CHALCOGENIDE MINERALIZATION IN THE ALUMINA–RICH FENITES OF THE KHIBINY ALKALINE COMPLEX (KOLA PENINSULA, RUSSIA)

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Apoxenolithic alumina-rich fenites in the Khibiny alkaline massif (Kola Peninsula, Russia) contain various and specific chalcogenide (mostly sulphide) mineralization. Chalcogenides occur mostly in essentially nepheline-feldspar rocks with variable quantities of other minerals (biotite, rutile, hercynite, corundum, ilmenite, pyrophan-ite, graphite, sillimanite, sekaninaite, native iron etc.). The most abundant are members of the pyrrhotite-troilite series, in some areas molybdenite is predominant. The other chalcogenides are subordinate however among them there occur both rather rare minerals (jaipurite CoS and westerveldite FeAs — the first finds in Russia, tungstenite WS_2 — the first find in Khibiny) and geochemically unique objects — edgarite $FeNb_3S_6$ and Ti-bearing iron sul-phides. Pyrite, marcasite, alabandite, chalcopyrite, sphalerite, löllingite, galena, cubanite, pentlandite also occur. The irregular distribution of sulphides in fenites (from 0.0 up to almost 70%) is due to the primary sulphur content in the protolith (Precambrian alumina-rich schists) which is considered to be its source. Activity of S^{2-} in some areas of the fenites reaches the record values for the Earth objects, which results in unique mineral associations with sul-phides containing Mn, W, V, and even Nb, Ti, Cr. The distribution analysis of metals (species-defining and "macro-impurities": from 0.n to n wt.%) among oxygen compounds and sulphides resulted in an empiric sequence of chalcophility decrease, i.e. affinity to S^{2-} (and, correspondingly, increase of lithophylity) of metals: Cu,Pb,Mo → Zn → Fe → Mn,W,V → Nb,Cr → Ti → Mg,Ca → Al,Be,*REE*. The formation of the sulphides in alumina-rich fen-ites in general took place at high temperatures (> 500−600˚C) and high reducing potential.
7 tables, 18 figures, 26 references.
Keywords: sulphides, pyrrhotite-troilite series, alabandite, tungstenite, jaipurite, westerveldite, chalcophility, fen-ites, Khibiny alkaline massif, Kola Peninsula.

The well-known Khibiny massif, the largest (1327 sq.km) alkaline complex in the world is located in the centre of Kola Peninsula, on the contact of Archean granite-gneisses of the Kola block and Proterozoic volcanic-sedimentary rocks of the Imandra-Varzuga series. This central-type intrusion is mainly composed of agpaitic feldspathoid rocks. Its core is formed by foyaites, and the periphery zone by khibinites which are referred to as a variety of foyaite by several researchers. In between the foyaites and khibinites there is a ring intrusion composed of melteigite-urtites and apatite-nepheline rocks accompanied by ristschorrites (Gor-stka, 1971) .

The numerous altered (fenitized) xeno-liths from several meters up to several kilo-metres in size are located at the contact zone between the foyaite core and ristschorrites. In general, they are located within Eveslog-chorr, Yukspor, Kukisvumchorr, Poachvum-chorr, Kaskasnyunchorr, Ristschorr and Partomchorr Mts., i.e. on the southern, south-western and western borders of the foyaite core. The majority of scientists agree that these xenoliths are the remnants of the host rocks in the roof of the Khibiny massif; they were altered — fenitized due to intrusion of alkaline magma. The nature of their protolith is still debatable. According to the structure-texture features, the fine-grained rocks of the altered xenoliths are often named hornfels; however by their genesis they are fenites. They are notable for their extraordinary wide mineral diversity. These are mostly enriched in Al up to highly alumina-rich rocks, com-posed of alkaline feldspars, nepheline, mica, andalusite, sillimanite, cordierite-sekaninaite series members, hercynite, corundum, etc.

The results of research of apoxenolithic rocks from Khibiny and their minerals are published in many papers by several scien-tists (Kupletskiy, 1923; Bonshtedt *et al*., 1937;

Men'shikov, 1978; Kostyleva-Labuntsova *et al.*, 1978[1,2]; Shlyukova, 1986; Barkov *et al.*, 1997, 2000[1,2], 2006; Men'shikov *et al.*, 1999, 2001; Yakovenchuk *et al.*, 2005; Korchak, 2008; Azarova, Shlyukova, 2008). Some aspects of mineralogy and geochemistry of these rocks were investigated by the authors (Yakovleva *et al.*, 2006[1,2], 2009).

In the fenitized xenoliths of the Khibiny massif there occurs very specific and in some areas rich in chalcogenides mineralization, however they were not systematically researched before. The present paper is devoted to it.

The material for investigation was collected from xenoliths situated on Kukisvumchorr (including Svintsoviy Ruchey, Lastochkino Gnezdo, the left bank of the upper reaches of the Tuliok river), Eveslogchorr (including Korundoviy Ruchey and Fersman Gorge), Kaskasnyunchorr, Yukspor (the head of Hackmann valley) and Partomchorr Mts. Literature data was also used.

Optical investigation of thin sections was performed using electronic microscope Axioplan 2 imaging (Carl Zeiss). BSE-images and energy-dispersive spectra of the minerals were obtained using SEM Jeol JSM-6480LV combined with EMPA equipment. The quantitative analysis was made using EMPA Camebax SX 50 at 15 kV, 30 nA and beam diameter — 3 µm. Standards: Fe, S — troilite, Mn — alabandite, Cu — covellite, Zn — sphalerite, Co — cobaltite, Ni — millerite, Ti — Ti, V — sulvanite, Cr — Cr_2O_3, Mo — molybdenite, W — tungstenite, Cd — $CdIn_2S_4$, As — arsenopyrite, Sb — stibnite.

Sulphide–bearing mineral associations from alumina–rich fenites of Khibiny massif

Sulphides and arsenides are dominant amongst chalcogenides within apoxenolithic alumina-rich fenites of Khibiny massif.

Sulphides occur in different amounts in all the types of these rocks. They are normally present as accessory minerals, but sometimes occur within the "ores" containing up to tens % of pyrrhotite (Yukspor Mt., Lastochkino Gnezdo, Kaskasnyunchorr Mt.) pr molybdenite (Lastochkino Gnezdo). The rocks enriched in sulphides are mostly feldspar and nepheline-feldspar varieties (and veinlets within them) that contain variable amounts of other minerals: ilmenite, biotite, rutile (Kas-

kasnyunchorr Mt., Eveslogchorr Mt., Poachvumchorr Mt., Lastochkino Gnezdo); biotite, corundum, sillimanite, pyrophanite, graphite, aenigmatite (Svintsoviy Ruchey); ilmenite, biotite, ulvö spinel (the upper reaches of the Tuliok River); biotite, sillimanite, sekaninaite, amphibole (the upper reaches of the Tuliok River, Lastochkino Gnezdo); ilmenite, hercynite, native iron (Partomchorr Mt.); biotite, minerals of the ilmenite-pyrophanite series, alkaline amphibole and pyroxene (Yukspor Mt., Lastochkino Gnezdo). Normally the rocks which predominantly consist of oxides and non-alkaline-alumina-rich silicates, contain less or no sulphides at all (mostly at Svintsoviy Ruchey and Corundoviy Ruchey). The neighbouring rocks on the one and the same locality can be different in sulphide content. Thus, in the xenolith at the Kaskasnyunchorr Mt. over a distance of several meters there are both "ore" (with up to 70 vol.% of pyrrhotite) and almost sulphide-free fenites with similar oxide-silicate mineral composition.

One of the most sulphide-rich and mineralogically and geochemically most interesting, is a specific type of fenite within the xenolith at Kaskasnyunchorr Mt., that was first described by Barkov *et al.* (1997, 2000[1,2]) and additionally studied by Korchak (2008) and by us. This fenite is a grey fine- to coarse-grained rock that consists predominantly of alkaline feldspars and nepheline (partially replaced by sodalite), each up to 75—80% in some areas. The other rock-forming minerals are: phlogopite, corundum, rutile and pyrrhotite (often Ti-, V- and Cr-bearing); the accessory minerals are: monazite-(Ce), fluorapatite, neighborite, chrysoberyl and graphite. The sulphides are diverse and unusual: the titanium-bearing varieties of pyrrhotite, pyrite and marcasite (all also occur without Ti), Fe enriched alabandite, chalcopyrite, sphalerite, wurtzite, galena, molybdenite (including its w-containing variety) and endemic niobium chalcogenides — edgarite $FeNb_3S_6$ and an unstudied sulphide of Nb, W, Mg and Al. Silicates and oxides here contain almost no iron. Such an unusual sulphide mineralization makes this rock unique.

Description of the minerals

All the researchers who studied fenitized xenoliths from Khibiny Mts., noted that *pyrrhotite* $Fe_{1-x}S$ is an abundant sulphide within alumina-rich rocks (Kupletskiy, 1923;

Bonshtedt *et al*., 1937; Kostyleva-Labuntsova *et al*., 1978[1,2]; Shlyukova, 1986; Korchak, 2008). This mineral forms separate irregular grains or massive aggregates, rarely — coarse-shaped hexagonal plate crystals. Pyrrhotite content varies from complete absence to almost 70% which is considered as "ore" associations. Individual grains are rarely over 1 cm in size, and are normally up to 1 mm. In the hornfels-like feldspar, nepheline-feldspar, biotite-feldspar, ilmenite-hercynite rocks, including corundum-bearing ones, pyrrhotite occurs as a fine impregnation. In pegmatiod varieties of fenites it occurs as continuous aggregates up to several centimetres.

