

Crystal Structure of K,F-Edenite from Khibini

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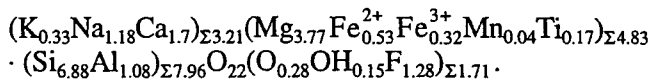
Abstract – The crystal structure of natural K-containing F-edenite was refined ($R = 0.029$). It is revealed from X-ray crystal structure analysis and IR spectroscopy data that the fluorine content is higher than that determined by chemical analysis. The “excess” Ca ions are proved to occupy the largest of the M octahedra [$M(2)$]. The distribution of cations through the $M(1)$ - $M(3)$ polyhedra corresponds to the linear correlation between the average $\langle M-O \rangle$ interatomic distances and the mean cation radii in these polyhedra.

Edenite, a Ca-amphibole discovered in the 19th century, has the idealized $\text{NaCa}_2\text{Mg}_5[\text{Si}_7\text{AlO}_{22}](\text{OH})_2$ composition. It differs from other Ca-amphiboles, such as tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, by the substitution of one Al atom for an Si atom and by filling the A position with Na cations. However, minerals of the above mentioned idealized composition are not found in nature, but synthesized in a laboratory [1]. The synthesis of edenite under low pressure was found to be inefficient in comparison with F-edenite.

According to the nomenclature of the International Mineralogical Association [2], edenites are Ca-amphiboles whose content of chemical elements (per formula unit) varies as follows: Si 7.25 to 6.75; Al 0.75 to 1.25; Ti < 0.5; Ca in the $M(4)$ position > 1.34; Na in the $M(4)$ position < 0.67; and (Na + K) in the A position > 0.5. Hence, magnesio-katophorite $\text{NaCaNaMg}_4(\text{Al}, \text{Fe}^{3+})[\text{Si}_7\text{AlO}_{22}](\text{OH})_2$ and richterite $\text{NaCaNaMg}_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$ appear to be the Ca-amphiboles closest to edenite in chemical composition; the former is characterized by a higher content of Na in the $M(4)$ position.

Despite the large number of publications on the structure refinement of different amphiboles, the crystal chemical features of natural edenite were not studied in detail until now, and a structural comparison of natural edenite with other minerals of the same group had never been performed [3, 4]. Earlier structural investigations of edenite [5, 6] were carried out, but with a low degree of accuracy. Therefore, the discovery of edenite in the Khibini alkali mass if (on the north-western side of the Yum'erchorr mountain, which is located on the Kola Peninsula) stimulated the X-ray crystal structure analysis of this mineral.

The average composition of edenite crystals was determined by using chemical and microprobe analyses:



The first unique feature of these crystals is the presence of K and F. Taking into account the relatively low content of K (< 0.5 per formula unit), we can consider this mineral to be a K-containing F-edenite.

The other specific feature of this mineral is its anomalously high total content of Ca and Na. Calcium and alkali amphiboles in which $[M(4) + A] > 3$ are found in high-calcareous or high-alkaline rocks. This feature can be considered a typomorphic feature. However, in this case, excess Ca or Na ions are allowed to occupy the relatively “tight” octahedral $M(1)$ - $M(3)$ positions [4, 6]. The verification of this assumption, using anomalously high-alkaline Khibinian edenite as an example, was one of the aims of this crystal-structure investigation.

The dark brown prismatic crystals of Khibinian edenite are characterized by the (010) plane of optic axes, $N_g = 1.638$, $N_m = 1.628$, $N_p = 1.618$, $N_g - N_p = 0.020$, and $2V = +84^\circ$. The unit-cell parameters refined on an Enraf-Nonius CAD-4 automated diffractometer are: $a = 9.911(3)$, $b = 18.030(9)$, $c = 5.279(2)$ Å, $\beta = 104.94(3)^\circ$, $V = 911.34$ Å³, $Z = 2$, $\rho_m = 3.01$, $\rho_{\text{calc}} = 3.08$ g/cm³, and sp. gr. $C2/m$.

