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Crystal structure of the new native sulfate-carbonate $Na_{25}BaTR_2(CO_3)_{11}(HCO_3)_4(SO_4)_2F_2CI$

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The authors make an x-ray structural study of the new natural Na,Ba,TR-fluoro,chloro-sulfatocarbonate Na₂₅BaTR₂(CO₃)₁₁(HCO₃)₄(SO₄)₂F₂Cl which was discovered by A. P. Khomyakov in Lovozero pegmatites (Syntex PI autodiffractometer, ω -method, R = 0.037, 518 reflections). The parameters of the hexagonal unit cell are: a = 8.811(7), c = 37.03(3) Å, space group $P6_3/m$, z = 2, $d_{calc} = 2.87$ g/cm³. The most probable statistical filling of the TR position (with minimal R index) is $Y_{0.55}Gd_{0.25}Dy_{0.20}$. In the crystal structure the Ba atoms lie in icosahedra, the TR in nine-pointed polyhedra, the Na in five-, six-, and seven-pointed polyhedra joined to the SO₄ tetrahedra; the F⁻ and Cl⁻ anions also form blocks parallel to the (0001) layers, the alternation of which along the c axis leads to a mixed framework structure.

The new natural Na, Ba, *TR*-fluoro, chloro-sulfatecarbonate was discovered by A. P. Khomyakov in Lovozero pegmatites in the interstices of the crystals of potassium feldspar together with nahcolite, trona, thermonatrite, sidorenkite, neiborite, aegirine, albite, cleiophane, etc.¹ The mineral forms irregular grains up to 0.5-1 cm in size, yellow-green, transparent, with a vitreous luster, perfect cleavage along (0001), $H \approx$ 4, stable in water, decomposing with effervescence in dilute solutions of various acids. From the results of quantitative electron-probe analysis we calculated the chemical formula of the mineral Na₅₁Ba₂*TR*₄^{*} (CO₃, HCO₃, OH, F, SO₄, Cl)_x, $x \approx$ 45 ($d_{exp} = 2.85$ g/cm³).

The x-ray diffraction data – the intensities of 518 independent nonzero $(I \ge 1.96\sigma(I))$ reflections (max sin $\theta/\lambda = 0.767 \text{ Å}^{-1})$ – were obtained from a single crystal with linear dimensions $0.075 \times 0.125 \times 0.175 \text{ mm}^3$ on a Syntex $P\bar{1}$ automatic diffractometer by the ω method with variable scanning rate 4-24 deg/min (Mo $K\alpha$ radiation, graphite monochromator). The parameters of the hexagonal unit cell were determined from x-ray oscillation – rotation patterns and scanning of the *hk*0 and *hk*1 layer lines, and refined on the same autodiffractometer: a = 8.811(7), c = 37.03(3) Å. Conversion of the intensities of $|F_{khl}|$ and the subsequent calculations were made on the E-XTL Syntex specialized computing system. The systematic extinctions among 000*l* with $l \neq 2n$ indicted two possible space groups: $P6_3$ and $P6_3/m$.

According to the above expression and analysis of the Patterson function, there was proposed the arrangement of the

Ba atoms in the space group $P6_3/m$ in the 000 positions and TR in the 000, 201 positions (in the first stage we used the atomic scattering curve of Gd). After least-squares refinement of the positional and thermal parameters of these atoms, in the cycle of successive approximations we located the lighter atoms S, Na, O, and C, which reduced R_{hkl} to 0.12. After making a correction for absorption for a crystal of arbitrary shape by means of the NWMAIN program,² the R index was reduced to 0.061. The most probable statistical filling of the TR positions by the cations Y, Gd, and Dy was established by refining the occupancy factor with fixed $B_{iso} = 0.3 \cdot 0.7 \text{ Å}^2$ and subsequent selection of the mixed curves of atomic scattering. The composition Y_{0.55}Gd_{0.25}Dy_{0.20}, corresponding to minimal R_{hkl} , agrees with the results of microprobe analysis. Calculation of the valence balance at the anions justified the exchange of two O atoms for F and Cl, which confirmed the subsequent refinement of the thermal corrections, and of some of the $(CO_3)^{2-}$ groups for $(HCO_3)^{-}$, which agrees with the splitting of the absorption band of the IR spectrum in the region 1300-1400 cm⁻¹. Thus in the concluding step ($R_{aniso} = 0.037$) we formulated the structural formula of the mineral as Na25BaTR2. $(CO_3)_{11}(HCO_3)_4(SO_4)_2F_2Cl (z = 2, d_{calc} = 2.87 \text{ g/cm}^3)$. The concluding coordinates of the basis atoms, the isotropic²) thermal corrections, and the interatomic distances are listed in Tables I and II.