The BSE images reveal that many of pyrrhotite grains are heterogeneous, sometimes there are individual grains containing regularly oriented bright lamellae in a dark matrix (Fig. 1). Such a composition, in general typical enough for this mineral (and sometimes is observed under optical microscope), is explained either by twinning (Kostyleva-Labuntsova *et al*. 1978[2]) or by exsolution of two phases similar in chemical composition (Ramdohr, 1962). In our case the brighter phase is enriched in iron compared to the darker one (empiric formulae $Fe_{0.95}S_{1.00}$ and $Fe_{0.93}S_{1.00}$ — analyses 4 and 5 in Table 1, respectively); under the optical microscope pyrrhotite grains look homogeneous. Due to these facts the assumption about solid solution explains the nature of this heterogeneity better.

In albite vein cross-cutting alumina-rich fenites at Kukisvumchorr Mt. we observed overgrowth and corrosion of both ilmenite and rutile by pyrrhotite (Fig. 2). In the same rock Shlyukova (1986) recorded overgrowth of ilmenite by pyrrhotite; this helps to conclude that sulphides were formed later than oxides in this mineral association. In other cases there are signs of co-growth of pyrrhotite and rock-forming silicates and oxides.

Accessory *troilite* FeS is less abundant. We found it only in four xenoliths at Kukisvumchorr Mt., Kaskasnyunchorr Mt., Yukspor Mt. and Partomchorr Mt. Troilite mostly coexists with pyrrhotite and forms rare grains up to 0.1 mm; their optical properties do not differ. At Kaskasnyunchorr Mt. troilite occurs in biotite-feldspar associations with variable quantities of nepheline, rutile, ilmenite, pyrrhotite, pyrophanite, fayalite, amphibole, pyroxene, muscovite, alabandite, chalcopyrite, sphalerite. In the annite-almandine-anorthoclase fenite at Kukisvumchorr Mt. troilite occurs as fine (up to 30 μm) platelets in association with native iron, hercynite, ilmenite, Ti-magnetite and rutile (Korchak, 2008; our data). In the predominantly potassic-feldspar-albite rock with muscovite and pyrophanite at Yukspor Mt. troilite coexists with predominant pyrrhotite. Their contents in the rock is together up to the first percents. Troilite from Partomchorr Mt. occurs in grains up to 0.2 mm, in intergrowths with native iron in nepheline and potassic feldspar matrix; in association there are also ilmenite, hercynite and magnetite forming rims over iron (Fig. 3) and also carbonic matter. Shlyukova (1986) reports that troilite, in a sodalite-orthoclase veinlet crossing a xenolith at Poachvumchorr Mt., occurs in association with native iron, magnetite, chalcopyrite, cubanite, sphalerite, V,Zr,Nb-bearing rutile, hercynite and bituminous matter.

The atomic ratios *Me:X* in minerals of pyrrhotite-troilite series are varied for

Fig. 1. Individual of pyrrhotite (Pyrr) consisting of two similar chemical varieties (light areas correspond to the enriched in iron), with ingrowths of cubanite (Cub) in anorthoclase matrix (Anorth), Kukisvumchorr Mt. (BSE-image).
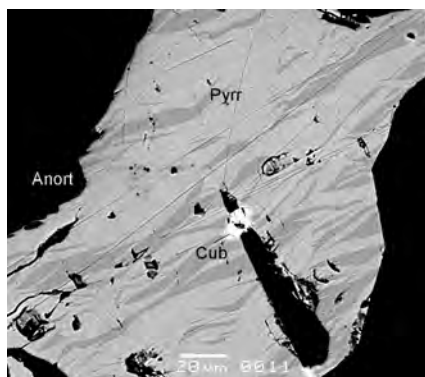
Fig. 2. Overgrowth and corrosion by pyrrhotite (Pyrr) of ilmenite (Ilm) and rutile (Rut) in albite (Ab) vein cross-cutting fenites of xenolith Lastochkino Gnezdo at Kukisvumchorr Mt. (BSE-image).

Table 1. **Chemical composition of pyrrhotite (1−21) and troilite (22−29) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
wt.%															
Ti	—	—	—	—	—	—	—	—	—	—	2.91	1.60	2.87	2.93	0.43
V	—	—	n/a	n/a	n/a	—	0.89	1.44	—	—	0.46	0.19	0.64	0.22	1.16
Cr	n/a	n/a	n/a	n/a	n/a	—	0.23	0.38*	0.06	0.07	—	—	—	—	n/a
Mn	0.07	—	—	—	—	—	0.08	0.19	—	—	—	—	—	0.08	—
Fe	63.15	61.40	60.96	62.44	61.62	60.56	59.39	58.54	59.62	61.29	56.84	60.30	55.91	59.86	57.84
Co	—	0.07	0.07	—	—	—	n/a	n/a	n/a	—	n/a	n/a	n/a	n/a	0.12
Ni	—	0.06	—	0.05	—	0.12	n/a	n/a	n/a	—	n/a	n/a	n/a	0.11	—
Cu	—	—	—	—	—	—	—	—	0.14	—	—	0.06	—	0.07	—
Zn	0.12	0.16	—	—	—	0.07	—	0.24	—	—	—	0.24	—	—	0.13
S	38.26	37.70	39.34	37.89	38.10	38.49	38.22	38.47	37.82	37.14	36.31	36.91	38.47	39.46	38.59
Total	101.60	99.39	100.37	100.38	99.72	99.24	98.80	99.26	97.81**	98.50	97.33**	99.29	97.89	102.73	98.27
apfu, for 1 S															
Ti	—	—	—	—	—	—	—	—	—	—	0.05	0.03	0.04	0.05	0.01
V	—	—				—	0.01	0.02	—	—	0.01	—	0.01	—	0.02
Fe	0.95	0.94	0.89	0.95	0.93	0.90	0.89	0.87	0.90	0.95	0.89	0.94	0.83	0.87	0.86
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Note: an. 1−6, 25, 27, 29 − Kukisvumchorr Mt., (including 1, 24 − the upper reaches of Tuliok River, 2−6, 25 − Lastochkino Gnezdo, 27, 29 − Svintsoviy Ruchey), an. 7−21, 23, 24 − Kaskasnyunchorr Mt., an. 22 − Partomchorr Mt., an. 26 − Yukspor Mt, an. 28 − Eveslogchorr Mt. An. 1−19, 22−26 − our data, an. 20, 21, 27−29 − literature data: 20 − Barkov et al., 2000₁;
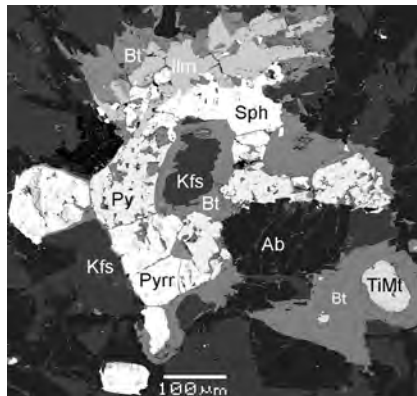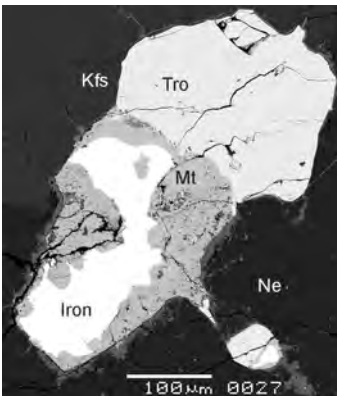

Fig. 3. Troilite (Tro) grain in close association with native iron (Iron) [which is surrounded by magnetite rim], potassic feldspar (Kfs) and nepheline (Ne), Partomchorr Mt. (BSE-image).

Fig. 4. Intergrowth of pyrite (Py), pyrrhotite (Pyrr) and sphalerite (Sph) in association with ilmenite (Ilm), biotite (Bt), Ti-magnetite (TiMt), albite (Ab) and potassic feldspar (Kfs) (BSE-image).

apoxenolithic fenites from Khibiny Mts., according to our and literature data, from 0.85 up to 1.06 (Table 1) within the continuous series. The phases which are more ferriferous that $Fe_{0.95}S_{1.00}$ we consider as troilite. In the rocks studied pyrrhotite with composition close to $Fe_{0.93}S_{1.00}$ is dominant. Minerals of this series contain impurities: Me = Ti, V, Ni, Cr; X = As. Unusual impurities − Ti (up to 3.9 wt.%), V (up to 1.9 wt.%) and Cr (up to 0.4 wt.%) − are typical for pyrrhotite from nepheline-feldspar rock with almost iron-free fluorophlogopite, rutile, corundum, alabandite, edgarite, W-bearing molybdenite and

tungstenite from Kaskasnyunchorr Mt. Pyrrhotite from this unique association was first described by Barkov *et al.* (1997) and additionally studied by us; in particular we determined its highest-vanadium-bearing (an. 16, Table 1) and chrome-bearing (an. 8, Table 1) varieties. It is significant that in other types of fenites within this xenolith there is different oxide-silicate mineralization (Yakovleva *et al.*, 2009).

