Crystal structure of betalomonosovite

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(Submitted October 4, 1974)
Kristallografiya, 20, 259-264 (March-April 1975)

The crystal structure of betalomonosovite $Na_7Ti_4Si_4P_2O_{23}(OH)_3$ was interpreted by a superposition method. The parameters of the triclinic lattice are as follows: a = 5.34, b = 14.26, c = 14.229 Å, α = 102°33', β = 105°52', γ = 89°06', space group $P\bar{1}$, Z = 2. The model was refined by the method of least squares in 1091 reflections to R_{hkl} = 15.4% (without individual temperature corrections). The structure is related to the lomonosovite structure. A distinguishing feature of the betalomonosovite is the rudimentary phosphorus–oxygen "chains" extending along the short direction of the unit cell.

According to the fairly unanimous statements of chemists and mineralogists,[1-3] betalomonosovite (or "metalomonosovite" according to the terminology given in ref. 1) must be considered to be an independent mineralogical form in the group of minerals headed by lomonosovite or murmanate. The similarity between betalomonosovite and lomonosovite in chemical composition, lattice parameters, optical characteristics, and certain other physical properties, however, led to the idea of their structural proximity, especially as the powder diagrams of these minerals differ mainly in the distribution of the intensities.

From the idea of the structural analogy between the two minerals a crystal-chemical model of betalomonosovite was proposed in ref. 4, in which the Na-phosphate part is as unstable as in the lomonosovite structure. From this it followed that the Na-phosphate component should be leached out from betalomonosovite as easily as from lomonsovite, and this was contradicted by the results.[5] Moreover, the structural solution proposed in ref. 4 does not agree with data from chemical analysis,[6] which primarily do not confirm the presence of trivalent titanium in minerals of the lomonosovite group and do not make it possible to isolate Mn (with a content of 0.4-2.3%) in an independent unit of the crystal-chemical formula of betalomonosovite. From the spectroscopic data[2] it follows that the position of phosphorus in betalomonosovite and lomonosovite differs in character and that $[P_2O_7]$ groups are not present in the two minerals in pits of its supposed existence in the models.[4] To investigate the differences between the structures of betalomonosovite and the previously interpreted[7] lomonosovite we undertook a full structural interpretation of betalomonosovite.

On 0kl -3kl scans obtained on an x-ray goniometer with Mo radiation 1091 independent zero reflections were recorded with their intensities, measured on a $2^{1/4}$ scale of blackness standards. The pseudoperiodicity detected on the oscillation x-ray patterns about the b axis and on the 1kl-3kl scans indicated the need (contrary to refs. 1, 4) to double the constant b. Thus, the triclinic unit-cell parameters of betalomonosovite, obtained from the rotational x-ray patterns and long-range reflections on zero Weissenberg patterns (0kl and h0l), have the following values: a = 5.34, b = 7.13 × 2 = 14.26, c = 14.229 Å, α = 102°33', β = 105°52', γ = 89°06°. The absence of a piezoeffect[4] and the character of the curve for the distribution of the experimental intensities, calculated according to ref. 8, showed that two space groups P1 and $P\bar{1}$ are possible. Interpretation of the structure in the noncentrosymmetric variant showed the expediency of changing to $P\bar{1}$, which had been established earlier for lomonosovite.[7] (In ref. 4 the P1 group was adopted for both structures.)

