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Crystal Structure of Magnesioferrikatophorite

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Abstract—The crystal structure of the Na,Ca-amphibole magnesioferrikatophorite found in carbonatites from the Turiy Cape (Kola Peninsula) was refined (Siemens P4 diffractometer, $\lambda \mathrm{Mo}K_\alpha$ radiation, 1481 independent reflections with $|F| > 4\sigma(F)$, anisotropic refinement, $R(F) = 0.039$). The parameters of the monoclinic unit cell are $a = 9.875(5)$ Å, $b = 18.010(8)$ Å, $c = 5.309(3)$ Å, $\beta = 104.39(5)°$, sp. gr. $C2/m$, $Z = 2$. The distribution of the cations over the crystallographically nonequivalent M(1–4)-positions was revealed by Mössbauer spectroscopy and X-ray diffraction analysis. The character of splitting of the A-position correlates with the characteristic features of the magnesioferrikatophorite composition. The resulting structural formula $(\mathrm{Na}_{0.87}\mathrm{K}_{0.13})_{\Sigma = 1} \cdot (\mathrm{Na}_{1.18}\mathrm{Ca}_{0.82})_{\Sigma = 2}(\mathrm{Mg}_{1.41}\mathrm{Fe}^{3+}_{0.42}\mathrm{Ti}^{4+}_{0.17})_{\Sigma = 2}\ (\mathrm{Fe}^{3+}_{1.31}\mathrm{Mg}_{0.69})_{\Sigma = 2}\ (\mathrm{Mg}_{0.60}\mathrm{Fe}^{2+}_{0.38}\mathrm{Mn}_{0.02})_{\Sigma = 1}(\mathrm{Si}_{3.16}\mathrm{Al}_{0.84})_{\Sigma = 4} \cdot \mathrm{Si}_4\mathrm{O}_{22}(\mathrm{O}_{1.05}\mathrm{OH}_{0.66}\mathrm{F}_{0.29})_{\Sigma = 2}$ agrees well with the electron microprobe analysis data. Based on the zonal character of the crystal and high Fe^{3+} content, the conditions of crystallogenesis are defined as oxidative against the background of a decrease in the Na potential in the course of the evolution of a mineral-forming system. *© 2003 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Amphiboles are characterized by pronounced variations in the structure and chemical composition. The number of the mineral species that belong to this group approaches 100. The compositions of amphiboles can be described by the general formula $A_{0-1}B_2C_5^{[6]}T_8^{[4]}\mathrm{O}_{22}(\mathrm{OH,F,Cl})_2$, where A is Na or K (coordination number ranges within 6–12), B is Ca, Na, Mn^{2+}, Fe^{2+}, Mg, or Li (coordination number ranges within 6–8, the M(4)-position), C is Mg, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al, or Ti^{4+} (coordination number is 6, the M(1–3)-positions), T is Si or Al (coordination number is 4, the T(1)- and T(2)-positions). The monoclinic amphibole under consideration with the idealized formula $\mathrm{Na_2CaMg_3Fe^{2+}Fe^{3+}Si_7AlO_{22}(OH)_2}$, sp. gr. $C2/m$, belongs to the *sodium–calcium subgroup*. For this subgroup, the contents of the chemical elements (the numbers of atoms per formula unit, apfu) vary in the following ranges: $(\mathrm{Ca} + \mathrm{Na})_B \geq 1.00$, $0.50 < \mathrm{Na}_B < 1.50$, $6.50 < \mathrm{Si} < 7.50$, $(\mathrm{Na} + \mathrm{K})_A > 0.50$. According to the modern amphiboles nomenclature [1], this mineral should be named magnesioferrikatophorite.

Although the structures of amphiboles of different compositions were refined in numerous studies, the crystal chemistry of the series of katophorites has been investigated insufficiently. In a number of earlier structure studies [2, 3], the specimens were described as katophorites, which they are not. According to the IMA-97 nomenclature, these compounds belong to other series of monoclinic amphiboles. In particular, the "katophorite varieties" (A1, A6, and A7) treated in [2] are riebeckite (A1) with the number of Al atoms per formula unit smaller than 0.5, arfvedsonite (A6) with three Na atoms per formula unit, and richterite (A7) containing two Na atoms, one Ca atom, and eight Si atoms per formula unit. The katophorite specimens A7 and A8, which were studied recently [3], contained two Al atoms per formula unit and, in fact, should be considered as magnesiotaramite.

Therefore, our study was stimulated by the lack of information on the crystallochemical features of katophorite species by a discovery of a new occurrence of the mineral of this series in carbonatites from the Turiy Cape (the Kola Peninsula, the North Shore of the Kandalaksha Bay of the White Sea), and also the possibility of analyzing the character of the cation distribution by modern methods of the Mössbauer spectroscopy and X-ray diffraction analysis.