Pyrite and *marcasite* occur in the pyrrhotite-bearing fenites, however their amount is rather small: rarely up to 5 % of the rock volume. Optical investigation revealed that

Table 1. **(cont.)**

	16	17	18	19	20	21	22	23	24	25	26	27	28	29
wt.%														
Ti	0.30	0.92	—	—	1.4−3.7	1.2−3.9	—	—	—	0.09	—	—		
V	1.86	1.22	—	—	0.2−0.6	0.2−0.4	—	—	0.16	0.08	—	—		0.01
Cr	n/a	n/a	n/a	n/a			n/a	—	0.10	0.06	—	—		
Mn	—	—	—	—	0.0−0.1	n/a	—	0.04	—	0.09	—	n/a		
Fe	57.11	56.43	58.72	58.31	56.2−58.5	56.1−59.2	63.92	63.57	61.49	65.92	65.26	62.75	63.60	62.89
Co	0.06	—	0.11	—			—	—	—	—	0.19			0.02
Ni	—	0.11	0.71*	0.52*			—	—	—	—	—			
Cu	—	—	—	—			—	—	0.07	—	—			
Zn	—	—	—	—			—	—	—	—	—			
S	38.94	38.52	39.12	38.47	38.9−40.1	38.5−40.7	34.57	34.74	36.59	35.90	36.13	37.49	36.47	36.72
Total	98.27	97.20	98.66	97.30			98.49	98.34	98.41	102.14	101.58	100.24	100.07	99.64
apfu, for 1 S														
Ti	0.01	0.02	—	—	0.02−0.06	0.02−0.07	—	—	—	—	—			
V	0.03	0.02	—	—	0.00−0.01	0.00−0.01	—	—	—	—	—			
Fe	0.84	0.84	0.86	0.87	0.82−0.85	0.79−0.87	1.06	1.05	0.96	1.05	1.04	0.96	1.00	0.98
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

*21 − Barkov et al., 1997; 27, 29 − Shlyukova, 1986; 28 − Yakovenchuk et al., 2005. * − corresponding to 0.01 apfu. ** − total also includes As (wt.%): 9 − 0.17 (0.00 apfu), 11 − 0.82 (0.01 apfu). Here and further in the tables 2−7 "dash" means values under detection limits, wt.% (0.00 apfu respectively); n/a − not analysed; the blank cell − no data.*

pyrite is considerably predominant among them. Disulphides of iron form separate grains up to 1 mm. Sometimes they co-grow with each other or occur as aggregates with pyrrhotite or sphalerite (Fig. 4). Disulphidization of pyrrhotite is typical: pyrite and marcasite form thin rims around its grains or along cracks (Fig. 5). Sometimes pyrite forms metacrystals in pyrrhotite (with multiple pyrite inclusions) and in non-sulphide minerals. We recorded pyrite in fenites from Kaskasnyunchorr, Kukisvumchorr, Yukspor and Eveslogchorr Mts., and marcasite − from Kaskasnyunchorr Mt.

The special feature of pyrite and marcasite from some of the rocks described is titanium impurity. Barkov *et al*. (1997, 2000₂) and the authors found titanium-bearing varieties of iron disulphides only at Kaskasnyunchorr Mt. in fenites with Ti-pyrrhotite; Korchak (2008) also recorded them in other xenoliths from the Khibiny Mts. Ti content in pyrite recorded by the authors (up to 3.9 wt.%: an. 2 in Table 2) is considerably higher than that previously published and is an absolute record for pyrite. It is significant that in the case of Ti-bearing pyrrhotite disulphidization, titanium is inherited by pyrite; Ti content may even increase comparative to pri-

mary pyrrhotite. Thus, pyrrhotite from this minerals association contains up to $0.03−0.05$ apfu Ti, and pyrite rim over it − contains 0.10 apfu Ti (an. 2 in Table 2). The other impurities are (Table 2): V (up to 0.7 wt.% including Ti-bearing pyrite from Kaskasnyunchorr Mt.), Mn (rarely up to 0.1 wt.%) and As (up to 1.4 wt.%).

During our work we assumed that titanium recorded by EMPA in iron sulphides is derived from microscopic rutile ingrowths. This assumption was not confirmed: energy-dispersive spectra of these minerals recorded using high-sensitive spectrometer INCA-Energy 350 with ATW-2 window showed no peak of oxygen, which will be apparent at Ti-content of $2−3$ wt.% as a part of TiO_2; O-content would be $1.3−2$ wt.% then. This ED spectrum is presented on Fig. 6 together with the spectrum of ilmenite $FeTiO_3$ that shows peaks of oxygen and metals that can be distinguished at this scale.

In a xenolith at Kaskasnyunchorr Mt. we made the first find of *pentlandite* for Khibiny $(Fe,Ni)_9S_8$ − $(Ni,Fe)_9S_8$ (previously mentioned from this massif "pentlandite" occurs as cobaltpentlandite according to spectral analysis; Kostyleva-Labintsova *et al*., 1978₂). It occurs as ingrowths up to 40 µm in
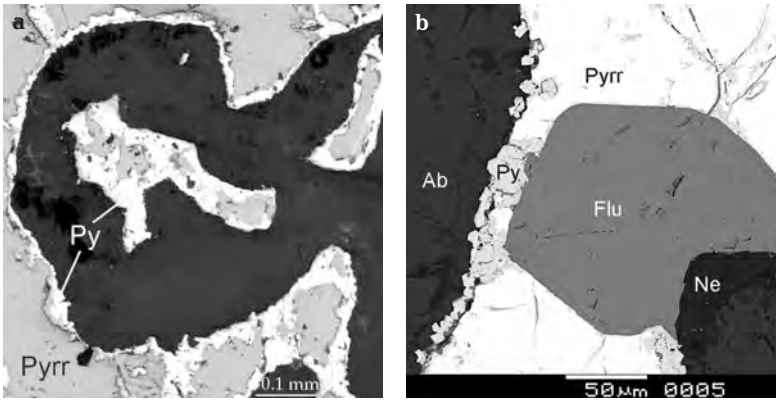
Fig. 5. Overgrowth and replacement of pyrrhotite (Pyrr) by pyrite (Py), in association with albite (Ab), nepheline (Ne) and fluorite (Flu), Kaskasnyunchorr Mt. (a — in reflected light, nicols //), b — BSE-image).

Table 2. **Chemical composition of pyrite (1−7) and marcasite (8−12) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6	7	8	9	10	11	12
wt.%												
Ti	0.13	3.92	—	1.6−2.7	0.56	0.0−2.7	0.64	0.7−2.7	1.42	1.37	1.06	0.98
V	—	0.15	—	0.2−0.3	—	0.0−0.7	—	0.2−0.4	0.19	0.09	0.53	—
Mn	—	0.08	—	n/a				0.0−0.1				
Fe	45.58	45.55	48.21	44.2−46.4	45.97	44.1−46.4	46.11	44.3−45.6	47.09	46.13	46.04	47.12
Co	n/a	n/a	0.07	n/a	—	—	—	0.00−0.03	—	—	—	—
Ni	n/a	n/a	0.10	n/a	—	0.0−0.1	0.02	0.00−0.04	—	—	—	—
As	1.36	0.74	—									
S	50.51	50.91	51.05	50.5−52.7	53.34	51.5−52.8	53.14	50.6−51.7	50.84	52.26	52.16	51.72
Total	97.45	97.20	99.43		99.31		99.27		97.93	98.39	98.20	98.84
apfu, for 2 S												
Ti	—	0.10	—	0.04−0.06	0.01	0.00−0.07	0.02	0.02−0.07	0.04	0.03	0.03	0.03
V	—	—	—	0.00−0.01	—	0.00−0.02	—	0.01	0.01	—	0.01	—
Fe	1.04	1.03	1.08	1.00−1.02	0.99	0.97−1.03	1.00	1.00−1.01	1.06	1.01	1.01	1.05
S	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

Note: an.: 1, 2, 4, 6, 8, 9 — Kaskasnyunchorr Mt., 3 — Lastochkino Gnezdo, 5, 10 — Eveslogchorr Mt., 7, 11, 12 — Marchenko peak. An. 1−3 — our data, an. 4−12 — literature data: 4, 8 — Barkov et al., 2000₁; 5−7, 10−12 — Korchak, 2008; 9 — Yakovenchuk et al., 2005.

pyrrhotite from an aegirine-ilmenite-nepheline-feldspar rock with muscovite, aenigmatite, alkaline amphibole, pyrrhotite and sphalerite (Fig. 7). The major impurities in pentlandite are Co (1.6−1.7 wt.%), and Cu (up to 0.2 wt.%). In its grain there are areas both in Fe- and Ni-dominant (an. 10−11 in Table 3).

