

THE CRYSTAL STRUCTURE OF NEPTUNITE

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Augite-like neptunite crystals, which have the metasilicate Si₂O ratio of 1:3, are usually classed with pyroxene or the pyroxenoids. Pyroxene chains have in fact been detected in the neptunite structure, but these chains are linked together into a three-dimensional oxygen-silicon framework, with the unusual formula [Si₄O₁₁]. Three kinds of alkali-metal cations, K, Na, and Li, are distributed in independent crystallographic positions.

Besides the formula of (Na, K)₂(Fe, Mn)Ti[Si₄O₁₂], mineralogy handbooks [1] give only a confused picture of the structure of neptunite, discussing whether the metasilicate Si₂O ratio of 1:3 is more likely to correspond to [Si₄O₁₂] rings or complex [Si₄O₁₂]₂ pyroxene chains.

The authors have obtained experimental material for the investigation of the problem in the form of x-ray goniometer photographs from two specimens of eight layer lines about the z axis (hk0-hk7) and of the zero layer about y (Mo radiation, sin θ/λ = 1.2). Both specimens were of mangiferous Lovozero neptunite; one was from the M. Pankaruaiv deposit, and has been described in detail not long ago [2], while the other was from the personal collection of one of the authors.

The monoclinic unit cell constants were in good agreement with literature results for mangan-neptunite; a = 16.41, b = 12.55, c = 10.03 Å; β = 115.5°; Z = 8. The crystals showed a considerable piezoelectric effect, but there were no visible indications that the structure differed from the holohedral space group C_{2h} = C2/c.

From the set of F_{hkl} obtained (~1600 nonzero reflections), three-dimensional Patterson functions were calculated, and the peaks on these were analyzed by a method proposed by one of the present authors [3]. It was established that the two heavy Mn and Ti atoms were arranged almost identically with respect to the two nonequivalent symmetry centers of the group C2/c, which led to condensation (superposition) of the Patterson function, making its inter-

pretation difficult. The coordinates of the other atoms were found from the peaks due to their interaction with the two key atoms [3], and the identification took into account both the weights of the peaks and the corresponding interatomic distances. The correctness of the interpretations was judged from their R factors; the atomic coordinates were refined by the least-squares method as their positions became fixed. As well as the Mn and Ti atoms lying in general positions, 4 Si atoms and 7 O atoms (O₄-O₇) were located, also in general positions, plus an atom in a special position of the twofold axis, assumed to be an alkali-metal atom. The distance, about 3 Å, between this latter atom and the nearest O atom was considerably greater than the ordinary Na-O distance. A study of chemical analysis results for neptunite revealed that it always contained potassium, and in almost identical amounts - about four atoms per unit cell. When the K was fixed at the fourfold position on the twofold axis, the number of unlocated alkali-metal cations was thus reduced from 16 to 12 per cell. It was much more simple to locate the missing oxygen atoms (O₈-O₁₂); since these were the shared corners of linked SiO₄ tetrahedra, then as a starting-point for refinement these were assigned the coordinates of the midpoints of lines joining adjacent Si atoms. A study of the resulting model showed that the remaining 12 alkali atoms could occupy a general position of multiplicity 8 close to the twofold screw axis and a special position of multiplicity 4 on the axis of rotation. In the treatment of this version, Na atoms

TABLE I. Atomic Coordinates, Isotropic Temperature Factors (B), and Standard Deviations (σ) for Neptunite

