The crystal structure of frankamenite

I. V. ROZHDESTVENSKAYA, L. V. NIKISHOVA

St Petersburg University, St Petersburg, 199034, Russia

AND

K. A. LAZEBNIK

Yakutian Institute of Geological Sciences, Siberian Department, Academy of Sciences, Yakutsk, 677891, Russia

Abstract

Frankamenite, $K_3Na_3Ca_5[Si_{12}O_{30}]F_3(OH)_1H_2O$, from the Yakutian charoitic rocks, has a triclinic unit cell with the dimensions: $a = 10.094(3)$, $b = 12.691(3)$, $c = 7.240(1)$ Å, $\alpha = 90.00(2)°$, $\beta = 111.02(2)°$, $\gamma = 110.20(2)°$, sp.gr. $= P\bar{1}$, $Z = 1$. Its crystal structure has been refined to $R_{aniso} = 0.059$ ($R_W = 0.060$) using the intensities of 2563 reflections.

The bases of the structure are zig-zag walls of Ca, Na octahedra joined by infinite octagonal cross-sectioned tubes of SiO_4 of the composition $(Si_{12}O_{30})$. Unlike canasite from the Khibini Mountains, the triclinic cell of frankamenite contains only one silicate tube. The atomic coordinates, interatomic distances and angles are topologically similar to those of canasite. Major differences are observed in the distribution of octahedral cations, which reflect the different anion compositions. Frankamenite exhibits six mixed Ca-Na positions, whereas canasite has only one such position. The H_2O molecule is located in the centre of the silicate tube between K^+ cations.

KEYWORDS: frankamenite, new mineral, crystal structure, charoitic rocks, Yakutia, Russia.
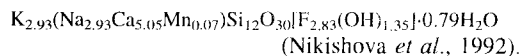
Introduction

A NEW mineral frankamenite is the fluorine-dominant analogue of the rare mineral canasite. The latter has so far been found only in pegmatites of the Khibini Mountains (Dorfman et al., 1959). Then a high F-content canasite-like mineral was reported from the charoitites in South Yakutia, Russia (Lazebnik and Lazebnik, 1981). There are significant physical and chemical differences between these two minerals which have been investigated by us in detail (Rozhdestvenskaya et al., 1988, Nikishova et al., 1992).

Recently the Commission on New Minerals and Mineral Names of the International Mineralogical Association has accepted our proposal to refine the nomenclature of canasite and the high-fluorine canasite-like mineral on the basis of our chemical and structural data. The fluorine-dominant analogue of canasite from charoitites has been approved as a new mineral frankamenite (94-050; Nikishova et al., 1996).

The mineralogical properties and structural characteristics of frankamenite are compared with those of canasite in this paper.

Initial study

Canasite from the Khibini occurs as greenish-yellow, transparent, idiomorphic grains up to 3 cm while the Yakutian mineral occurs as semi-transparent, prismatic crystals of gray, lilac, blue or green colour. Some prisms can reach to 10–15 cm in size. Prisms up to 0.5 cm thick are usually transparent and show perfect cleavage. The average of twelve chemical analyses of frankamenite, determined on an electron microprobe, gave the formula:

$$K_{2.93}(Na_{2.93}Ca_{5.05}Mn_{0.07})Si_{12}O_{30}|F_{2.83}(OH)_{1.35}|\cdot0.79H_2O$$
$$\text{(Nikishova et al., 1992).}$$

The mineral is distinguished from canasite by an excess free water (1–2 molecules of H_2O per formula unit) and F is dominant over OH.

X-ray powder patterns of canasite and frankamenite are similar, except there are twelve weak reflections in the high 2θ region for frankamenite. All reflections can be indexed on a monoclinic unit cell close to that established for canasite from Khibini. The extinction symbol is C1-1; however,

TABLE 1. Crystallographic data of minerals with the $Si_{12}O_{30}$ tube radical

	Frankamenite Present study $K_3Na_3Ca_5(Si_{12}O_{30})\cdot(OH)F_3H_2O$	Canasite Rozhdestvenskaya *et al.* (1988) $K_3Na_3Ca_5(Si_{12}O_{30})\cdot(OH)_{2.5}F_{1.5}$	Miserite Scott (1976) $KCa_5(Si_2O_7)\cdot[Si_6O_{15}](OH)F$
$a(\text{Å})$	10.094(3)	18.836(4)	10.100(5)
$b(\text{Å})$	12.691(3)	7.244(1)	16.014(7)
$c(\text{Å})$	7.240(1)	12.636(2)	7.377(5)
$\alpha(°)$	90.00(2)	90.0	96.42(3)
$\beta(°)$	111.02(2)	111.76(2)	111.15(3)
$\gamma(°)$	110.20(2)	90.0	76.62(2)
$V(\text{Å}^3)$	804.5(7)	1601.3(8)	1081.9(8)
Z	1	2	2
sp.gr.	$P1$	Cm	$P\bar{1}$
$d_m(g/cm^3)$	2.68	2.707	2.926(2)
$d_c(g/cm^3)$	2.69	2.67	2.83
$\mu(cm^{-1})$	17.9	17.9	—

