.1 -23.9	<8.6 +8.7	16.5 -17.2	<9.3 +6.3	28.4 +34.3	<9.9 -2.9	22.2 +26.1	<10.6 +5.1	<11.0 +9.0	<11.4 -3.0	21.1 -23.9				

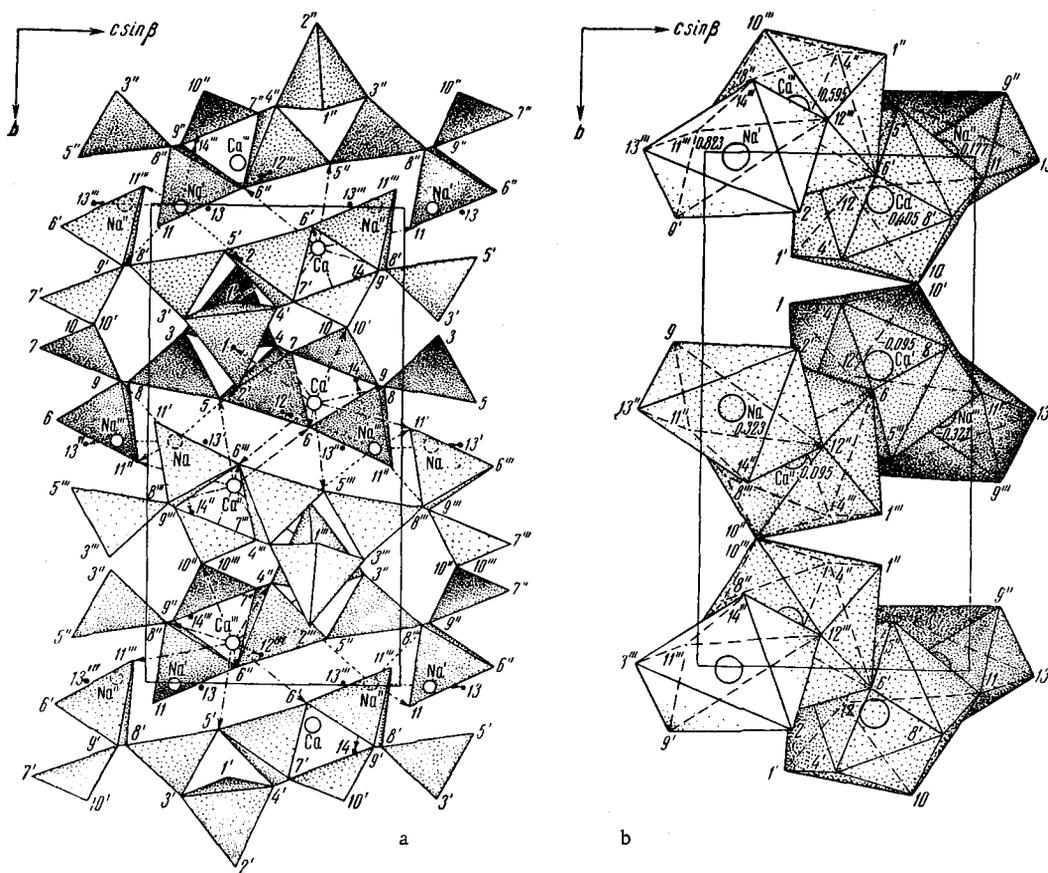


Fig. 3. Projection of the structure of probertite in polyhedra along the a axis: a) Full structure; figures indicate O atoms, Na - O bonds shown by dashed and Ca - O by dot-dashed lines; b) groups of Ca and Na polyhedra.

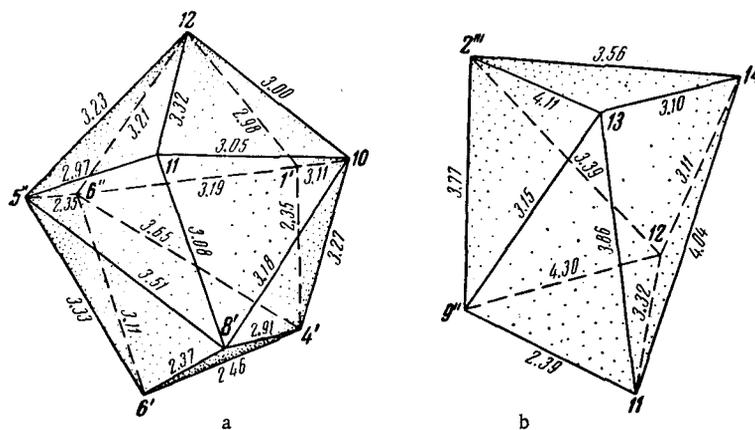


Fig. 4. Coordination polyhedra in the probertite structure: a) Around Ca atoms; b) around Na. Projection along c . Length of O - O edges given in Å.

with the water molecule (O_{12}). The Ca polyhedra in turn are connected with each other by a common edge $O_6^I - O_6^{II}$ formed by two centrosymmetrically connected oxygen atoms. These island quartets of cations are linked into a single structure by borate chains, each of which stretches (within the cell limits) between three (Na, Ca) island groups. Hy-

drogen bonds play an important part in merging the island groups and chains into a single unit. The chemical formula of probertite is thus written as $CaNa[B_5O_7(OH)_4] \cdot 3H_2O$, as predicted in [17], but not in [18].