The IR spectroscopic data[2] make it possible to suppose that the individuality of betalomonosovite is determined not by the "murmanite" component but by the "lomonosovite" component (the space between the stacks), which undergoes substantial changes. The interpretation confirmed this supposition. The three-dimensional Patterson function and its P(uw) and P(vw) projections differ from those for lomonosovite by the greater diffuseness of the peaks and the redistribution of their weights. The struc-

TABLE 1. Coordinates of Basis Atoms of Betalomonosovite

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ti_1	0.778	0.312	0.008	O_6	0.530	0.401	0.934
Ti_2	0.245	0.189	0.992	O_7	0.966	0.416	0.096
Ti_3	0.058	0.477	0.221	O_8	0.067	0.077	0.917
Ti_4	0.936	0.024	0.777	O_9	0.826	0.086	0.216
P_1	0.158	0.131	0.445	O_{10}	0.219	0.446	0.781
P_2	0.728	0.736	0.518	O_{11}	0.577	0.233	0.239
Si_1	0.559	0.329	0.199	O_{12}	0.434	0.278	0.778
Si_2	0.453	0.173	0.801	O_{13}	0.865	0.370	0.246
Si_3	0.518	0.118	0.181	O_{14}	0.188	0.106	0.749
Si_4	0.484	0.388	0.819	O_{15}	0.278	0.074	0.206
Na_1	0.800	0.050	0.010	O_{16}	0.690	0.434	0.774
Na_2	0.143	0.452	0.977	O_{17}	0.353	0.400	0.238
Na_3	0.103	0.236	0.264	O_{18}	0.673	0.121	0.757
Na_4	0.930	0.258	0.750	O_{19}	0.169	0.025	0.376
Na_5	0.829	0.141	0.622	O_{20}	0.828	0.460	0.638
Na_6	0.660	0.478	0.375	O_{21}(OH)	0.208	0.228	0.430
Na_7	0.342	0.003	0.637	O_{22}	0.814	0.290	0.596
O_1	0.481	0.300	0.081	O_{23}	0.895	0.123	0.466
O_2	0.522	0.191	0.915	O_{24}(OH)	0.414	0.379	0.532
O_3	0.983	0.209	0.061	O_{25}(OH)	0.832	0.366	0.464
O_4	0.003	0.279	0.923	O_{26}	0.390	0.130	0.533
O_5	0.404	0.099	0.066				

TABLE 2. Interatomic Separations in the Betalomonosovite Structure (Å)

Ti_1 octahedron	Ti_2 octahedron	Ti_3 octahedron	Ti_4 octahedron	Na_1 polyhedron	Na_2 polyhedron	Na_3 polyhedron	Na_4 polyhedron
Ti_1-O_7 1.81	Ti_2-O_8 1.83	Ti_3-O_7 1.74	Ti_4-O_8 1.91	Na_1-O_8 2.28	Na_2-O_7 2.29	Na_3-O_{13} 2.31	Na_4-O_{22} 2.25
Ti_1-O_4 1.91	Ti_2-O_5 1.88	Ti_3-O_{10} 1.83	Ti_4-O_{15} 1.91	Na_1-O_8 2.29	Na_2-O_7 2.34	$Na_3-O_{21}(OH)$ 2.31	Na_4-O_4 2.34
Ti_1-O_3 1.98	Ti_2-O_3 1.90	Ti_3-O_8 1.84	Ti_4-O_{18} 1.97	Na_1-O_5 2.30	Na_2-O_6 2.37	Na_3-O_9 2.48	Na_4-O_{18} 2.44
Ti_1-O_5 2.06	Ti_2-O_1 2.00	Ti_3-O_{17} 1.89	Ti_4-O_{14} 1.98	Na_1-O_3 2.37	Na_2-O_4 2.47	Na_3-O_{15} 2.52	Na_4-O_{14} 2.55
Ti_1-O_1 2.14	Ti_2-O_4 2.02	Ti_3-O_{20} 1.95	Ti_4-O_9 2.00	Na_1-O_5 2.50	Na_2-O_6 2.61	Na_3-O_{11} 2.64	Na_4-O_{12} 2.62
Ti_1-O_2 2.17	Ti_2-O_2 2.07	Ti_3-O_{13} 2.00	Ti_4-O_{19} 2.05			Na_3-O_3 2.72	Na_4-O_{12} 2.79
						Na_3-O_{11} 2.74	Na_4-O_{16} 2.79
						Na_3-O_{17} 2.85	Na_4-O_{10} 3.00