EXPERIMENTAL

Chemical composition and the zonal character of the crystal (electron microprobe data). The mineral was discovered in a drill core. In this deposit, massive calcite carbonatite in some places is enriched with apatite, phlogopite, amphibole, and pyrrhotite. Amphibole occurs as black prismatic crystals (up to 7 × 1.5 × 1 mm) formed predominantly by the {110} and {100}

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faces with poorly formed vertices. Its content in the rock reaches 3–5%.

Chemical analysis of the crystals was performed on a CAMEBAX SX 50 instrument (CAMECA); the accelerating voltage was 15 kV; the current intensity was 30 nA (analyst N.N. Korotaeva).

The formula coefficients were calculated for 46 negative charges, i.e., formally, for the anhydrous anionic basis [23(O)]. Then, the formula was converted to the calculated basis 23(O) + $\Sigma(T + C) = 13$, where T and C are the cations in the tetrahedral and octahedral positions of the amphibole structure. The empirical formula was determined by averaging the results of chemical analyses at 10 points performed for two grains. The Fe^{3+} content in the formula was determined from the requirement of its electroneutrality. The resulting formula can be written as $(Na_{0.75}K_{0.13})_{\Sigma 0.88}(Na_{1.45}Ca_{0.55})_{\Sigma 2.00} \cdot (Mg_{2.72}Fe^{2+}_{1.07}Fe^{3+}_{1.02}Ti^{4+}_{0.17}Mn_{0.02})_{\Sigma 5.00}(Si_{7.21}Al_{0.76} \cdot Fe^{3+}_{0.03})_{\Sigma 8.00}O_{22}(OH_{1.71}F_{0.29})_{\Sigma 2.00}$.

Chemical analysis revealed the zonal character of the crystals. For one of the crystals, the composition was determined at eight points along the elongation axis. The Ca : Na ratio changes substantially in moving from the specimen center to its periphery. In the central portion, the grain is enriched with Na (the Na content is higher than 1.5 apfu and the Ca content is lower than 0.5 apfu) and its composition corresponds to ferric-nyböite (idealized formula $Na_3Mg_3Fe^{3+}_2Si_7AlO_{22}(OH)_2$). At the specimen periphery, where the Ca content is higher (Na < 1.5 apfu, and Ca > 0.50 apfu), the composition corresponds to magnesioferrikatophorite. The volume of the ferric-nyböite core is less than the volume of the peripheral zone of the magnesioferrikatophorite crystal.

Analysis of the Mössbauer spectra of magnesioferrikatophorite performed at the preliminary stage of the investigation allowed us to distinguish between divalent and trivalent iron ions and showed that Fe^{3+} ions substantially dominate over Fe^{2+}. The refined empirical formula of the magnesioferrikatophorite specimen (Table 1) can be written as follows:

$$(Na_{0.74}K_{0.12})_{\Sigma 0.86}(Na_{1.45}Ca_{0.55})_{\Sigma 2.00}$$

$$\cdot (Mg_{2.71}Fe^{3+}_{1.34}Fe^{2+}_{0.76}Ti^{4+}_{0.17}Mn_{0.02})_{\Sigma 5.00}$$

$$\cdot (Si_{7.15}Al_{0.76}Fe^{3+}_{0.09})_{\Sigma 8.00}O_{22}(OH_{1.47}F_{0.29}O_{0.24})_{\Sigma 2.00}.$$

Evidently, the compositional characteristics of this amphibole are directly associated with the characteristic chemical features of the host rocks, which is indicative of a high oxidizing potential of the mineral-forming medium and a slight decrease in the activity of Na in the course of the evolution of crystallogenesis. In addition, it was demonstrated [4] that the composition of amphiboles serves as a certain indicator that allows one to estimate the silica content in magma. Amphiboles, which are relatively depleted of silica (Si < ~7.00 apfu), are formed in silicon-undersaturated rocks, whereas amphiboles formed in silicon-saturated and silicon-oversaturated rocks are characterized by a higher Si content (~7.00 < Si < 8.00 apfu). Based on the silica content in the specimen under study, the latter can be related to high-silica amphiboles. Taking into account the characteristic geochemical features of the carbonatite systems, it would be more correct to consider the medium as deficient in aluminum but rather as enriched with silica.

Table 1. Average chemical composition of magnesioferrikatophorite

Component	wt %
Na_2O	7.76
K_2O	0.67
CaO	3.50
MgO	12.53
MnO	0.19
FeO*	6.23
$Fe_2O_3^*$	12.32
Al_2O_3	4.42
TiO_2	1.51
SiO_2	49.23
F	0.62
$-O{=}F_2$	–0.26
Sum	98.72

* Divalent and trivalent iron ions are distinguished based on the Mössbauer spectroscopic data.