The interatomic distance and bond angles in the probertite structure are given in Table 3. We

TABLE 3. Interatomic Distances (in Å) and Bond Angles in the Probertite Structure

B _I -Tetrahedron		B _{II} -Tetrahedron		B _{IV} -Tetrahedron	
B _I —O ₁ [*]	1.48	B _{II} —O ₄	1.44	B _{IV} —O ₆	1.50
B _I —O ₂	1.47	B _{II} —O ₆	1.54	B _{IV} —O ₈	1.52
B _I —O ₃	1.49	B _{II} —O ₆	1.50	B _{IV} —O ₉	1.44
B _I —O ₄	1.44	B _{II} —O ₇	1.46	B _{IV} —O ₁₁ ^{**}	1.45
Mean	1.47	Mean	1.48 ₆	Mean	1.48
O ₁ [*] —O ₂ [*]	2.44	O ₄ —O ₅	2.45	O ₆ —O ₈	2.37
O ₁ [*] —O ₃	2.41	O ₄ —O ₆	2.46	O ₆ —O ₉	2.43
O ₁ [*] —O ₄	2.34	O ₄ —O ₇	2.38	O ₆ —O ₁₁ ^{**}	2.42
O ₂ [*] —O ₃	2.37	O ₅ —O ₆	2.35	O ₈ —O ₉	2.43
O ₂ [*] —O ₄	2.42	O ₅ —O ₇	2.42	O ₈ —O ₁₁ ^{**}	2.44
O ₃ [*] —O ₄	2.42	O ₆ —O ₇	2.47	O ₉ —O ₁₁ ^{**}	2.39
Mean	2.40	Mean	2.42	Mean	2.41
O ₁ [*] —B _I —O ₂ [*]	111.5°	O ₄ —B _{II} —O ₅	110.5°	O ₆ —B _{IV} —O ₈	103.4°
O ₁ [*] —B _I —O ₃	108.5°	O ₄ —B _{II} —O ₆	113.6°	O ₆ —B _{IV} —O ₉	111.5°
O ₁ [*] —B _I —O ₄	106.6°	O ₄ —B _{II} —O ₇	110.3°	O ₆ —B _{IV} —O ₁₁ ^{**}	110.1°
O ₂ [*] —B _I —O ₃	106.4°	O ₅ —B _{II} —O ₆	101.3°	O ₈ —B _{IV} —O ₉	110.3°
O ₂ [*] —B _I —O ₄	112.5°	O ₅ —B _{II} —O ₇	107.6°	O ₈ —B _{IV} —O ₁₁ ^{**}	110.6°
O ₃ [*] —B _I —O ₄	111.3°	O ₆ —B _{II} —O ₇	113.1°	O ₉ —B _{IV} —O ₁₁ ^{**}	111.5°
Mean	109.5°	Mean	109.4°	Mean	109.6°
B _{III} -Triangle		B _V -Triangle		Ca-Polyhedron	
B _{III} —O ₃	1.42	B _V —O ₇	1.38	Ca—O ₅ [*]	2.38
B _{III} —O ₅	1.34	B _V —O ₉	1.32	Ca—O ₈ [*]	2.40
B _{III} —O ₈	1.35	B _V —O ₁₀ [*]	1.42	Ca—O ₁₀ [*]	2.42
Mean	1.37	Mean	1.37	Ca—O ₁₂ ^{**}	2.43
O ₃ —O ₅	2.39	O ₇ —O ₉	2.38	Ca—O ₄ [*]	2.48
O ₃ —O ₈	2.33	O ₇ —O ₁₀ [*]	2.33	Ca—O ₆ [*]	2.49
O ₅ —O ₈	2.39	O ₉ —O ₁₀ [*]	2.39	Ca—O ₁ [*]	2.58
Mean	2.37	Mean	2.37	Ca—O ₃ [*]	2.70
O ₃ —B _{III} —O ₅	125.2°	O ₇ —B _V —O ₉	124.0°	Ca—O ₁₁ [*]	2.84
O ₃ —B _{III} —O ₈	114.9°	O ₇ —B _V —O ₁₀ [*]	113.0°		
O ₅ —B _{III} —O ₈	120.3°	O ₉ —B _V —O ₁₀ [*]	122.3°		
Sum	360.4°	Sum	359.3°		
		Na-Octahedron			
Na—O ₉	2.34	Na—O ₁₁ ^{**}	2.43	Na—O ₁₂ ^{**}	2.49
Na—O ₁₄ ^{**}	2.39	Na—O ₂ [*]	2.48	Na—O ₁₃ ^{**}	2.72

O* = atom of OH group.

