

Spinel-Group Minerals in Rocks of the Khibiny Alkaline Pluton, Kola Peninsula

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Abstract—Seven spinel-group minerals in various geological settings have been revealed in the rocks of the Khibiny pluton. Hercynite, gahnite, and vuorelainenite occur only in xenoliths of hornfels after volcanic and sedimentary rocks, whereas spinel and magnesiochromite occur in alkaline ultramafic rocks of dike series. Franklinite has been discovered in a low-temperature hydrothermal vein. Ubiquitous magnetite is abundant in foyaite, foidolites, alkaline ultrabasic rocks, and pegmatite and hydrothermal veins and may even be the main mineral in some foidolite varieties. The spinel-group minerals are characterized by various chemical compositions due to the fractionation of nepheline syenites resulting in formation of the Main ring of foidolites and apatite–nepheline ore. Like most other minerals found throughout the pluton, magnetite is characterized by variation in the chemical composition along the radial line from the contact with country Proterozoic volcanic rocks to the geometric center of the pluton. Toward the center, the total Ti and Mn contents in magnetite increase from 5–15 up to 40 at %.

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INTRODUCTION

The spinel group comprises cubic ($Fd\bar{3}m$) oxides with a structure formed by the close packing of oxygen atoms with tetrahedral and octahedral interstices occupied by tri- and divalent cations. In standard spinel (spinel, hercynite, gahnite, magnesiochromite, vuorelainenite, franklinite, etc.), tetrahedral interstices are occupied by divalent cations, whereas octahedral interstices are occupied by trivalent cations. In inverted spinel (magnetite, magnesioferrite, etc.), tetrahedral interstices are occupied by tri- or tetravalent cations, whereas octahedral interstices are occupied by divalent and other cations. Many members of the spinel group are characterized by continuous miscibility of cations in one or both positions (spinel–hercynite, spinel–magnesiochromite, spinel–chromite, magnesiochromite–chromite, etc.). If cation miscibility is absent in a certain temperature interval, exsolution textures appear, for instance, lamellae of spinel–hercynite and ilmenite in magnetite.

Seven minerals of the spinel group have been identified in the Khibiny pluton with confidence: vuorelainenite, gahnite, hercynite, magnesiochromite, magnetite, franklinite, and spinel proper. In addition, Khibiny samples are suggested to contain ulvospinel (Kostyleva-Labuntsova et al., 1978) based on recalculation of the chemical analysis of titanium-bearing magnetite. This paper presents a characterization of the

above-mentioned minerals largely based on original data. Minerals were identified with EPMA and XRD. BSE images were obtained on a LEO-1450 SEM.

GEOLOGICAL SETTING

The Khibiny alkaline pluton, the world's largest, is located in the western part of the Kola Peninsula at the boundary of the Archean granite gneisses of the Kola Block and the Proterozoic Imandra–Varzuga volcanic–sedimentary complex. Foyaite, the major rock of the pluton, occupies more than 70% of its volume. The foyaite body is divided into two approximately equal parts by the Main ring zone, 50–500 m wide in the north and 1500–2000 m wide in the south. The Main ring zone, composed of melteigite–urtite and apatite–nepheline rocks, is surrounded by 0.1- to 2-km-wide zones of metasomatically altered nepheline syenite of the lyavochorrite–rischorrite series.

The Main ring zone is characterized by a symmetrical zonal structure over most of its extent: foyaite–rischorrite–foidolite–apatite–nepheline rock–foidolite–rischorrite–foyaite (Fig. 1). This zoning is emphasized by an almost continuous ring of xenoliths of volcanic and sedimentary rocks of the Lovozero Formation transformed into hornfels and afterward fenitized at the rischorrite–foyaite boundary. Young dikes of alkaline and alkaline ultramafic rocks, volcanic pipes, and pegmatite and hydrothermal veins are also related to the Main ring (Yakovenchuk et al., 2005). The Minor semi-ring zone (up to 500 m wide) of foidolites and hornfels

