

# Self-Organization of the Khibiny Alkaline Massif (Kola Peninsula, Russia)

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## 1. Introduction

The world's largest Khibiny alkaline massif occupies the area of about 1327 km<sup>2</sup> in the extreme West of the Kola Peninsula, at the contact of rocks of the Imandra-Varzuga Proterozoic greenstone belt and the Archaean metamorphic complexes of the Kola-Norwegian megablock (Fig. 1). According to Pb-Pb, Rb-Sr and Sm-Nd dating (Arzamastsev et al., 2007), the age of the main rock types of the Khibiny massif is 380-360 million years.

About 70% of the massif area is occupied by nepheline syenites (foyaite) monotonous in composition which are, in most works, subdivided into two equal parts: foyaite proper (in the center) and "khibinite" (surrounding them), separated from each other by a zone rock complex of the Main Ring. Besides, practically every geological map of the Khibiny massif highlights the concentric zones of massive and trachytic khibinite and foyaite, along the edge and in the center, and on both sides of the Main Ring, respectively.

Within the Main Ring, foidolites (melteigite-ijolite-urtite), high-potassic poikilitic nepheline syenite (rischorrite) and less widespread malignite, as well as titanite-nepheline, titanite-apatite and apatite-nepheline rocks are of crucial importance. The same complex of rocks can be related to the so-called irregular-grained nepheline syenite ("lyavochorrite"), transitive to rischorrite in accordance with modal composition, texture-structural features and geological position (see Fig. 1). The rock complex of the Main Ring fills a conic fault in which the angle between the axis and generatrix varies between 50-70° close to the surface and 10-40° at the depth of more than 1 km. On the day surface, rocks of this complex occupy 30 % of the total area of the massif, the share of foidolites, rischorrite and lyavochorrite making up 10 vol. % each. Apatite-nepheline and titanite-apatite-nepheline rocks form fractal ore stockworks (Fig. 2) in the apical parts of the foidolite ring, being related to it by gradational transitions. The thickness of apatite-rich foidolites ranges from 200 m in the south-western part of the Main Ring up to the first meters in its north-eastern part.

Within the Main Ring and, especially, in the adjoining parts of nepheline syenites (on both sides of the Ring), there are a lot of xenoliths (from half a meter up to several kilometers across) of volcanogenic-sedimentary rocks metamorphosed to hornfels and fenitized (Korchak et al., 2011). Xenoliths, though occupying less than 1 % of the total day surface of the massif, are in constant association with the much wider spread fine-grained alkaline and nepheline syenites obviously representing the result of a more or less deep fenitization of volcanogenic-sedimentary rocks metamorphosed to hornfels.

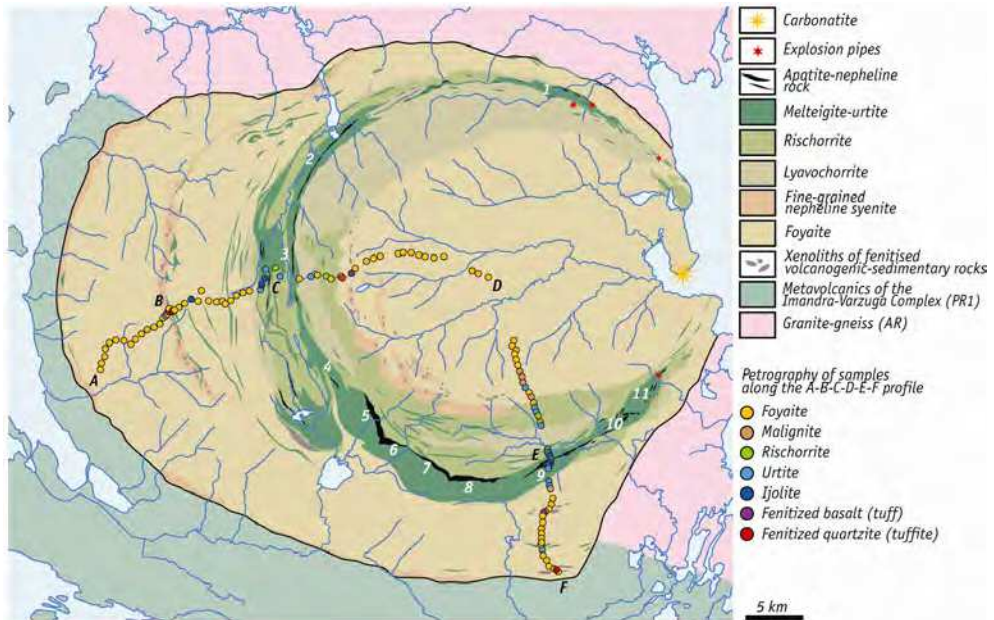


Fig. 1. Simplified geology map of the Khibiny massif (after Snyatkova et al., 1983). Apatite-nepheline deposits: 1 – Valepakhk, 2 – Partomchorr, 3 – Kuelporr, 4 – Snezhny Zirk, 5 – Kukisvumchorr; 6 – Yuksporr; 7 – Apatitovy Zirk; 8 – Plato Rasvumchorr; 9 – Koashva; 10 – Niorkpakhk; 11 – Oleniy Ruchei. A-B-C-D-E-F – profile with sampling points.

Fine-grained alkaline and nepheline syenites (3 % of the massif's total area) are concentrated within three ring zones: at the border of the massif, on the periphery of the Main Ring and within the Small Semiring (see Fig. 1). The latter, up to 500 m wide, located in the foyaite part of the massif external relatively the Main Ring, is composed of fine-grained alkaline and nepheline syenites (fenites?) with xenoliths of volcanogenic-sedimentary rocks and also by bodies of melteigite, urtite, and malignite. Fine-grained alkaline and nepheline syenites of the outer zone are bedded as separate, up to 200 m wide, lenses and strips; they usually have gradational contacts with foyaite and are often present as xenoliths within the latter.

Dyke rocks of the Khibiny massif are represented, for the most part, by hypabyssal analogues of its plutonic rocks: alkali-feldspar trachyte, phonolite and melanephelinite, mainly concentrated near the Main Ring, as well as by monchiquite and carbonatite composing veins and explosion pipes in its eastern part (Ivanyuk et al., 2009). Pegmatite and hydrothermal veins, which include an unusually great number of mineral species (about 300), are common throughout the massif, with their main concentration within rischorrite and foidolites of the Main Ring. In foyaite, there are ordinary clinopyroxene-nepheline-microcline veins, but, as the Main Ring is approached, their mineral composition becomes more and more varied – up to 80 minerals in a vein (Yakovenchuk et al., 2005).

Generally speaking, the geological events were mostly occurring within the Main Conic Fault and it is this structure that controls the bodies of apatite-nepheline rocks, brecciating

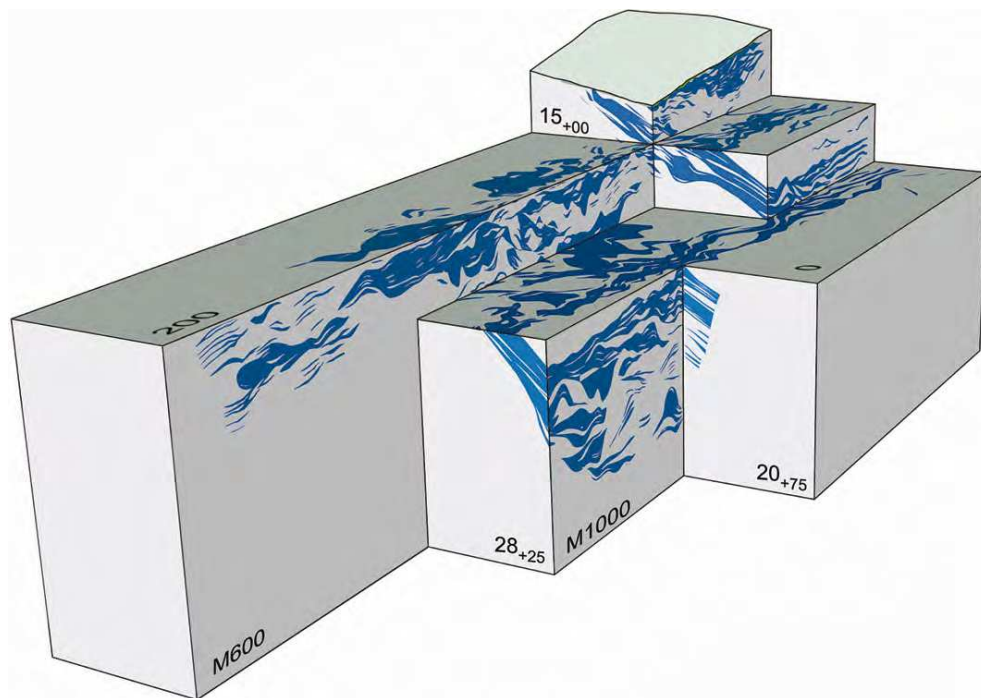


Fig. 2. Block-diagram of the Koashva deposit. Greenish-grey – ijolite-urtite, blue – apatite-nepheline rock (foiolites with  $P_2O_5 \geq 4$  wt. %).

and folding zones, explosion pipes, dykes of phonolites, alkali-ultrabasic rocks and foidites; zones of albitization and aegirinization of nepheline syenites bearing eudialyte, astrophyllite, loparite, rinkite, and pyrochlore mineralization; pegmatite and hydrothermal veins, zones of contemporary mineral formation, and epicentres of earthquakes (Goryainov et al., 1998). Besides the Main Ring, the Small Semiring, and a number of some less pronounced conic tectonic structures, the massif also reveals later subvertical radial faults diverging from the extreme eastern point of the massif (the latter is marked, in addition, by stockworks of carbonatite veins) similar to cracks resulting from hammering on glass. Although no essential displacements were found within the radial faults, all zones of foliation, crushing, spreusteinization, and chemical decomposition of nepheline syenites and foidolites are related to them.

Similar to the majority of stretching fractures, the Main Ring fault has a fractal morphology of percolation clusters ( ${}^3D = 2.54$ ): fractal dimension of the foidolite cluster shown in Fig. 1 is  ${}^3D \approx {}^2D + 1 = 2.5$ , approximately equal to that of apatite-ore clusters of the Koashva deposit (see Fig. 2)  ${}^3D \approx {}^2D + 1 = 2.7$  and fluorapatite clusters in apatite-nepheline rock  ${}^3D \approx {}^2D + 1 = 2.6$  (Fig. 3) in an interval of scales from 0.001 up to 3 kms. Processes of fractal fault network formation kept recurring with accumulation of critical pressure in the rising massif – every time with a smaller power effect. Notably, the morphology and fractal dimension of the forming structures (pegmatites, hydrothermalites, and modern clusters of sodium carbonates) always corresponded to those of percolation clusters (Goryainov et al., 1998; Ivanyuk et al., 2009).

