

MODULAR STRUCTURE OF THE VEATCHITE POLYTYPES AND OF THE RELATED PENTABORATES

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This paper describes a crystal chemical analysis of natural and synthetic veatchite-related pentaborates based on a modular approach. The structures of three polytypes of veatchite $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, as well as similar veatchite synthetic modifications, are built up of three-layer stacks isolated from each other and formed by Ca(Sr, Ba)-polyhedra, connected on both sides with boron-oxygen networks. B-O-sheets are built of $[\text{B}^t_2\text{B}^a_3\text{O}_8(\text{OH})]^{2-}$, pentagroups, formed by two B-tetrahedra and three B-triangles. From the positions seen using this modular approach, the structures of the veatchite derivative pentaborates – volkovskite, biringuccite, gowerite and nasinite – have been examined. The fundamental building block (FBB or basic structure) of pentaborates is the volume unit with a formula $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) and metric characteristics $a^* \sim 6.7\text{\AA}$, $b^* \sim 6.7\text{\AA}$, $c^* \sim 10.8\text{\AA}$, $\alpha^* \sim 105^\circ$, $\beta^* \sim 75^\circ$, $\gamma^* \sim 120^\circ$. Possible basic models of veatchite-like polytype modifications with the symmetry $P\bar{1}$, $P11n$, $P12_1$ have been derived by geometrical construction of hypothetical structures. The most probable basic structure has been defined by analysis of interatomic distances and energy testing with using a universal model of the interatomic potentials. The diversity of mineral species in the pentaborates group under consideration are associated with variations of composition, symmetry of blocks and ways of their joining in structure.

6 figures, 7 tables, 22 references.

Keywords: modular approach, a polytypism, pentaborate, veatchite, volkovskite, biringuccite, gowerite, nasinite, structural energy.

The first structural investigation of a natural strontium pentaborate – veatchite $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, published simultaneously both by Russian (Rumanova, Gandymov, 1971; Rumanov, *et al.*, 1971) and American (Clark, Christ, 1971) authors, revealed two polymorphic monoclinic modifications: *p*-veatchite (sp. gr. $P2_1$) and veatchite (sp. gr. *Aa*). The structure of a high-calcium variety of *p*-veatchite was refined subsequently (Rastsvetayeva, *et al.*, 1993). In more recent work (Grice, Pring, 2012), results of structure refinement of new finds of monoclinic *p*-veatchite and veatchite (in this publication veatchite-1*M* and veatchite-2*M*, respectively) and description of the triclinic structure of veatchite-A (veatchite-1) (Kumbasar, 1979) were presented. The currently recognized structures of 15 natural and synthetic veatchite-like and derivative pentaborates, with crystallographic characteristics, are shown in Table 1. The structural base of veatchite-like phases is comprised of three-layer stacks (Fig. 1) isolated from each other, with a central part of *M*-polyhedra ($M = \text{Ca}, \text{Sr}, \text{Ba}$), united in layers from both sides of which boron-oxygen networks occur. Building units of the network (Fig. 2) are penta-

groups $[\text{B}^t_2\text{B}^a_3\text{O}_8(\text{OH})]^{2-}$, formed of two B-tetrahedra and three B-triangles one of which is apical with an OH-group at a free vertex. The apical B-triangle is located perpendicular to the plane of a boron-oxygen sheet towards to the neighboring three-layer stack. As a result, this sheet becomes polar. Reproducing by means of horizontal translation motion, lying in the plane of a boron-oxygen sheet, pentagroups form 9-member rings of a trigonal configuration. In the center of the rings there are *M*-cations, surrounded by two types of polyhedra with ten- and eleven-vertices, which are rigidly connected with a B-polyhedra of pentaborate sheets by common edges and faces. The free vertex of the *M*1-ten-vertex polyhedron is occupied by an H_2O molecule, and *M*2-eleven-vertex polyhedron has common (OH)-edge with the additional $\text{B}(\text{OH})_3$ -triangle isolated from a boron-oxygen network of a stack. The neighboring three-layer stacks are connected along the vertical period only through hydrogen bonds, achieved by participation of H_2O -molecules and OH-groups of apical and additional B-triangles. This feature of crystal structure of veatchite explains possibility of shift and rotation of the neighboring three-

Table 1. Crystallographic characteristics of veatchite-like pentaborates

Mineral, formula	Space group Z	Unit cell parameters (Å, degr.)			Transformation matrixes			Block parameters (Å, degr.)		
		a	b	c				a	b	c
		α	β	γ				α	β	γ
<i>p</i> -veatchite {Sr[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	<i>P</i> 2 ₁ 2	6.70 90.00	20.80 119.15	6.60 90.00	-1 1 -0.55	0 0 -0.5	0 1 -0.21	6.70 103.8	6.73 73.9	10.89 121.1
High-calcium <i>p</i> -veatchite {(Ca,Sr)[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	<i>P</i> 2 ₁ 2	6.686 90.00	20.614 119.17	6.594 90.00	-1 1 -0.55	0 0 -0.5	0 1 -0.21	6.69 103.8	6.72 73.9	10.80 121.1
Veatchite-1M {Sr[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	<i>P</i> 2 ₁ 2	6.713 90.00	20.704 119.21	6.627 90.00	-1 1 -0.55	0 0 -0.5	0 1 -0.21	6.71 103.8	6.75 73.9	10.85 121.0
Veatchiter {Sr[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	<i>Aa</i> 4	20.86 90.00	11.738 92.10	6.652 90.00	0 0 -0.5	-0.5 0.5 -0.23	-0.5 -0.5 0	6.75 103.6	6.75 78.4	10.77 120.9
Veatchite-2M {Sr[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	<i>Cc</i> 4	6.607 90.00	11.713 92.00	20.685 90.00	-0.5 -0.5 0	-0.5 0.5 -0.23	0 0 -0.5	6.75 103.6	6.75 78.4	10.69 120.4
Veatchite-1A {Sr[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}}	\bar{P} 2	6.638 87.86	6.739 82.70	20.982 60.48	1 0 0	-1 1 -0.5	0 0 0.5	6.74 105.9	6.74 75.9	10.90 121.0
{Ca[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O} (I)}	<i>P</i> 1 1	6.665 103.68	6.617 77.98	10.605 120.93	1 0 0	0 1 0	0 0 1	6.67 103.7	6.62 78.0	10.61 120.9
{Ca[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O} (II)}	<i>P</i> 1 1	6.544 76.66	6.606 88.48	10.596 60.94	1 0 0	-1 1 0	0 0 -1	6.67 103.3	6.61 78.3	10.60 120.9
{Ca[B ₅ O ₈ (OH)] • {H ₂ O}}	<i>P</i> 2 ₁ / <i>c</i> 4	6.530 90.00	19.613 119.21	6.530 90.00	-1 1 -0.64	0 0 0.5	0 1 -0.39	6.53 108.9	6.61 73.6	10.47 120.4
{Ba[B ₅ O ₈ (OH)] • {H ₂ O} (I)}	\bar{P} 2	6.785 100.07	6.831 91.98	10.629 119.46	0 1 0	-1 1 0	0 0 1	6.83 102.0	6.86 79.9	10.63 120.6
{Ba[B ₅ O ₈ (OH)] • {H ₂ O} (II)}	\bar{P} 2	6.781 102.55	6.901 91.51	9.737 119.72	0 1 0	-1 1 0	0 0 1	6.90 104.1	6.87 77.4	9.74 121.0
Volkovskite {Ca[B ₅ O ₈ (OH)] ₂ • {B(OH) ₃ • H ₂ O}} ₂ • {KCl • 2H ₂ O}}	<i>P</i> 1 1	6.50 95.68	23.96 119.6	6.62 90.59	0 -1 0.11	0 0 0.43	1 -1 0.22	6.62 102.2	6.60 78.4	10.53 121.1
Biringuccite {Na[B ₅ O ₈ (OH)] ₂ • {Na • H ₂ O}} ₂	<i>P</i> 2 ₁ / <i>c</i> 4	11.196 90.00	6.561 93.89	20.757 90.00	0 0.5 0	-1 0.5 -0.11	0 0 0.5	6.56 95.4	6.49 85.9	10.41 120.4
Gowerite {Ca[B ₅ O ₈ (OH)] • {B(OH) ₃ • 3H ₂ O}}	<i>P</i> 2 ₁ / <i>c</i> 4	12.882 90.00	16.360 121.62	6.558 90.00	0.5 0 0.12	0 0 0.5	0 1 -0.18	6.44 103.5	6.56 75.3	8.52 121.6
Nasinite {Na[B ₅ O ₈ (OH)] • {Na • 2H ₂ O}}	<i>Pna</i> 2 ₁ 4	12.015 90.00	6.518 90.00	11.173 90.00	0 0 0.5	-1 0.5 0.56	0 0.5 0	6.52 105.2	6.47 58.7	7.03 120.3

layer stacks from each other and, as a result, the formation of polytypes with a close horizontal parameters and the vertical parameter of which differing in multiples of a number.