Atom	x, y, z, B	σ	Atom	x, y, z, B	σ	Atom	x, y, z, B	σ
Mn	0.163	0.001	Si ₆	0.232	0.001	O ₆	0.049	0.003
	0.185	0.002		0.521	0.002		0.948	0.006
	0.308	0.001		0.399	0.003		0.531	0.006
	0.52	0.10		0.47	0.27		1.27	0.95
Ti	0.099	0.011	Si ₄	0.147	0.001	O ₇	0.113	0.003
	0.939	0.002		0.141	0.003		0.818	0.003
	0.116	0.002		0.539	0.003		0.277	0.006
	0.38	0.17		1.00	0.33		1.66	0.98
K	0.000	0.03	O ₁	0.166	0.003	O ₈	0.105	0.003
	0.560	0.003		0.286	0.003		0.517	0.003
	0.250	0		0.249	0.005		0.181	0.006
	0.30	0.30		0.07	0.55		0.59	0.56
Na	0.241	0.002	O ₂	0.003	0.003	O ₉	0.166	0.003
	0.22	0.02		0.172	0.003		0.597	0.005
	0.805	0.003		0.118	0.007		0.729	0.005
	2.28	0.75		3.00	1.10		0.61	0.56
Li	0.000	0	O ₃	0.201	0.003	O ₁₀	0.339	0.003
	0.071	0.010		0.307	0.006		0.374	0.006
	0.230	0		0.587	0.006		0.471	0.006
	0.239	1.29		3.00	1.50		0.80	0.74
Si ₁	0.000	0	O ₄	0.123	0.003	O ₁₁	0.289	0.003
	0.028	0.001		0.033	0.006		0.631	0.006
	0.278	0.003		0.233	0.006		0.470	0.006
	0.091	0.003		1.10	0.81		1.46	0.92
Si ₂	0.103	0.001	O ₅	0.202	0.003	O ₁₂	0.516	0.003
	0.816	0.003		0.071	0.006		0.738	0.006
	0.411	0.003		0.580	0.006		0.524	0.006
	0.55	0.27		-0.55	0.10		0.68	0.70

were placed in both positions. Structure refinements carried out independently from the amplitudes of the two (zero) zones hk0 and h0l resulted in considerably different x-coordinate values for the same atoms. It appears that in the treatment of a structure of this complexity, it is necessary to give up the idea of an independent analysis of projections. To use all the three-dimensional set of amplitudes in this preliminary refinement stage would involve a large expenditure of computer time, and so a compromise version was chosen (a modification of F. A. Brusentsev's program) to carry out simultaneous least-squares refinement over the two zones hk0 and h0l. Here the x coordinates were refined from all 260 amplitudes, y from the 136 F_{hk0} amplitudes, and z from the remaining 124 F_{h0l}.

A puzzling feature of the refinement was the extremely large value of the isotropic temperature factor B for the atoms in one of the fourfold positions. A recently published chemical analysis [2], the first to detect the considerable amount of Li present in Lovozero mangan-neptunites, explained this anomaly. Calculations of the average contents of a unit cell, from its density and volume, led to the detailed formula Na_{7.56}K_{3.80}Mn_{3.88}Ca_{0.05}Mn_{5.77}Fe_{2.15}Fe_{0.05}Mg_{0.04}Ti_{7.75}Si_{31.45}Al_{0.08}O_{95.5}(OH, F)₆, and to the conclusion that the second fourfold position was occupied entirely by light Li atoms, so that nep-

tunite contains three kinds of alkali atoms, distributed among different crystallographic positions. It also emerged that one of the 12 oxygen atoms (O₁) in the formula did not participate in the oxygen-silicon radical, so that the modified formula of lithium mangan-neptunite was KNa₂Li(Mn, Fe)₂Ti₂O₃[Si₄O₁₂], after rounding off the numbers, with four such formula units present in a centered cell.

Table 1 lists the coordinates of the principal atoms, the individual isotropic temperature factors, and the standard deviations calculated from the matrix, while the main interatomic distances are shown in Table 2; R(hk0 + h0l) = 23.5%.