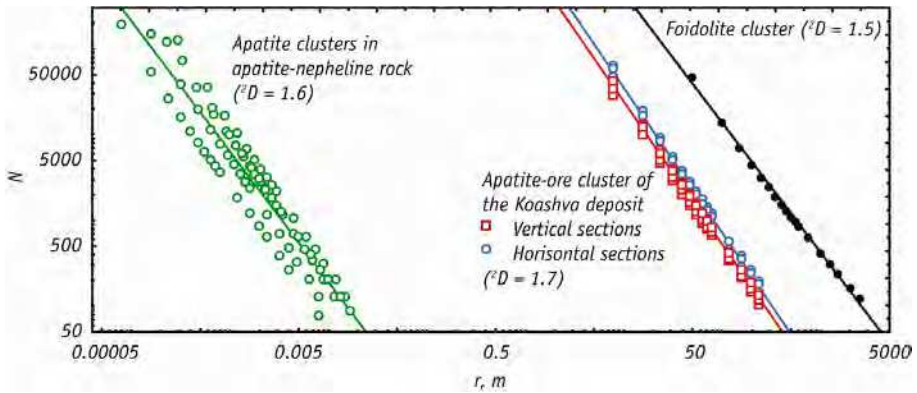


Fig. 3. The  $\ln$  of number of boxes  $N(r)$  with side length  $r$  needed to cover clusters of foidolite, apatite-nepheline rock and fluorapatite as a function of  $r$ .

Despite its rather simple structure, not only the genesis of the Khibiny massif but also the age ratio of the rock complexes discussed above, have generated heated debates till nowadays. A lot of genetic models have been proposed to explain the concentric-zoned structure of the massif (Fig. 4). The reason for such a variety of genetic models is ambiguity of the rock ratio and proximity of their absolute ages. In order to correlate the results of tectonic, geochemical and mineralogical researches within a uniform concept, we have carried out own systemic study of the Khibiny massif, including its mineral, petrographic and geochemical zonation along the profile from the Khibiny railway station (the *A* point in Fig. 1) to the massif center, Mt. Vantomnyutsk (point *D*) and further across the Koashva deposit (the *E* point) to the contact with host rocks at the foot of Mt. Kitchepahk (the *F* point). We also have re-interpreted the structures of the Khibiny apatite deposits on the basis of the data obtained during their mining. This work summarizes the results of research, which was partly published in a number of our works (Yakovenchuk et al., 2005, 2008, 2010a–d; Ivanyuk et al., 2009, 2010; Konopleva et al., 2008; Pakhomovsky et al., 2009).

## 2. Petrography

According to *QAPF* classification, the conventional boundary of nepheline syenites with foidolites passes at the line of  $\text{Fsp}_{60}\text{Ne}_{40}$ , and with alkaline syenites – at the line of  $\text{Fsp}_{90}\text{Ne}_{10}$  (Fig. 5). According to the color index *M*, the nepheline syenites are subdivided into foyaitite (0–30% of dark-coloured minerals), malignite (30–60%), and shonkinite (more than 60% of dark-coloured minerals). For foidolites, a division into urtite (10–30% of dark-coloured minerals), ijolite (30–70%) and melteigites (70–90%) is generally accepted. The estimation of the volumetric proportion of minerals in samples selected by us along the *A–B–C–D–E–F* profile (see Fig. 1) was made by counting the areas occupied by these minerals on polished sample sections (about  $20 \times 20$  cm). The minerals were diagnosed by using microprobe analysis and powder X-ray diffractometry.

*Foyaitite* represents medium- to coarse-grained leucocratic greenish-grey rocks composed of tabular up to equant crystals of potassium feldspar (usually with albite perthites) whose interstices in the aggregate are filled with euhedral grains of nepheline and prismatic crystals of dark-coloured minerals, with domineering clinopyroxenes of aegirine-diopside

series, and also alkaline and Na-Ca amphiboles (richterite-ferrichterite, magnesiokatophorite-katophorite, magnesioarfvedsonite-arfvedsonite, etc.) among the latter. The rock-forming minerals are nepheline, microcline, orthoclase, albite, aegirine, augite, Na-Ca- and Na-amphiboles, aenigmatite, titanite, eudialyte, lamprophillite, and annite. The widest spread accessory minerals include magnetite, loparite-(Ce), pyrochlore, sodalite, rinkite, astrophyllite, barytolamprophyllite, ilmenite, lorenzenite, rosenbuschite, fluorapatite, fluorite, and pyrrhotite. Secondary minerals are represented mainly by zeolites (natrolite, gonnardite, analcime, etc.), illite, pyrite, anatase, and goethite.

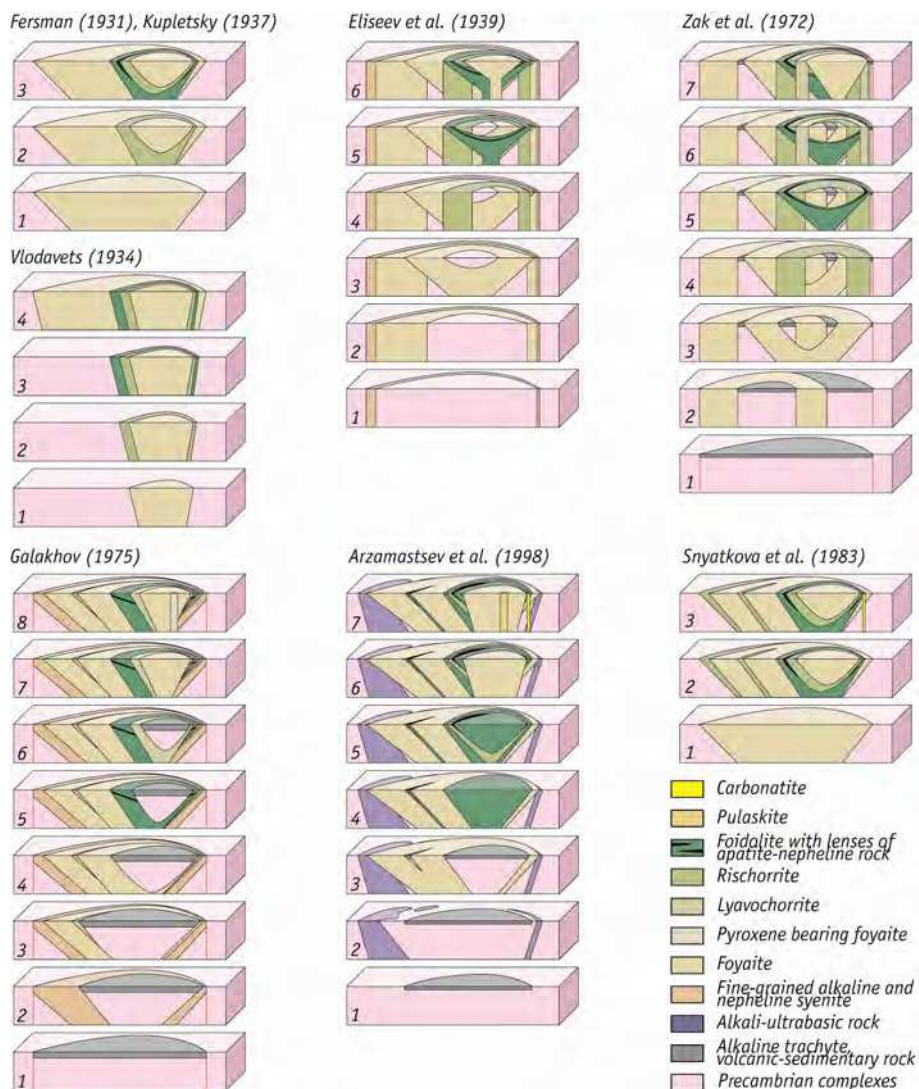


Fig. 4. Genetic models of the Khibiny massif.

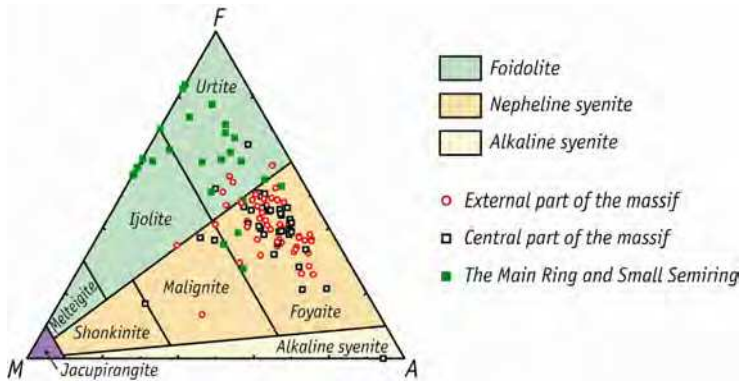


Fig. 5. Modal composition of alkaline rocks estimated using grain squares of feldspar (A), nepheline+kalsilite+sodalite (F), and dark coloured minerals (M) in polished hand-sized specimens sampled along the A-B-C-D-E-F profile.

The quantitative proportion of feldspar, nepheline and dark-coloured minerals in foyaite along the A-B-C-D-E-F profile varies over a rather wide range (see Fig. 5), generally corresponding to the composition of  $Fsp_{44}Ne_{40}M_{16}$ . The average mineral composition of foyaite in the part of the massif external relatively the Main Ring ("khibinite"),  $Fsp_{44}Ne_{40}M_{16}$ , is practically identical to that of the rocks in the central part of the massif,  $Fsp_{43}Ne_{40}M_{17}$ . It should be noted that, in accordance with classification *QAPF*, about 10 % of the samples corresponding to foyaite according to its position in the A-B-C-D-E-F profile, its structural-textural features, and the set and composition of minerals composing them, are referred to the foidolite field. Above all, these samples differ from the feldspar ijolite-urtite of the Main Ring, similar to them in modal composition, due to the tabular shape of microcline-perthite crystals and an utter absence of "web-footed" metacrysts of orthoclase with poikilitic inclusions of nepheline and kalsilite.

The content of major minerals in foyaite changes symmetrically relative to the Main Ring along the A-B-C-D-E-F profile (Fig. 6). The share of alkaline feldspar in the rock composition decreases towards the contacts with foidolites proportionally to the width of the latter in the profile: less intensively in the area at Mt. Marchenko Peak (the C point); more intensively in the area at Mt. Koashva (the E point). This change is compensated by increasing contents of nepheline in the C point and dark-coloured minerals in the E point. In the former case, this results in the formation of leucocratic foyaite transitive to urtite (or even urtite, still corresponding to foyaite in composition); in the latter case - in mesocratic nepheline syenite and malignite. The consecutive increasing of feldspar content (at the expense of nepheline) from the Main Ring towards the outer parts and centre of the massif results in the occurrence of alkaline syenites, described in (Ramsay & Hackman, 1894; Korobeynikov & Pavlov, 1990) under the name of umptekite (A) and pulaskite (D).

On the whole, the distribution of accessory minerals in foyaite along the A-B-C-D-E-F profile appears as extremely non-uniform. However, practically all curves of the occurrences of certain mineral species (Fig. 7) proved to be symmetric relatively the center of the massif, this concerning both widespread minerals (biotite, sodalite, ilmenite, magnetite, etc.) and rare species (banalsite, rosenbuschite, strontioapatite, etc.). Titanite and fluorapatite are through minerals of foyaite, whereas lamprophyllite, biotite, aenigmatite, astrophyllite,

and lozenzenite mainly concentrate either in the central part of the massif (biotite, astrophyllite) or in its outer parts. The occurrence of the majority of accessories (barytolamprophyllite, rinkite, rosenbuschite, pyrochlore, ilmenite, magnetite, fluorite, etc.) decreases as the Main Ring is approached. Conversely, eudialyte and sodalite become here an integral attribute of the rocks.