In the crystal structure of the mineral, the Ba atoms, lying in icosahedra, and TR in nine-pointed polyhedra, and the Na in five-, six-, and seven-pointed polyhedra, form three types of







FIG. 1. Projection of structure of Na, Ba, *TR*-sulfate – carbonate on (0001) plane. We mark three types of "layers" at levels $z \approx 0$, 0.5 (a), z = 0.2-0.3 (b), and $z \approx 0.1$, 0.4 (c).



FIG. 2. Alternation of layer –blocks in the structures of Na, Ba, *TR*-fluoro, chloro-sulfate–carbonate Na₂₅Ba*TR*₂(CO₃)₁₁·(HCO₃)₄(SO₄)₂F₂Cl(a), juanite BaCe(CO₃)₂F (b), bayunbite NaBaCe₂(CO₃)₄F (c), donneyite (Na, *TR*)Sr· (CO₃)₂·H₂O (d), and tuliokite Na₆BaTh(CO₃)₆·6H₂O (e).



Atom	x/a	y/b	z	B, Λ^2
Ba	0	0	0	0,48(5)
TR	0	0	0,19842(8)	0,50(3)
S	15	243	0,3930(2)	0,1(2)
Cl	1 13	243	14	0,9(8)
Na1	0,0995(9)	0,4478(9)	0,0333(2)	0,5(1)
Na2	0,0989(9)	0,4497(9)	0,3249(2)	1,1(2)
Na3	И	23	0,6916(3)	0,3(2)
Na4	0,1123(9)	0,6707(9)	0,6064(2)	0,9(2)
Na5	0,357(1)	0,377(1)	14	0,8(2)
Na6	0	0	0,3974(3)	0,7(2)
F	И	2/3	0,5022(5)	0,2(3)
01	0,251(2)	0,113(2)	0,0594(3)	0,7(3)
02	0,224(1)	0,088(1)	0,1509(3)	0,1(2)
03	0,092(2)	0,656(2)	0,7202(3)	0,9(3)
04	0,109(1)	0,466(1)	0,6493(3)	0,5(3)
05	0,186(2)	0,025(2)	14	0,7(4)
06	0,332(1)	0,038(1)	0,5230(3)	0,4(3)
07*	0,150(2)	0,510(1)	0,5591(3)	0,3(3)
08	0,248(1)	0,292(1)	0,3106(3)	0,1(2)
09	0,187(1)	0,496(1)	0,4058(3)	0,9(3)
O10	13	243	0,3519(5)	0,2(6)
C1	0,077(2)	0,348(2)	0,5465(4)	0,3(4)
C2	0,355(3)	0,072(3)	14	0,2(5)
C3	0.069(2)	0,316(2)	0,6628(4)	0,2(4)

TABLE I. Coordinates of Basis Atoms and Individual Isotropic Temperature Corrections

*Oxygen atoms partly replaced by OH groups.

TABLE II. Interatomic Distances (Å)

Ba-icosahedron	TR-nine-vertex polyhedron	Nal-seven-vertex polyhedron	
Ba — 01 2,91(1) × 6 06 2,90(1) × 6 Average 2,90	$\frac{TR - O2 2,46(1) \times 3}{O5 2,45(1) \times 3}$ $\frac{O8 2,42(1) \times 3}{Average 2,44}$	Na1 O1 2,61(1) O6 2,63(1) O6' 2,42(2) O6'' 2,44(1) O7 2,59(2) O9 2,35(1) F 2,38(1) Average 2,49	
Na2-five-vertex polyhedron	Na3-octahedron	Na4-seven-vertex polyhedron	
Na2 - O2 2,57(1) O3 2,23(1) O4 2,48(2) O8 2,40(2) O10 2,22(1) Average 2,38	Na3 — O3 2,34(2) × 3 O4 2,44(1) × 3 Average 2,39	$\begin{array}{c} \text{Na4} & & \text{O1} & 2,42(1) \\ & \text{O2} & 2,45(1) \\ & \text{O4} & 2,40(1) \\ & \text{O4}' & 2,60(1) \\ & \text{O7} & 2,39(1) \\ & \text{O7}' & 2,62(1) \\ & \text{O9} & 2,35(1) \\ & \text{Average} & 2,46 \end{array}$	
Na5-octahedron	Na6-octahedron	S-tetrahedron	
Na5 — Cl 2,67(1) O3 2,56(2) \times 2 O5 2,68(2) O8 2,40(1) \times 2 Average 2,54	Na6 O1 2,47(2) \times 3 O2 2,50(1) \times 3 Average 2,49	$S - O9 1,47(1) \times 3$ O10 1,54(2) Average S - O 1,49 O - O 2,43	
C1-triangle	C2-triangle	C3-triangle	
$\begin{array}{c} C1 - 01 \ 1,32(2) \\ 06 \ 1,23(2) \\ 07 \ 1,31(2) \end{array}$ $\begin{array}{c} C1 - 0 \ 1,285 \\ 0 - 0.2 \ 23 \end{array}$	$C2 - 031,28(2) \times 2$ 051,33(4) Average C2 - 01,295 0223	$\begin{array}{c} C3 - O2 \ 1,30(2) \\ O4 \ 1,29(2) \\ O8 \ 1,32(2) \\ C3 - O \ 1,30 \\ O - O \ 2,36 \end{array}$	