the presence of the additional reflections prompted us to carry out a more detailed investigation of the Yakutian mineral. Its optical, X-ray powder and electron microscope data are given elsewhere (Nikishova *et al.*, 1992).

Selected area electron diffraction patterns from a number of crystal fragments had oblique lattices. The arrangment of reflections was at variance with the space group and the unit-cell setting accepted for canasite (Table 1). In all cases the repeat period along the length of the crystal remained constant at ~ 7.2 Å. That was the unique axis for Cm, but the angles between the axes of reciprocal lattice were not 90° (Fig. 1). This indicated that the unit cell of frankamenite can be either monoclinic with another setting or triclinic with different unit cell dimensions. The single crystal determination was undertaken in order to confirm our supposition. The poor quality and strong twinning made it extremely difficult to choose a suitable single crystal. After a prolonged search a single crystal in the form of a thin prism measuring 0.05 × 0.05 × 0.2 mm was selected for data collection.

The crystal structure of canasite from Khibini has been determined and refined in space group Cm (Chiragov *et al.*, 1969; Chiragov *et al.*, 1972; Rozhdestvenskaya *et al.*, 1988). However, for frankamenite we found some inconsistencies with monoclinic symmetry.

The initial structural refinement in space group Cm was not satisfactory. It revealed a different distribution of Ca and Na cations in the octahedral positions compared with the structure of canasite. Further, we obtained negative thermal parameters for some Si

and O atoms and observed a bifurcation for peaks corresponding to the Si and O atom positions on Fourier maps. Taking into account the SAED patterns
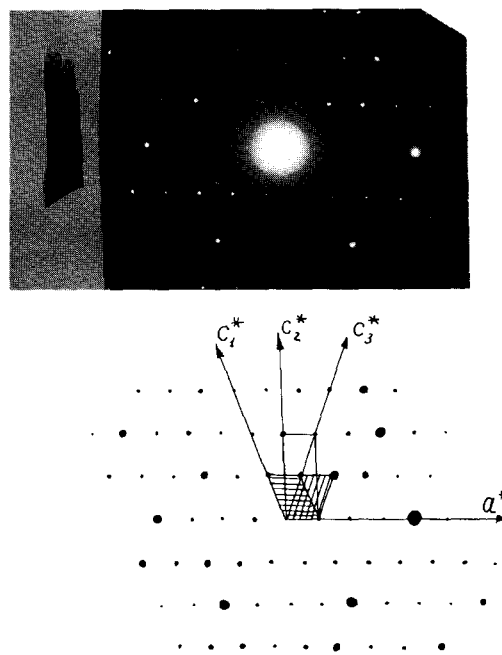

FIG. 1. The typical SAED pattern showing triclinic symmetry. Three different oblique nets are illustrated. The axes mark refers to the triclinic set.

a triclinic cell was then selected with the following relationship to the monoclinic cell:

$$\bar{a}_{tr} = (\tfrac{1}{2}\bar{a}_m + \bar{b}_m); \quad \bar{b}_{tr} = \bar{c}_m; \quad \bar{c}_{tr} = -\bar{b}_m \text{ (Fig. 2)}.$$

This transition from Cm to $P1$ permits indexing of additional reflections in the powder patterns by integer values of hkl and with minimal deviations of d_{calc} from d_{exp} and also removes the contradictions in the SAED data (Nikishova et al., 1992).

Triclinic cell dimensions were derived by transforming the Cm cell (Table 1). The latter was refined for 23 reflections ($35° < 2\theta < 40°$) carefully measured on an automatic four-circle X-ray P2₁ diffractometer with Mo-$K\alpha$ radiation.

Refinement of the structure

A set of intensities for space group $P1$ was obtained by transforming the data collected in Cm. 2717 intensities ($I > 2\sigma_I$) were measured by the ω-method using variable scan rates of 3 to 30 grad/min, Mo-$K\alpha$ radiation, $2\theta_{max} = 80°$ within a reflection hemisphere from $\bar{h}0\bar{l}$ to hkl. The intensities were corrected for LP factors. Absorption corrections were applied during later stages of the refinement.

