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THE CRYSTAL STRUCTURE OF TUNDRITE

The mineral tundrite, discovered by E. I. Semenov in the Lovozero alkaline massif (^{1}), is a sodium titanosilicate of the rare earths with sharply pronounced selectivity with respect to cerium. The most reliable chemical analyses of Lovozero and Greenland samples of tundrite are given in Table 1. In addition to the principal elements (Ce, Na, Ti, Si), the mineral contains from 0.7 to 3.2 wt.% CaO, 2.9-6.1 wt.% Nb_2O_5, up to 1% Fe_2O_3, and minor impurities of Th, K, P, etc. The difficulties associated with the variable composition of the mineral and the scatter of the experimental data make, at the first stages of the investigation, only two formulas more probable: $NaTR_2TiSiO_7(OH) \cdot 4H_2O$ or $Na_{3-y}TR_xTi_2Si_2O_{14}(OH)_2 \cdot 8H_2O$.

For triclinic crystals of tundrite–of acicular habit–perfect cleavage along (010) is characteristic. The unit-cell parameters are: $a = 7.57 \pm 0.03$; $b = 13.98 \pm 0.06$; $c = 5.03 \pm 0.02$ Å; $\alpha = 101°30'$; $\beta = 70°25'$; $\gamma = 101°30'$. The difference from the figures given earlier (^{1}) is connected with a certain arbitrariness in the choice of axes in the triclinic lattice. The cell contains one molecule of composition $Na_{3-y}TR_xTi_2Si_2O_{14}(OH)_2 \cdot 8H_2O$. The strong piezoelectric effect must correspond to the Fedorov group $P1$.

Table 1

Chemical analyses of tundrite (wt. %)*

Components	Lovozero	Greenland
Nb_2O_5	2.90	4.26
TiO_2	12.65	10.14
SiO_2	9.67	10.15
ThO_2	0.80	0.70
TR_2O_3	46.75	49.92
Fe_2O_3	0.71	0.46
CaO	3.20	0.74
Na_2O	6.20	6.25
H_2O	15.12	14.85
K_2O	–	1.31

Components	Lovozero	Greenland
	98.00	93.78

* Analyst M. E. Kazakova.

The three-dimensional set of intensities comprised reflections from the layers $hk0$ $-hk4$ and $0kl$–$3kl$ (Weissenberg goniometer, Mo$K\alpha$ radiation, max $\sin\theta/\lambda = 1.2$ Å^{-1}) with a double visual estimate on a $\sqrt[4]{2}$-scale of blackening standards. At the first stage of the analysis no correction for absorption was introduced.

From the distribution of maxima of the three-dimensional Patterson function $P(uvw)$, there first of all followed the presence in the cell of four heavy atoms, identified as Ce. In accordance with the chemical-analysis data, such a conclusion requires isomorphous entry into this quartet of all the impurity Ca, and subsequently we proceed from the formula with $x = 4$: $\mathrm{Na_{3-y}Ce_4Ti_2Si_2O_{14}(OH)_2 \cdot 8H_2O}$.

At the second stage of the analysis, on the constructed distributions of electron density $\sigma(xy)$, $\sigma(yz)$, and $\rho(xyz)$, the average atoms Ti and Si were localized. Their inclusion in the subsequent stages of refinement made it possible to find the lighter Na, O, H_2O. For control and greater confidence, the localization of these atoms was carried out both from the usual projections $\sigma(xy)$ and $\sigma(xz)$, the most effective of which was the first (along the short c axis = 5.03 Å), and from weighted $\sigma^{\cos\,\sin}_{1,2,3}(xyz)$, constructed from the coordinates of Ce, Ti, Si. Satisfactory values of the R-factors without allowance for thermal corrections were: $R_{hkl} = 0.247$; $R_{hk2} = 0.25$; $R_{hk3} = 0.29$–

allowed the model constructed at this stage to be regarded as sufficiently probable.

A curious feature of the model that immediately attracted attention was the layered (parallel to xz) arrangement of the overwhelming number of atoms and the concentration of the smaller Ti^{4+} and Si^{4+} only in one half of the cell. The almost strict periodicity ($\sim 1/12\,b$) in the arrangement of the atomic layers made it possible to choose sections of the three-dimensional $\rho(xyz)$ economically. The remaining unclear details of the structure were specified from difference syntheses $\Delta\rho(xyz)$.

At the stage of structural determination reached, $R_{hkl} = 0.187$ at $B = 1.45$ Å^2 (max $\sin\theta/\lambda = 1.2$ Å^{-1}). The corresponding $R_{hk0} = 0.148$. The coordinates of 35 basis atoms (102 parameters) are given in Table 2.