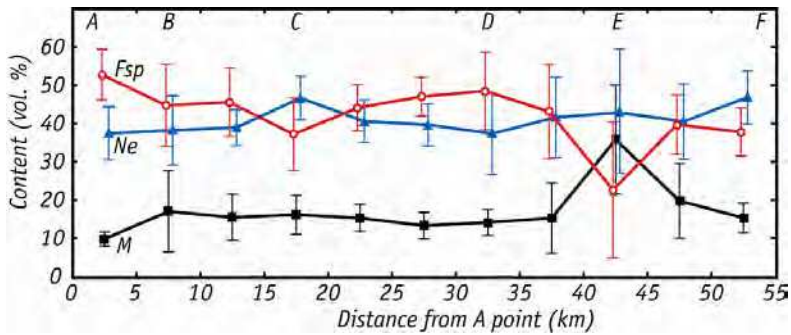


Fig. 6. Variation of alkaline feldspar (Fsp), nepheline (Ne) and dark coloured minerals (M) contents along the A-B-C-D-E-F profile (mean plus-minus standard deviation).

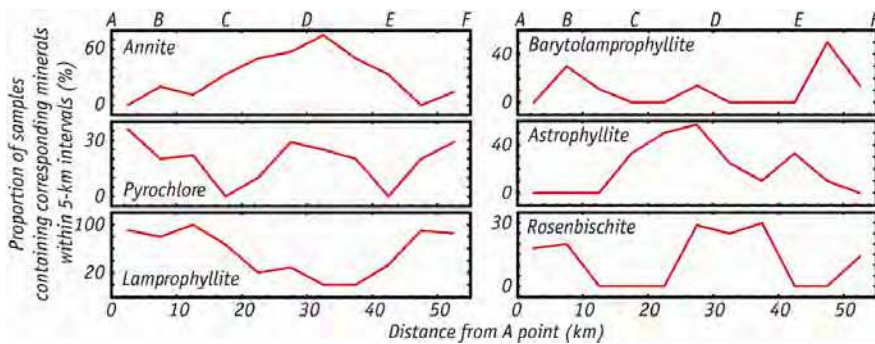


Fig. 7. Variation of accessory mineral contents along the A-B-C-D-E-F profile.

The texture of foyaite can be both massive and trachytic. Field observations of the majority of researchers have noted the trachytic variety of foyaite at contacts with foidolites of the Small Semiring and the Main Ring, and also to the western and southern contacts of the massif with host metamorphic rocks (Tihonenkov, 1963; Zak et al., 1972; Galakhov, 1975; etc.). At the same time, trachytic foyaite was often found (Snyatkova et al., 1983) to be alternating with massive foyaite. The definition of foyaite trachtyoid structure, i.e. the definition of the degree of orientation of potassium feldspar tabular crystals in the rock, has been made by us in the polished sections of foyaite samples picked along the A-B-C-D-E-F profile. From the diagram showing the variation of standard deviation of the  $b$  axis orientation in potassium feldspar tabular crystals from their average direction,  $\sigma_{Fsp}$  (Fig. 8a), it follows that, contrary to the common belief, the degree of foyaite isotropism gradually increases moving from the outer and central parts of the massif towards the Main Ring, near which foyaite grades into entirely isotropic rischorrite.

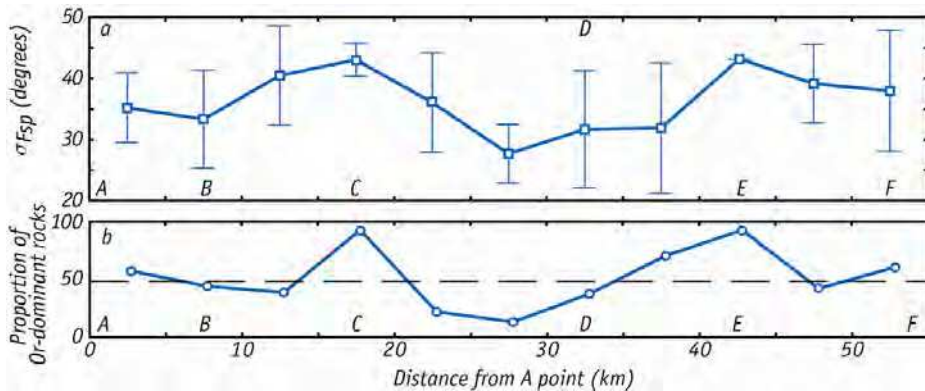


Fig. 8. Variation of standard deviation (a) of the *b* axis orientation in potassium feldspar tabular crystals from their average direction ( $\sigma_{Fsp}$ ) and the presence of orthoclase-dominant rocks (b) along the A-B-C-D-E-F profile.

X-ray diffraction analysis of potassium feldspar has shown (Fig. 8b) that orthoclase-dominant foyaite occurs less frequently moving from the outer part towards the center of the massif and it is against this background that a sharp “orthoclase” maximum is observed near the Main Ring (Ivanyuk et al., 2010). Since orthoclase, compared to microcline, is a higher-temperature modification of potassium feldspar, its diminishing share towards the massif center allows to suggest gradual decreasing of the temperature of feldspar (re)crystallization in this direction while the foyaite intrusions were consolidating. Apparently, the transition of microcline foyaite to orthoclase foyaite, finally turning to rischorrite near the Main Ring, accompanying the textural isotropization of these rocks, occurred owing to the warming-up of fault parts of the massif by foidolite melt.

Data on the chemical composition of foyaite are presented in Table 1. As is peculiar to plutonic rocks, the empirical distributions of principal components in foyaite (Si, Al, Na, K and Fe oxides) correspond to the normal law. Logarithmically normal (exponential) distributions of MgO, CaO, SrO, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, F and Cl contents are due to enrichment of the foyaite parts contacting with the Main Ring with these components (such as fluorapatite, titanite, and other minerals).

*Malignite*, a melanocratic (*M*<sub>30-60</sub>) variety of nepheline syenites, has a rather limited distribution in the Khibiny massif being mostly concentrated on the periphery of the rischorrite-foidolite ring. Contacts of malignite with ambient foyaite can be both gradational (more often) and sharp. The latter case is usually realized within various tectonic zones where malignite and foyaite often interchange. Macroscopically, malignite represents fine- or medium-grained composed of nepheline, orthoclase-perthite, aegirine, aenigmatite, and iron-dominant Na-Ca and alkaline amphiboles (ferroeckermannite, ferrichterite, arfvedsonite, etc.). The average composition of malignite, observed by us along the A-B-C-D-E-F profile, makes Fsp<sub>31</sub>Ne<sub>28</sub>M<sub>41</sub> (see Fig. 5). Malignite is characterized by a gneissose structure caused by oriented arrangement of aegirine fibers, prismatic crystals of amphiboles and lamprophyllite, elongated segregations of aenigmatite and eudialyte. Eudialyte (up to 5 vol. %) and titanite (up to 7 vol. %) are typical constituents of malignite. Other characteristic accessories are fluorapatite, aenigmatite, lamprophyllite, baryto-lamprophyllite, rinkite, ilmenite, and pyrrhotite.



	Distribution ( $r^2$ )	$n$	Content (wt. %)				
			Mode	Mean	Min	Max	$\sigma$
SiO <sub>2</sub>	Normal (0.952)	143	53.75	54.74	47.48	63.67	2.15
TiO <sub>2</sub>	Lognormal (1.000)	143	0.86	0.88	0.20	5.34	0.56
ZrO <sub>2</sub>	Lognormal (0.955)	86	0.07	0.10	0.02	0.30	0.05
Al <sub>2</sub> O <sub>3</sub>	Normal (0.998)	143	21	20.95	13.61	28.6	1.91
Fe <sub>2</sub> O <sub>3</sub>	Lognormal (0.997)	143	1.5	2.26	0.24	7.57	1.10
FeO	Normal (0.992)	143	1.75	1.78	0.39	6.46	0.84
MnO	Lognormal (0.997)	139	0.14	0.19	0.08	0.71	0.10
MgO	Lognormal (0.989)	143	0.42	0.49	0.07	2.57	0.32
CaO	Lognormal (0.998)	143	1.12	1.18	0.45	6.53	0.73
SrO	Lognormal (0.933)	112	0.22	0.11	0.01	0.58	0.09
Na <sub>2</sub> O	Normal (0.996)	143	9.50	9.47	5.78	13.15	1.13
K <sub>2</sub> O	Normal (0.999)	143	5.50	5.83	1.14	9.91	0.8
P <sub>2</sub> O <sub>5</sub>	Exponential (0.999)	124	0.06	0.18	0.00	1.30	0.14
CO <sub>2</sub>	Lognormal (0.993)	84	0.10	0.12	0.03	1.87	0.2
H <sub>2</sub> O	Cauchy (0.991)	143	0.75	1.09	0.24	3.01	0.48
S <sub>tot</sub>	Exponential (0.999)	64	0.01	0.04	0.01	0.26	0.05
Cl	Exponential (0.996)	123	0.01	0.04	0.00	0.33	0.05
F	Exponential (0.955)	120	0.13	0.15	0.00	0.64	0.09

Table 1. Chemical composition of foyaite ( $n$  – quantity of samples,  $\sigma$  – standard deviation).

*Rischorrite*, or poikilitic nepheline syenite, is a leucocratic massive medium- to coarse-grained rock easily identifiable during a field research owing to its characteristic poikilitic structure. This structure is due to the presence of large (up to 20 cm in diameter) equant metacrysts of orthoclase, overflowed with poikilitic inclusions of nepheline, kalsilite and dark-coloured minerals, in fine-, medium-grained mass of euhedral grains of nepheline cemented by dark-coloured minerals (mainly aegirine and potassicarfvedsonite). The average composition of rischorrite taken by us along the *A-B-C-D-E-F* profile makes  $Fsp_{36}Ne_{44}M_{20}$ . It should be noted, however, that, similarly to the case with foyaite, the boundary between rischorrite and feldspar urtite was drawn absolutely formally, according to *QAPF* classification. Actually, they form a continuous series of rocks genetically related among themselves by processes of orthoclase poikiloblasts forming. The rock-forming minerals are nepheline, sodalite, orthoclase, aegirine, arfvedsonite, potassicarfvedsonite, potassic-ferroeckermannite, magnesioarfvedsonite, annite, titanite, aenigmatite, ilmenite, lamprophillite, astrophyllite, and fluorapatite. The accessories include eudialyte, lorenzenite, pectolite, rinkite, yuksporite, fersmanite, lomonosovite, murmanite, loparite-(Ce), ancylite-(Ce), magnetite, sphalerite, djerfisherite, and pyrrhotite. Also found are kalsilite, natrolite, goethite, wadeite, and catapleite present as secondary minerals.

The data on the average chemical composition of rischorrite are given in Table 2. Empirical distributions of components in these rocks are essentially different from those in foyaite. So, normal distribution of FeO and logarithmically normal distribution of Fe<sub>2</sub>O<sub>3</sub> in foyaite “change places” on transition to rischorrite. This inversion reflects a transition from essentially calcium-rich pyroxenes and amphiboles, dominating in foyaite, to aegirine and arfvedsonite peculiar to rischorrite. Normal distribution of Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O concentrations in foyaite is replaced by *Q*-normal on transition to rischorrite, which suggests introducing of these components in protorischorrite in the course of their nephelinization on the contact

with foidolites. The content of  $K_2O$ ,  $CaO$ ,  $P_2O_5$ ,  $Cl$ ,  $F$ , and  $H_2O$  in rischorrite is characterized by bimodal distributions in which the first maximum is quite comparable to the average content of the given components in foyaite. The second maximum is, obviously, related to introducing of considered components from foidolites during a fluid-metasomatic alteration of foyaite overlying them, and transformation of the latter into rischorrite.