The experimental data were collected on a diffractometer from a spherical sample 0.35 mm in diameter ($\text{MoK}\alpha$ radiation, graphite monochromator, $\sin \theta / \lambda \leq 0.7$ Å⁻¹). The data set included 1323 reflections. After averaging the equivalents, 1032 reflections with $I > 2\sigma(I)$ remained. The calculations were performed using the AREN program package [7]. The coordinates of 13 atoms from [8] were used in the procedure of phase refinement [9]. Six iterations lowered the R index from 46.9 to 20.6%, and the modified

Table 1. Atomic coordinates, equivalent thermal parameters (B_{eq}), and occupation factors (q) in the K,F-edenite structure

Atom	$B_{eq}, \text{\AA}^2$	x/a	y/b	z/c	q
$M(1)$	0.71(2)	0	0.0890(0)	0.5	1
$M(2)$	0.68(2)	0	0.1776(0)	0	1
$M(3)$	0.84(2)	0	0	0	1
$M(4)$	0.95(2)	0.5	0.2220(0)	0.5	1
$T(1)$	0.59(1)	0.2797(0)	0.0845(0)	0.3011(0)	1
$T(2)$	0.54(1)	0.2883(0)	0.1715(0)	0.8071(0)	1
$A(m)$	3.0(1)	0.5	0	0	0.49(1)
$A(2)$	2.7(1)	0.4576(5)	0	0.903(1)	0.25(1)
$O(1)$	0.70(3)	0.1103(1)	0.0851(0)	0.2197(2)	1
$O(2)$	0.77(3)	0.1194(1)	0.1702(0)	0.7261(2)	1
$F[O(3)]$	0.98(4)	0.1038(1)	0	0.7143(3)	1
$O(4)$	0.98(3)	0.3632(1)	0.2488(0)	0.7921(2)	1
$O(5)$	1.12(3)	0.3474(1)	0.1344(0)	0.1026(2)	1
$O(6)$	0.99(3)	0.3448(1)	0.1170(0)	0.5997(2)	1
$O(7)$	1.12(4)	0.3408(2)	0	0.2912(4)	1

F synthesis revealed the whole structure, including the atom in the A position. The least-squares refinement using the atomic factors of Mg for $M(1)$ and $M(3)$, Fe for $M(2)$, Ca for $M(4)$, and Na for A atoms led to $R = 11.2\%$. The $M(1)$ and $M(3)$ atoms had too low thermal parameters (~ 0.2), while for the $M(2)$ atom, this value was

rather high (2.15), and for the A atom it was anomalously high ($5.1 \text{ \AA}^2$). Combining the mixed curves, we examined the complete occupancy of each position, the averaged data of the chemical analysis, the standard crystal-chemical characteristics, and the valence balances of the anions. The least-squares refinement with allowance for isomorphic substitutions resulted in $R = 7.1\%$. At this stage, the difference Fourier synthesis with allowance for the series-termination effect revealed splitting of the A position. Both the central $A(m)$ and the $A(2)$ subpositions are occupied by Na and K atoms. The K atoms are mainly located in the former subposition. The final refinement of the positional and thermal parameters (the data were corrected for absorption using the DIFABS program [10], $\mu = 17 \text{ mm}^{-1}$) in the isotropic approximation reduced the R index to 4.56%, and the anisotropic refinement including extinction correction ($E = 0.0000065$) resulted in $R = 2.9\%$. The final positional and equivalent thermal parameters of atoms and interatomic distances are listed in Tables 1 and 2, respectively.

The inclusion of excess Ca ions (0.21 atoms per formula unit) into the $M(2)$ octahedron is justified by both the dimensions of this polyhedron and Brown's valence balance [11]. The calculations of valence balance were based on main amphibole composition, and the cations in the T , $M(1) - M(3)$, and $M(4)$ positions were approximated as Si, Mg, and Ca atoms, respectively. Table 3 shows that F and $O(4)$ atoms are the most in bond strength deficient. The arrangement of Na