Molybdenite MoS$_2$ is a common accessory mineral in alumina-rich fenites Khibiny; but sometimes its content is quite high for it to be an ore-forming mineral (Fig. 8). Thus, in the Lastochkino Gnezdo area this mineral occurs in small stockwork zones with its concentration up to 30%. The chemical composition of such an "ore" molybdenite is close to ideal, and accessory molybdenite in the same association contains up to 0.3 wt.% W (an. 2 in

Table 4). In corundum-pyrrhotite-anorthoclase rock at Kaskasnyunchorr Mt. molybdenite is significantly enriched in tungsten, it occurs as zoned tabular crystals up to 60 µm in association with Ti,V-bearing varieties of pyrrhotite, pyrite and marcasite, with alabandite, edgarite, tungstenite, fluorophlogopite, rutile, corundum, monazite-(Ce) and graphite. Here Barkov *et al.* (2000₂) found molybdenite with up to 5.8 wt.% of W, and the authors — with up to 22.7 wt.% of W (Table 4). In the same association molybdenite without tungsten, including zoned crystals with areas enriched and depleted in W occurs. Fig. 9 illustrates that W-bearing molybdenite was formed later than the tungsten-free. Sometimes there is Fe impurity — up to 1.3 wt.% in the molybdenite composition (Table 4). Ac-
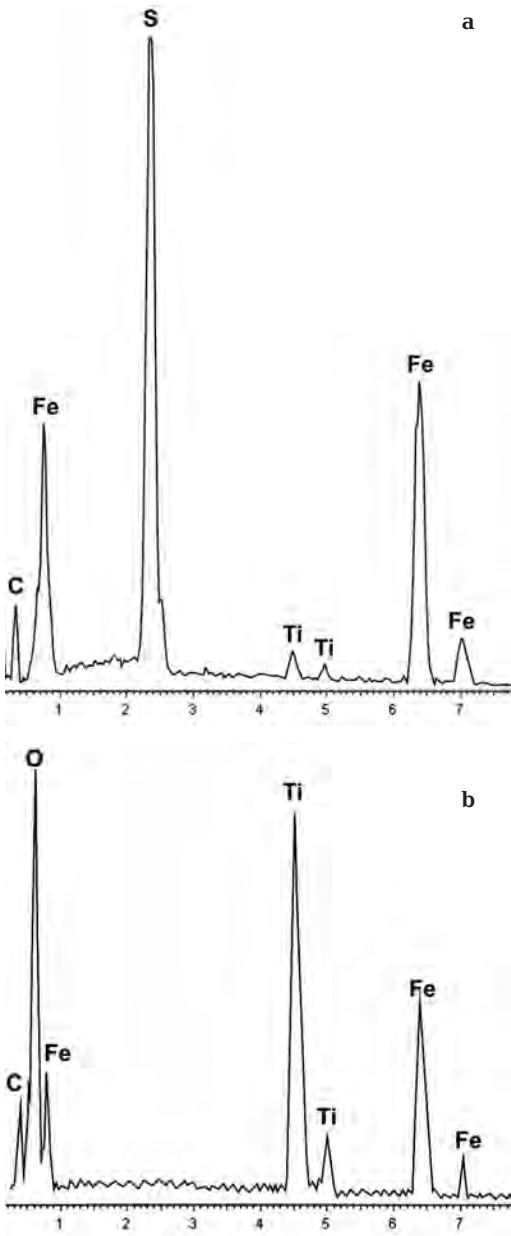
Fig. 6. Energy dispersive spectra of Ti-bearing pyrrhotite (a) and ilmenite (b) from a xenolith on Kaskasnyunchorr Mt. Peak of C corresponds to the carbon film of the sample.

cording to Korchak (2008), in apoxenolithic fenites molybdenite-2*H* occurs.

Tungstenite WS_2 was first discovered by the authors in Khibiny in predominantly feldspar rock — fenitized xenolith — with corundum, rutile and topaz at Kaskasnyunchorr Mt. (it was independently found by Mikhail M. Moiseev, personal communication), and also in association with Ti-pyrrhotite and edgarite. It occurs as soft dark-grey hexagonal or irregular platelets up to 1 mm, with metallic lustre and is visually indistinguishable from graphite. The chemical composition of the mineral is well-stoichiometric, and the impurities content below the EMPA detection limit (an. 8 in Table 4).

Alabandite MnS is a typical accessory mineral of corundum-pyrrhotite-orthoclase, nepheline-feldspar, corundum-nepheline, muscovite-anorthoclase and sodalite-albite-anorthoclase rocks of xenoliths from Kaskasnyunchorr Mt. (Barkov *et al.*, 1997; Yakovenchuk *et al.*, 2005; our data). We also found it in corundum-bearing pyrrhotite-feldspar rock in xenoliths from Kukisvumchorr Mt. (the upper reaches of the Tuliok river) and titanite-biotite-nepheline-feldspar fenite from Yukspor Mt. (Hackmann valley). The mineral occurs as rounded grains up to 0.5 mm, usually in intergrowths with pyrrhotite (Fig. 10). By its optical characteristics it corresponds to alabandite. It is represented by the ferriferous variety (6.0 — 9.8 wt.% Fe; Table 5), and one sample revealed 0.85 wt.% As.

The endemic mineral *edgarite* $FeNb_3S_6$ occurs in corundum-pyrrhotite-anorthoclase fenite from xenoliths at Kaskasnyunchorr Mt. This unique niobium sulphide discovered by
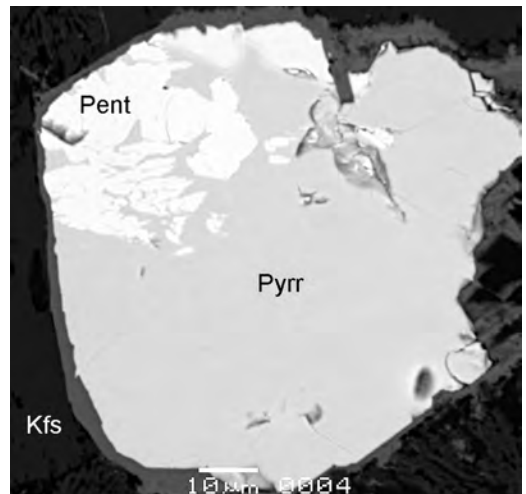

Fig. 7. Pentlandite (Pent) ingrowths in pyrrhotite (Pyrr) grain, in a matrix of potassic feldspar (Kfs), Kaskasnyunchorr Mt. (BSE-image).

Table 3. **Chemical composition of chalcopyrite (1 − 4), cubanite (5, 6), bornite (?) (7), jaipurite (8, 9) and pentlandite (10, 11) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6	7	8	9	10	11
					wt.%						
Mn	0.04	0.08	0.07		−			−	−	−	−
Fe	30.85	31.23	31.49	29.83	43.25	40.54	18.57	5.71	6.64	36.59	27.48
Co	−	−	−		−			56.53	56.06	1.60	1.72
Ni	−	0.08	0.09		0.05			1.90	2.18	29.34	36.38
Cu	32.70	33.09	33.64	33.76	20.77	23.78	59.35	−	0.08	0.16	−
S	34.88	32.65	34.38	35.28	35.53	35.75	24.32	33.97	33.85	32.79	32.09
Total	98.47	97.13	99.67	98.87	99.60	100.07	102.24	98.11	99.00*	100.48	97.67
	apfu, for 2 S (chalcopyrite), 3 S (cubanite), 4 S (bornite), 1 S (jaipurite), for total = 17 atoms (pentlandite)										
Fe	1.02	1.10	1.05	0.97	2.10	1.95	1.75	0.10	0.11	5.05	3.91
Co	−	−	−		−			0.92	0.90	0.20	0.23
Ni	−	−	−		−			0.03	0.03	3.85	4.92
Cu	0.95	1.02	0.99	0.97	0.89	1.01	4.93	−	−	0.02	−
S	2.00	2.00	2.00	2.00	3.00	3.00	4.00	1.00	1.00	7.88	7.94

Note: an: 1, 4−7 − Kukisvumchorr Mt., 2, 10, 11 − Kaskasnyunchorr Mt., 3, 8, 9 − Yukspor Mt. An. 1−3, 5, 8−11 − our data, an. 4, 6, 7 − literature data: 4, 7 − Korchak, 2008; 6 − Yakovenchuk et al., 2005. • − total also includes 0.19 wt. % Zn.

Table 4. **Chemical composition of molybdenite (1 − 7) and tungstenite (8) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6	7	8
				wt.%				
Fe	0.36	0.50	−	n/a	−	0.0 − 1.3	−	−
Mo	60.85	60.92	60.11	48.34	43.28	51.9 − 58.8	59.94	−
W	−	0.32	−	14.87	22.70	0.1 − 5.8	−	73.48
S	35.81	36.06	39.30	37.46	32.32	39.5 − 41.1	39.77	25.60
Total	97.02	97.80	99.41	100.67	98.30		99.71	99.08
				apfu, for 2 S				
Fe	0.01	0.02	−		−	0.00 − 0.04	−	−
Mo	1.16	1.14	1.00	0.86	0.90	0.88 − 0.97	1.01	−
W	−	−	−	0.14	0.25	0.00 − 0.05	−	1.00
S	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

Note: an.: 1, 2, 7 − Kukisvumchorr Mt. (including 1, 7 − the upper reaches of Tuliok River, 2 − Lastochkino Gnezdo, 3−6, 8 − Kaskasnyunchorr Mt.). An. 1−5, 8 − our data, an. 6, 7 − literature data: 6 − Barkov et al., 2000₂, 7 − Korchak, 2008.