Si_1 tetrahedron	Si_2 tetrahedron	Si_3 tetrahedron	Si_4 tetrahedron	Na_5 polyhedron	Na_6 polyhedron	Na_7 polyhedron
Si_1-O_{11} 1.57	Si_2-O_2 1.53	Si_3-O_5 1.54	Si_4-O_{12} 1.55	Na_5-O_{22} 2.23	Na_6-O_{17} 2.26	Na_7-O_{23} 2.21
Si_1-O_1 1.59	Si_2-O_{18} 1.57	Si_3-O_{15} 1.59	Si_4-O_6 1.55	Na_5-O_{23} 2.30	$Na_6-O_{24}(OH)$ 2.27	Na_7-O_{14} 2.24
Si_1-O_{17} 1.61	Si_2-O_{12} 1.60	Si_3-O_{11} 1.66	Si_4-O_{16} 1.62	Na_5-O_{26} 2.33	$Na_6-O_{25}(OH)$ 2.27	Na_7-O_{18} 2.46
Si_1-O_{13} 1.65	Si_2-O_{14} 1.61	Si_3-O_9 1.67	Si_4-O_{10} 1.65	Na_5-O_{18} 2.36	Na_6-O_{13} 2.61	Na_7-O_{26} 2.63
				Na_5-O_{19} 2.37	Na_6-O_{20} 2.71	Na_7-O_{19} 2.69
				Na_5-O_{14} 2.38	Na_6-O_{19} 2.91	Na_7-O_{19} 2.71
					Na_6-O_{18} 2.92	Na_7-O_{15} 2.97
					Na_6-O_{29} 2.96	Na_7-O_9 3.00

P_1 tetrahedron		P_2 tetrahedron	
$P_1-O_{21}(OH)$	1.49	P_2-O_{20}	1.44
P_1-O_{26}	1.50	P_2-O_{22}	1.46
P_1-O_{23}	1.52	$P_2-O_{25}(OH)$	1.57
P_1-O_{19}	1.62	$P_2-O_{24}(OH)$	1.62

ture was interpreted by a superposition method on the basis of the "Kristall" set of programs.[9,10] The search for the shift vectors required for construction of the minimum function was realized by means of the programs in ref. 11. Twenty six-atom fragments, which agree with the Patterson distribution with the point peaks coinciding with an accuracy of ~ 0.25 Å, were found among the 50 strongest peaks for the interatomic vectors. Analysis of the isolated fragments by the method in ref. 11 led to one independent four-atom variant, which was used to construct a fourth-rank minimum function. The obtained fragment of the structure coincided with lomonosovite and contained two vectors between the Ti atoms and one each between Ti−Si and Ti−O. Maxima of all the cations appeared on a superposition synthesis, constructed after inversion of the Fourier function.[9] By the electron density function calculated from the coordinates of these cations with the origin of the coordinates of Ti_1 it was possible to localize the 22 O atoms. The remaining four O anions were localized on the electron density syntheses after refinement of the model by the method of least squares. Without allowance for individual temperature corrections the obtained discrepancy factor R_{hkl} was 15.4%. (A correction for absorption was not made during the calculation of the structure amplitudes on account of the irregular form of the sample.) The final atomic coordinates are given in Table 1 (the origin of the coordinates was transposed for convenience in comparison with the data for lomonosovite), and the corresponding interatomic separations are given in Table 2.

As seen from Figs. 1 and 2, of the two pairs of titanium atoms related by the pseudocenter one lies at the "core" of a triple mica-like stack, and the second lies in its armor network ("chain mail"). In view of the increased weight of the peaks on the electron density map for the Ti_3-Ti_4 pair it can be considered that the Ti_1 and Ti_2 atoms are "pure," whereas Ti_3 and Ti_4 are isomorphously substituted by Zr, Nb, Mg, Fe, and Mn, which are distributed statistically among these positions in the unit cell.