Mössbauer spectroscopy. The Mössbauer spectra were recorded on an instrument of the electrodynamic type using a Co^{57} (Rh) source at 300, 80, and 10 K. The experimental spectra were processed using the UNIVEM program [5]. The isomer shifts are given relative to α-Fe (main standard).

The mathematical processing of the spectrum measured at 300 K at a rate of ±8 mm/s allowed us to single out three doublets (Fig. 1), with two of them being unambiguously attributed to Fe^{2+} and Fe^{3+}, respectively (characteristic isomer shifts), with the third one being attributed to Fe^{4+} (isomer shift $\delta_3 = -0.10$ mm/s, quadrupole splitting $\delta_3 = 0.25$ mm/s) [6]. According to experimental data [7], similar parameters of the Mössbauer spectrum correspond to Fe^{3+} located in the vicinity of Ti^{4+}. The assignment of the Mössbauer-spectrum doublets to the structural positions in magnesioferrikatophorite was made with due regard for the known crystal chemistry data for amphiboles [6, 8] and the results of our X-ray diffraction study. The parameters of the spectrum are given in Table 2. The experiment was performed at a high rate (±8 mm/s) and confirmed

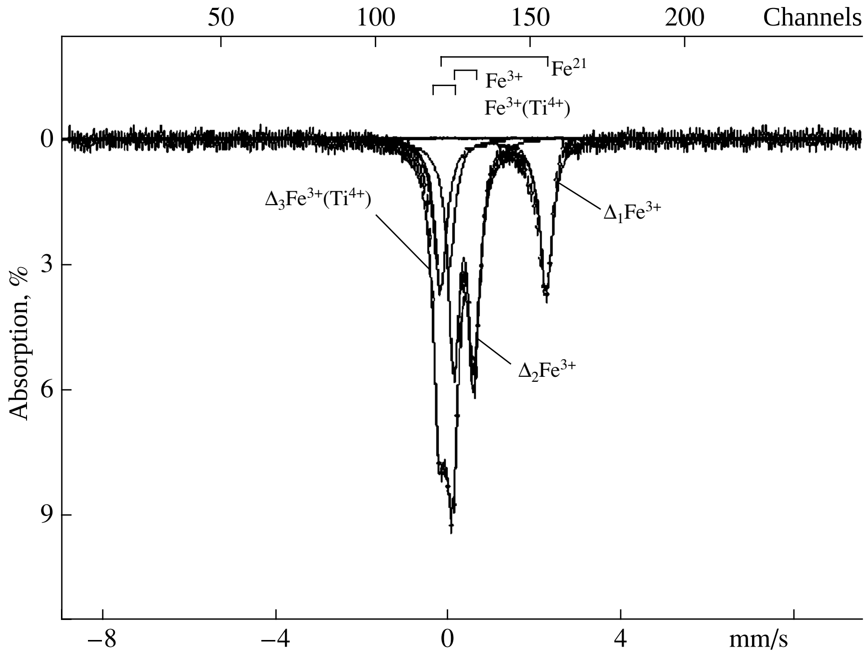

Fig. 1. Mössbauer spectrum of magnesioferrikatophorite.

the absence of magnetic splitting in the Mössbauer spectrum.

X-ray diffraction study. The crystallographic characteristics, the principal parameters of the X-ray diffraction study, and the details of the structure refinement are given in Table 3. The unit-cell parameters were determined by the least-squares refinement with the use of the angular characteristics of 22 reflections in the range $20° \leq 2\theta \leq 32°$. The empirical absorption correction was applied using the ψ-scan.

The crystal structure was refined starting from the atomic coordinates of K-edenite [9] within the sp. gr. $C2/m$ using 1481 independent reflections with $I_0 > 2\sigma(I_0)$ by the SHELX97 program package [10]. The refinement was performed with the anisotropic thermal parameters up to $R(F) = 0.039$. At the first stage, the occupancies of five cation positions, namely, $M(1)$, $M(2)$, $M(3)$, $M(4)$, and A, were refined.

The subsequent determination of the distribution of isomorphous cations over the crystallographically nonequivalent positions was based on the following: (1) the refinement of the electron contents of the cation positions, (2) the correspondence between the structural formula and the data from electron microprobe analysis, (3) the electroneutrality of the chemical formula, (4) the requirements of the valence balance, and (5) the approximate equality of the average interatomic distances to the sums of the ionic radii of the cation and anion in the corresponding polyhedra. However, there are some limitations in the refinement of the mixed occupancies of the nonequivalent cation positions. Since the scattering abilities of Fe^{3+}, Fe^{2+}, and Mn, on the one hand, and Al and Mg, on the other hand, are virtually indistinguishable, the mutual replacement of cations that belong to the same group has almost no effect on the reflection intensities. This fact made it expedient to refine the distribution of the Fe^{3+} and Fe^{2+} ions over the nonequivalent positions using the Mössbauer spectroscopy data.