Table 2. Interatomic distances ($\text{\AA}$) in the K,F-edenite structure

<i>T</i> tetrahedra					
<i>T</i> (1)—O(1)	1.622(1)			<i>T</i> (2)—O(4)	1.591(1)
O(7)	1.645(1)			O(2)	1.617(1)
O(5)	1.649(1)			O(5)	1.658(1)
O(6)	1.649(1)			O(6)	1.670(1)
	⟨1.641⟩				⟨1.634⟩
<i>M</i> octahedra					
<i>M</i> (1)—O(1)	2.055(1) × 2	<i>M</i> (2)—O(4)	2.008(1) × 2	<i>M</i> (3)—F	2.033(1) × 2
O(2)	2.059(1) × 2	O(2)	2.095(1) × 2	O(1)	2.059(1) × 4
F	2.076(1) × 2	O(1)	2.160(1) × 2		⟨2.050⟩
	⟨2.063⟩		⟨2.088⟩		
Ca, Na, K polyhedra					
<i>M</i> (4)—O(4)	2.351(1) × 2	<i>A</i> (<i>m</i>)—O(7)	2.470(2) × 2	<i>A</i> (2)—O(7)	2.472(6)
O(2)	2.424(1) × 2	O(5)	2.979(1) × 4	O(7)	2.596(6)
O(6)	2.576(1) × 2	O(6)	3.099(1) × 4	O(6)	2.711(3) × 2
O(5)	2.746(1) × 2		⟨2.925⟩	O(5)	2.959(3) × 2
	⟨2.524⟩			O(5)	3.105(3) × 2
		<i>A</i> (<i>m</i>)— <i>A</i> (2)	0.569(4)	O(7)	3.141(5)
		<i>A</i> (2)— <i>A</i> (2)	1.139(6)		⟨2.860⟩

cations in the *M* octahedra would still further increase the significant deficit of bond strength at the F anion and worsen the situation for the O(4) atom. Thus, although direct evidence of the inclusion of Ca into the *M* octahedra is absent, the location presence of Ca ions is more probable than the presence of Na ions in the *M*(2) positions.

The amphibole structural type is well known. It is characterized by the presence of infinite ribbons parallel to *c* and consists of six-membered rings of (Si,Al)-tetrahedra. The *a* period (9.91 Å) corresponds to the distance between the ribbons related by translation. The ribbons of tetrahedra are binded via the *M*(1) - *M*(3) octahedra and the *M*(4) and *A* polyhedra (the figure).

As is the case in most amphiboles, the *A* position in the K,F-edenite structure is split. According to [4], this disorder is, to a great extent, associated with the types of alkali cations located in this position. The K atoms are usually displaced in the (010) plane, while the Na cations are shifted along the 2-fold axis. Apparently, the disorder of the *A* cations in the (010) plane (the figure) is due to the presence of K cations in the sample under study.

The comparison of *T*(1)-O and *T*(2)-O average distances (Table 2) indicates that Al is localized in the *T*(1) position. The Si/Al ratio found in the *T*(1) position is supported by the correlation between the average *T*(1)-O bond length and the Al content [12, 13].

The absence of OH groups in the O(3) position and, consequently, its complete occupation by F⁻ anions, were confirmed by the results of the refinement of the atomic scattering factors. Despite the fact that the scattering factors of F and O atoms have close values, the efficiency of the method in determining the ratio of F to OH anions was substantiated [14]. Apparently, the F content was slightly underestimated in the chemical analysis due to the inaccuracy of the distillation method. The absence of the OH group in the O(3) position is also confirmed by the absence of an absorption band between 3600 and 3700 cm⁻¹ in the IR spectra of K,F-edenite.

The almost complete occupancy of the O(3) position by fluorine atoms favours the absence of Ti atoms in the *M*(1) and *M*(3) positions. It was shown in [15] that the presence of significant amounts of Ti in these positions suggests that the isomorphic substitution according to the scheme $\text{Ti}^{4+} + 2\text{O}^{2-} \rightarrow (\text{Mg}, \text{Fe}^{2+}) + 2(\text{OH}, \text{F})$ takes place; hence, the O(3) position should at least be partially occupied by O atoms. However, the low content of Ti⁴⁺ makes this type of isomorphism improbable. That is why we accepted an alternative variant, that the Ti⁴⁺ ions were located in the *M*(2) position, which improved the valence balance of the anions coordinated by the central alkali cation.

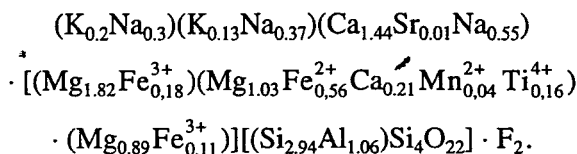
Thus, the low *R* value (0.029) was achieved in the refinement, and the model of the structure is reasonable in terms of cationic composition, isotropic temperature factors, and interatomic distances and corresponds to

Table 3. Valence balance (according to Brown) at the anions of the K,F-edenite structure