Of the five pairs of Na atoms found in lomonosovite[7] three pairs are retained in the independent part of the betalomonosovite cell, i.e., one (Na_1 and Na_2) in the core, a second (Na_3 and Na_4) in the chain mail, and a third (Na_6 and Na_7) in the space between them. In addition the unpaired atom Na_5 is situated in the space between the stacks, disrupting the centrosymmetry of the betalomonosovite subcell. The oxygen polyhedra around all the Na atoms are of irregular form. The Na_1 and Na_2 polyhedra are to a first approximation reminiscent of the Na octahedra extended along the b axis in the walls of lomonosovite, but the cations are largely displaced towards one vertex and have lost their bond with the second. The distances from

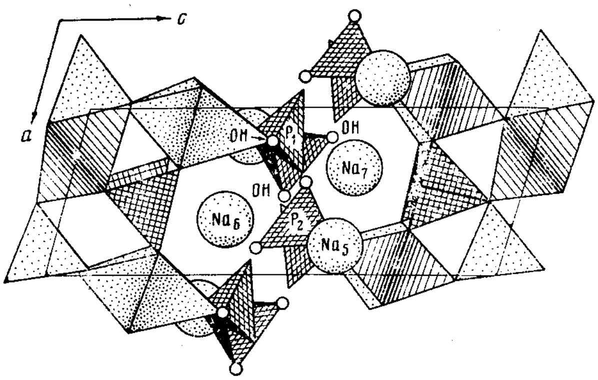

Fig. 1. Projection of the betalomonosovite structure onto the xz plane in Pauling polyhedra. In Figs. 1 and 2 the positions of the Na_5, Na_6, and Na_7 atoms and OH groups are shown by circles.

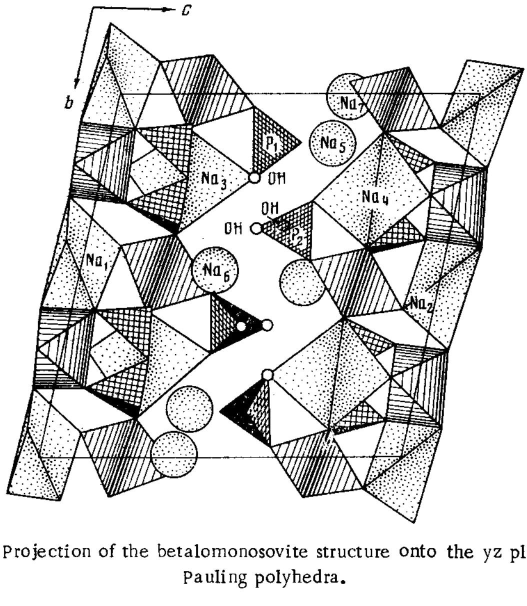

Fig. 2. Projection of the betalomonosovite structure onto the yz plane in Pauling polyhedra.

Na_1 and Na_2 to the vertices of the semioctahedra (tetragonal pyramids) are 2.28-2.50 and 2.29-261 Å, respectively, whereas the distances to the "withdrawn" sixth vertex are 2.84 Å in one octahedron and 3.15 Å in the other. The loose eight-cornered polyhedra around Na_3 and Na_4 very exactly repeat the hexagonal bipyramids in the "chain mail" of lomonosovite. The unpaired Na_5 atom lies at the center of a compact but strongly distorted octahedron. (The corresponding polyhedron in lomonosovite has five corners.) The Na_6 and Na_7 pair with coordination number 8 lies in extensive cavities, which represent a combination of trigonal prisms and two pyramidal caps. (In lomonosovite they correspond to octahedra.)