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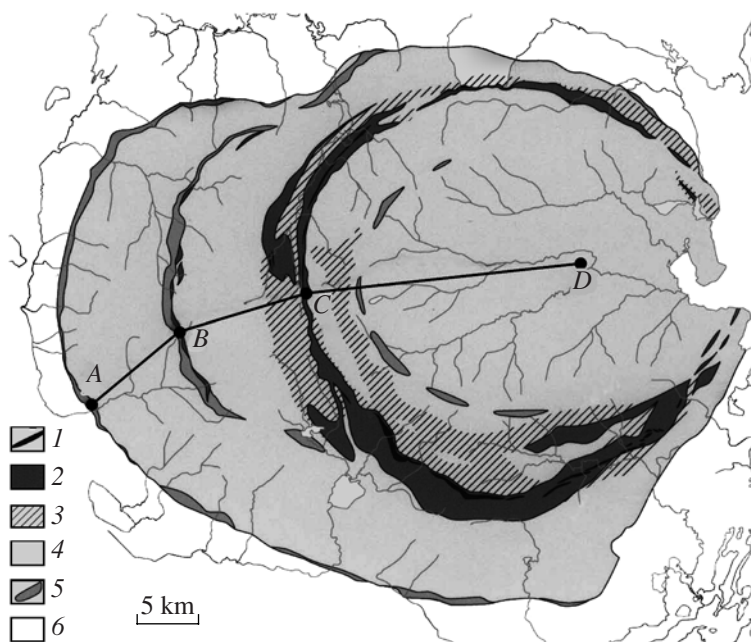


Fig. 1. Geological sketch map of the Khibiny pluton, simplified after O.L. Snyatkova and N.K. Mikhnyak. (1) Apatite–nepheline rock, (2) melteigite–urtite, (3) rischorrite, (4) foyaite, (5) xenoliths of hornfels after volcanic and sedimentary rocks, (6) Archean and Proterozoic metamorphic complexes. A–B–C–D is the line of sampling; 75 samples were taken at distances of 200–500 m from one another.

after volcanic and sedimentary rocks is traced outside of the Main ring zone.

Analysis of the mineral assemblages of more than 500 samples of different rocks and veins from the Khibiny pluton has shown that hercynite and vuorelainenite occur only in hornfels and fenitized xenoliths of volcanic and sedimentary rocks, while spinel and magnesiochromite occur in alkaline ultramafic rocks of dike

series. Franklinite has been found in a low-temperature hydrothermal vein. Ubiquitous magnetite is abundant in foyaite, foidolites, alkaline ultrabasic rocks, and pegmatite and hydrothermal veins and occurs as the major mineral in some foidolite varieties.

DESCRIPTION OF MINERALS

Vuorelainenite MnV_2O_4 has been found in fenitized and hydrothermally altered phlogopite–nepheline–albite hornfels from a large xenolith of volcanic and sedimentary rocks in foyaite at Mount Kaskasnyunchorr (Yakovenchuk et al., 2005). *Vuorelainenite* (along with vanadium crichtonite, karelianite, and an unknown sulfide of iron, vanadium, and chromium) composes thin (up to 70 μm) rims around rutile inclusions in pyrrhotite (Fig. 2). In addition to the mentioned minerals, this assemblage contains natrolite, titanite, rengerite, zircon, baddeleyite, srilankite, zirconolite, rhodochrosite, calcite, pyrite, monazite-(Ce), fluorapatite, and britholite-(Ce).

Gahnite ZnAl_2O_4 has been detected in fine-grained muscovite–anorthoclase–sekaninaite hornfels from xenoliths of volcanic and sedimentary rocks in foyaite at Mount Eveslogchorr (Yakovenchuk et al., 2005). *Gahnite* occurs as individual subhedral crystals and rare segregations of dark green grains (up to 80 μm in diameter) intergrown with ilmenite, ferrocolumbite, sillimanite, and quartz (Fig. 3).

Hercynite FeAl_2O_4 is a typomorphic accessory mineral of hornfels after volcanic and sedimentary rocks at

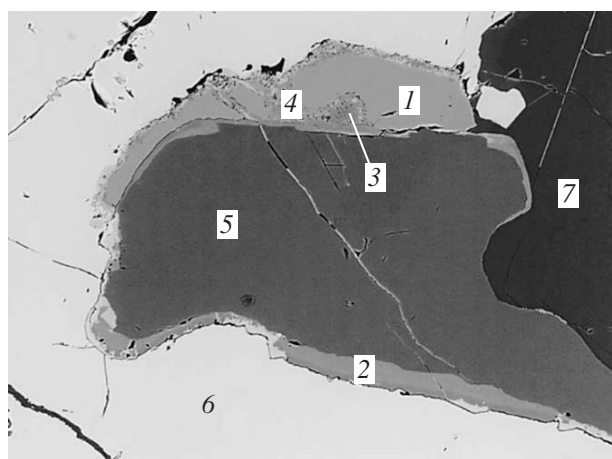


Fig. 2. A rim of vuorelainenite (1), crichtonite (2), karelianite (3), and an unknown heterogeneous sulfide of iron, vanadium, and chromium (4) around a rutile grain (5) in pyrrhotite (6); (7) calcite. Phlogopite–nepheline–albite hornfels from xenoliths in foyaite at Mount Kaskasnyunchorr. BSE image, 480 $\times$ 360 μm .