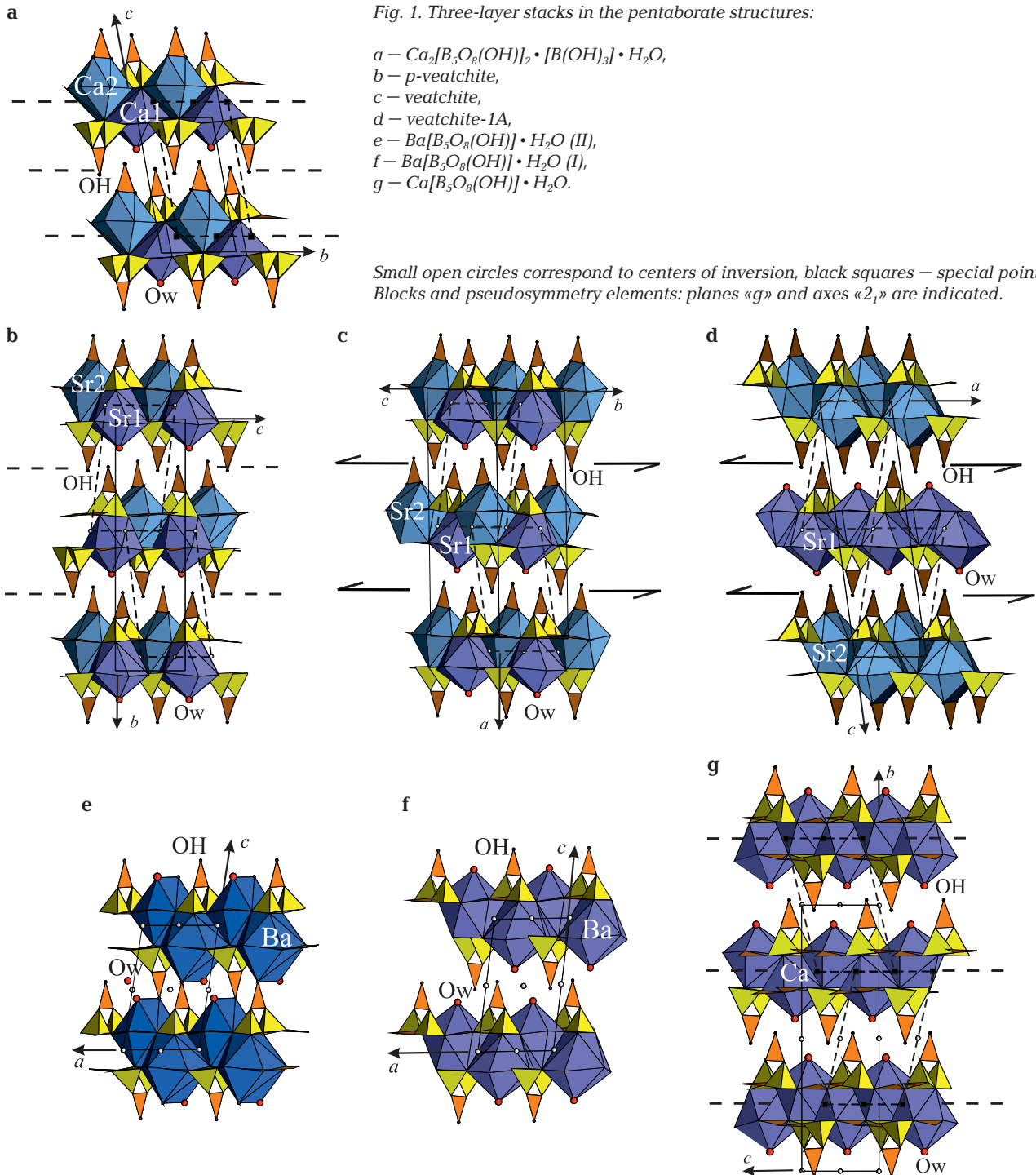
Crystal chemical investigations of the veatchite mineral group and related natural and synthetic phases, performed previously (Rastsvetayeva, *et al.*, 1993; Belokoneva, *et al.*, 2000; Grice, Pring, 2012), have been continued by our group (Yamnova, *et al.*, 2009; Yamnova *et al.*, 2011) using a modular approach (Ferraris *et al.*, 2004; Yamnova, *et al.*, 2008; Rastsvetayeva, Aksenov, 2011). As a fundamental construction unit (both of the module and basic structure) the volume block with parameters $a^* \sim 6.7\text{\AA}$, $b^* \sim 6.7\text{\AA}$, $c^* \sim 10.8\text{\AA}$, $\alpha^* \sim 105^\circ$, $\beta^* \sim 75^\circ$, $\gamma^* \sim 120^\circ$, the composition of which corresponds to a formula $\{M[B_5O_8(OH)]\}_2 \cdot \{[B(OH)_3], H_2O\}_2$ ($M = Ca, Sr, Ba$), was separated, where the first braces corresponding to the stack occupation, and the second to the interstack space occupation. Variability of symmetry linkage between atoms within the block and variability of their composition, as well as ways of separate blocks integration into structures leads to polytype occurrence. The purpose of this work is the search of the most probable base model of veatchite-related pentaborate. For the possible hypothetical structures, built on the base of a known structure, a testing of interatomic distances, and further energetical estimation by results of calculations of interatomic potential parameters is held.

Peculiarities of symmetry linkage in structures of veatchite polytypes

Peculiarities of symmetry linkage in structures of veatchite-like pentaborates have been considered from OD-theory positions by E.L. Belokoneva with coauthors (2000) where the pseudo-symmetry elements (the center of inversion in the structure of a monocline veatchite and the glide plane in a veatchite related structure of volkovskite, K-Ca-pentaborate) connecting couples of boron-oxygen layers belonging to one stack were revealed. The analysis performed later by our group (Yamnova *et al.*, 2009; Yamnova *et al.*, 2011) showed existence of a new pseudo-symmetry elements connecting the layers, related to neighbor stacks: "a glide plane (g)" (Fig. 1a, b) and "screw axe 2_1 " (Fig. 1c, d). These operations are not crystallographic and are therefore in quotes. The glide component in both cases is $\sim 1/3T_d$, where $T_d \sim 11.7\text{\AA}$ is the b parameter of the veatchite

