

CRYSTAL STRUCTURE OF URALBORITE $\text{Ca}_2[\text{B}_4\text{O}_4(\text{OH})_8]$

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The mineral uralborite,¹ a hydrated calcium metaborate, was discovered and described by Malinko in 1961 [1]. She was kind enough to make it available to the crystal chemistry laboratory of the All-Union Scientific-Research Institute of Mineral Raw Materials for detailed structural analysis. The presence of another calcium metaborate, vimsite [2], was detected in the given samples after careful x-ray study.

The fact that vimsite was found with uralborite makes one doubt the chemical analysis of the latter given in [1]. After repeated microchemical analysis of uralborite (T. I. Stolyarova, chemical laboratory of All-Union Scientific-Research Institute of Mineral Raw Materials), it was concluded that the chemical formula of the mineral $\text{CaB}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with the ratio $\text{CaO} : \text{B}_2\text{O}_3 : \text{H}_2\text{O} = 1 : 1 : 2$, which is derived from the full chemical analysis (wt. %): SiO_2 4.00, Al_2O_3 1.12, Fe_2O_3 2.13, CaO 35.27, MgO 0.67, B_2O_3 38.06, H_2O^+ 19.08, $\Sigma = 100.33\%$, was correct, and it was used as the basis for a detailed x-ray study.

The parameters of the monoclinic cell, as refined by the powder method (RKU-114) are: $a = 6.92 \pm 0.01 \text{ \AA}$; $b = 12.35 \pm 0.02 \text{ \AA}$; $c = 9.80 \pm 0.02 \text{ \AA}$; $\beta = 83^\circ$. At specific weight $d = 2.60 \text{ g/cm}^3$ the cell contains $z = 8$ units of $\text{CaB}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

The main experimental material for the structural interpretation of uralborite was obtained from the development of the layer lines (Weissenberg photographs with Mo radiation) around the a , b , and c axes: $0kl - 5kl$, $hk0$, $hk1$, $h0l$, $h1l$ (max $\sin \theta / \lambda = 0.95 \text{ \AA}^{-1}$). The intensities of the reflections were determined from a standard $\sqrt{2}$ blackening scale. Systematic extinctions on the developments pointed clearly to the Fedorov group $C_{2h}^5 = P2_1/n$. The structure of uralborite, just as that of vimsite [3], was resolved in accordance with the previous-

ly calculated gravity criterion ($r' = 1, 2$) by the heavy-atom method [4].

Detailed analysis of the Patterson charts $p(uw)$ and $p(vw)$ and the initial syntheses of electron density enabled us to localize the Ca atoms in the xz and yz projections in the common positions. The light O and B atoms were localized from the three-dimensional full and differential syntheses of electron density, which had been made from the coordinates found for the Ca atoms.

The resulting model of the structure was refined by the method of least squares on an M-20 computer in the Moscow University Computation Center according to the programming carried out by Tarnopol'skii and Andrianov [5]. The definitive coordinates of the basal atoms of uralborite (54 parameters) are given in Table 1. The divergence factor R_{hkl} , which corresponds to these coordinates for 1600 independent and zero reflections, is 15.1% ($B = 0.4 \text{ \AA}^2$).

The interatomic distances are shown in Table 2. Considering the valence balance and the empirical chemical formula it follows from them that uralborite, like vimsite, has no "entire" H_2O molecules and the O^{2-} and OH^- groups are separated specifically in the anion fraction.

All the boron atoms in the uralborite structure are in fourfold coordination and form a basic compact group with four B tetrahedra which are crystallographically independent but are bound by the common vertices. As usual, the O atoms are common to two neighboring B atoms, and the eight anions participating in the coordination of only one B (and Ca) are represented by OH^- groups, i.e., the formula of the insular boron-oxygen radical in

¹Named after the Urals, where it was found.

