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This volume contains papers on the newly discovered mineral species – aleksandrovite, the Sn-analogue of baratovite, and åskagenite-(Nd), a new mineral of epidote supergroup. Discoveries of the rare minerals – irarsite (from ores of the Shanuch deposit in Kamchatka), orickite, jaipurite, westerveldite, edgarite, tungstenite and other chalcogenides (from the Khibiny massif in Kola peninsula) are described. New data on accessory minerals from the Semeninskaya pit in the Aduy pegmatite field in the Ural Mts., on arsenosulvanite and other sulphides from the Lebedinoe deposit in the Aldan Mts., on the composition and features of native gold from an ore occurrence in South-Eastern Kamchatka, are given. Zoned crystals of monazite-(Ce) from granite pegmatites of the Ilmeny Mts. are studied, including radiology dating. Problems of mineralogy and geochemistry of tetravalent uranium, uranium ores and sulfide-oxide associations in modern submarine pyrites, are covered.

In the chapter "*Mineral museums and collections*" there is a paper on the exhibition in the Fersman Mineralogical Museum RAS dedicated to the 125th anniversary of Alexander N. Labuntsov – the discoverer of apatite deposits in the Khibiny Mts.

The next chapter – "*Personalities*" – for the first time brings forward letters found in the RAS archives from Alexander N. Labuntsov to academician Vladimir I. Vernadsky.

The "*Mineralogical notes*" chapter includes description of rare intergrowth twins of magnetite from the Kurzhunkul deposit, Kazakhstan, and discussion of previous mistakes in the calculation of the chemical composition of some minerals.

The "*Discussions*" is represented by the paper on the problems of the definition of a valid mineral species and metastable mineralization.

The journal is of interest to mineralogists, geochemists, geologists and also researchers of Natural History museums, collectors and amateurs.

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New Minerals and Their Varieties, New Finds of Rare Minerals, Mineral Paragenesis

ALEKSANDROVITE[1], $KLi_3Ca_7Sn_2[Si_6O_{18}]_2F_2$ – A NEW TIN MINERAL

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Aleksandrovite, $KLi_3Ca_7Sn_2[Si_6O_{18}]_2F_2$ is a new mineral, the tin analogue of baratovite. It was discovered in a moraine boulder of microcline-calcite rock, along with quartz, albite, aegirine-hedenbergite pyroxene, in the Darai-Pioz glacier (Tajikistan). The mineral association is represented by baratovite, fluorite, miserite, Sn-bearing titanite, bazirite, pabstite, Sn-bearing sogdianite, sugilite, turkestanite, fluorapatite (apatite-(CaF)). The new mineral occurs in two types: a) minute (up to 50 – 70 μm) lamellar grains with no zoning visible under BSE, and b) crystals (up to 0.8 mm) and aggregates of zoned and sectorial grains with separate zones of aleksandrovite, and baratovite or katayamalite. The mineral is colourless, transparent, with vitreous lustre and pearl lustre on cleaved surface. Streak colour is white. Cleavage is perfect along (001). Density (measured) = 3.05(2) g/cm^3, density (calculated) = 3.07(2) g/cm^3. Microhardness is 300 kg/mm^2. Mohs hardness is 4 – 4.5. It fluoresces light-blue under short wave UV (254 nm). The mineral is biaxial, optically negative: $n_p = 1.629(2)$, $n_m = 1.635(4)$, $n_g = 1.638(2)$ (589 nm); $2V$ (calculated) = $-70.3°$. Dispersion is strong, $r > v$. Elongation is positive, angle of extinction varies from 0° to 22°. Aleksandrovite is monoclinic, $C2/c$, $a = 17.01(2)$, $b = 9.751(6)$, $c = 21.00(2)$ Å, $\beta = 112.45(8)°$, $V = 3219(7)$ Å^3, $Z = 4$. The strongest X-Ray lines are as follows: (d in Å *(I) (hkl)*): 4.86(21)(31 – 1); 3.712(33)(312); 3.234(100)(006); 3.206(34)(223); 3.039(28)(025); 2.894(42)(314); 2.425(42)(008); 1.950(25)(426). Chemical analysis (EMPA, an average out of 17 analyses; Li_2O – ICP OES, H_2O – calculated; wt.%): SiO_2 – 48.01, Al_2O_3 – 0.07, TiO_2 – 2.86, SnO_2 – 12.84, ZrO_2 – 1.27, Nb_2O_5 – 0.11, Fe_2O_3 – 0.27, Ce_2O_3 – 0.04, MgO – 0.05, CaO – 25.52, SrO – 0.39, Na_2O – 0.20, K_2O – 2.91, Li_2O – 3.01, F – 1.71, H_2O – 0.39, (-O=F_2) = -0.72, total 99.12. Empiric formula of aleksandrovite – $(K_{0.93}Na_{0.10})_{1.03}Li_{3.02}(Ca_{6.82}Sr_{0.06}Mn_{0.04}Mg_{0.02})_{6.94}(Sn_{1.28}Ti_{0.54}Zr_{0.15}Fe_{0.05}Nb_{0.01})_{2.03}(Si_{11.98}Al_{0.02})_{12}O_{36.00}[F_{1.35}(OH)_{0.65}]_{2.00.}$

IR spectrum of aleksandrovite is similar to that of baratovite, the strongest absorption strips are: 1083, 1024, 974, 950, 673, 607, 568, 520, 470, 440 cm^{-1}. Compatibility index is $1 - (K_p/K_c) = -0.005$. The mineral is named to honour of the well-known Russian geochemist, geologist and mineralogist Stanislav Mikhailovich Aleksandrov (born in 1932) for his great contribution in geology, geochemistry and mineralogy of tin. The type specimen is stored in the Fersman Mineralogical Museum RAS in Moscow (registration number 3825/1).

5 tables, 6 figures, 19 references.

Keywords: aleksandrovite, baratovite, katayamalite, Darai-Pioz, tin minerals, alkaline rocks.

During examination of the field materials collected by the authors in 2004 and 2007 in Darai-Pioz alkaline massif (Tajikistan) a new tin mineral was discovered. The chemical composition can be expressed as the simplified formula $KLi_3Ca_7Sn_2[Si_6O_{18}]_2F_2$. It was named aleksandrovite to honour Stanislav Mikhailovich Aleksandrov (born in 1932), the well-known Russian geochemist, geologist and mineralogist, for his great contribution in geology, geochemistry and mineralogy of tin.

Aleksandrovite is the tin analogue of baratovite, $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$ and fluorine-tin analogue of katayamalite, $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH,F)_2$.

Before concentration on the description of the new mineral we shall dwell on the history of the investigation of baratovite and katayamalite, because the view of their chemical composition and nomenclature differed over many years.

Baratovite was described as a new mineral discovered within quartz-albite-aegirine rocks with miserite from Darai-Pioz massif in 1975 by Vyacheslav D. Dusmatov with coauthors. According to the wet chemical analysis (Table 1, an. 1) the suggested formula was $KLi_2Ca_8Ti_2Si_{12}O_{37}F$ (Dusmatov *et al.*, 1975). That differs by the number of atoms per formula unit from the one approved at present: Ca (8 *apfu* instead of 7 apfu), Li (2 *apfu* instead of 3 apfu) and F (1 *apfu* instead of 2 *apfu* in the extreme fluoric end member). Unfortunately, in this paper there is no data on the sample preparation for chemical analysis, on the methods of determination of the chemical compounds, or on whether the water content was measured. Absence of these data makes

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[1] – the mineral was considered and recommended for publication by the Commission on New minerals and mineral names of Russian mineralogical society and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA on 4th of May 2009.

Table 1. **Chemical composition of baratovite, katayamalite and aleksandrovite (wt.%)**

Comp.	Baratovite	Katayamalite	Aleksandrovite	
	1	2	3	
			average	variation limits
SiO_2	50.46	52.31	48.01	47.32 – 48.79
Al_2O_3			0.07	0.01 – 0.27
TiO_2	9.55	10.99	2.86	0.88 – 3.89
SnO_2			12.84	10.73 – 16.03
ZrO_2	2.28		1.27	0.18 – 3.01
Nb_2O_5	0.72		0.11	0.00 – 0.28
Fe_2O_3	0.50	0.29	0.27	0.01 – 0.74
Ce_2O_3			0.04	0.00 – 0.23
MgO			0.05	0.01 – 0.25
MnO	0.12	0.22	0.17	0.10 – 0.25
CaO	30.36	28.25	25.52	24.98 – 25.87
SrO			0.39	0.01 – 1.48
Na_2O	0.70	0.22	0.20	0.01 – 0.56
K_2O	2.96	2.89	2.91	2.76 – 3.06
Li_2O	2.05	3.25	3.01*	
F	1.05	0.34	1.71	1.10 – 2.01
H_2O		1.21	0.39**	
$-O=F_2$	-0.44	-0.14	-0.72	
Total	100.31	99.83	99.12	

Note: calculated for (Si + Al) = 12 atoms

1 – baratovite, Darai-Pioz, Tajikistan. Analyst A.V. Bykova (Dusmatov et al., 1975) $(K_{0.90}Na_{0.28})_{1.18}Li_{1.96}(Ca_{7.75}Mn_{0.03})_{7.78}(Ti_{1.71}Zr_{0.26}Fe_{0.09}Nb_{0.08})_{2.14}Si_{12}O_{37.23}F_{0.79}$.

2 – katayamalite, Iwaki, Japan. EMPA. Li_2O *– flame photometry,* H_2O *– thermal-gravimetry,* Fe_2O_3 *– titrometry (Murakami et al., 1983)* $(K_{0.85}Na_{0.10})_{0.95}Li_{3.00}(Ca_{6.94}Mn_{0.04})_{6.98}(Ti_{1.90}Fe_{0.05})_{1.95}Si_{12}O_{35.78}(OH)_{1.85}F_{0.25}$.

3 – aleksandrovite, EMPA,average from 17 analyses. $Li_2O^{\star}$ *– ICP OES,* $H_2O^{\star\star}$ *– calculated. Analyst L.A. Pautov,* $(K_{0.93}Na_{0.10})_{1.03}Li_{3.02}(Ca_{6.82}Sr_{0.06}Mn_{0.04}Mg_{0.02})_{6.94}(Sn_{1.28}Ti_{0.54}Zr_{0.15}Fe_{0.05}Nb_{0.01})_{2.03}(Si_{11.98}Al_{0.02})_{12}O_{36.00}[F_{1.35}(OH)_{0.65}]_{2.00}$.

evaluation of correctness of the original baratovite formula difficult.

The crystal structure of baratovite was studied (R = 5.6%) by P.A. Sandomirskiy with co-authors on the sample from Darai-Pioz kept in the Fersman Mineralogical Museum RAS (Sandomirskiy *et al.*, 1976). The picturesque description of baratovite crystal structure is given in the famous "Essays on structural mineralogy" by Nikolay V. Belov and Elizaveta N. Belova (1978). Later, the baratovite structure was refined (R = 3.4%) by Silvio Menchetti and Cesare Sabelli (Menchetti, Sabelli, 1979), also on the sample from Darai-Pioz obtained from Alexander S. Povarennykh. The study of the structure in both works was not accompanied by the chemical composition determination, and there is no evidence of correlation between the specimens of baratovite studied and the type material. In both cases the authors suggest the formula $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$. According to the structural data, the mineral does not contain hydroxyl-groups. However, Werner H. Bauer and Dethard Kassner (Baur, Kassner, 1992) doubted this and suggested the formula $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(F,OH)_2$. They concluded this on the basis of comparison of the structures of baratovite and similar to it katayamalite $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH,F)_2$. Our study established that the hydroxyl-groups are present in baratovite, at least in some specimens from Darai-Pioz. The content of H_2O^+, determined by the Penfield method, varies from 0.44 to 1.02 wt.% in the studied samples. The presence of hydroxyl-groups is also confirmed by the IR-spectroscopy data. For the hypothetical mineral the water and fluorine contents with intermediate composition $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_{1.00}(OH)_{1.00}$ would be 0.65 and 1.37 wt.% respectively. Thus, samples of the mineral with H_2O content over 0.65 wt.% should formally be attributed to katayamalite. It is possible that the difference in fluorine content according to the chemical analysis by A.V. Bykova (Dusmatov *et al.*, 1975) and to the structural research of baratovite (Sandomirskiy *et al.*, 1976; Menchetti, Sabelli, 1979) is related to variations in the fluorine-hydroxyl ratio in different samples of this mineral from Darai-Pioz.

Ekaterina Reguir with co-authors (1999) performed over 30 analyses of baratovite from quartz-albite-aegirine rocks from the Darai-Pioz complex (in the paper there are only 2 analyses of baratovite with no data on fluorine- and water content) and indicate that the new analytical data correlated well with the structural formula suggested by Pavel A. Sandomirskiy with co-authors (1976) and almost identical to katayamalite analyses.

Katayamalite was discovered and described by Nobuhide Murakami with co-authors in 1983 in aegirine syenite from Iwaki island, Ehime Pref., on the South-West of Japan (Murakami *et al.*, 1983), and its structure was interpreted by Toshio Kato and Nobuhide Murakami (Kato, Murakami, 1985). Katayamalite differs from baratovite by triclinic symmetry and by predominance of OH over F (water content was determined using thermogravimetric analysis). Werner H. Bauer and Dethard Kassner indicated that triclinic value of katayamalite is extremely low, and the α and γ angles deviation from 90° is within the experimental error limits (Baur, Kassner, 1992). On this basis they conclude the identity of baratovite and katayamalite structures. Thus, at present katayamalite is recognised as a hydroxyl-dominant mineral, and baratovite, according to the structural study – as fluorine-dominant, although it is in contradiction with the results of the first chemical analysis (Dusmatov *et al.*, 1975).

We draw your attention to the history of the study of fluorine and hydroxyl ratio in baratovite and katayamalite because aleksandrovite has wide variations of fluorine concentration. After calculating some of aleksandrovite analyses (for 12 Si atoms), the fluorine coefficient appeared to be less than one, and therefore the mineral of such a chemical composition is formally not aleksandrovite but its hydroxyl analogue. Unfortunately until now we could not find sufficient quantity of such a material for the detail study.

The variations of cations composition in the minerals of baratovite group have been studied to a lesser degree. In this paper we tried to fill this gap up by presenting the characteristics of isomorphism in the octahedral position, predominantly occupied by titanium in baratovite and by tin in aleksandrovite.

Type locality

The alkaline massif Darai-Pioz is located on the joint of three sub-latitudinal ridges – Turkestanskiy, Alaiskiy and Zeravshanskiy in the upper reaches of the Darai-Pioz river, the left tributary of the Obi-Kabud (Yarkhych) river which belong to the Surkhob river basin. The first data on this massif were obtained by Alexander V. Moskvin during Tajik-Pamirs expedition in 1932–1936 (Moskvin, 1937). During 1946–1947 the specific works on rare-metal mineralization in alkaline rocks in the Alai and Turkestan ridges were held under the leadership of Yuriy A. Arapov. Since 1960 detailed mineralogical research of the Darai-Pioz massif, mostly by Vyacheslav D. Dusmatov, lead to the revelation of unique mineralization of lithium, boron, zirconium and *REE* (Dusmatov, 1968; 1971 etc.). The extremely complex high-mountainous relief and overlapping of considerable parts of the outcrops by glaciers and moraines make geological research difficult. The total area of the outcrops are nearly 16 sq. km. On the north the massif intrudes through Silurian limestone strata, and on the south – through terrigene-schistose strata with limestones and Middle-Upper Carboniferous effusion interlayers. The external part of the massif consists of sub-alkaline biotite granites of the 2nd phase of the Turkestan complex (300–290 Ma) and their tourmalinized and greisened varieties. Further towards the centre there are interrupted rings of biotite granites changing in some areas to granosyenites and alkaline granites. The core of the massif is composed of quartz- and aegirine syenites. In the north-eastern part of the massif there are outcrops of cancrinite foyaites (247±6 Ma). All the intrusive rocks are crossed by the dykes of fine-grained biotite granites with tourmaline. The fenitized varieties of the rocks, sometimes with bafertisite, calcybeborosilite-(Y) and thorite are widespread. In the moraine of the Darai-Pioz glacier blocks of rather peculiar aegirine-microcline-quartz-albite rocks with miserite, baratovite occur; these rocks are described by Reguir *et al.* (1999). The massif is locally albitized (203±8 Ma), carbonatized and graphitized. The vein rocks are various. Amongst them there are several types: muscovite-microcline-quartz pegmatites with schorl (limited occurrence); aegirine-microcline-quartz pegmatites with polylithionite, leucosphenite, stillwellite-(Ce), pyrochlore, sogdianite etc. (286±7 Ma); aegirine-microcline-sogdianite pegmatites with stillwellite-(Ce), titanite, danburite, rarely – with quartz; aegirine-microcline-quartz pegmatites with neptunite, eudialyte, titanite; aegirine-microcline-reedmergnerite pegmatites with pectolite, eudialyte, leucosphenite; syenite pegmatites with turkestanite; microcline-calcite-pectolite veins with turkestanite. The petrology and mineralogy of the massif is described in detail in a number of publications (Dusmatov, 1968, 1971; Belakovskiy, 1991; Grew *et al.*, 1993 etc.). It is significant that carbonatites – essentially calcite rocks, sometimes with quartz (Dusmatov, 1971; Mayorov, Gavrilin, 1971) are widespread in the massif, and aleksandrovite is related exactly with them. It is possible that these rocks are not genetically similar, and are under intensive research at present (Faiziev *et al.*, 2008; Gafurov, 2008).

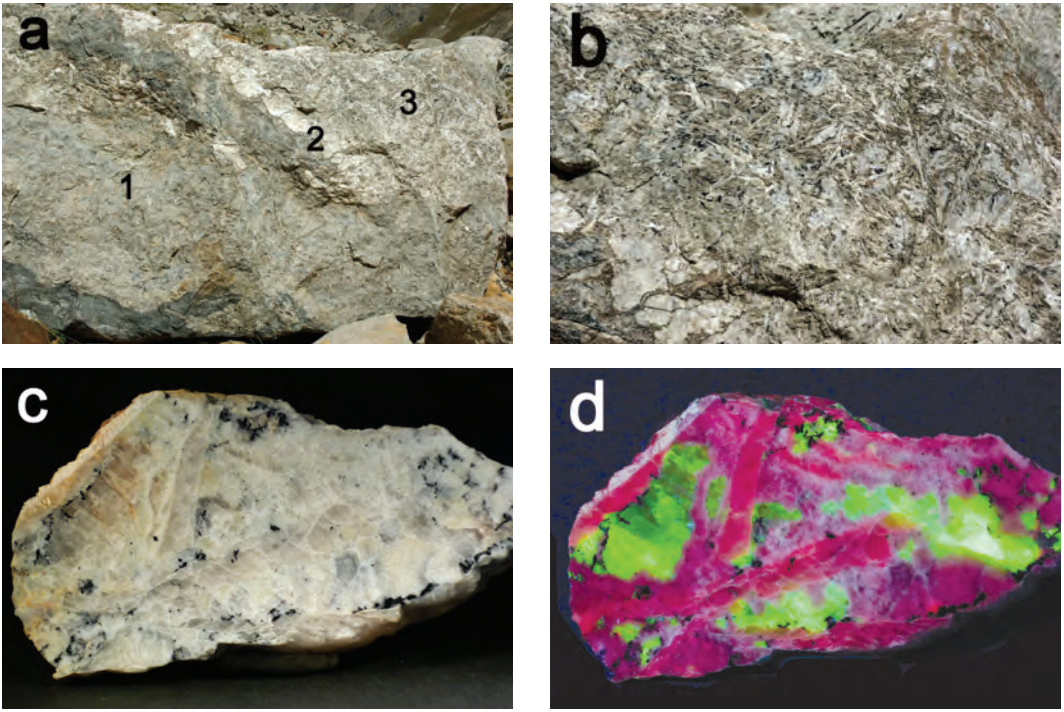
There is only fragmentary data on the geochemistry and mineralogy of tin in the Darai-

Pioz massif. Certain speciality was mentioned by V.V. Mogarovsky (1987). The average content of tin in the rocks of the massif is 8 – 12 ppm according to his data. The enrichment in tin was observed in titanite – 0.13 wt.% SnO_2 (Dusmatov, 1971), up to 8.1 wt.% SnO_2 (Reguir *et al.*, 1999); in bazirite 2.9 wt.% SnO_2 (Reguir *et al.*, 1999), in sogdianite up to 1.4 wt.% SnO_2 (Pautov *et al.*, 2000). The only proper tin mineral in the Darai-Pioz massif before aleksandrovite discovery was pabstite (Pautov, 2003).

Aleksandrovite was found in a large boulder (Fig. 1) in a vein within microcline-calcite rock with pyroxene and quartz from the Darai-Pioz glacier moraine. The vein has complex zoned structure. It is composed of (from periphery towards the centre): 1 – leucocratic medium-grained pyroxene-microcline rock, 2 – inequigranular quartz-pyroxene-microcline rock with large segregations (ovoids) of calcite, 3 – coarse-grained microcline-calcite rock with aegirine, quartz, albite. The host rock is an intensively altered clay slate. Microcline-calcite rock (Fig. 1 a – d) is composed of disorderly located coarse (10 – 15 × 8 – 15 × 0.5 – 1.5 cm) grains of white calcite flattened along (001). Calcite comprises the framework of the rock, and interstitions are filled with aggregates of pale-grey oval zoned microcline crystals (1 – 2 cm across) and fine-grained aggregates of albite, quartz, calcite, apatite. Pyroxene is represented by columnar grains up to 1 cm long, often associated with the boundary between large plates of calcite and feldspar aggregate. Some interstitions between calcite plates are filled with translucent colourless quartz with irregular but very bright yellowish-green fluorescence under short wave UV (254 nm). Some areas of such a rock (on the border with the Zone 2) consist predominantly of fine-grained quartz-albite aggregates with miserite. In one of these areas aleksandrovite was found.

The predominant minerals in association with aleksandrovite are calcite, microcline and quartz, the minor phases are albite, pyroxene, the accessory phases – baratovite, fluo-

Fig. 1. The rock and specimens with aleksandrovite: a – the general view of the boulder of microcline-calcite rock with pyroxene and quartz, size 2 × 2 × 3.5 m (1 – syenite zone, 2 – transition zone from syenite to quartz-microcline-calcite rock (large oval segregation of calcite are visible), 3 – quartz-microcline-calcite rock zone); b – the fragment of the previous image (zone 3) – quartz-microcline-calcite rock; c & d – rock sample from the zone 3, under incandescent light (c) and SW UV illumination (d). Quartz fluoresces bright-green, platy calcite – pinkish-red, microcline – pinkish-purple. Black grains – aegirine-hedenbergite. Size 6 × 14 cm.



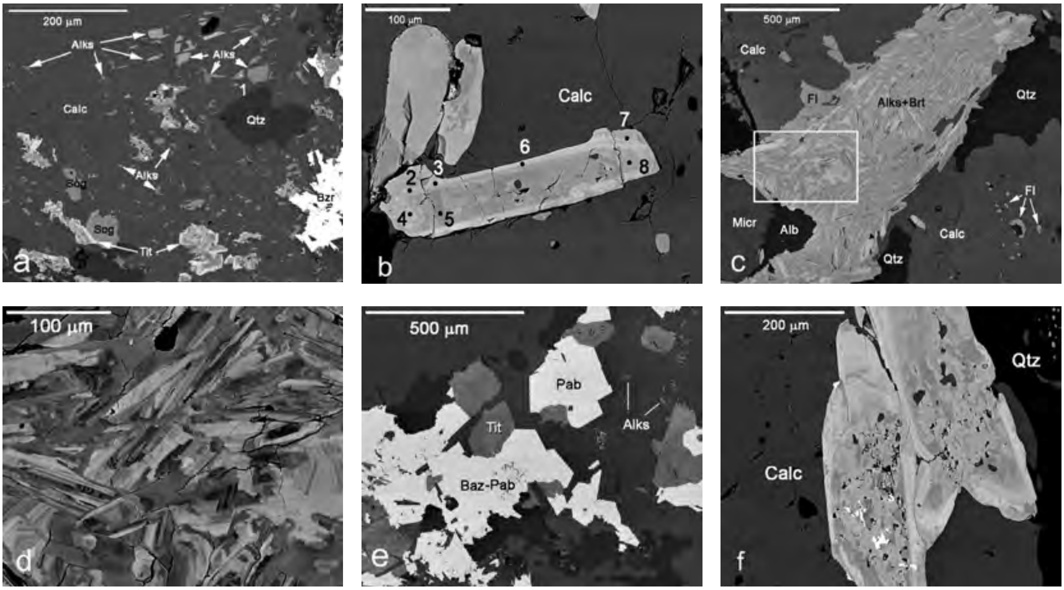


Fig. 2. Aleksandrovite grains in quartz-aegirine-albite-microcline-calcite rock. BSE images of polished thin sections. Labelled points — analysed minerals using EMPA (the numbers correspond to the ones in the Table 3). Alks — aleksandrovite, Brt — baratovite or katayamalite, Tit — titanite, Bzr — bazirite, Sog — sogdianite, Calc — calcite, Qtz — quartz, Micr — microcline, Alb — albite, Fl — fluorite.

a — small (5—60 µm) and relatively homogeneous grains of aleksandrovite with no visible zonation, in calcite. This was the source of aleksandrovite for obtaining physical properties, X-ray data and determination of Li content. Aggregates of distinctly zoned and sectorial Sn-bearing titanite (the paler areas are enriched in tin) and Sn-bearing sogdianite are located in the lower part of the image; b — zoned crystal, its central part corresponds to baratovite-katayamalite and periphery paler part — to aleksandrovite; c — an aggregate of sectorial-zoned grains of the minerals of aleksandrovite-baratovite series in quartz-albite-microcline-calcite rock; d — the fragment of the previous image (marked with white frame), with details of the complex sectorial-zoned structure of the grains; e — aggregates of crystals of the minerals of bazirite-pabstite series (Baz-Pab) with tin-bearing titanite in quartz-calcite aggregate; aleksandrovite is represented by thin platy grains; f — an aggregate of relatively large crystals with complex layout pale areas are corresponded to aleksandrovite, grey — to baratovite or katayamalite. White ingrowths in the crystals — are tin-bearing bazirite. Small isometric crystals in the upper right corner of the image belong to fluorite. Images are obtained using SEM CamScan-4D.

rite, miserite, titanite, bazirite, pabstite, sogdianite, sugilite, turkestanite and fluorapatite. Calcite is characterized by the relatively high content of barium and strontium, and by enrichment in light *REE* (according to ICP-MS analysis: Ba — 1030, Sr — 4530, Mn — 1010, Ce — 165, Y — 38 ppm) which is typical for calcite from carbonatites. Microcline is represented by the zoned crystals enriched in barium (separate crystals contain up to 2.0 wt.% BaO). Pyroxene crystals in the rock are poorly terminated. Their chemical composition corresponds to aegirine-hedenbergite. A typical mineral in the above-described association is tin-bearing titanite, that occurs in zoned-sectorial, blocked and split crystals. The constant companion of aleksandrovite is bazirite which forms a continuous solid solutions series with pabstite (Fig. 2e). Selective chemical compositions of the minerals from the association with aleksandrovite are presented in the Table 2.

Aleksandrovite occurs in different shapes and forms. For convenience one can assign two "extreme" types: minute (up to 50—70 µm) lamellar grains with no zoning visible under BSE, separate grains (Fig. 2a) and larger (up to 0.8 mm) crystals and aggregates of zoned and sectorial grains with separate zones of aleksandrovite (paler colour under BSE) and baratovite or katayamalite (Fig. 2b — d, f, Fig. 3).

All the data of the physical properties of aleksandrovite were obtained from grains of type I. In order to separate the grains we dissolve the second half of the polished section with non-zoned aleksandrovite, in 5% HNO_3 at room temperature. The insoluble residue was thoroughly washed with deionized water, rinsed with acetone and dried at room temperature. Several transparent, non-included

Table 2. **Chemical composition of the minerals from association with aleksandrovite, EPMA data (wt.%)**

Comp.	titanite			sogdianite	bazirite	pabstite		pyroxene
	1	2	3	4	5	6	7	8
SiO_2	26.68	28.11	29.45	65.77	39.37	37.10	38.69	50.16
Al_2O_3	0.15*	0.61	0.89	0.01	–	–	–	0.13
TiO_2	21.78	24.94	30.82	0.03	–	–	1.89	0.16
Nb_2O_5	1.09	1.04	1.05	–	–	–	–	–
ZrO_2	1.96	0.76	0.99	15.08	25.29	1.17	3.41	–
SnO_2	21.08	14.63	7.36	9.07	1.90	28.76	24.20	–
FeO	0.92	2.02	2.35	–	0.19*	–	–	24.38
MnO	0.04*	0.04*	0.08*	–	–	–	–	2.50
MgO	0.06*	0.27*	0.00	–	–	–	–	1.65
BaO	–	–	–	–	33.26	32.41	32.37	–
CaO	24.42	25.70	26.86	0.06	–	–	–	13.81
Na_2O	0.14*	0.00	0.21*	0.09	–	–	–	5.81
K_2O	–	–	–	4.10	–	–	–	–
Li_2O				4.09**				
Total	98.32	98.11	100.06	98.30	100.01	99.44	100.56	98.60

*Note: obtained using SEM CamScan 4D with energy dispersive spectrometer Link ISIS, U = 20 kV, I = 4 nA. * = <2 sigma. ** calculated content. "–" component content is under limits of EDS analysis. Analyst L.A. Pautov.*
Titanite (calculated for O = 5): 1) $Ca_{0.98}Na_{0.01}(Ti_{0.61}Sn_{0.31}Zr_{0.04}Fe_{0.03}Nb_{0.02})_{1.01}Al_{0.01}Si_{1.00}O_5$,
2) $Ca_{1.00}(Ti_{0.68}Sn_{0.21}Zr_{0.01}Fe_{0.06}Nb_{0.02})_{0.98}Al_{0.03}Si_{1.02}O_5$,
3) $Ca_{0.99}Na_{0.01}(Ti_{0.79}Sn_{0.10}Zr_{0.02}Fe_{0.07}Nb_{0.02})_{1.00}Al_{0.04}Si_{1.01}O_5$.
Sogdianite (calculated for Si = 12): 4) $K_{0.95}Na_{0.03}Ca_{0.01}Li_{3.00}(Zr_{1.34}Sn_{0.66})_{2.00}Si_{12}O_{30.02}$.
Bazirite (calculated for O = 9): 5) $Ba_{0.99}(Zr_{0.94}Sn_{0.06}Fe_{0.01})_{1.01}Si_{3.00}O_9$.
Pabstite (calculated for O = 9): 6) $Ba_{1.03}(Sn_{0.93}Zr_{0.05})_{0.98}Si_{3.01}O_9$, *7)* $Ba_{0.99}(Sn_{0.75}Zr_{0.13}Ti_{0.11})_{0.99}Si_{3.01}O_9$.
Pyroxene (aegirine-hedenbergite) (calculated for O = 6): 8) $Ca_{0.58}Na_{0.44}Mg_{0.10}Mn_{0.08}Fe^{+2}_{0.33}Fe^{+3}_{0.47}(Si_{1.98}Al_{0.01})_{1.99}O_6$.

grains of the new mineral were separated under binocular microscope with UV shortwave control, and put onto elecroconductive carbonic tape. The chemical composition of the separated grains was obtained from many spots using EMPA JXA-50A with energy dispersive spectrometer. Afterwards the grains were used for measurements of density, optical properties, obtaining X-ray data and for lithium content determination.