unit cell. Shift amplitude of the adjacent sheets in the structure of triclinic veatchite-1A is different and is $\sim 1/4T_d$. The stack layers in all three veatchite polytype modifications are connected by the inversion center; further, for both monocline p -veatchite (Fig. 1b) and veatchite (Fig. 1c) those elements are pseudosymmetry elements (in so far as isolated $B(OH)_3$ -triangles and H_2O molecules, located in interstitial space do not submit to them), while in the structure of veatchite-1A triclinic modification (Fig. 1d) those elements are true symmetry elements. In this case stacks of different composition has alternate in the structure: with cationic filling of Sr1 10-vertex polyhedra, coordinated by water molecules, and of Sr2 11-vertex polyhedra, coordinated by isolated $B(OH)_3$ -triangles. It should be noted that in this triclinic structure the vertical glide plane, located perpendicular to $T_d \sim 11.7\text{\AA}$ and broken with isolated $B(OH)_3$ -triangles and water molecules, remains as pseudo-symmetry element. In the structure of monoclinic veatchite which symmetry is described by a Aa space group, this plane is true. The centers of inversion connecting sheets both for a stack and adjacent stacks in structures of two modifications of $Ba[B_5O_8(OH)] \cdot H_2O$ (II) (Fig. 1e) (Belokoneva *et al.*, 2008) and $Ba[B_5O_8(OH)] \cdot H_2O$ (I) (Fig. 1f) (Pushcharovsky *et al.*, 2000) are the true elements of symmetry, too. In the structure of synthetic $Ca[B_5O_8(OH)] \cdot H_2O$ (Fig. 1g) (Yamnova *et al.*, 2003) layers of the adjacent stacks are connected by the center of inversion, and layers of one stack – with the glide plane, and in this case true symmetry has remained (space group $P2_1/c$). In the acentric structure of synthetic Ca-pentaborate $Ca_2[B_5O_8(OH)]_2 \cdot [B(OH)_3] \cdot H_2O$ (Fig. 1a) with a mixed filling of interstitial space (Yamnova *et al.*, 2009) a pair of a stack layers is connected with " g " plane noted above, but the shift vector in this case is $\sim 1/2T_d$. As well as in case of veatchites, isolated $B(OH)_3$ -triangles and molecules of H_2O do not submit to both operations.

The alternation and symmetry linkage of the sheets, located at four levels along the axis, perpendicular to the sheet plane in structures of three veatchite polytypes (Fig. 2a, b, c), volkovskite (Fig. 2d) (Rastsvetayeva *et al.*, 1992) and synthetic $Ca[B_5O_8(OH)] \cdot H_2O$ (Fig. 2e) are shown. The layers belonging to a single three-layer stack are put into square brackets in figure: one stack in the central part of elements figure, and the others (two halves of the neighboring stacks) are in the



top and lower parts. In the same figure a module-blocks $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ with pseudo-hexagonal section – triclinic "protocells" shown. Horizontal axes a^* and b^* are oriented in such a way that "apical" B-triangles of pentagroups are parallel to a long rhombus diagonal ($T_d \sim 11.7\text{\AA}$). In the identified blocks atoms occupy similar positions, but there are differences: 1) in symmetry linkage and filling of interstitial space within the blocks, and 2) in ways that the identified blocks consolidate along the

vertical axis. Nodes (points) of blocks are chosen in the pseudo- or true inversion centers (small white circles at Fig. 1 and 2), and also in the special points (small black squares in the figures) are linked to symmetry elements, i.e. are equidistant from pairs of *M*-positions and located on the right lines connecting them. The length of the a^* and b^* vectors are identical to horizontal translations of unit cells of the actual structures, and the c^* vector length corresponds to distance between the nodes located in the neighbor-

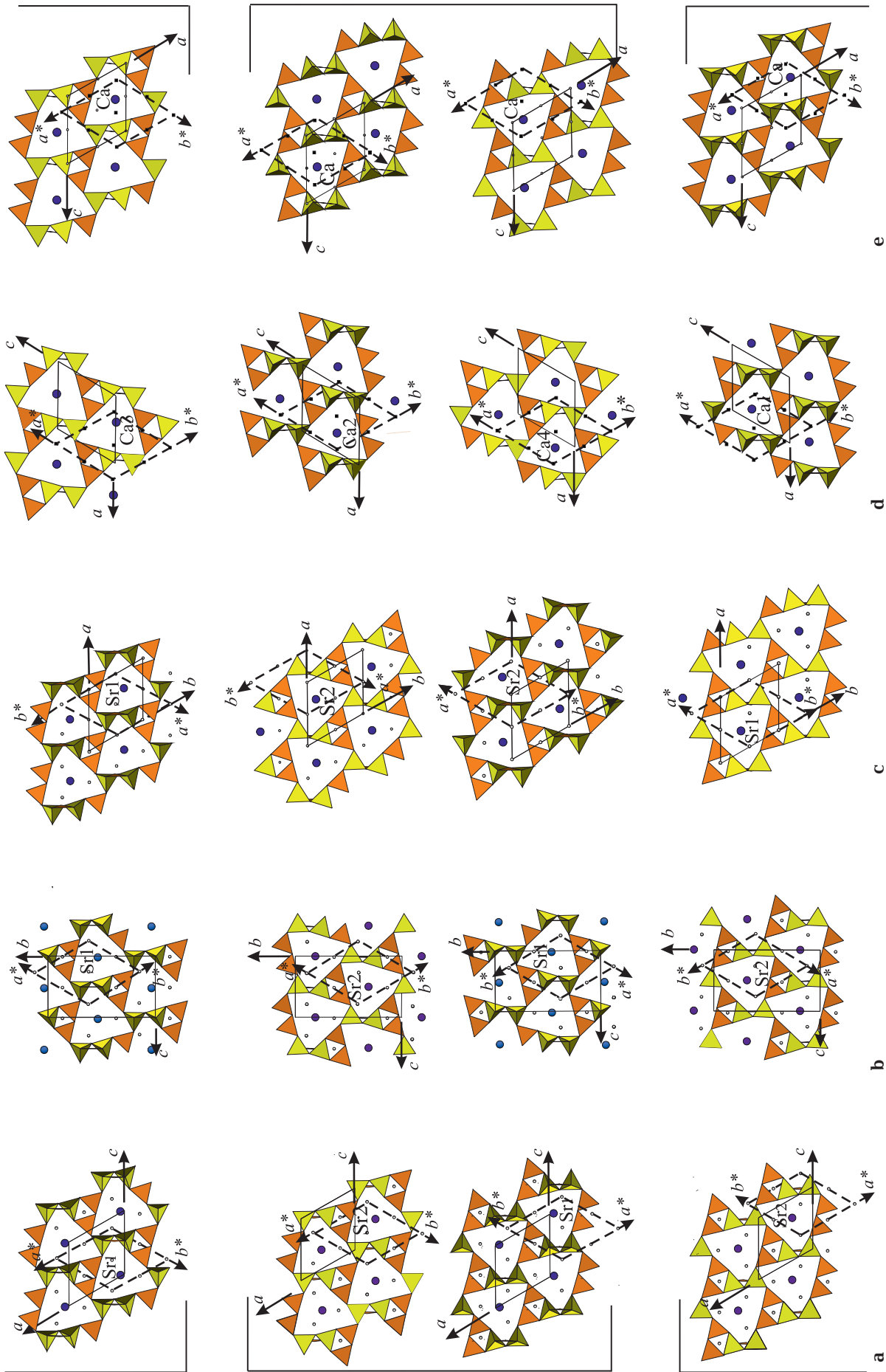


Fig. 2. Alternation of layers at four levels in the structures of pentaborates: a – p-veatchite, b – veatchite, c – veatchite -1A, d – volkovskite, and e – $\text{Ca}[\text{B}_5\text{O}_{10}(\text{OH})] \cdot \text{H}_2\text{O}$. Square brackets indicate the layers joined into stacks. Dashed lines represent blocks. Small open circles correspond to (a, b) pseudocenters of inversion and (c, e) true centers of inversion, black squares – special points.

ing three-layer stacks. In the structure of veatchite-1A (Fig. 1d; 2c) and Ba-pentaborate (Fig. 1e, f) the nodes of the blocks coincides with the true centers of inversion, in the structures of monoclinic polytypes – with the inversion pseudo-centers (Fig. 1b, c; and 2a, b). In the structures of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Fig. 1a), volkovskite (Fig. 2d) and $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 1g and 2e) the nodes of the blocks are chosen in the special points located on the glide planes. The block nodes coordinates (x, y, z), defined for actual structures, were a basis for calculation of the transformation matrixes from unit cell of each structure to triclinic blocks (modules) which metric characteristics are provided in Table 1.