Barkov *et al*. (2000[1]) is not a rarity here. It occurs as lamellar inclusions (up to 0.15 µm) in titanium-bearing pyrrhotite and alabandite, and as aggregates (up to 1 mm) of dark-grey platelets overgrowing faces of pyrrhotite crystals (Barkov *et al*., 1997, 2000[1,2]; our data; fig. 11). Visually edgarite resembles dark molybdenite and indistinguishable from graphite and tungstenite from the same association. The chemical composition of edgarite is (wt.%): Ti up to 0.09, V up to 0.41, Mn up to 0.13, Fe 8.84 − 10.60, Nb 52.33 − 54.10, S 35.30 − 37.13, which corresponds to the formula $(Fe_{0.82-1.00} Mn_{0.00-0.01})(Nb_{2.95-3.17} V_{0.00-0.04} Ti_{0.00-0.01}) S_6$ (Barkov *et al*., 1997, 2000[1]; Korchak, 2008).

Chalcopyrite $CuFeS_2$ is a common accessory mineral from alumina-rich fenites from Khibiny. It does not form significant aggregations. Usually it occurs as small (up to 50 µm), irregularly shaped grains, often intergrown with grains of pyrrhotite and other sulphides (fig. 12). Chemical composition of the mineral is close to ideal. Significant impurities are: Zn − up to 0.2 wt.%, Ni, Mn, As − up to 0.1 wt.% (Table 3). Emulsion impregnation of chalcopyrite in sphalerite is typical (see below).

In albite-hercynite-sillimanite rock with corundum and ilmenite at Kukisvumchorr Mt. chalcopyrite is surrounded by a fine rim of pure copper sulphide (Fig. 13), probably *chalcocite* Cu_2S or a related phase. Shlyukova (1986) reported similar from drill core sample from bore hole No 557.
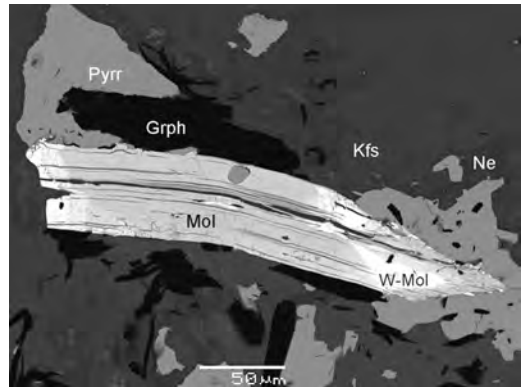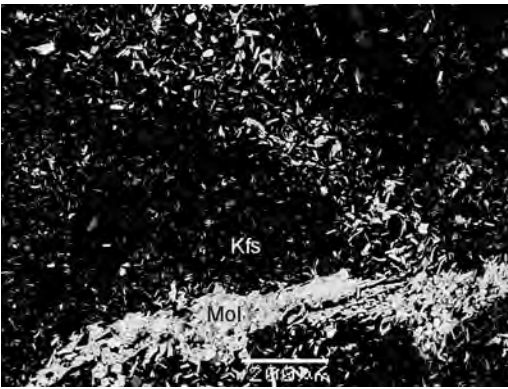
Fig. 8. Molybdenite (Mol) in the predominantly potassic feldspar (Kfs) fenites of Lastochkino Gnezdo (BSE-image).
Fig. 9. Molybdenite crystal from Kaskasnyunchorr Mt. containing areas with different chemical composition — with tungsten (W-Mol) (up to 14.9 wt. % W) and without it (Mol), in association with graphite (Grph), pyrrhotite (Pyrr), nepheline (Ne) and potassic feldspar (Kfs) (BSE-image).
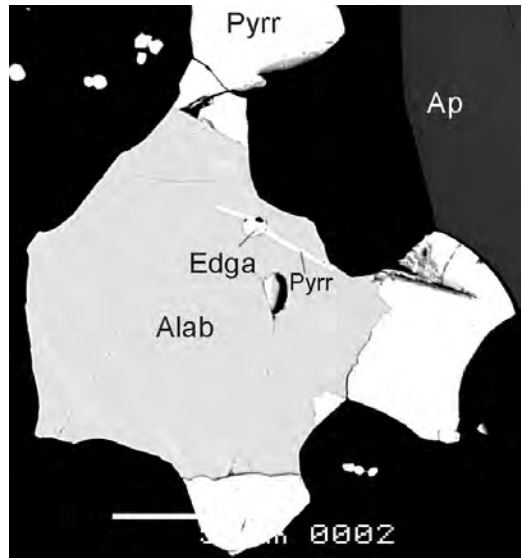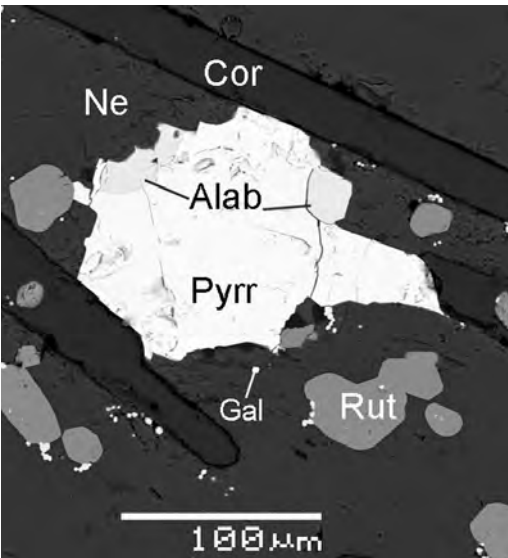

Fig. 10. Alabandite (Alab) and pyrrhotite (Pyrr) intergrowth in corundum-nepheline (Cor-Ne) rock, in association with rutile (Rut) and galena (Gal), Kaskasnyunchorr Mt. (BSE-image).
Fig. 11. Lamellar inclusion of edgarite (Edga) in alabandite (Alab) grain in close association with pyrrhotite (Pyrr) and fluorapatite (Ap), Kaskasnyunchorr Mt. (BSE-image).

Fine (up to 0.1 mm) grains of *bornite* Cu_5FeS_4 in intergrowths with chalcopyrite (Shlyukova, 1986; Korchak, 2008) occur in a corundum-bearing pegmatite which crosscuts a xenolith at Kukisvumchorr Mt. By its chemical composition, the mineral was identified by Korchak (2008) as bornite despite high Fe content (Table 3).

Cubanite $CuFe_2S_3$ is very rare. Its finds were recorded in annite-almandine-feldspar rock from xenoliths at Kukisvumchorr Mt. in close association with pyrrhotite, *rasvumite*

KFe_2S_3, sometimes with chalcopyrite, sphalerite (Shlyukova, 1986).

We found cubanite in a biotite-feldspar rock from a xenolith at Kukisvumchorr Mt. with pyrrhotite, löllingite and molybdenite (Fig. 1; Table 3).

Sphalerite ZnS is a typical accessory mineral of many fenitized xenoliths (Kukisvumchorr, Yukspor, Poachvumchorr and Kaskasnyunchorr Mts.). However here it does not occur in aggregations and is not as abundant as in pegmatites and hydrothermal bodies in

Table 5. **Chemical composition of alabandite from alumina-rich fenites, Kaskasnyunchorr Mt.**

	1	2	3	4	5	6	7
wt.%							
Mn	56.27	55.52	56.61	58.43	55.89	54.72	54.8−56.9
Fe	8.41	6.97	6.59	6.06	7.73	9.75	6.0−7.6
S	36.88	35.82	34.75	36.07	35.85	35.27	35.9−37.8
Total	101.56	99.16*	97.95	100.56	99.47	99.74	
apfu, for 1 S							
Mn	0.89	0.90	0.95	0.94	0.91	0.91	0.87−0.90
Fe	0.13	0.11	0.11	0.09	0.12	0.16	0.09−0.12
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Note: an. 1−4 − our data, an. 5−7 − literature data: 5 − Yakovenchuk et al., 2005; 6 − Korchak, 2008, 7 − Barkov et al., 2000₁.
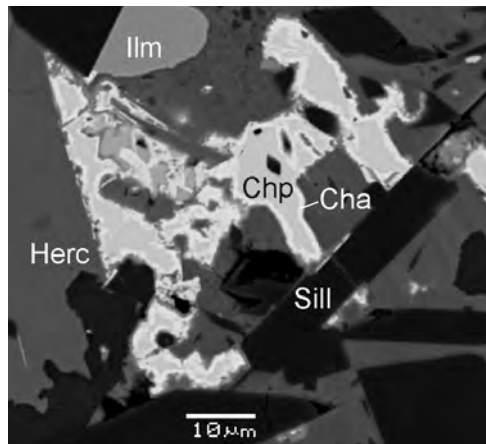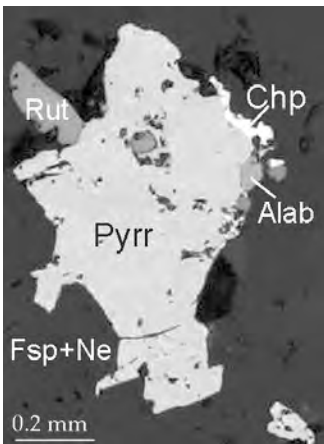** − total also includes 0.85 wt.% As (0.01 apfu).*

Fig. 12. Chalcopyrite (Chp), pyrrhotite (Pyrr) and alabandite (Alab) intergrowth in the feldspar-nepheline (Fsp+Ne) rock with rutile (Rut), Kaskasnyunchorr Mt. (in reflected light, nicols //).