The Mn (with 1/4 Fe impurity) and Ti atoms, which had similar scattering abilities, were identified from the interatomic distances; the smaller octahedron was assigned to Ti. This also gave sensible values of B for Ti and Mn.¹

The neptunite structure contains infinite, zigzag, highly elaborate columns in "baroque" style, and in these columns pairs of Ti and Mn octahedra alter-

¹In view of the small difference between the Ti and Mn octahedra, and the fact that the piezochroism of neptunite has been emphasized by mineralogists [2], it is possible that neptunite contains trivalent Ti and Mn ions of equal radii (cf. analyses of seidozerite and laventite [4]), formed according to the equilibrium reaction Ti³⁺ + Mn²⁺ ≈ Ti³⁺ + Mn³⁺.

TABLE 2. Principal Interatomic Distances in Neptunite (from the coordinates in Table 1)

Mn-octahedron:	Mn-O	1.97; 2.07; 2.18; 2.19; 2.219; 2.31;
	O-O	2.84-3.16 (edge) and 4.03-4.49 (diagonals)
Ti-octahedron:	Ti-O	1.80; 1.98; 2.02; 2.13; 2.19; 2.28;
	O-O	2.55-3.15 (edge) and 4.06-4.10 (diagonals)
Si-tetrahedron:	Si-O	1.55; 1.59; 1.61; 1.63;
	O-O	2.52-2.71
Si ₂ -tetrahedron:	Si-O	1.40; 1.62; 1.63; 1.66;
	O-O	2.40-2.68;
Si ₃ -tetrahedron:	Si-O	1.57; 1.60; 1.61; 1.66;
	O-O	2.56-2.77
Si ₄ -tetrahedron:	Si-O	1.61; 1.67; 1.67; 1.70;
	O-O	2.55-2.85
Li-octahedron:	Li-O	1.97(2); 2.04(2); 2.28(2);
	Na-octahedron:	Na-O
K-polyhedron:	K-O	2.79(2); 2.84(2); 2.98(2); 3.18(2);
		3.20(2); 3.75(2);

rate, these being linked together through shared edges. The columns run along the diagonals of the centered C-face (*ab* plane), giving rise to the (110) cleavage. The columns are framed on two sides by parallel infinite chains of Si tetrahedra (Fig. 1), as in the pyroxenes. The glide plane (*c*) translates a

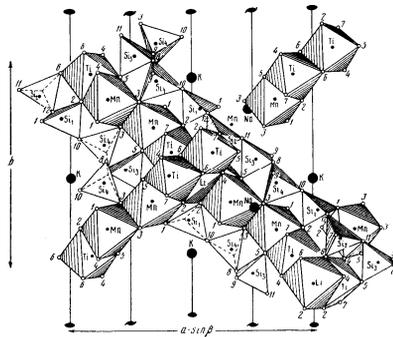


Fig. 1. Neptunite. A piece out of the main architectural pattern: columns of "baroque" type crisscrossing at an angle of 80°, each column containing alternating pairs of Ti and Mn octahedra. On two sides the columns are framed by "pyroxene" chains of Si tetrahedra. There are shown only for the lowest column. The upper column has one octahedron removed where it passes over the lower column. At the points where the columns are closest together they are linked through a "shackle-bolt" octahedron containing a Li atom.

column of octahedra parallel to [110] plus its oxygen-silicon framework into a similar column parallel to [110] and crossing over its original line at an angle of 80° and with a difference in level of *c*/2.

Crisscrossing $[\text{Si}_4\text{O}_{12}]_{\infty}$ pyroxene chains were detected recently in the structure of Zn-chalcolite [5], but there they were isolated, while in neptunite the crisscrossing metasilicate chains from columns at different levels are not isolated; instead they are linked together in such a way (Fig. 2) that along [001] = *c* almost completely straight chains of Si tetrahedra are formed (the *c*-constant is roughly equal to four times the edge of a SiO_4 tetrahedron).