Table 2. Parameters of the doublets in the Mössbauer spectrum of magnesioferrikatophorite ($T = 300$ K and $V = \pm 8$ mm/s)

Cations	Isomer shift δ (mm/s)	Quadrupole splitting Δ (mm/s)	Relative area (%)
Fe^{3+} (Ti^{4+})	−0.1000	0.2500	20.09
Fe^{3+}	0.3789	0.5010	43.93
Fe^{2+}	1.0409	2.4690	35.98

The final coordinates and atomic-displacement parameters are listed in Table 4. The distribution of the cations over the positions is presented in Table 5. The local valence balance calculated in [13] is indicated in Table 6. The average interatomic distances in the coordination polyhedra have standard values ($\langle M(1)\text{–O}\rangle = 2.083$ Å, $\langle M(2)\text{–O}\rangle = 2.061$ Å, $\langle M(3)\text{–O}\rangle = 2.088$ Å, $\langle M(4)\text{–O}\rangle = 2.539$ Å, $\langle T(1)\text{–O}\rangle = 1.644$ Å, $\langle T(2)\text{–O}\rangle = 1.635$ Å, $\langle A(m)\text{–O}\rangle = 2.765$ Å, and $\langle A(2)\text{–O}\rangle = 2.713$ Å).

The overall view of the structure drawn using the ATOMS program [14] is shown in Fig. 2.

Table 3. Crystallographic characteristics and details of the X-ray diffraction study

Unit-cell parameters, Å, deg	a = 9.875(5), b = 18.010(8), c = 5.309(3), β = 104.39(5)
Sp. gr.; Z	$C2/m$; 2
V, Å^3	914.6
ρ_{calcd}, g/cm^3	3.211
μ (mm^{-1})	2.81
Molecular weight	1768.82
Crystal dimensions (mm)	0.15 × 0.10 × 0.06
F_{000}	872
Diffractometer	Siemens P4
Wavelength, Å	0.71069
$2\theta_{max}$, deg	70.08
otal number of reflections	4014
Total number of independent reflections	2072
Number of independent reflections with $I_0 > 2\sigma(I_0)$	1481
R_{int}, %	6.87
Method of refinement	Least-squares procedure based on F^2
Number of parameters in the refinement	145
Final $R(F)$ for reflections with $I_0 > 2\sigma(I_0)$	0.039
$R(F)$ for all independent reflections	0.064
wR (F^2)	0.102
$S = GOF$	1.047
$\Delta\rho_{max}$, e/Å^3	0.8
$\Delta\rho_{min}$, e/Å^3	–0.93

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Tetrahedral *T*(1)- and *T*(2)-positions. According to the electron microprobe analysis data, there are approximately eight Si + Al atoms per formula unit, which supports the conclusion about the tetrahedral coordination of aluminum in the structure. The structures of monoclinic amphiboles have two nonequivalent positions, namely, $T(1)$ and $T(2)$, characterized by a distorted tetrahedral coordination and the point symmetry 1.

A comparison of the average distances $\langle T(1)\text{–O}\rangle$ = 1.644 Å and $\langle T(2)\text{–O}\rangle$ = 1.635 Å shows that aluminum is located only in the $T(1)$ position. The Si : Al ratio in this position (3.16 and 0.84 apfu for Si and Al, respectively) was determined based on the correlation between the average $\langle T(1)\text{–O}\rangle$ bond length and the Al content [15]

$$^{T(1)}\text{Al (apfu)} = [\langle T(1)\text{–O}\rangle - 1.6187] \times 33.2055.$$

A somewhat larger average distance $\langle T(2)\text{–O}\rangle$ = 1.635 Å falls within the range 1.628–1.635 Å typical of these tetrahedra and is consistent with the corresponding distances in the Ca-containing amphiboles studied earlier.

Octahedral positions. In addition to the tetrahedral cations, the octahedral cations are also of importance in the formation of the amphibole structure type. These polyhedra are linked to form the ribbons containing three nonequivalent cation positions, namely, $M(1)$, $M(2)$, and $M(3)$, characterized by different point symmetry groups (2, 2, and $2/m$, respectively). The cations located in these positions have a pseudooctahedral coordination. The $M(4)$ position characterized by the point symmetry 2 and surrounded by eight anions holds a special place in the structure. However, not all these anions form bonds with the central cation.

The total scattering power of the $M(1)$, $M(2)$, and $M(3)$ positions is provided by the sum of electrons of the cations located in these positions or, to put it differently, the sum of the average atomic numbers per position. Analogous calculations can be performed based on the chemical analysis data for one formula unit. A correlation between these two estimates can be considered as a correctness criterion for the structure-refinement data [2]. Figure 3 shows the plot characterizing the consistency of the electron contents of the $M(1)$, $M(2)$, and $M(3)$ positions determined from the X-ray diffraction and chemical analysis data for amphiboles studied earlier [2]. The position of the point corresponding to magnesioferrikatophorite in this plot confirms the correctness of the proposed model of the cation distribution over the $M(1)$, $M(2)$, and $M(3)$ positions.