Chemical composition

The chemical composition of aleksandrovite was studied for non-zoned fine grains, due to the small amount of material from the zoned crystals for lithium detection. The composition of the mineral was measured using CamScan 4D SEM scanning electron microscope with EDS energy dispersive spectrometer Link ISIS, operated at 20 kV, absorbed current on metallic cobalt at 4nA and beam diameter of 1 μm, and also using X-ray microanalyser Camebax-microbeam with four WDS wave spectrometers at 20 kV (10 kV for F), beam current at 20 nA and beam diameter of 1 μm. Standards we used are as follows: microcline USNM 143966 (K, Al), jadeite STD 048 (Na), wollastonite STD 097 (Si, Ca), diopside USNM 117733 (Mg), $SrSO_4$ (Sr), $MnTiO_3$ (Mn), $CePO_4$ USNM 168484 (Ce), SnO_2 (Sn), ZrO_2 (Zr), $LiNbO_3$ (Nb), ilmenite USNM 96189 (Ti, Fe), MgF_2 (F). Calculation of concentrations for EDS analysis was made by Phi-Rho-Z method, for WDS – by ZAF-correction (PAP-correction for F). The average composition on the basis of analyses of 17 grains is presented in the Table 1.

For lithium determination, two grains about 50 μm were extracted from the carbonic conductive tape (after EDS analysis composition control) and decomposed with HF + H_2SO_4 in a glass-carbonic crucible. After evaporation of the solution, the residue was dissolved in HNO_3 and then diluted with water until 5% nitric acid. The solution obtained was analysed using ICP-OES Vista MPX by VARIAN. For calculation of the lithium content in aleksandrovite we used the method of lithium concentration in solution, by the ratio of another elements concentration in the mineral (which was determined by microprobe analysis). As such an elements we chose potassium and calcium, which concen-

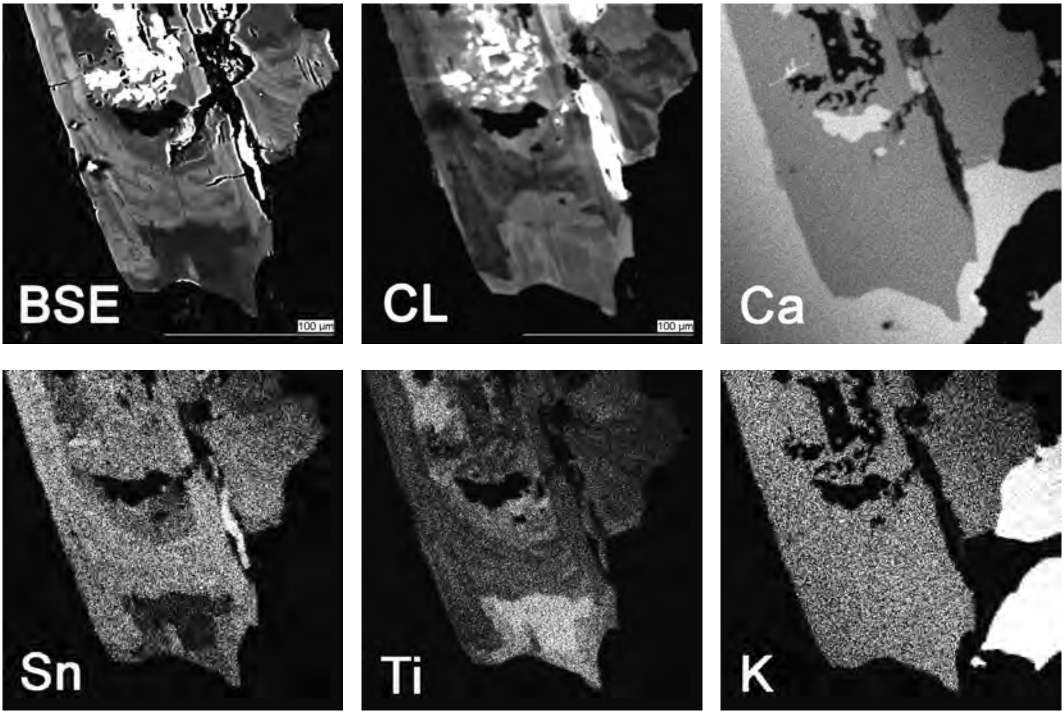


Fig. 3. Twinned zoned-sectorial crystal with grey areas (under BSE) corresponded to aleksandrovite and dark-grey — to baratovite. The crystal is in an aggregate with calcite, microcline and quartz. White grains — the minerals of bazirite-pabstite series. CL — cathodoluminescent image, Ca — characteristic X-ray images in CaKα, Sn — SnLα, Ti — TiKα, K — KKα. Images are obtained using Camebax-microbeam microanalyser.

trations are less inconstant according to microprobe analyses and to scanning of the mineral grains along profiles (Fig. 4). The lithium content calculated according to Li/K and Li/Ca ratios, appeared to be quite similar (divergence in Li content after normalization to K and Ca is 0.03%).

The water content was not determined due to the small amount of the new mineral available for this.

The empirical formula of aleksandrovite (calculated for 38 anions): $(K_{0.93}Na_{0.10})_{e1.03}Li_{3.02}(Ca_{6.82}Sr_{0.06}Mn_{0.04}Mg_{0.02})_{\Sigma 6.94}(Sn_{1.28}Ti_{0.54}Zr_{0.15}Fe_{0.05}Nb_{0.01})_{\Sigma 2.03}(Si_{11.98}Al_{0.02})_{\Sigma 12.00}O_{36}[F_{1.35}(OH)_{0.65}]_{\Sigma 2.00}$.

Idealised formula of aleksandrovite is $KLi_3Ca_7Sn_2Si_{12}O_{36}F_2$.

During the study of the zoned crystals of the mineral the wide variations of octahedral cations (Ti, Sn, Zr etc.) and additional anions (F, OH) were revealed. The typical images of the zoned crystals are shown on the Figure 2 (b—d, f) and Figure 3, the results of microprobe analyses — in the Table 2. Figure 5 shows the triangular diagram Ti-Sn-Zr (at.%), with the analyses obtained and represented in this paper, and also analyses of the minerals similar to baratovite from quartz-albite-pyroxene-microcline-calcite rocks of Darai-Pioz, both from our and literature data. It is evident that by the octahedral site predominant occupation one can distinguish the following minerals: baratovite and katayamalite — prevalence of titanium, aleksandrovite — tin, and an unnamed zirconium analogue. As was mentioned above, we suggest to combine all these minerals into the baratovite group.

X–ray data

The X-ray data for aleksandrovite were obtained using diffractometer DRON-2, the results calculated are presented in the Table 4. Due to the rather limited quantity of material available for investigation, the sample was prepared by putting the mineral powder onto the oriented monocrystal plate of "non-diffractive" silicon in order to obtain a satisfactory X-Ray powder-diffraction pattern. Using the Debye-Scherrer method quite a strong veil due to intensive X-Ray luminescence was ob-

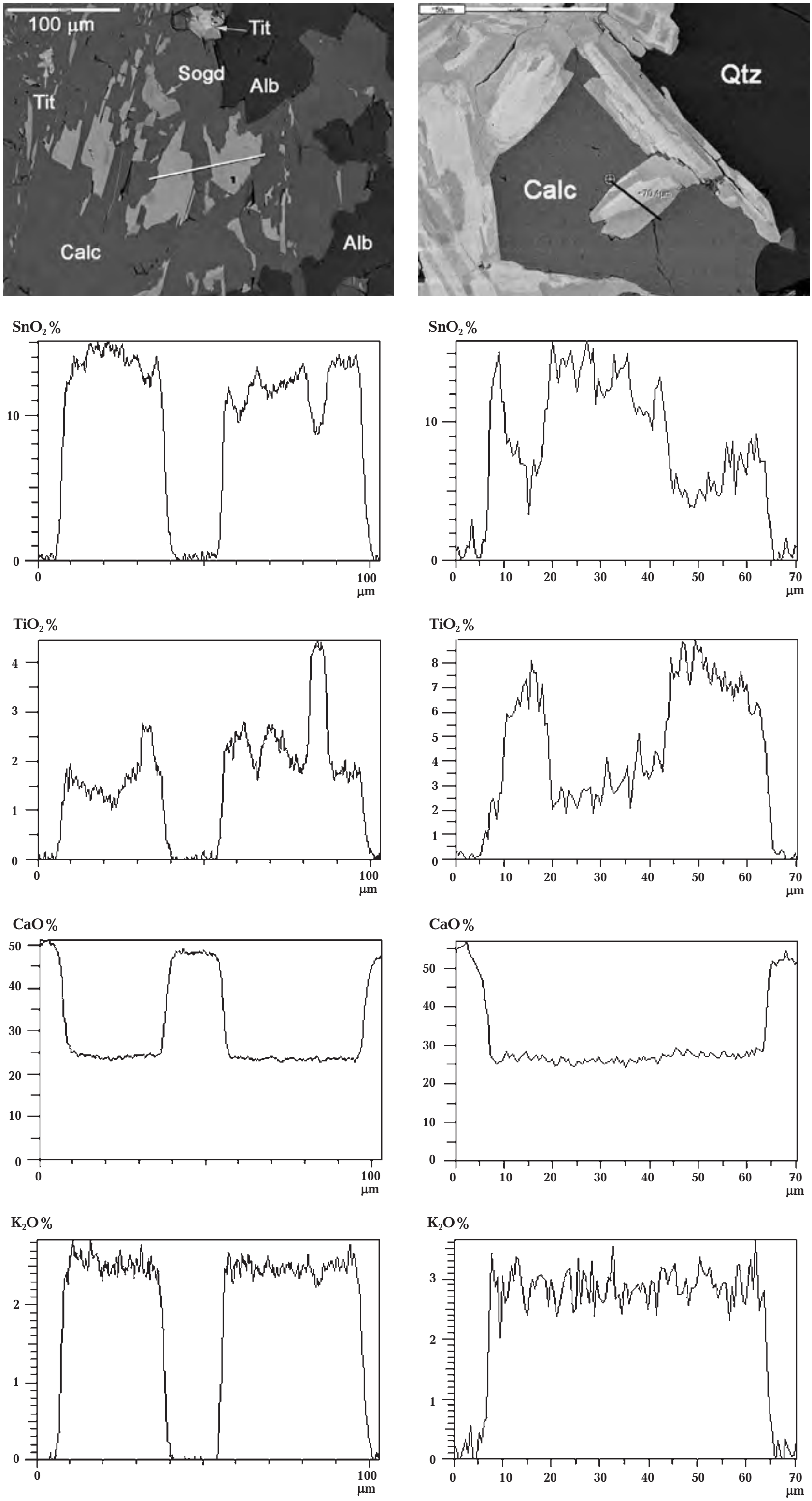


Fig. 4. Elements distribution along the scanning profiles in characteristic X-ray radiation, in aleksandrovite grain and in the zoned grain, where paler areas under BSE correspond to aleksandrovite and the darker – to baratovite. Vertical scales show wt.%. Images and profiles are obtained using CamScan 4D with energy dispersive spectrometer Link ISIS.

Table 3. **Chemical composition of the minerals of baratovite group shown on Fig. 2a, 2b, EMPA data (wt.%)**

Comp.	1	2	3	4	5	6	7	8
SiO_2	48.35	48.08	48.24	48.56	49.63	48.86	48.46	48.66
Al_2O_3	0.01	0.20	0.19	0.19	0.07	0.13	0.16	0.11
TiO_2	3.43	2.93	2.90	2.26	6.01	3.97	3.52	4.23
Fe_2O_3	0.21	0.31	0.26	0.41	0.29	0.27	0.31	0.31
CaO	26.39	26.26	26.34	26.14	26.67	26.43	26.70	26.75
MnO	0.16	0.23	0.16	0.20	0.15	0.11	0.14	0.15
SnO_2	11.49	12.43	12.99	11.38	2.04	9.06	11.74	7.53
ZrO_2	1.10	1.01	0.71	3.06	6.08	2.66	0.84	3.95
Nb_2O_5	0.15	0.12	0.19	0.17	0.00	0.08	0.08	0.19
Na_2O	0.12	0.15	0.18	0.19	0.15	0.26	0.13	0.18
K_2O	2.87	2.95	2.96	2.91	3.03	2.89	3.00	2.92
Li_2O	3.06	3.00*	3.01*	3.04*	3.10*	3.05*	3.02*	3.03*
F	2.27	2.00	1.15	2.00	1.02	1.07	2.65	1.46
H_2O^{**}	0.13	0.26	0.66	0.26	0.76	0.71	0.00	0.53
	99.75	99.94	99.97	100.78	99.01	99.56	100.76	100.02
-O=F	0.95	0.84	0.48	0.84	0.43	0.45	1.11	0.61
Total	98.80	99.10	99.49	99.94	98.58	99.11	99.65	99.41
				Apfu (Si+Al = 12)				
K	0.91	0.93	0.94	0.91	0.93	0.90	0.95	0.92
Na	0.06	0.07	0.09	0.09	0.07	0.13	0.06	0.09
A	***0.97***	***1.00***	***1.03***	***1.00***	***1.00***	***1.03***	***1.01***	***1.01***
Ca	7.02	6.99	6.99	6.89	6.90	6.93	7.06	7.05
Mn	0.03	0.05	0.03	0.04	0.03	0.02	0.03	0.03
M1	***7.05***	***7.04***	***7.02***	***6.93***	***6.93***	***6.95***	***7.09***	***7.08***
Sn	1.14	1.23	1.28	1.12	0.20	0.88	1.15	0.74
Ti	0.64	0.55	0.54	0.42	1.09	0.73	0.65	0.78
Zr	0.13	0.12	0.09	0.37	0.72	0.32	0.10	0.47
Nb	0.02	0.01	0.02	0.02	0.00	0.01	0.01	0.02
Fe	0.04	0.06	0.05	0.08	0.05	0.05	0.06	0.06
M2	***1.97***	***1.97***	***1.98***	***2.01***	***2.06***	***1.99***	***1.97***	***2.07***
Li	**3.05**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
Si	12.00	11.94	11.94	11.94	11.98	11.96	11.95	11.97
Al	0.00	0.06	0.06	0.06	0.02	0.04	0.05	0.03
T	12	12	12	12	12	12	12	12
F	1.78	1.57	0.90	1.56	0.77	0.83	2.06	1.14
OH	0.22	0.43	1.10	0.44	1.23	1.17	0.00	0.86

Note: an. 1, 2, 4, 7 — aleksandrovite, 3, 6 — possibly hydroxyl-analogue of aleksandrovite, 8 — baratovite, 5 — katayamalite, analyses obtained using Camebax-microbeam, 15 kV, 30 nA (WDS). Li_2O^* — calculated content. Analyst L.A. Pautov.

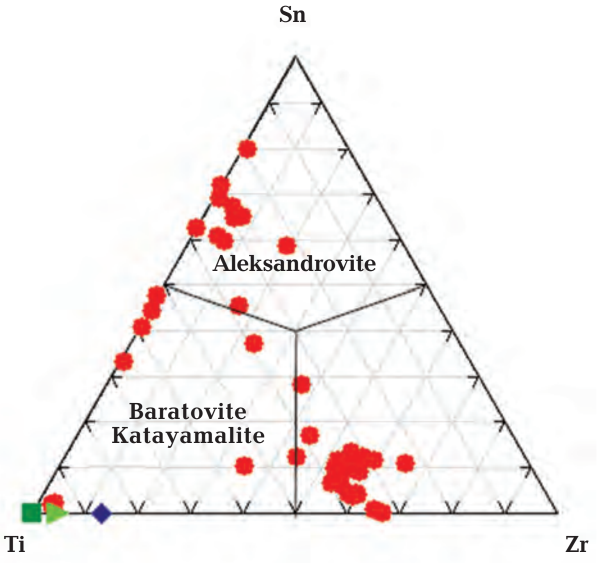


Fig. 5. Variations of octahedral cations content (atomic numbers) in the minerals of baratovite group. Blue rhombus — baratovite (Dusmatov et al., 1975), pale-green triangle — baratovite (Reguir et al., 1999), dark-green square — katayamalite (Murakami et al., 1983), red rounds — minerals of baratovite group (the author's data).

Table 4. **Calculation of the powder X-ray data of aleksandrovite**

$d_{exp.}$	$I_{exp.}$	$d_{calc.}$	*hkl*	$d_{exp.}$	$I_{exp.}$	$d_{calc.}$	*hkl*
9.74	8	9.704	0 0 2	2.395	3	2.403	5 1 3
7.78	4	7.858	2 0 0	2.347	4	2.374	3 3 3
		7.715	2 0 -2	2.313	3	2.316	6 0 2
7.16	5	7.121	1 1 1	2.190	6	2.190	3 3 -7
5.76	6	5.755	1 1 2			2.188	7 1 0
4.86	21	4.874	3 1 -1	2.090	5	2.092	6 2 2
		4.852	0 0 4			2.089	7 1 1
		4.848	3 1 -2	2.066	3	2.065	8 0 -6
4.62	9	4.615	3 1 0			2.064	0 4 5
		4.611	1 1 -4	2.049	4	2.048	5 3 -7
4.25	15	4.250	4 0 -2	2.015	6	2.015	1 3 7
4.19	4	4.184	3 1 1	1.991	7	1.991	1 1 9
4.11	16	4.122	2 2 -2	1.973	4	1.974	6 2 3
		4.104	3 1 -4			1.972	0 2 9
3.90	13	3.895	2 2 1	1.950	25	1.952	4 2 6
3.864	9	3.862	1 1 4			1.948	8 2 -4
3.712	33	3.712	3 1 2	1.940	18	1.940	5 3 -8
3.635	6	3.633	3 1 -5	1.912	4	1.912	2 2-10
3.567	8	3.565	2 0 4	1.895	4	1.896	7 3 -1
3.534	3	3.520	2 2 -4			1.895	3 3 -9
3.495	5	3.498	2 0 -6	1.847	16	1.847	7 3 0
3.444	14	3.439	0 2 4			1.847	4 4 -7
3.267	10	3.271	1 1 5	1.814	4	1.814	9 1 -2
3.234	100	3.235	0 0 6	1.802	4	1.803	0 2 10
3.206	34	3.208	2 2 3	1.785	4	1.785	3 3 7
		3.206	5 1 -2			1.785	6 4 0
		3.204	4 2 -2	1.772	5	1.772	2 2 9
3.102	12	3.103	1 3 1			1.772	9 1 -1
3.061	10	3.059	4 2 0	1.744	5	1.746	9 1 -8
3.039	28	3.037	0 2 5			1.746	3 5 -5
2.988	3	2.992	5 1 0			1.743	6 2 5
2.963	14	2.958	1 3 2	1.719	9	1.720	0 4 8
2.944	14	2.942	5 1 -5			1.719	2 0-12
2.894	42	2.893	3 1 4			1.719	9 1 0
		2.893	4 2 1			1.718	7 3 2
2.826	6	2.827	1 1 6			1.718	6 4 -7
2.777	9	2.772	1 3 3	1.705	5	1.705	6 2-11
2.752	9	2.750	5 1 -6			1.705	5 1-12
		2.748	3 3 -3	1.695	5	1.696	1 5 -6
2.698	11	2.697	4 2 2			1.696	6 0-12
2.664	3	2.661	3 3 1	1.671	2	1.671	4 4 -9
2.601	3	2.605	4 0 4	1.645	6	1.645	7 3 3
		2.605	5 1 2	1.634	3	1.634	10 0 -8
2.570	6	2.572	1 3 4			1.633	9 3 -4
		2.572	6 0 -6	1.616	8	1.616	9 3 -6
2.547	3	2.547	5 1 -7			1.616	6 4 3
		2.544	4 0 -8			1.615	7 3-10
2.525	4	2.526	3 3 2			1.615	0 4 9
		2.526	3 1 -8	1.602	5	1.602	8 4 -4
2.450	5	2.450	6 2 -3			1.602	6 2-12
2.425	42	2.426	0 0 8				
		2.424	6 2 -4				

Note: obtained using diffractometer DRON-2, FeKα — radiation, 0.5°/min. Internal standard — quartz. Analyst — L.A. Pautov.

served. To prevent this we used a strip of black paper as a shield X-Ray film. Aleksandrovite by the set of reflections and their intensities on the powder X-ray diffraction data is similar to baratovite. Mineral is monoclinic, space group $C2/c$ (on the analogy of baratovite), the cell parameters are a = 17.01(2), b = 9.751(6), c = 21.00(2) Å, β = 112.45(8)°, V = 3219(7) Å^3, Z = 4.

Physical properties

Aleksandrovite — is a colourless and transparent mineral with vitreous lustre and pearl lustre on the cleaved surface. Streak is white. Cleavage is perfect along (001), fracture is even. A density was found using the flotation method in thallium malonate formate (Clerici solution) is 3.05(2) g/cm^3. Calculated density is 3.07(2) g/cm^3. Microhardness of the mineral (an average value out of 15 measurements using PMT-3, loaded with a 50 g weight) VHN = 300 kg/mm^2 (value dispersion is 276—319). Mohs hardness is estimated to be 4—4.5. It fluoresces light-blue under short-wave UV light (254 nm).

Aleksandrovite is optically biaxial negative. The indices of refraction measured at 589 nm on the spindle needle in immersion liquids are: n_p = 1.629(2), n_m = 1.635(4), n_g = 1.638(2); 2V (calculated) = −70.3°. Dispersion of optical axis is strong, $r > v$. In thin sections (0.03 mm thick) aleksandrovite differs from baratovite by the higher interference colour (aleksandrovite has white and baratovite has up to grey colour the highest), notable lower refractive indices and optical sign. In the zoned crystals between baratovite and aleksandrovite zones the Becke bright line is easily visible. The anomalous interference colours are observed in the close-to-extinction positions. Elongation is positive. The angle of extinction on the sections with distinct cleavage fractures (parallel to the elongation of the grains) varies from nearly straight extinction to 22°.

Unfortunately, the small size of homogenous aleksandrovite crystals, its relatively low birefringence and anomalous extinction of many grains made the Fedorov universal stage method of optical orientation investigation inapplicable.

IR spectrum of aleksandrovite was detected in microtablet with KBr using spectrometer Specord 75IR. Aleksandrovite IR-spectrum is similar to that of baratovite (Fig. 6), the major absorption strips are: 1083, 1024, 974, 950, 673, 607, 568, 520, 470, 440 cm^{-1}.

Compatibility index according to Gladstone-Dale relation is 1 – (K_p/K_c) = -0.005 (superior) for D_{calc} (density calculated) = 3.07 and -0.005 for D_{meas} (density measured) = 3.05 g/cm^3 .

The comparative characteristics of aleksandrovite and baratovite are given in the Table 5.

The type specimen with aleksandrovite is stored in the Fersman Mineralogical Museum RAS in Moscow (registration number 3825/1).

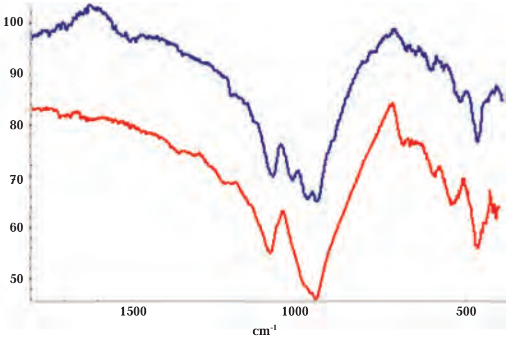


Fig. 6. IR-spectra of aleksandrovite (the upper spectrum) and baratovite, (Darai-Pioz massif) № 80873 from the Fersman Mineralogical Museum RAS collection (the lower spectrum).

Acknowledgements

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Table 5. **Comparative characteristics of aleksandrovite and baratovite**

	Aleksandrovite	Baratovite*
Formula	$KLi_3Ca_7Sn_2Si_{12}O_{36}F_2$	$KLi_3Ca_7(Ti,Zr)_2Si_{12}O_{36}F_2$
Singony	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
a, Å	17.01	16.94
b, Å	9.751	9.746
c, Å	21.00	20.907
β	112.45	112.50
Z	4	4
Intensive	4.86	4.8288
lines of	3.712	3.6966
powder	3.234	3.2192
X-ray	3.206	3.1913
data, *d/n*	3.039	3.0510
	2.894	2.8839
	2.425	2.4144
	1.950	1.9437
Density (calculated), g/cm^3	3.05(2)	2.92
Optical sign	(–)	(+)
n_p	1.629	1.672
n_m	1.635	1.672
n_g	1.638	1.673

Note: * — X-ray data are from JCPDS 33-0811

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ÅSKAGENITE-(Nd), $Mn^{2+}NdAl_2Fe^{3+}(Si_2O_7)(SiO_4)O_2$, A NEW MINERAL OF THE EPIDOTE SUPERGROUP[1]

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A new epidote-supergroup mineral åskagenite-(Nd) was discovered in specimens from a granite pegmatite outcropped at the Åskagen deposit near the town of Filipstad, Värmland, Sweden, in association with potassic feldspar, quartz, bastnäsite, thorite, the Nd-dominant analogue of allanite-(Ce), brookite, gadolinite-(Y) and allophane. The new mineral forms coarse prismatic and flattened crystals up to 1×4 cm in size. Åskagenite-(Nd) is black, with resinous lustre and brown streak, translucent in thin fragments; brittle, Mohs' hardness 6, fracture conchoidal. $D_{meas} = 3.737(5)$ g/cm^3 (for a metamict sample); $D_{calc} = 4.375$ g/cm^3 (for a sample heated at 600°C during 1 h in nitrogen). Åskagenite-(Nd) is optically isotropic, $n = 1.712(2)$. IR spectrum is given. Chemical composition (electron microprobe, water determined by Alimarin method, Fe^{2+}:Fe^{3+} by Mössbauer data, valency of Mn by XANES spectroscopic data, wt.%): CaO 0.27, Y_2O_3 2.27, La_2O_3 0.44, Ce_2O_3 7.99, Pr_2O_3 1.76, Nd_2O_3 11.21, Sm_2O_3 3.01, Yb_2O_3 0.21, ThO_2 0.72, MnO 7.98, FeO 7.75, Fe_2O_3 9.16, Al_2O_3 15.85, SiO_2 29.51, H_2O 0.55, total; 98.75. Crystal-chemical formula: $(Mn^{2+}_{0.69}Fe^{2+}_{0.26}Ca_{0.03})_{\Sigma 0.98}(Nd_{0.41}Ce_{0.30}Y_{0.12}Sm_{0.10}Pr_{0.07}La_{0.02}Yb_{0.01}Th_{0.02})_{\Sigma 1.05}(Al_{0.90}Fe^{3+}_{0.10})_{\Sigma 1.00}Al_{1.00}$ $(Fe^{3+}_{0.60}Fe^{2+}_{0.40})_{\Sigma 1.00}Si_{2.99}O_{11}O[O_{0.63}(OH)_{0.37}]_{\Sigma 1.00}$. Strong lines of X-ray powder-diffraction pattern of a heated sample *d*, Å (*I*; *hkl*) are: 3.50(46; -211), 3.22(50; -212, 201), 2.897 (100; -301), 2.850(73; 020), 2.687(73; 120), 2.121(48; -403), 1.630(59; 124). Unit-cell parameters are: $a = 8.78(1)$ Å, $b = 5.710(6)$ Å, $c = 10.02(1)$ Å, $\beta = 114.6(2)°$; $V = 456.7(8)$ Å^3, $Z = 2$; space group $P2_1/m$. Type material is deposited in the collections of the Technische Universität, Bergakademie Freiberg, Germany; inventory numbers are 82194 and 82218.
3 tables, 5 figures, 14 references.
Keywords: åskagenite-(Nd), epidote supergroup, pegmatite, Åskagen.

Introduction

According to the recommended nomenclature of epidote-group minerals that was approved recently by the IMA CNMNC, epidote group unites monoclinic (space group $P2_1/m$) minerals with the general crystal-chemical formula is $A1A2M1M2M3(Si_2O_7)(SiO_4)\varnothing4\varnothing10$, where $A1$ = Ca, Mn^{2+}; $A2$ = Ca, *REE*, Sr, Pb; $M1$ = Al, Fe^{3+}, V^{3+}, Mn^{3+}, Cr^{3+}; $M2$ = Al, Fe^{3+}; $M3$ = Al, Fe^{3+}, V^{3+}, Mn^{3+}, Cr^{3+}, Mg, Fe^{2+}, Mn^{2+}; $\varnothing4$ = O, F; $\varnothing10$ = OH and sometimes subordinate O (Armbruster *et al.*, 2006).

Subsequently, in accordance with new rules of the standartization of mineral group hierarchies (the proposal 09-A-bis), epidote group was renamed into epidote supergroup (Mills *et al.*, 2009), whereas clinozoisite (epidote), allanite and dollaseite subgroups were renamed into corresponding groups.

General formulae for members of these groups are:

Epidote group —
$A1^{2+}A2^{2+}M1^{3+}M2^{3+}M3^{3+}(Si_2O_7)(SiO_4)O(OH)$;
Allanite group —
$A1^{2+}A2^{3+}M1^{3+}M2^{3+}M3^{2+}(Si_2O_7)(SiO_4)O(OH)$;
Dollaseite group —
$A1^{2+}A2^{3+}M1^{2+}M2^{3+}M3^{2+}(Si_2O_7)(SiO_4)F(OH)$.