Fig. 13. The rim of a pure copper sulphide (chalcocite? − Cha) on chalcopyrite (Chp) in albite-hercynite-sillimanite (Herc, Sill) rock with ilmenite (Ilm), Kukisvumchorr Mt. (BSE-image).

the Khibiny massif. Sphalerite occurs in almost every association of alumina-rich fenites as separate grains up to 0.2 mm or intimate intergrowths with pyrrhotite (Fig. 14), pyrite and ilmenite. Its chemical composition varies significantly (Table 6). The high Fe content (11.9−20.9 wt.%) is typical for all the samples of sphalerite from alumina-rich fenites. Mn content varies from almost complete absence to 14.1 wt.% (Kaskasnyunchorr Mt.; Yakovenchuk *et al.*, 2005); the authors determined 10.0 wt.% Mn in the sample from Yukspor Mt. (Table 6). Sometimes sphalerite contains fine, submicroscopic, emulsion impregnation of chalcopyrite that explains the high Cu content compared to that of Fe in several samples (up to 15.0 wt.% Cu, Kukisvumchorr Mt. − an. 2 in Table 6). The analysis of sphalerite with emulsion impregnation of chalcopyrite (Fig. 15) from a xenolith from the upper reaches of the Tuliok river (Kukisvumchorr Mt.) was performed using EMPA with defocused (10×10 μm) beam (an. 6 in

Table 6). The composition, $(Zn_{0.55}Fe_{0.28}Cu_{0.17}Cd_{0.01})_{1.01}S_1$, possibly corresponds to the primary solid solution exsolved into the phases $(Zn,Fe,Cd)S$ and $CuFeS_2$ under cooling conditions.

Wurtzite-2*H* ZnS occurs as fine grains in a natrolite veinlet cross-cutting phlogopite-anorthoclase fenite with pyrrhotite, monazite-(Ce), rutile and alabandite at Kaskasnyunchorr Mt. Wurtzite contains significant Mn impurity (15.9−16.1 wt.%) and minor Ga and Cd (both 0.1 wt.%) (Table 6).

Galena PbS is a rare mineral in alumina-rich fenites. Normally it occurs as grains up to 50 μm in intergrowths with other sulphides. Galena from Kaskasnyunchorr occurs as grains, with segregations up to 3 mm, in: (1) corundum-nepheline rocks with pyrrhotite, alabandite and rutile (Fig. 10), and (2) orthoclase veinlets cross-cutting anorthoclase-freudenbergite-rutile rock. The chemical composition of this mineral is Pb 86.68, S 13.43, total 100.11 wt.% (Korchak, 2008).
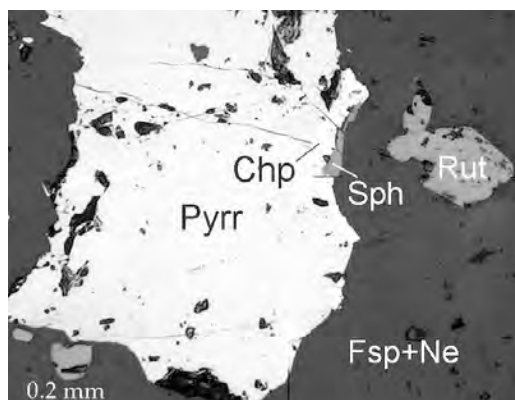
Fig. 14. Sphalerite (Sph), pyrrhotite (Pyrr) and chalcopyrite (Chp) intergrowth in feldspar-nepheline (Fsp+Ne) rock with rutile (Rut), Kaskasnyunchorr Mt. (in reflected light, nicols //).
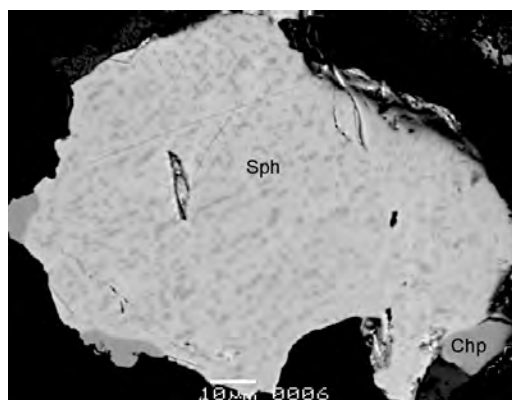
Fig. 15. Emulsion impregnation of chalcopyrite in sphalerite, Kaskasnyunchorr Mt. (BSE-image).

Table 6. **Chemical composition of sphalerite (1 – 14) and wurtzite (15, 16) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6**	7	8	9	10	11	12	13	14	15	16
							wt.%									
Mn	1.17	0.06	0.15	0.30	0.05	0.02	0.14	0.08	7.47	9.97	0.63	14.07	1.08	0.28	16.12	15.94
Fe	20.94	17.46	14.23	18.27	16.69	15.69	16.82	12.90	14.08	19.27	14.73	18.75	14.81	11.89	15.57	15.47
Cu	1.67	15.00*	6.63*	0.45	14.03*	10.81*	0.27	4.88*	2.41	0.04						
Zn	41.49	31.43	43.68	46.78	32.45	36.73	46.44	46.23	39.93	37.08	50.04	33.23	48.03	53.65	33.13	33.21
Cd	n/a	n/a	n/a	n/a	1.11	1.35	0.37	n/a	n/a	—					0.13	0.12
S	33.55	33.22	32.64	33.28	32.94	32.57	33.56	33.21	34.00	36.14	32.58	33.34	33.73	34.42	34.66	34.57
Total	98.82	97.17	97.33	99.08	97.27	97.17	97.66***	97.40***	97.89	102.56***	97.98	99.39	97.65	100.24	99.72***	99.43***
							apfu, for 2 S									
Mn	0.02	—	—	—	—	—	—	—	0.13	0.16	0.01	0.25	0.02	—	0.27	0.27
Fe	0.36	0.30	0.25	0.31	0.29	0.28	0.29	0.23	0.24	0.31	0.26	0.32	0.25	0.20	0.26	0.26
Cu	0.03	0.23	0.10	0.01	0.21	0.17	—	0.07	0.04	—						
Zn	0.60	0.46	0.65	0.69	0.48	0.55	0.68	0.68	0.58	0.50	0.75	0.49	0.70	0.76	0.47	0.47
Cd					0.01	0.01	—		—							
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

*Note: an.: 1–7 – Kukisvumchorr Mt., (including 1 – the upper reaches of Tuliok River, 2–7 – Lastochkino Gnezdo), 8, 9, 12, 15, 16 – Kaskasnyunchorr Mt., 10 – Yukspor Mt., 11 – Eveslogchorr Mt., 13, 14 – Marchenko peak. An. 1–10 – our data, an. 11–16 – literature data: 11, 14 – Korchak, 2008; 12, 13, 16 – Yakovenchuk et al., 2000; 15 – Barkov et al., 2000₁. * – large content of Cu is due to fine emulsion ingrowths of chalcopyrite. ** – electron microprobe analysis with defocused beam (10×10 μm). *** – total also include (wt. %): 7 – 0.06 Co, 8 – 0.10 Co, 10 – 0.06 Ni, 15 – 0.11 Ga, 16 – 0.12 Ga.*

We made the first find of *jaipurite* CoS in Russia. It occurs as ingrowths up to 30 μm in pyrrhotite from an aegirine-biotite-nepheline xenolithic rock in the head of the Hackmann valley, Yukspor Mt. (Fig. 16). It occurs in association with chalcopyrite and sometimes with galena. Impurities of Fe (5.7 – 6.6 wt.%) and Ni (1.9 – 2.2 wt.%) are significant.

Also, the authors made the first find of *westerveldite* FeAs in Russia, in xenoliths at

Kukisvumchorr Mt. (the upper reaches of the Tuliok river). It was found in ilmenite-biotite-feldspar fenite with pyrrhotite, molybdenite, zircon and britholite-(Ce). It occurs as rounded ingrowths up to 10 μm in pyrrhotite (Fig. 17). Sulphur impurity in westerveldite from Khibiny varies from 1.0 to 4.6 wt.% (Table 7).

Löllingite FeAs$_2$ from alumina-rich fenites in Khibiny is more abundant than westerveldite. It occurs as an accessory mineral in

many associations, mostly in xenoliths from Kukisvumchorr and Kaskasnyunchorr Mts. (Shlyukova, 1986; Korchak, 2008; our data). Normally this arsenide occurs in close association with sulphides − chalcopyrite, sphalerite, molybdenite, galena and especially with pyrrhotite, in which it forms elongated ingrowths up to 50 μm (Fig. 18).

The larger separate segregations of löllingite (up to 0.3 mm) occur in oxide-silicate aggregates (low-sulphide and sulphide-free associations; possibly the appearance of lö llingite is due to sulphur deficiency). A tan-

gible impurity of Co − up to 3.2 wt.% (Table 7) is typical for löllingite from Khibiny alumina-rich fenites; the other impurities are (wt.%): Ni (up to 1.7), Cu (up to 0.1), Sb (up to 2.8) and S (up to 1.1).

In sekaninaite-corundum-quartz-almandine-orthoclase veins within fenites in xenoliths from Eveslogchorr Mt. Yakovenchuk *et al.* (2005) found a 1 cm isometric segregation of *arsenopyrite* FeAsS within orthoclase (Table 7).