Octahedral *M*(1) and *M*(3) positions. The atoms in the $M(1)$ and $M(3)$ positions are coordinated by four O atoms and two OH$^-$ anions [O(3)]. In the $M(1)$ octahedra, the O(3) anions are in the *cis* positions, whereas O(3) anions in the $M(3)$ octahedra are in the *trans* positions. An $M(1)$ octahedron shares five edges with the surrounding octahedra and only one edge with a $M(4)$ polyhedron, whereas an $M(3)$ octahedron shares all the six edges with the adjacent octahedra; i.e., it is the central polyhedron of the octahedral ribbon.

The results of the structure refinement of approximately 550 monoclinic amphibole specimens demonstrated that an increase in the electron content in the $M(1)$ position is accompanied by an increase in the electron content in the $M(2)$ position [2]. A slight deviation from this correlation was observed only for Li-containing amphiboles, in whose structures the light Li atoms are located, primarily, in the $M(3)$ octahedra. The cation distribution found in the magnesioferrikatophorite structure is in good agreement with the above-

Table 4. Final atomic coordinates and atomic-displacement parameters in the magnesioferrikatophorite structure

Position	*x*/*a*	*y*/*b*	*z*/*c*	U^{*}_{eq}, Å^2
M(1)	0	0.08874(6)	0.5	87(2)
M(2)	0	0.18063(4)	0	96(2)
M(3)	0	0	0	70(2)
M(4)	0	0.27810(7)	0.5	150(2)
A(*m*)**	0.5	0	0	1004(55)
A(2)**	0.44870(3)	0	0.88028(4)	339(9)
T(1)	0.28009(8)	0.08562(4)	0.2968(2)	75(2)
T(2)	0.28894(7)	0.17158(4)	0.8049(1)	68(1)
O(1)	0.1098(2)	0.0882(1)	0.2144(4)	95(3)
O(2)	0.1194(2)	0.1711(1)	0.7313(4)	106(4)
O(3)=OH	0.1084(3)	0	0.7108(5)	101(5)
O(4)	0.3640(2)	0.2495(1)	0.7948(4)	124(4)
O(5)	0.3494(2)	0.1323(1)	0.0927(4)	153(4)
O(6)	0.3427(2)	0.1176(1)	0.5932(4)	137(4)
O(7)	0.3384(3)	0	0.2867(6)	149(6)

* $U_{\mathrm{eq}} \times 10^4$.

** The nomenclature of the *A*-positions in amphiboles with the symmetry *C*2/*m* [11]: *A*(*m*), *x*, 1/2, *z*; *A*(2), 0, *y*, 0; *A*(2/*m*), 0, 1/2, 0.

mentioned correlation between the electron contents of the *M*(1) and *M*(3) positions. In Fig. 4, the point corresponding to magnesioferrikatophorite lies in the lenticular region, which also includes the electron contents of the *M*(1) and *M*(3) positions of most of the known amphiboles. In these structures, the Fe^{2+} ($r^{[6]}$Fe^{2+} = 0.78 Å) and Mg^{2+} ($r^{[6]}$Mg^{2+} = 0.72 Å) cations with large ionic radii occupy the largest *M*(3) octahedra.

Location of Ti^{4+} in the octahedral *M*(1) position. Electron microprobe analysis showed that the Ti^{4+} content in the specimen is ~0.17 apfu. In accordance with the earlier studies of amphiboles [16, 17], the Ti^{4+} ion was always placed into the *M*(2) octahedron of a relatively small volume. This was explained by the fact that $^{[6]}$Ti^{4+} is a small-size cation with high valence ($r^{[6]}$Ti^{4+} = 0.605 Å). Its role in the amphibole structures is analogous to the role played by other cations of the *C* group (Fe^{3+}, Mn, Mg, Al, etc.). In a more recent study of the structure of $^{[6]}$Ti-containing richterite [18], Ti^{4+} was found to occupy the *M*(1) position, which fact was attributed to the heterovalent substitution according to the following scheme:

$$^{[M(1)]}(\mathrm{Ti}^{4+}) + 2^{[\mathrm{O}(3)]}\mathrm{O}^{2-} \Leftrightarrow {}^{[M(1)]}(\mathrm{Mg,Fe}) + 2^{[\mathrm{O}(3)]}\mathrm{OH}^{-}.$$

Later on, the Ti^{4+} ion was found both in the *M*(1) and *M*(2) positions in the structures of amphiboles of various compositions.