Åskagenite-(Nd), a new epidote-supergroup mineral described in the present article, is the first representative of a new group whose general formula can be written as follows: $A1^{2+}A2^{3+}M1^{3+}M2^{3+}M3^{3+}(Si_2O_7)(SiO_4)O_2$.

The name was given after the locality and reflects the predominance of Nd over other *REE* in the site *A*2.

Type material is deposited in the collections of the Technische Universität, Bergakademie Freiberg, Germany. Inventory numbers are 82194 (holotype) and 82218 (cotype).

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[1] — Åskagenite-(Nd) is approved by the IMA Commission on New Minerals, Nomenclature and Classification on December 1, 2009, IMA no. 2009-073.

Occurrence, general appearance and physical properties

Åskagenite-(Nd) was discovered in specimens collected at the beginning of 20th century in a small (5×20 m) working at the Åskagen quarry, near the former mining settlement Torskebäcken located 12 km ENE of Filipstad town, Värmlands län, Sweden (Wilke, 1997). The Åskagen quarry exploited for quartz from 1882 to 1916 is located within leptite zone developed along the eastern coast of the lake Yngen.

The working, where the new mineral was found, crosses a pegmatite body. In the latter, in association with åskagenite-(Nd) the following minerals are identified: potassic feldspar, quartz, bastnäsite, thorite, the Nd-dominant analogue of allanite-(Ce), brookite, gadolinite-(Y), as well as late allophane.

The new mineral forms coarse prismatic and flattened crystals up to 1×4 cm in size, with orthogonal cross-section (Fig. 1). Åskagenite-(Nd) is black, translucent in thin fragments, with resinous lustre and brown streak. It is brittle, with conchoidal fracture. Mohs' hardness is 6. Cleavage is not observed. Measured density is $D_{meas} = 3.737(5)$ g/cm^3 (for a metamict sample); $D_{calc} = 4.375$ g/cm^3 (for a sample heated at 600°C during 1 h in nitrogen).

Åskagenite-(Nd) is weakly radioactive that is the cause of its metamict state. As a result, the mineral is optically isotropic, $n = 1.712(2)$. Optical properties of åskagenite-(Nd) heated at 600°C during 1 h in nitrogen could not be determined due to the small size of single crystals and the presence of submicroscopic pores and cracks.

Chemical composition

Chemical composition of åskagenite-(Nd) was investigated by electron microprobe, with the scanning electron microscope Tescan Vega II XMU with the EDS mode spectrometer INCAx-sight at the accelerating voltage of 20 kV, electron beam current of 0.5 nA and electron beam diameter of 0.157 μm. The beam was restered on the area 16×16 μm. Four local analyses have been carried out. Mean values of the contents of constituents and their ranges are given in Table 1.

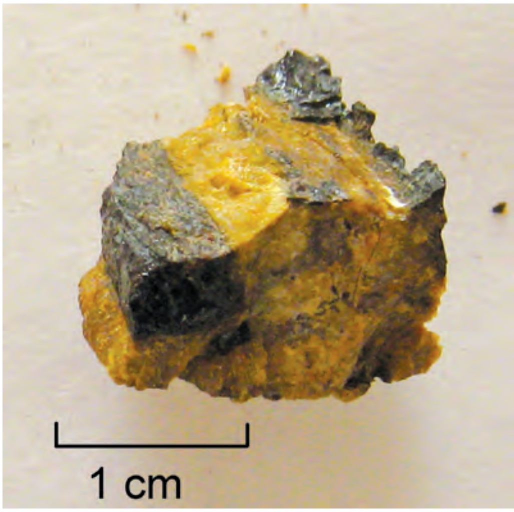
H_2O was determined by the Alimarin method (Penfield method modified for small samples with selective sorption of H_2O on $Mg(ClO_4)_2$ from gaseous products obtained by heating the mineral in oxygen at 1060°C). CO_2 was not analysed because of the absence of bands corresponding to C-O vibrations in the IR spectrum.

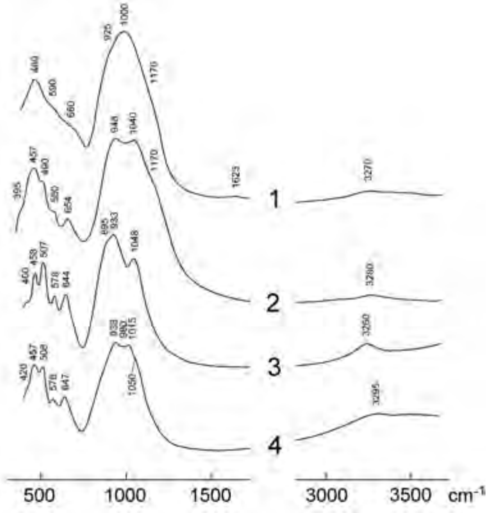
The empirical formula calculated on 13 oxygen atoms, taking into account the valencies of Fe and Mn (by Mössbauer and XANES data) is: $(Mn^{2+}_{0.69}Fe^{2+}_{0.26}Ca_{0.03})_{\Sigma 0.98}(Nd_{0.41}Ce_{0.30}Y_{0.12}Sm_{0.10}Pr_{0.07}La_{0.02}Yb_{0.01}Th_{0.02})_{\Sigma 1.05}(Al_{1.90}Fe^{3+}_{0.70}Fe^{2+}_{0.40})_{\Sigma 2.98}Si_{2.99}O_{12.63}(OH)_{0.37}$. The simplified formula of åskagenite-(Nd) is $Mn^{2+}NdAl_2Fe^{3+}(Si_2O_7)(SiO_4)O_2$.

Gladstone-Dale compatibility is $1 - (K_p/K_c) = 0.012$ (superior) for initial (metamict) åskagenite-(Nd), with measured density.

Fig. 1. Crystal of åskagenite-(Nd) in pegmatite.

Fig. 2. IR spectra of initially metamict åskagenite-(Nd) (1), åskagenite-(Nd) heated at 600˚C during 1 h in nitrogen (2), Nd-rich allanite-(Ce) from Khaldzan Buragtag, Mongolia (3) and Nd-rich allanite-(Y) from Åskagen, Sweden (4).





XANES, IR and Mössbauer data. The valency of Mn and Fe

In order to obtain IR spectra, mineral samples have been mixed with anhydrous KBr, pelletized, and analysed using a Specord 75 IR spectrophotometer. IR spectrum of pure KBr-disk was subtracted from the overall spectrum. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of frequency measurement is ± 1 cm^{-1}; the mean resolution for the region 400 – 1600 cm^{-1} is 0.8 cm^{-1}.

The IR spectrum of åskagenite-(Nd) (Figure 2, curve 1) contains two strong bands with maxima at 469 and 1000 cm^{-1} and several shoulders. The absence of distinct band maxima in the range 550 – 900 cm^{-1} is a generic property of the majority of metamict silicates. A very weak band at 1623 cm^{-1} indicates the presence of trace amounts of H_2O. The IR spectrum of åskagenite-(Nd) heated at 600°C, during 1 h in nitrogen (Figure 2, curve 2) is similar to the spectra of allanite group minerals (Figure 2, curves 3 and 4). A very weak band at 3280 cm^{-1} corresponds to stretching vibrations of OH groups.

Mössbauer spectrum has been obtained using the modified WISSEL spectrometer, with registration simultaneously in 512 channels and signal accumulation during 308 hours at the temperature of 293 K.

In the Mössbauer spectrum of åskagenite-(Nd) (Figure 3) two doublets are present. The doublet with an isomer shift of 0.2869 mm/s, quadrupole splitting of 0.9139 mm/s and relative area of 51.5% corresponds to Fe^{3+}. The doublet with isomer shift of 0.9402 mm/s, quadrupole splitting of 2.1830 mm/s and relative area of 48.5% corresponds to Fe^{2+}. Thus the Fe^{3+}:Fe^{3+} ratio in åskagenite-(Nd) is 51.5:48.5.

Fine structure of the X-ray absorption spectrum near edge structure (XANES) is very sensitive to the electronic state of an absorbing atom, as well as to its local environment. In order to determine the state of Mn in åskagenite-(Nd), its XANES spectrum was compared with X-ray spectra of standard samples.

Table 1. **Analytical data for åskagenite-(Nd)**

Comp.	wt.%	Range	Probe standard
CaO	0.27	0.00 – 1.43	Wollastonite
Y_2O_3	2.27	2.02 – 2.82	Y
La_2O_3	0.44	0.40 – 0.49	$LaPO_4$
Ce_2O_3	7.99	7.83 – 8.15	$CePO_4$
Pr_2O_3	1.76	1.47 – 1.90	$PrPO_4$
Nd_2O_3	11.21	11.06 – 11.45	$NdPO_4$
Sm_2O_3	3.01	2.82 – 3.33	$SmPO_4$
Yb_2O_3	0.28	0.00 – 0.48	$YbPO_4$
ThO_2	0.72	0.58 – 0.77	ThO_2
MnO*	7.98	7.79 – 8.48	Mn
FeO**	7.75	15.85 – 16.13***	Fe
Fe_2O_3**	9.16		
Al_2O_3	15.85	15.60 – 15.97	Al_2O_3
SiO_2	29.51	29.32 – 29.90	SiO_2
H_2O	0.55		
Total	98.75		

Note: * – According to XANES data, all Mn is bivalent. ** – Total iron content analysed as FeO is 16.00 wt.% and divided over FeO and Fe_2O_3 according to the results of Mössbauer spectroscopy.
*** – For total iron measured as FeO.

XANES spectra were obtained on the X-ray beamline of the synchrotron radiation source ANKA (SUL-X Beamline) in the Synchrotron Radiation Laboratry for Environmental Studies, Karlsruhe Institute of Technology, Campus North. The samples have been prepared as pellets (with cellulose as matrix stuff) and as raw fragments of the mineral using fluorescence-mode and transmission-mode data-logging, in the range of energies from 6530 to 6630 eV, the

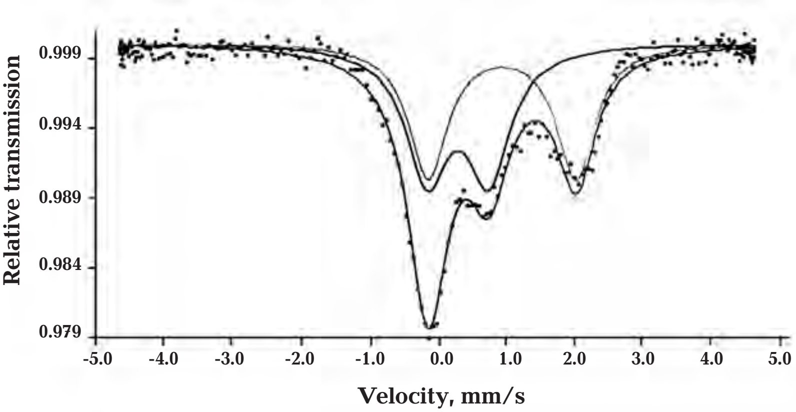


Fig. 3. Mössbauer spectrum of åskagenite-(Nd).

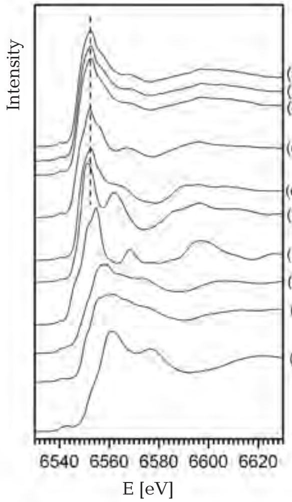


Fig. 4. Mn K-edge XANES spectra of åskagenite-(Nd) (a – c, three measurements), $Mn^{2+}SiO_3$ (d), $Mn^{2+}SO_4 \cdot H_2O$ (e), $Mn^{2+}CO_3$ (f), MnO (g), Mn_2O_3 (h), $Mn^{3+}PO_4$ (i) and MnO_2 (j).

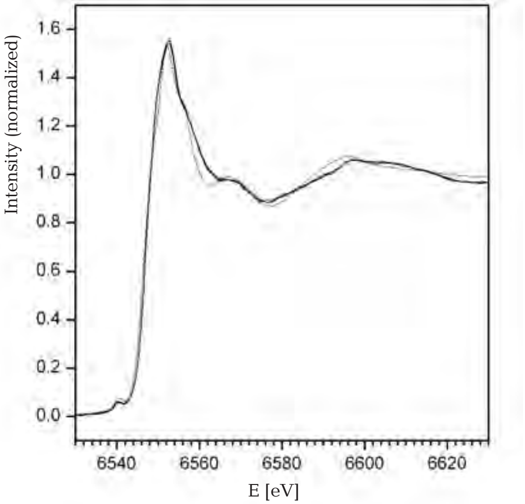


Fig. 5. Comparison of Mn K-edge XANES spectra of åskagenite-(Nd) (solid lines) and $Mn^{2+}SiO_3$ (dashed line).

Table 2. **X-ray powder-diffraction data for åskagenite-(Nd) heated at 600°C during 1 hour in nitrogen**

I_{meas}, %	d_{meas}, Å	d_{calc}, Å	*hkl*
23	9.12	9.11	001
12	8.01	7.98	100
16	5.05	5.05	101
18	4.63	4.64	110
17	4.00	3.99	200
46	3.50	3.48	-211
50	3.22	3.23	-212
		3.20	201
100	2.897	2.900	-301
73	2.850	2.855	020
73	2.687	2.688	120
52	2.606	2.611	-303
38	2.534	2.526	202
23	2.394	2.393	-221
22	2.394	2.322	220
15	2.300	2.299	113
37	2.15*	2.145	-401
48	2.121	2.122	-403
27	2.038	2.042	203
		2.034	-321
25	1.979	1.983	104
35	1.876	1.873	114
46	1.644	1.646	-306
59	1.630	1.629	124
15	1.580	1.582	-316
14	1.546	1.548	330
29	1.456	1.457	304
		1.455	-334
33	1.404	1.405	-612, 140
		1.404	-141

Note: * – broad reflection.

beam sizes at the sample surface being 100×200 μm. In the working range of energies, other components except Mn do not absorb X-ray irradiation. The detectable contribution of the Nd L-series becomes apparent only above 6700 eV.

The Mn K-edge spectrum of åskagenite-(Nd) with the main resonance line at 6553 eV is very close to the spectrum of $Mn^{2+}SiO_3$ (Mn^{2+} in anhydrous silicate matrix), and little different from spectra of compounds with Mn^{2+} in other matrices. It is strongly different from spectra of compounds with Mn^{3+} and Mn^{4+} (Figures 4 and 5). Thus we conclude that all manganese in åskagenite-(Nd) is divalent.

X-ray diffraction

Åskagenite-(Nd) is metamict, amorphous. Its X-ray powder-diffraction pattern contains only a broad halo with the maximum near 3 Å.

After heating in a nitrogen atmosphere (heating rate 5°C per minute up to 600°C, then one hour at a constant temperature of 600°C, and thereafter with rapid cooling to room temperature) åskagenite-(Nd) gives a distinct X-ray powder diffraction pattern. X-ray powder diffraction data were collected using a PANalytical X'Pert PRO diffractometer with Soller slit and X'Cellerator detector. The data (in Å for $CuK\alpha_1$) are given in Table 2. Heated sample is monoclinic, space group $P2_1/m$; refined unit-cell parameters are: $a = 8.78(1)$ Å, $b = 5.710(6)$ Å, $c = 10.02(1)$ Å, $\beta = 114.6(2)°$; $V = 456.7(8)$ Å^3, $Z = 2$.

Table 3. **Comparative data for åskagenite-(Nd) and some related epidote supergroup minerals (all monoclinic, $P2_1/m$, Z = 2)**

Mineral	**Åskagenite-(Nd)**	**Epidote-(Sr)**	**Epidote-(Pb)**	**Allanite-(Ce)**	**Allanite-(La)**	**Mangani-androsite-(Ce)**	**Mangani-androsite-(La)**
Simplified formula	$Mn^{2+}NdAl_2Fe^{3+}(Si_2O_7)(SiO_4)O_2$	$CaSrAl_2Fe^{3+}(Si_2O_7)(SiO_4)O(OH)$	$CaPbAl_2Fe^{3+}(Si_2O_7)(SiO_4)O(OH)$	$CaCeAl_2Fe^{2+}(Si_2O_7)(SiO_4)O(OH)$	$CaLaAl_2Fe^{2+}(Si_2O_7)(SiO_4)O(OH)$	$Mn^{2+}CeMn^{3+}AlFe^{2+}(Si_2O_7)(SiO_4)O(OH)$	$Mn^{2+}LaMn^{3+}AlFe^{2+}(Si_2O_7)(SiO_4)O(OH)$
Unit cell data							
a, Å	8.78	8.928	8.958	8.932	8.914	8.901	8.896
b, Å	5.71	5.652	5.665	5.770	5.726	5.738	5.706
c, Å	10.02	10.244	10.304	10.1575	10.132	10.068	10.083
β, °	114.6	114.46	114.4	114.69	114.87	113.425	113.88
V, $Å^3$	456.7	470.5	476.2	475.6	469.1	471.81	468.0
Strongest reflections of the X-ray powder pattern: *d*, Å – *I*, %	3.50 – 46	3.50 – 42	3.49 – 50	3.53 – 43	3.506 – 20	3.514 – 41	3.504 – 40
	3.22 – 50	3.26 – 23	2.91 – 100	2.920 – 100	2.901 – 100	2.896 – 100	2.897 – 100
	2.897 – 100	2.92 – 100	2.81 – 40	2.886 – 28	2.860 – 40	2.869 – 35	2.857 – 45
	2.850 – 73	2.83 – 32	2.71 – 40	2.714 – 66	2.692 – 60	2.713 – 39	2.707 – 60
	2.687 – 73	2.72 – 41	2.60 – 50	2.627 – 41	2.611 – 50	2.707 – 39	2.615 – 60
	2.606 – 52	2.61 – 42	2.18 – 40	2.182 – 36	2.174 – 25	2.6225 – 53	2.178 – 60
	2.121 – 48	2.58 – 49	1.90 – 40	2.158 – 23			2.145 – 60
	1.630 – 59						
Density, g/cm^3	3.737 (meas)*;		4.03 (meas);	3.5-4.2 (meas);	3.93 (meas);		>4.03 (meas);
	4.375 (calc)	3.74 (calc)	4.03 (calc)	4.11 (calc)	3.94 (calc)	4.21 (calc)	4.21 (calc)
Optical data:							
Refraction indices	Isotropic, mean refraction index is 1.712*	α = 1.737 β = 1.780 γ = 1.792	α = 1.788 β = 1.81 γ = 1.830	Mean 1.54-1.72* α = 1.69-1.79 β = 1.70-1.815 γ = 1.71-1.83	α = 1.755 β = 1.760 γ = 1.765	Mean refraction index is 1.80 (calc)	Mean refraction index is 1.877 (calc)
Optical sign, 2V	No data	(-) 62	(-) 50	(-) or (+) 40-123	(+/-) 90	(+) 80.6	No data
Sources	This work	Minakawa *et al.*, 2008	Dollase, 1971; Dunn, 1985; Holtstam, Langhof, 1994	Vlasov, 1966; Dollase, 1971; Deer *et al.*, 1986	Orlandi, Pasero, 2006	Cenki-Tok *et al.*, 2006	Bonazzi *et al.*, (1996)

*Note: * — Data for metamict samples.*

Discussion

The distribution of ionic species between various sites is determined by ionic radii. In particular, Al^{3+} ($r = 0.535$ Å) preferentially occupies the *M*2 and *M*1 sites, whereas Fe^{3+} ($r = 0.645$ Å) present in amounts 1 apfu concentrates in the *M*3 site. In order to determine site population in an epidote-group mineral, one must know valencies of species-determining components.

Taking into account that the valencies of Fe and Mn in åskagenite-(Nd) have been determined by non-destructive methods and following the accepted rules for the assignment of ionic species to the various key sites (Armbruster *et al.*, 2006), the empirical formula of åskagenite-(Nd) can be rewritten as

$$(Mn^{2+}_{0.69}Fe^{2+}_{0.26}Ca_{0.03})_{\Sigma 0.98}(Nd_{0.41}Ce_{0.30}Y_{0.12}Sm_{0.10}Pr_{0.07}La_{0.02}Yb_{0.01}Th_{0.02})_{\Sigma 1.05}(Al_{0.90}Fe^{3+}_{0.10})_{\Sigma 1.00}Al_{1.00}(Fe^{3+}_{0.60}Fe^{2+}_{0.40})_{\Sigma 1.00}Si_{2.99}O_{11}O[O_{0.63}(OH)_{0.37}]_{\Sigma 1.00}.$$

In Table 3, comparative data for åskagenite-(Nd) and some related epidote group minerals are given. Åskagenite-(Nd) has the smallest unit cell volume among epidote group minerals, even smaller than those of manganiandrosite-(Ce) and manganiandrosite-(La), both of which contain Mn^{2+} in the *A*1 site. As compared with manganiandrosite-(Ce) and manganiandrosite-(La), in åskagenite-(Nd), Fe^{3+} prevails over the larger cation Fe^{2+} and Mn^{2+} is partially substituted by the smaller cation Fe^{2+}. Probably, this is the main cause of the lowering of unit cell dimensions.

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IRARSITE DISCOVERY IN COPPER–NICKEL ORES OF SHANUCH DEPOSIT (KAMCHATKA)

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In sulfide copper-nickel ores of the Shanuch deposit (Kamchatka) new for this deposit mineral – irarsite was found. The deposit is associated spatially and geneticly with stocks and dikes of the Dukukskiy basite-hyperbasite complex of Eocene age. Three mineral associations are distinguished in its ores: pentlandite-pyrrhotite, magnetite-chalcopyrite-pyrrhotite and pyrite-marcasite one. It is established, that irarsite forms microinclusions in sulfoarsenides, more seldom in pentlandite of magnetite-chalcopyrite-pyrrhotite association of massive sulfide ores. In irarsite composition there are constantly admixtures of iron, nickel and cobalt, sometimes of rhodium and platinum.

2 tables, 3 figures, 9 references.
Keywords: irarsite, sulfoarsenides, mineral associations, copper-nickel ores.

Irarsite – (Ir,Ru,Rh,Pt)AsS – a rare sulfoarsenide of elements of platinum group. It was discovered by A.D. Genkin with coauthors (Genkin *et al.*, 1966) in chromite ores of the Onfervacht deposit (Bushveld complex, RSA). The mineral is an end member of the hollingworthite-irarsite row. The most often irarsite is found together with gold, chromite and minerals of elements of platinum group in placers of Australia, Myanmar, Finland and Russia. The source of noble metals mineralization is represented by stratified massifs of rocks of ultrabasic-basic composition: dunites, gabbro-pyroxenites and others (Genkin *et al.*, 1991; Shcheka *et al.*, 1991; Nekrasov *et al.*, 1994; Cabri *et al.*, 1996; etc.). Information in literature about occurrence of irarsite in commercial copper-nickel ores is scarce. It is mentioned presence of irarsite in the ores of the Noril'sk deposit (Dodin *et al.*, 2000). V.V. Distler and I.P. Laputina found it among disseminated copper-nickel mineralization in some horizons of stratified ultrabasite (gabbro-norites-lerzolites) massif at the Kola Peninsula (Distler, Laputina, 1981).

The authors carried out mineralogical study of ore body No 1 of the Shanuch deposit. Rare and ore-forming minerals were analysed using X-ray spectral microanalyzer JEOL JXA-8100. In doing so in massive copper-nickel ores irarsite in association with sulfoarsenides was established.

Short description of the Shanuch deposit

The Shanuch copper-nickel deposit is located at the southern part of the Kamchatka peninsula and is confined to median massif of the same name (Stepanov, Trukhin, 2007). At the area of the deposit are distributed crystalline schists of the Kamchatka series of late Proterozoic and gneissoid granites of the Krutogorovskiy complex of early Cretaceous. Nickel-bearing formations are represented by stocks and dikes of the Dukukskiy basite-hyperbasite complex of Eocene age. Copper-nickel mineralization is spatially conjugated with one of dike swarms oriented subvertically. The best studied ore body No 1 has in vertical section lens-like form with a bulge in the central part. According to texture features one could distinguish four main types of ores: massive, densely impregnated, impregnated and breccial ones. It should be noted some zoning in their distribution in the limits of the ore body (Fig. 1). Thus, the central part of the latter is composed of predominantly massive ores. At near root and in subsurface parts of the ore body they are changed by breccial ores, which are predominant here. At the surface one could observe an iron hat of small thickness, composed of oxidized ores. Horizontal sections display conform zoning: the central part of ore body is most often composed of massive and densely impregnated ores, which towards periphery are changed by breccial ones then by veinlet-impregnated and impregnated ores. In the ore mineral composition pyrrhotite, pentlandite, violarite and chalcopyrite predominate, pyrite, magnetite, millerite, mackinawite are less abundant, seldom occurrence is noted for gersdorffite, sulfoarsenides, sphalerite, galena, molybdenite, scheelite, as well as for native gold and platinoids (Poletaev, 2004). The highest gold con-

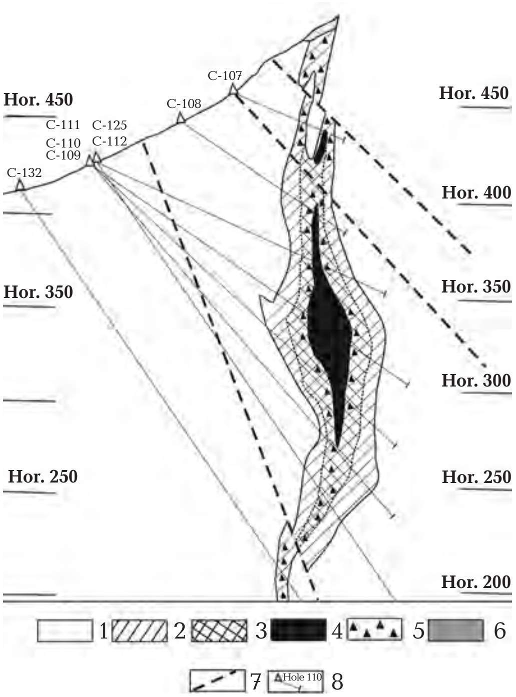

Fig 1. Sketch section of the ore body №1 from the Shanuch deposit. 1. Country rocks. 2–6. Ore types: 2 – impregnated; 3 – dense-impregnated; 4 – continuous (massive); 5 – breccias; 6 – oxidized ores. 7. Faults. 8. Boreholes and their numbers.

tents are marked in the middle part of ore body, enriched in nickel, copper and cobalt. Along dip and rise of ore body concentration of gold diminishes. Contents in ores of palladium and platinum gradually increase up the rise towards the central part of ore body, where maximum quantity of massive ores is concentrated.

The ores are characterized by the same mineral associations, among which one could distinguish pentlandite-pyrrhotite, magnetite-chalcopyrite-pyrrhotite and pyrite-marcasite ones. Two first associations are productive for copper-nickel mineralization. Sulfoarsenides with irarsite are spatially related to massive sulfide ores, in which magnetite-chalcopyrite-pyrrhotite association is developed.

Investigation results for sulfoarsenides and irarsite

Sulfoarsenides occur in all types of ores: massive, densely impregnated, impregnated and breccial ones. Usually they are represented by idiomorphic grains, which do not exceed 10 microns (seldom are found more large grains up to 50 microns), which are established in pyrrhotite, chalcopyrite and pentlandite. Crystals of skeletal form are observed very seldom. As regards their optical characteristics the minerals of this group don't differ from gersdorffite. The minerals have white color, high reflective ability; double reflection and anisotropy were not reported. By chemical composition and paragenesis one might distinguish two groups of sulfoarsenides. Sulfoarsenides with cobalt content of 5–9 wt.% are related to the first group. Minerals of the first group are often observed as intergrowths with pentlandite, forming coarse-looped structures of decay of solid solution in pyrrhotite, and are spatially attracted towards chalcopyrites of late generations, associated with monoclinic pyrrhotite and magnetite. Sulfoarsenides of the first group contain microinclusions of chalcopyrite, tellurobismuthite and argentite. Sulfoarsenides with cobalt content from 9 to 15.23 wt.% are related to the second group. Their composition is displayed in Table 1. These sulfoarsenides are spatially confined to pentlandite and pyrrhotite of early generations and often contain microinclusions of irarsite. Presence in sulfoarsenides of the second group admixtures of Ir, Rh, Pt is caused by occurrence of inclusions of such minerals as irarsite and sperrylite.

Chemical composition of sulfoarsenides of both groups is rather correctly calculated for the formula: (Ni,Co, Fe)AsS with insignificant deficit of the sum of nickel, cobalt and iron. Thus, one could note wide isomorphic substitution in the system of natural phases CoAsS – FeAsS – NiAsS, established by V.V. Distler and I.P. Laputina for another deposit (Distler, Laputina, 1979).

Irarsite is a rare mineral in the ores of the deposit (Fig. 2). Usually it forms microinclusions of rounded (Fig. 2a, f) and elongated oval (Fig. 2c) form 2–6 microns in size, locating in the central parts of idiomorphic micrograins of sulfoarsenides. Sometimes irarsite grains are found in pentlandite (Fig. 2b). Very seldom idiomorphic microcrystals (Fig. 2e) and grains of skeletal form (Fig. 2d) are observed. In one case in small idiomorphic crystal of irarsite was found micrograin (less than 1 micron) possibly of sperrylite (Fig. 3). As regards optical characteristics irarsite is not practically different from sulfoarsenides. The mineral has reflective ability close to 45% and, according to relief of relatively large (more than 5 microns; Fig. 2c) grains, higher hardness in comparison with sulfoarsenides;

Table 1. **Chemical composition of sulfoarsenides, wt.%**

№ an.	Fe	Ni	Co	As	Ir	Pt	Rh	S	Total
1	5.23	17.89	13.40	45.69	–	–	–	19.11	101.32
2	6.04	13.94	15.23	46.20	1.82	–	–	19.07	102.30
3	7.87	15.26	11.58	43.30	–	–	–	18.94	96.95
4	10.62	14.22	12.31	41.10	1.86	0.85	–	21.93	102.89
5	6.78	15.30	14.61	45.28	–	–	–	18.72	100.69
6	10.57	16.33	12.35	38.50	–	–	–	20.89	98.64
7	6.10	13.42	13.05	43.81	5.86	–	1.59	17.56	101.39
8	6.18	16.20	14.53	46.54	–	–	–	18.68	102.13

Calculation of the analyses for apfu in (Ni, Co, Fe)AsS

№ an.	Fe	Ni	Co	As	Ir	Pt	Rh	S
1	0.16	0.51	0.38	1.01	–	–	–	0.94
2	0.18	0.39	0.42	1.02	0.02	–	–	0.97
3	0.24	0.45	0.33	0.98	–	–	–	1.00
4	0.30	0.38	0.33	0.87	0.02	0.01	–	1.09
5	0.20	0.43	0.41	1.01	–	–	–	0.95
6	0.31	0.45	0.34	0.84	–	–	–	1.06
7	0.19	0.39	0.38	1.01	0.05	–	0.03	0.95
8	0.18	0.45	0.40	1.02	–	–	–	0.95

Note. An. 1 – sp. 107-4; an. 2–4 – sp. 110-34 (an. 2 and an. 4 – with irarsite micro-admixture); an. 5–6 – sp. 107-4; an. 7–8 – sp. 110-22 (an. 7 – with irarsite micro-admixture).