A distinctive feature of the betalomonosovite structure is the "rudimentary chains" (according to the terminology in ref. 12), formed by P tetrahedra and extending along the short direction of the unit cell (Fig. 1). One of the P tetrahedra (the P_2 orthotetrahedron) occupies a position analogous to that in lomonosovite, and the second (P_1) is turned towards the opposite side and links the two adjacent translationally identical P_2 orthotetrahedra in a phosphorus–oxygen chain. As seen from the yz projection (Fig. 2), the links of the chain are isolated tetrahedra connected by hydrogen bonds. A similar rudimentary phosphorus–oxygen chain has been described[12] in $Ca(H_2PO_4)_2$. In the unit cell of betalomonosovite there are two such undulating chains, related by a center of symmetry. The linkage of the isolated P tetrahedra into chains proved possible for the betalomonosovite structure on account of the greater compactness of the space between the stacks (shortening of the constant c by 0.6 Å), the decrease in the number of Na atoms compared with lomonosovite, and the presence of water.

The balance of valences according to Pauling indicates a considerable deficiency of valence forces converging at the free vertices of the P_2 tetrahedron (1.41 and 1.41) and at the bridging O atom common to the P_2 tetrahedron and the large Na polyhedron (1.37). Such a situation does not arise in the lomonosovite structure on account of the contribution from the three additional Na atoms. The presence of water in the mineral in the form of OH groups (according to chemical and thermal analyses[1,2]) makes it possible to suppose that the O_{21}, O_{24}, and O_{25} atoms are substituted by OH groups. The insertion of OH groups into the small tetrahedra has now become the usual feature in hydrated borates (uralborite, vimsite, kurnakovite, etc.) and in hydrated phosphates.[13,14]

Thus, the composition of the layer between the stacks, obtained from the structural analysis, agrees completely with the data in ref. 2, where it was described as a double anhydrous sodium phosphate $Na_2HPO_4 \cdot NaH_2PO_4$ or $Na_3H_3 \cdot PO_4)_2$.

Substitution of two O atoms by the OH group led to considerable distortion of the P tetrahedron: $P_2-O = 1.44$-1.62 Å. As indicated in ref. 13, these values are typical of disubstituted $[PO_2X_2]^{-1}$ groups.

From chemical analysis of the mineral with density[2] 2.90-2.95 g/cm^3 it follows that it is necessary to place the 42 atoms $Na_6Ti_4Si_4P_2O_{22}(OH)_4$ in independent parts of the unit cell. (The other variants of the formula proposed in refs. 1, 3, and 15 differ in the amount of Na, anions, and water.) From our structural analysis it follows that the detailed crystal-chemical formula of betalomonosovite has the form $Na_2Ti_2[Na_2Ti_2Si_4]O_{18}Na_3[PO_3(OH)][PO_2(OH)_2]$ with Z = 2 (86 atoms in the centrosymmetric unit cell).

Thus, the interpretation of the betalomonosovite structure confirms the suggestion put forward in ref. 2 that the more stable position of P and Na in the betalomonosovite structure compared with lomonosovite is explained by hydrogen bonds. The shortened $O_{21}(OH)-O_{24}(OH)$ and $O_{21}{}''(OH)-O_{25}(OH)$ distances of 2.36 and 2.76 Å respectively demonstrate the existence of strong hydrogen bonds between the links of the chain. The initially paradoxical effect that anhydrous lomonosovite $Na_5Ti_2[Si_2O_7][PO_4]O_2$ is decomposed by water more readily than the water-containing betalomonosovite becomes understandable. Our conclusions also agree with the indication[16] that orthophosphates (disubstituted and trisubstituted) as derivatives of tribasic phosphoric acid are insoluble in water and form stable compounds.

The one further distinctive feature of betalomonosovite mentioned in ref. 2, i.e., the existence of imperfect cleavage along $(0\bar{1}2)$, can be explained by the weakness of the bond between the phosphorus–oxygen chains (Fig. 2).

The authors thank V. I. Simonov for constant interest in the work.

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