Table 5. Distribution of the cations over the positions in the magnesioferrikatophorite structure

Position	Electron content	Occupancy of the position	Electron content with due regard for the real occupancy	Sum of ionic radii* of the cation and anion	Average cation–anion distance
M(1)	31.27	1.41Mg + 0.42Fe^{3+} + 0.17Ti^{4+}	31.59	2.075	2.083
M(2)	39.83	1.31Fe^{3+} + 0.69Mg	42.39	2.051	2.061
M(3)	16.95	0.60Mg + 0.37Fe^{2+} + 0.02Mn	17.06	2.118	2.088
M(4)	29.29	1.18Na + 0.82Ca	29.38	2.535	2.539
A(*m*)	11.58	0.56Na + 0.13K	8.58	2.448	2.765
A(2)		0.31Na	3.41	2.380	2.713

* The ionic radii were taken from [12].

Table 6. Local valence balance at the anions in the magnesioferrikatophorite structure

	M(1)	*M*(2)	*M*(3)	*M*(4)	*A*(*m*)	*A*(2)	*T*(1)	*T*(2)	Σ
O(1)	0.38	0.33	0.35				0.99		2.05
O(2)	0.37	0.40		0.23				1.01	2.01
O(3)=OH	0.37		0.37						0.74
O(4)		0.55		0.28				1.08	1.91
O(5)				0.08	0.05	0.01	0.95	0.92	2.01
O(6)				0.16		0.02	0.95	0.88	2.01
O(7)					0.16	0.04 + 0.02	0.94 × 2		2.10

In the magnesioferrikatophorite structure, the O(3) position is occupied by O^{2-} by more than 50%. Hence, it is reasonable to assume that the Ti^{4+} ion occupies the *M*(1) position together with Fe^{3+}, which is confirmed by the Mössbauer spectroscopy data. This distribution leads to an improvement of the valence balance, and the average interatomic distance $\langle M(1)\text{–O}\rangle = 2.083$ Å becomes approximately equal to the sum of the ionic radii of the cation and anion (2.075 Å). The involvement of Ti^{4+} in the *M*(1) octahedra is also consistent with the estimate of the electron content in this position.

Octahedral *M*(2) position. In the amphibole structures, the atoms in the *M*(2) position with the point symmetry 2 are coordinated by six O atoms. The *M*(2) octahedron is generally occupied by cations with rather small radii. This octahedron shares three edges with the adjacent *M*(1) and *M*(3) octahedra and one edge with the *M*(4) polyhedron. In the magnesioferrikatophorite structure, the *M*(2) octahedron is also characterized by the smallest average bond length $\langle M(2)\text{–O}\rangle = 2.061$ Å as compared to the *M*(1) and *M*(3) octahedral positions. The *M*(2) octahedra are occupied by more than 50% by the Fe^{3+} cations ($r^{[6]}Fe^{3+} = 0.645$ Å), which is confirmed by the Mössbauer spectroscopy data. In addition, Mg atoms are also located in the *M*(2) octahedra.

The relatively low symmetry of the *M*(2) octahedron is attributed to the fact that four of the total six O atoms involved in this octahedron (O(4) and O(2)) are simultaneously bound to the large cations in the *M*(4) position. According to [8], the effect of these cations is seen from a decrease in the corresponding bond lengths in the *M*(2) octahedra. As a result, the average distances $\langle M(2)\text{–O}(4)\rangle = 1.961$ Å and $\langle M(2)\text{–O}(2)\rangle = 2.072$ Å in the magnesioferrikatophorite structure are substantially shorter than $\langle M(2)\text{–O}(1)\rangle = 2.151$ Å.

The *M*(4) position. Taking into account eight neighboring anions, the coordination polyhedron about the *M*(4) position is either a distorted cube or a tetragonal antiprism sharing seven edges with the adjacent polyhedra, namely, four edges with the SiO_4 tetrahedra and three edges with the *M*(2) octahedra.

The *M*(4) position holds a special place in the amphibole structures. Since this position is occupied by different cations, it influences the isomorphism in the amphibole series and plays an important role for choosing the name of a mineral species. It is the change in the Ca : Na ratio in the *M*(4) position that is responsible for the zonal nature of the crystal studied. Thus, the com-