	Distribution ( $r^2$ )	$n$	Content (wt. %)				
			Mode	Mean	Min	Max	$\sigma$
$SiO_2$	Cauchy (0.897)	80	51.5	51.48	47.02	56.93	2.33
$TiO_2$	Normal (0.997)	80	1.25	1.23	0.28	3.15	0.51
$ZrO_2$	Exponential (0.962)	13	0.05	0.12	0.02	0.60	0.18
$Al_2O_3$	Q-normal (0.984)	80	21.00	20.87	12.07	25.07	2.37
$Fe_2O_3$	Cauchy (0.965)	80	2.50	2.70	0.03	8.05	1.57
$FeO$	Lognormal (0.975)	80	1.96	2.50	0.90	10.66	1.94
$MnO$	Lognormal (0.995)	78	0.12	0.17	0.06	0.93	0.13
$MgO$	Normal (0.805)	80	0.62	0.68	0.07	2.37	0.41
$CaO$	Bimodal	80	0.75 and 1.75	1.40	0.19	3.81	0.73
$SrO$	Exponential (0.979)	61	0.06	0.15	0.01	0.93	0.13
$Na_2O$	Q-normal (0.952)	80	8.50	8.35	3.77	12.82	1.84
$K_2O$	Bimodal	80	<u>7.50</u> and 10.50	8.40	4.13	14.12	2.24
$P_2O_5$	Bimodal	70	<u>0.05</u> and 0.50	0.16	0.01	0.81	0.18
$CO_2$	Exponential (0.945)	55	0.05	0.10	0.02	1.01	0.20
$H_2O$	Bimodal	47	<u>0.70</u> and 1.10	1.00	0.16	2.48	0.50
$S_{tot}$	Exponential (0.995)	20	0.03	0.06	0.00	0.74	0.19
$Cl$	Bimodal	27	<u>0.03</u> and 0.14	0.04	0.01	0.15	0.04
$F$	Bimodal	66	<u>0.15</u> and 0.60	0.12	0.01	0.68	0.11

Table 2. Chemical composition of rischorrite ( $n$  – quantity of samples,  $\sigma$  – standard deviation. More intensive maximum of bimodal distribution is underlined).

It is remarkable that foidolites, having the lowest potassium contents in the Khibiny rocks, should cause a potassic metasomatism of ambient foyaite. It is known (Hayward et al., 2000) that silicon, superfluous relative to the stoichiometric values of 4 atoms of Si per molecule in nepheline, along with the inverse process, is compensated by removing or introducing of an equivalent quantity of potassium (sodium takes no part in this process). As is shown by the dependence of Na and K contents on the proportion of Si, Al and  $Fe^{3+}$  in nepheline from various rocks of the Khibiny massif (Fig. 9), potassium content in nepheline from foidolites of the Main Ring is extreme and the rest potassium must be accumulated in a residual fluid.

Autometasomatic alteration of foidolites (including apatite-nepheline rocks) by residual potassium-rich fluids during the intrusion cooling has resulted in substitution of nepheline for kalsilite, the formation of orthoclase, biotite, potassic amphiboles, wadeite and other K-minerals. Simultaneous steaming operation of overlying foyaite by such fluids is the reason of kalsilite-orthoclase poikiloblasts forming in these rocks:  $NaAlSi_3O_8 + K^+ \leftrightarrow KAlSi_3O_8 + Na^+$  and  $Na_3KAl_4Si_4O_{16} + 3K^+ \leftrightarrow 4KAlSiO_4 + 3Na^+$ . For this reason, the content of  $K_2O$  in rischorrite is in inverse proportion to the content of  $Na_2O$ , whereas foyaite exhibits no such

correlation, and it is positive in foidolites. The releasing sodium takes part in the formation of albitites and aegirinites, spatially adjacent to rischorrite, as well as ultra-agpaitic veins abundant in rischorrite.

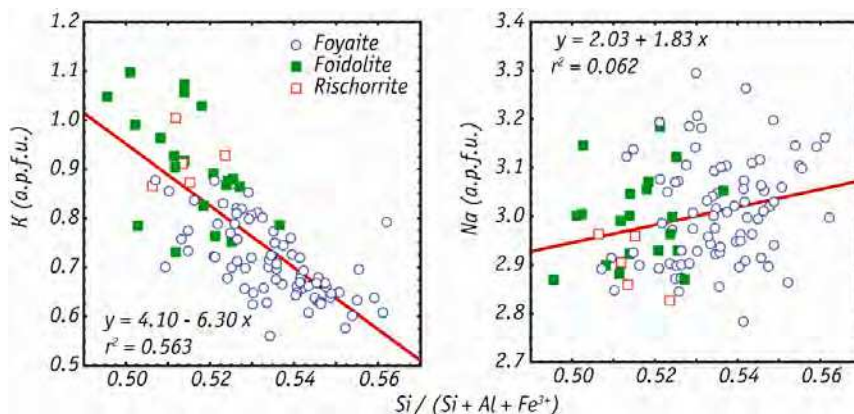


Fig. 9. Potassium (a) and sodium (b) dependence on Si-Al relation in nepheline.

*Lyavochorrite* (irregular-grained nepheline syenite) is a variety of foyaite which can be related to the rock complex of the Main Ring according to a number of features, including its geological position (see Fig. 1). Basically, these are medium- to coarse-grained greenish-grey leucocratic rocks composed of equant crystals of orthoclase-perthite (up to 3 cm in diameter), where interstices in the aggregate are filled with euhedral grains of nepheline, as well as aegirine-augite crystals and Na-Ca amphiboles (predominantly, richterite-ferrichterite). *Lyavochorrite* is similar to rischorrite, primarily owing to the presence of poikilitic metacrysts of orthoclase. However, orthoclase poikiloblasts is not so widespread in *lyavochorrite*; its morphology is less pronounced; and it is often seen to coexist with tabular orthoclase and even with microcline-perthite. *Lyavochorrite* includes titanite, lamprophillite, eudialyte, rinkite, aenigmatite, götzenite, ilmenite, magnetite, loparite-(Ce), fluorapatite, and graphite as accessories; the secondary minerals are natrolite, cancrinite, sodalite, albite, goethite, wadeite, etc.

The mineral composition of *lyavochorrite* falls within the range of  $\text{Fsp}_{43-77}\text{Ne}_{18-43}\text{M}_{4-23}$ . A gradational transition from foyaite of the outer part relative to the Main Ring of the Khibiny massif (khibinite) through *lyavochorrite* to foyaite of the central part is observed (Tikhonenkov, 1963). Similar to foyaite, the *lyavochorrites* may contain parts with increased contents of nepheline which belong to foidolites (in accordance with *QAPF* classification). The majority of components of the *lyavochorrite* composition are characterized by bimodal distributions (Table 3), confirming the idea of hybridisms of these rocks (Tikhonenkov, 1963; Snyatkova et al., 1983). If foyaite has served as a basis for its formation, it is not surprising that one of the maxima in such distributions appears be close to the average content of this component in foyaite, and the second maximum is determined either by introducing or withdrawing of this component. Accordingly, *lyavochorrite* should be regarded as a variety of an "underdeveloped" rischorrite which, along with common rischorrite, was formed under the influence of foidolite intrusion upon the overlying foyaite, although only in places where the width of this intrusion was rather insignificant (see Fig. 1).

	Distribution ( $r^2$ )	$n$	Content (wt. %)				
			Mode	Mean	Min	Max	$\sigma$
SiO <sub>2</sub>	Bimodal	18	<u>54.00</u> and 55.75	53.66	51.2	56.2	1.43
TiO <sub>2</sub>	Bimodal	12	0.98 and <u>1.13</u>	1.13	0.91	1.26	0.11
ZrO <sub>2</sub>		5	0.06	0.07	0.06	0.19	0.07
Al <sub>2</sub> O <sub>3</sub>	Bimodal	18	<u>17.75</u> and 21.00	20.41	17.79	22.71	1.64
Fe <sub>2</sub> O <sub>3</sub>	Bimodal	18	<u>1.50</u> and 5.50	3.18	1.74	8.32	1.76
FeO	Bimodal	18	<u>1.90</u> and 2.70	1.88	1.29	3.53	0.51
MnO	Bimodal	12	<u>0.10</u> and 0.14	0.13	0.08	0.18	0.03
MgO	Normal (0.840)	12	0.70	0.68	0.03	1.16	0.29
CaO	Q-normal (0.957)	12	1.45	1.34	1.04	1.48	0.15
SrO	Bimodal	12	0.01 and <u>0.06</u>	0.07	0.01	0.08	0.02
Na <sub>2</sub> O	Bimodal	18	8.75 and <u>10.25</u>	9.87	7.70	10.8	0.92
K <sub>2</sub> O	Bimodal	18	<u>5.75</u> and 6.75	6.00	5.02	8.00	0.72
P <sub>2</sub> O <sub>5</sub>	Bimodal	13	<u>0.15</u> and 0.35	0.19	0.1	0.57	0.13
CO <sub>2</sub>		5	0.06	0.06	0.03	0.08	0.02
H <sub>2</sub> O	Normal (0.778)	12	0.65	0.61	0.39	0.96	0.17
S <sub>tot</sub>		7	0.04	0.03	0.00	0.18	0.06
Cl	Bimodal	9	<u>0.08</u> and 0.30	0.07	0.01	0.31	0.10
F	Bimodal	8	<u>0.05</u> and 0.15	0.07	0.04	0.19	0.05

Table 3. Chemical composition of lyavochoirite ( $n$  – quantity of samples,  $\sigma$  – standard deviation. More intensive maximum of bimodal distribution is underlined).

*Melteigite-urtite of the Main Ring and Small Semiring.* Unaltered urtite represents fine-, medium-grained greenish-grey rocks with either massive and gneissose texture. They are formed by euhedral crystals of a nepheline, in which interstices in the aggregate are filled with grains of clinopyroxenes of the diopside-aegirine-augite series, KNaCa-amphiboles (potassicrichterite, potassicferrorichterite, etc.), annite, titanite, magnetite, ilmenite, and eudialyte. Nepheline crystals quite often occur as poikilitic inclusions in large (up to 10 cm in diameter) metacrysts of aegirine-augite, potassicrichterite, and orthoclase. The content of orthoclase poikiloblasts in urtite varies continuously from zero up to the threshold value of urtite transition to rischorrite (see Fig. 5). Quite often one encounters here late albite forming fine-grained segregations and stringers in an intimate association with natrolite and aegirine. In ijolite and melteigite, nepheline becomes less widespread, its proportion to dark-coloured minerals remaining the same. These rocks are also characterized by a porphyritic shape owing to the presence of rather large short-prismatic crystals of nepheline in the fine-grained mass of nepheline and dark-coloured minerals. The characteristic accessory minerals of melteigite-urtite are forsterite, fluorapatite, aenigmatite, lamprophillite-barytolamprophyllite, astrophyllite, lorenzenite, pectolite, rinkite, loparite-(Ce), pyrochlore, fluorite, pyrrhotite, sphalerite, and chalcopyrite. The secondary minerals include kalsilite, natrolite, albite, orthoclase, and goethite all of which were formed after nepheline; aegirine, potassicrichterite, potassicarfvedsonite and anatase (after titanite and lamprophyllite).