The structure of frankamenite was refined on 2563 reflections with $F > 4\sigma_F$ in space groups $P1$ and $P\bar{1}$ using CSD program package (Akselrud et al., 1989) on a CM-4 computer. The weighting scheme was $1/w = \sigma^2 + 0.005F^2$. The atomic coordinates of canasite of Rozhdestvenskaya et al. (1988) were transformed into the triclinic setting and used as the starting coordinates.

During the earlier stages we carried out a refinement of octahedral and K^+ cation occupancy using a limited number of reflections: 1180 reflections with $Sin\theta < 0.5$. These refinements revealed that Ca and Na are ordered onto some octahedral sites and disordered on others. The position of free water was located on a difference Fourier synthesis and its occupancy was also refined. This refinement, with isotropic temperature factors, yielded $R = 0.077$, $R_w = 0.113$. At this stage we used the program DIFABS (Wolkers and Stewart, 1983) which permits correction of diffraction data for absorption, in a sample of an arbitrary form, thereby reducing R to 0.072 and R_w to 0.078. In the final stages, the crystal structure was refined with anisotropic temperature factors (265 variables in sp.gr. $P\bar{1}$ and 528 in sp.gr. $P1$). Refinements gave similar site occupancies and atomic coordinates for both space groups and equal R-factors. The final R_{hkl} is 0.059, R_w is 0.064 and GOF is 1.

It is reasonable to assume that the decrease in symmetry from a noncentric Cm results in $P1$ rather than $P\bar{1}$ symmetry. That was confirmed by statistical testing. The observed $\bar{E}$ and $(\bar{E}^2 - 1)$ values are

0.883 and 0.757, respectively, while the theoretical values are 0.883 and 0.736 in the acentric case and 0.798 and 0.968 in the centric case. The values of atomic coordinates and interatomic distances are very close in space groups $P1$ and $P\bar{1}$. The refined atomic coordinates with B_{iso} and the site occupancies are given in Tables 2 and 3 respectively.[1]

Comparison of the frankamenite and canasite structures.

In general terms, the crystal structure of frankamenite is composed of zig-zag walls of Ca-Na octahedra joined together by infinite octagonal cross-sectioned tubes of Si-O tetrahedra with the composition $(Si_{12}O_{30})$ and are topologically similar to the canasite structure. The latter was described in detail by Rozhdestvenskaya et al., 1988. Some of its important features are considered here.

Octahedral positions. In the structure of canasite the Na and Ca cations are generally ordered over the various octahedral sites. Two octahedral sites $M(1)$ and $M(6)$ are occupied by Na^+, one position, $M(4)$, by Na^+ and Ca^{2+} cations, and the rest by Ca^{2+} cations (Fig. 2 and Table 3).

In the triclinic structure of frankamenite, of the eight octahedral positions only $M(1)$ is completely occupied by Na^+ and $M(2)$ by Ca^{2+} cations. The rest are mixed Ca, Na positions. Note that the purely sodic and purely calcic octahedra $M(1)$ and $M(2)$ alternate along C_T in one column (Fig. 2). In the subsequent columns, the $M(3)$ and $M(4)$ octahedra are isomorphically occupied by almost equal amounts of Ca^{2+} and Na^+. The rest of the octahedral positions $M(5)-M(8)$ are isomorphically occupied by Na and Ca approximately in the ratio 1:2. The overall octahedral atomic composition is $Na_{3.14}Ca_{4.86}$. This value differs slightly from the average chemical composition but falls within the range of compositions found by microprobe analysis. Mean cation–oxygen distances remain practically unchanged compared with those canasite (Rozhdestvenskaya et al., 1988).

The distribution of Ca and Na cations in the octahedral positions violate the mirror symmetry and face-centring of the monoclinic cell and leads to $P1$ symmetry. The triclinic unit cell is the smallest structure fragment containing one silicate tube.

The silicate tube and the positions of K and H_2O. Mean Si–O distances, mean O–Si–O angles, and

[1] Tables of the observed structure factors and anisotropic temperature factors are available from the editorial office.