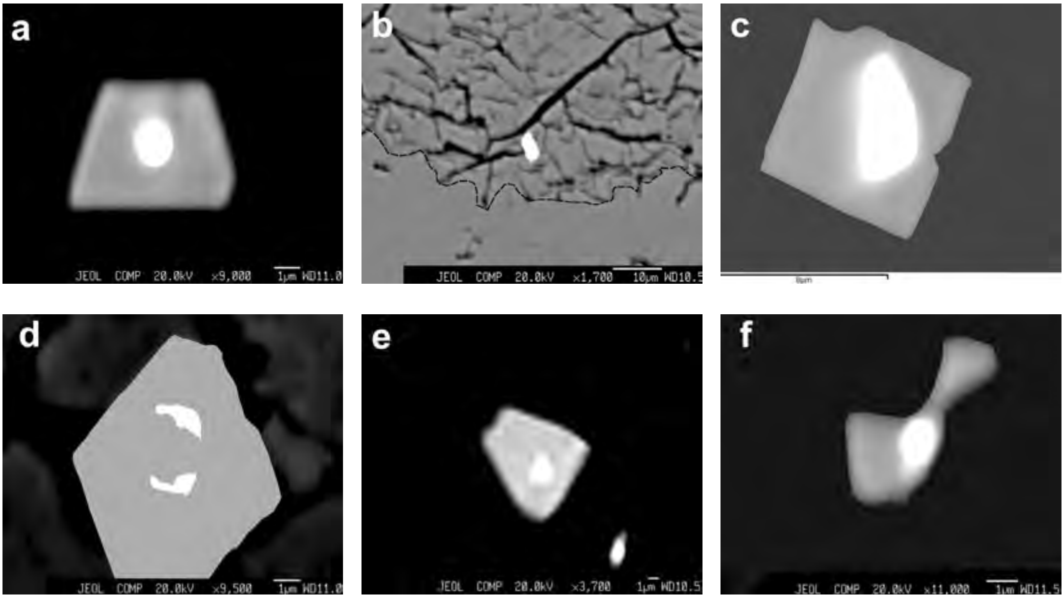

Fig. 2. Segregation shapes of irarsite and its interrelation with ore minerals:
a – rounded phenocryst of irarsite (white) in idiomorphic crystal of sulfoarsenide (pale-grey);
b – Idiomorphic grain of irarsite (white) in pentlandite (grey);
c – isometric rounded grain of irarsite (white) in sulfoarsenide (pale-grey);
d – irarsite hopper-crystal (white) in sulfoarsenide (pale-grey);
e – idiomorphic grain of irarsite (white) in idiomorphic sulfoarsenide (pale-grey);
f – rounded grain of irarsite (white) in sulfoarsenide (pale-grey). BSE images, using JXA JEOL-8100.

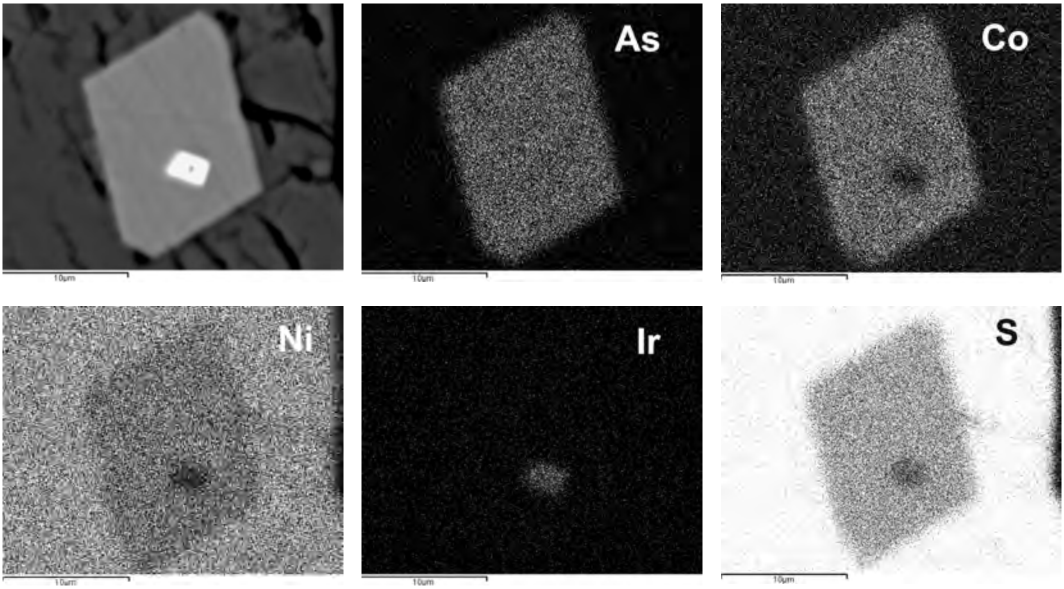

Fig. 3. Idiomorphic crystals of sulfoarsenide and irarsite with inclusions of sperrylite-(?), BSE image and characteristic emission of As, Co, Ni, Ir and S (sp. 107-4).

Table 2. **Chemical composition of irarsite, wt.%**

№, an.	Fe	Ni	Co	As	Os	Ru	Rh	Ir	Pt	S	Total
1	3.36	5.61	4.34	32.49	–	–	0.96	38.57	–	12.60	97.93
2	3.04	5.08	3.01	30.86	–	–	–	44.49	–	11.64	98.12
3	2.71	4.53	2.64	28.83	–	–	–	44.00	6.00	11.35	100.06
4	3.47	3.96	1.20	30.88	–	–	–	45.19	5.43	10.68	100.81
5	3.61	4.02	1.49	29.86	–	–	–	45.06	5.07	11.50	100.61
6	3.80	5.76	4.86	33.82	–	–	0.92	31.79	6.92	12.51	100.38
7	4.20	5.89	4.77	34.49	–	–	1.03	30.75	6.98	13.35	101.46
8	2.33	7.97	4.29	32.52	–	–	0.92	36.08	–	13.32	97.43
9	–	–	–	24.96	1.48	–	2.65	59.62	1.20	10.79	100.70
10	–	–	–	34.50	–	9.40	7.20	23.00	12.60	11.60	98.30

Calculation of the analyses for apfu in irarsite (Ir,Ru,Rh,Pt,Fe,Ni,Co)AsS

№, an.	Fe	Ni	Co	As	Os	Ru	Rh	Ir	Pt	S
1	0.14	0.23	0.18	1.02	–	–	0.02	0.48	–	0.93
2	0.13	0.12	0.13	1.03	–	–	–	0.58	–	0.91
3	0.13	0.19	0.11	0.99	–	–	–	0.59	0.08	0.91
4	0.16	0.18	0.05	1.06	–	–	–	0.62	0.07	0.86
5	0.15	0.18	0.06	1.02	–	–	–	0.60	0.07	0.92
6	0.15	0.23	0.19	1.04	–	–	0.02	0.38	0.09	0.90
7	0.17	0.22	0.18	1.03	–	–	0.02	0.35	0.09	0.94
8	0.09	0.32	0.16	1.04	–	–	0.02	0.42	–	0.95
9	–	–	–	0.99	0.02	–	0.05	0.92	0.02	1.00
10	–	–	–	1.18		0.24	0.18	0.30	0.17	0.93

Note. Analyses: 1–8 – irarsite, Shanuch deposit (Kamchatka); an. 1–3 – sp. 107-4 (an. 1, 2 – edge, irarsite; an. 3 – centre: irarsite with sperrylite-? micro-admixture); an. 4–5 – sp. 132-15 (irarsite inclusion in oxidised pentlandite); an. 9 – irarsite from copper-nickel ores from ultrabasic rocks from Kola peninsula, after Distler et al., 1981; an 10 – irarsite from platinum ores from Onverwacht mine, RSA, after Genkin et al., 1966.

double reflection and anisotropy were not observed. In chemical composition of irarsite predominate iridium, arsenic and sulfer, that supports diagnostics of this mineral. It has constantly admixtures of iron, nickel and cobalt, sometimes of rhodium and platinum (Table 2). It should be noted that hightened concentrations of platinum in irarsite are caused in one case (specimen 107-4) by presence at the spot of analysis of sperrylite microinclusion (?), in other cases — platinum is evenly distributed through the whole irarsite grain (specimen 132-15, Fig. 2b; specimen 110-34, Fig. 2c). In the whole, the mineral is satisfactorily calculated for formula close to the theoretical one (Ir, Rh, Pt, Fe, Ni, Co)AsS, displaying insignificant deficit of sulfur and surplus of arsenic. Presence of admixtures of nickel, cobalt and iron, presumably, is specific feature of irarsites at the Shanuch deposit. It is related to localization of irarsite in massive cobalt-copper-nickel ores of this deposit. It should be considered also wide isomorphism of elements of iron and platinum groups in the minerals of cobaltite and pyrite (Genkin *et al.*, 1966). Heightened contents of platinum and rhodium in irarsite are characteristic for the central and lower parts of the ore body (in contrast to the upper one). Close by composition irarsites are known in ores of the deposits of Myanmar, Columbia, Canada (Cabri *et al.*, 1996), Russia (Distler, Laputina, 1981; Shcheka *et al.*, 1991; Nekrasov *et al.*, 1994).

Conclusion

In sulfide copper-nickel ores of the Shanuch deposit at Kamchatka for the first time irarsite, which associated with sulfoarsenides was discovered. Irarsite forms microinclusions of rounded and oval form, sometimes idiomorphic small crystals and grains of skeletal form in grains of sulfoarsenides and in pentlandite. The irarsite formula is close to theoretical one with admixture of Ni, Co and Fe. This find adds a list of minerals of the platinum group elements (Poletaev, 2004), discovered in the ores of the Shanuch deposit.

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NEW DATA ON THE ACCESSORY MINERALS OF THE SEMENINSKAYA PIT OF THE ADUY PEGMATITE FIELD (URALS)

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Composition and forms of separations of two specimens of "euxenite" from the collections of A.E. Fersman (from the funds of the Fersman Mineralogical Museum, RAS) found to be samarskite-(Y) as well as new findings of samarskite-(Y), ferro- and manganocolumbite, monazite-(Ce), gahnite and spessartine from quartz-albite aggregates of chamber granitic pegmatite from the Semeninskaya pit have been investigated. Samarskite grains are partly replaced by fersmite, and in zones of alteration contain silica (probably opal).

2 tables, 5 figures, 7 references.
Keywords: granitic pegmatites, former collections, composition of accessory minerals, rare earths, evolution of composition.

Among the other mines of the Central Aduy pegmatite field on the territory of the modern Rezhevsky state nature-mineralogical reserve Semeninskaya pit is famous by its history of foundation (probably in the second half of the XIX century), survey and taking of aquamarine, heliodor, smoky quartz and amethyst. It was colorfully described in several publications (Fersman, 1962; Emlin *et al*., 2002; Malikov *et al*., 2007, etc.).

Vein of granitic pegmatite striking in 30–50° of NE direction and stretching during 125 m with a 8–12 m thickness (up to 0.5–1 m in its thinning part) is traced up to the depth of 39 m by two shafts (Fig. 1) and during 80 m down the dip by boreholes of exploration drilling. Granitic graphic pegmatite of the vein is distinguished by relatively thick inner zone (up to 1–4 m) of coarse-grained albite with muscovite, microcline, quartz, and accessory minerals.

After their attendance of the mine in 1912–1913 A.E. Fersman and B.A. Lindener passed several specimens with "euxenite" to the Mineralogical Museum of the Russian Academy of Sciences. In the same time the owner of the mine M. Belykh at the instance of A.E. Fersman organized the revision of the mine dumps (Malikov *et al*., 2007) in order to search for accessory minerals. Alongside with berill, A.E. Fersman noted magnetite, spessartine, euxenite, and monazite in the vein. According to the results of the geological-exploration works of the Isetsky geological-exploration party in 1977–1980, accessory minerals rarely occurred in the graphic quartz-two-feldspar zone of the vein, but more frequent (and in more large separations) they were found in boundary part between the block two-feldspar zone and zone of coarse-grained albite as well as in cavities within the albitic zone (according to the data of M.B. Arinshtein; see Emlin *et al*., 2002). We have not found publications concerning the composition of these minerals except our data about monazite (Popova *et al*., 2007). We have also found ferro- and manganocolumbite, samarskite-(Y), gahnite, and fluorapatite in aggregates with albite and quartz in the mine dumps. Below we give the results of investigation of some minerals (also including "euxenite" of the specimens № 21934 and № 21935 from the funds of the Fersman Mineralogical Museum (FMM). Unfortunately, we could not affirm the presence of this mineral. Separations of "euxenite" proved to be samarskite-(Y). Macrodiagnostics of these minerals is not so simple; samarskite in spalls is frequently similar with euxenite and polycrase seemingly.

Samarskite-(Y) from the specimens of FMM occurs as brown-black and black-brown grains up to 1 sm in size forming ingrowths in albite with specific reddening around them (Fig. 2a). The grain from the specimen № 21934 is brown-black and contains ingrowths of albite and microinclusions of monazite-(Ce) near its margin. Composition of samarskite-(Y) mostly consists of Nb, Fe, Y, sum of *TR* equals to 10.54 wt.%. It also contains few Ti that differ it from euxenite and reveal its similarity with samarskite-(Y). Its empirical formula is well calculated to typical formulas ABO_4 (Table 1, analysis 1): $(Fe_{0.38}Y_{0.28}REE_{0.16}U_{0.12}Th_{0.02})_{0.96}(Nb_{0.85}Ti_{0.10}Ta_{0.09})_{1.04}O_{3.87}$.

Some deficit of oxygen appears to be due to partial hydrous alteration of metamict mineral. Samarskite is partially altered. Debye powder pattern of the grain calcined up to 1000°C contains the following main lines (*d/n*, Å; *I*): 3.99 (9); 3.16 (10); 3.01 (9); 2.48 (9); 1.883 (8); 1.825 (9); 1.561 (7) (analyst E.D. Zenovich; analysed at: URS-2.0, RKD-57.3 mm, Fe-anode). These lines are most close to X-ray pattern of the altered

Fig. 1. Headframe of the shaft on the Semeninskaya vein, 2009. (Photo by O.L. Buslovskaya).

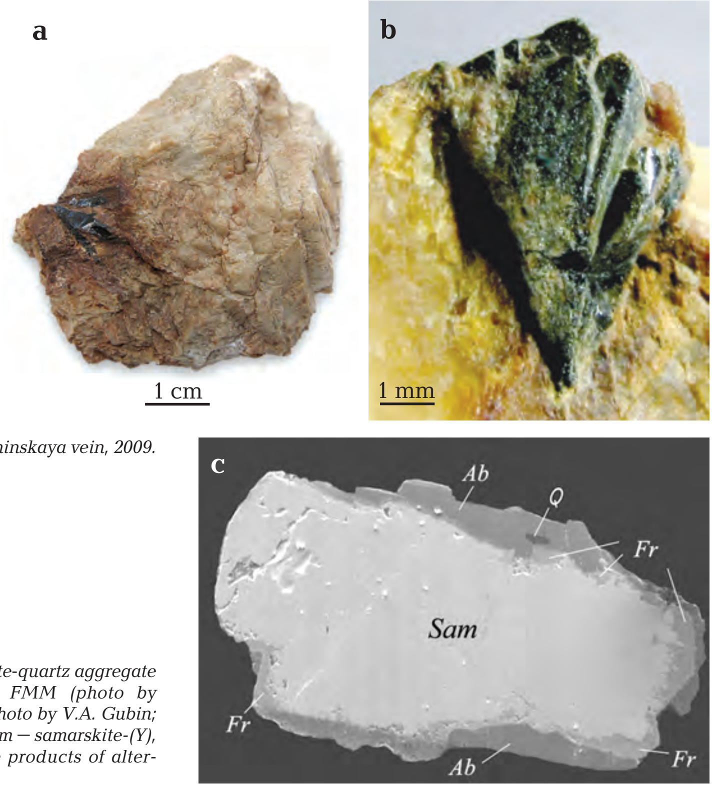


Fig. 2. Samarskite-(Y) in albite (a) and albite-quartz aggregate (b, c). a — specimen № 21934 from FMM (photo by V.Y. Karpenko); b, c — specimen Г1 (b — photo by V.A. Gubin; c — photo by V.A. Kotlyarov; BSE image. Sam — samarskite-(Y), Fr — fersmite (predominating among the products of alteration), Ab — albite, Q — quartz.

Table 1. **Composition of samarskite and pseudomorphs upon it in the Semeninskaya pit from the Aduy**

№ an.	1		2		3		4	5
	wt.%	apfu	wt.%	apfu	wt.%	apfu	wt.%	apfu
TiO_2	2.81	0.10	3.88	0.14	3.20	0.11	9.50	7.94
FeO	9.80	0.38	8.34	0.33	8.55	0.34	7.10	5.83
MnO	–	–	–	–	–	–	0.17	1.41
CaO	–	–	–	–	–	–	4.92	4.71
Nb_2O_5	40.55	0.85	39.64	0.85	38.60	0.82	38.07	47.40
Ta_2O_5	6.94	0.09	8.28	0.11	7.39	0.09	21.15	12.85
Y_2O_3	11.40	0.28	11.24	0.28	11.92	0.30	–	1.46
Ce_2O_3	–	–	–	–	–	–	1.45	0.85
Nd_2O_3	0.88	0.01	1.15	0.02	0.88	0.01	0.72	0.56
Sm_2O_3	1.33	0.02	1.25	0.02	1.49	0.02	–	0.17
Eu_2O_3	0.78	0.01	0.81	0.01	0.79	0.01	–	–
Gd_2O_3	2.68	0.04	2.70	0.04	2.61	0.04	–	0.10
Dy_2O_3	2.25	0.04	2.56	0.04	2.19	0.03	–	–
Tb_2O_3	0.61	0.01	0.83	0.01	0.50	0.01	–	–
Yb_2O_3	2.01	0.03	2.17	0.03	1.80	0.03	–	–
ThO_2	2.12	0.02	2.17	0.02	1.95	0.02	7.70	5.57
UO_2	11.58	0.12	8.76	0.09	14.45	0.15	2.50	2.90
Total	95.84	2.00	93.78	2.00	96.32	2.00	93.28	91.75
	TR = 10.54	O = 3.87	*TR* = 11.47	O = 3.92	*TR* = 10.26	O = 3.89	*TR* = 2.17	*TR* = 1.68
n	4		3		6		5	2

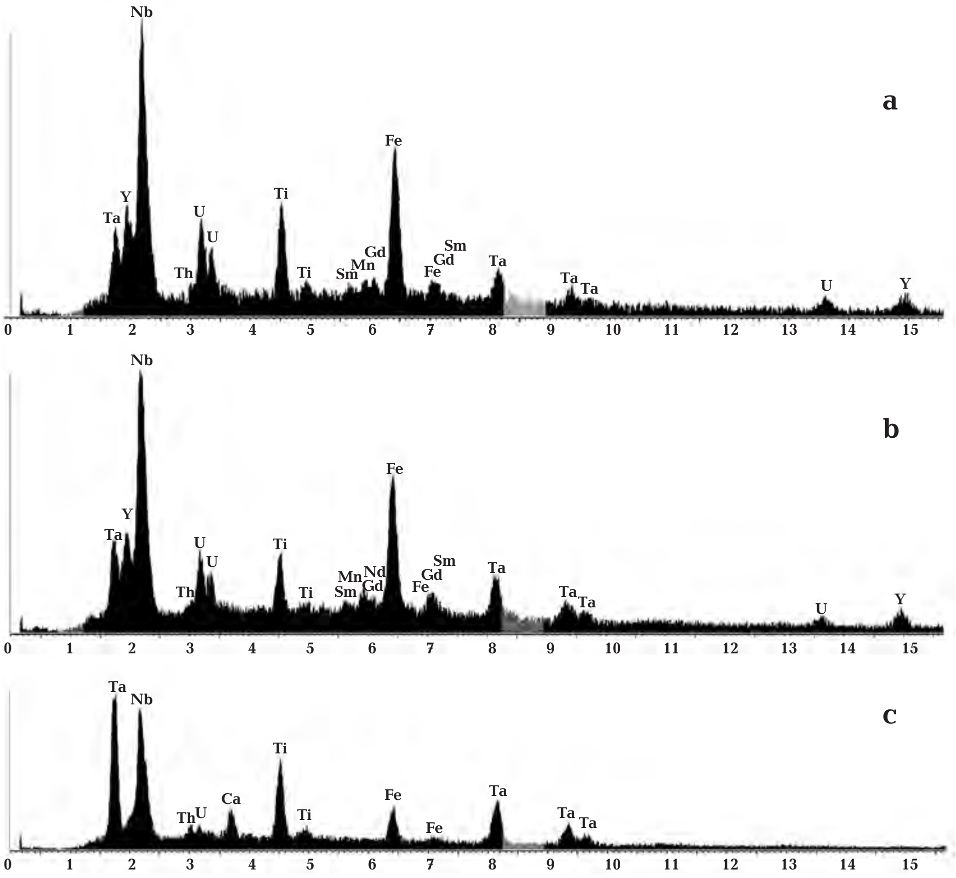
Note: Analyses 1–3 —samarskite-(Y): 1 — specimen № 21934 FMM, 2 — specimen № 21935 FMM, 3 — specimen Г1; analyses 4, 5 — fersmite pseudomorph replacing samarskite-(Y), specimen Г1. Average concentrations are shown (n — number of analyses) according to the data of microprobe analysis (REMMA-202M with energy-dispersion spectrometer Link LZ-5, analyst V.A. Kotlyarov; JXA-733 with wave-dispersion spectrometers, analyst E.I. Churin).

Table 2. **Composition of monazite-(Ce) from the Semeninskaya pit (wt.%)**

№ an.	Grain	Site	SiO_2	P_2O_5	CaO	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	ThO_2	UO_2	Total
1	1	center	–	27.97	–	3.67	21.28	3.79	17.07	17.20	6.03	2.07	–	99.08
2		center	0.11	27.79	0.05	2.85	20.14	5.68	16.16	16.56	7.90	2.48	0.20	99.91
3		margin	–	27.99	–	3.54	20.54	3.39	16.80	18.19	6.66	2.12	–	99.23
4		margin	0.34	27.57	–	2.86	20.36	5.83	16.22	16.25	7.18	2.66	0.34	99.59
5	2	center	1.31	26.59	0.16	5.81	28.39	4.24	16.55	6.70	1.85	5.87	1.28	99.17
6		center	2.17	25.51	0.08	5.59	29.42	6.37	16.97	7.00	–	6.91	–	100.02
7		margin	1.62	26.72.	0.11	5.38	28.47	6.02	17.31	7.36	–	6.55	–	99.54
			Empirical formulas (based on 2 cations)											
1		center	$(Ce_{0.32}Nd_{0.25}Sm_{0.24}Gd_{0.08}La_{0.06}Pr_{0.06}Th_{0.02})_{1.03}P_{0.97}O_{3.98}$											
3		margin	$(Ce_{0.31}Nd_{0.25}Sm_{0.26}Gd_{0.09}La_{0.05}Pr_{0.05}Th_{0.02})_{1.03}P_{0.97}O_{3.98}$											
5		center	$(Ce_{0.43}Nd_{0.24}Sm_{0.10}La_{0.09}Pr_{0.06}Th_{0.05}Gd_{0.02}Ca_{0.01}Y_{0.01}U_{0.01})_{1.02}(P_{0.93}Si_{0.05})_{0.98}O_{3.99}$											
7		margin	$(Ce_{0.43}Nd_{0.25}Sm_{0.10}Pr_{0.09}La_{0.08}Th_{0.06})_{1.01}(P_{0.92}Si_{0.06})_{0.98}O_{3.99}$											

Note: Analyses 1, 3, 7 – microprobe analyzer JXA-733 Superprobe (analyst E.I. Churin), (analyses 1, 3 are proceeded with the help of energy-dispersion spectrometer INCA, analysis 7 – with the help of wave-dispersion spectrometers); analyses 2, 4–6 – REMMA-202M with energy-dispersion spectrometer Link LZ-5 (analyst V.A. Kotlyarov); sum of the analysis 5 includes 0.42 wt.% of Y_2O_3. Dash – not detected.

Fig. 3. Energy-dispersion spectra of samarskite-(Y) (a, b) and replacing it fersmite (c):
a – specimen № 21934 FMM; b, c – specimen Г1.



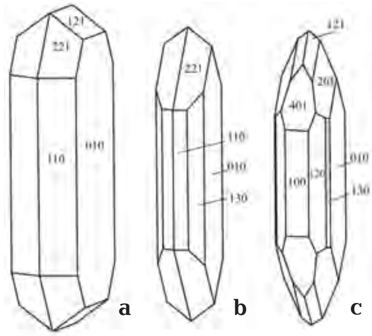


Fig. 4. Form of ferrocolumbite crystals from the Semeninskaya vein.

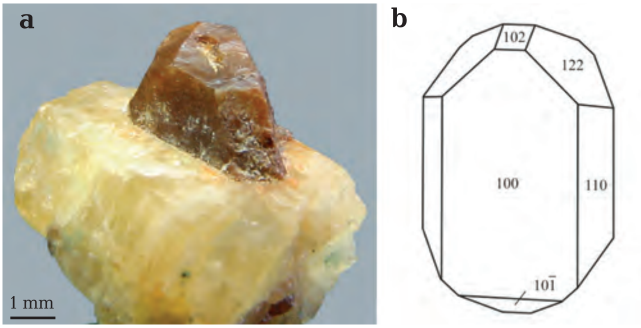


Fig. 5. Monazite-(Ce) from the Semeninskaya vein: a — monazite in yellow beryl from albite (photo by V.A. Gubin), b — idealized form of crystal.

samarskite (samarskite altered) from the data base JCPDS.

Samarskite-(Y) from the other specimens of FMM (№ 21935) is black-brown in color and also contains microinclusions of albite near its margins. During the microprobe investigations it was established that only central part of the grain relatively not altered. Its composition differs from the former specimen by lower amounts of Fe and U oxides and by higher amounts of Ti, Ta and rare earths. Its empirical formula $(Fe_{0.33}Y_{0.28}REE_{0.17}U_{0.09}Th_{0.02})_{0.89}(Nb_{0.85}Ti_{0.14}Ta_{0.11})_{1.10}O_{3.92}$ (Table 1, analysis 2).

In 1975 V.A. Gubin has found in albite-quartz aggregate fan-shaped joint of elongated tabular brown-black small crystals of samarskite-(Y) 6 mm in size with the following habitus forms: {100}, {010} and {011} (Fig. 2b). According to its composition, it is close to the specimens from FMM with a little higher concentration of UO_2 (Table 1, analysis 3); its formula $(Fe_{0.34}Y_{0.30}REE_{0.17}U_{0.15}Th_{0.02})_{0.98}(Nb_{0.82}Ti_{0.11}Ta_{0.09})_{1.02}O_{3.89}$.

The mineral that partly replaces crystals and grains of samarskite-(Y) from their periphery (Fig. 2c) is characterized by relatively high concentrations of CaO (up to 3 — 5 wt.%) and practically does not contain yttrium and rare earth elements of its group. Amounts of Ti, Ta and Th are twice or thrice higher than in samarskite-(Y) but U concentration is low (Fig. 3, table 1, analyses 4 — 5). Due to the presence of microrelicts of samarskite, we could not obtain its satisfactory analyses. Both varieties distinguished by the Fe, Nb and Ta ratio are very close in their composition to the ferrous fersmite. Their calculated formulas are as follows: $(Fe_{0.40}Ca_{0.35}Th_{0.12}REE_{0.06}U_{0.04}Mn_{0.01})_{0.98}(Nb_{1.16}Ti_{0.48}Ta_{0.39})_{2.03}O_{6.0}$ (analysis 4) и $(Ca_{0.33}Fe_{0.32}Mn_{0.08}Th_{0.08}Y_{0.05}U_{0.04}REE_{0.03})_{0.93}(Nb_{1.42}Ti_{0.40}Ta_{0.23})_{2.05}O_{6.04}$ (analysis 5). Several reflections of Debye powder pattern of the calcined grain of the altered samarskite correspond to fersmite. Except for assumed fersmite, in sites of the samarskite alteration during the analysis we have found micrograins of manganocolumbite, monazite-(Ce), and zircon. In a number of analyses there is increased concentration of SiO_2 (up to 3 — 15 %), probably due to hypergene opal or microinclusions of albite.

Manganocolumbite from the inclusion in the altered samarskite (fersmite) has a following composition (wt.%): FeO 9.30; MnO 12.94; Nb_2O_5 70.41; Ta_2O_5 3.01; TiO_2 2.42; WO_3 0.21; UO_2 1.47; total 99.76 (admixture of U, probably, it is caused by surrounding minerals — samarskite-(Y) and fersmite). Analysis is calculated to the following formula: $(Mn_{0.62}Fe_{0.44})_{1.06}(Nb_{1.81}Ti_{0.10}Ta_{0.05})_{1.96}O_{5.96}$.