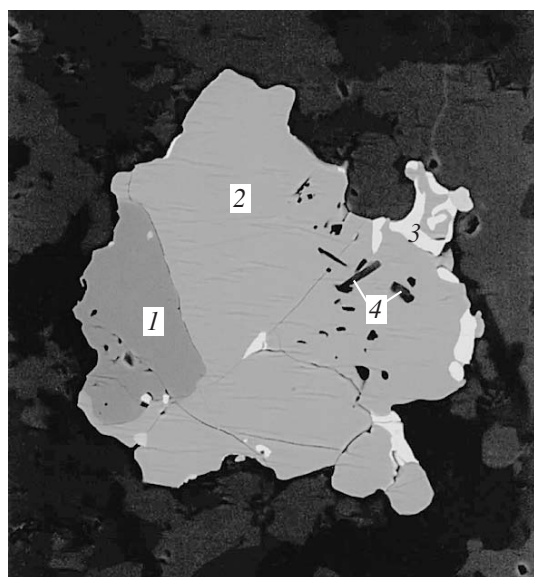


Fig. 3. Intergrowth of gahnite (80 μm long) (1), ilmenite (2), ferrocolumbite (3), and sillimanite (4) grains in an orthoclase-sekaninaite hornfels from a xenolith in foyaite at Mount Eveslogchorr; BSE image.



Fig. 4. Hercynite crystals (up to 8 mm in diameter) from an orthoclase veinlet in hornfels at Mount Kukisvumchorr.

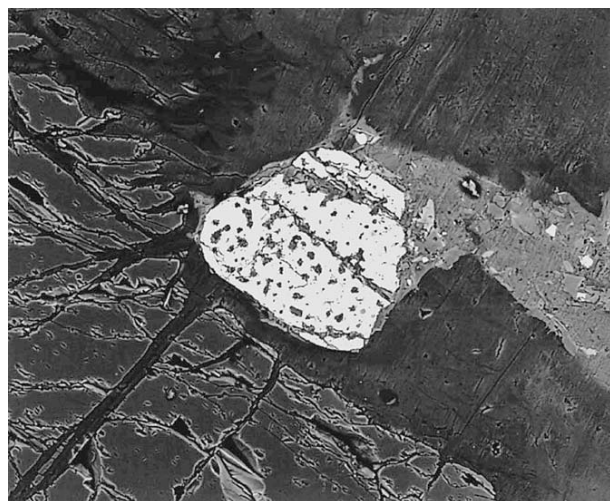


Fig. 5. Magnesiochromite crystal (0.2 mm in diameter) in serpentinized forsterite from an olivine melanephelinite dike in foidolite at Mount Koashva; BSE image.

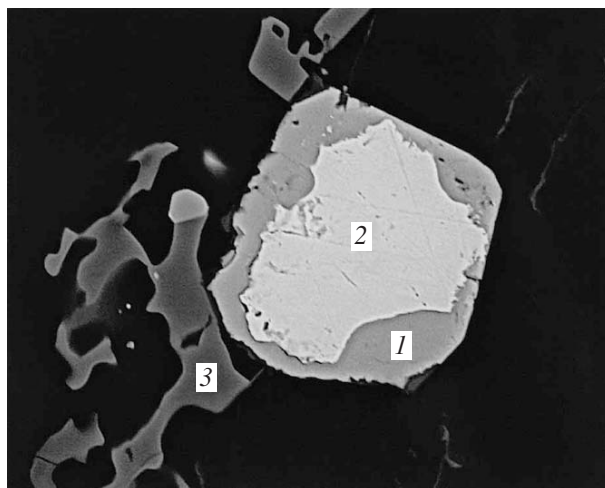


Fig. 6. Magnetite (1) replacing a native iron crystal (2, 30 μm in diameter) in sillimanite-albite hornfels at Mount Partomchorr; (3) hercynite; BSE image.

Mounts Poachvumchorr, Kaskasnyunchorr, Kukisvumchorr, Yuksporr, and Eveslogchorr (Kostyleva-Labuntsova et al., 1978; Shlyukova, 1986; Yakovenchuk et al., 2005). Spinel-orthoclase, corundum-spinel-orthoclase, and garnet-spinel-orthoclase hornfels and crosscutting corundum-orthoclase veins are characterized by the highest concentrations (up to 50 vol %) of small (up to 2 mm) octahedral hercynite crystals and rounded grains. In crosscutting corundum-orthoclase veins, dark green to black and perfectly faceted octahedral hercynite crystals often attain 1 cm in diameter (Fig. 4).