I. V. ROZHDESTVENSKAYA *ET AL.*

TABLE 2. Atomic coordinates (standard deviations) and isotropic thermal parameters of frankamenite (sp. gr. $P1$)

Position	x/a	y/b	z/c	$B(Å^{-2})$
K(1)	0.000(2)	0.4991(2)	0.478(2)	3.4(2)
K(2)	0.3167(7)	0.4984(5)	0.1586(9)	1.78(14)
K(3)	0.6847(6)	0.5018(4)	0.8410(7)	1.77(13)
M(1)	0	0	0	1.1(2)
M(2)	0.0098(8)	−0.0025(7)	0.5078(11)	0.68(7)
M(3)	0.5081(6)	0.0062(4)	0.2536(8)	0.90(12)
M(4)	0.3295(6)	0.1588(5)	−0.0831(8)	0.88(12)
M(5)	0.6700(5)	0.8411(4)	0.5870(7)	0.84(10)
M(6)	0.4906(7)	−0.0069(5)	0.7460(9)	0.94(14)
M(7)	0.3295(6)	0.1585(5)	0.4128(8)	0.97(12)
M(8)	0.6704(5)	0.8413(4)	0.0848(7)	0.73(10)
Si(1)	0.0367(7)	0.2468(5)	0.8014(10)	0.59(13)
Si(2)	0.2888(7)	0.7521(5)	0.9306(9)	0.65(13)
Si(3)	0.2757(7)	0.3678(6)	0.6372(10)	0.61(14)
Si(4)	0.4078(7)	0.6312(6)	0.7031(10)	0.66(14)
Si(5)	0.0371(7)	0.2461(6)	0.2348(10)	0.79(13)
Si(6)	0.2890(7)	0.7516(6)	0.3578(10)	0.79(14)
Si(7)	0.9625(6)	0.7533(5)	0.1977(8)	0.71(13)
Si(8)	0.7110(6)	0.2483(4)	0.0690(8)	0.60(12)
Si(9)	0.7248(6)	0.6322(4)	0.3633(8)	0.67(12)
Si(10)	0.5919(6)	0.3691(4)	0.2962(8)	0.70(12)
Si(11)	0.9632(6)	0.7535(5)	0.7649(8)	0.61(12)
Si(12)	0.7116(6)	0.2481(5)	0.6420(8)	0.72(12)
O(1)	0.066(2)	0.1331(15)	0.780(2)	1.2(4)
O(2)	0.165(2)	0.3552(14)	0.766(2)	1.3(4)
O(3)	0.420(2)	0.2855(15)	0.208(2)	1.5(4)
O(4)	0.392(2)	0.4992(14)	0.697(2)	1.2(4)
O(5)	0.310(2)	0.6425(14)	0.836(2)	1.2(4)
O(6)	0.130(2)	0.7582(14)	0.782(2)	1.3(4)
O(7)	0.566(2)	0.1333(14)	0.025(2)	1.4(4)
O(8)	0.635(2)	0.7170(13)	0.316(2)	1.4(4)
O(9)	0.053(2)	0.2829(12)	0.028(2)	1.1(4)
O(10)	0.264(2)	0.7090(12)	0.132(2)	1.2(4)
O(11)	0.065(2)	0.1322(11)	0.284(2)	1.0(4)
O(12)	0.164(2)	0.3555(12)	0.401(2)	1.3(4)
O(13)	0.310(2)	0.6434(13)	0.477(2)	1.5(4)
O(14)	0.130(2)	0.7576(12)	0.349(2)	1.6(4)
O(15)	0.568(2)	0.1333(12)	0.540(2)	1.4(3)
O(16)	−0.066(2)	0.8668(12)	0.218(2)	1.2(3)
O(17)	0.832(2)	0.6447(12)	0.232(2)	0.9(3)
O(18)	0.582(2)	0.7127(12)	0.792(2)	1.3(3)
O(19)	0.606(2)	0.5009(11)	0.306(2)	1.0(3)
O(20)	0.688(2)	0.3561(12)	0.161(2)	1.2(3)
O(21)	0.872(2)	0.2450(13)	0.220(2)	1.7(3)
O(22)	0.430(2)	0.8658(12)	0.969(2)	1.1(3)
O(23)	0.367(2)	0.2853(12)	0.684(2)	1.2(3)
O(24)	−0.054(2)	0.7172(11)	0.975(2)	1.0(3)
O(25)	0.737(2)	0.2900(12)	0.870(2)	1.1(3)
O(26)	−0.066(1)	0.8663(11)	0.712(2)	0.9(3)
O(27)	0.835(1)	0.6448(11)	0.597(2)	1.1(3)
O(28)	0.690(2)	0.3560(12)	0.524(2)	1.1(3)
O(29)	0.871(2)	0.2425(12)	0.652(2)	1.3(3)
O(30)	0.431(2)	0.8666(12)	0.461(2)	1.2(3)
OH(1)	0.262(2)	0.0310(14)	0.630(2)	0.6(5)
OH(2)	0.738(2)	0.9679(14)	0.370(2)	1.5(4)
F(1)	0.275(2)	0.0381(12)	0.139(2)	2.1(4)
F(2)	0.722(1)	0.9657(11)	0.859(2)	1.8(3)
H_2O	0.004(4)	0.498(4)	−0.039(4)	4.0(6)