High-manganese ferrocolumbite in the aggregate of albite with yellow beryl, quartz and muscovite was found by V.A. Gubin in 1969 in the form of plates fragments of coarse crystals (2.6 mm wide). It also occurs in schlich of the shaft dump. Its larger grains (2 — 5 mm) have elongated-tabular shape with the ratio $c : b = 3$ and facets {110}, {010}, {221}, {021}. Its smaller grains (1 mm and less) are more elongated with the ratio $c : b = 4$ and appearance of facets of additional prisms {120}, {130}, {401}, {261} and pinacoid {100} (Fig. 4). Its composition (wt.%): FeO 10.71; MnO 9.56; Nb_2O_5 69.52; Ta_2O_5 8.19; TiO_2 1.96; total 99.94 (conditions of recording: REMMA-202M, equipped with Link LZ-5 energy dispersion spectrometer, analyst V.A. Kotlyarov); empirical formula $(Fe_{0.51}Mn_{0.47})_{0.98}(Nb_{1.81}Ta_{0.13}Ti_{0.08})_{2.02}O_6$.

In the pegmatite vein Puzyr` (380 m to the north of the Semeninskaya pit) ferrocolumbite similar in composition occurs in graphic pegmatite and high-ferrous manganocolumbite occurs in the block zone (Emlin *et al.*, 2002). In the Yuzhnaya mine high-ferrous manganocolumbite is described in topazes from druse cavities. In the block zone occurs ferrocolumbite with significantly lower (two times or more) concentrations of Mn and Ta (Shagalov *et al.*, 2004).

Monazite-(Ce) is found as ingrowths of partly faceted red-brown grains up to 4 – 25 mm in size in albite and yellowish translucent beryl (from cavity in albite). Monazite crystals have tabular shape (Fig. 5). This monazite (Table 2, analyses 1 – 4) is distinguished from the monazites of other veins of the Aduy field by highest concentrations Nd and Sm and lowest – Th (Popova *et al.*, 2007); micrograin of the monazite-(Ce) enriched in Nd and Sm is found also in samarskite-(Y) from the specimen № 21934 FMM. Other type of monazite-(Ce) crystals (elongated-tabular yellow-brown, probably from the block zone of pegmatite) is characterized by lower concentration of Sm_2O_3 (6 – 7 wt.%), more high – Ce_2O_3 and ThO_2 (Table 2, analyses 5 – 7) and is closer in composition to the monazites from the block zone of the Yuzhnaya pegmatite vein (Vakhrusheva *et al.*, 2004) and muscovite-quartz-albite zone of the Telephonka vein (Popova, Churin, 2009).

Gahnite in quartz-albite aggregate is found in the form of green-black and dark blue-green crystals and grains (up to 2 – 5 mm and larger) with parts of habitus facets {111}, {110} (narrow), regularly with predominant induction surfaces with albite and quartz. ZnO content in it is about 33 wt.%, calculated formula is as follows: $(Zn_{0.72}Fe_{0.24}Mn_{0.03})_{0.99}Al_{2.01}O_4$. According to their form and composition, they are similar to gahnite crystals from quartz-albite zone of the Telephonka pegmatite (Emlin *et al.*, 2002). Orange-red spessartine contains about 61% of Mn-end-member (16 – 17 wt.% of FeO), and red-orange variety from albite contains 77% of Mn-end-member (10 – 11 wt.% of FeO).

New data on the accessory minerals of the Semeninskaya pit confirm its individuality (marked by A.E. Fersman due to its thick albite zone of the vein). Specimens of "euxenite" from the collections of A.E. Fersman investigated by us are proved to be samarskite-(Y) partly replaced by fersmite and microinclusions of other minerals. Columbites evolutionated in composition from earlier ferruginous to late manganese that is typical of many veins of granitic pegmatites from different regions. Irrespective of Sm_2O_3 concentration in monazites of different veins from the Aduy field, share of Sm in composition of monazite-(Ce) grew during its crystallization.

The data given in the article show expediency of revision of mineralogy of many other veins of the ancient mines and deposits of the last years, especially in rich mineralogical collections of museums.

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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, pyrophanite, 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 sulphides. 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 sulphides 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 seguence 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 fenites 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, fenites, 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 (Gorstka, 1971) .

The numerous altered (fenitized) xenoliths from several meters up to several kilometres in size are located at the contact zone between the foyaite core and ristschorrites. In general, they are located within Eveslogchorr, Yukspor, Kukisvumchorr, Poachvumchorr, 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, composed 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 scientists (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 (Kaskasnyunchorr 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

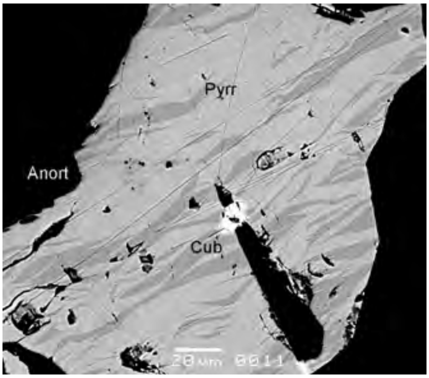


Fig. 1. Individual of pyrrhotite (Pyrr) consisting of two similar chemical varieties (light areas correspond to the enriched in iron), with ingrowths of cubanite (Cub) in anorthoclase matrix (Anorth), Kukisvumchorr Mt. (BSE-image).

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., 2000_1*;*

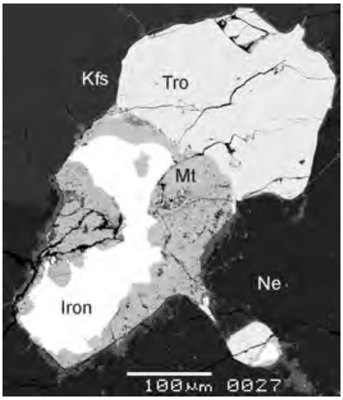


Fig. 3. Troilite (Tro) grain in close association with native iron (Iron) [which is surrounded by magnetite rim], potassic feldspar (Kfs) and nepheline (Ne), Partomchorr Mt. (BSE-image).

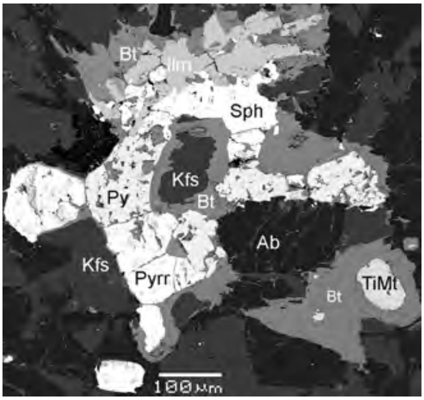


Fig. 4. Intergrowth of pyrite (Py), pyrrhotite (Pyrr) and sphalerite (Sph) in association with ilmenite (Ilm), biotite (Bt), Ti-magnetite (TiMt), albite (Ab) and potassic feldspar (Kfs) (BSE-image).

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, 2000_2) 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 primary 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.*, 1978_2). It occurs as ingrowths up to 40 μm in

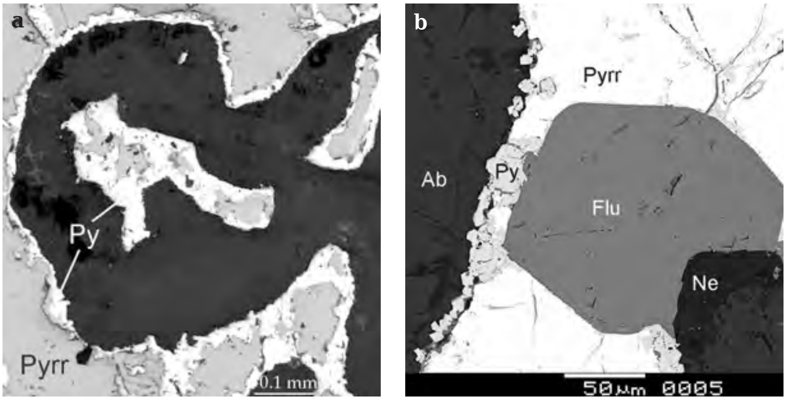


Fig. 5. Overgrowth and replacement of pyrrhotite (Pyrr) by pyrite (Py), in association with albite (Ab), nepheline (Ne) and fluorite (Flu), Kaskasnyunchorr Mt. (a — in reflected light, nicols //), b — BSE-image).

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., 2000$_1$; 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.* (2000$_2$) 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). According 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

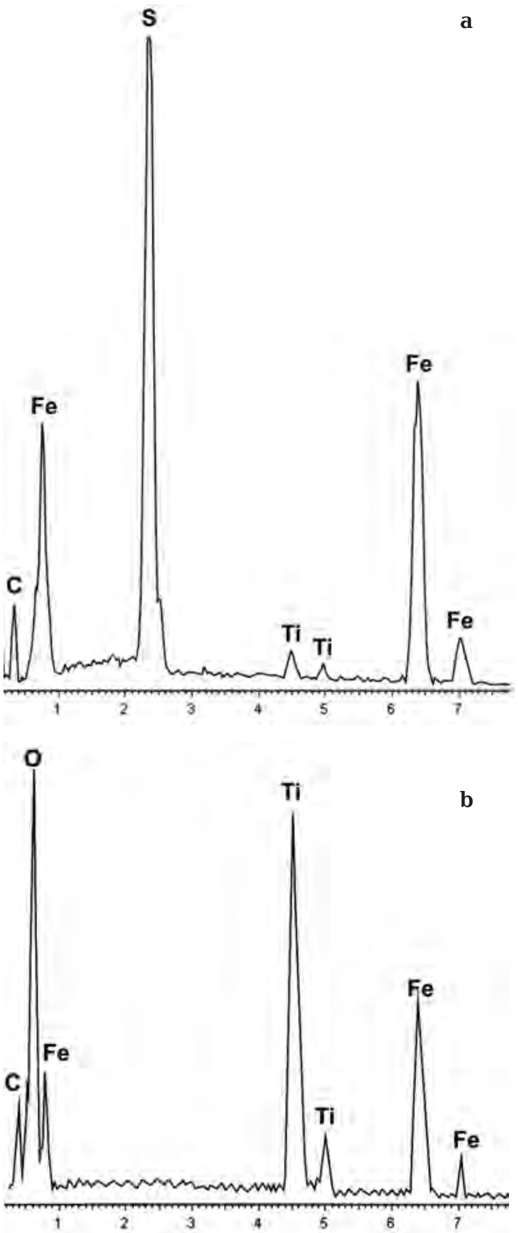


Fig. 6. Energy dispersive spectra of Ti-bearing pyrrhotite (a) and ilmenite (b) from a xenolith on Kaskasnyunchorr Mt. Peak of C corresponds to the carbon film of the sample.

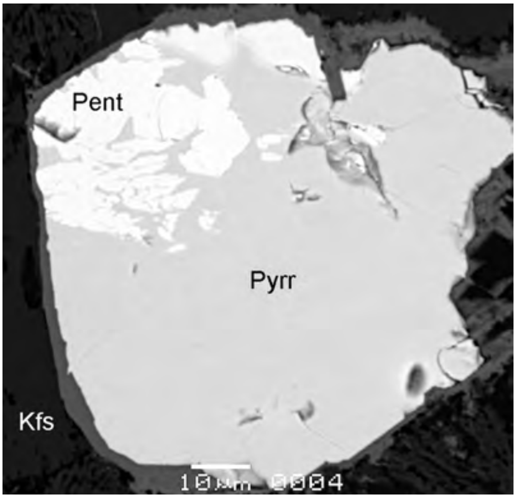


Fig. 7. Pentlandite (Pent) ingrowths in pyrrhotite (Pyrr) grain, in a matrix of potassic feldspar (Kfs), Kaskasnyunchorr Mt. (BSE-image).

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**

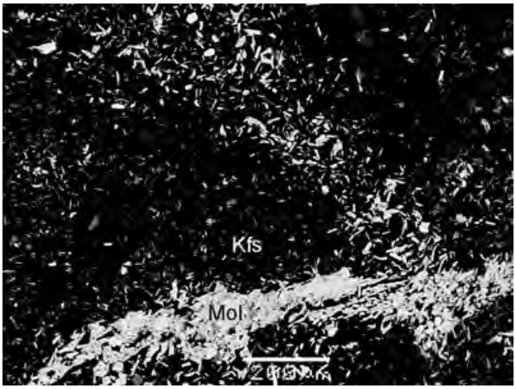
	1	2	3	4	5	6	7	8
				wt.%				
Fe	0.36	0.50	–	n/a	–	0.0–1.3	–	–
Mo	60.85	60.92	60.11	48.34	43.28	51.9–58.8	59.94	–
W	–	0.32	–	14.87	22.70	0.1–5.8	–	73.48
S	35.81	36.06	39.30	37.46	32.32	39.5–41.1	39.77	25.60
Total	97.02	97.80	99.41	100.67	98.30		99.71	99.08
				apfu, for 2 S				
Fe	0.01	0.02	–		–	0.00–0.04	–	–
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., 2000_2, 7 — Korchak, 2008.

Barkov *et al.* (20001) 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 $(\mathrm{Fe}_{0.82\text{-}1.00}\mathrm{Mn}_{0.00\text{-}0.01})(\mathrm{Nb}_{2.95\text{-}3.17}\mathrm{V}_{0.00\text{-}0.04}\mathrm{Ti}_{0.00\text{-}0.01})\mathrm{S}_6$ (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.



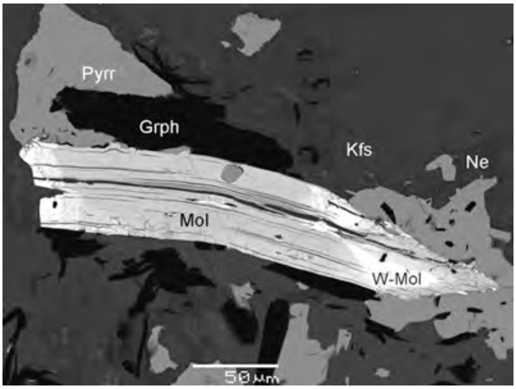
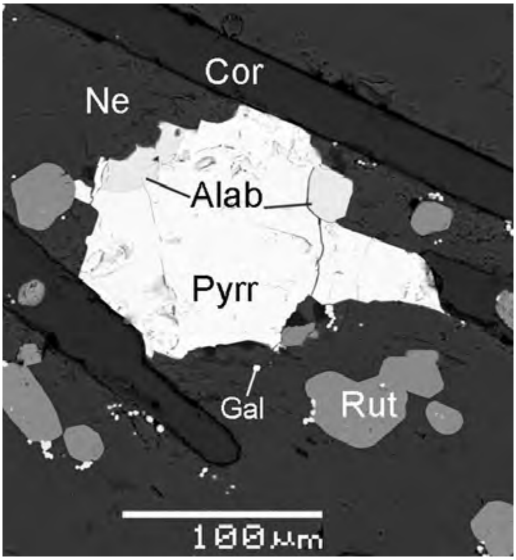


Fig. 8. Molybdenite (Mol) in the predominantly potassic feldspar (Kfs) fenites of Lastochkino Gnezdo (BSE-image).
Fig. 9. Molybdenite crystal from Kaskasnyunchorr Mt. containing areas with different chemical composition — with tungsten (W-Mol) (up to 14.9 wt. % W) and without it (Mol), in association with graphite (Grph), pyrrhotite (Pyrr), nepheline (Ne) and potassic feldspar (Kfs) (BSE-image).



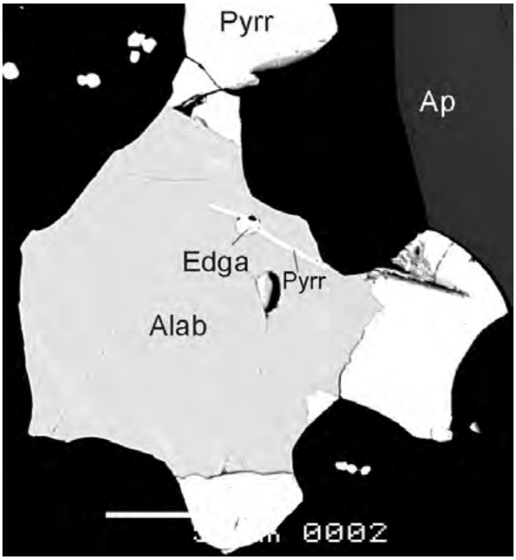


Fig. 10. Alabandite (Alab) and pyrrhotite (Pyrr) intergrowth in corundum-nepheline (Cor-Ne) rock, in association with rutile (Rut) and galena (Gal), Kaskasnyunchorr Mt. (BSE-image).
Fig. 11. Lamellar inclusion of edgarite (Edga) in alabandite (Alab) grain in close association with pyrrhotite (Pyrr) and 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., 2000$_1$.
** – total also includes 0.85 wt. % As (0.01 apfu).*

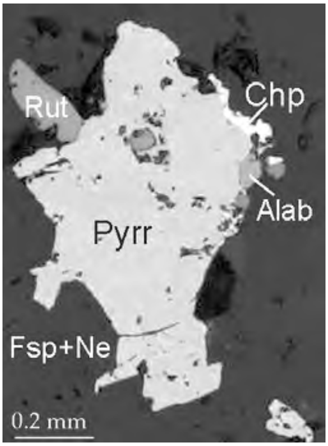


Fig. 12. Chalcopyrite (Chp), pyrrhotite (Pyrr) and alabandite (Alab) intergrowth in the feldspar-nepheline (Fsp+Ne) rock with rutile (Rut), Kaskasnyunchorr Mt. (in reflected light, nicols //).

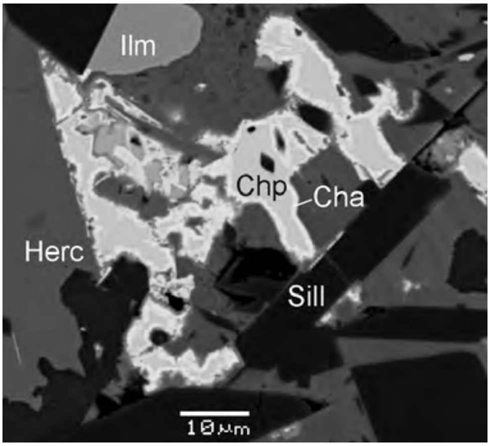
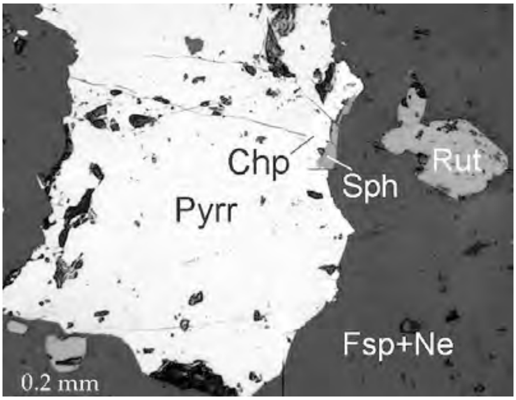


Fig. 13. The rim of a pure copper sulphide (chalcocite? – Cha) on chalcopyrite (Chp) in albite-hercynite-sillimanite (Herc, Sill) rock with ilmenite (Ilm), Kukisvumchorr Mt. (BSE-image).

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-2H 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).



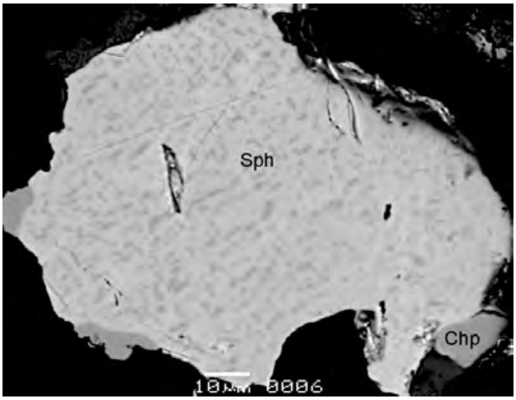


Fig. 14. Sphalerite (Sph), pyrrhotite (Pyrr) and chalcopyrite (Chp) intergrowth in feldspar-nepheline (Fsp+Ne) rock with rutile (Rut), Kaskasnyunchorr Mt. (in reflected light, nicols //).

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., 2000$_1$. * — 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 löllingite is due to sulphur deficiency). A tangible 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 insulficiently studied sulphides which were

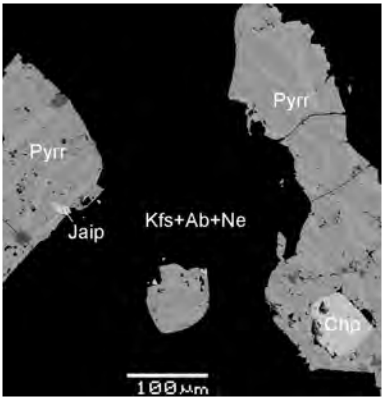


Fig. 16. Jaipurite (Jaip) ingrowth in pyrrhotite (Pyrr) in association with chalcopyrite (Chp) in potassic-feldspar-albite-nefeline (Kfs+Ab_Ne) rock, Yukspor Mt. (BSE-image).

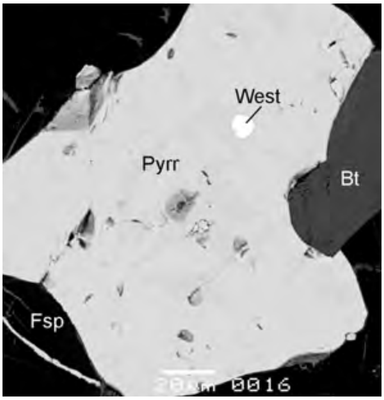


Fig. 17. Inclusion of westerveldite (West) in pyrrhotite (Pyrr) in association with biotite (Bt) and feldspar (Fsp), Kukisvumchorr Mt. (BSE-image).

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 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 (pre-eminently S and Mn) were found.

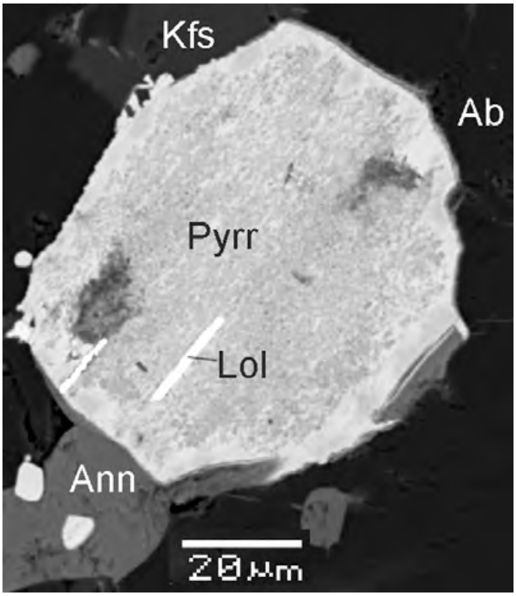


Fig. 18. Ingrowths of lö llingite (Lol) in pyrrhotite (Pyrr) in annite-potassic-feldspar-albite rock (Ann, Kfs, Ab), Lastochkino Gnezdo (BSE-image).

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, Eveslogchorr 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 meteorites. 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 — containing 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 → Zn → Fe → Mn,W,V → Nb,Cr → Ti → Mg,Ca → 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.

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FEATURES OF ARSENOSULVANITE FROM THE LEBEDINOE DEPOSIT, CENTRAL ALDAN

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The results of examination of arsenosulvanite from the Lebedinoe deposit are discussed. The comparison with available published data of arsenosulvanite and colusite indicated that arsenosulvanite studied here is significantly different from colusite in both content of species-forming minerals and set of admixtures. Based on the electron microprobe data, X-ray diffraction study, and taking into account data by Frank-Kamenetskaya (2002) that arsenosulvanite and colusite are two structural modifications of compound $V_2Cu_{24}As_6S_{32}$, we conclude arsenosulvanite as independent and incorrectly discredited mineral species (Burke, 2006).

2 figures, 4 tables, 25 references.
Keywords: arsenosulvanite, sulvanite, colusite, Lebedinoe deposit.

Introduction

A.G. Betekhtin (1941) described arsenosulvanite, $Cu_3(As,V)S_4$, for the first time from the ore of unknown deposit in Mongolia. The specimens placed at Betekhtin's disposal were "bronze-yellow; the Mohs hardness 3.5; density 4.01; megascopally and microscopically, they were not different from sulvanite and were isotropic". According to two bulk analyses, a new mineral contained Cu, S, As, and V; the content of latter is significantly lesser (4.16, 5.20 wt.%) than in sulvanite, Cu_3VS_4 (11.8 – 13.7 wt.%). Concentration of As in the new mineral was 11.67 and 12.8 wt.%. Betekhtin measured As in arsenosulvanite few times to resolve a problem of probable As→V substitution and revealed oscillating As concentration with the least concentration of 5.1 wt.%. Microscopically, inclusions of other minerals in the samples studied were not observable. Despite this, physical properties of arsenosulvanite were not significantly variable. This fact provided the basis for the conclusion of isomorphic substitution of As for V in the structure of this mineral. In addition, Betekhtin (1941) discussed chemical similarity of arsenosulvanite and enargite and luzonite, which are polymorphous modifications (orthorhombic and monoclinic, respectively) of Cu_3AsS_4, and similar physical properties and crystal structure of arsenosulvanite, $Cu_3(As,V)S_4$ (cubic), and sulvanite. It turns out that there is probably isomorphic substitution in the Cu_3AsS_4-$Cu_3(As,V)S_4$ series, i.e., isomorphic substitution between orthorhombic or monoclinic enargite or luzonite and cubic sulvanite occurs. This contradiction could be resolved that arsenosulvanite is not cubic or Cu_3AsS_4 compound should have cubic modification, or admixture of V stabilizes high-temperature cubic Cu_3AsS_4 allowing retention of arsenosulvanite, $Cu_3(As,V)S_4$, at low temperature.

Later, arsenosulvanite was found at the Lebedinoe deposit in Russia, as well as at deposits in Bulgaria, Bolivia, Hungary, Canada, Serbia, and USA.

Kachalovskaya *et al.* (1975) suggested that in reflected light, colusite, arsenosulvanite, and sulvanite are hardly different. Pink-beige colusite, beige-yellowish-greenish arsenosulvanite, and grayish-greenish sulvanite are difficult to be distinguished in intimate intergrowths. "Arsenosulvanite is extremely weakly anisotropic in yellowish brown color. Due to anisotropy, fine-grained and local unclear lattice structure of arsenosulvanite grains is exhibited". These authors reported that relief of arsenosulvanite and colusite is notably higher than that of sulvanite.

Mikheev (1941) performed the first X-ray structural study of the mineral. The structure of arsenosulvanite is similar to "the structure of sphalerite, ZnS, with Zn atoms being substituted by As and V atoms in apices of cube and Cu atoms being substituted for Zn atoms in center of faces". The cubic structure obtained is close to the structure of sulvanite, but differs from the latter in atom arrangement in the unit cell. According to Mikheev (1941), it is caused by the admixture of As. Space group is $P\bar{4}3m$; the unit-cell parameter $a = 5.257$ Å.

Later, Orlandi *et al.* (1981), Khoroshilova (1987, 2002), and Frank-Kamenetskaya *et al.*

(2002) who studied the structure of arsenosulvanite compared structures and chemical compositions of arsenosulvanite, sulvanite, and colusite. As a result, the crystal chemical conception of arsenosulvanite was changed. Previously, the simplified chemical formula $Cu_3(As,V)S_4$ and cubic structure of the sphalerite type with $a = 5.257(3)$ Å derived from X-ray powder diffraction data (Mikheev, 1941) were assigned to sphalerite. Frank-Kamenetskaya *et al.* (2002) revealed cubic cell containing 32 S atoms with double period 10.5 – 10.6 Å in comparison with sphalerite and sulvanite, i.e., superstructure *C2a2a2a*.

Various researchers suggested the following formulas of arsenosulvanite: $Cu_3(As,V)S_4$ (Mikheev, 1941); $Cu_{26}V_2(As, Sb, Sn, Ge)_6S_{32}$ (Orlandi *et al.*, 1981); $Cu_{24}V_2As_6S_{32}$ (Khoroshilova *et al.*, 1984); $Cu_{24+x}V_2(As, Sb)_{6-x}S_{32}$, where $x = 0 - 2$ (Spry *et al.*, 1994). Frank-Kamenetskaya *et al.* (2002) reported the bulk composition of colusite, arsenosulvanite, and V-As-bearing germanite as $Cu^{+}_{24+x+2y}V^{5+}_{2}$ $(As, Sb)^{5+}_{6-x-y}$ $(Sn,Ge)^{4+}_{x}V^{3+}_{y}S_{32}$, where $0 \le x \le 2$, $0.5 \ge y \ge 0$. According to Frank-Kamenetskaya *et al.* (2002), the arrangement of cations in the structures of arsenosulvanite and colusite results in the generalized crystal chemical formula $Cu^{M}_{2-x}V^{M}_{2}Cu_{26-y}(As,Ge,Sn,Sb,V)_6S_{32}$, where Cu^{M}, V^{M} are cations at the interstitial sites ($0.2 \le x \le 2.0$, $2.7 \ge y \ge 0$, respectively). Variable composition of the structures studied is caused by heterovalent isomorphic substitution at the sphalerite site 6*c* (space group $P\bar{4}3n$). Charge imbalance arising as a result of substitution of the As pentavalent cations by cations of lower valence is compensated by additional Cu^{+} cations. Non-stoichiometric compositions are due to vacancies at interstices and sphalerite sites partly occupied by Cu (T'1, T2, T4) and V (T'2) cations. The cited paper clearly indicates that colusite and arsenosulvanite in strict sense are different minerals. Their structures consist of framework of CuS_4 and $(As,Ge,Sb)S_4$ apex-shared tetrahedrons. The main difference is occupation of interstitial sites of tetrahedral framework, where differently ordered V and Cu atoms are arranged (Frank-Kamenetskaya *et al.*, 2002): in colusite, the interstices are occupied by V but in arsenosulvanite, by Cu.

Thus, the contradiction noted by Betekhtin (1941) that consisted in similar chemical composition of arsenosulvanite, and of enargite and luzonite, which are polymorphous modifications of Cu_3AsS_4 (orthorhombic and monoclinic, respectively) as well as in similar physical properties and crystal structure of arsenosulvanite, $Cu_3(As,V)S_4$ (cubic), and of sulvanite is not yet solved. Moreover, Burke (2006) discredited arsenosulvanite as mineral species on the basis of Spry *et al.* (1994). These authors studied the structure of colusite and taking into account data by Riedel and Paterno (1976) who examined the Cu_3VS_4-Cu_3AsS_4 system and revealed intermediate cubic compound $Cu_{12}VAs_3S_{16}$ with X-ray diffraction pattern similar to that of colusite and arsenosulvanite, interpreted an intermediate compound $Cu_{12}VAs_3S_{16}$ or ($Cu_{24}V_2As_6S_{32}$) (that is arsenosulvanite) as Sn-free colusite. However, Spry *et al.* (1994) referred to previous studies rather than gave own data of arsenosulvanite. Nevertheless, they concluded the identity of arsenosulvanite and colusite that provided the basis for discreditation of the former (Burke, 2006). In this case, Burke (2006) did not refer to Frank-Kamenetskaya *et al.* (2002) although this could prevent the discreditation of arsenosulvanite. The aim of this study is to bring out the actual problem of arsenosulvanite as independent mineral species.