The content of main components of these rocks is characterized by symmetric distributions (normal or Cauchy); the minor ones have logarithmically normal or exponential distributions (Table 4). Distributions of Fe, Mg and Mn oxides are caused by an essential

quantitative domination of urtite over their more melanocratic analogues. In the case of CaO, F, Cl and C, distributions are due to re-deposition of fluorapatite from melteigite-urtite into apatite-nepheline rocks.

	Distribution ( $r^2$ )	$n$	Content (wt. %)				
			Mode	Mean	Min	Max	$\sigma$
SiO <sub>2</sub>	Cauchy (0.998)	268	42.5	43.13	10.8	60.47	4.61
TiO <sub>2</sub>	Normal (0.976)	268	2.30	2.99	0.42	18.46	2.01
ZrO <sub>2</sub>	Cauchy (0.985)	46	0.10	0.11	0.01	0.28	0.05
Al <sub>2</sub> O <sub>3</sub>	Normal (0.988)	261	19.5	18.85	1.81	29.89	5.46
Fe <sub>2</sub> O <sub>3</sub>	Exponential (0.941)	268	2.50	7.60	1.11	29.23	2.96
FeO	Exponential (1.000)	252	1.84	4.33	0.45	27.69	2.87
MnO	Lognormal (1.000)	232	0.10	0.21	0.04	1.56	0.18
MgO	Lognormal (0.994)	245	1.50	1.68	0.03	8.40	1.65
CaO	Lognormal (0.922)	246	5.50	5.67	0.31	19.74	3.46
SrO	Cauchy (1.000)	202	0.25	0.27	0.01	1.86	0.19
Na <sub>2</sub> O	Normal (0.993)	267	10.50	10.15	0.64	15.21	2.37
K <sub>2</sub> O	Normal (0.956)	269	5.00	4.70	0.25	11.21	1.67
P <sub>2</sub> O <sub>5</sub>	Exponential (0.998)	257	1.00	0.69	0.04	14.30	1.60
CO <sub>2</sub>	Exponential (1.000)	185	0.10	0.22	0.00	2.15	0.17
H <sub>2</sub> O	Normal (0.999)	235	0.66	0.80	0.00	3.29	0.45
S <sub>tot</sub>	Exponential (0.998)	46	0.01	0.07	0.01	0.43	0.08
Cl	Exponential (0.999)	77	0.04	0.05	0.00	0.27	0.05
F	Exponential (0.956)	212	0.12	0.30	0.01	1.47	0.17

Table 4. Chemical composition of foidolites ( $n$  – quantity of samples,  $\sigma$  – standard deviation).

*Apatite-nepheline rocks* are foidolites more or less enriched with fluorapatite up to monomineral apatitilite. These are spotty greenish-grey rocks often forming a stockwork of later fluorapatite veinlets in melteigite-urtite. Major minerals of the considered rocks are the same as in ijolite-urtite: fluorapatite, nepheline, diopside-aegirine-augite, potassicrichterite, potassicferrorichterite, orthoclase, titanite, magnetite, and ilmenite. Accessory minerals include aegirine, potassicarfvedsonite, eudialyte, lamprophillite, annite, calcite, ancylite-(Ce), and burbankite. Anatase, astrophyllite, kalsilite, natrolite, illite, goethite, wadeite, gaidonnayite, and pyrite occur as secondary minerals.

Apatite-nepheline rocks (Fig. 10) are traditionally subdivided into a number of textured-substantial types differing, above all, by fluorapatite concentration; they are spotty, lens-shaped banded, block-shaped, reticulate, ingrained, and brecciated. All of these varieties of apatite-nepheline rocks exhibit a clear structural-textural anisotropy marked by an oriented arrangement of elongated crystals of fluorapatite and dark-coloured minerals; by fluorapatite veinlets and, accordingly, lens-shaped fragments of melteigite-urtite separated by these veinlets; by lens-shaped segregations of titanite, clinopyroxene, etc. On the whole, the structural-textural orientation of these rocks coincides with the contours of the Main Ring.

Among the specified ore types, the dominating varieties are reticulate and lens-shaped banded, differing only by the shape of ijolite-urtite blocks and the thickness of fluorapatite veinlets enveloping these blocks. The richest spotty ores are, as a matter of fact, the thickest (up to 1.5 m) layers of lens-shaped banded ores, while the poorest massive (ingrained) ores

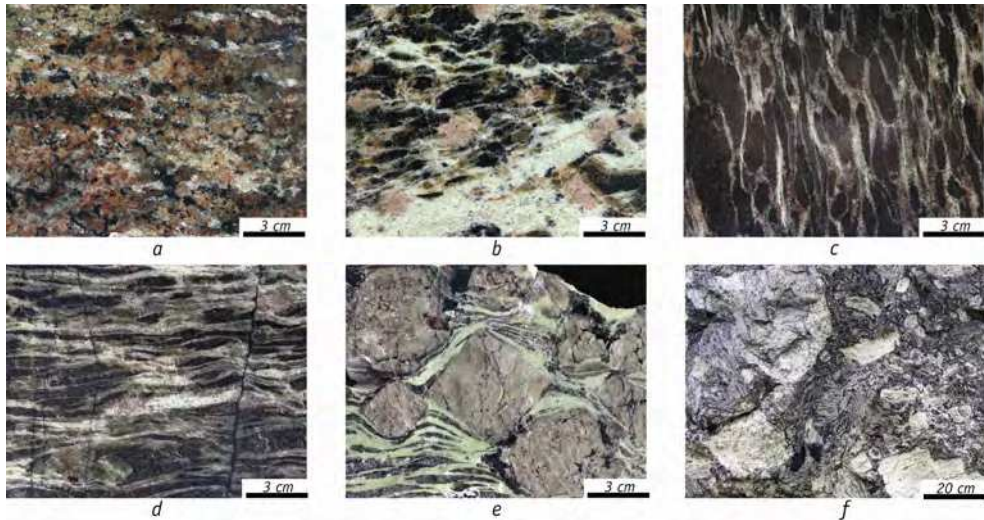


Fig. 10. Main textural types of apatite-nepheline rock: a – spotty, b – stockwork-like; c – reticulate; d – lens-shaped banded; e – block-shaped; f – brecciated.

are an implicitly pronounced variety of reticulate ores. Block-shaped ores are a result of recrystallization of reticulate or lens-shaped banded ores, in the course of which separate crystals of nepheline from ijolite-urtite lenses cluster in larger (up to 8 cm) metacrysts inside which relics of ijolite-urtite are often included. The geometry of apatite clusters on sections of these rock types is characterized by similar fractal dimension of  $1.63 \leq {}^2D \leq 1.75$  (see Fig. 3). The value of their full fractal dimension determined by Mandelbrot's rule (Mandelbrot, 1983) is  ${}^3D \approx 2.6-2.7$  and it is close to the dimension of apatite-ore and foidolite stockworks.

Brecciated ores, commonly found in all Khibiny deposits, occur as volumetric breccia organized similarly to “a blurred floe”, in which fragments of apatite-nepheline rock of different sizes (from sub-centimeter up to several tens meters) and shapes are cemented by rather melanocratic foidolite (see Fig. 10f). The composition of the latter commonly corresponds to ijolite-urtite enriched with apatite and orthoclase. Sometimes, however, the cement is absent and differently oriented fragments appear to be compactly lap-fitted to each other. But, irrespective of the quantitative proportion of apatite-nepheline rock fragments and ijolite-urtite cement in breccias, the occurrence of fragments with increasing area decreases according to the power law with the parameter equal 0.6, i.e. the distribution of apatite-nepheline rock fragments in size is fractal with the dimension of  $D \approx 1.2$ .

Another textural variety of apatite-nepheline rocks atypical of magmatogene deposits is the plicated ores widespread in apatite-rich zones of Kukisvumchorr, Yukspor, and Rasvumchorr deposits (Yakovenchuk et al., 2005; Ivanyuk et al., 2009). The fractal dimension of separate foidolite layers in plicated spotty-banded apatite-nepheline ores ranges from 1.0 up to 1.2 in a wide enough interval of scales (from several millimeters up to several meters), which makes the appearance of these rocks indistinguishable from those of iron quartzite and other metamorphic rocks.

The chemical composition of apatite-nepheline rocks varies in a wide range of values (Table 5) being limited, on the one hand, by the composition of original melteigite-urtite and, on

the other hand - by fluorapatite content (up to 90 vol. %). The content of the main components of the rocks in question ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ , and F) is characterized by symmetric distributions (normal or Cauchy) reflecting a tendency of the mineral composition to an equilibrium fluorapatite+nepheline+aegirine association. As these three minerals compose 95 vol. % of these rocks, the contents of Si, Al, Na, K, on the one hand, and the contents of F, Ca, P, on the other hand, are in a negative linear dependence. If we extend the sampling by apatite-titanite rocks, one of the major components will become titanium, the content of its oxide being distributed according to the Cauchy law. The content of the majority of trace components is distributed according to the exponential law which is primarily caused by the essential predominance of urtite over more melanocratic constituents of the apatite-nepheline rock protolyte.

	Distribution ( $r^2$ )	$n$	Content (wt. %)				
			Mode	Mean	Min	Max	$\sigma$
$\text{SiO}_2$	Cauchy (0.980)	238	23.60	20.38	1.07	38.94	8.04
$\text{TiO}_2$	Exponential (0.999)	238	1.10	1.91	0.05	10.14	1.46
$\text{ZrO}_2$	Bimodal	10	<u>0.05 и 0.09</u>	0.07	0.01	0.14	0.04
$\text{Al}_2\text{O}_3$	Cauchy (0.993)	238	12.50	11.08	0.47	27.28	5.17
$\text{Fe}_2\text{O}_3$	Cauchy (0.948)	238	2.20	2.67	0.08	16.22	2.20
$\text{FeO}$	Exponential (0.993)	225	1.30	2.20	0.00	15.41	1.46
$\text{MnO}$	Exponential (0.990)	139	0.07	0.12	0.02	0.46	0.08
$\text{MgO}$	Exponential (0.994)	224	0.50	0.66	0.02	3.06	0.47
$\text{CaO}$	Cauchy (0.957)	224	27.50	29.19	4.08	51.25	9.69
$\text{SrO}$	Bimodal	14	<u>0.25 и 2.25</u>	2.11	0.02	4.43	1.14
$\text{Na}_2\text{O}$	Normal (0.995)	238	6.00	5.67	0.26	14.28	2.64
$\text{K}_2\text{O}$	Cauchy (0.960)	238	2.75	2.49	0.03	5.78	1.15
$\text{P}_2\text{O}_5$	Cauchy (0.956)	236	20.50	20.99	2.12	40.65	8.16
$\text{CO}_2$	Exponential (0.996)	126	0.12	0.22	0.00	1.27	0.21
$\text{H}_2\text{O}$	Lognormal (0.980)	139	0.49	0.56	0.11	1.96	0.37
$\text{S}_{\text{tot}}$	Exponential (0.872)	18	0.02	0.03	0.00	0.20	0.05
Cl	Exponential (0.990)	29	0.03	0.05	0.00	0.29	0.07
F	Normal (0.989)	139	1.90	1.88	0.23	3.34	0.77

Table 5. Chemical composition of apatite-nepheline rock ( $n$  – quantity of samples,  $\sigma$  – standard deviation. More intensive maximum of bimodal distribution is underlined).