Each of these vertical oxygen-silicon chains is connected with four parallel chains (Fig. 2) through nonparticipating pairs of tetrahedra from horizontal chains. In this way the oxygen-silicon radicals in neptunite form a three-dimensional framework, independently of the other components, with a somewhat unusual formula. It can be seen from Fig. 2 that only two tetrahedra from each four-membered link of a horizontal chain take part directly in the joining of horizontal chains on different levels, so that the formula of the framework works out as $2\text{Si}_4\text{O}_{12} - 2\text{O} = \text{Si}_6\text{O}_{22} = 2[\text{Si}_4\text{O}_{11}]_{\infty, \infty, \infty}$.

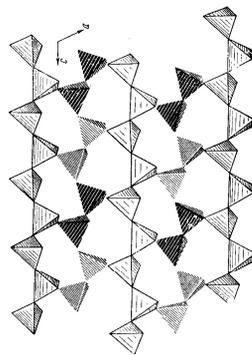


Fig. 2. Neptunite. The horizontal oxygen-silicon chains of $[\text{Si}_4\text{O}_{12}]_{\infty}$ pyroxene type which frame the main columns. The upper and lower chains pass from left to right and upwards, and the middle chain to the right and downwards. In each link of four tetrahedra the first and the fourth join the chain to other chains lying at a higher level, and at the same time form vertical chains parallel to the *c* axis, also with a repeat unit of four tetrahedra: the second and third tetrahedra of each link join the chain to parallel vertical chains. These latter tetrahedra are shaded in two different ways: one set points up from the plane of the drawing, and the other set points down.

Unfortunately it is difficult to show on a flat drawing how this three-dimensional framework only includes half the Si tetrahedra in the neptunite structure. Above the plane of the drawing a second system of chains begins (Fig. 3), parallel both to the "main" chains framing the columns of octahedra and the vertical chains parallel to the [001] axis. These form a three-dimensional oxygen-silicon framework which is completely analogous to that described above, the two frameworks being related by a center of symmetry, but not sharing any common components, even though the two open frameworks of SiO_4 tetrahedra repeatedly interpenetrate each other, even within a single unit cell volume (Fig. 3). It can also be considered that the oxygen-silicon radical in neptunite is made up of four vertical chains (per unit cell) of the pyroxene type but with branching $[\text{Si}_2\text{O}_6 + \text{O}]_{\infty}$ chains like those found in astrophyllite [6], although in neptunite these somewhat twisted vertical chains are linked together via their side chains with four neighboring

chains (from different cells), to form one of the two frameworks.

Let us return now to the more complex details of the structure. In the places where the crisscrossing Mn, Ti columns are at their closest they are linked together through Li octahedra (acting like the shackle-bolts in scaffolding) which have three edges shared with two Ti octahedra and one Mn octahedron of the lower column, and three other edges (related by a twofold axis to the opposite edges of the Li octahedron) shared with similar octahedra of the upper column (Fig. 4). Parallel to the (110) face, translationally-identical columns of Mn, Ti octahedra (Fig. 4) form a trellis-type wall containing crosslinks of two kinds: pairs of Li octahedra, between which "protrude" segments of almost perpendicular columns (Fig. 4), and pairs of large Na octahedra in the same plane as the columns. The Na octahedra come into contact with the main column in similar fashion to the Li octahedra, between pairs of identical-type octahedra, with a further side edge shared with an octahedron of a second type (in accord with their sizes, Li is between two Ti, and Na between two Mn). The pairs of Li octahedra shown in Fig. 4, pierced by columns passing in the other direction, fix the axis parallel to [001], about which the trellis wall mentioned may be rotated to transform into the analogous [110] wall which has its main horizontal columns lying at the level *c*/2 below the columns in the (110) wall. The intersecting trellis walls cut the neptunite structure up into compartments parallel to [001] - rhombic "pits" with angles of 80 and 100°. There are two of these "pits" in a centered cell, and a column of large 12-cornered K polyhedra passes along the central axis of the compartment, these polyhedra being connected together through shared edges. In the acute angles of these compartments the vertical oxygen-silicon chains described above pass. The pairs of Si tetrahedra (from the horizontal chains) which do not participate in these pass through the compartment walls between the Li and Na crosslinks and form the two independent $[\text{Si}_4\text{O}_{11}]_{\infty, \infty, \infty}$ oxygen-silicon frameworks.