Analytical techniques

The thin polished sections were studied with an OPTON microscope. Magnification from ×60 to ×1250 was used; the main operating magnification was ×200. The chemical composition was determined with a CamScan-4D scanning electron microscope equipped with a Link ISIS EDS operating at accelerated voltage 20 kV and beam current of 4 nA. Back-scattered electron images of the objects studied here were obtained. X-ray powder patterns were obtained by photomethod with an URS-50 diffractometer in RKD-57.3 mm camera, Fe*K*α radiation, Mn filter.

Mode of occurrence, physical properties, and chemical composition

M.I. Novgorodova placed at our disposal the specimens from the Lebedinoe mine (Orochon deposit, dump of prospecting pit No 7) collected by A.I. Fastalovich in 1941 and stored in the collection by N.V. Petrovskaya.

Petrovskaya (1973) reported the Lebedinoe ore field in her book "Native Gold":

"Some fields of Late Cambrian gold mineralization, including Lebedinoe are located on the margins of epicratonic troughs in the area of tectonic activation of the ancient Aldan shield".

"The rocks of ancient sequences are highly dislocated and altered as a result of intrusion of large synorogenic granitic plutons. The nearly horizontal sequence of the Cambrian weakly metamorphosed dolomite of 200 m thick overlaps eroded surface of the ancient sequences. Both structural units are intruded by numerous small plutons of the Upper Jurassic-Lower Cretaceous age". These are predominantly stocks, laccoliths, and dykes of intermediate rocks of elevated alkalinity. The mineralization is hosted mainly in the upper structural unit. Altered wall-rocks are ankeritized dolomite and sericitized and silicified igneous rocks.

"The intrusive bodies and crystalline rocks of basement are cut by steep veins composed of quartz (80–90 %); metasomatic sulfide-carbonate bodies (occasionally as vein apophysises) are hosted in dolomite along horizontal faults". The metasomatic bodies consist of ankerite (30%) firstly formed as a result of acting of ore-bearing fluids on the Cambrian dolomite sequence. Ore minerals are dominated by pyrite; significant chalcopyrite was identified; and substantial hematite in some veins was observable. Fastalovich and Petrovskaya (1940), and Petrovskaya (1973) reported abundant galena, sphalerite, pyrrhotite, galenobismutite, and tennantite-tetrahedrite and extremely rare vanadium sulfide, sulvanite. Supergene minerals are varied iron hydroxides, jarosite, copper oxides (cuprite), copper sulfides (chalcocite and covellite), copper and lead carbonates (malachite, azurite, and cerussite), sulfates (gypsum and melanterite), and manganese minerals (Fastalovich and Petrovskaya, 1940).

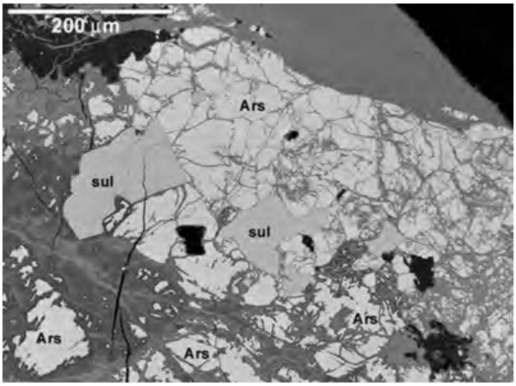
Pyrite, chalcopyrite, fahlores, famatinite, bornite, pyrrhotite, covellite, digenite, anilite, sulvanite, and two phases with the higher relief were found in thin polished sections along with quartz and carbonate. Sulvanite was found only in one of 18 samples studied here as four irregular-shaped grains of ~150×80, ~100×80, ~40×30, and ~40×20 microns in size among arsenosulvanite (Fig. 1). In reflected light, sulvanite is light yellow, isotropic. Two phases with higher relief than that of sulvanite are similar to arsenosulvanite, but they are highly anisotropic. According to chemical study, they are arsenosulvanite. Their light yellow color is slightly lighter than sulvanite (Fig. 1), but darker than that of fahlores (Fig. 2); bireflectance is weak; the anisotropy of one of these phases varies from light gray with greenish tint to pale lilac; the color of the second phase varies from light grey with weak lilac tint to deep pink. Polysynthetic twins are characteristic of the second phase. In addition, secondary minerals formed after ore minerals are planned to study in the future.

Twenty seven electron microprobe point analyses of sulvanite and arsenosulvanite and calculated formulas are given in Table 1 and Table 2, respectively. According to the idealized formula of arsenosulvanite, $Cu_{24}V_2As_6S_{32}$, suggested by Frank-Kamenetskaya *et al.* (2002), the compositions were calculated on the basis of 64 atoms.

The first three analyses in the Tables correspond to that of sulvanite containing low As, Sb, and Pb. It is nearly pure sulvanite. The other compositions correspond to sufficiently pure arsenosulvanite. In arsenosulvanite, 0.0 – 2.9 wt.% Sb that is up to 0.76 *apfu* (an. 24) were detected. Iron content is lower: up to 0.18 *apfu* (an. 18). Two grains of sulvanite which are different in intensity of anisotropy in reflected light are approximately identical in chemical composition. The grain with stronger anisotropy is low-Fe, whereas another grain is Fe-free. Different anisotropy is caused most likely by different sections of the grains. Polysynthetic twins are well observable in sample 242/5 from location 1 (Tables 1, 2, an. 25 – 27). Only 0.50 – 1.71 wt.% Sb corresponding to 0.2 – 0.44 *apfu* were detected in them.

The compositions of sulvanite from the other deposits are given in Tables 1 and 2 (an. 28 – 36).

The sample for the X-ray diffraction study was prepared by the following way: the grains previously measured with electron microprobe were extracted from polished sections and placed into resin ball. The comparison of the X-ray diffraction pattern of arsenosulvanite obtained in this study with those reported by Mikheev (1941) and Kachalovskaya *et al.* (1975) indicated that the former is closer to the X-ray diffraction pattern given by Mikheev (1941) (Table 3). The X-ray diffraction pattern given in this study shows additional weak reflections with intensities I = 1 – 2 (2.52, 1.934, 1.405, 1.365, 1.164) indexed in



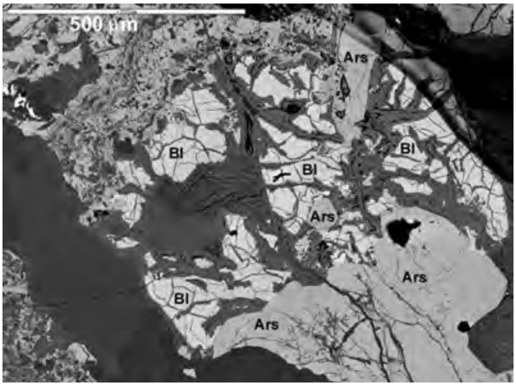


Fig. 1. An assemblage of arsenosulvanite (Ars) (light grey, fractured) and sulvanite (sul) (with pronounced boundaries, darker than arsenosulvanite) enclosed in segregation of secondary minerals (arsenates, sulfates, copper carbonates) and quartz. Sample 242/3 (location 2). BSE image.

Fig. 2. An assemblage of arsenosulvanite (Ars) (light grey, fractured) and tennantite-tetrahedrite (Bl) (light grey) enclosed in segregation of secondary minerals. Sample 242/6 (location 1). BSE image.

space group $P\bar{4}3n$ and are absent in the X-ray diffraction patterns by Mikheev (1941) and Kachalovskaya *et al.* (1975). The strong reflections of sulvanite (5.42, 2.41, 1.910, 1.796, 1.626) are also absent testifying the absence of this mineral in our sample. In the X-ray diffraction pattern obtained by Kachalovskaya *et al.* (1975), there are strong reflections of sulvanite indicating the impurity of this mineral.

Discussion

As aforementioned, the samples of arsenosulvanite studied here are characterized by nearly constant composition (Table 2, an. 1 – 27). Insignificant Fe and Sb were detected. Content of V in these samples exceptionally analysis 26 (where it is 2.01 *apfu*) and in the samples from Japan deposits (Table 2, an. 35, 36) does not exceed 2 *apfu*. The concentration of V reaches 2.26 *apfu* in previously published compositions of sulvanite from the Lebedinoe deposit (Table 2, an. 28 – 30). Arsenosulvanite from Mongolia is the Fe-richest (2.54 – 3.30 *apfu*) (Table 2, an. 31, 32). It should be noted that the compositions were determined by bulk chemical analysis rather than electron microprobe. In addition, only these samples are isotropic. Taking into account this two remarks, elevated vanadium concentration in the compositions of sulvanite from Mongolia are explained by the following reasons: (1) the analyzed samples are cubic colusite rather than arsenosulvanite and therefore they are isotropic and contain more than 2 *apfu* V, and (2) the selection of homogeneous material for bulk analysis is very difficult, therefore mechanical impurity of any V-bearing mineral is possible, for example, mentioned by Petrovskaya (1941) vanadium-mica that fills fractures in sulvanite together with malachite, azurite, and brown iron hydroxides. A.G. Betekhtin who discovered arsenosulvanite noted that *"bright green powder films as oxidizing products are extremely characteristic of weathered surface of arsenosulvanite grains".* He suggested that it is certain intermediate variety between copper vanadates, turanite, $Cu_5(VO_4)_2(OH)_4$, or volborthite, $(Cu,Zn,Ni)_3V_2O_7(OH)_2 \cdot 2H_2O$, and copper arsenate, tyrolite, $CaCu_5^{2+}(AsO_4)_2(CO_3)(OH)_4 \cdot 6H_2O$, or erythrine, $Co_3(AsO_4)_2 \cdot 8H_2O$. Taking into account the highest qualification of Betekhtin, our second suggestion is unlikely. However, currently, mineralogists run into phenomenon, when megascopally homogeneous material turns out composed of two phases as revealed by microscopic study with high magnification. Therefore, the second unlike explanation of high content of vanadium (more than 2 *apfu*) is not worth rejection. Consequently, it may be suggested that up to 2 *apfu* V incorporate into arsenosulvanite. Number of As or total As and Sb is close to 6 *apfu* (5.65 – 6.34 *apfu*), i.e., 6±0.35 *apfu*. Content of S ranges from 31.46 to 32.28 *apfu*. Cu content is the most variable from 23.72 to 24.86 *apfu*.

Electron microprobe data of colusite by Spry *et al.* (1994) are given in Table 4. They are recalculated on the sum of 64 atoms for comparison with data of arsenosulvanite.

According to the electron microprobe data, content of V in 12 samples of colusite

Table 1. **Bulk chemical and electron microprobe data of sulvanite and arsenosulvanite**

№ an.	Description of phase	Cu	Fe	V	As	Sb	S	∑
1	Light yellow	52.05	–	13.22	–	0.03	34.22	99.96*
2	isotropic sulvanite	52.64	–	13.14	0.08	–	34.97	100.83
3		52.25	–	13.30	–	0.02	35.29	100.86
Average		52.31	–	13.22	0.03	0.02	34.83	100.55
4	Light yellow slightly	50.20	–	3.09	13.61	0.15	32.87	99.92
5	darker than sulvanite;	51.10	–	3.26	13.75	–	32.66	100.77
6	anisotropy from -	50.99	–	3.24	13.78	0.10	32.57	100.68
7	light grey with greenish	50.34	–	3.25	13.65	0.58	32.65	100.47
8	tint to pale violet; relief	50.42	–	3.20	13.87	0.74	32.98	101.21
9	is higher than that of	50.60	–	3.06	12.55	2.49	32.95	101.65
10	sulvanite	50.85	–	3.14	14.22	0.45	32.24	100.90
11		50.01	–	3.21	13.21	2.06	32.36	100.85
12		50.30	–	3.17	12.04	2.44	32.52	100.47
13		50.83	–	3.05	13.68	1.01	32.68	101.25
14	Light yellow slightly	50.48	–	3.16	14.84	–	34.11	102.59
15	darker than sulvanite;	49.99	–	3.15	14.76	–	34.05	101.95
16	anisotropy from pale light	49.89	0.13	3.21	15.15	–	33.76	102.14
17	violet to deep pink-light	48.99	0.20	3.19	14.78	–	33.63	100.79
18	violet; relief is higher than	48.52	0.33	3.13	13.99	0.18	32.49	98.66
19	that of sulvanite;	48.99	0.09	3.06	15.05	–	33.44	100.63
20	polysynthetic twins are clear	48.97	0.07	3.19	14.51	0.77	33.19	100.70
21		48.95	0.15	3.11	15.14	0.17	33.62	101.14
22		49.15	–	2.94	14.61	–	33.22	99.92
23		49.09	–	3.01	14.94	0.18	33.89	101.11
24		48.34	0.05	3.01	13.35	2.94	32.72	100.41
25		50.20	–	3.19	13.89	1.71	33.07	102.06
26		49.87	–	3.31	13.28	1.68	33.13	101.27
27		49.47	–	3.15	13.94	0.50	33.13	100.19
28	Weakly anisotropic	50.35	–	3.7	13.35	–	32.55	99.95
29	arsenosulvanite	50.40	–	3.69	13.52	–	32.39	100.00
30		50.40	–	3.60	13.49	–	32.50	99.99
31	Isotropic	48.84	–	4,16	12.80	–	33.14	99.95**
32	arsenosulvanite	46.65	–	5.20	11.67	–	31.66	99.00**
33	Weakly anisotropic	48.8	–	3.7	12.4	–	31.7	96.6
34	arsenosulvanite	50.6	–	3.4	13.2	–	32.22	100.04
35	Arsenosulvanite	46.2	3.4	3.1	10.2	3.9	31.8	99.6***
36	Arsenosulvanite	49.4	–	3.2	12.3	–	33.9	98.8

*Notes: analyses: bulk chemical (31, 32) and electron microprobe (1–30, 33–36); samples: 242/3 (location 2), analysis 1–13; 242/6 (location 1), analysis 14–22; 242/6 (location 3), analysis 23 and 24; 242/5 (location 1), analysis 25–27. *Including 0.44 wt. % Pb. Average of three point analyses of sulvanite is 0.15 wt. % Pb. **Including insoluble residue, wt. %: 1.01 (an. 31) and 3.82 (an. 32). *** Including 1.0 wt. % Sn. In addition, in analysis 34, 0.62 wt. % Ge was detected. Dash denotes that the element was not analyzed. (1–30) Lebedinoe deposit, South Yakutia: (1–27) this study, (28) Novikov et al. (1974), average of two measurements; (29, 30) Khoroshilova (1987); (31, 32) Mongolia (Betekhtin, 1941); (33, 34) Bor, Serbia: (33) Kachalovskya et al. (1975), (34) Cvetkovi and Karanovi (1993); (35) Hayakawa, Japan (Ishiyama et al., 1990); (36) Osarizawa, Japan (Taguchi and Kizawa, 1974).*

Table 2. **Formulas of sulvanite and arsenosulvanite given in Table 1 calculated on the sum of 64 atoms**

№ an.	Formula	Mineral	Valence balance Δ, %
1	$Cu^{+}_{24.40}Pb_{0.06}V^{5+}_{2.00}V^{5+}_{5.73}Sb_{0.01}S_{31.79}$	Light yellow isotropic sulvanite	0.6
2	$Cu^{+}_{24.34}V^{5+}_{2.00}V^{5+}_{5.58}As^{5+}_{0.03}S_{32.04}$		2.6
3	$Cu^{+}_{24.10}V^{5+}_{2.00}V^{5+}_{5.65}Sb^{5+}_{0.01}S_{32.25}$		3.2
Average	$Cu^{+}_{24.28}Pb_{0.02}V^{5+}_{2.00}V^{5+}_{5.65}As^{5+}_{0.01}Sb^{5+}_{0.01}S_{32.03}$		2.1
4	$Cu^{+}_{24.56}V^{5+}_{1.88}(As_{5.65}Sb_{0.04})^{5+}_{5.69}S_{31.86}$	Light yellow slightly darker than sulvanite; anisotropy from light grey with greenish tint to pale violet; relief is higher than that of sulvanite	2.0
5	$Cu^{+}_{24.86}V^{5+}_{1.98}As^{5+}_{5.67}S_{31.49}$		0.2
6	$Cu^{+}_{24.85}V^{5+}_{1.97}(As_{5.70}Sb_{0.02})^{5+}_{5.72}S_{31.46}$		0.6
7	$Cu^{+}_{24.60}V^{5+}_{1.98}(As_{5.66}Sb_{0.15})^{5+}_{5.81}S_{31.62}$		0.5
8	$Cu^{+}_{24.46}V^{5+}_{1.94}(As_{5.70}Sb_{0.18})^{5+}_{5.88}S_{31.70}$		0.2
9	$Cu^{+}_{24.59}V^{5+}_{1.85}(As_{5.18}Sb_{0.63})^{5+}_{5.81}S_{31.74}$		0.9
10	$Cu^{+}_{24.85}V^{5+}_{1.93}(As_{5.89}Sb_{0.12})^{5+}_{6.01}S_{31.22}$		3.2
11	$Cu^{+}_{24.54}V^{5+}_{1.96}(As_{5.50}Sb_{0.52})^{5+}_{6.02}S_{31.47}$		2.3
12	$Cu^{+}_{24.73}V^{5+}_{1.94}(As_{5.02}Sb_{0.63})^{5+}_{5.65}S_{31.69}$		1.1
13	$Cu^{+}_{24.73}V^{5+}_{1.85}(As_{5.64}Sb_{0.26})^{5+}_{5.90}S_{31.51}$		0.7
14	$Cu^{+}_{24.00}V^{5+}_{1.88}As^{5+}_{5.98}S_{32.14}$	Light yellow slightly darker than sulvanite; anisotropy from pale light violet to deep pink-light violet; relief is higher than that of sulvanite; polysynthetic twins are clear	1.6
15	$Cu^{+}_{23.89}V^{5+}_{1.88}As^{5+}_{5.98}S_{32.25}$		2.0
16	$Cu^{+}_{23.86}V^{5+}_{1.92}As^{5+}_{6.14}Fe^{2+}_{0.07}S_{32.00}$		0.5
17	$Cu^{+}_{23.69}V^{5+}_{1.93}As^{5+}_{6.06}Fe^{2+}_{0.10}S_{32.22}$		0.9
18	$Cu^{+}_{24.04}V^{5+}_{1.93}(As_{5.88}Sb_{0.04})^{5+}_{5.92}Fe_{0.18}S_{31.91}$		0.3
19	$Cu^{+}_{23.76}V^{5+}_{1.85}As^{5+}_{6.20}Fe^{2+}_{0.05}S_{32.14}$		0.2
20	$Cu^{+}_{23.83}V^{5+}_{1.94}(As_{5.99}Sb_{0.20})^{5+}_{6.19}Fe^{2+}_{0.04}S_{32.01}$		0.8
21	$Cu^{+}_{23.64}V^{5+}_{1.87}(As_{6.20}Sb_{0.04})^{5+}_{6.24}Fe^{2+}_{0.08}S_{32.17}$		0.02
22	$Cu^{+}_{24.01}V^{5+}_{1.79}As_{6.05}S_{32.15}$		1.7
23	$Cu^{+}_{23.66}V^{5+}_{1.81}(As_{6.10}Sb_{0.04})^{5+}_{6.14}S_{32.38}$		2.1
24	$Cu^{+}_{23.82}V^{5+}_{1.85}(As_{5.58}Sb_{0.76})^{5+}_{6.34}Fe^{2+}_{0.03}S_{31.96}$		1.4
25	$Cu^{+}_{24.27}V^{5+}_{1.93}(As_{5.69}Sb_{0.44})^{5+}_{6.13}S_{31.68}$		1.9
26	$Cu^{+}_{24.21}V^{5+}_{2.00}(As_{5.47}Sb_{0.42})^{5+}_{5.89}V^{3+}_{0.01}S_{31.88}$		0.1
27	$Cu^{+}_{24.15}V^{5+}_{1.91}(As_{5.77}Sb_{0.12})^{5+}_{5.89}S_{32.04}$		1.4
28	$Cu^{+}_{24.64}V^{5+}_{2.00}(V^{3+}_{0.26}As_{5.54})^{5+}_{5.80}S_{31.56}$	Weakly anisotropic arsenosulvanite	0.0
29	$Cu^{+}_{24.68}V^{5+}_{2.00}(V^{3+}_{0.25}As_{5.62})^{5+}_{5.87}S_{31.44}$		1.0
30	$Cu^{+}_{24.67}V^{5+}_{2.00}(V^{3+}_{0.20}As_{5.60})^{5+}_{5.80}S_{31.53}$		0.3
31	$Cu^{+}_{23.94}V^{5+}_{2.00}(V^{3+}_{0.54}As_{5.32})^{5+}_{5.86}S_{32.19}$	Isotropic arsenosulvanite	3.4
32	$Cu^{+}_{23.74}V^{5+}_{2.00}(V^{3+}_{1.30}As_{5.04})^{5+}_{6.34}S_{31.93}$		1.6
33	$Cu^{+}_{24.64}V^{5+}_{2.00}(V^{3+}_{0.33}As_{5.31})^{5+}_{5.64}S_{31.72}$	Weakly anisotropic arsenosulvanite	2.0
34	$Cu^{+}_{24.83}V^{5+}_{2.00}(V^{3+}_{0.08}Ge^{4+}_{0.27}As^{5+}_{5.49})_{5.84}S_{31.33}$		1.5
35	$Cu^{+}_{23.07}Fe_{1.93}V^{5+}_{1.93}(Sb^{5+}_{1.02}As^{5+}_{4.32}Sn^{4+}_{0.27})_{5.61}S_{31.47}$		2.2
36	$Cu^{+}_{24.19}V^{5+}_{1.95}As^{5+}_{5.09}S_{32.77}$		9.4

Notes: Analyses 29, 30, and 34–36 taken from Frank-Kamenetskaya et al., 2002.

Table 3. **Comparison of X-ray diffraction patterns of arsenosulvanite, colusite, and sulvanite**

				Arsenosulvanite						Colusite*		Sulvanite	
	This study			Mikheev,1941, $a = 5.257 \pm 3$ Å			Kachalovskaya *et al.*, 1975, $a = 10.52$ Å			JCPDS 44-1474		Levy, 1966	
№	*I*	*d/n*, Å	*hkl*	*I*	*d/n*, Å	*hkl*	*I*	*d/n*, Å	*hkl*	*I*	*d/n*, Å	*I*	*d/n*, Å
1							3	5.32	200	3	5.311	10	5.42
2							1	4.80	210	3	4.75		
3	1	4.32	211				1	4.36	211	4	4.337		
4	4	3.34	310	4	(3.339)	211, 310	5	(3.37)	310β				
5	10	3.01	222	9	3.034	111	10	3.05	222	100	3.066	10	3.12
6	1	2.86	321				1	2.82	321	2	2.839		
7	4	2.62	400	3	2.627	200	4	2.65	400	9	2.656	4	2.69
8	1	2.52	223							2	2.576		
9	2	2.47	411				1	2.47	411				
10							1	2.43	331			8	2.41
11	1	2.35	420				1	2.36	420	1	2.375		
12	1	2.29	332				1	2.25	332	1	2.265		
13	3	2.04	510	5	(2.048)	220β	4	(2.06)	510β, 431β				
14	2	1.934	521							1	1.974		
15							1	1.906	521			10	1.910
16	9	1.849	440	10	1.859	220	9	1.867	440	41	1.878		
17							1	1.810	530, 433	4	1.822	5	1.796
18	2	1.737	610	3	(1.746)	313β	3	(1.757)	600β, 442β				
19	1	1.636											
20							1	1.627	541			6	1.626
21	8	1.573	622	9	1.584	311	8	1.591	622	14	1.601		
22										1	1.533	1	1.552
23	2	1.510	444	1	1.518	222	1	1.521	444				
24	1	1.470					1	1.452	720, 641				
25	1	1.405	642										
26	1	1.365	371, 553, 731										
27				0,5	(1,328)	331β	1	(1,336)	732β, 651β				
28	3	1.308	800	6	1.314	400	4	1.320	800	2	1.328		
29	2	1.254	453										
30	5	1.203	662	7	1.207	331	5	1.210	662	3	1.218		
31							1	1.194	752	1	1.188		
32	1	1.182	840	2	1.180	420	1	1.183	840	3	1.084		
33	1	1.164	833										
34	2	1.121	664				1	1.125	664				
35	2	1.094	931	1	(1,111)	513β	1	1.103	931				
36	7	1.072	844	9	1.074	422	6	1.077	844				
37	4	1.013	10.22	7	1.014	511	3	1.015	10.22	1	1.022		

Notes: * *— Butte, Montana, USA.*

Table 4. **Electron microprobe data of colusite (Spry *et al.*, 1994)**

№ an.	Cu	V	Fe	Zn	Ge	Sn	As	Sb	S	∑
1	50.8	3.2				7.3	8.6	1.1	30.1	100.0
2	49.5	3.0				5.31	8.6	1.1	31.6	99.1
3	50.1	3.3			0.63	0.26	13.6	1.4	31.2	100.49
4	49.5	3.1			1.1	6.6	8.8	0.92	30.2	100.22
5	50.41	3.52	0.58	0.35	2.85	3.17	8.12		29.69	98.69
6	47.98	2.95	1.10	0.07	0.14	8.42	3.61	6.59	29.77	101.06
7	49.40	3.18	0.35	0.33	4.52		8.64	0.34	33.13	101.24
8	48.5	2.7			6.2		10.0		32.3	99.7
9	47.4	2.2	1.8			7.6	7.5	1.4	31.2	99.3
10	49.3	2.7				5.9	12.1		28.2	98.2
11	50.4	3.6				1.3	10.7		31.9	97.9
12	49.5	3.05	1.5			4.65	11.05		30.55	100.30

Formula calculated on the sum of 64 atoms

	Formula	Valence balance Δ, %
1	$Cu^{+}_{25.95}V^{5+}_{2.00}As^{5+}_{3.55}Sn^{4+}_{2.00}V^{3+}_{0.04}S_{30.47}$ or	
	$Cu^{+}_{25.95}V^{5+}_{2.00}(As^{5+}_{3.55}Sn^{4+}_{2.00}V^{3+}_{0.04})_{5.59}S_{30.47}$	1.1
2	$Cu^{+}_{25.03}V^{5+}_{1.89}(As_{3.69}Sb_{0.29})^{5+}_{3.98}Sn^{4+}_{1.44}S_{31.66}$ or	
	$Cu^{+}_{25.03}V^{5+}_{1.89}[(As_{3.69}Sb_{0.29})^{5+}_{3.98}Sn^{4+}_{1.44}]_{5.42}S_{31.66}$	5.0
3	$Cu^{+}_{24.85}V^{5+}_{2.00}(As_{5.72}Sb_{0.36})^{5+}_{6.08}(Sn_{0.07}Ge_{0.27})^{4+}_{0.34}V^{3+}_{0.04}S_{30.68}$ or	
	$Cu^{+}_{24.85}V^{5+}_{2.00}[(As_{5.72}Sb_{0.36})^{5+}_{6.08}(Sn_{0.07}Ge_{0.27})^{4+}_{0.34}V^{3+}_{0.04}]_{6.46}S_{30.68}$	8.0
4	$Cu^{+}_{25.21}V^{5+}_{1.97}(As_{3.80}Sb_{0.24})^{5+}_{4.04}(Sn_{1.80}Ge_{0.49})^{4+}_{2.29}S_{30.48}$ or	
	$Cu^{+}_{25.21}V^{5+}_{1.97}[(As_{3.80}Sb_{0.24})^{5+}_{4.04}(Sn_{1.80}Ge_{0.49})^{4+}_{2.29}]_{6.33}S_{30.48}$	5.4
5	$Cu^{+}_{25.73}Fe_{0.34}V^{5+}_{2.00}As^{5+}_{3.51}(Sn_{0.87}Ge_{1.27})^{4+}_{2.14}V^{3+}_{0.24}S_{30.03}$ or	
	$Cu^{+}_{25.73}Fe_{0.34}V^{5+}_{2.00}[As^{5+}_{3.51}(Sn_{0.87}Ge_{1.27})^{4+}_{2.14}V^{3+}_{0.24}]_{5.89}S_{30.03}$	5.0
6	$Cu^{+}_{25.03}Fe_{0.65}V^{5+}_{1.92}(As_{1.60}Sb_{1.60})^{5+}_{3.20}(Sn_{2.35}Ge_{0.06})^{4+}_{2.41}S_{30.78}$	
	$Cu^{+}_{25.03}Fe_{0.65}V^{5+}_{1.92}[(As_{1.60}Sb_{1.60})^{5+}_{3.20}(Sn_{2.35}Ge_{0.06})^{4+}_{2.41}]_{5.65}S_{30.78}$	0.0
7	$Cu^{+}_{24.44}Fe_{0.20}V^{5+}_{1.21}(As_{3.62}Sb_{0.09})^{5+}_{3.71}Ge^{4+}_{1.96}S_{32.48}$ или	
	$Cu^{+}_{24.44}Fe_{0.20}V^{5+}_{1.21}[(As_{3.62}Sb_{0.09})^{5+}_{3.71}Ge^{4+}_{1.96}]_{5.67}S_{32.48}$	11.8
8	$Cu^{+}_{23.90}V^{5+}_{1.68}As^{5+}_{4.15}Ge^{4+}_{2.67}S_{31.60}$ or	
	$Cu^{+}_{23.90}V^{5+}_{1.68}[As^{5+}_{4.15}Ge^{4+}_{2.67}]_{6.82}S_{31.60}$	0.8
9	$Cu^{+}_{24.23}Fe_{1.05}V^{5+}_{1.40}(As_{3.25}Sb_{0.37})^{5+}_{3.62}Sn^{4+}_{2.08}S_{31.61}$ or	
	$Cu^{+}_{24.23}Fe_{1.05}V^{5+}_{1.40}[(As_{3.25}Sb_{0.37})^{5+}_{3.62}Sn^{4+}_{2.08}]_{5.70}S_{31.61}$	5.5
10	$Cu^{+}_{25.87}V^{5+}_{1.77}As^{5+}_{5.38}Sn^{4+}_{1.66}S_{29.32}$ or	
	$Cu^{+}_{25.87}V^{5+}_{1.77}[As^{5+}_{5.38}Sn^{4+}_{1.66}]_{7.04}S_{29.32}$	14.1
11	$Cu^{+}_{25.22}V^{5+}_{2.00}As^{5+}_{4.54}Sn^{4+}_{0.35}V^{3+}_{0.25}S_{31.64}$ or	
	$Cu^{+}_{25.22}V^{5+}_{2.00}[As^{5+}_{4.54}Sn^{4+}_{0.35}V^{3+}_{0.25}]_{5.14}S_{31.64}$	5.1
12	$Cu^{+}_{24.86}Fe_{0.86}V^{5+}_{1.91}As^{5+}_{4.71}Sn^{4+}_{1.25}S_{30.41}$ or	
	$Cu^{+}_{24.86}Fe_{0.86}V^{5+}_{1.91}[As^{5+}_{4.71}Sn^{4+}_{1.25}]_{5.96}S_{30.41}$	6.0

Notes: 0.35 wt. % Zn (analysis 5); 0.07 wt.% Zn and 0.40 wt. % Mo (analysis 6); 0.04 wt. % Ni and 0.12 wt. % Bi (analysis 7); 0.03 wt. % Mo (analysis 9). (1) Butte, Montana (Levy, 1967); (2) Butte, Montana (Springer, 1969); (3, 4) Lorano, Italy (Orlandi et al., 1981); (5) Gai, Russia (Pshenichnyi et al., 1974); (6) Kairagach, Uzbekistan (Spiridonov et al., 1984); (7) San Fernando, Cuba (Krapiva et al., 1986); (8) unknown deposit, Kazakhstan (Mitryaeva et al., 1968); (9) Chizeuil, France (Delfour et al., 1984); (10, 11) Bor, Serbia (Kachalovskaya et al., 1975); (12) Medet, Bulgaria (Strashimirov, 1982).

from varied deposits ranges from 1.21 to 2.25 *apfu* (San Fernando deposit, Cuba and Bor deposit, Serbia, respectively). Number of As or the sum of As and Sb in colusite varies from 3.20 to 6.08 *apfu* (Kairagach deposit, Uzbekistan and Lorano deposit, Italy). The content of the other elements is as follows, *apfu*: 0 – 1.60 Sb, 0 – 2.67 Ge, 0 – 2.08 Sn, 0 – 1.05 Fe, 23.90 – 25.90 Cu, 29.32 – 32.48 S.