TABLE 1. Coordinates of the Basal Atoms of Uralborite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Ca ₁	0.698	0.259	0.238	O ₈	0.556	0.248	0.729
Ca ₂	0.719	0.401	0.864	O ₉ (OH)	0.517	0.293	0.039
O ₁	0.870	0.072	0.405	O ₁₀ (OH)	0.729	0.399	0.613
O ₂ (OH)	0.585	0.070	0.277	O ₁₁ (OH)	0.851	0.419	0.076
O ₃	0.756	0.097	0.651	O ₁₂ (OH)	0.639	0.455	0.281
O ₄ (OH)	0.576	0.099	0.877	B ₁	0.742	0.008	0.338
O ₅ (OH)	0.913	0.152	0.067	B ₂	0.825	0.153	0.519
O ₆ (OH)	0.852	0.220	0.822	B ₃	0.682	0.164	0.769
O ₇	0.637	0.235	0.484	B ₄	0.597	0.308	0.596

uralborite is $[B_4O_4(OH)_8]^{4-}$. As is seen in Fig. 1, the three B tetrahedra in the boron-oxygen radical form a triple ring similar to the silicon-oxygen ring of $[Si_3O_9]$, while the fourth is joined to it through a common vertex. This radical may be regarded as an interesting characteristic of the structure of uralborite and, primarily, as a new radical of tetrahedra not known earlier; the discovery of this radical changes the position of uralborite in the classification of borates. Despite the earlier classification [6, 7], which related it to the chain group, it comes under the category of insular groups. The addition (external) of the fourth tetrahedron to the triple ring did not change the meta-character of the radical $[B_3+O_{12}] = [BO_3]_4$.

Two independent Ca atoms are located at the eight vertices of dodecahedra which are approximately equal in volume. These delta-dodecahedra (all the faces are triangles) are joined through the

common edge into pairs which, being subordinated to the clino-plane n at two levels, extend along the long diagonal ($a + c$) of the (010) projection into an endless band; the neighboring pairs in the band are also connected through the common edges. This band is connected through the vertices on both sides in the direction of the diagonal ($a - c$) with two translationally identical bands, forming an endless layer of Ca polyhedra (Fig. 2). For the period $b = 12.34 \text{ \AA}$ there are two such layers at levels $y = 1/4$ and $y = 3/4$, which form the "engineering" foundation of the structure. The layers of Ca polyhedra in uralborite remind one of the layers of Sc octahedra with the corundum pattern, six-member loops in the thortveitite structure [8, 9]. The boron-oxygen radicals $[B_4O_4(OH)_8]^{4-}$ are inscribed in the sixfold rings of the Ca polyhedra, cementing and being joined to them through the common edges (in two levels of the Ca polyhedra along a pair of very short edges, Table 2) and common vertices. The section of the structure perpendicular to the a axis (Fig. 3) clearly shows the cementing of the

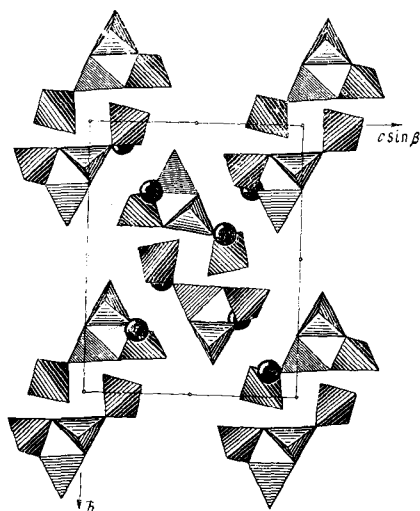


Fig. 1. Uralborite, the yz projection. The oxygen tetrahedra are shown. The spheres denote the Ca atoms of the cell.

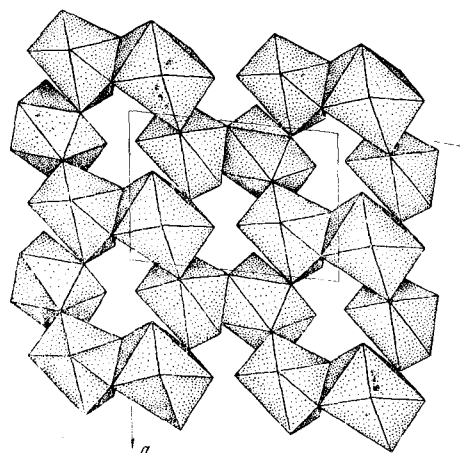


Fig. 2. Uralborite. Layers of Ca polyhedra.