TABLE 3. Distribution of Na and Ca atoms in the canasite and frankamenite structures

Octahedral positions	Frankamenite Present study	Canasite Rozhdestv. *et al.*, 1988
$M(1)$	Na	Na
$M(2)$	Ca	Ca
$M(3)$	$Na_{0.52}Ca_{0.48}$	Ca
$M(4)$	$Na_{0.46}Ca_{0.54}$	$Na_{0.44}Ca_{0.43}R^a_{0.13}$
$M(5)$	$Na_{0.30}Ca_{0.70}$	Ca
$M(6)$	$Na_{0.31}Ca_{0.69}$	Na
$M(7)$	$Na_{0.27}Ca_{0.73}$	$Na_{0.44}Ca_{0.43}R^a_{0.13}$
$M(8)$	$Na_{0.28}Ca_{0.72}$	Ca^b

a – R = Fe, Mn, Mg, Al, Ti
b – For monoclinic canasite $M(7)$ and $M(8)$ positions are identical with $M(4)$, $M(5)$, respectively, through the m-symmetry operation of the space group.

FIG. 2. The relation of monoclinic and triclinic cell vectors stand out against a background of the canasite structure octahedral wall. Common origin at $M(1)$.

shifting of Si atoms towards non-bridging oxygens are similar in both minerals. The greatest differences are noted between values of the Si—O—Si angles for the four chains which compose a silicate tube in frankamenite and canasite (Fig.3).

The angles vary between 149.3 and 144.4° in frankamenite and 151.9—138.4° in canasite. These changes are related to the manner of ordering of the cations in the octahedral positions and the size of the vertical edges to which the silicate radical adjoins (Table 4).

In the canasite structure the pairs of $M(3)$, $M(6)$ octahedra and $M(4)$, $M(5)$ octahedra are occupied by different cations (Table 3). These octahedra are located on different sides of an octahedral wall (Fig. 3). In frankamenite the occupancies of $M(3)—M(6)$ octahedra are similar. This results in similar lengths for the octahedral vertical edges and close angle values for the Si_2O_7 vertical diorthogroups of the I—IV chains which compose a silicate tube (Fig. 3, Table 4).

The position K(1) shows incomplete occupancy (0.87) by K atoms;this was also observed in canasite. Translated by half c from the K(1) position in

frankamenite there is an H_2O molecule. The occupancy of this position is 0.78. The oxygen of H_2O is connected to K(2) with a O—K(2) contact of 2.982 Å.

The hydrogen positions of the H_2O molecule remain uncertain. But it can be assumed that hydrogens are hydrogen bonded to O(9) and O(10) because the shortest H_2O—O(9) and H_2O—O(10) bonds are 2.979 and 2.895 Å, respectively and also the angle O(9)—H_2O—O(10) is 118°.

The H_2O molecule compensates for part of the alkaline cation's positive charge and weakens the interaction between this cation and the anions of the next silicate tube. Moreover the hydrogen bonds of this molecule with the oxygens O(9) and O(10) decrease the anion's radical negative charge.

The influence of the F^- and $(OH)^-$ anions disposition on cation ordering. As in the canasite structure, we were unable to locate hydrogen on the OH group in the frankamenite structure. It is, however, possible to make some suggestions about the disposition of these ions within the structure. Comparison of both structures shows that the cation ordering mechanism is associated with the chemical
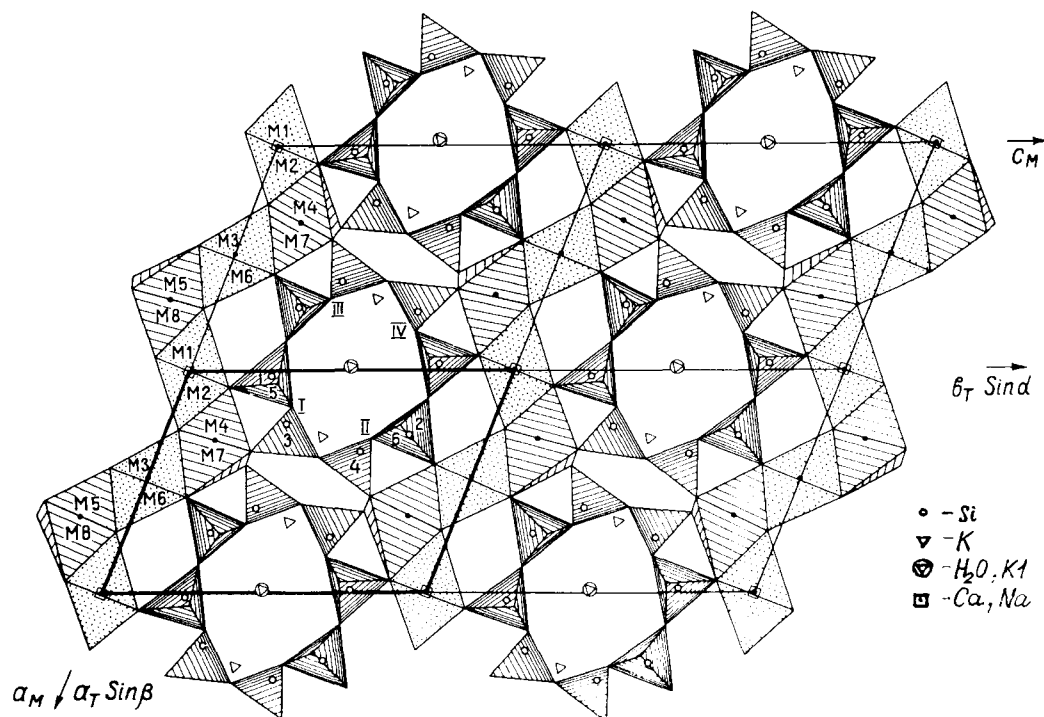