Table 2

Coordinates of basis atoms in the structure of tundrite

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ce_1	0	0	0	O_5	0.751	0.140	0.478	O_{17}	0.512	0.820	0.385
Ce_2	0.570	0.998	0.677	O_6	0.895	0.135	0.930	O_{18}	0.434	0.833	0.930
Ce_3	0.134	0.446	0.057	O_7	0.197	0.297	0.704	O_{19}	0.931	0.835	0.238
Ce_4	0.688	0.444	0.824	O_8	0.568	0.306	0.458	O_{20}	0.995	0.817	0.692
Ti_1	0.959	0.223	0.593	O_9	0.410	0.459	0.680	O_{21}	0.645	0.996	0.200
Ti_2	0.738	0.223	0.209	O_{10}	0.377	0.374	0.196	O_{22}	0.895	0.998	0.601
Si_1	0.302	0.079	0.315	O_{11}	0.787	0.301	0.921	O_{23}	0.033	0.460	0.606
Si_2	0.382	0.361	0.505	O_{12}	0.934	0.303	0.338	O_{24}	0.791	0.450	0.298
O_1	0.265	0.965	0.147	O_{13}	0.189	0.632	0.396	Na_1	0.340	0.225	0.928
O_2	0.135	0.130	0.343	O_{14}	0.152	0.605	0.900	Na_2	0.477	0.688	0.596
O_3	0.505	0.142	0.165	O_{15}	0.695	0.627	0.166	Na_3	0.190	0.750	0.206
O_4	0.309	0.059	0.650	O_{16}	0.749	0.591	0.626				

In the triclinic cell of tundrite there are 4 heavy atoms Ce^{3+} (plus Ca^{2+}), 3 Na^{1+} cations, 2 each of Ti^{4+} and Si^{4+}, and 24 lighter O^{2-}, $(OH)^{1-}$, and H_2O. The rare-earth cations are accommodated in irregular 9-vertex polyhedra. Tetravalent titanium is true to the coordination most usual for it—octahedral. Silicon is normally surrounded by anions in a tetrahedron. Of the 3 Na cations, one, in the densely occupied part of the cell, is in an octahedron, while the other 2 (in the rather empty half of the cell) are in trigonal prisms.

The interatomic distances are within acceptable limits: in the Si_1-tetrahedron, Si—O is 1.55–1.78 Å, with O—O 2.57–2.76 Å. In the Si_2-tetrahedron, Si—O is 1.51–1.66 Å, with O—O 2.51–2.78 Å. In the fairly regular Ti-octahedra, Ti_1—O is 1.93–2.16 Å and Ti_2—O is 1.87–1.95 Å, respectively. Six neighbors surround Na in a compact sphere with slight deviations from the mean: Na_1—O 2.47 Å, Na_2—O 2.52 Å, and Na_3—O 2.39 Å. The next neighboring anions are farther than 3.0 Å away (3.2–3.68 Å and more). Among the large polyhedra around Ce, the Ce_2-9-vertex polyhedron can be distinguished.

In it, the 9 Ce_2—O distances are divided into two groups. Four distances (the first coordination sphere) are substantially shorter than the other five (the second coordination sphere): 2.29–2.36 Å and 2.71–2.87 Å, respectively, with an average of 2.58 Å. In the remaining polyhedra: for Ce_4, all Ce—O distances are within the narrow range 2.44–2.68 Å; for Ce_1 and Ce_3, only one distance (≈ 2.31 Å) falls out of the ensemble surrounding the central cation approximately uniformly (2.51–2.86 Å—Ce_1-polyhedron and 2.46–2.85 Å—Ce_3-polyhedron).

The clearly expressed layered character of the structure of tundrite appears in Fig. 1. Parallel to the plane (010), at intervals slightly different from $b/2$, are walls of Ce^{3+} (plus Ca^{2+})-polyhedra, which are connected by common edges in the direction of the *a* axis and by common vertices along *c*. The intervals between parallel walls are uneven. In the narrower gaps are placed infinite (parallel ⋯

along the c axis) columns of Ti octahedra of the brookite (columbite) type. Two translationally identical columns are linked to one another by isolated Si orthotetrahedra (Fig. 2). Isolated Na atoms (in octahedra) also act as additional links between the columns. Along the c axis there is an alternation of polyhedra of the same type, empty and filled. As a result, the Ti, Si, and Na polyhedra (-octahedra) combine into a very dense layer—a "core" of "medium" cations (plus Na), armored on both sides by rings of Ce polyhedra (antimica!) and separated from the translationally identical (antimica) packet by a wide corridor (≈ 8 Å) with very poor cationic filling. Not counting the Ce atoms in the corridor walls, along its entire length within the cell there are only two cations (Na_2 and Na_3). Each of them is surrounded by a distorted trigonal prism of 6 H_2O molecules. The occupied Na prisms are joined along horizontal edges into a zigzag chain along the c axis.