TABLE 2. Interatomic Distances in the Structure of Uralborite (Å)

B ₁ tetrahedron		B ₂ tetrahedron	
B ₁ —O ₂ (OH)	1.51	B ₂ —O ₃	1.49
B ₁ —O ₁	1.41	B ₂ —O ₇ *	1.46
B ₁ —O ₁₂ (OH)*	1.50	B ₂ —O ₁	1.50
B ₁ —O ₁₁ (OH)*	1.49	B ₂ —O ₉ (OH)*	1.52
O ₁ —O ₂ (OH)	2.47	O ₃ —O ₇ *	2.45
O ₁ —O ₁₂ (OH)*	2.39	O ₃ —O ₁	2.46
O ₁ —O ₁₁ (OH)*	2.43	O ₃ —O ₉ (OH)	2.41
O ₂ (OH)—O ₁₁ (OH)*	2.33	O ₇ *—O ₁	2.45
O ₂ (OH)—O ₁₂ (OH)*	2.42	O ₇ *—O ₉ (OH)	2.43
O ₁₁ (OH)*—O ₁₂ (OH)*	2.39	O ₁ —O ₉ (OH)	2.42
Average			
B ₁ —O(OH)	1.48	B ₂ —O(OH)	1.49
O—O(OH)	2.41	O—O(OH)	2.44
B—O—B angles			
B ₁ —O ₁ —B ₂	129°8'	B ₂ —O ₃ —B ₃	117°40'
B ₃ tetrahedron		B ₄ tetrahedron	
B ₃ —O ₈	1.47	B ₄ —O ₁₀ (OH)	1.47
B ₃ —O ₆	1.44	B ₄ —O ₇ *	1.50
B ₃ —O ₆ (OH)	1.51	B ₄ —O ₈	1.50
B ₃ —O ₄ (OH)	1.46	B ₄ —O ₅ (OH)	1.43
O ₃ —O ₈	2.40	O ₁₀ (OH)—O ₇ *	2.43
O ₃ —O ₆ (OH)	2.42	O ₁₀ (OH)—O ₈	2.42
O ₃ —O ₄ (OH)	2.41	O ₁₀ (OH)—O ₅ (OH)	2.37
O ₆ —O ₈ (OH)	2.37	O ₇ *—O ₈	2.47
O ₆ —O ₄ (OH)	2.36	O ₇ *—O ₅ (OH)	2.42
O ₆ (OH)—O ₄ (OH)	2.43	O ₈ —O ₅ (OH)	2.33
Average			
B ₃ —O(OH)	1.47	B ₄ —O(OH)	1.50
O—O(OH)	2.40	O—O(OH)	2.41
B—O—B angles			
B ₃ —O ₇ *—B ₄	117°30'	B ₃ —O ₈ —B ₄	122°7'
Ca ₁ polyhedron		Ca ₂ polyhedron	
Ca ₁ —O ₂ (OH)	2.48	Ca ₂ —O ₈	2.64
Ca ₁ —O ₇	2.41	Ca ₂ —O ₆ (OH)	2.43
Ca ₁ —O ₉ (OH)	2.48	Ca ₂ —O ₁₀ (OH)	2.45
Ca ₁ —O ₅ (OH)	2.49	Ca ₂ —O ₃ *	2.43
Ca ₁ —O ₁₁ (OH)	2.68	Ca ₂ —O ₁₁ (OH)	2.38
Ca ₁ —O ₈ *	2.47	Ca ₂ —O ₂ (OH)	2.59
Ca ₁ —O ₁₂ (OH)	2.48	Ca ₂ —O ₁ *	2.42
Ca ₁ —O ₆ *	2.41	Ca ₂ —O ₉ (OH)	2.49
O ₂ (OH)—O ₉ (OH)	3.68	O ₈ —O ₆ (OH)	2.37**
O ₂ (OH)—O ₆ (OH)	3.06	O ₈ —O ₁₀ (OH)	2.42**
O ₂ (OH)—O ₇	3.02	O ₈ —O ₃ (OH)	3.06
O ₂ (OH)—O ₈	3.94	O ₈ —O ₁	3.01
O ₂ (OH)—O ₅ (OH)	3.05	O ₆ (OH)—O ₁₀ (OH)	3.20
O ₅ (OH)—O ₈ *	2.33**	O ₆ (OH)—O ₂ (OH)*	3.06
O ₅ (OH)—O ₉ (OH)	3.29	O ₆ (OH)—O ₁₁ (OH)	3.50
O ₅ (OH)—O ₁₁ (OH)	3.33	O ₆ (OH)—O ₉ (OH)	3.08
O ₁₁ (OH)—O ₉ (OH)	2.85	O ₉ (OH)—O ₁₁ (OH)	2.87
O ₁₁ (OH)—O ₈ *	3.01	O ₉ (OH)—O ₁ *	2.42**
O ₁₁ (OH)—O ₁₂ (OH)	2.39**	O ₁₁ (OH)—O ₁ *	3.90
O ₁₂ (OH)—O ₇	3.41	O ₁₁ (OH)—O ₂ (OH)*	3.17
O ₁₂ (OH)—O ₈ *	3.81	O ₁ *—O ₁₀ (OH)	3.57
O ₁₂ (OH)—O ₆ (OH)	2.90	O ₂ (OH)*—O ₁₀ (OH)	3.13
O ₁₂ (OH)—O ₉ (OH)	3.29	O ₃ *—O ₂ (OH)*	3.14
O ₇ —O ₈ *	3.35	O ₃ *—O ₁₀ (OH)	3.38
O ₇ —O ₆ (OH)	2.98	O ₃ *—O ₁ *	3.31
O ₉ (OH)—O ₆ (OH)	2.86	O ₃ *—O ₁₁ (OH)	3.27
Average			
Ca ₁ —O(OH)	2.49	Ca ₂ —O(OH)	2.48
O—O(OH)	3.15	O—O(OH)	3.21