Alternation of boron-oxygen sheets based on the separated blocks in structures of the veatchite related pentaborates are schematically shown in Figure 3, where hypothetical models are constructed by combinations

both of true- and pseudo-elements of symmetry with retaining the mutual arrangement of fragment, which is similar to that of real structures. The pentagroups of boron-oxygen sheets shown as triangles on the scheme, are on borders of blocks and belongs to a three-layer stack. The structures of veatchite-like pentaborates can be divided into three types by symmetry linkage of atoms within the marked blocks. The first type – "the glide plane, g ", is found in the structures: Ca-pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Fig. 3a), volkovskite (Fig. 3b), p -veatchite (Fig. 3c) and hypothetical model (Fig. 3d); the second type – "a screw axes, 2_1 " – in the structures of monoclinic and triclinic veatchite (Fig. 3f), and also in two hypothetical models (Fig. 3e, g); and the third type – the center of inversion (i) – in Ba-pentaborates (Fig. 3h) structures, Ca-pentaborate $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 3i) and in hypothetical model (Fig. 3j). Both transla-

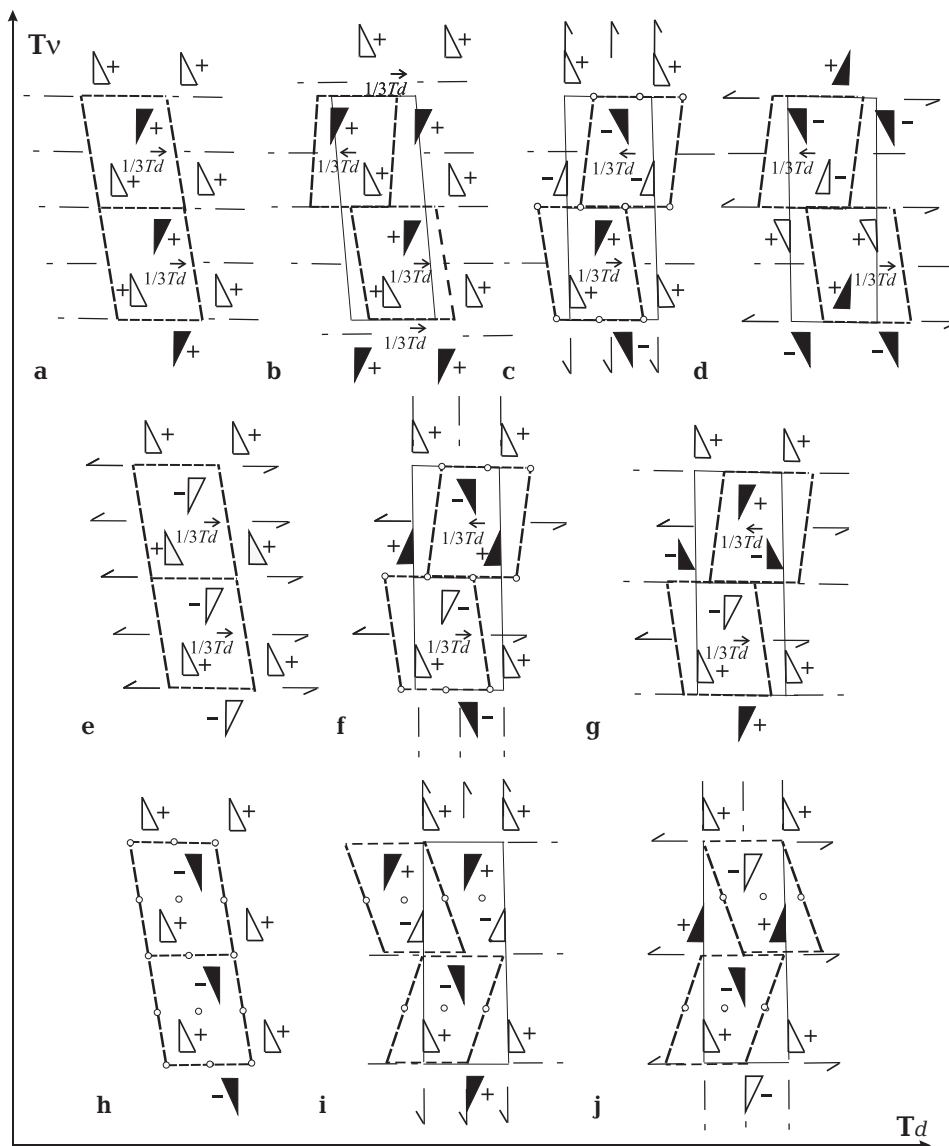


Fig. 3. Schematic diagrams illustrating the symmetry relationships between the layers in the structures of pentaborates: a – $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, b – volkovskite, c – p -veatchite, d – hypothetical model, e – hypothetical model, f – veatchite and veatchite-1A, g – hypothetical model, h – $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (II) and $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (I), i – $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$, and j – hypothetical model. Closed and open triangles represent the left and right figures (pentaborate groups of the boron-oxygen layer), respectively. Dashed lines indicate the blocks, and the letters T_v and T_d denote the vertical and diagonal translations, respectively.

Table 2. The unit cell characteristics of triclinic and monoclinic hypothetical models of pentaborates with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ (1-1, 1-2, 1-3, 1-4) and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ (2-1, 2-2, 2-3, 2-4)

Unit cell parameters	Model 1-1	Model 1-2	Model 1-3	Model 1-4
	Model 2-1	Model 2-2	Model 2-3	Model 2-4
a, Å	6.665	6.665	6.665	10.430
b, Å	6.617	6.617	6.617	11.738
c, Å	10.605	10.605	10.605	6.652
α , degr.	103.68	90	90	90
β , degr.	77.98	90	90	92.1
γ , degr.	120.93	120.93	120.93	90
Symmetry	(i)	(i)	(n)	(2 ₁)
Transformation matrixes	x, y, z	x, y, z	x, y, z	x, y, z
	-x, -y, -z	-x, -y, -z	x+1/2, y+1/2, -z	-x, y+1/2, -z

tion-identical blocks, and those, connected by operation of true elements of symmetry of space groups of actual structures alternate along (\mathbf{T}_v), axis, perpendicular to the plane of sheets.

Geometrical construction and testing of possible basic models of veatchite polytypes

The structure models built up of blocks connected with \mathbf{T}_x , \mathbf{T}_y , \mathbf{T}_z translation are the base models of the veatchite-like structures (Fig. 3a, e, h). In this case the basic model obeying the true symmetry (space group $P\bar{1}$) (Fig. 3h), with uniform filling of the interstitial space with H_2O molecules, realized in the structures of two modifications (I, II) of synthetic $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$, reported by E.L. Belokoneva and co-authors (Belokoneva *et al.*, 2000) as the *MDO*-polytype. Two other models have non-crystallographic (translation component $\sim 1/3\mathbf{T}_d$) symmetry of "g" (Fig. 3a) and "2₁" (Fig. 3e). Thus the first model is found in Ca-pentaborate's structure of synthetic $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, as investigated by ourselves (Yamnova *et al.*, 2009) and refined later (Yamnova *et al.*, 2012), while the second model remains hypothetical.