Hercynite is usually associated with annite, almandine, sodalite, nosean, quartz, sillimanite, zircon, ilmenite, pyrrhotite, native iron, fluorapatite, and monazite-(Ce).

Magnesiochromite MgCr_2O_4 is typical of alkaline ultramafic rocks of the dike series and volcanic pipes in ijolite-urtite from the eastern part of the pluton. Fine (up to 0.5 mm in diameter) idiomorphic magnesiochromite grains were revealed in dikes of alkaline picrites and carbonatites of Tul'ilukht Bay and in xenoliths of spinel peridotite and picritic cement of volcanic pipes at Mount Namuaiv (Arzamastsev et al., 1988),

Table 1. Microprobe analyses of normal spinellide, wt %

Component	Chr		Hc					Vuo	Ghn	Sp		
	1	2	3	4	5	6	7	8	9	10	11	12
MgO	11.90	12.96	—	0.18	3.12	7.78	2.16	0.33	0.19	21.79	12.93	24.09
Al ₂ O ₃	11.69	8.89	57.74	57.53	64.90	58.12	58.45	—	59.09	54.02	24.72	62.58
SiO ₂	0.00	0.32	0.57	0.24	—	0.13	0.58	—	0.33	0.11	—	—
CaO	—	0.44	—	—	—	—	—	—	—	—	—	—
TiO ₂	4.51	2.16	0.07	—	0.05	0.52	0.35	0.11	0.47	0.21	1.55	0.14
V ₂ O ₃	0.16	0.20	0.08	—	1.75	0.07	0.12	37.47	—	—	0.08	0.00
Cr ₂ O ₃	33.95	49.84	—	—	—	—	—	28.75	—	1.00	30.97	0.35
MnO	0.40	0.37	0.21	0.31	1.03	0.75	1.46	22.80	0.64	0.26	0.31	0.22
FeO	33.78	22.47	41.38	24.76	22.76	28.52	34.37	8.84	13.41	19.92	25.73	10.61
NiO	0.15	—	—	—	—	—	—	—	—	—	0.08	0.17
ZnO	0.07	—	0.19	16.63	1.35	2.99	1.87	—	25.57	0.21	0.01	0.81
Total	96.60	97.84	100.24	99.65	94.96	98.87	99.35	96.30	99.70	97.52	96.38	98.97

Note: (Chr) magnesiochromite, (Hc) hercynite, (Vuo) vuorelainenite, (Ghn) gahnite, (Sp) spinel. (1) Melanephelinite dike at Mount Koashva; (2) carbonated picrite from volcanic pipe in urtite at Mount Namuaiv; (3–9) hornfels after volcanic and sedimentary rocks from xenoliths in foyaites at Mounts Kaskasnyunchorr (3, 8), Eveslogchorr (4, 9), Partomchorr (5), Yumjechorr (6), and Kukisvumchorr (7); (10) melilitolite of Mount Putelichorr (Arzamastsev et al., 1988); (11) alkali picrite dike in the Oleny Creek Valley (Arzamastsev et al., 1988); (12) pyroxene dike at Mount Khibinpahkchorr.

Table 2. Microprobe analyses of magnetite, wt %

Component	1	2	3	4	5	6	7	8	9	10	11
MgO	—	—	—	—	—	—	—	—	0.10	6.23	6.68
Al ₂ O ₃	0.30	0.43	—	0.19	0.55	2.55	0.66	0.44	0.79	4.63	2.19
SiO ₂	0.31	0.33	0.15	0.18	0.44	0.55	0.16	0.39	0.39	—	0.02
CaO	—	—	0.16	—	0.11	0.05	—	0.11	0.35	—	—
TiO ₂	19.79	18.19	2.93	23.68	13.94	17.55	29.96	6.83	12.63	3.12	2.27
V ₂ O ₃	0.31	0.47	0.59	0.37	0.31	0.06	0.23	0.17	0.39	0.11	—
Cr ₂ O ₃	—	—	—	—	—	—	—	0.15	0.07	0.31	0.89
MnO	2.43	3.18	0.30	2.82	2.97	5.18	5.38	2.38	0.78	1.10	0.85
FeO	74.14	73.95	89.52	68.18	77.32	68.46	61.54	83.13	78.44	78.62	86.76
NiO	—	—	—	—	—	—	—	—	—	0.28	—
ZnO	0.13	—	—	0.43	0.14	0.45	—	—	—	0.09	—
ZrO ₂	—	—	—	—	0.23	—	—	—	—	—	—
Nb ₂ O ₅	—	—	—	0.14	—	—	—	—	—	—	—
Total	97.40	96.54	93.74	95.98	96.00	95.84	94.92	95.58	93.95	94.48	99.66

