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CRYSTAL STRUCTURE OF VINOGRADOVITE

$Na_4Ti_4[Si_2O_6]_2[Si_4O_{10}]O_4 \cdot nH_2O$

In 1950 E. I. Semenov (^{1}) discovered, in the alkaline pegmatites of the Kola Peninsula, a new acicular mineral, later named vinogradovite in honor of Academician A. P. Vinogradov. An X-ray study of this mineral confirmed its monoclinic symmetry. The unit-cell parameters, determined from oscillation and rotation photographs, are $a = 5.35$, $b = 8.56$, $c = 24.22$ Å; $\beta = 101°$. With great difficulty it proved possible to select a single-crystal fragment of a flattened vinogradovite needle suitable for obtaining from it a complete three-dimensional set of experimental structural amplitudes. In the overwhelming majority of cases, the acicular crystals of vinogradovite give very low-quality Laue patterns, which may indicate intense twinning of these mineral specimens.

In all, using Mo radiation on an equi-inclination Weissenberg goniometer, 8 layer-line photographs ($0kl$—$7kl$) were obtained on rotation about the elongation axis of the crystal; on them 1308 independent reflections different from zero were recorded. Of the two Fedorov space groups possible from systematic absences, $A2/a$ and Aa, the intensity statistics (^{2}) unambiguously indicated the group of monoclinic holohedry. The successful solution of the structure within the group $A2/a$ confirmed this conclusion.

The chemical formula of vinogradovite, $Na_5Ti_4AlSi_6O_{24} \cdot 3H_2O$, as emphasized by the authors (^{1}), is approximate. This formula and the specific gravity of the mineral $d = 2.878$ require the placement, in the above-mentioned cell, of $Na_{10}Ti_8Al_2Si_{12}O_{48} \cdot 6H_2O$. The symmetry group $A2/a$ is characterized by general 8-fold and special 4-fold positions (on 2-fold rotation axes and at inversion centers) and does not permit, in an elementary way, the placement within it of 10 Na atoms, 2 Al atoms, and 6 H_2O molecules. As the solution of the structure showed, the ideal chemical formula of vinogradovite is somewhat different.

The heaviest atoms, Ti, entering into the composition of vinogradovite cannot be used for structure analysis by the heavy-atom method, since they account for less than 20% of the scattering matter. The basis for solving the structure was the three-dimensional Patterson function, on which (using the regularities in the arrangement of vectors between atoms related by the $A2/a$ symmetry) Ti—Ti vectors were localized. The centrosymmetric Ti—Ti vector was used to construct

Fig. 1. Projection of the structure of vinogradovite onto the yz plane in Pauling polyhedra (positions of Na atoms are indicated by circles)

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the plane (projection yz) minimization function and the three-dimensional superposition synthesis. The solution was substantially delayed by the attempt to place 12 Si atoms in the vinogradovite cell: in one general position and on a 2-fold rotation axis. Progress was achieved only after combining the Al and Si atoms and increasing their total number (contrary to the approximate formula) to 16 atoms. At present the discrepancy factors are $R_{0kl} = 16.6\%$ (for 134 independent reflections) and $R_{hkl} = 21.5\%$ (for 1308 reflections). The corresponding coordinates of the basic atoms are given in Table 1. The projection of the vinogradovite structure is shown in Fig. 1 and corresponds to the formula $Na_4Ti_4[Si_2O_6]_2[Si_4O_{10}]O_4 \cdot nH_2O$, in which Al is combined with Si into a single dimetaradical.

The large value of the dimension $c = 24.22$ Å is weakened by the centering of the face $A = bc$, which makes it possible to have in the primitive cell, with the same a and b the third parameter $c' = 12.78$ Å. The whole architecture of vinogradovite, its main motifs, proved to be "subordinate" to the shortest dimension along the needle axis, $a = 5.35$ Å, characteristic of pyroxenes. Parallel to this direction in vinogradovite there do indeed extend two pyroxene chains (four per complete cell; they are polar, and enantiomorphic pairs are related by centers of symmetry) with the metasilicate formula $[Si_2O_6]_\infty$. With their free prongs these metachains rest on "swaying" columns of Ti octahedra joined by oblique ("polar") edges. This linkage of two kinds of polyhedra repeats very closely what occurs in ramsayite $Na_2Ti_2Si_2O_9$, with the same two parameters (5.23; 8.57 Å) (^{3}).