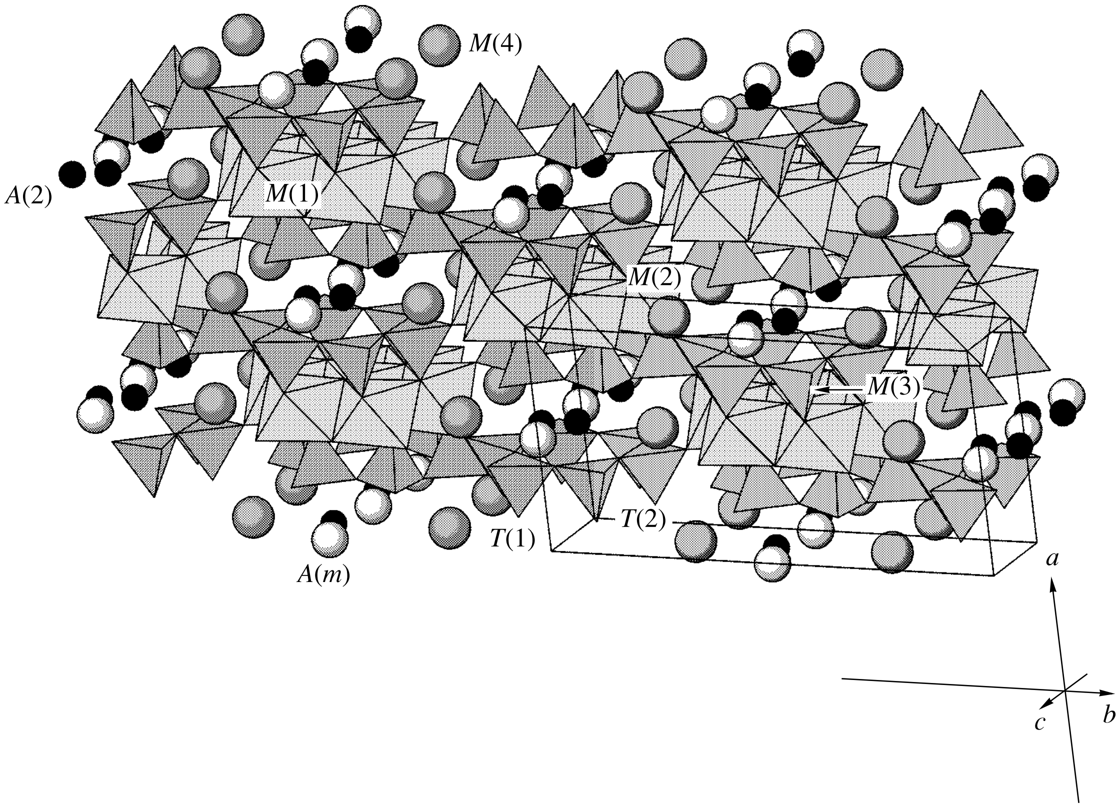

Fig. 2. Overall view of the magnesioferrikatophorite structure; the *A*(2), *A*(*m*), *M*(4) positions are indicated by solid, empty, and shaded circles, respectively.

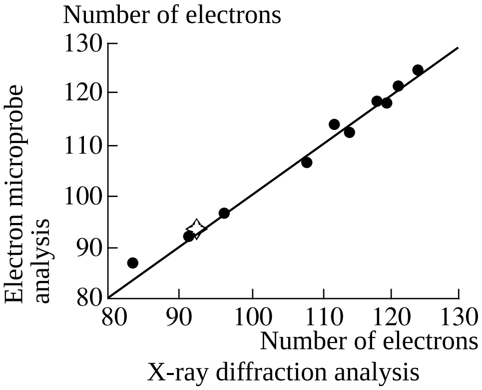

Fig. 3. Total electron content of the *M*(1), *M*(2), and *M*(3) positions in the magnesioferrikatophorite structure (white cross) according to the electron microprobe and X-ray diffraction analysis data in comparison with various amphiboles studied earlier [2].

positions of its core and the periphery correspond to different mineral species, namely, to ferric-nyböite and magnesioferrikatophorite, respectively.

According to [8], the size of the *M*(4) position depends on the sizes of the cations located in other octahedral positions. Thus, an increase in the ⟨*M*(1,2,3)–O⟩ distances averaged over three octahedra is accompanied by an increase in the average ⟨*M*(4)–O⟩ distance. In the magnesioferrikatophorite structure, the average interatomic distances ⟨*M*(4)–O⟩ = 2.539 Å and ⟨*M*(1,2,3)–O⟩ = 2.077 Å agree with the correlation reported in [8].

The *M*(4) position is very “elastic” as to the sizes and coordination of the cations entering this position. In monoclinic amphiboles with the symmetry group *C*2/*m*, this position is occupied by the cations of the *B* group, namely, by Ca ($r^{[8]}\mathrm{Ca}^{2+}$ = 1.12 Å) and Na ($r^{[8]}\mathrm{Na}^{+}$ = 1.18 Å).

Structural position *A*. The largest polyhedra occupied by the *A* cations are located between the adjacent silicon–oxygen ribbons along the *a* axis. These polyhedra are formed by 12 oxygen anions. The bridging anions between the SiO_4 tetrahedra form two ditrigonal rings at the opposite bases of the *A* polyhedra.