Note: (1–5) Foyaites at Mounts Yumjechorr (1–3), Yudychvumchorr (4), and Vantomnyutsk (5); (6–8) hornfels after volcanic and sedimentary rocks from xenoliths in foyaites at Mounts Yumjechorr (6), Kukisvumchorr (7), and Eveslogchorr (8); (9) carbonated picrite from volcanic pipe in urtite of Mount Namuaiv; (10) pyroxenite dike at Mount Khibinpahkchorr; (11) melilitolite at Mount Putelichorr (Arzamastsev et al., 1990).

where magnesiochromite occurs as subhedral octahedral crystals. In an olivine melanephelinite dike cutting urtites of Mount Koashva, rounded octahedral magnesiochromite crystals (Fig. 5) are associated with phlogopite, magnetite, and dolomite in serpentinized forsterite (Yakovenchuk et al., 2005).

Magnetite FeFe₂O₄ usually occurs as a high-Ti variety—titanomagnetite. Magnetite is a mineral found throughout all rocks in the Khibiny pluton. Its content varies from <0.5 vol % in nepheline syenite to 11 vol % in ijolite–urtite and more than 80 vol % in melteigite (Kostyleva-Labuntsova et al., 1978). Magnetite is usu-

ally scattered in rock as small (up to 5 mm in diameter) rounded grains that make up lenticular ore segregations (up to 15 cm in diameter) along with pyrrhotite and ilmenite. Veins composed of 60–80 vol % magnetite and 20–40 vol % aegirine, fluorapatite, biotite, titanite, and nepheline were detected in apatite–nepheline rocks at Mount Kukisvumchorr (Bonshtedt et al., 1937). Large (up to 30 cm) magnetite segregations are characteristic of aegirine–microcline, aegirine–nepheline–microcline, and titanite–aegirine–nepheline veins in foidolites and apatite–nepheline rocks at Mounts Koashva, Rasvumchorr, and Kukisvumchorr. There are also rare more or less distinct mosaic and skeletal magnetite crystals. They are usually octahedral, though crystals from ijolite–urtite are characterized by small additional rhombic dodecahedral and cubic faces as well (Ivanova et al., 1970). Hornfels after volcanic and sedimentary rocks occasionally contain rare disseminations of minute (up to 0.1 mm) magnetite crystals associated with predominant hercynite, ilmenite, pyrrhotite, and native iron. Magnetite forms partial or complete pseudomorphs after native iron (Fig. 6). In addition, very fine (up to 0.02 mm in diameter) exsolution magnetite lamellae are segregated on the {111} plane of hercynite crystals in xenoliths of volcanic and sedimentary rocks from foyaite at Mounts Poachvumchorr (Shlyukova et al., 1973) and Kukisvumchorr (our data). Small magnetite grains with rounded exsolution inclusions of spinel were found in dikes of alkaline ultramafic rocks (Arzamastsev et al., 1988; Yakovenchuk et al., 2005). Magnetite usually contains exsolution lamellae of ilmenite, hercynite, or spinel, but the ulvospinel segregations mentioned by some authors (Dudkin et al., 1964; Dudkin, 1968; Kostyleva-Labuntsova et al., 1978) have not been detected even as a result of detailed SEM investigations.

Franklinite ZnFe_2O_4 was identified by Pekov et al. (2000) in an aegirine–natrolite hydrothermal vein in nepheline syenite of Mount Yukspor, where this mineral is observed as reddish brown pseudomorphs after large grains of Fe-rich sphalerite. Franklinite has been identified from the X-ray powder pattern and characteristic X-ray spectrum.

Spinel $\text{Mg}(\text{Al},\text{Cr})_2\text{O}_4$ is a common product of exsolution of high-alumina magnetite in picrite, pyroxenite, and melilitolite. In magnetite grains, spinel occurs as fine (up to 20 μm) rounded inclusions with exsolution lamellae of ilmenite (Arzamastsev et al., 1988; Yakovenchuk et al., 2005). Small crystals of high-Cr spinel (up to 0.1 mm in diameter) are present in alkaline ultramafic rocks and carbonatites from the eastern part of the Main ring (Arzamastsev et al., 1988).