In order to determine the probability of *MDO*-polytypes formation, the symmetry of which would result in $P\bar{1}$, $P11n$ and $P12_11$ true space groups (with translation components $1/2\mathbf{T}_d$ for monoclinic groups), the structure models of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ with uniform interstitial filling have been constructed. The metric characteristics and atomic coordinates of the real structure of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Yamnova *et al.*, 2009), in which H_2O molecules and $\text{B}(\text{OH})_3$ triangles alternately replace each other were used as initial model

for the building of models with symmetry (i) (space group $P\bar{1}$) and (n) (space group $P11n$) This model was chosen because of the coincidence of its metric characteristics to the basic block, and also the rather small number of parameters necessary to further carry out a power analysis. The coordinates of atoms (Clark, Christ, 1971) corresponding to a half-volume of a monoclinic veatchite cell ($a' = 1/2a = 10.4\text{Å}$) with symmetry (2₁) (space group $P12_11$) for both compositions, were used as the initial model (in a real structure of which the identified blocks possess non-crystallographic symmetry "2₁" with translation $\sim 1/3\mathbf{T}_d$ along the $b = 11.7\text{Å}$ axis).

Characteristics of the unit cells of the constructed models are provided in Table 2, the transformed atomic coordinates are in Tables 3–6, and "lateral" projections of hypothetical structures in Fig. 4. For models with symmetry (i), two options for the unit cell are used: triclinic "scalene", and "rectangular"; for models with symmetry (n) and (2₁) – only "rectangular" monoclinic.

The structural model of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ with two additional interstitial B-triangles and (i)-symmetry seems improbable, as in this case distances between the OH-tops of the isolated B-triangles and the O(OH)-tops of the apical B-triangles from the adjacent three-layer stack (those are noted with thick lines and 1 and 2 figures) are too short (1.78Å and 1.93Å for 1-1 model (Fig. 4a); 1.66Å and 1.77Å for 1-2 model (Fig. 4b)). For monoclinic models with the same composition, with symmetry (n) and (2₁) (not presented on the figure), similar distances are as follows: 1.26Å and 1.27Å (1-3 model); 1.45Å and 1.52Å (1-4 model). The same options were used for the building of hypothetical structures for $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$. For triclinic models with symmetry (i)

Table 3. Atomic coordinates of the models (1-1, 1-2, 1-3) with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$

Atom	x/a	y/b	z/c
Ca1	0.2300	0.2850	0.1150
B1	0.3320	-0.2000	0.1180
B2	-0.0950	0.6580	0.1610
B3	-0.2810	-0.0960	0.1740
B4	-0.3580	0.2130	0.1370
B5	-0.2230	-0.1850	0.3740
B6	0.1790	0.4070	0.4180
O1	-0.1010	-0.1550	0.1110
O2	0.5010	0.7290	0.1100
O3	-0.2050	0.1470	0.1520
O4	0.4020	0.0390	0.1330
O5	0.6900	0.4320	0.1250
O6	0.1080	0.6270	0.1060
O7	-0.0990	0.7090	0.3060
O8	-0.3260	-0.1040	0.3140
(OH)9**	0.1350	-0.5550	0.5510
(OH)10*	-0.2480	-0.1650	0.5070
(OH)11**	0.1340	0.5080	0.3360
(OH)12**	0.2760	0.2730	0.3480

Table 4. Atomic coordinates of the models (1-4) with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2\text{H}_2\text{O}$

Atom	x/a	y/b	z/c
Ca1	0.2300	0.2850	0.1150
B1	0.3320	-0.2000	0.1180
B2	-0.0950	0.6580	0.1610
B3	-0.2810	-0.0960	0.1740
B4	-0.3580	0.2130	0.1370
B5	-0.2230	-0.1850	0.3740
O1	-0.1010	-0.1550	0.1110
O2	0.5010	0.7290	0.1100
O3	-0.2050	0.1470	0.1520
O4	0.4020	0.0390	0.1330
O5	0.6900	0.4320	0.1250
O6	0.1080	0.6270	0.1060
O7	-0.0990	0.7090	0.3060
O8	-0.3260	-0.1040	0.3140
(OH)9*	-0.2480	-0.1650	0.5070
Ow	0.1700	0.3700	0.3380

Table 5. Atomic coordinates of the models (2-1, 2-2, 2-3) with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$

Atom	x/a	y/b	z/c
Ca1	0.1100	0.0400	0.5300
Ca1-1	0.1100	0.5400	0.0300
B1	0.1500	0.3310	0.7240
B1-1	0.1500	0.8310	0.2240
B2	0.1900	0.4850	0.4850
B2-1	0.1900	0.9850	0.9850
B3	0.1500	0.2880	0.3650
B3-1	0.1500	0.7880	0.8650
B4	0.1900	0.6950	0.5140
B4-1	0.1900	0.1950	0.0140
B5	0.4100	0.5950	0.5000
B5-1	0.4100	0.0950	0.0000
B6	-0.4300	0.2100	0.0100
B6-1	-0.4300	0.7100	0.5100
O1	0.1300	0.2970	0.9190
O1-1	0.1300	0.7970	0.4190
O2	0.1300	0.4430	0.6780
O2-1	0.1300	0.9430	0.1780
O3	0.1500	0.2520	0.5690
O3-1	0.1500	0.7520	0.0690
O4	0.1500	0.4000	0.3220
O4-1	0.1500	0.9000	0.8220
O5	0.3300	0.4930	0.5060
O5-1	0.3300	0.9930	0.0060
O6	0.1300	0.5940	0.4240
O6-1	0.1300	0.0940	0.9240
O7	0.1500	0.2010	0.2330
O7-1	0.1500	0.7010	0.7330
O8	0.3300	0.6990	0.5050
O8-1	0.3300	0.1990	0.0050
(OH)9*	0.5300	0.5920	0.5070
(OH)9-1*	0.5300	0.0920	0.0070
(OH)10**	-0.5500	0.2100	0.0000
(OH)10-1**	-0.5500	0.7100	0.5000
(OH)11**	-0.3300	0.3000	0.0200
(OH)11-1**	-0.3300	0.8000	0.5200
(OH)12**	-0.3500	0.1100	0.0100
(OH)12-1**	-0.3500	0.6100	0.5100

Note: In the following tables: * – OH-group of the apical B-triangle of B-O-network; ** – OH- group of the additional B- triangle.