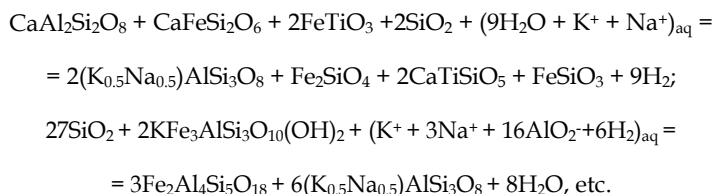
The apatite-titanite and nepheline-titanite ores, generally occurring along the top contact of apatite-nepheline rocks, are formed as the result of enrichment of apatite-nepheline rocks and overlying melteigites-urtite with titanite {also with fluorapatite in melteigites-urtite}. Initially, titanite forms a fairly sparse network of veinlets in ijolite-urtite which, however, is quickly condensed, forming, already after some meters, apatite-titanite or nepheline-titanite rocks with relics of nepheline and oval segregations of recrystallized aegirine-augite. The characteristic accessories of these rocks are orthoclase, natrolite, magnetite, ilmenite, potassicferrichterite, and calcite. The proportion between the contents of main components in apatite and nepheline-titanite ores is close to that in apatite-nepheline rocks. The  $\text{TiO}_2$  content in these rocks is weakly ( $r^2 < 0.5$ ) dependent on the quantity of

any other component, linearly decreasing with increase in their total content (with the deduction of  $\text{SiO}_2$  and  $\text{CaO}$ ), because of a superimposed character of titanite mineralization.

*Alkaline syenites* in the Khibiny massif play an extremely subordinated role in comparison with nepheline syenites with which, as a rule, they are related by a gradational transition. As it has been noted, in extreme western (the *A* point in Fig. 1) and central (the *D* point) parts of the Khibiny massif is located foyaite with an increased content of alkaline feldspar at the expense of nepheline. In places, the proportion of these minerals exceeds the classification limit of  $\text{Ne}/(\text{Fsp}+\text{Ne})=0.1$  between alkaline and nepheline syenites (see Fig. 5). Alkaline syenites are white or light-grey fine-, medium-grained massive rocks made of an aggregate of tabular crystals of microcline- or orthoclase-perthite (75-99 vol. %) whose interstices are filled with grains of nepheline, aegirine-augite and magnesioarfvedsonite. As a rule, dark-coloured minerals form a uniform impregnation in the feldspar mass. Less frequently, they occur as separate clusters (up to 50 cm in diameter) imparting a taxite-like appearance to the rock. Accessory minerals of alkaline syenites are titanite, astrophyllite, phlogopite, sodalite, cancrinite, fluorapatite, fluorite, calcite, magnetite, and pyrrhotite.

*Volcanogenic-sedimentary rocks metamorphosed to hornfels* spatially related to rock complexes of the Small Semiring and Main Ring (see Fig. 1) occur in foyaite as lens-shaped xenoliths from half meter up to 3 kms long and up to 600 m wide, and are almost always separated from foyaite by a zone of fine-grained alkaline or nepheline syenites (fenites after hornfels). Macroscopically, hornfels are fine-grained rocks (the average grain size is 0.07 mm) with a characteristic conchoidal fracture the color of which varies from white, light-grey, pale-violet, blue, green and brown of different hues to dark-grey and black. The structure of these rocks changes from massive to high-contrast banded, lens-shaped banded, taxitic and porphyritic. The microtexture is typically hornfels, or poikiloblastic - in the presence of large metacrysts of amphiboles, corundum, nepheline and aenigmatite.

Hornfels are characterized by wide variations of mineral composition within an isolated xenolith, an individual sample, or even a separate thin section. In total, the considered rocks include more than 170 minerals, more than 30 of which are rock-forming (including crichtonite-loveringite, sekaninaite, topaz, fayalite and freudenbergite). However, despite the varied and rather exotic mineral composition of hornfels and fenites forming after them, recalculation of the chemical composition of these rocks to normative components using the CIPW method has revealed three groups of rocks. The first two of them correspond to more or less intensively fenitized quartzite and basalt, the third one corresponds to alkaline trachyte and phonolite (fenite.) In fact, the introduction of aluminium and alkaline metals in these rocks during their thermal metamorphism initially generates a variety of hornfels and fenites (Yakovenchuk et al., 2005; Korchak et al., 2011):





### 3. Chemical zonation

The symmetric petrographic zonation of the Khibiny massif relatively the axial part of the Main Ring with bodies of apatite-nepheline rocks (see Fig. 1) predetermines the presence of a similar geochemical zonation. Such zonation, noted by many researchers (Fersman, 1931; Zak et al., 1972; Galakhov, 1975; etc.), is expressed in consecutive increasing of Ca, Sr, Ti, P and F contents from the outer and central parts of the massif to the axial zone of the Main Ring at the expense of Si, Al, Mg, Fe, Na and K. But our prime interest when stating the task was not this obvious zonation. We were interested in the hidden zonation of foyaitite complex capable of throwing light on the Khibiny massif evolution.

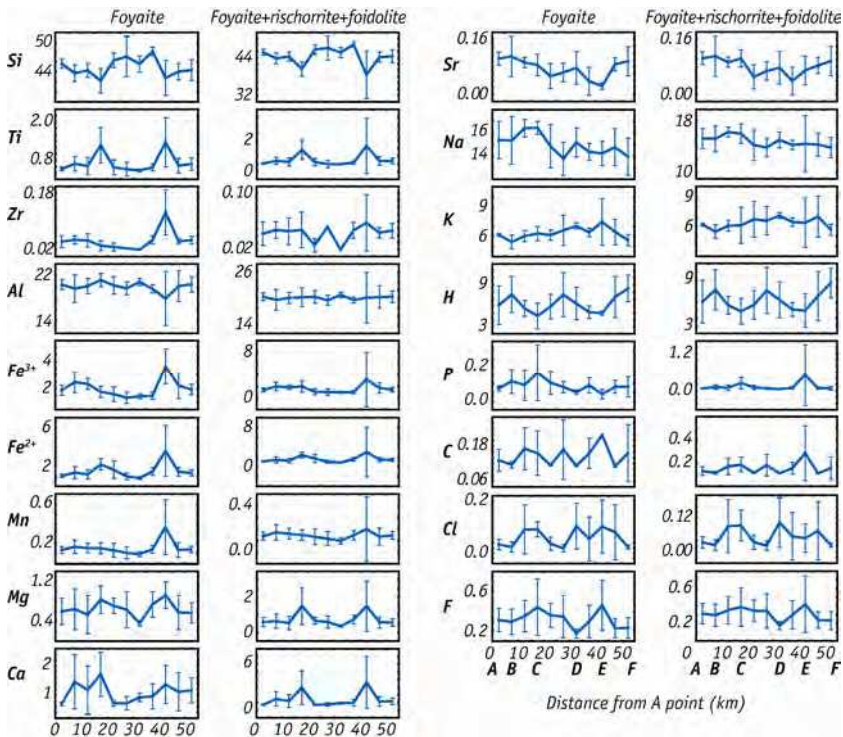


Fig. 11. Variation of chemical composition of alkaline rocks along the A-B-C-D-E-F profile.

Figure 11 represents a change in the chemical composition of rocks of the Khibiny massif, the data on which are 5-km interval-averaged along the A-B-C-D-E-F profile (see Fig. 1). Comparing these diagrams reveals that the Main Ring determines the composition of not only rischorrite but also foyaitite, its influence becoming evident already at a distance of 5-10 kms away from the Main Ring! Consequently, of all the earlier proposed models of the Khibiny massif zonation origin, it is O. L. Snyatkova and colleagues' model (1983), in its turn developing the conceptions of A. E. Fersman (1931) about a relation of zonation with intruded foidolite melts along the ring fault (see Fig. 4), that represents the facts.

On the whole, in proximity of the Main Ring one observes substantial decreasing of the quantity of Si, Sr and H<sub>2</sub>O in foyaitite composition, compensated by increasing contents of all

other elements, Ti, Zr, Ca, Mn, Fe, Mg, F, and Cl in the first place. At the same time, there are essential distinctions in foyaite composition adjacent to enriched in apatite-nepheline rock part of the Main Ring (Mt. Koashva, the *E* point) and its pure part (Mt. Marchenko Peak, the *C* point), mostly in regard to phosphorus and aluminium. Foyaite appears essentially enriched with Al, Na, P and Ca (i.e., accordingly, with nepheline and fluorapatite) in the area at Mt. Marchenko Peak, whereas foyaite from the Koashva deposit area (the *E* point) is obviously depleted in these elements due to increased contents of K, Fe, Mn, Zr and C (i.e., accordingly, biotite, K-amphiboles, kalsilite, orthoclase, and eudialyte). However, if the sampling data on composition first include rischorrite, and then ijolite-urtite, these distinctions practically disappear and the concentration profiles take a symmetric view relative to the center of the massif.

Otherwise, the rather monolithic "barren" areas of the Main Ring contain nepheline syenites essentially enriched with nepheline and fluorapatite as the result of steaming by foidolite-connected fluids. Foidolites in "ore" areas filled a great yawning fracture without causing such an intensive enrichment of host foyaite with nepheline and fluorapatite. But here emerge numerous processes of potassium metasomatism of ambient foyaite (up to formation of rischorrite), foidolites and even dykes of alkali-ultrabasic rocks. The formation of the Main Ring complex was completed when foidolites were fractured along the same "ring" filling this cluster with fluorapatite, which may partly be due to redistribution of the latter from ambient foidolites.

#### 4. Typomorphic minerals

Studying the rocks of the Khibiny massif along the *A-B-C-D-E-F* profile, we have authentically identified more than 100 minerals, comprehensively described in (Yakovenchuk et al., 2005). In this work, prominence is given to typomorphic minerals: nepheline, feldspars, amphiboles, clinopyroxenes, and fluorapatite.

*Nepheline* is a rock-forming mineral of foidolites, nepheline and alkaline syenites, fenite and pegmatite-hydrothermal veins where its content varies from the first per cent up to 90 vol. % (see Fig. 5 and 6). Silica content in nepheline changes according to temperature of rock forming (Yakovenchuk et al., 2010c): 4.3 a.p.f.u in hornfels and foyaite (about 900 °C), 4.2 a.p.f.u in foidolite (about 500 °C), 4.1 a.p.f.u in rischorrite and apatite-nepheline rock (about 400 °C), and 4.0 a.p.f.u in pegmatite-hydrothermal veins (about 200 °C). The chemical composition of nepheline in foyaite samples picked along the *A-B-C-D-E-F* profile (see Fig. 1) shows a regular change at moving from the outer and central parts of the massif towards the Main Ring (Fig. 12).