CHEMICAL COMPOSITION OF MINERALS

The chemical composition of spinel-group minerals from rocks of the Khibiny pluton was determined on a

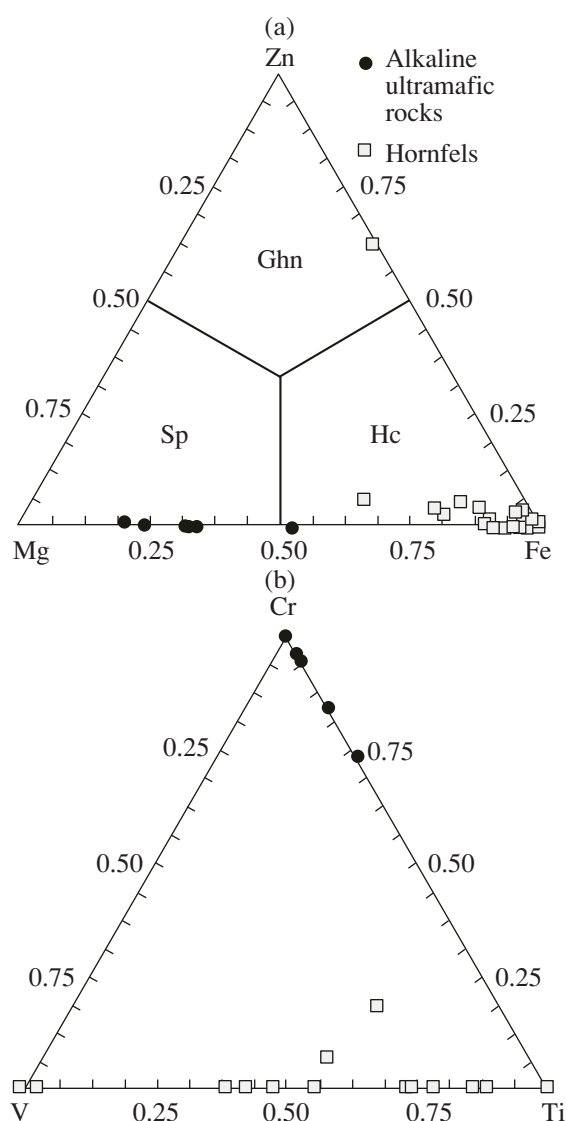


Fig. 7. Chemical compositions of aluminospinel from the Khibiny pluton, at %: (a) species-forming cations in the tetrahedral position and (b) admixture cations in the octahedral position.

Cameca MS-46 microprobe at the Geological Institute, Kola Scientific Center, Russian Academy of Sciences. Selected microprobe analyses of the spinel-group minerals with the normal spinel structure (aluminospinel, magnesiochromite, and vuorelainenite) and magnetite are presented in Tables 1 and 2, respectively.

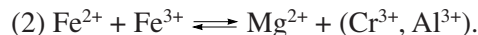
The composition of aluminospinel from hornfels after volcanic and sedimentary rocks varies from virtually pure hercynite to gahnite (xenoliths in foyaite at Mount Eveslogchorr) and magnesium hercynite (other xenoliths), which is similar in composition to spinel from alkaline ultramafic rocks (Fig. 7). Aluminum in octahedral positions of aluminospinel from hornfels after volcanic and sedimentary rocks is partially substituted by titanium and vanadium up to the formation of vuore-

Table 3. Principal component analysis of magnetite compositions, at %

Variable	Eigenvector		
	1	2	3
Mg	0.269	-0.929	0.033
Al	-0.160	-0.745	0.127
Si	-0.205	0.192	-0.836
Ca	0.022	0.158	-0.856
Ti	-0.929	0.178	-0.004
V	0.309	0.609	-0.278
Cr	0.330	-0.855	-0.043
Mn	-0.832	0.125	0.069
Fe	0.932	0.243	0.014
Zn	-0.31	0.107	0.506
Eigenvalue	2.267	2.701	1.790
Contribution to dispersion, %	29	27	18

Note: Loads exceeding 0.5 are boldfaced.

shown that the Khibiny pluton is characterized by two schemes of isomorphism (Table 3, Fig. 8):



The first scheme is typical of foyaite, foidolite, veins, and hornfels after volcanic and sedimentary rocks. The second scheme is characteristic of alkaline ultramafic rocks and some hornfels varieties. Therefore, the majority of analyzed samples are characterized by a negative linear correlation between (Ti + Mn) and Fe, which is close to the theoretical relationship (Fig. 9).

Along the line that crosses the Khibiny pluton from the contact with country metavolcanic rocks to the geometric center (Fig. 1), the chemical composition of “titanomagnetite” that appears uniform under an electron microscope varies symmetrically relative to the Main ring (Yakovenchuk et al., 2005). Closer to the Main ring, the total of Ti and Mn in magnetite increases from 5–15 to 40 at % at the expense of a decrease in Fe and V (Fig. 10).

lainenite. Aluminum from ultramafic rocks is replaced by chromium up to the formation of magnesiochromite.