*Atoms which are connected with the corresponding basal atoms by the symmetry elements of the group.

**The common edges are shortened in accordance with the Pauling rule.

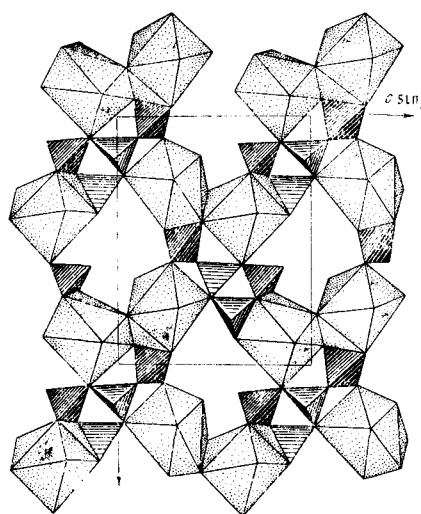


Fig. 3. Uralborite. Section $x = 1/4$. The geometry of the joining of the Ca polyhedra through boron-oxygen radicals in the direction of the b axis.

two layers by the B tetrahedra into a three-dimensional structure. The mutual binding of the layers through the boron-oxygen groups is so strong that, despite the layered position of the Ca polyhedra, there is no cleavage in the mineral. In accordance with the interpretation of its structure, the mineral's formula is $\text{Ca}_2[\text{B}_4\text{O}_4(\text{OH})_8]$.

LITERATURE CITED

1. S. V. Malinko, *Zap. Vsesoyuzn. Mineralog. Obshch.*, Part 90, No. 6 (1961).
2. D. P. Shashkin, M. A. Simonov, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, **182**, 821 (1968) [*Sov. Phys.-Dokl.*, **13**, 974 (1969)].
3. D. P. Shashkin, M. A. Simonov, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, **182**, No. 6 (1968).
4. M. A. Simonov, Candidate's Dissertation, *Crystal Structure of Sodium-Cadmium Silicates* [in Russian] (1969).
5. B. L. Tarnopol'skii and V. I. Andrianov, *Zh. Struk. Khim.*, **4**, No. 3, 434 (1963).
6. G. B. Bokii and V. B. Kravchenko, *Zh. Struk. Khim.*, **7**, No. 6 (1966).
7. A. S. Povarennykh, *Crystallochemical Classification of Mineral Types* [in Russian], Kiev (1966).
8. N. V. Belov, *Crystal Chemistry of the Silicates with Large Cations* [in Russian], *Izd. Akad. Nauk SSSR* (1961).
9. W. H. Zachariasen, *Zs. Kristallogr.*, **73**, 1 (1930).