Atom	<i>T</i> (1)	<i>T</i> (2)	<i>M</i> (1)	<i>M</i> (2)	<i>M</i> (3)	<i>M</i> (4)	<i>A</i> (<i>m</i>)	<i>V_i</i>	Δ _{<i>i</i>}
O(1)	1.01		0.38	0.28	0.37			2.04	0.04
O(2)		1.02	0.37	0.34		0.29		2.02	0.02
F			0.26 × 2		0.29			0.81	0.19
O(4)		1.09		0.43		0.35		1.87	0.13
O(5)	0.93	0.91				0.12	0.04	2.00	0
O(6)	0.93	0.88				0.19		2.03	0.03
O(7)	0.94 × 2							2.04	0.04
Σ								12.81	0.45

Note: *D* = 3.5%; |Δ|_{max} = 9.5%. The *T*(1) and *T*(2), *M*(1) - *M*(3), and *M*(4) cations are identified as silicon, magnesium, and calcium, respectively; isomorphic admixtures were disregarded.

the linear correlation [4] between the mean interatomic distance $\langle \text{M}-\text{O} \rangle = 2.070$ and the mean cation radius $\langle r \rangle = 0.718$ Å in *M*(1) - *M*(3) polyhedra of this mineral. The crystal-chemical formula reflects the composition of the *A*(*m*), *A*(2), *M*(4), *M*(1), *M*(2), *M*(3), *T*(1), and *T*(2) positions, indicated in parentheses:



The structural features found in this mineral agree with the characteristics of other Ca-amphiboles. However, there are some features unique to Khibinian F-edenite.

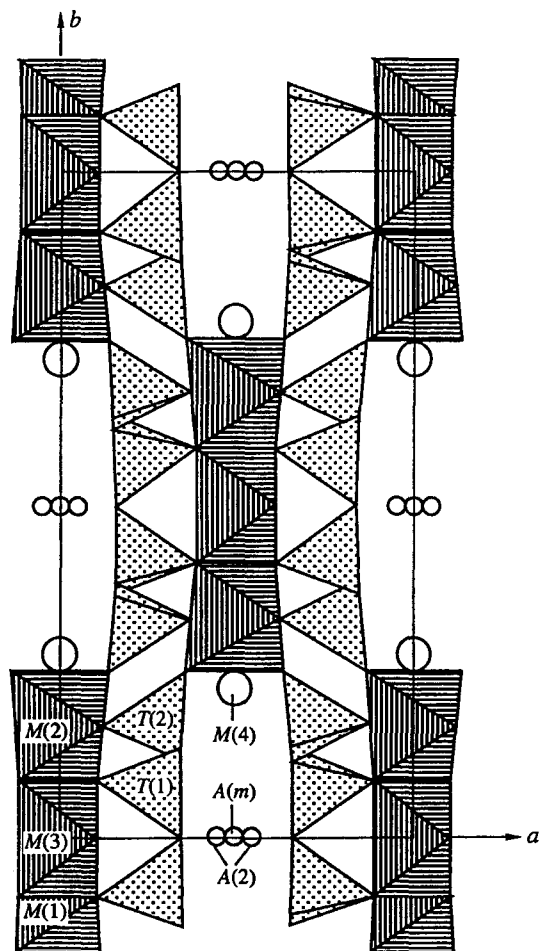
(1) Contrary to the structures of other amphiboles, a partially ordered distribution of Mg and Fe²⁺ ions in different octahedra is observed in the edenite studied, and the estimation of the temperature of formation of the mineral, which is based on the Mg/Fe²⁺ ratio in the *M*(1) and *M*(3) positions, does not seem possible.

(2) The splitting of the *A* position due to the high K content leads to the disorder of the *A* cations in the (010) plane, because K is distributed over both subpositions.

(3) The anomalous increase of the *M*(2) octahedron relative to the *M*(1) and *M*(3) octahedra results mainly from its occupation predominantly by Fe²⁺ and Mn²⁺ ions (along with the presence of a smaller Ti⁴⁺ ion) and by the possible inclusion of Ca atoms.

The problem of the location of excess Na or Ca cations in the structure of this amphibole can hardly be solved unambiguously. However, we can safely assume that in the process of filling the *A* positions by the Na and K atoms under basic conditions, the excess Na ions migrate to the *M*(4) position and partially displace Ca

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Projection of the K,F-edenite structure onto the (001) plane. The $M(1)$ - $M(3)$ octahedra are shaded, and the $M(4)$ and A positions are shown by large and small circles, respectively.

to the adjacent $M(2)$ position. The migration of Na ions to an M octahedron seems less possible.

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