The principal component analysis of magnetite composition with normalizing and varimax rotation has

DISCUSSION

The Khibiny foyaite pluton is characterized by quite distinct petrographic and geochemical zoning, which is symmetrical to the Main Ring Fault, composed of melt-

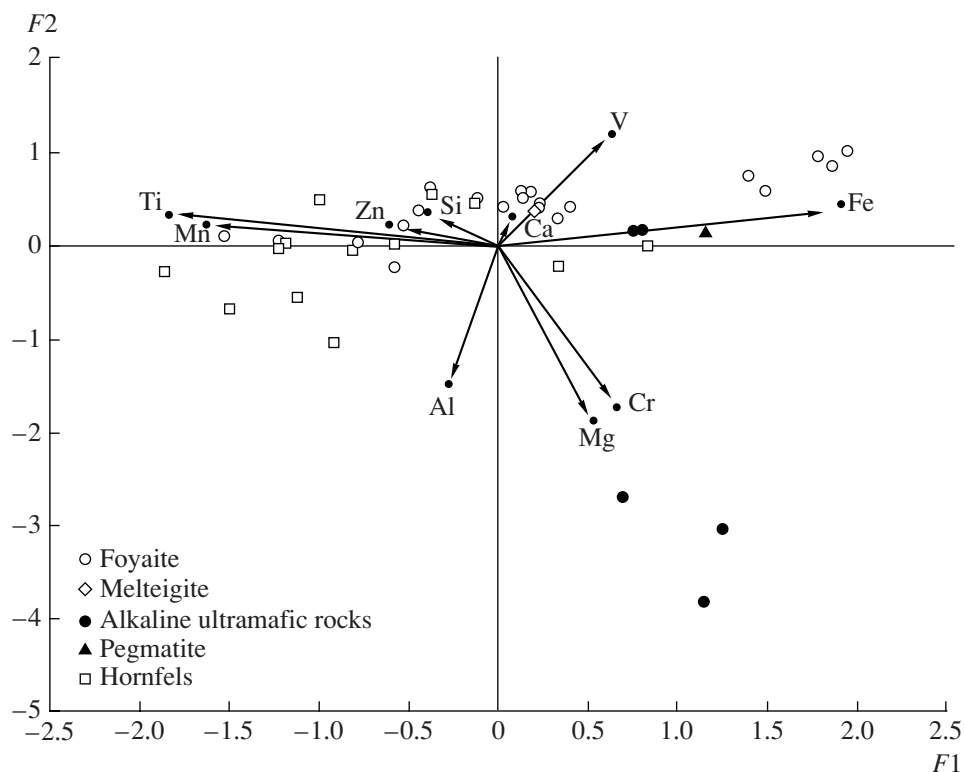


Fig. 8. Composition of magnetite from the Khibiny pluton in coordinates of the first two principal components. Lengths of vector variables and vector objects are not agreed.

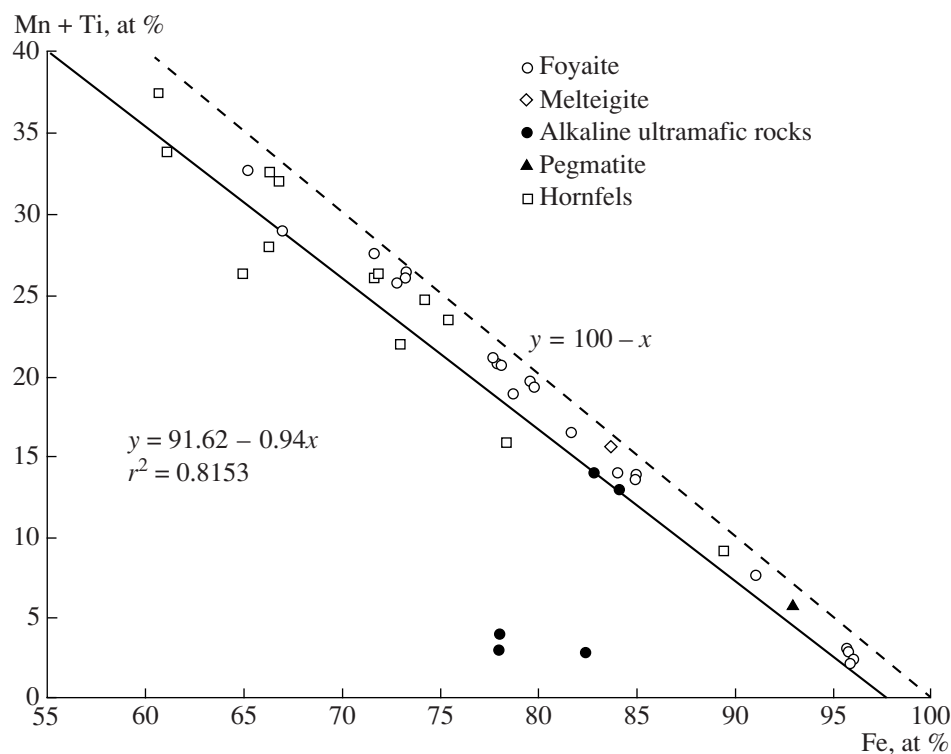


Fig. 9. Relationship between Fe, Ti, and Mn contents in magnetite from the Khibiny pluton.