Fig. 1. Projection of the structure of vinogradovite onto the yz plane in Pauling polyhedra (positions of Na atoms are indicated by circles)

A new feature, characteristic only of vinogradovite, is the silica ribbons $[Si_4O_{10}]_\infty$, not linked with the pyroxene ones and subordinate to the same parameter $a = 5.35$ Å. These doubled chains are obtained as a result of condensation (geometrically, by means of a pseudo-plane of symmetry) of two pyroxene chains; but whereas in the well-known amphibole ribbons only every second tetrahedron of the chain participates in the condensation ($2[Si_2O_6]_\infty - O = [Si_4O_{11}]_\infty$), in vinogradovite ribbons all tetrahedra are involved in the condensation ($2Si_2O_6 - 2O = Si_4O_{10}$). Silica ribbons in epididymite–eudidymite (^{4}) and in sillimanite–mullite (^{5}) are characterized by the same dimetasilicate ratio $4 : 10 = 2 : 5$, but in the first two, three pairs of tetrahedra fall within the

Fig. 2. Vinogradovite $[Si_4O_{10}]_\infty$ (a), epididymite $[Si_6O_{15}]_\infty$ (b), and orthoclase $[Si_8O_{20}]_\infty$ (c) ribbons

Figure 2: Fig. 2. Vinogradovite $[Si_4O_{10}]_\infty$ (a), epididymite $[Si_6O_{15}]_\infty$ (b), and orthoclase $[Si_8O_{20}]_\infty$ (c) ribbons

repeat period along the chain axis: $[Si_6O_{15}]_\infty$, whereas in the other two there is only one pair: Z_2O_5, where $Z_2 = Si + Al$. In Fig. 2 are reproduced ribbons close in geometry, made up of tetrahedra of vinogradovite, epididymite, and orthoclase (a framework fragment).

Table 1

Coordinates of the basis atoms of vinogradovite

Atoms	x/a	y/b	z/c
Ti	0.711	0.096	0.349
Si_1	0.274	0.090	0.233
Si_2	0.272	0.100	0.065
Na	0.803	0.192	0.149
O_1	0.250	0.160	0.000
O_2	0.997	0.042	0.079
O_3	0.023	0.013	0.208
O_4	0.042	0.068	0.385
O_5	0.782	0.241	0.292
O_6	0.332	0.083	0.300
O_7	0.625	0.250	0.394

Along the $c'(c)$ axis the characteristic details of the structure are arranged in three independent layers: metachains (two), columns of Ti octahedra (two), and dimetachains. The last layer is the most open (one dimetachain in the primitive cell, two in the complete cell), and between the silica ribbons there remain very spacious ($\sim 4 \times 4$ Å^2) channels filled with zeolitic water. Narrower channels are formed in the layer with Ti octahedra, but it is precisely here that the Na cations are located; these can be "shifted," which is characteristic of zeolites of the natrolite group.

Until now, the simultaneous presence in a mineral of two different silica-oxygen radicals had been known only for epidote—zoisite (orthite) and, presumptively, for vesuvianite, where independent island orthogroups $[SiO_4]$ and diortho $[Si_2O_7]$ groups alternated within a single structure (^{6,7}).

In vinogradovite we have the first case of the joint coexistence in a single structure of two independent infinite, one-dimensional silica-oxygen radicals—the metachains $[Si_2O_6]_\infty$ and the dimetalent $[Si_4O_{10}]_\infty$.

Fig. 2. Vinogradovite $[Si_4O_{10}]_\infty$ *(a)*, epididymite $[Si_6O_{15}]_\infty$ *(b)*, and orthoclase $[Si_8O_{20}]_\infty$ *(c)* ribbons

Zigzags of two kinds of channels with zeolitic water determine the perfect cleavage (001). The optical features of vinogradovite are curious. Chains of three kinds, parallel to [100], should make vinogradovite positive, but the metachains $[Si_2O_6]_\infty$, with the aid of Ti columns, join into powerful walls, tipping the balance pan in the negative direction with a small $N_g - N_p = 0.030$.

Comparison of the formulas of ramzaite and vinogradovite, as well as of the parameters of their cells, shows that upon transformation of the former—weathering—the SiO_2 is completely retained and the amount of $Ti + Na$, replaced by H_2O, is reduced by half. The two parameters that remain determine the ever-present connection (intergrowth, overgrowth) of secondary vinogradovite with primary ramzaite.

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CITED LITERATURE

1. E. I. Semenov, E. M. Bomshte[d]-Kupetskaya et al., DAN, **109**, No. 3, 617 (1956).
2. E. R. Howells, D. C. Phillips, D. Rogers, Acta Crystallogr., **3**, 216 (1950).
3. N. V. Belov, *Structure of Ionic Crystals and Metallic Phases*, Moscow, 1947, p. 108.
4. E. A. Pobedimskaya, N. V. Belov, DAN, **129**, No. 4, 900 (1959).
5. W. L. Bragg, G. F. Claringbull, *Crystalline Structure of Minerals*, Moscow, 1967, p. 190.
6. N. V. Belov, I. M. Rumanova, Proceedings of the Institute of Crystallography, Academy of Sciences of the USSR, issue 9, 103 (1954).
7. B. E. Warren, D. L. Modell, Zs. Kristallogr., **78**, 422 (1931).

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