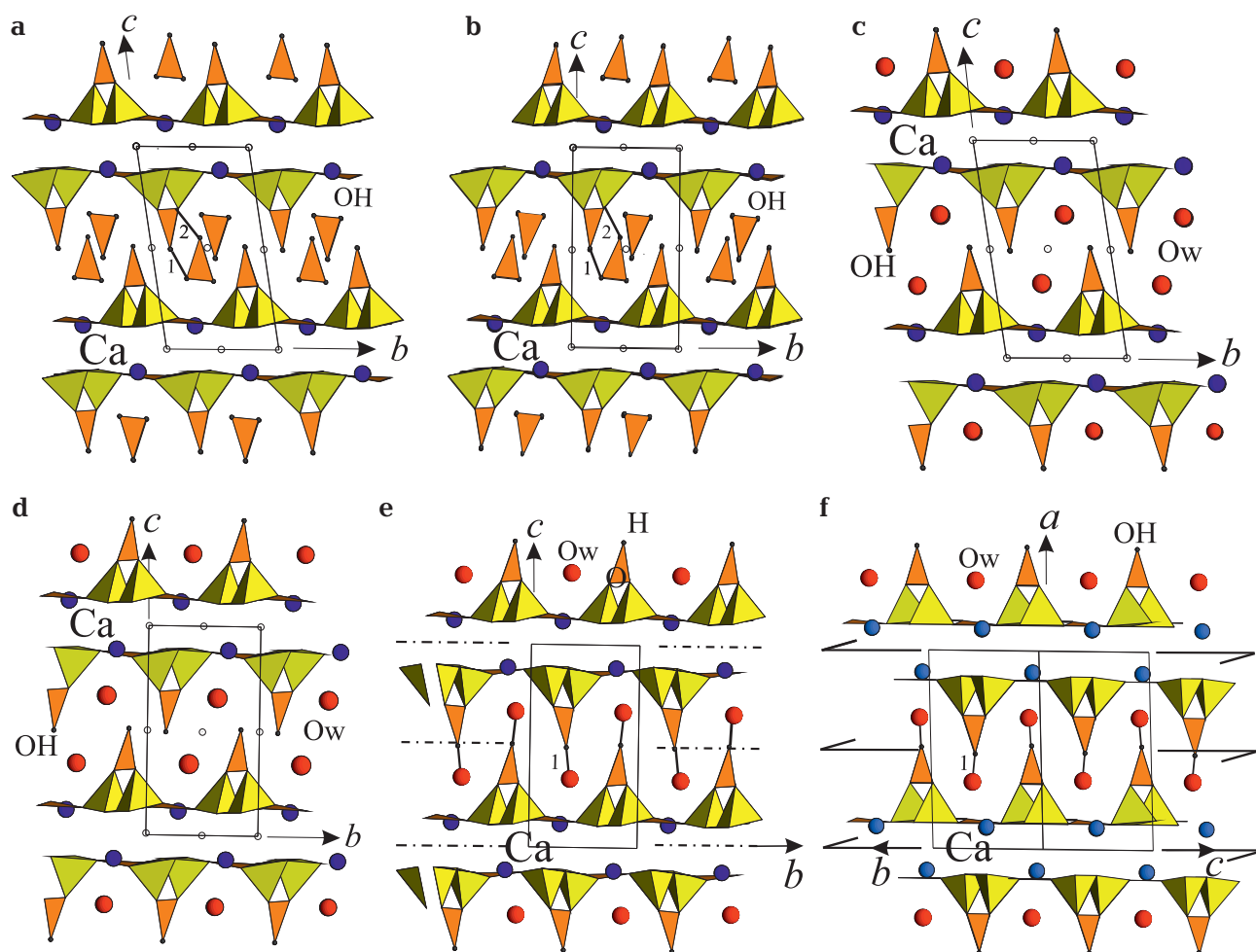


Fig. 4. Hypothetical models of the pentaborate structures with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$: a – model 1-1, b – model 1-2, c – model 2-1, d – model 2-2, e – model 2-3, and f – model 2-4. Bold lines and digits (1, 2) denote the "short" interatomic distances.

with "scalene" and "rectangular" cell an interatomic distances, the values found are not far beyond standard values (Fig. 4c, d), but for monoclinic models with symmetry (n) (Fig. 4e) and (2_1) (Fig. 4f), distances between atoms of oxygen in a water molecule and the OH-top of the apical B-triangle were inadmissible small (1.78\AA for the first model and 1.41\AA for the second). Thus, monoclinic models with a true symmetry of 2_1 and n are improbable as basic structures.

Theoretical modeling of the basic structure of veatchite polytypes

The universal set of parameters of the interatomic potentials optimized for structural modeling of borates was applied to a power analysis of possible basic structures of veatchite-like polytypes (Eremin, Urusov, 2013). In the current study to develop the potential primary model, the simplest crystal structure of CaB_2O_4 borate, containing only BO_3 triangles, was chosen. At the initial stage

of modeling, the following set was used: in addition to the Coulomb interaction of all ions, the cation-oxygen and oxygen-oxygen repulsion, described by the Buckingham potential, was considered. As result of a test calculation series we found that, 1) the B-O interaction does not allow a satisfactory description within the model with a formal charges on atoms, and 2) the Buckingham potential for this pair of atoms is also inapplicable owing to what for the description of B-O interaction in the mentioned work (Eremin, Urusov, 2013) the Morse potential was applied. In order the anions polarization effect to be included in calculation, the shell-type model was applied for oxygen atoms. Besides, an introduction of the additional contribution, described by three-particle harmonious potential, was required for the additional stabilization of valence angles coordination in boron polyhedra. The effective charges estimated from test procedures on oxygen in CaB_2O_4 were transferred without change to the other model species, SrB_4O_7

Table 6. Atomic coordinates of the models (2-4) with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$

Atom	x/a	y/b	z/c
Ca1	0.1100	0.0359	0.5256
Ca1-1	0.1100	0.5359	0.0256
B1	0.1500	0.3310	0.7240
B1-1	0.1500	0.8310	0.2240
B2	0.1900	0.4850	0.4850
B2-1	0.1900	0.9850	0.9850
B3	0.1500	0.2880	0.3650
B3-1	0.1500	0.7880	0.8650
B4	0.1900	0.6950	0.5140
B4-1	0.1900	0.1950	0.0140
B5	0.4100	0.5950	0.5000
B5	0.4100	0.0950	0.0000
O1	0.1300	0.2970	0.9190
O1-1	0.1300	0.7970	0.4190
O2	0.1300	0.4430	0.6780
O2-1	0.1300	0.9430	0.1780
O3	0.1500	0.2520	0.5690
O3-1	0.1500	0.7520	0.0690
O4	0.1500	0.4000	0.3220
O4-1	0.1500	0.9000	0.8220
O5	0.3300	0.4930	0.5060
O5-1	0.3300	0.9930	0.0060
O6	0.1300	0.5940	0.4240
O6-1	0.1300	0.0940	0.9240
O7	0.1500	0.2010	0.2330
O7-1	0.1500	0.7010	0.7330
O8	0.3300	0.6990	0.5050
O8-1	0.3300	0.1990	0.0050
(OH)9*	0.5200	0.5920	0.5070
(OH)9-1*	0.5200	0.0920	0.0070
Ow	0.3500	0.0710	0.5320
Ow-1	0.3500	0.5710	0.0320

Table 7. Unit cell parameters and structural energy (E_{str}) of the hypothetical models $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$

Parameter	Model 2-1	Model 2-2	Model 2-3 ₁	Model 2-3 ₂
	(i)	(i)	(n)	(n)
a, Å	6.665	6.665	6.665	6.665
b, Å	6.617	6.617	6.617	6.617
c, Å	10.605	10.605	10.605	10.605
α , degr.	103.68	90	90	103.68
β , degr.	77.98	90	90	77.98
γ , degr.	120.93	120.93	120.93	120.93
E_{str} , eV	-987.56	-955.86	-896.18	-938.33

(Perloff, Cluster, 1966), used for optimization of B-O interaction in the tetrahedron of BO_4 . Thus, for preservation of electroneutrality in the unit cell, the B-charge in tetrahedral surrounding appeared above a similar charge in triangular coordination that corresponds to the crystal chemical rule of dependence of an ion charge on coordination number.

In our study, the two models of composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ and symmetry (*i*) in "scalene" (2-1 model) and "rectangular" (2-2 model) variants, which are the most probable basic models according the previous results, were used. For comparison within the same unit cells with right (2-31 model) and oblique (2-32 model) corners, two structures of similar composition with symmetry (*n*) were tested. The structural energy (E_{str}) of all four geometrical models was estimated in the calculation mode with fixed atoms coordinates specified in Table 5. The 2-1 model with symmetry (*i*) and a triclinic cell (Fig. 4c) appeared to be the most energy favorable, as shown in Table 7. The other variants appeared more energy-expensive, that is why their realization is improbable. Results of comparison of structural energies of tested crystal structures confirmed data, obtained at geometrical construction of a possible basic models of veatchite-like structures.

