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CRYSTAL STRUCTURE OF PHENAKSITE

FeNaK[Si_4O_{10}] (KNaFe[Si_4O_{10}])

The Khibiny mineral phenaksite—a K, Na, Fe silicate—was discovered in 1959 by M. D. Dorfman (1). The parameters of the triclinic cell of phenaksite reported in (2) were refined from CuK$\alpha_1\alpha_2$ doublets on zero-level Weissenberg photographs: $a = 6.98$, $b = 8.24$, $c = 9.98$ Å; $\alpha = 114°12'$, $\beta = 80°14'$, $\gamma = 115°36'$. At a density of 2.74 g/cm^3 such a cell contains $Z = 2$ units of composition $KNaFeSi_4O_{10}$. The formula obtained on the basis of chemical analysis of two samples (1) is corrected by the present structural study.

The experimental X-ray material consisted of 2100 nonzero reflections on Weissenberg photographs $0kl$–$7kl$, $h0l$–$h5l$ (Mo radiation, $\sin\vartheta/\lambda \leq 1.2$ Å). Intensities were estimated by the $\sqrt[4]{2}$-scale of blackening standards. For layers older than the 2nd, a correction for spot shape according to Phillips (3) was introduced. For crystals of $1 \times 0.2 \times 0.2$ mm^3, no absorption corrections were introduced.

The initial model of the phenaksite structure was obtained from analysis of the three-dimensional Patterson function. An attempt to use the presence of the heavier Fe atoms and the symmetry (statistical tests made the group $P\bar{1}$ more probable) was unsuccessful because of the large number of overlapping interatomic vectors, and we turned to the method of multiple peaks (4), which in our laboratory has led to success in deciphering a number of structures (5, 6). However, the presence in phenaksite of atoms of different weight ($Z_{\mathrm{Fe}} = 26$, $Z_{\mathrm{Si}} = 14$) substantially hindered the practical realization of this method.

Table 1

Coordinates of the basis atoms in phenaksite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
K	0.140	0.809	0.010	O_3	0.632	0.424	0.167
Na	0.525	0.270	0.410	O_4	0.431	0.838	0.286
Fe	0.049	0.299	0.407	O_5	0.791	0.798	0.220
Si_1	0.669	0.913	0.213	O_6	0.790	0.139	0.280

Fig. 1. Fenaksite KNaFe[Si4O10]. Projection of the structure along the y axis. A tubular ribbon of Si tetrahedra is highlighted

Figure 1: Fig. 1. Fenaksite KNaFe[Si4O10]. Projection of the structure along the y axis. A tubular ribbon of Si tetrahedra is highlighted

Fig. 2. Fenaksite. Projection along the z axis with highlighted Si tetrahedra

Figure 2: Fig. 2. Fenaksite. Projection along the z axis with highlighted Si tetrahedra

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Si_2	0.230	0.631	0.270	O_7	0.033	0.629	0.205
Si_3	0.380	0.304	0.131	O_8	0.175	0.589	0.448
Si_4	0.803	0.632	0.273	O_9	0.760	0.655	0.436
O_1	0.630	0.856	0.041	O_{10}	0.251	0.192	0.237
O_2	0.294	0.457	0.133				

In extracting the basis system from the vector system, instead of two peaks as in (^{4}), 7 peaks of the Patterson function were used. As a result it was possible to isolate a basis system containing 11 peaks; however, it was not possible to identify them on the basis of the Patterson function.

The first synthesis of electron density was therefore obtained using a single averaged f_{Si}-curve. The positions of these 11 atoms were refined by least squares with allowance for individualized thermal corrections, and on

at the third stage of successive approximations of the electron density, all atoms in the complete model of the structure were fixed.

Although the procedure for selecting the basic system was carried out without taking into account a center of symmetry, the latter was clearly manifested in the final model of fenaksite.

The final values of all 51 positional parameters are given in Table 1 and are characterized by $R = 14.8\%$ ($B_{\mathrm{obs}} = 0.6$ Å^{-1}). The interatomic distances do not fall outside the usual limits (Table 2).

The crystal structure of fenaksite in polyhedra is shown in Figs. 1, 2, 3. The principal architectural component of the structure proved to be a tubular silicate radical $[Si_8O_{20}]_\infty$ of a new type. Most clearly,

Fig. 1. Fenaksite KNaFe[Si_4O_{10}]. Projection of the structure along the *y* axis. A tubular ribbon of Si tetrahedra is highlighted

Fig. 2. Fenaksite. Projection along the *z* axis with highlighted Si tetrahedra

it is described as the result of "condensation" of two vlasovite chains according

to the scheme
$2[Si_4O_{11}]_\infty - 2O = [Si_8O_{20}]_\infty$. Tubular radicals with the dimetasilicate gross formula Si_2O_5 were found in 1960 in narsarsukite (7) and recently in kanasite (8) (Fig. 3). In the former, a tube with a square cross-section is formed as a result of the "story-by-story" joining of pairs of diorthogroups according to the law of a screw two-start 4-fold axis (4_2), with the rods parallel to the tube axis. In kanasite, the tube has an 8-sided cross-section; four "parallel" rods are arranged on one "story" and two diorthogroups "perpendicular" to them on the next. In fenaksite the tube has a 6-sided cross-section; on each story two diorthogroups are arranged, but, in contrast to narsarsukite, the story with "parallel" (to the tube axis) rods alternates with a story where the rods are perpendicular (to the tube axis), which makes the tubular ribbon a condensate of two vlasovite chains.

Table 2

Interatomic distances in fenaksite (Å)

Polyhedra	Distance	Values	Distance	Values	Polyhedra	Distance	Values	Distance	Values
Si tetrahedra	Si–O	1.55-1.69	O–O	2.54-2.73	Na polyhedron (c.n. 5)	Na–O	2.44-2.79	O–O	2.9-4.00
Si tetrahedra	Si–O	Av. 1.61	O–O	Av. 2.64	Na polyhedron (c.n. 5)	Na–O	Av. 2.53	O–O	Av. 3.58
Fe polyhedron (c.n. 5)	Fe–O	1.98-2.31	O–O	2.9-3.36	K polyhedron (c.n. 10)	K–O	2.73-3.41		
Fe polyhedron (c.n. 5)	Fe–O	Av. 2.12	O–O	Av. 3.08	K polyhedron (c.n. 10)	K–O	Av. 3.04		

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

In each SiO_4 tetrahedron, three oxygen vertices are shared with other Si tetrahedra; the free vertex is bonded to an Fe atom in a coordination five-vertex polyhedron (a distorted tetragonal pyramid with one more distant base vertex: 2.33 Å, as against 1.98 ÷ 2.16 Å in the others). Two Fe five-vertex polyhedra have a common edge, and they, together with ana-

logical but somewhat enlarged Na five-vertex polyhedra form columns that extend along the *a* axis (Fig. 4). In the K atoms the coordination is 10. The proposed structure satisfactorily explains two perfect cleavages along the planes (010) and 001), i.e., parallel to the axis of the tube.

Fig. 3. Tubular silicon-oxygen radicals with the dimetasilicate formula $[Si_2O_5]_n$:
a—narsarsukite; *b*—phenaksite; *c*—canasite

Fig. 4. Phenaksite. Projection along the x axis. Si tetrahedra and Fe five-vertex polyhedra are shown

The authors express their gratitude to M. D. Dorfman for providing phenaksite samples for the study and take the liberty of suggesting that the name of the first discoverer of both canasite and phenaksite be attached to the new tubular silicon-oxygen ribbon in phenaksite.

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