FIG. 3. Interrelationship of coordinate axes of unit cells of Na, Ba, TR, fluoro, chloro-sulfate-carbonate, juanite, bayunbite, donneyite-1, and tuliokite in (0001) projection. The shaded region is the initial cell with parameter $a \approx 5$ Å. Black disks mark positions of large cations, occupied in all the structures; shaded disks mark positions which are vacant or occupied by ions S⁶⁺, Na⁺, F⁻, Cl⁻.

layer blocks, where the denser Ba, Na, CO₃, F "layers" (Fig. 1a) and the twinned *TR*, Na, CO₃Cl blocks (Fig. 1b) alternate along the *c* axes with loose Na, SO₄ "layers" (Fig. 1c). The separate "layers" are joined by common O-vertices, while in the twinned block the pairs of *TR*-nine-pointed polyhedra are joined by a common face lying in the mirror symmetry plane at levels z = 1/4 and 3/4. The isolated SO₄ tetrahedra and the F and Cl atoms, lying on the triad axes, join sets of three Na polyhedra. Alternation of the layers joined by common vertices and faces along the *c* axis creates a mixed framework structure (Fig. 2a).

The structure of Na, Ba, TR-fluoro, chloro-sulfate-carbonate can be regarded as a derivative of the structures of the minerals of the TR-carbonate group, similar in composition and symmetry: juanite BaCe(CO₃)₂F (Ref. 3) (a = 5.070, c =38.408 Å, z = 6, space group R3m), bayunbite NaBaCe₂. $(CO_3)_4F$ (Ref. 4) (a = 5.0875, c = 23.168 Å, z = 2, space group $P6_3/mmc$), and donneyite-1 (Na, TR)Sr(CO₃)₂·H₂O, Ref. 5 (a = 5.211, c = 18.377 Å, z = 3, space group R3m). In the structures of these minerals (Fig. 2b, c, d) along the c axis of the unit cell there alternate layers of large cations Ba²⁺ and TR^{3+} close-packed along the triad and hexad axes, the smaller Na⁺ and anions F^- and the triangles CO_3^{2-} , the planes of which are parallel to (0001). Like our mineral, in the structure of bayunbite the denser Ba, CO₃- and Ce, CO₃-layers alternate with loose Na, F layers, while in the structure of donneyite-1 the dense Sr, CO₃- and (Na, TR)-layers alternate with loose CO₃, H₂O-D-layers with disordered arrangement of the atoms. But in the structure of alkali-free juanite the dense Ba, F, Ce, CO3- and Ba, CO3 layers are uniformly distributed over the whole length of the c axis of the R cell. As seen from Fig. 3, some of the positions occupied by the large cations Ba^{2+} and TR^{3+} in the structures of minerals with parameter $a \approx 5$ Å in the structure of Na, Ba, TR-fluoro, chloro-sulfate-carbonate are either replaced by the lighter S, Na, F, and Cl, or remain vacant, thus increasing the parameter a by a factor of $\sqrt{3}$. With the structures of the above minerals we can also associate the structure of the previously studied Na,Ba,Th-carbonate tuliokite Na₆BaTh(CO₃)₆·6H₂O (Ref. 6) (a = 14.175, c = 8.605 Å, z = 3, space group $R\bar{3}$), in which some of the positions of the large cations are replaced by triads of Na-polyhe dra linked by the 3₁ axis. In this structure (Fig. 2e) layers of close-packed large cations Ba²⁺ and Th³⁺ also alternate along the c axis, but the distance between the centers of the atoms within the layers is longer than the interlayer distances. Thus infinite columns are formed along the c axis, from Th-Ba-Th-icosahedra, on the peripheries of which there are sets of six Na-polyhedra, creating a dense framework structure.

According to Ref. 1, the complex chemical composition of Na, Ba, TR-fluoro, chloro-sulfate-carbonate reflects the multicomponent character of the residual differentiates of the agpaite magmas, and its formula symbolizes the union of the main features of ultraagpaicity – limitingly high alkalinity and enrichment with various volatile and rare elements. The appearance of both Khibiny donneyite and tuliokite minerals, similar to our studied one – concentrators of yttrium and heavy rare earths – is possible with the general cerium characteristics of alkaline rocks in the epithermal stage of formation of ultraagpaite pegmatites, in which there is fixation of the most deficient elements of nepheline-syenite magmas in the solid phases.

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