The *A* position is generally occupied by large K and Na cations. In monoclinic amphiboles with the symmetry group *C*2/*m*, this position is often split with respect to this position in an inversion center (0.5, 0, 0) because, first of all, of the larger size of the *A* cavity. The structural features associated with splitting of the *A* positions were considered in a number of studies. In [19], it was indicated that alkali cations occupy the *A*(2) or *A*(*m*) positions if the O(3) positions are occupied by OH groups or F^- anions, respectively. In terms of the valence balance [8], splitting of the *A* position led to the conclusion that the location of potassium in the *A*(2/*m*) position gives rise to an excessive sum of valence forces at this cation, whereas a deficiency of valence forces takes place if this position is occupied by Na.

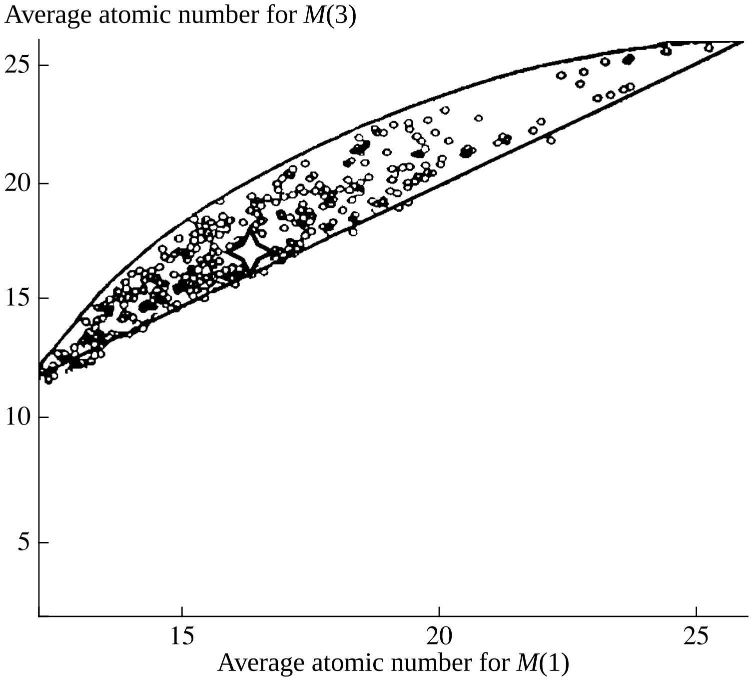

Fig. 4. Average atomic numbers in the *M*(1) and *M*(3) positions in the magnesioferrikatophorite structure (white cross within the lenticular region) in comparison with the electron contents of the same positions for different amphiboles studied earlier [2].

In the magnesioferrikatophorite structure, the *A* position is also split into two subpositions, namely, *A*(2) and *A*(*m*). This effect can be associated with the following facts:

(1) the presence of small amounts of K (~0.12 apfu) in the structure, which was confirmed by the electron microprobe analysis data; the large potassium cation ($r^{[12]}K^+ = 1.64$ Å) is located in the *A*(*m*) subposition together with Na ($r^{[12]}Na^+ = 1.27$ Å), whereas sodium can simultaneously occupy both subpositions [20], which is quite reasonable, because the average bond length $\langle A(m)\text{–O}\rangle = 2.765$ Å is larger than $\langle A(2)\text{–O}\rangle = 2.713$ Å;

(2) the presence of three types of cations (OH^-, F^-, and O^{2-}) in the O(3) position responsible for the redistribution of ^{A}Na over the *A*(2) and *A*(*m*) subpositions [3];

(3) the involvement along with Si also of aluminum in the tetrahedral *T*(1) position (Al content is 0.84 apfu); the positional disorder was attributed [21, 22] to the necessity of preservation of the valence balance at the anions involved in the bonds with the *T*(1) and *A* cations. In the presence of Al in the *T*(1) tetrahedra, Na atoms occupy the *A*(2) subposition, whereas, because of the larger size, the K atoms are located in the *A*(*m*) subposition.

Therefore, in the magnesioferrikatophorite structure, the Na atoms are located in both split subpositions, whereas the K atoms occupy only the *A*(*m*) subposition. The compositions of the cation positions in the structure are reflected by the refined crystallochemical formula of magnesioferrikatophorite $(Na_{0.87}K_{0.13})_{\Sigma A = 1}(Na_{1.18}Ca_{0.82})_{\Sigma M(4) = 2}(Mg_{1.41}Fe^{3+}_{0.42}Ti^{4+}_{0.17})_{\Sigma M(1) = 2}(Mg_{0.69}Fe^{3+}_{1.31})_{\Sigma M(2) = 2}(Mg_{0.60}Fe^{2+}_{0.38}Mn_{0.02})_{\Sigma M(3) = 1}(Si_{3.16}Al_{0.84})_{\Sigma T(1) = 4}Si_4O_{22}(O_{1.05}OH_{0.66}F_{0.29})_{\Sigma 2}$.

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