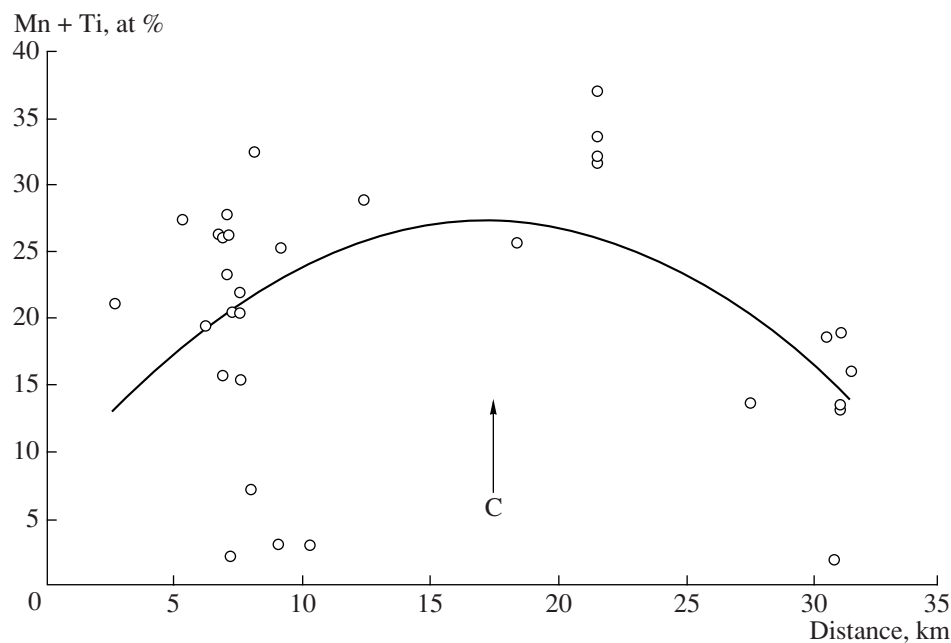


Fig. 10. Variation of Mn and Ti contents in magnetite from the margin to the center of the Khibiny pluton along the line A-B-C-D. The arrow shows the position of the Main ring (point C in Fig. 1).

eigite-urtite and apatite-nepheline rocks (Goryainov et al., 2005). The variation in the chemical composition of most minerals found throughout (potassium feldspar, nepheline, fluorapatite, amphibole, pyroxene, eudia-

lyte, lamprophyllite, sodalite, ilmenite, etc.) is symmetrical with regard to this fault zone as well. Many trends expressed in foyaites are traced farther to rischorrite, foidolite, and apatite-nepheline rocks. The zoning in

the pluton is manifested in more or less advanced fractionation with concentration of trace elements originally dispersed in rock-forming silicates rather than in a mere increase or decrease in contents of particular elements. Thus, closer to the Main ring, the Mn content increases in eudialyte but decreases in ilmenite and amphibole, the K content increases in amphibole but decreases in feldspar and nepheline, the Ca content increases in pyroxene and titanite but decreases in fluorapatite and amphibole, and so on. The Ti content in magnetite from foyaite increases from the margins and center of the pluton toward the Main ring. At a distance of 3 km from the Main ring, magnetite almost completely disappears in foyaite, having been replaced by ilmenite.

Taking into consideration the fractal geometry of apatite deposits with a topology corresponding completely to the topology of tension fractures (Ivanyuk et al., 2002; Goryainov et al., 2005) and the character of ancient and recent tectonic unloading of the continually emerging Khibiny pluton (Goryainov et al., 1998), it becomes clear that the zoning was formed as a result of fractionation initiated by the origin of a conic fault in a completely consolidated foyaite body subjected to dilatancy and accompanied by the injection of foidolite melt into the fault zone. In our opinion, the nature of global fractionation of large rock volumes may be interpreted in terms of the theory of dissipative structures (Goryainov and Ivanyuk, 2001). One possible mechanism of such self-organization is offered by the concept of aqua-complexes developed by Stenina et al. (1984, 2005).

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