In the structure of ilvaite, which has the orthosilicate formula $\text{CaFe}^{2+}\text{Fe}_2\text{Si}_2\text{O}_7\text{OH}$, the fact that

²On the left of Fig. 1, half of one of these "compartments" can be seen, with a K atom at its center and a "vertical" $[\text{Si}_4\text{O}_{12}]_{\infty}$ chain in the acute angle. This last point shows that one of the oxygen-silicon frameworks will be made up of perpendicular and horizontal chains lying to the left of both columns in the orientations shown in Fig. 1, while the second framework will be formed from the chains lying to the right of both columns in Fig. 1.

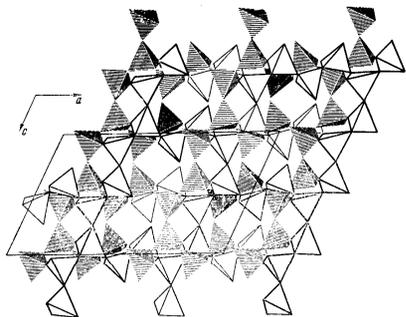


Fig. 3. The two independent oxygen-silicon frameworks in the structure of neptunite.

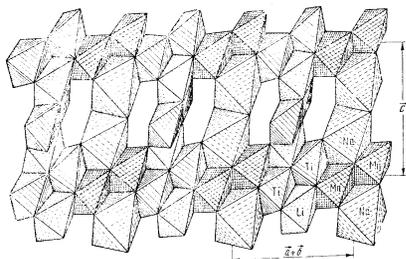


Fig. 4. Trellis-type walls of cation octahedra, lying parallel to the (110) plane. Two translationally identical columns of alternating pairs of Ti and Mn octahedra are linked together in their own (110) plane by pairs of Na octahedra, and also through Li octahedra which lie on either side of almost perpendicular similar columns passing in the other direction, [110].

the eighth O atom does not enter into the oxygen-silicon radical makes the structure a diorthosilicate, $\text{CaFe}^{\text{III}}\text{Fe}_2^{\text{IV}}\text{OSi}_2\text{O}_7\text{OH}$. In a similar way the 12th O atom in epidote [4] was taken out, as $\text{Ca}_2\text{Al}_2\text{FeSi}_2\text{O}_{12}\text{OH} = \text{Ca}_2\text{Al}_2\text{FeO}[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{OH}$. In neptunite, with a formula of the metasilicate type, removal of the 12th O atom from the radical has turned the mineral into a three-dimensional framework silicate.

The general formula $[\text{Si}_4\text{O}_{11}]$ thus corresponds to three "polymorphic" radicals; an amphibole and a vlasovite [7] radical, both these being $[\text{Si}_4\text{O}_{11}]_{\infty}$

ribbons, and a neptunite $[\text{Si}_4\text{O}_{11}]_{\infty, \infty, \infty}$ framework radical. In each type, there are two kinds of Si tetrahedron, one with three shared corners and one unshared, and the other with unshared corners $2\text{SiO}_2 \times 3_{0,5+1} \times 1 + 2\text{SiO}_2 \times 0_{0,5+2} \times 1 = \text{Si}_4\text{O}_{11}$.

The arrangement of oxygen-silicon chains shown in Fig. 2, with linked diortho groups, clearly explains why neptunite twins according to the pyroxene law on the twin plane (100).

The present study of the structure of neptunite must not be assumed to be completely exhaustive.

It is necessary to refine the Na coordinates and some of the O coordinates, and also refine the whole structure on the basis of the noncentrosymmetric group Cc, which increases the number of independent parameters from 59 to 123.

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