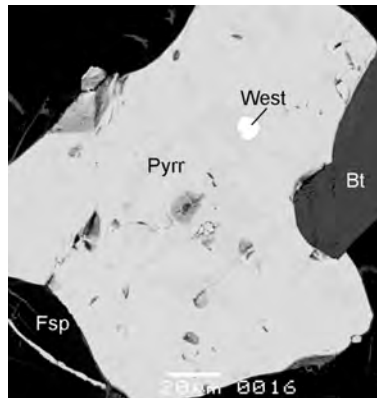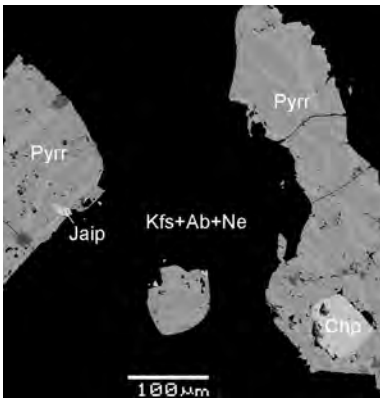The information by Korchak (2008) on two insufficiently studied sulphides which were

Fig. 16. Jaipurite (Jaip) ingrowth in pyrrhotite (Pyrr) in association with chalcopyrite (Chp) in potassic-feldspar-albite-nefeline (Kfs+Ab_Ne) rock, Yukspor Mt. (BSE-image).

Fig. 17. Inclusion of westerveldite (West) in pyrrhotite (Pyrr) in association with biotite (Bt) and feldspar (Fsp), Kukisvumchorr Mt. (BSE-image).

Table 7. **Chemical composition of löllingite (1 − 6), westerveldite (7 − 9) and arsenopyrite (10) from alumina-rich fenites of the Khibiny massif**

	1	2	3	4	5	6	7	8	9	10
					wt.%					
Mn	−	−	−	−			0.13	0.09	−	
Fe	26.25	26.66	23.52	24.44	25.7 − 27.0	26.74	44.75	44.93	45.38	34.02
Co	2.66	2.89	2.88	3.22	1.1 − 1.2	0.33	−	−	−	0.11
Ni	−	−	0.12	1.70	0.3 − 0.4	0.63	0.08	−	0.14	0.40
Cu	−	−	−	0.14			−	−	−	0.28
As	71.25	70.31	70.46	69.11	70.3 − 71.3	71.97	56.04	52.81	50.81	46.62
Sb	−	−	0.48	2.83			−	−	−	
S	0.57	0.65	0.48	1.06	0.2 − 0.5	0.33	0.96	3.26	4.57	18.59
Total	100.73	100.51	97.94	102.50		100.00	101.96	101.09	100.90	100.02
	apfu, for total = 3 atoms (of löllingite), As + S = 1 (westerveldite), As + S = 2 (arsenopyrite)									
Fe	0.95	0.96	0.88	0.92	0.95 − 1.02	0.99	1.03	1.00	0.99	0.98
Co	0.09	0.10	0.10	0.11	0.04	0.01	−	−	−	−
Ni	−	−	−	0.06	0.01	0.02	−	−	−	0.01
Cu	−	−	−	−			−	−	−	0.01
As	1.92	1.90	1.97	1.93	1.97 − 1.99	1.98	0.96	0.87	0.83	1.00
Sb	−	−	0.01	0.05			−	−	−	
S	0.04	0.04	0.03	0.07	0.01 − 0.03	0.02	0.04	0.13	0.17	1.00

Note: an.: 1−5, 7−9 − Kukisvumchorr Mt., (including 1, 5, 7−9 − the upper reaches of Tuliok River, 2−4 − Lastochkino Gnezdo), 6 − Kaskasnyunchorr Mt., 10 − Eveslogchorr Mt. An. 1−4, 7−9 − our data, an. 5, 6, 10 − literature data: 5 − Shlyukova, 1986; 6, 10 − Yakovenchuk et al., 2005.

found in alumina-rich fenites from xenoliths of Kaskasnyunchorr Mt. is very interesting.

Thus, *the phase $Mg_2AlNb_2S_4$* occurs in mica-like swirly grains up to 0.1 mm in anorthoclase rock with pyrite, pyrrhotite, alabandite, Ba-orthoclase, chrysoberyl, monazite-(Ce) and both an undetermined Al, Ti-oxide and Ca,Mg,Al-fluoride. The empirical formula calculated on 4 atoms of sulphur is the following: $(Mg_{1.63}Ca_{0.03}Fe_{0.03}Mn_{0.01})_{1.70}(Al_{1.05}V_{0.03})_{1.08}$ $(Nb_{1.66}W_{0.22}Si_{0.17})_{2.05}S_4$ (Korchak, 2008). Unfortunately, in the paper by Yu. A. Korchak there is no data on oxygen content given in this phase. Judging by the set of the components and shape of individuals and aggregates, we suppose it might well belong to the group of hybrid layer hydroxide-sulphides with successive structures composed by sulphide modules M_xS (M = Fe, Cu, Ni, V) and brucite packets $A(OH)_y$ (A = Mg, Ca, Fe, Al; y = 2−3) (Organova, 1989). This group contains valleriite $4(Fe,Cu)S \cdot 3(Mg,Al)(OH)_y$, haapalaite $4(Fe,Ni)S \cdot 3(Mg,Fe)(OH)_2$, tochilinite $6FeS \cdot 5Mg(OH)_2$, vyalsovite $FeS \cdot Ca(OH)_2 \cdot Al(OH)_3$ and yushkinite $V_{0.4}S \cdot 0.6(Mg,Al)(OH)_y$. It is possible that , "the phase $Mg_2AlNb_2S_4$" in fact corresponds to a formula close to $2(Nb,W)S_2 \cdot 2Mg(OH)_2 \cdot Al(OH)_3$.

The phase $Fe(V,Cr_2)S_2$ was found in phlogopite-nepheline-albite fenite as a fine (up to 10 µm) rim in between pyritized pyrrhotite and vuorelainenite MnV_2O_4. It is associated with alabandite, crichtonite, rutile, rengeite and rhodochrosite. The empirical formula calculated for 2 atoms of sulphur is the following: $(Fe_{0.79}Zn_{0.04}Mn_{0.03})_{0.86}(V_{1.20}Cr_{0.56})_{1.76}S_2$ (Korchak, 2008).

Discussion of results and conclusions

Sulphide mineralization is widespread in apoxenolithic alumina-rich fenites of the Khibiny massif, as the other chalcogenides, e.g. arsenides, are rare. Mineralogical analysis of the sulphide-bearing parageneses reveals three major feature of mineralization in this conditions: 1) enrichment in sulphur; 2) high reductive conditions; 3) high temperatures. The last two features are typical in general for all alumina-rich fenites of Khibiny. These rocks formed due to the impact of the huge masses of foyaite magma, even in their centre, the large xenoliths contain sillimanite, often with andalusite (but not kyanite), anorthoclase (usually exsolved) and
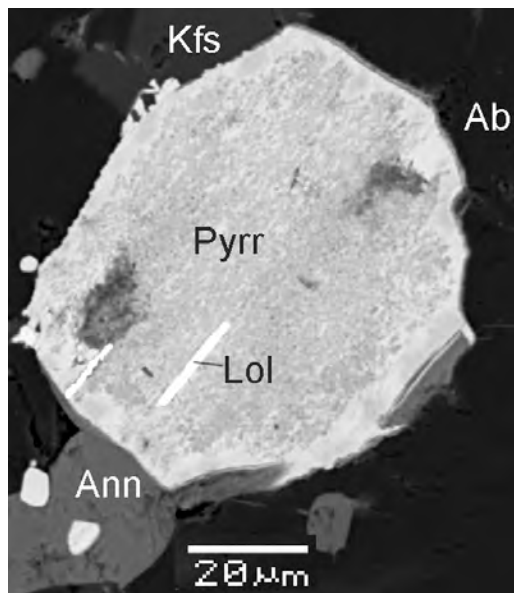

Fig. 18. Ingrowths of lö llingite (Lol) in pyrrhotite (Pyrr) in annite-potassic-feldspar-albite rock (Ann, Kfs, Ab), Lastochkino Gnezdo (BSE-image).

have a number of other indications of the high-temperature (>600−800°C) origin. The close association of native iron and troilite at Partomchorr (fig. 3) demonstrates signs of magmatic crystallization which refers to temperatures over Fe−FeS eutectic point: nearly 990°C (Minerals, 1974). The peculiarities of sphalerite, such as the significant Fe content and emulsion chalcopyrite also indicate high crystallization temperature. The overwhelming majority of mineral associations in the fenites described were formed in sharp reductive conditions; it is proved by the number of minerals of iron and their chemical composition. Thus, the typical and sometimes rock-forming minerals here are biotite and hercynite with extremely low Fe^{3+} content (Yakovleva *et al*., 2006[1,2]), native iron is common (Yakovenchuk *et al*., 2005; our data), and phases with Fe^{3+} including magnetite are rare. In alumina-rich fenites of Khibiny graphite is widespread, however there are almost no carbonates and no oxide forms of the other elements with variable valency (preeminently S and Mn) were found.