Features of pentaborate structures related to veatchite: volkovskite, biringuccite, gowerite and nasinite

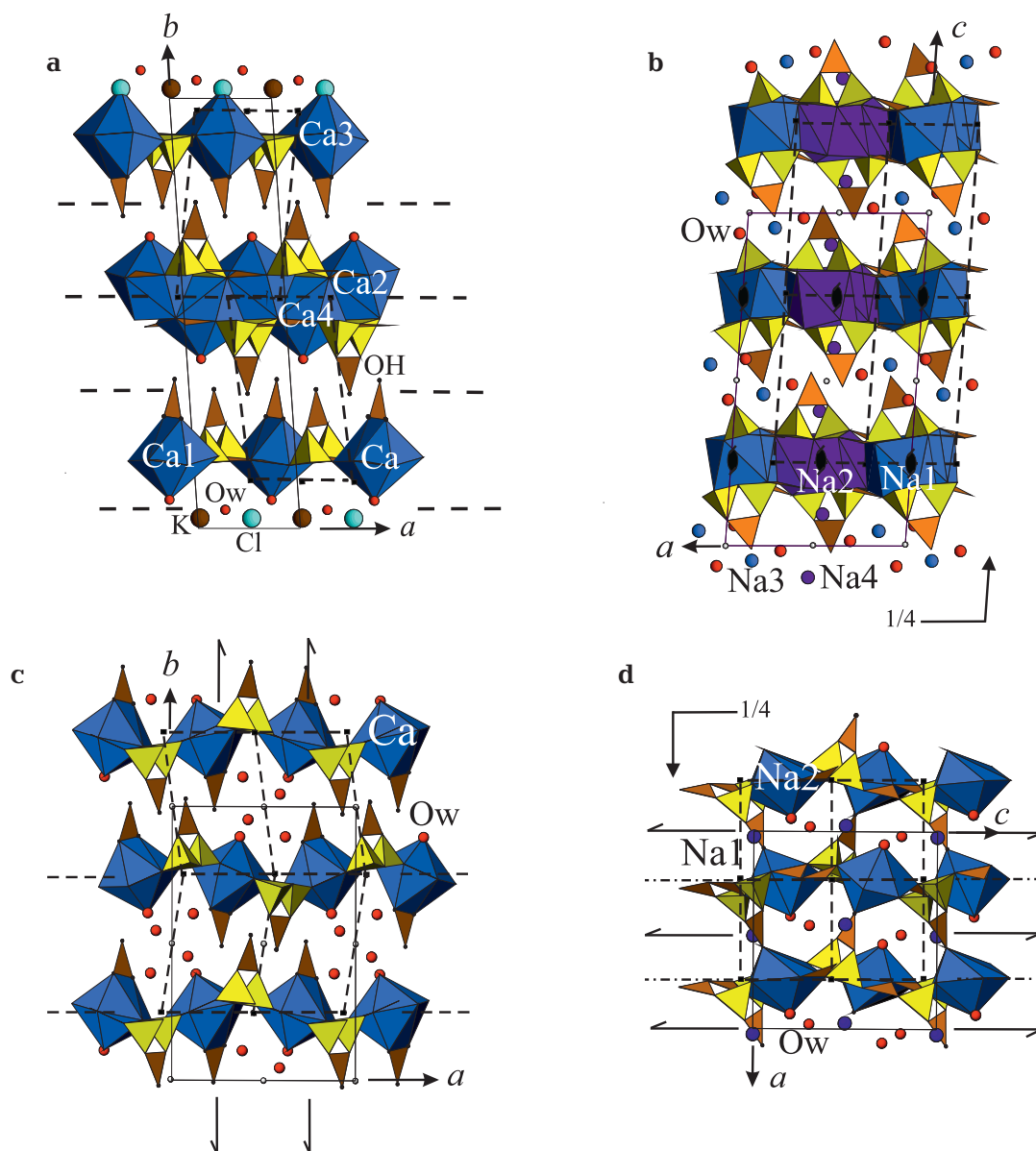
Symmetry of the separated block of composition $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$, (*M* = Ca, Sr, Ba) defines 1) the type of bonds between boron-oxygen sheets from the neighboring three-layer stacks of the veatchite-like structures and 2) the stacks shift of the one from each other. With regard to composition, theoretically, according to the general formula of the veatchite-like species, for every two *M*-cations in a three-layer stack there are either two isolated $\text{B}(\text{OH})_3$ -triangles or two H_2O molecules, or single molecule of both composition. The other composition of both a three-layer stack and an interstitial space leads to distortion or change of the veatchite-like structure that is observed in natural pentaborates as follows: volkovskite $\text{KCa}_4[\text{B}_{22}\text{O}_{32}(\text{OH})_{10}\text{Cl}] \cdot 4\text{H}_2\text{O}$ (Ras-tsvetayeva *et al.*, 1992), biringuccite $\text{Na}_4[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ (Corazza *et al.*, 1974), gowerite $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot [\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}$ (Konnert *et al.*, 1972) and nasinite $\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$ (Corazza *et al.*, 1975).

In the volkovskite structure (Fig. 5a), one of two three-layer stacks topologically completely corresponds to that described above. The second stack differs from the first by introduction of K and Cl atoms and of H₂O molecules between the top and lower half of a three-layer stack. As a result, the crystal chemical formula of the mineral can be written down as $[\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{B}(\text{OH})_3\} \cdot \text{H}_2\text{O}]_2 \cdot \{\text{KCl} \cdot 2\text{H}_2\text{O}\}$, which corresponds to alternation along the *b* axis of two blocks and a $\{\text{KCl} \cdot 2\text{H}_2\text{O}\}$ -layer in the structure of the mineral. A symmetry linkage of boron-oxygen layers in the volkovskite structure (Fig. 2d; 3b) is similar to that in the structure of synthetic $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$: the layers of a stack are connected by the glide plane of the shift components $\sim 1/2\text{T}_a$

and layers of the next stacks – with non-crystallographic $\sim 1/3\text{T}_a$. Thus, the positions of the H₂O-molecules and isolated B-triangles are subject to action only by the first plane. Nodes of the separated blocks are located in special points: on the glide planes, connecting calcium-boron-oxygen layers of a three-layer stack, and also equidistant from pairs of atoms Ca3 – K and Ca1 – Ow (oxygen atom of H₂O molecule). Metric characterizations of the chosen blocks and the transformation matrix for them are provided in Table 1.

In the structures of the Ca(Sr,Ba)-pentaborates previously discussed, neutrality is achieved via an equal ratio of cations and pentagroups in the three-layer stacks ($\text{M}^{2+} : [\text{B}_5\text{O}_8(\text{OH})]^{2-} = 1:1$) The same ratio is

Fig. 5. «Lateral» projections of the structures: a – volkovskite, b – biringuccite, c – gowerite, and d – nasinite. Blocks and pseudosymmetry (a) and true symmetry (b-d) elements are indicated.



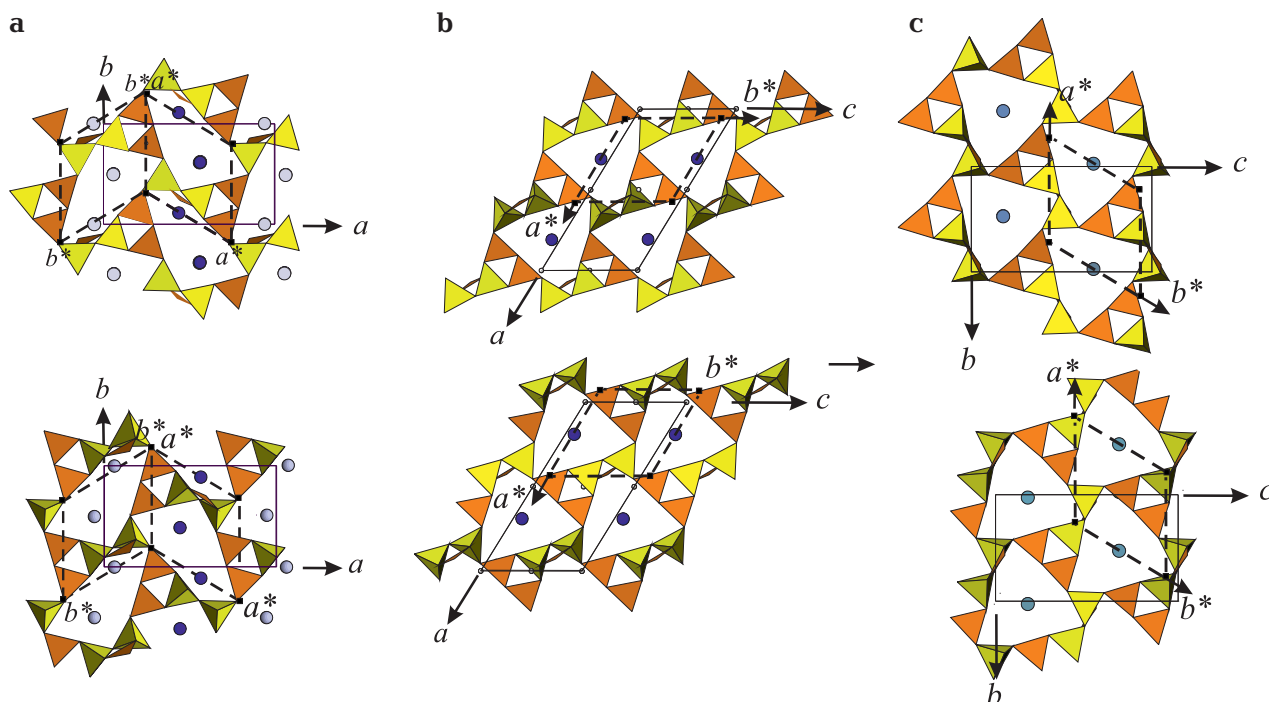


Fig. 6. Alternation of layers at two levels in the structures: a – biringuccite, b – gowerite, and c – nasinite. Dashed lines represent blocks.