Thus, colusite is characterized by wide ranges of V content and total As and Sb, whereas these values in arsenosulvanite are close to 2 and 6 ± 0.35 *apfu*. Significant Ge and Sn are frequent in colusite, whereas these elements are rare and insignificant in arsenosulvanite. Admixture cations in colusite are resulted from the larger isomorphic capacity of the structure of colusite in contrast to arsenosulvanite. These minerals are significantly different in chemical composition.

Conclusions

(1) Arsenosulvanite and colusite are different mineral species.

(2) Discreditation of arsenosulvanite (Burke, 2006) is incorrect.

(3) Reinvestigation of arsenosulvanite including structural study is required to approve it as mineral species.

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SULFIDE MINERALIZATION OF THE LEBEDINOE DEPOSIT, CENTRAL ALDAN

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The results of examination of minerals from the Lebedinoe deposit are discussed. In addition to previously described mineral species, digenite, anilite, spionkopite, yarrowite, pyrrohotite-*5c*, and minerals of the fahlore family (Zn-bearing tetrahedrite – sandbergerite, tetrahedrite-tennantite, and tennantite) were identified in the ore of the deposit. Anisotropic arsenosulvanite with well-formed polysynthetic twins has been found.
6 figures, 3 tables, 7 references.

Keywords: digenite, anilite, spionkopite, yarrowite, fahlores, Lebedinoe deposit.

Introduction

Margarita I. Novgorodova gave us for investigation the specimens from the Lebedinoe deposit (ore body Orochon, prospecting pit No 7 dumps) collected by A.I. Fastalovich in 1941 and stored in the collection by N.V. Petrovskaya.

The Lebedinoe deposit was described in detail in the article by Nenashava and Karpenko (this volume) according to Fastalovich and Petrovskaya (1940), and Petrovskaya (1973). Here, we give brief description only. The sequence of the Cambrian weakly metamorphosed dolomite overlapping eroded surface of granite plutons cutting ancient rocks is intruded by the Upper Jurassic-Lower Cretaceous numerous small bodies. These are predominantly stocks, laccoliths, and dykes of intermediate rocks of elevated alkalinity. The metasomatic sulfide-carbonate bodies occasionally as vein apophysises are hosted in dolomite along horizontal fractures (Petrovskaya, 1973). The primary ore minerals are dominated by pyrite; chalcopyrite occurs also; hematite is identified in some veins; galena, sphalerite, pyrrhotite, galenobismutite, tetrahedrite, native gold, bornite, cobaltite, and sulvanite are less frequent. Supergene minerals are iron hydroxides, jarosite, cuprite, chalcocite, covellite, malachite, azurite, cerussite, gypsum, and melanterite (Fastalovich and Petrovskaya, 1940).

Analytical techniques and results

The thin polished sections were studied with an OPTON microscope. The chemical composition was determined with a CamScan-4D scanning electron microscope equipped with a Link ISIS EDS operating at accelerated voltage 20 kV and beam current of 4 nA.

Microscopically, heterogeneous objects studied here are composed of ore minerals (pyrite, galena, and bornite are major minerals) enclosed in quartz-carbonate-arsenate matrix. The grains of fahlores, sulvanite, arsenosulvanite, and famatinite were found in galena. In addition, the segregations of pyrrhotite, covellite, digenite, anilite, spionkopite, yarrowite were determined with electron microprobe.

Fahlores are mainly antimonial. Tetrahedrite enriched in Zn, sandbergerite (Table 1, an. 1–24), was identified to be associated with galena, famatinite, arsenosulvanite, and anglesite (Fig. 1, 2). Content of Zn is variable (5.14–8.07 wt.% corresponding to 1.32–2.04 *apfu*). Concentration of Sb ranges from 23.53 to 28.16 wt.% that exceeds 3 *apfu* corresponding to 3.25 and 3.85 *apfu*. There is no clear correlation between Zn and As, but Sb and Zn+Ag are positively correlated. Such correlation was previously reported by Mozgova and Tsepin (1983) for fahlores. Anglesite Pb[SO_4] occurs at the contact between sandbergerite and galena (Fig. 1, 2). Its composition is as follows, wt.%: 67.06 Pb, 10.82 S, 21.38 O, total is 99.26. Formula is: $Pb_{0.97}S_{1.01}O_{4.01}$.

The intermediate members of the tetrahedrite-tennantite series and tennantite (Table 1, an. 25–31) are associated with sulvanite, arsenosulvanite, and Cu-Ca arsenate (probably, tyrolite, $Ca_2Cu_5^{2+}(OH,O)_4\,(AsO_4)_2(CO_3)\cdot 6H_2O$, or clinotyrolite, $Ca_2Cu_9^{2+}(OH,O)_{10}[(AsO_4),(SO_4)]_4\cdot 10H_2O$) (Fig. 3).

As and Sb are negatively correlated in the intermediate members of the tetrahedrite-tennantite series and tennantite. Arsenate formed after arsenosulvanite occasionally fills veinlets, where grains of tennantite are

Table 1. **Electron microprobe data of tennantite-tetrahedrite, wt.%**

№ an.	Sample	Cu	Ag	Fe	Zn	Cd	Pb	Sb	As	S	Se	∑
1	242 (loc. 1)	34.90	2.83	0.40	6.91	1.10	0.71	25.70	1.68	23.75		97.98
2		35.80	1.72	0.26	6.41	1.05	0.78	25.54	1.64	24.13		97.33
3		35.77	1.58	0.33	6.44	0.82	0.87	26.62	0.59	24.17		97.34*
4		38.06	1.61	0.32	7.01	0.79	0.90	26.47	1.47	24.59		101.22
5		37.89	1.96	0.14	6.52	0.92	0.85	27.53	0.43	24.80		101.04
6		38.75	1.00	0.18	6.34	0.79	1.29	25.54	1.85	24.18		99.92
7		37.83	1.87	0.33	6.56	1.27	0.06	28.16	0.06	25.03		101.17
8		35.38	4.37	0.50	6.83	0.28	1.25	25.88	1.99	24.92	0.42	101.82
9		37.22	1.68	0.50	6.34	1.28	0.99	27.61	0.34	24.26	0.22	100.44
10		38.85	1.87	0.49	6.43	0.89	1.30	28.23	0.33	24.51	0.05	100.95
11	242 (loc. 4)	35.98	4.11	0.36	6.79	0.74	0.93	27.31	0.23	24.22		100.67
12	242 (loc. 2)	38.16	0.65	0.15	7.21	0.40	0.26	25.21	2.11	25.10		99.25
13		37.66	0.91	0.19	8.06	0.15	1.12	24.79	2.20	24.94	0.41	100.43
14		37.70	0.92	0.19	8.07	0.17	0.00	24.69	2.21	25.12	0.41	99.48
15	242 (loc. 3)	36.02	2.63	0.22	7.09	0.35	0.47	26.96	0.25	24.61	0.37	99.23
16		37.81	1.91	0.31	7.48	0.39	0.78	26.33	0.72	24.99	0.13	100.85
17	242 (loc. 6)	35.53	2.78	0.55	6.68	1.93	1.61	26.84	0.00	23.96		100.31
18		33.86	5.40	0.69	5.73	1.45	0.15	25.33	0.96	23.89		97.96
19		35.41	2.89	0.64	5.66	1.42	1.40	26.49	0.05	23.34	0.18	97.48
20		35.30	2.28	0.65	5.71	1.82	1.60	26.82		23.82		98.0
21		35.09	2.54	0.48	5.77	1.78	1.08	26.06	0.09	23.08	0.13	96.41
22		36.74	2.76	0.91	5.39	2.01	1.37	26.73	0.40	24.80		101.11
23	242 (loc. 5)	37.47	2.35	0.00	5.14	2.23	0.83	23.53	3.02	24.87		99.44
24		35.91	3.38	0.53	5.68	2.10	1.60	25.36	0.93	24.25		99.74
25	242/1 (loc. 1)	41.14	0.18	0.56	7.30	0.27	0.32	15.03	9.45	26.58		100.83
26		42.07	0.16	0.57	7.67	0.17	0.89	14.09	9.43	26.31		101.36
27	242/6 (loc. 1)	45.64		5.69	0.27			1.89	19.58	28.74		101.81
28		45.80		6.07				1.36	20.42	28.95		102.60
29		45.20		5.44				1.77	20.39	28.79		101.59
30	242/5 (loc. 1)	45.06		6.79	0.43			1.53	19.18	28.84		101.83
31		46.61		5.23	0.35			1.47	19.02	28.55		101.23

№ an.	Sample	Formula calculated on the sum of 29 atoms	Valence balance Δ, %
1	242 (loc. 1)	$(Cu_{9.51}Ag_{0.45})_{9.96}(Zn_{1.83}Fe_{0.12}Cd_{0.17}Pb_{0.06})_{2.18}(Sb_{3.65}As_{0.39})_{4.04}S_{12.82}$	3.0
2		$(Cu_{9.73}Ag_{0.28})_{10.01}(Zn_{1.69}Cd_{0.16}Fe_{0.08}Pb_{0.06})_{1.99}(Sb_{3.62}As_{0.38})_{4.00}S_{12.99}$	0.1
3		$(Cu_{9.74}Ag_{0.26})_{10.00}(Zn_{1.71}Cd_{0.12}Fe_{0.10}Pb_{0.07})_{2.00}(Sb_{3.78}As_{0.14}Ge_{0.03})_{3.95}S_{13.04}$	0.8
4		$(Cu_{9.97}Ag_{0.25})_{10.22}(Zn_{1.79}Cd_{0.12}Fe_{0.10}Pb_{0.07})_{2.08}(Sb_{3.62}As_{0.33})_{3.95}S_{12.76}$	2.7
5		$(Cu_{9.97}Ag_{0.30})_{10.27}(Zn_{1.67}Cd_{0.14}Fe_{0.04}Pb_{0.07})_{1.92}(Sb_{3.78}As_{0.10})_{3.88}S_{12.93}$	0.3
6		$(Cu_{10.27}Ag_{0.16})_{10.43}(Zn_{1.64}Cd_{0.12}Fe_{0.06}Pb_{0.10})_{1.92}(Sb_{3.53}As_{0.41})_{3.94}S_{12.70}$	2.6
7		$(Cu_{9.90}Ag_{0.29})_{10.19}(Zn_{1.67}Cd_{0.19}Fe_{0.10})_{1.96}(Sb_{3.85}As_{0.01})_{3.86}S_{12.90}$	1.1
8		$(Cu_{9.27}Ag_{0.68})_{9.95}(Zn_{1.74}Fe_{0.15}Cd_{0.04}Pb_{0.10})_{2.03}(Sb_{3.54}As_{0.44})_{3.98}(S_{12.94}Se_{0.09})_{13.03}$	0.4
9		$(Cu_{9.91}Ag_{0.26})_{10.17}(Zn_{1.64}Cd_{0.19}Fe_{0.15}Pb_{0.08})_{2.06}(Sb_{3.84}As_{0.08})_{3.92}(S_{12.80}Se_{0.05})_{12.85}$	1.3
10		$(Cu_{9.78}Ag_{0.29})_{10.07}(Zn_{1.66}Cd_{0.13}Fe_{0.15}Pb_{0.11})_{2.05}(Sb_{3.91}As_{0.08})_{3.99}(S_{12.89}Se_{0.01})_{12.90}$	1.3
11	242 (loc. 4)	$(Cu_{9.61}Ag_{0.65})_{10.26}(Zn_{1.76}Cd_{0.11}Fe_{0.11}Pb_{0.08})_{2.06}(Sb_{3.81}As_{0.05})_{3.86}S_{12.82}$	1.2
12	242 (loc. 2)	$(Cu_{10.00}Ag_{0.10})_{10.10}(Zn_{1.84}Cd_{0.06}Fe_{0.05}Pb_{0.02})_{1.97}(Sb_{3.44}As_{0.47})_{3.91}S_{13.03}$	1.1
13		$(Cu_{9.82}Ag_{0.14})_{9.96}(Zn_{2.04}Fe_{0.06}Cd_{0.02}Pb_{0.09})_{2.21}(Sb_{3.37}As_{0.49})_{3.86}(S_{12.88}Se_{0.09})_{12.97}$	0.1
14		$(Cu_{9.82}Ag_{0.14})_{9.96}(Zn_{2.04}Fe_{0.06}Cd_{0.03})_{2.13}(Sb_{3.36}As_{0.49})_{3.85}(S_{12.97}Se_{0.09})_{13.06}$	1.0

Table 1. **Cont.**

№ an.	Sample	Formula calculated on the sum of 29 atoms	Valence balance Δ, %
15	242 (loc. 3)	$(Cu_{9.62}Ag_{0.41})_{10.03}(Zn_{1.84}Fe_{0.07}Cd_{0.05}Pb_{0.04})_{2.00}(Sb_{3.76}As_{0.06}Te^{4+}_{0.03})_{3.83}(S_{13.03}Se_{0.07})_{13.10}$	2.2
16		$(Cu_{9.88}Ag_{0.30})_{10.18}(Zn_{1.90}Fe_{0.09}Cd_{0.06}Pb_{0.06})_{2.11}(Sb_{3.59}As_{0.16})_{3.75}(S_{12.94}Se_{0.03})_{12.97}$	1.0
17	242 (loc. 6)	$(Cu_{9.58}Ag_{0.44})_{10.02}(Zn_{1.75}Fe_{0.17}Cd_{0.29})_{2.21}(Sb_{3.78}Te_{0.06})_{3.84}S_{12.80}$	1.6
18		$(Cu_{9.28}Ag_{0.87})_{10.15}(Zn_{1.52}Cd_{0.23}Fe_{021}Pb_{0.01})_{1.97}(Sb_{3.62}As_{0.22}Bi_{0.14})_{3.98}S_{12.98}$	0.3
19		$(Cu_{9.80}Ag_{0.47})_{10.27}(Zn_{1.52}Cd_{0.22}Fe_{0.20}Pb_{0.12})_{2.06}(Sb_{3.82}As_{0.01})_{3.83}(S_{12.79}Se_{0.04})_{12.81}$	1.0
20		$(Cu_{9.69}Ag_{0.37})_{10.06}(Zn_{1.52}Cd_{0.28}Fe_{0.20}Pb_{0.14})_{2.06}Sb_{3.84}S_{12.95}$	0.2
21		$(Cu_{9.81}Ag_{0.42})_{10.23}(Zn_{1.57}Cd_{0.28}Fe_{0.15}Pb_{0.09})_{2.09}(Sb_{3.80}As_{0.02}Bi_{0.02}Te^{4+}_{0.02})_{3.86}(S_{12.79}Se_{0.03})_{12.82}$	1.4
22		$(Cu_{9.72}Ag_{0.43})_{10.15}(Zn_{1.39}Fe_{0.28}Cd_{0.30}Pb_{0.11})_{2.08}(Sb_{3.69}As_{0.09})_{3.78}S_{13.00}$	1.3
23	242 (loc. 5)	$(Cu_{9.92}Ag_{0.37})_{10.29}(Zn_{1.32}Cd_{0.33}Pb_{0.07})_{1.72}(Sb_{3.25}As_{0.68})_{3.93}S_{13.05}$	2.2
24		$(Cu_{9.66}Ag_{0.54})_{10.20}(Zn_{1.49}Cd_{0.32}Fe_{0.16}Pb_{0.13})_{2.10}(Sb_{3.56}As_{0.21})_{3.77}S_{12.93}$	0.6
25	242/1	$(Cu_{10.13}Ag_{0.03})_{10.16}(Zn_{1.74}Fe_{0.16}Cd_{0.04}Pb_{0.02})_{1.96}(As_{1.97}Sb_{1.93})_{3.90}S_{12.97}$	0.6
26		$(Cu_{10.33}Ag_{0.02})_{10.35}(Zn_{1.83}Fe_{0.16}Cd_{0.02}Pb_{0.07})_{2.08}(As_{1.96}Sb_{1.81})_{3.77}S_{12.80}$	0.8
27	242/6 (loc. 1)	$Cu_{10.00}(Cu^{2+}_{0.43}Fe_{1.48}Zn_{0.06})_{1.97}(As_{3.79}Sb_{0.23})_{4.02}S_{13.01}$	0.8
28		$Cu_{10.00}(Cu^{2+}_{0.37}Fe_{1.56})_{1.93}(As_{3.92}Sb_{0.16})_{4.02}S_{12.99}$	0.5
29		$Cu_{10.00}(Cu^{2+}_{0.35}Fe_{1.42})_{1.77}(As_{3.96}Sb_{0.21})_{4.17}S_{13.06}$	0.3
30	242/5 (loc. 1)	$Cu_{10.00}(Cu^{2+}_{0.25}Fe_{1.76}Zn_{0.10})_{2.11}(As_{3.70}Sb_{0.18})_{3.88}S_{13.01}$	0.6
31		$Cu_{10.00}(Cu^{2+}_{0.70}Fe_{1.36}Zn_{0.08})_{2.14}(As_{3.70}Sb_{0.18})_{3.88}S_{12.98}$	0.2

Notes: (1–24) Zn-bearing tetrahedrite (sandbergerite), (25, 26) tennantite-tetrhedrite, (27–31) tennantite. Including, wt. % : 0.15 Ge (an. 3), 0.26 Te (an. 15), 0.43 Te (an. 17), 0.12 Te (an. 21), 0.50 Bi (an. 18), and 0.19 Bi (an. 21).

Table 2. **Electron microprobe data of famatinite, wt.%**

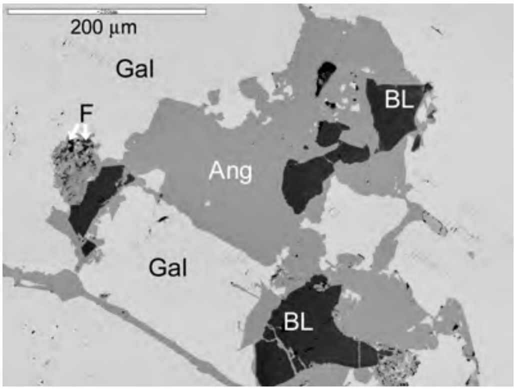
№ an.	Sample	Cu	Ag	Zn	Cd	Sb	Pb	S	Σ
1	242 (loc. 1)	42.71	0.58		0.42	26.26	0.88	28.65	99.56*
2	242 (loc. 6)	42.56	0.28	0.10	0.02	24.95	2.39	29.10	99.65**
3		41.00	0.38	0.11		24.56	3.78	28.21	98.04

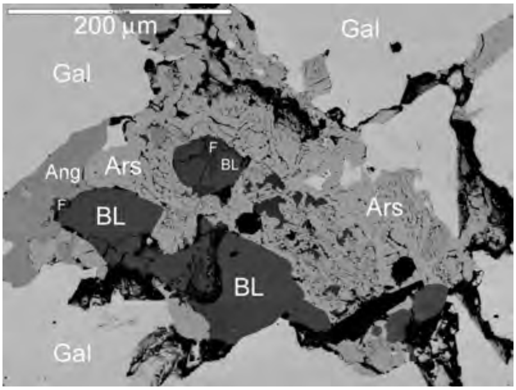
№ an.	Sample	Formula calculated on the sum of 64 atoms	Valence balance Δ, %
1	242 (loc. 1)	$(Cu^{+}_{7.81}Ag_{0.19})_{8.00}(Cu^{2+}_{16.15}Fe_{0.04}Cd_{0.13}Pb_{0.15})_{16.47}Sb_{7.68}S_{31.85}$	0.4
2	242 (loc. 6)	$(Cu^{+}_{7.91}Ag_{0.09})_{8.00}(Cu^{2+}_{15.89}Zn_{0.06}Cd_{0.01}Pb_{0.41})_{16.37}Sb_{7.28}S_{32.25}Se_{0.10}$	3.3
3		$(Cu^{+}_{7.87}Ag_{0.13})_{8.00}(Cu^{2+}_{15.73}Zn_{0.06}Pb_{0.66})_{16.45}Sb_{7.37}S_{32.17}$	2.1

*Notes: Including * Fe – 0.06, ** Se – 0.25.*

Fig. 1. Segregations of sandbergerite (BL) and famatinite (F) enclosed in galena (Gal) and anglesite (Ang). BSE image.

Fig. 2. Grains of sandbergerite (BL), famatinite (F), and anglesite (Ang) enclosed in matrix of galena (Gal) and arsenosulvanite (Ars). BSE image.





found. Betekhtin (1941), who described arsenosulvanite for the first time, denoted probable occurrence of tyrolite in the ore of the Lebedinoe deposit. He suggested that bright green powder crusts, which are oxidizing products of arsenosulvanite, are certain intermediate variety between copper vanadates, turanite, $Cu_5(VO_4)_2(OH)_4$, or volborthite, $(Cu,Zn,Ni)_3V_2O_7(OH)_2 \cdot 2H_2O$), and copper arsenate, tyrolite, $CaCu^{2+}_5(AsO_4)_2(CO_3)(OH)_4 \cdot 6H_2O$, or erythrine, $Co_3(AsO_4)_2 \cdot 8H_2O$.

As aforementioned, famatinite is associated with sandbergerite and galena. It occurs as small grains up to 10 microns in size. In reflected light, this mineral has weak pink tint in comparison with sandbergite and is anisotropic (Fig. 1, 2; Table 2).

Sulvanite and arsenosulvanite are discussed in this volume in the article by Nenasheva and Karpenko.

The composition of galena (Fig. 1, 2) close to theoretical is as follows, wt.%: 87.44 and 86.30 Pb and 13.82 and 13.46 S, total is 101.26 and 99.76. Valence balance is 2.0 and 0.9%, respectively. Formula is as follows: $PbS_{1.02}$ and $PbS_{1.01}$.

Four compositions of pyrite (Fig. 4 – 6; Table 3, an. 1 – 4) are not different from each other, exceptionally compositions 2 and 3, where small content of Cu was detected 0.87 and 0.71 wt.%, respectively that correspond to 0.02 and 0.1 *apfu*. Ramdohr (1962) noted that copper admixture in pyrite is caused most likely by mechanical contamination, but in our cases it is microimpurity.

The grain of pyrrhotite-5*C* $Fe^{2+}_7Fe^{3+}_2S_{10}$ (Table 3, an. 5) containing Cu impurity was identified in association with arsenosulvanite, pyrite, chalcopyrite, and copper arsenate, probably tyrolite. The calculated formula of this pyrrhotite is $Fe_{8.67}Cu_{0.31}S_{10.01}$ or $(Fe_{6.67}Cu_{0.31})^{2+}_{6.98}Fe^{3+}_{2.00}S_{10.01}$ that corresponds ideally to theoretical composition.

Compositions of bornite are close to theoretical $Cu_{5+x}FeS_{4-x}$, Cu_5FeS_4 or $Cu_{5-x}FeS_{4+x}$ (Table 3, an. 6 – 8; Fig. 4 – 6).

The results of the examination of the material that looks like covellite in reflected light are of interest. Large areas (up to 300×200 microns) are broken down by cleavage in plates up to 10 – 15 microns wide (Fig. 5, 6). In reflected light, the mineral is light blue; bireflectance ranges from light gray with bluish tint to bright light blue; anisotropy varies from light gray to pink, bright blue, and orange. Compositions of different plates are recalculated to formulas corresponding to different minerals of the Cu-S system: compositions 13 and 14 (Table 3) are recalculated to the formula corresponding to anilite, $Cu_7S_4 \rightarrow Cu^{+}_{6}Cu^{2+}S_4$; composition 15 (Table 3) corresponds to the mixture of spionkopite $Cu_{39}S_{28} \rightarrow Cu^{+}_{22}Cu^{2+}_{17}S_{28}$ and yarrowite $Cu_9S_8 \rightarrow Cu^{+}_{2}Cu^{2+}_{7}S_8$; and compositions 9 and 10 (Table 3) corresponds to covellite CuS or $3CuS \rightarrow Cu^{+}_{2}S \cdot Cu^{2+}[S_2]$ (Fig. 5, 6). It is easy to note that amount of bivalent copper increases toward covellite indicating increasing of mineralizing fluid acidity during mineral formation. According to the experimental data, sulfides containing lesser Cu (Cu^+ and Cu^{2+}) are more stable with pH decreasing. They are uncharged because of partial oxidation of Cu to bivalent state. Rickard (1973) synthesized djurleite $Cu_{31}S_{16} \rightarrow Cu^{+}_{30}Cu^{2+}S_{16}$ (pH > 7.5) and covellite (pH < 7) at low temperature close to oxidative zone as a result of interaction of Na_2S and Cu_2O. Experimental data (Whiteside and Goble, 1986) of copper leaching from synthetic chalcocite and digenite

Fig. 3. Tennantite (Tn) in veinlet of Cu-Ca arsenate (Arst), (probable tyrolite) enclosed in arsenosulvanite (Ars). BSE image.

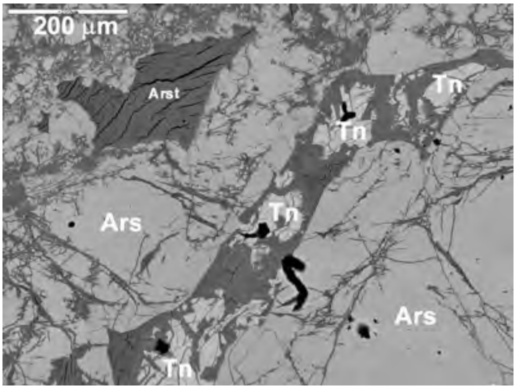
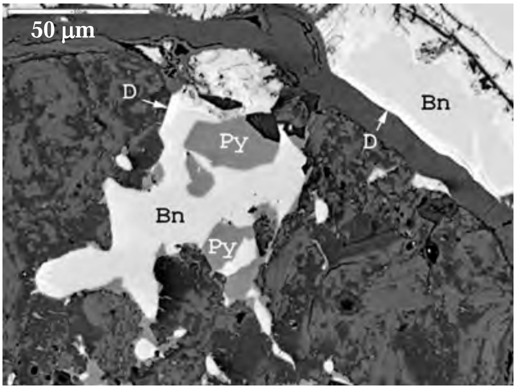
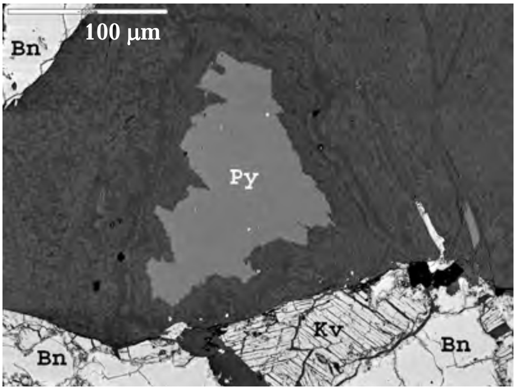


Fig. 4. Bornite (Bn), pyrite (Py), and digenite (D) enclosed in Cu carbonates and Cu-Ca arsenates. BSE image.





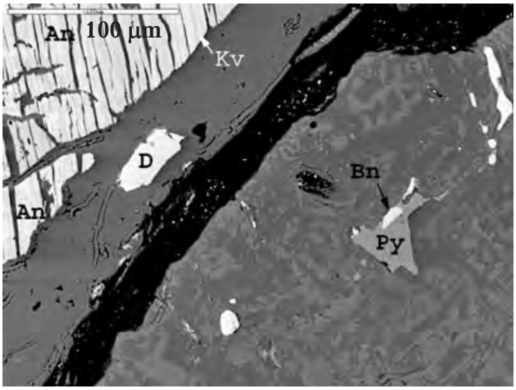


Fig. 5. Pyrite (Py), covellite (Kv), bornite (Bn) enclosed in intergrown Cu carbonates and Cu-Ca arsenates. BSE image.