FIG. 3. Projection of the canasite structure along the elongated axis. Triclinic cell is shown by thick line. I,II,III,IV mark the four pectolite-like chains forming the $Si_{12}O_{30}$ tube. $M(1)$, $M(2)$ are alternately Na and Ca octahedra, while $M(3)—M(8)$ are mixed Ca,Na positions.

TABLE 4. Si—O—Si angles in the pyroxenoid chains of the silicate radical (space group $P\bar{1}$)[a]

	Si—O—Si	Frankamenite (grad)	l(Å)[b]	Si—O—Si	Canasite (grad)	l(Å)[b]
	Si(1)—O(2)—Si(3)	132.9		Si(1)—O(2)—Si(3)	130.5	
I	Si(1)—O(9)—Si(5)	149.3	3.66	Si(1)—O(17)—Si(1)[c]	151.9	3.70
	Si(5)—O(12)—Si(3)	133.0		Si(1)—O(2)—Si(3)[c]	139.5	
	Si(2)—O(5)—Si(4)	133.5		Si(2)—O(5)—Si(4)	135.0	
II	Si(2)—O(10)—Si(6)	144.4	3.71	Si(2)—O(18)—Si(2)	148.6	3.63
	Si(6)—O(13)—Si(4)	134.2		Si(4)—O(5)—Si(2)[c]	135.0	
	Si(2)—O(5)—Si(4)	133.5		Si(6)—O(10)—Si(5)	132.6	
III	Si(2)—O(10)—Si(6)	144.4	3.71	Si(5)—O(19)—Si(5)[c]	133.4	3.43
	Si(6)—O(13)—Si(4)	134.2		Si(6)—O(10)—Si(5)	132.6	
	Si(1)—O(2)—Si(3)	132.9		Si(7)—O(13)—Si(8)	134.3	
IV	Si(1)—O(9)—Si(5)	149.3	3.66	Si(8)—O(20)—Si(8)[c]	141.9	3.58
	Si(3)—O(12)—Si(5)	133.0		Si(7)[c]—O(13)—Si(8)[c]	134.3	
	Si(2)—O(6)—Si(5)	144.0		Si(5)—O(9)—Si(1)	144.2	
d	Si(1)—O(14)—Si(6)	143.9		Si(8)—O(6)—Si(2)	142.0	
	Si(3)—O(4)—Si(4)	144.9		Si(3)—O(4)—Si(4)	145.8	
	Si(3)—O(4)—Si(4)	144.9		Si(6)—O(11)—Si(7)	149.2	

a - For the purpose of saving space the bond angles are given in space group $P\bar{1}$. Those connected by a pseudocentre of symmetry are very close.
b - The length of octahedral edge, covered by the vertical Si_2O_7 group.
c - Symmetry-identical atoms
d - Angles in the horizontal Si_2O_7 groups.

composition of the anions and depends on the kind of anions not connected to the silicate radical. In these structures, there are three anion types: F^-, O^{2-} and $(OH)^-$ groups. The charge on the OH groups can be considered to be greater than -1 as H on the group is hydrogen bonded to another oxygen. The under-bonding on the O of the OH group must be compensated for by the cations in its coordinate sphere. There are four octahedral cations which give approximately 1/6 part of their charge to the anion. Therefore, the compensation of an F^- charge requires $2Na^+ + 2Ca^{2+}$, of an $(OH)^-$ charge - $1Na^+ + 3Ca^{2+}$; and of an $[(OH)^-, O^{2-}]$ charge - $4Ca^{2+}$. The cations are redistributed at the octahedral positions according to the anion distribution. We observed just such a pattern in these structures (Tables 3 and 5).