O** = atom of H₂O molecule

see from the table that in the borate tetrahedra the mean B—O distance lies between 1.47 and 1.48 Å for edges 2.40 to 2.42 Å and bond angles O—B—O 109.4° to 109.6°. In the B triangles the mean distance B—O = 1.37 Å for mean edge lengths O—O = 2.37 Å, which corresponds to the distance found in other borates (see, for example, [8-12]). In the B triangles the three "valence" angles O—B—O around the B_{III} and B_V atoms add up to 360.4° and 359.3° respectively, which, within the limits of error, locates the boron atoms in the plane of the oxygen triangles.

In the Ca nonahedron, six of the Ca—O distances lie within the narrow limits of 2.38 to 2.49 Å and three longer ones remain within 2.58 to 2.84 Å, the rest exceeding 3.7 Å. In the Na polyhedron five Na—O distances lie very close together (2.34 to 2.49 Å) and only Na—O₁₃ = 2.72 Å, the rest exceeding 3.5 Å.

The distribution of protons between the oxygen atoms and the separation of the OH groups from the water molecules was effected on the basis of a valence balance computed by Pauling's second rule. The hydrogen bonds were fixed by finding the short-

TABLE 4. Shortest O—O Vectors not Constituting Edges of Coordination Polyhedra

O—O Vector	Length of O—O vector in Å	OH(H ₂ O) proton donor	O—O Vector	Length of O—O vector in Å	OH(H ₂ O) proton donor
O ₁₂ ^{**} —O ₁₃ ^{**}	2.70	O ₁₂ ^{**} or O ₁₃ ^{**}	O ₁ [*] —O ₁₁ [*]	2.81	O ₁₁ [*]
O ₁₄ [*] —O ₄ [*]	2.70	O ₁₄ [*]	O ₇ —O ₁₂ ^{**}	2.86	O ₁₂ ^{**}
O ₃ [*] —O ₁₀ [*]	2.71	O ₁₀ [*]	O ₃ —O ₁₄ ^{**}	2.92	O ₁₄ ^{**}
O ₁₃ ^{**} —O ₁₄ ^{**}	2.77	O ₁₃ ^{**}	O ₇ —O ₁ [*]	2.97	O ₁ [*]
O ₂ [*] —O ₁₃ ^{**}	2.79	O ₂ [*] or O ₁₃ ^{**}			

O* = O atom in OH group.

OO* = O atom in H₂O molecule.

est O—O vectors not constituting edges of coordination polyhedra, on condition that at least one of the O considered belonged to an OH group or water. The nine such shortest distances appear in Table 4. None exceeds 2.96 Å and all may be regarded as corresponding to hydrogen bonds. The next in magnitude, O₈—O₁₄^{**} = 3.05 Å, O₈^{*}—O₁₁^{*} = 3.07 Å, and O₃^{*}—O₁₁^{*} = 3.08 Å, are too large, while the remaining distances are longer still (exceeding 3.2 Å).

LITERATURE CITED

1. A. S. Eakle, *Amer. Mineralogist*, **14**, 11, 427 (1929).
2. W. H. Barnes, *Amer. Mineralogist*, **34**, 1, 19 (1949).
3. W. T. Schaller, *U. S. Geol. Surv. Prof. Paper*, **158**, 137 (1930).
4. J. R. Clark and C. L. Christ, *Amer. Mineralogist*, **44**, 7-8, 712 (1959).
5. Kh. M. Kurbanov, I. M. Rumanova, and N. V. Belov, *Dokl. AN SSSR*, **152**, 5, 1100 (1963) [*Soviet Physics - Doklady*, Vol. 8, p. 956].
6. I. M. Rumanova, *Dokl. AN SSSR*, **98**, 3, 399 (1954).
7. E. G. Fesenko, I. M. Rumanova, and N. V. Belov, *Kristallografiya*, **1**, 2, 171 (1956).
8. P. M. Sayre, *Acta crystallogr.*, **5**, 1, 60 (1952).
9. W. H. Zachariasen, *Acta crystallogr.*, **5**, 1, 68 (1952).
10. N. Morimoto, *Mineral. J. Japan*, **2**, 1, 1 (1956).
11. C. L. Christ, J. R. Clark, and H. T. Evans, *Acta crystallogr.*, **11**, 11, 761 (1958).
12. C. L. Christ and J. R. Clark, *Z. Kristallogr.*, **114**, 5-6, 321 (1960).
13. I. M. Rumanova and A. Ashirov, *Kristallografiya*, **8**, 4, 517 (1963) [*Soviet Physics - Crystallography*, Vol. 8, p. 414].
14. S. V. Borisov, V. P. Golovachev, and N. V. Belov, *Kristallografiya*, **3**, 3, 269 (1958) [*Soviet Physics - Crystallography*, Vol. 3, p. 274].
15. I. M. Rumanova, *Kristallografiya*, **3**, 6, 664 (1958) [*Soviet Physics - Crystallography*, Vol. 3, p. 672].
16. I. M. Rumanova, *Kristallografiya*, **4**, 2, 143 (1959) [*Soviet Physics - Crystallography*, Vol. 4, p. 127].
17. A. F. Gorbov, *Tr. Vses. n.-i. inst. galurgii*, **40**, 392 (1960).
18. C. L. Christ, *Amer. Mineralogist*, **45**, 3-4, 334 (1960).

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