Fig. 1. Structure of tundrite in polyhedra. Projection xy. The core is clearly distinguished—a framework of Ti octahedra and Si tetrahedra (linear hatching), and the packet walls on both sides, made of large Ce polyhedra. Empty circles are Na atoms. Arrows denote Na—H_2O bonds in trigonal prisms: solid line—to ligands within the given cell, dashed line—to translationally identical atoms

Tundrite columns of Ti octahedra, fastened by Si tetrahedra and enclosed between walls of large Ce polyhedra, recall the characteristic features of sphene (titanite) $CaTiSiO_5$, with chains of Ti octahedra and with Si orthotetrahedra between the walls of large (Ca) polyhedra. The titanium chains differ in motif (the Ti octahedra have only common vertices), but the Si tetrahedra, as in tundrite, unite neighboring Ti chains into an openwork framework. More essentially, in sphene every corridor between cationic walls is occupied by Ti columns, whereas in tundrite only every second one is.

Fig. 2. Fragment of the structure of tundrite. The titanium-silicon-oxygen framework is the core of the packet in projection onto the xz plane

The available chemical analyses of the mineral give from 2.2 to 2.8 Na atoms per cell, whereas the structural analysis rather convincingly reveals three positions occupied by light cations (Na). The most probable appears to be a statistical distribution of $2 - y$ Na cations (one

Na in the octahedron inside the packet) in the interpacket gap inside prisms made up of H_2O molecules.

The question of identifying the anions, and of distinguishing O, OH, and H_2O, is likewise not solved immediately. The principal argument for the proposed specific solutions was the sums of valence strengths converging on the anions (Table 3). The ligands from the coordination spheres of Si and Ti must be regarded as normal anions O^{2-}.

Table 3

Local balance of valences in the structure of tundrite (without taking bond lengths into account)

Anion	Si^{4+}	Ti^{4+}	Ce^{3+}	Na^{+}	$\Sigma\omega$ /ni
O_1	1.0	–	2$×1/3\|—\|2−1/3\|\|O_{2}$	1.0	2/3
O_3	1.0	2/3	1/3	1/6	2+1/6
O_4	1.0	–	2$×1/3\|1/6\|2−1/6\|\|O_{5}$	–	2$×2/3\|1/3\|—\|2−1/3\|\|O_{6}$
O_8	1.0	2/3	1/3	1/6	2+1/6
O_9	1.0	–	2$×1/3\|—\|2−1/3\|\|O_{10}$	1.0	–
O_{16}	–	–	1/3	1/6	1/2
O_{17}	–	–	1/3	2$×1/6\|2/3\|\|O_{18}$	–
O_{20}	–	–	1/3	1/6	1/2

For all anions from the interpacket space and those bonded to $Na_2{}^{1+}$ and $Na_3{}^{1+}$ (and partly to Ce^{3+}), an insignificant sum of valence strengths converges, and they should naturally be taken as neutral H_2O molecules. It may be noted that it is precisely with these anions that the Ce^{3+} atom has the longest Ce–O bonds (on average 2.70 Å, as against 2.55 Å for the others). Of the remaining four light atoms (O_{21}, O_{22}, O_{23}, O_{24} in Table 2), each is located at the junction of three Ce polyhedra and draws to itself a sum of positive strengths equal to unity, which should characterize the groups $(OH)^{1-}$ (their presence is also confirmed by thermal analysis ([1])). A more "chemical" analysis shows that the four positions just indicated must be statistically occupied by both $(OH)^{-}$ ions and O^{2-}, in order to avoid a deficit of negative charges necessary for neutralizing the cationic framework of the structure. Thus, the chemical formula of tundrite (from the results of the structure determination) may be represented as

$$Na_{3-y}(Ce,Ca)_4(Ti,Nb)_2(SiO_4)_2(O,OH)_8 \cdot 8H_2O.$$

The characterization of tundrite as an orthosilicate with a layered structure, but at the same time with columns of Ti octahedra, corresponds to the morphology of the mineral, with perfect cleavage on (010) and an acicular habit of crystals with the elongation axis along c.

In the continuing refinement of the structure, one of the aims is to establish the degree of pseudocentricity of tundrite and the reasons causing the disappearance of a true center of symmetry in the structure.

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Note: Figure translations are in progress. See original paper for figures.

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