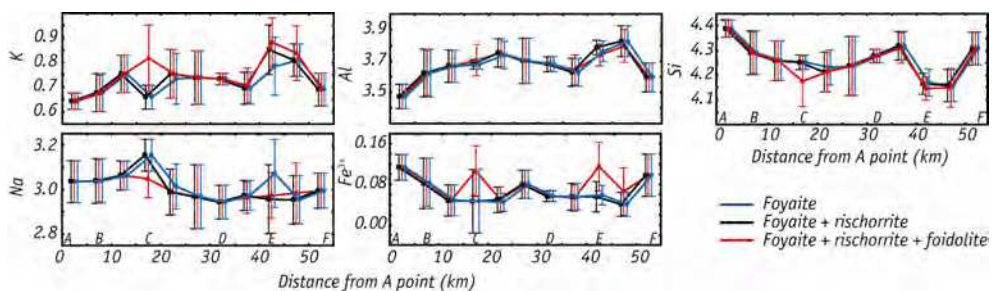


Fig. 12. Variation of nepheline composition along the *A-B-C-D-E-F* profile.

Thus, the change in nepheline composition from the outer and central parts of the massif towards the Main Ring can generally be expressed by the formula:  $\square_B + (\text{Si}^{4+} + \text{Fe}^{3+})_T \leftrightarrow \text{K}^+_{\text{B}} + 2\text{Al}^{3+}_{\text{T}}$ . Near the Main Ring, the substitution of Si for Al in nepheline from foyaitite is accompanied by increasing of Na content in it (on the average, up to 3.2 *a.p.f.u.*), whereas in nepheline from foidolites the preferred substitution of Si for trivalent Fe is compensated by K and Ba:  $\square_A + \text{K}_B + \text{Si}_T \leftrightarrow \text{Na}_A + \square_B + \text{Al}_T$  (in foyaitite), and  $\text{Na}_A + \square_B + \text{Si}_T \leftrightarrow \square_A + \text{K}_B + \text{Fe}^{3+}_T$  (in foidolites). As a result, the high-potassium and iron-rich nepheline of foidolites is essentially different in composition from the high-sodium and iron-poor nepheline of the adjacent foyaitite and, partly, rischorrite. Besides, the initially potassium-rich ijolite-urtite melt seems to have caused not only the subsequent wide development of orthoclasing and kalsilitizing processes within foidolites (including apatite-nepheline rocks), but the alteration of ambient nepheline syenites as well.

*Microcline* and *orthoclase* are major minerals of alkaline and nepheline syenites, feldspar-bearing ijolite-urtite, fenite, hornfels of volcanogenic-sedimentary rocks, phonolites, alkali-feldspar trachytes and pegmatite-hydrothermal veins. Orthoclase essentially dominates in rischorrite, foidolites, fine-grained nepheline syenites and hornfels (in hornfels, together with anorthoclase); microcline is more common in pegmatite veins, while foyaitite contains both the modifications, although in different proportions (Ivanyuk et al., 2010). Orthoclase-bearing foyaitite is generally concentrated within the 5-km outer zone of the massif, and also on the periphery of the Main Ring where its gradational transformation to lyavochorrite and rischorrite is observed. Changing of the potassium feldspar composition in samples of the Khibiny rocks picked along the A-B-C-D-E-F profile (see Fig. 1) is shown in Fig. 13.

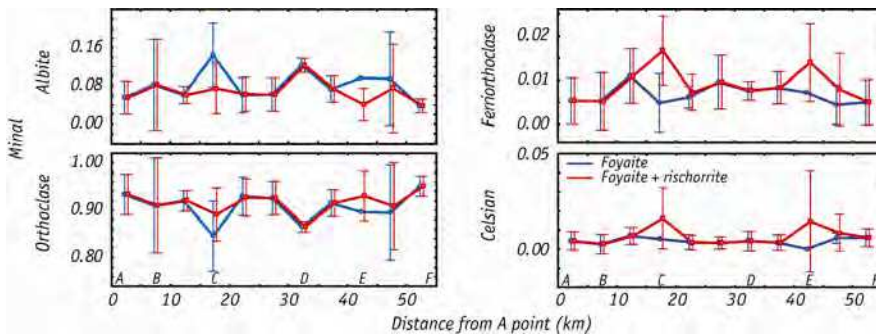


Fig. 13. Variation of K-feldspar composition along the A-B-C-D-E-F profile.

The "purest" orthoclase is concentrated in outer parts of the foyaitite complex, whereas in the center of the massif and in the Main Ring area the feldspar is represented by a variety transitive to anorthoclase. Orthoclase of rischorrite, compared to that of foyaitite, is essentially enriched with ferri-orthoclase and celsian constituents. The role of Ba and Fe increased at the final stages of orthoclase poikiloblasts formation owing to which the marginal zones of such poikiloblasts, both in rischorrite and in ijolite-urtite, are quite often represented by iron-rich hyalophane. Taking into account the data on foyaitite complex textural zonation (see Fig. 8), it becomes obvious that this complex initially had monotonous zonation with an orthoclase-dominant outer zone and microcline-dominant central part, and that the orthoclase-bearing rocks near the Main Ring were formed due to warming-up and metasomatic alteration of ambient foyaitite by fluidized foidolite melts filling the ring fault.

The *clinopyroxenes* of the Khibiny massif, predominating in the majority of rocks, are represented by diopside, hedenbergite, augite, aegirine-augite and aegirine (Yakovenchuk et al., 2005; Yakovenchuk et al., 2008). Diopside is a rock-forming mineral of alkali-ultrabasic rocks, alkali-feldspar trachytes, melteigite-urtite, metamorphosed to hornfels volcanogenic-sedimentary rocks of basalt composition and their host foyaitite. Hedenbergite is observed in fenitized hornfels (after tuffite) where it together with aegirine forms parallel-columnar coronas around fayalite inclusions in albite. Aegirine-augite is the main mineral of all types of nepheline syenites (5–50 vol. %), foidolites (up to 90 vol. %), apatite-nepheline rocks, fenitized rocks of the massif frame and xenoliths of volcanogenic-sedimentary rocks in foyaitite. In foyaitite of the outer and central parts of the massif, it predominates among the other iron-magnesium-bearing silicates and quite often occupies a position subordinated in relation to aegirine, alkaline amphiboles, and annite in foyaitite, lyavochorrite and rischorrite of the Main Ring zone. Aegirine is a ubiquitous primary and/or secondary mineral forming marginal zones around diopside-aegirine-augite crystals or separate needle-like crystals obviously formed later than the other clinopyroxenes (Yakovenchuk et al., 2005).

Diagrams of a change in clinopyroxene composition (Fig. 14) along the *A-B-C-D-E-F* profile (see Fig. 1) shows, above all, a different degree of rock differentiation in the Main Ring in its rich (the Koashva deposit, the *E* point) and poor ore (Mt. Marchenko Peak, the *C* point) parts. As the Main Ring is approached in the area at Mt. Marchenko Peak, the clinopyroxenes of foyaitite feature increasing contents of Ca, Mg and  $\text{Fe}^{2+}$  at the expense of Na and  $\text{Fe}^{3+}$ , which proceeds on transition to rischorrite attaining the maximum in ijolite-urtite. Quite opposite is the situation in the area of the Koashva deposit, where the clinopyroxene of foyaitite is represented by aegirine with traces of Ca, Mg and  $\text{Fe}^{2+}$ . However, the concentrations of these elements increase on transition to rischorrite and foidolites, with ijolite-urtite also containing clinopyroxenes of the diopside-hedenbergite series.

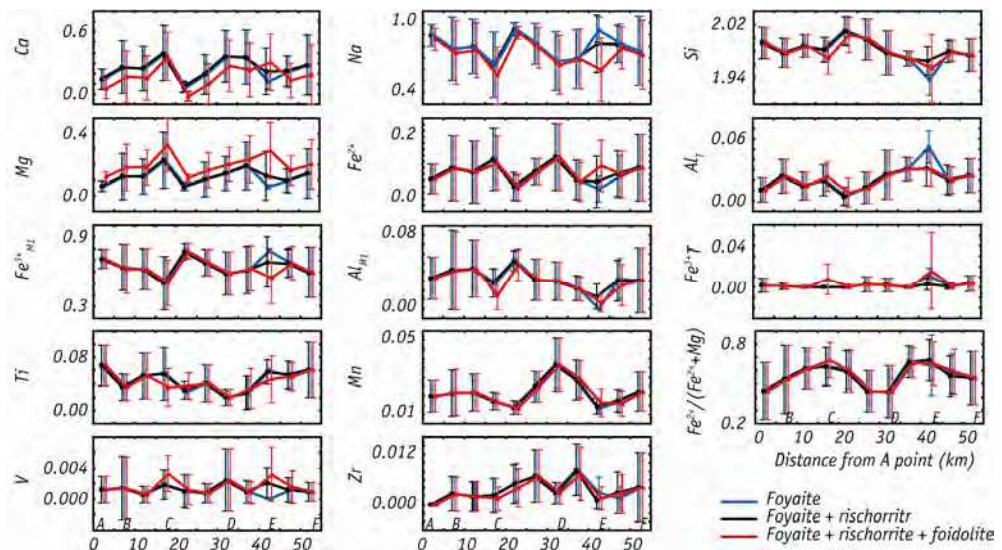


Fig. 14. Variation of clinopyroxene composition along the *A-B-C-D-E-F* profile.

Diagram of the change of the Mg and Fe<sup>2+</sup> ratio in clinopyroxene composition demonstrates consecutive increasing of the hedenbergite constituent from the border of the massif to the Main Ring, where all rocks contain clinopyroxene with a maximal content of Fe<sup>2+</sup>, followed by an abrupt decrease in Fe<sup>2+</sup> concentration to the center of the massif. The Mn content in the clinopyroxene composition decreases from the border to the Main Ring, suddenly rising in the massif's central part. The local maxima of Ti and V contents in clinopyroxenes are confined to the rock complexes of the Main Ring, whereas the increased content of Zr shows the position of the albitization ring at the contact between rischorrite and foyaite in the central part of the massif. Moreover, clinopyroxene in all types of rocks found on the Main Ring area are deficient in silicon compensated by aluminium and/or iron.

*Amphiboles* of the Khibiny massif are rather variegated (Konopleva et al., 2008): the total number of members in this group, scattered within the massif according to its general zonation (Fig. 15), was found to be 25. Foyaite contains richterite, ferrichterite, ferroeckermannite, arfvedsonite, magnesioarfvedsonite, katophorite, ferrikatophorite, magnesioferrikatophorite, ferrinyboite, and ferric-ferronyboite. Rischorrite is mostly characterized by the presence of potassicarfvedsonite, foidolites - of potassicrichterite. Dykes of alkali-ultrabasic rocks and alkali-feldspar trachytes contain pargasite, ferro-pargasite, hastingsite, magnesiohastingsite, and kaersutite; pegmatite-hydrothermal veins include potassicrichterite, potassicarfvedsonite, arfvedsonite, and magnesioarfvedsonite; in xenoliths of metamorphized volcanogenic-sedimentary rocks are present edenite, fluorendenite, magnesioferrikatophorite, arfvedsonite and ferric-ferronyboite.