found in the structure of biringuccite, $\text{Na}_4[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O} = \{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{Na} \cdot \text{H}_2\text{O}\}_2$, the base of which (Fig. 5b) is also composed of three-layer stacks (two boron-oxygen sheets, between which Na1- and Na2-cations are enclosed). In this case the three-layer stacks have a negative charge, which is compensated for by additional Na^+ (Na3 and Na4) cations entering into the interstitial space with H_2O -molecules. As a result, the polyhedra, around the Na3 and Na4 cations are combined via common O-vertices and edges, with the Na1- and Na2-polyhedra of a three-layer stack in a three-dimensional framework. This leads to a strong distortion of the sodium-boron-oxygen network in the biringuccite structure (Fig. 6a). Unlike the structures of divalent cation pentaborates, $[\text{B}_2^t\text{B}_3^a\text{O}_8(\text{OH})]^{2-}$ pentagroups in the biringuccite sheet are connected not by horizontal translations, as in the above-described structures, but by reflection in pseudoplanes (a), which are located on levels $y \sim 0$ and $\sim 1/2$ and which alternate with planes (c) of the mineral's true symmetry. Despite these differences, one can also separate a building block, similar by its metric characteristics and composition: a pseudo-hexagonal triclinic cell (Table 1) with the formula $\{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{Na} \cdot \text{H}_2\text{O}\}_2$, within the mineral structure. Atoms in the separated blocks have connected with true inversion centers, while in blocks adjacent to the **a** axis, a similar arrangement of the atoms

inverts the positions of Na3-, Na4-atoms and H_2O molecules in the interstices. There are four such blocks alternating in the structure: adjacent blocks along the **b** axis have connected by translation, and those adjacent along the **a** axis, by reflection in **a** pseudoplanes.

The analysis of atomic distances which was carried out above in hypothetical structures established a small probability of a structure model with the composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ with two additional interstitial B-triangles. Such a ratio of cations and isolated B-triangles, together with the trebled quantity of H_2O -molecules in comparison with the synthetic pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ is found in the gowerite structure $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot [\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}$, the basis of which is formed from a non-polar (with various orientations of apical B-triangles) calcium-boron-oxygen sheets (Fig. 5c), not connected to each other. The mechanism of such a transition from the veatchite-similar structure can be presented as follows: as H_2O -molecules and $\text{B}(\text{OH})_3$ isolated triangles are increased in the interstitial space, a reversal of some pentagroups with inversion of apical B-triangles of boron-oxygen networks occurs, leading to "destruction" of three-layer stacks and bonding of structures with non-polar sheets. In this structure, following the principles described above, it is also possible to separate the block with nodes in specific points on the planes (a),

corresponding to the composition $\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot [\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}$, where the first part of the formula corresponds to the calcium-boron-oxygen sheet composition, and the second one to the interstitial space occupation.

There are four blocks in the gowerite unit cell, connected by symmetry elements of the $P2_1/a$ space group. Sheets, similar to those of gowerite, are also present in the structure of nasinite $\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$ (Fig. 5d), in the composition of which a doubled number of H_2O -molecules occurs, in contrast to biringuccite $\text{Na}_4[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O} = 2 \times \{\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}\}$. In the structure of nasinite, as well as in that of biringuccite, a negative charge of sodium-boron-oxygen networks is compensated by entry of additional Na together with two H_2O molecules to the interstitial space. As in biringuccite, sheet and interstitial Na-polyhedra forms the framework. The possible mechanism of structural transition of biringuccite – nasinite is similar to that for gowerite, as described above. In the nasinite structure, using special points on clinoplates (n), it is possible to separate the block of composition $\{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{\text{Na} \cdot 2\text{H}_2\text{O}\}$: there are 4 blocks in the unit cell, connected by reflection in the planes (n) and (a) of the $Pna2_1$ space group. In the gowerite and nasinite structures, the hexagonal configuration of boron-oxygen layers with cations in triangular nests remains similar to veatchite, with Ca in the gowerite structure (Fig. 6b) and Na in nasinite (Fig. 6c). Metric characteristics of the blocks, separated by special points, are comparable to similar parameters in other veatchite-like structures (Table 1). In the separated blocks of the gowerite and nasinite structures, the arrangement of atoms and their quantity differs from that of the veatchite-like structures. In the gowerite and nasinite structure blocks, the volume of which is comparable with that of veatchite, there are half as many atoms in the cation-boron-oxygen network and twice as many in the interstitial space. This corresponds to a looser structures, in which cation-boron-oxygen networks do not unit into three-layer stacks, but evenly alternate with interstitial space.

Conclusions

The comparative crystal chemical analysis of minerals of the veatchite group and related natural and synthetic compounds has

allowed us to separate the module – block $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) as the fundamental construction unit with specific metric characteristics and atomic arrangement. Testing the hypothetical structures – constructed on the basis of this block has shown that theoretically the most probable basic model of the veatchite-like pentaborate polytypes with polar boron-oxygen sheets is the structure of composition $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{H}_2\text{O}\}_2$ with a triclinic scalene unit cell and symmetry (i). This model, found in two Ba-pentaborate structures as the *MDO*-polytype, is the fundamental building block for synthetic Ca-pentaborate $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$, in which structure the blocks neighboring on horizontal axes are connected by translational motion, and those, adjacent along a vertical axis are connected by operation of true elements of symmetry. Scalene translation along the T_v direction, perpendicular to the plane of boron-oxygen sheets, providing a certain shift of three-layer stacks from each other, apparently, is a necessary condition of a stable structure obtaining (as in this case an interstitial volume, sufficient for displacement of two water molecules, has created). Therefore, the existence of monoclinic *MDO*-polytypes of a similar composition and structure, the symmetry of which follows the space group $P11n$ and $P12_11$, is improbable: there are no examples of structures built of blocks of this kind among known veatchite-like natural and synthetic phases. The structures formed of blocks $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ with close metric characteristics, but with mixed interstitial filling and with " g " and " 2_1 " symmetry and a non-crystallographic glide component, are the most widespread. A block with " g " symmetry, found in the structure of the investigated Ca-pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ is a basic model for the volkovskite and p -veatchite structures, and a block of similar composition, with symmetry " 2_1 ", is a basic model for the veatchite and triclinic veatchite-1A structures.

Variations in the composition of the separated block lead to transformation of the veatchite structure and the appearance of new structural types. The structures of volkovskite and biringuccite, in which polarity of boron-oxygen sheets and the "three-layer stack" character of the veatchite structure remains, can be considered as transition forms to the structures of gowerite and nasinite, with non-polar boron-oxygen sheets.

Thus, in all the structures derived from veatchite, the fundamental building block remains, which is comparable to the structure and parameters with that of veatchite, which allow to assume a genetic linkage of the specified groups minerals.

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