The proposed distribution of cations and anions for both structures is in good agreement with the calculation of the valence efforts (V_a) by Pyatenko (1972) and the value of the summary cation charge (Z) in four octahedral positions (Tables 3 and 5).

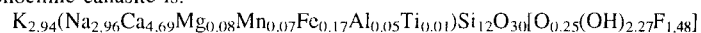## Crystal structures of miserite and frankamenite

Canasite and frankamenite are not the only silicate structures containing a tubular radical of the composition ($Si_{12}O_{30}$). Similar tubes have been noted in miserite (Scott, 1976). The coexistence of miserite and frankamenite in charoitic rocks suggests a genetic link between the minerals. Now that a better correspondence between the unit cell dimensions of frankamenite and miserite has been established (Table 1, Fig. 4), a more reliable and convincing comparison of the two structures can be made than was possible in previous work (Rozhdestvenskaya et al., 1988).

These structures display similarities in the linkage of the silicate tubes to the zig-zag octahedral walls, and in the positions of K, F and OH (Fig. 4). The main difference is that the walls in the structure of miserite are twice as thick. It is possible to accommodate extra K atoms and H_2O in the tube channels to fill vacancies with Na atoms and to
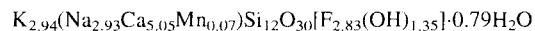
TABLE 5. Octahedra coordinating the univalence anion positions, summary cation charge (Z) and anion bond valence sums (V_a)

Position of anion	octahedra[d]	Canasite[a]			Frankamenite[b]		
		anions	Z	V_a^c	anions	Z	V_a^c
F(1)	$M(1),M(3),$ $M(4),M(7)$	F,OH	6.12	1.27	F	5.91	1.04
F(2)	$M(2),M(4),$ $M(6),M(7)$	F,OH	6.12	1.18	F,OH	6.97	1.17
F(3)	$M(2),M(3),$ $M(5),M(8)$	O,OH	8.00	1.33	F,OH	6.89	1.17
F(4)	$M(1),M(5),$ $M(6),M(8)$	F	6.00	1.01	F	5.95	1.04

a - Crystal chemical formula for monoclinic canasite is:

$$K_{2.94}(Na_{2.96}Ca_{4.69}Mg_{0.08}Mn_{0.07}Fe_{0.17}Al_{0.05}Ti_{0.01})Si_{12}O_{30}[O_{0.25}(OH)_{2.27}F_{1.48}]$$

b - for triclinic frankamenite is:

$$K_{2.94}(Na_{2.93}Ca_{5.05}Mn_{0.07})Si_{12}O_{30}[F_{2.83}(OH)_{1.35}]\cdot0.79H_2O$$

c - V_a were calculated according to the method proposed by Pyatenko (1972)

d - The Ca, Na occupancies of all octahedra are listed in Table 3.

partially replace Ca atoms in the miserite octahedral walls with Na atoms. It may be supposed that frankamenite was formed during K-Na metasomatism of charoitites and inherited fragments of the miserite structure.

Conclusion

The different conditions of the Yakutian and Khibini mineral formation defined the different anion compositions. The most important result is the
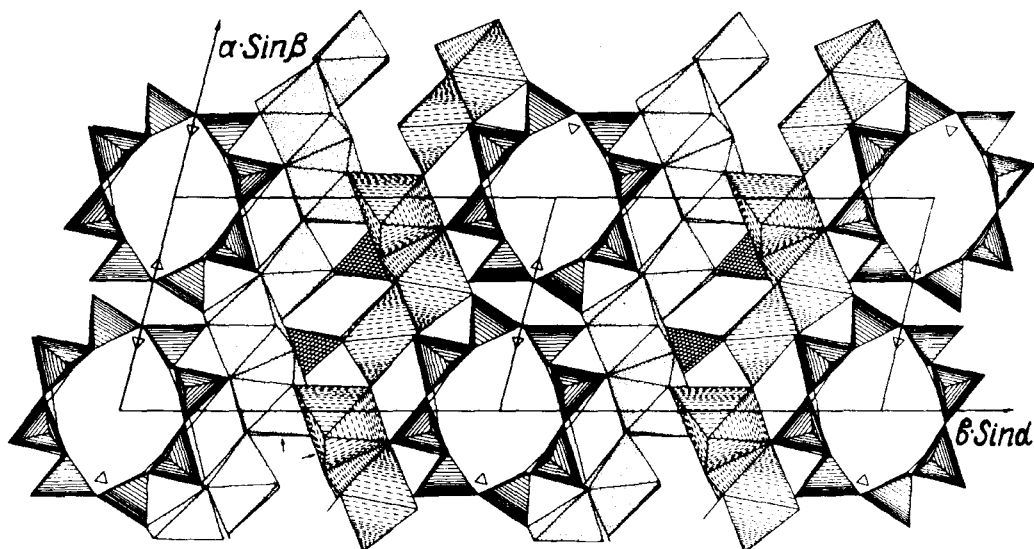