We observed, both amongst different xenoliths and within each of them that sulphur forms solely as a S^{2-} into the minerals described and their distribution is rather uneven. Pyrrhotite content in the rock can

vary from zero (Svintsoviy Ruchey, Eves-logchorr Mt.) up to 70 vol.% ("ore" areas in fenites: Kaskasnyunchorr Mt., Hackmann valley), and the molybdenite content sometimes reaches 30 vol.% (Lastochkino Gnezdo). Along with that the content of sulphides can decrease to minimum just several meters away from their segregations. It is likely that such an inequality indicates that the source of sulphur was not the fenitizing fluid but the xenolith protolith, and therefore the distribution of sulphides was inherited by one of S-bearing minerals in the primary rock. This conclusion is confirmed by sulphur isotopic data. The minerals from fenitized xenoliths are enriched in light isotope (-1.2 to -8.4 ‰ ^{34}S) which corresponds to the predominantly exogenic source of sulphur. On the other hand, the minerals from magmatic rocks and pegmatites are enriched in heavy S isotope (-0.8 up to $+2.2$‰ ^{34}S) that corresponds to its endogenic source (Shlyukova *et al.*, 1967; Shlyukova, 1986).

The above mentioned extremely unusual mineral association in a xenolith at Kaskasnyunchorr Mt. deserves special discussion. In this mineral association there are endemic niobium sulphide — edgarite; pyrrhotite and Fe disulphides that contain several wt.% of Ti (that was first recorded for Earth objects), V and up to 0.4 wt.% Cr; molybdenite which is oftenly enriched in W (up to 22.7 wt.%); and also alabandite, tungstenite, sphalerite, wurtzite and an understudied sulphide (possibly hydroxide-sulphide) Nb, Mg and Al. This association was first described by Barkov *et al.* (1997, 2000$_{1,2}$) who noticed extremely high S^{2-} activity . Oxygen bearing compounds of iron do not exist in this rock, and Fe impurity in silicates and oxides is insignificant. The most ferriferous mineral is fluorophlogopite containing $0.04-1.3$ wt.% FeO. In that way, not only are Fe, Zn, Mo found in sulphide form but also Mn, Nb, V, Cr, W and also partially Ti.

In our opinion, this remarkable association deserves attention because of the geochemistry issues of metals and their affinity to S^{2-} (i.e. relative chalcophility). It is significant that the order of the elements distribution between the phases (first of all, between oxygen-containing and oxygen-free) is become apparent at both the mineral-forming and "macro-impurities" level (from $0.n$% to tens %), and not at "micro-level" as in mete-orites. Relying on the distribution of metals between oxygen-containing compounds and sulphides in the rock described, and also in the other associations of alumina-rich fenites in Khibiny, along with the data on the other Earth formations and meteorites, one can draw up an empirical sequence of chalcophility decrease (and lithophylity increase respectively) of metals: Cu,Pb,Mo → Zn → Fe → Mn,W,V → Nb,Cr → Ti → Mg,Ca → Al,Be,*REE*.

Here is a brief discussion of this line. In nature Al, Be and *REE* are unknown in chalcogenides. Sulphides of Mg and Ca are typical only for enstatite chondrites — meteorites of extremely reductive type, enriched in sulphur (Leitch, Smith, 1982). Alkaline metals distribution between the sulphides and oxygen-containing/haloid compounds are utterly specific (Urusov, 1975; Pekov, 2005), and therefore are not discussed here. The other side of the line (Cu, Pb, Mo, Zn, Fe) also raise no questions. Sulphides of Mn, W and V although not very abundant are still not exotic for Earth conditions. The intermediate part of the sequence is the most interesting and has not been studied previously.

The assortment and chemical composition of minerals associated with edgarite paragenesis indicate that at this value of S^{2-} activity, not only do Cu, Pb, Mo, Zn and Fe, but also Mn, W, V, Cr and even Nb reveal a chalcophile character and form sulphides; whereas Mg, Al, Ca, Be and *REE* "remain lithophyle". Ti occupies an intermediate position distributing between oxygen-containing compound (rutile) and chalcogenide (pyrrhotite). From this it is concluded that Nb and Cr are more chalcophile than Ti. This conclusion is particularly important for Nb the content of which in meteorites is incredibly low, and it is not possible to estimate its relative affinity to S^{2-} according to the meteorite data. In other associations of alumina-rich xenoliths from Khibiny (Kaskasnyunchorr, Kukisvumchorr and Yukspor Mts.) sulphides with Mn (alabandite, high-manganese sphalerite), W (W-bearing molybdenite), V (V-bearing pyrrhotite) co-exist with oxygen-containing compounds of Cr (Cr-bearing spinels and other oxides, various silicates) and Nb (pyrochlore, Nb-bearing ilmenite, zirconolite, titanite). This indicates the higher affinity to S^{2-} (chalcophility) of Mn, W and V comparing to that of Cr and Nb.

It is worthwhile emphasising once again that the uniqueness of conditions where edgarite formation became possible, is due to the combination of very high values of sulphur activity and reductive potential. The distinct indicators of such conditions are sulphides containing typical lithophyle metals as species-forming components (edgarite, tungstenite, alabandite, and in other localities — also patrónite, daubréelite, oldhamite, niningerite) or as considerable impurities (in our fenites — iron sulphides with Ti, V, Cr, molybdenite with W, sphalerite enriched in Mn — up to 14 wt.% Mn). The more to the right the metal is located in the suggested empirical sequence of chalcophility, is the higher sulphur activity indicated by its sulphide state. On the other hand, the presence of the metals from the left part of the line in form of oxygen compounds demonstates low S^{2-} activity : is it well-known from the example of Zn which is included in a composition of spinel group oxides and/or silicates in such conditions. In the fenites discussed it is Zn-bearing hercynite (Fe,Zn) Al_2O_4 in the first instance.

In the fenites described, along with the increase of S^{2-} activity accompanied by the increase in the number of sulphides, the content of Mn increases in ilmenite (content of Fe decreases, as it was "scavenged" by sulphides) until its manganese analogue formation — pyrophanite $MnTiO_3$. During further increase of S^{2-} potential pyrophanite is displaced by alabandite MnS. Thus, the Mn/Fe ratio in the ilmenite group minerals may be an indicator of S^{2-} activity in these rocks with the predominance of Fe over Mn.

Reductive conditions of the mineral-forming process in alumina-rich fenites from Khibiny is likely due to the presence of carbonaceous matter in the primary xenolith rocks. We assume that this protolith is Precambrian metapelites spread around the Khibiny massif. These also could be alumina-rich Proterozoic metamorphites — separate horizons within the Imandra-Varzuga complex series (Shlyukova, 1986; Azarova, Shlyukova, 2008), or more ancient muscovite and kyanite schists with almandine, staurolite, rutile etc. (Yakovleva *et al.*, 2006[2], 2009). The considerable enrichment of Archean alumina-rich schists of the Kola Peninsula in carbonaceous matter (Bel'kov, 1963) testifies to the latter assumption, whereas in the Imandra-Varzuga series carbonate rocks — con-

taining oxidised carbon — along with alumina-rich rocks ones occur. The conclusion made by Korchak (2008) about protolith of alumina-rich apo-xenolith fenites of Khibiny as terrigene and metabasic rocks of Paleozoic Lovozero suite, seems erratic to us. First of all, our opinion is based on the contradiction of the general geochemical features of fenitized xenoliths and the assumption that rocks are depleted in Al and enriched in Ca and Mg. For the protolith as alumina-rich metapelites and not metabasites indicaes to the fact that fenites are enriched in Cr and V (components-impurities in the Al position in alumina-rich minerals of muscovite and kyanite schists; see Yakovleva *et al.*, 2009) comparing with Ni: its content in sulphides is insignificant and the finds of the mineral with species-defining Ni; pentlandite, is single.

Thus, in summary:

1. In apoxenolithic alumina-rich fenites of the Khibiny massif there occurs both a diverse and specific chalcogenide mineralization with the prevalence of sulphides, first of pyrrhotite-troilite series and molybdenite in some areas. The amount of other chalcogenides is insignificant, however among them there occur quite rare minerals (jaipurite CoS and westerveldite FeAs — the first finds in Russia, tungstenite WS_2 — the first find in Khibiny) and geochemically unique phases — edgarite $FeNb_3S_6$ and Ti-bearing iron sulphides: pyrrhotite, pyrite and marcasite.

2. Activity of S^{2-} in some areas of the fenites reaches record values for natural terrestrial phases, which results in unique mineral associations with sulphides containing Mn, W, V, and even Nb, Ti, Cr. The analysis of the distribution of metals (species-forming and "macro-impurities": from 0.*n* to *n* wt.%) among oxygen compounds and sulphides, including data on other formations and meteorites, resulted in an empirical sequence of chalcophility decrease, i.e. affinity with S^{2-} (and, correspondingly, an increase of lithophylity) of metals: Cu,Pb,Mo $\rightarrow$ Zn $\rightarrow$ Fe $\rightarrow$ Mn,W,V $\rightarrow$ Nb,Cr $\rightarrow$ Ti $\rightarrow$ Mg,Ca $\rightarrow$ Al,Be,*REE*.

3. The content of sulphides in fenites varies widely from 0.0 up to almost 70%, and sometimes adjacent enriched ("ore") and sulphide depleted areas. This is due to the irregular distribution of primary sulphur content in the protolith which is considered to be the sulphur source (it correlates with isotope analysis data: Shlyukova, 1986).

4. The formation of the sulphides in alumina-rich fenites in general took place at high temperatures (>500−600°C) and high reducing potential. It resulted from the impact of large masses of hot foyaite magma and the presence of a considerable amount of carbonaceous matter in the most probable protolith − Precambrian alumina-rich schists.

Acknowledgements

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