*Fluorapatite* is a through accessory mineral of all the Khibiny massif rocks, becoming a rock-forming mineral in apatite-nepheline rocks. The content of fluorapatite is 0.2-1.0 vol. % in nepheline syenites, 1-7 vol. % in melteigite-urtite, achieving up to 98 vol. % in apatite-nepheline rocks. An examination of fluorapatite composition along the mentioned profile (Fig. 16) has shown that fluorapatite is released from Na, REE, and Si impurities in favour of Ca, Sr and P, as the foidolite ring is approached from the outer and central parts of the massif:  $REE^{3+} + Si^{4+} \leftrightarrow (Ca, Sr)^{2+} + P^{5+}$  and  $Na^{+} + REE^{3+} \leftrightarrow 2(Ca, Sr)^{2+}$ . The behaviour of Ca

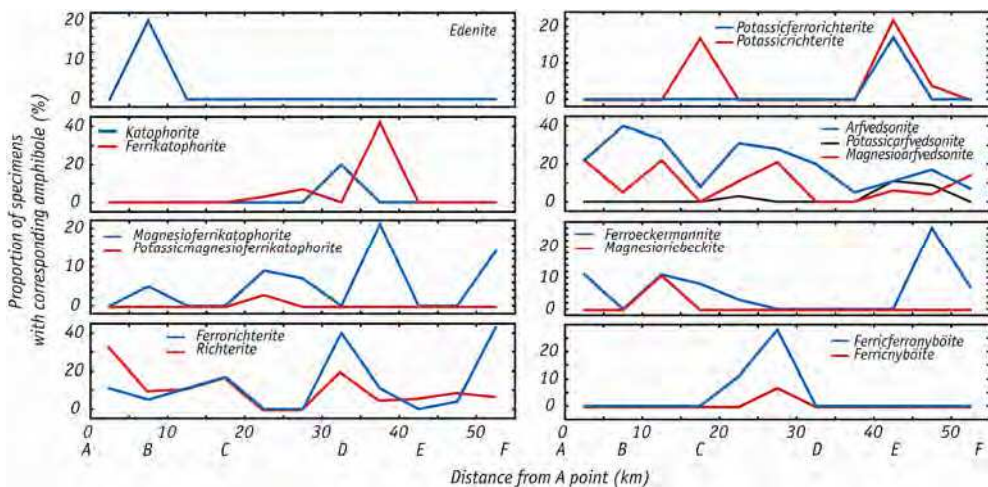


Fig. 15. Variation of amphibole composition along the A-B-C-D-E-F profile.

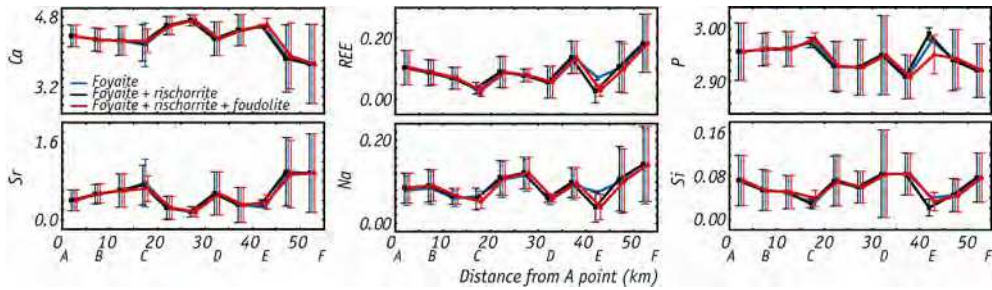


Fig. 16. Variation of fluorapatite composition along the A-B-C-D-E-F profile.

and Sr is different in the ore and barren parts of the Main Ring; the larger deposit the lower Sr content. It is important that similar behaviour of these elements was also observed within the apatite deposits: the higher the ore grade (high content of  $P_2O_5$ ) in fluorapatite, the smaller the quantity of Sr in its composition.

The above cited data on the features of rock-forming and accessory minerals composition within the Khibiny massif indicate that the majority of "through" minerals change the composition as the Main Ring is approached. The extreme contents of some of the elements in mineral compositions, which are related to the Main Ring, are usually superimposed on original monotonous zonation of the foyaite complex, manifesting itself in gradational change of the contents of these elements from the border to the center of the massif. During the formation of substantial zonation of the Khibiny massif, there occurred both plain concentration of elements in the composition of suitable phases and their redistribution between coexisting minerals parallel with their self-cleaning from impurities. In the course of this process, the first to be formed are transitive metastable phases. At the next stage, numerous rare minerals are crystallized in situ, both in interstices of rock-forming minerals of the same rocks and in various types of pegmatite-hydrothermal veins. The zone of maximal differentiation in the mineral chemical composition is confined to the Main Ring, as is the zone of maximal differentiation of rocks.

The plot of quantity of rock-forming and accessory minerals in a rock along the A-B-C-D-E-F profile (Fig. 17) has an intensive minimum in the area of the Koashva deposit and a weak minimum in the area of the Marchenko deposit. These minimums correspond to the maximal quantity of mineral species known at these intervals. It means that the great mineral diversity of apatite deposits is related to pegmatites and zones of a later mineralization in both of which the impurities were moved during the ore zone formation. These impurities can be produced by accessory minerals destruction as well as by rock-forming minerals self-cleaning. The larger thickness of foidolite intrusion in the area of the Koashva deposit causes more long and intensive metasomatic and hydrothermal processes, longer chains of mineral transformations and, finally, larger mineral diversity.

Origin of the most of rare minerals by means of self-cleaning of rock-forming minerals causes good correlation between composition of host rocks, rock-forming minerals and mineral diversity (Fig. 18): the largest apatite deposit has the simplest mineral composition of ores, closest to ideal composition of rock-forming minerals, highest mineral diversity and longest list of firstly discovered minerals. Application of our rule to above described profile through the Khibiny massif helped us to discover 8 new minerals with interesting technological properties (see Fig. 17): cerite-(La) (Pakhomovsky et al., 2002), chivruaiite

(Men'shikov et al. 2006), ivanyukite-Na, ivanyukite-K and ivanyukite-Cu (Yakovenchuk et al. 2009), punkaruavite (Yakovenchuk et al. 2010a); strontiofluorite and polezhaevite-(Ce) (Yakovenchuk et al. 2010b,d).

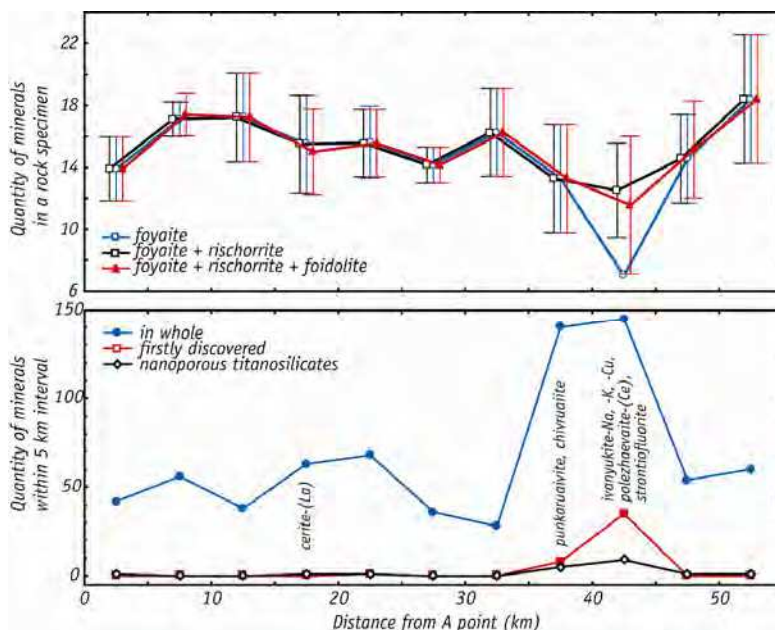


Fig. 17. Variation of quantity of mineral in alkaline rock along the A-B-C-D-E-F profile.

## 5. Conclusion

A thorough geological, petrographic, geochemical and mineralogical investigation of the world's largest Khibiny massif of nepheline syenites and foidolites has provided some essentially new information concerning this unique object and the genesis of its huge apatite deposits. The model of the Khibiny massif formation, in the light of the data obtained, can be seen as the following sequence of events: 1 – formation of a shallow-water mass of terrigene and volcanogenic-sedimentary rocks of the Lovozero suite (quartzite, sandstone, olivine basalt and their tufas); 2 – formation of foyaite massif with a monotonous zonation from the border to the center of the massif as a result of decreasing temperature of rock formation; 3 – formation of the Main and Small Conic faults in the consolidated day-surface part of the massif, owing to its expansion (dilatancy) near the day surface and filling of the faults by foidolite melts; 4 – consolidation and bursting of ijolite-urtite along the same ring, the position of which is determined by a stress field in the still extending Khibiny massif; extrusion to the fractures of residual fluid enriched with Ca, P, F, Cl, C, and H and development of fluorapatite stockworks; apatitization of ambient foyaite, kalsilite-orthoclase metasomatism (poikiloblasting process) and formation of the lyavoehorrite-rischorrite series rock; 5 – development of zones of fractal plication and breccias, due to relieving of stresses still persisting along the Main Conic fault, and formation of fractal stockworks of pegmatite-hydrothermal veins within the day-surface parts of apatite-ore bodies; 6 – formation of a

system of radial fractures, dykes of alkaline, alkali-ultrabasic rocks and carbonatites, explosion pipes and zones of a low-temperature hydrothermal alteration of the rocks concentrated near the day-surface part of the Main Ring; 7 – completion of formation of a characteristic fractal relief of the Khibiny Tundra due non-uniform uplifting of various parts of the massif accompanied by earthquakes and tremors; 8 – man-caused alterations due to excavation and moving of huge rock masses, accompanied by mountain bumps, earthquakes and intensive low-temperature mineral formation within the Main Ring.

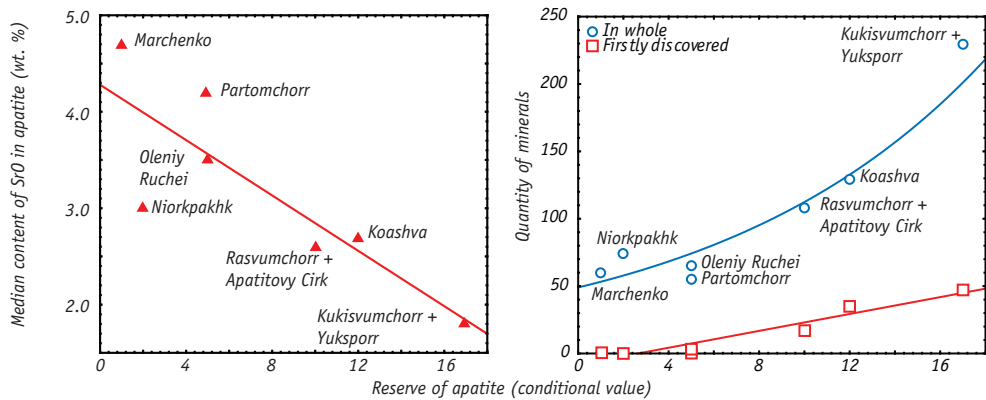


Fig. 18. Relation between size of apatite deposit, composition of apatite and quantity of minerals known in this deposit.

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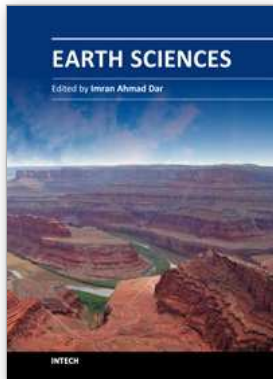
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## **Earth Sciences**

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