FIG. 4. The projection of the miserite structure along the c axis is represented as the polyhedra, according to the atomic coordinates of Scott (1976). In the cavities of the Ca polyhedral walls the Si_2O_7 diorthogroups are shaded.

revelation of the effect of anions on the structure and on some properties of these canasite species. A doubled fluorine content in frankamenite results in a different distribution of Ca^{2+} and Na^+ from canasite, increasing the number of isomorphically occupied positions. This leads to reduction of monoclinic symmetry to $P1$. The triclinic unit cell of frankamenite represents the minimal fragment of the structure, containing one silicate tube.

Water, which is localized in the tube $(Si_{12}O_{30})$, together with K atoms, neutralizes some valency effects of the anions and alkaline cations, and thereby weakens the strength of the frankamenite structure. The high number of $(OH)^-$ groups in canasite results in structure stabilization due to hydrogen bonding between the octahedral walls and the tubular radical. In contrast, a higher fluorine content weakens the strength of the frankamenite structure.

Acknowledgements

References

Akselrud, L.G., Crun, Yu.N., Zavalii, P.Yu., Pecharsky, V.K. and Fundamensky, V.S. (1989) CSD - universal program package for single crystal and/or powder srtucture data treatment. *XII European Cryst. meeting, Moscow. Collected Abstacts*, B3, 155.

Chiragov, M.I. and Mamedov, H.S. (1972) Crystal structure of canasite $K_3Ca_5Na_3(Si_{12}O_{30})(OH,F)_4$. *U.zap. Azerb. Univer., Ser. geol-geogr.*, no. 4,

14—9 (in Russian).

Chiragov, M.I., Mamedov, H.S. and Belov, N.V. (1969) On the crystal structure of canasite - $Ca_5Na_4K_2(Si_{12}O_{30})(OH,F)_4$. *Dokl. Acad. Nauk USSR*, 185, 672—4 (in Russian).

Dorfman, M.D., Rogachev, D.Ya., Gorotshenko, Z.I. and Uspenskaya, E.I. (1959) Canasite - a new mineral. *Ann. Miner. Mus. AN USSR.*, 9, 158—66 (in Russian).

Lazebnik, K.A. and Lazebnik, Yu.D. (1981) The rare silicates - miserite, canasite, fedorite in the charoite rocks. In *Mineralogy and Geochemistry of the ultrabasic and basic rocks of Yakutia.* (Kovalsky, V.V., ed.) Yakutsk, 32—50 (in Russian).

Nikishova, L.V., Lazebnik, K.A., Rozhdestvenskaya, I.V., Dazebnik, Yu.D. and Yemel'ayanova, N.N. (1992) Triclinic canasite from charoitites of Yakutia. *Mineral. Zhurn.*, 14, no. 1, 71—7 (in Russian).

Nikishova, L.V., Lazebnik, K.A., Rozhdestvenskaya, I.V., Yemel'yanova, N.N. and Lazebnik, Yu.D. (1996) Frankamenite $K_3Na_3Ca_5(Si_{12}O_{30})F_3-(OH)\cdot H_2O$ — new mineral. Triclinic species of canasite from charoitites. *Zap. Vses. Mineral. Obshch.*, 125, pt 2, 106—8 (in Russian).

Pyatenko, Yu.A. (1972) On a common approach to the analysis of local valency balance in inorganic structures. *Crystallographia*, 17, 773—9 (in Russian).

Rozhdestvenskaya, I.V., Nikishova, L.V., Bannova, I.I. and Lazebnik, Yu.D. (1988) Canasite: refinement and characteristics of the structure, structural typomorphism. *Mineral. Zhurn.*, 10, no. 4, 31—44 (in Russian).

Scott, J.D. (1976) Crystal structure of miserite a Zoltai type 5-structure. *Canad. Mineral.*, 14, 515—28.

Wolkers, N. and Stewart, D. (1983) An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr.*, A39, 158—65.