Fig. 6. Covellite (Kv), annilite (An), bornite (Bn), digenite (D), and pyrite (Py) in matrix of supergene minerals. BSE image.

Table 3. **Electron microprobe data of sulfides, wt.%**

№ an.	Sample	Fe	Cu	S	∑	Formula	Valence balance Δ, %
1	245/1 (loc. 1)	45.92		51.87	97.79	$FeS_{1.97}$	
2	245/1 (loc. 3)	45.72	0.87	52.08	98.67	$FeCu_{0.02}S_{1.98}$	
3		44.91	0.71	52.23	97.85	$FeCu_{0.01}S_{2.02}$	
4	245/1 (loc. 5)	46.38		52.41	98.79	$FeS_{1.97}$	
5	242/6 (loc. 3)	57.41	2.32	38.04	97.77	$Fe_{8.67}Cu_{0.31}S_{10.01}$ or	
						$(Fe_{6.67}Cu_{0.31})^{2+}_{6.98}Fe^{3+}_{2.00}S_{10.01}$	0.2
6	245/1 (loc. 3)	12.63	60.27	25.75	98.65	$Cu_{4.80}Fe_{1.14}S_{4.06}$	1.2
7	245/1 (loc. 5)	11.00	63.80	25.45	100.25	$Cu_{5.03}Fe_{0.98}S_{3.98}$	0.4
8		11.28	62.48	25.46	99.22	$Cu_{4.97}Fe_{1.02}S_{4.01}$	0.1
9	245/1 (loc. 5)		71.22	29.79	101.01	$Cu_{1.09}S_{0.91}$	
10			71.91	28.47	100.38	$Cu_{1.12}S_{0.88}$	
11	245/1 (loc. 1)	0.76	78.35	21.79	100.90	$Cu^{+}_{7.96}Cu^{2+}_{1.00}Fe_{0.10}S_{4.94}$	2.8
12		0.66	78.21	22.20	101.07	$Cu^{+}_{7.90}Cu^{2+}_{1.00}Fe_{0.08}S_{5.01}$	0.4
13	245/1 (loc. 1)		77.37	22.29	99.66	$Cu^{+}_{6.00}Cu^{2+}_{1.00}S_{4.00}$	0.0
14			77.50	23.18	100.68	$Cu^{+}_{5.91}Cu^{2+}_{1.00}S_{4.09}$	3.0
15			72.27	27.78	100.05	$Cu^{+}_{12.00}Cu^{2+}_{11.84}S_{18.16}$*	1.8

*Notes: (1–4) Pyrite, (5) pyrrhotite-5C, (6–8) bornite, (9, 10) covellite, (11, 12) digenite, (13, 14) anilite, and (15) intermediate composition between spioncopite $Cu_{39}S_{28} \rightarrow Cu^{+}_{22}Cu^{2+}_{17}S_{28}$ and yarrowite $Cu_9S_8 \rightarrow Cu^{+}_{2}Cu^{2+}_{7}S_8$ (15). *This formula calculated for intermediate composition between spionkopite and yarrowite.*

with iron sulfate acidic solution testify that action of this reagent upon digenite results in the formation of anilite followed by spionkopite, yarrowite, and covellite. The conclusion of decreasing pH with temperature decreasing is supported by relicts of digenite as small euhedral grains up to 20–30 microns in size enclosed in supergene minerals, carbonates, copper arsenates, iron sulfates (Fig. 6; Table 3, an. 11, 12). Occasionally bornite is rimmed by digenite (Fig. 4). In compositions 10 and 11, 0.76 and 0.66 wt.% Fe were detected, respectively, corresponding to 0.10 and 0.08 *apfu*. Digenite is stable in alkaline environment.

Conclusions

Previously unknown minerals were found at the Lebedinoe deposit. These are minerals of the chalcocite polysomatic series depleted in copper in comparison with chalcocite: digenite, anilite, and mixture (probably fine intergrowths) of spionkopite and yarrowite. In addition anisotropic arsenosulvanite and anglesite are described.

Digenite, anilite, spinonkopite, and yarrowite indicate changing acidity of fluid during mineralizing process. Digenite is stable within wide range of temperature and alkaline environment, whereas anilite and spionkopite and yarrowite are stable within narrow range of temperature from 0 to 30°C and from 0 to 157°C, respectively are formed in acidic environment. Covellite is stable at 0—507°C and acidic environment.

Fahlores of the Lebedinoe deposit are Zn-bearing tetrahedrite — sandbergerite associated with galena, anglesite, arsenosulvanite, and famatinite and tetrahedrite-tennantite and tennantite associated with sulvanite, arsenosulvanite, and Cu-Ca arsenate (probably, tyrolite or clinotyrolite).

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NATIVE GOLD FROM MUTNOVSKOE ORE OCCURRENCE, SOUTH-EASTERN KAMCHATKA, RUSSIA

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Native gold from hydrothermal ore veins from the South-Eastern Kamchatka region is described. Silver content in the mineral measured by microprobe varies from 14.4 up to 32 wt.%. There are also Bi, Te and Se in the mineral composition. The heterogeneous structure of the gold grains observed gives their low microhardness. The conclusion on the correlation between physical properties, composition and conditions of mineral formation is made. 3 tables, 5 figures, 14 references.

Keywords: native gold, hydrothermal gold deposit, Mutnovskoe ore occurrence, South-Eastern Kamchatka.

Brief geological overview of the region

Mutnovskoe ore occurrence is located in erosion-tectonic caldera of the Miocene-Pleistocene volcano in the south-east of Kamchatka (Aprelkov, Sheimovich, 1964; Aprelkov, Kharchenko, 1968). In terms of geology this area represents two structural levels (Lonshakov, 1979). The lower level consists of Oligocene-Miocene volcanic rocks and volcanic sediments crossed with intrusive bodies. The rocks of the lower level host the ore. Volcanic rocks are represented by fine fragmentary clastic tuffs of acidic and intermediate composition interbedded with andesite and andesite-basalt lava flows. They are present in the central part of the caldera. Intrusive massif with complex structure and composition that varies from quartz diorite to gabbro-diabase, is located in the same part of caldera. The massif is saturated with dacitic and quartz porphyry dikes. Volcanoclastic tuffs and tuffaceous sandstone are localized in the north-eastern part of the caldera. The upper structural level on the margins of the caldera consists of Upper Miocene-Pliocene and Lower Pleistocene volcanics covering underlying level with angular and azimuthal unconformity. Basaltic, andesite-basaltic lavas and rhyolite tuffs represent the upper volcanic rocks.

All ore hosting rocks are altered. Chemical analyses of rock samples taken across the ore body cross-section, show that propylitic alteration is characteristic for gabbro-diorite rocks. The comparison between altered and "fresh" rocks reveals that alteration resulted from potassium metasomatism with supply of K_2O and SiO_2 and removal of Na_2O and CaO (Table 1, an. 1 – 7). Argillic alteration is more developed in tuffs and andesite, which got depleted in K_2O, Na_2O and CaO, but enriched in silica (Table 1, an. 8 – 13).

The ore bodies are represented by hydrothermal veins and veinlets which alternate with completely altered and strongly silicified rocks. They usually extend submeridionally or to the north-west and north-east. The veins dip is steep and subvertical; the thickness varies from some centimeters to several meters. The biggest ore body reaches 2 – 3 meters in some places and widens up to 10 – 15 m (in the north upper part) splitting into multiple veins and veinlets. Vein clusters change to one or two veins at depth, which is typical for low depth gold deposits according to some authors (Nekrasov, 1976).

The veins vary in mineral composition: there are quartz, quartz-sulfide and quartz-carbonate veins. Quartz-sulfide veins dominate in the southern part of the area while quartz and quartz-carbonate ones are more abundant in the north. Pyrite, sphalerite and galena are the most common sulfide minerals in quartz-sulfide veins (Borisova *et al.*, 1983). Minor ore minerals include chalcopyrite, fahlore; the less abundant are luzonite, hessite, altaite, sylvanite, proustite, pyrargyrite, selenium bearing berryite and cupropavonite (Borisova *et al.*, 1986, Borisova, Meshalkin, 1991).

Characteristics of native gold

Native gold was observed in the crushed ore samples of the biggest ore body. It is represented by very small (0.01 mm) films, clumpy and interstitial particles in quartz. More rarely native gold was found as separated free grains of 0.01 – 0.1 mm in size. Such

Table 1. **Chemical composition of hydrothermally altered rocks of Mutnovskoe ore occurrence, wt.%**

№ an.	d, m	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	S_{total}	LOI	Total
Profile 1																
1	550	51.00	0.68	23.10	3.79	3.52	0.14	2.23	10.21	3.18	0.77	0.14	1.17	0.07	–	100.00
2	5.5	51.96	1.03	17.10	4.27	4.69	0.33	5.17	8.94	3.17	1.38	0.22	–	n.d.	1.64	99.90
3	4.5	49.16	1.13	16.36	3.93	4.90	0.62	0.88	16.30	2.30	1.38	0.26	–	n.d.	2.80	100.03
4	2.5	53.36	1.55	12.70	7.69	2.43	1.95	6.51	1.41	0.61	2.58	0.26	–	n.d.	8.26	99.31
5	1.5	51.25	1.74	17.19	1.78	8.15	0.68	1.76	7.36	2.30	2.40	0.21	–	n.d.	4.60	99.42
6	0.5	63.51	0.83	12.02	7.87	0.07	0.86	2.29	1.78	0.74	2.28	0.26	–	n.d.	6.85	99.36
7	0.05	57.94	0.94	15.93	4.93	0.74	1.49	4.81	1.34	1.08	4.74	0.30	–	n.d.	6.53	100.77
Profile 2																
8	5.3	74.80	0.65	13.60	0.54	0.23	0.042	0.40	0.05	0.12	6.69	0.036	1.98	0.08	–	99.22
9	4.3	72.60	0.41	14.90	0.44	0.26	0.078	0.43	0.05	0.10	7.78	0.052	1.92	0.05	–	99.07
10	3.3	75.80	0.78	10.40	3.80	0.18	0.080	0.65	0.09	0.05	3.70	0.140	3.12	0.34	–	99.13
11	2.3	84.20	0.80	8.60	0.31	0.15	0.091	0.53	0.05	0.025	2.11	0.060	2.24	0.03	–	99.20
12	1.3	89.60	1.04	5.70	0.02	0.17	0.068	0.31	0.05	0.016	1.35	0.026	1.52	0.02	–	99.89
13	0.4	94.60	1.15	1.30	0.13	0.06	0.017	0.06	0.05	0.029	0.22	0.028	1.49	0.02	–	99.15

Note: d – distance from the sample location to the ore body, n.d. – not determined, Analyses 1–7 are slightly altered gabbro-diorite and propylitic rocks; analyses were done at spectral-chemical laboratory of Lomonosov Moscow State University, analyst V.N. Zhihareva. Analyses 8–13 are argillic altered tuffs and andesites; samples were analyzed at the central analytic laboratory of GEOCHI RAS, analysts E.V. Besrogova and N.V. Budarina.

grains usually have applanate, dendrite, wire-like or isometric shape. The color of the gold particles is mainly yellow, sometimes with red or white tint.

Scanning electron microscopy (SEM) study of the particles morphology showed that there are flat or stepped areas on the surface of applanate and dendrite grains (Fig. 1). Subblock and granular structure of some grains was observed under higher magnification. Sometime some unidentified inclusions of porous and honeycomb phases were seen in gold grains (Fig. 2). Lighter strings of presumably more pure gold on the boundary of the blocks were observed in some cases (Fig. 3). Interstitial gold in quartz has curved boundaries that follow the contours of quartz grains or resemble amoeba-like pads on it (Fig. 4).

The structural peculiarities observed, that are granular and block structure, stepped pattern as well as phase heterogeneity of grains, are common for native gold in general, whereas very fine grains and ultra small size of their surface elements are characteristic for gold ores of low depth deposits (Petrovskaya, 1973, Novgorodova, 1983). Relation of gold grains with quartz show that they crystallized simultaneously or, sometime, gold formed a little later than adjacent quartz.

The studied gold can contain up to 32 wt.% of silver. Bi, more rarely Se and Te are also present in its composition (Table 2). According to Nina V. Petrovskaya (Petrovskaya, 1980), impurity of bismuth usually characterizes gold from deposits of medium depths, while Te and Se are the typical admixture for the mineral from ores of low depth deposits. Fineness of the gold from Mutnovskoe corresponds to the most common gold found in nature (Petrovskaya, 1973). The highest fineness characterizes one of the smallest grains (Table 2, an. 3). We did not observe any compositional zoning of the grains; although morphological or phase heterogeneity found under electron microscope could be caused by various Ag content. For instance, porous and honeycomb inclusions can possibly have higher Ag content because they look darker (Fig. 2) and therefore have lighter overall atomic weight. The paler veinlets at the blocks edges (Fig. 3) probably correspond to the composition with higher Au content than the matrix. Possibly, these gold veinlets formed as a result of matter rearrangement within or after the ore deposition. It is also possible that the heterogeneity in gold may represent inclusions of other minerals containing bismuth or tellurium.

X-ray powder diffraction data of native gold are given in the Table 3. The unit-cell parameter is 4.076 Å; it corresponds to gold-silver alloys with about 70 at.% Ag (Moiseyenko, 1977) confirming the determined composition of the mineral.

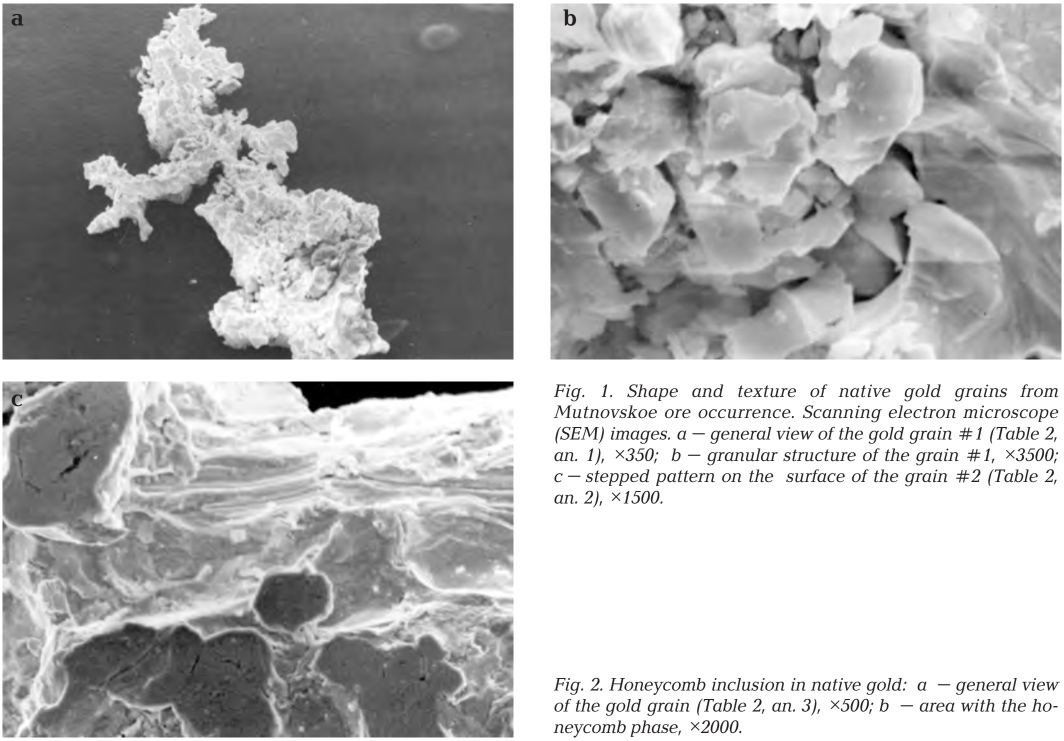
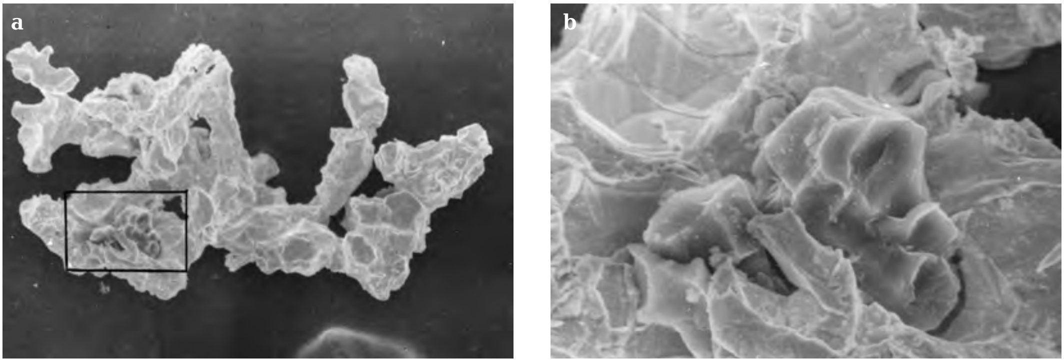


Fig. 1. Shape and texture of native gold grains from Mutnovskoe ore occurrence. Scanning electron microscope (SEM) images. a — general view of the gold grain #1 (Table 2, an. 1), ×350; b — granular structure of the grain #1, ×3500; c — stepped pattern on the surface of the grain #2 (Table 2, an. 2), ×1500.

Fig. 2. Honeycomb inclusion in native gold: a — general view of the gold grain (Table 2, an. 3), ×500; b — area with the honeycomb phase, ×2000.



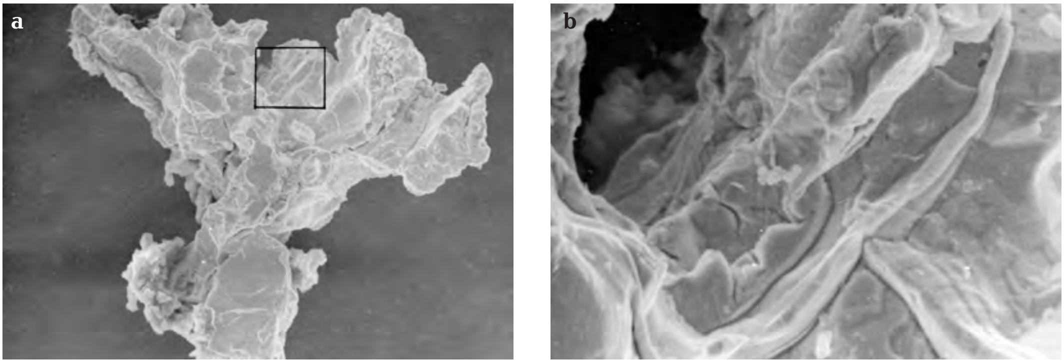


Fig. 3. Subblock structure of a gold grain: a — general view of the gold grain #4 (Table 2, an. 4), ×500; b — area with bright veinlets (possibly purer gold) on the blocks boundaries, ×3500.

Table 2. **Composition of the native gold by EPMA, wt.%**

№ an.	Size of the gold grains, μm	Au	Ag	Bi	Total	Fineness
1	5	78.8	19.5	n.d.	98.3	802
2	100	79.7	19.3	n.d.	99.0	805
3	5	82.4	14.4	n.d.	96.8	851
4	10	74.4	22.8	n.d.	97.2	765
5	10	75.0	22.9	n.d.	97.9	766
6	20–30	68.3	28.7	0.4	97.4	701
7	20–30	64.1	32.0	0.6	96.7	663
8	20–30	66.4	29.2	0.7	96.3	690
9	20–30	67.9	27.7	0.5	96.3	705
10	20–30	69.0	27.1	0.6	96.7	714
11	20–30	66.1	29.3	0.5	96.0	689

Note: accelerating voltage 22 kV, Au, Ag and Cu pure metals, PbTe, ZnSe were used as etalons. Analyses 1–5 were done by analyst L.T. Soshkina with JXA 50A microprobe. Cu, Bi, Te and Se were not detected (n.d.) Analyses 6–11 were done by analyst V.M. Chubarov with Camebax 244 microprobe. Cu, Se, Te, Zn, Pb, Fe, Sn and Sb were not detected except of analyses # 9 (Se and Te 0.1 wt. %). Low sums of the analyses are possibly due to the small grain size.

Table 3. **X-ray diffraction data for the native gold**

This study data		A.S.T.M., # 4-0786		
a_o = 4.076 Å		a_o = 4.0786 Å		
I	*d*	*I*	*d*	*hkl*
100	2.349	100	2.355	111
50	2.035	52	2.039	200
40	1.438	32	1.442	220
60	1.227	26	1.230	311
45	1.178	12	1.1774	222
10	1.0185	6	1.0196	400
30	0.9338	23	0.9358	331
40	0.9116	22	0.9120	420
		23	0.8325	422

Note: diffractogram was obtained with DRON 1 diffractometer with Co X-ray source using quartz as an internal etalon. Parameters of the unit cell were measured with a precision method by E.A. Borisova.

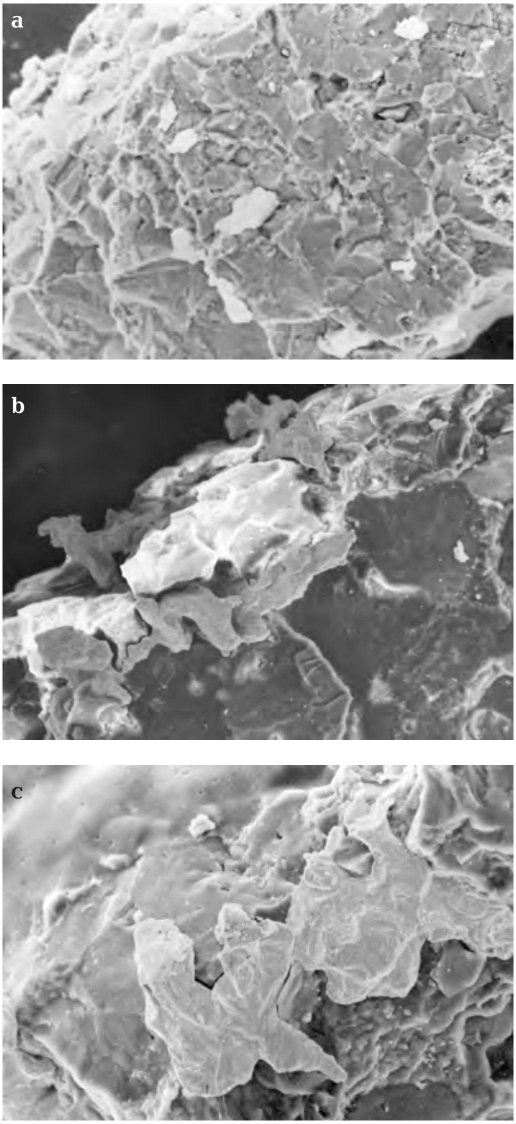


Fig. 4. Relations between native gold and adjacent quartz grain (SEM image); native gold – white and bright grey, quartz – dark grey. a, b – ×350; c – ×750.

Microhardness was measured for the biggest gold grain found. It varies in the range of 15–20 kg/mm^2 (3 measurements on PMT-3 with 5 g load) that is much lower than it was described for native gold before (Petrovskaya, 1980, Moiseyenko, 1977). This is most likely due to heterogeneity and internal structure of the grains which were observed under SEM. Also it needs to be mentioned that the Mutnovskoe ore occurrence is located in young region with active tectonics (Okrugin *et al.*, 2010). Therefore it could be possible that ores and gold suffered numerical temperature fluctuations resulted from temperature anomalies typical for the region and within the erosion-tectonic caldera. Temperature fluctuations might result in recrystallization of the gold grains and disorder of their structure. Nina V. Petrovskaya presumed that the low gold microhardness is related to structural disorder resulted from recrystallization, induced by near-intrusive heat (Petrovskaya, 1973). Valentin G. Moiseyenko provided data on heated and quenched Au-Ag alloys been softer and

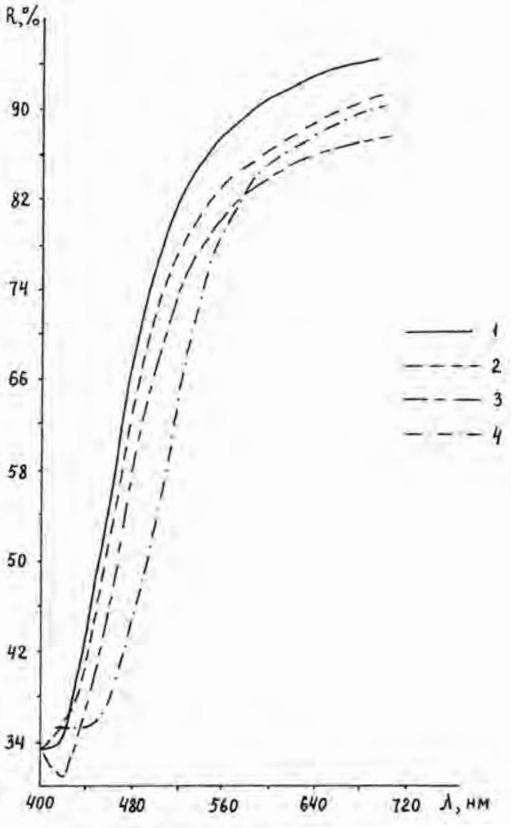


Fig. 5. Spectral reflection curves of the native fold from Mutnovskoe ore occurrence: 1 and 2 – gold grain #2 (Table 2, an. 2), 3 – gold grain #3 (Table 2, an. 3); 4 – reference data for native gold (Identification..., 1973).

more malleable in comparison to ones gradually heated and cooled (Moiseyenko, 1977).

The curves of reflectance spectrum measured on two gold grains (Table 2, an. 2, 3), are shown on Figure 5. According to the partial dispersion $\alpha = R_{640}/R_{480}$ and the correlation between α and gold fineness (Identification..., 1973) composition of the second gold grain (an. 3) includes more Au than that of the first one (an. 2) as it has been determined by microprobe too (Table 2). The shape of reflectance spectrum curves of the two grains are also different. The curve of the second grain (an. 3) has a dip at 420 nm and more gradual rise in the red part of the spectrum which is characteristic for gold with high fineness.

Conclusions

Gold particles from Mutnovskoe ore occurence are very fine in size, have complex morphology, structure heterogeneity and inclusions of unidentified phases. Fineness of the studied gold is in the range of 660–850 which is most common for native gold-silver alloys. The mineral contains 14.4 to 32 wt.% of Ag and sometime has Bi, Te, and Se in its composition. Physical properties of the gold connected to its composition and complex grain structure. The studied native gold is characteristic for low depth hydrothermal deposits (Petrovskaya, Safonov, 1976) formed in conditions of frequent temperature change.

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MONAZITES OF THE LATE GRANITIC PEGMATITES FROM ILMENY MOUNTAINS: AN AGE CHEMICAL DATING OF ZONAL AND SECTORIAL CRYSTALS

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Crystals of monazite-(Ce) from granitic amazonite pegmatite of the Blyumovskaya mine (N 50) and amazoniteless granitic pegmatite of the mine N 244 from the Ilmeny mountains of the Southern Urals are investigated. Heterovalent isomorphism according to the scheme $[(Th^{4+},U^{4+},Pb^{2+})_{1-x}Ca_x^{2+}] + Si^{4+} \leftrightarrow (REE^{3+},Y^{3+}) + P^{5+}$ is revealed in composition of the investigated monazites. Monazite-(Ce) from the granitic amazonite pegmatite of the Blyumovskaya mine with a semi-specious stones mineralization is enriched in Th and Pb and it is characterized by sharp sectoriality of composition with higher concentrations of ThO_2 (32 – 33 wt.%), UO_2 and PbO in pyramids of growth <110> and $<32\bar{2}>$, and with the lowest concentrations of these components in <101> pyramids. According to chemical dating, age of monazite from the Blyumovskaya mine accounts for 240 ± 11 – 12 million years. Monazite-(Ce) from granitic amazoniteless pegmatite of the mine N 244 is zonal with smaller concentrations of Th, U and Pb in the central zones of crystal. According to the ratio La_2O_3-Nd_2O_3 in monazite of the mine N 244, this vein is attributed to the late granitic pegmatites (formed before amazonite ones). Radiological age of the monazite from this vein is a little bit more ancient than from the Blyumovskaya (247 ± 16 million years) that corresponds with the data on sequence of formation of different pegmatites in the Ilmeny mountains.
4 tables, 6 figures, 11 references.

Keywords: monazite-(Ce), chemical dating of radiological age, granitic pegmatites of the Ilmeny mountains.

Structure of pegmatites and localization of monazite-(Ce)

Blyumovskaya mine was founded in 1835 by the fifth "gem stone" party under the direction of mining engineer F.F. Blum on a place of P.A. Versilov`s prospecting shaft on the latidunally directed hill situated in 2.5 km from the confluence of Cheremshanka river into the Ilmenskoe lake. The mine strips a vein of amazonite pegmatites with a length of about 150 m and thickness reaching up to 4 – 8 m (Minerals., 1949) in gneisses with amphibolite interbeds of the Ilmenogorsky stratum (PR1*il*). This vein has got its historical popularity not only because of the largest in the Ilmeny mountains (for that time) transparent crystals of topaz, but also due to the first findings of samarskite that was used during researches of radioactivity and gave to the world a new chemical element – samarium. In 1897 Blyumovskaya mine was examined by the participants of the VII International mineralogical congress. Pegmatite of this mine was one of the objects for A.E. Fersman during the development of pegmatite formation model and substantiation of the crystallographic induction law during cocrystallization of minerals.

In the vein, from selvage to the center occur coarse- and finegraphic zones with yellowish and pinkish microcline, fine- and coarsegraphic zones with greenish amazonite and albite, block zone with bluish-green amazonite, albite, topaz, and beryl. In eastern wall of the Academichesky passage, block zone is intersected by quartz-albite blastomylonite with accessory samarskite-(Y) (Melnikov, 1882; Popov, Popova, 2006). Crystals of monazite-(Ce) tabular along (100) and varying from 1 – 2 mm up to 1 – 2.5 sm in size have sites of induction surfaces (Fig. 1) with associating minerals: biotite (siderophyillite), almandine, ilmenorutile, ferrocolumbite, samarskite-(Y), and zircon (Fersman, 1940). Crystals of monazite – (Ce) generally have tabular shape with predominance of habitus form {100}, also crystals reveal areas of facets of the following different simple forms (in relative abundance): {110}, {120}, {101}, $\{\bar{1}01\}$, and {102}, other are rare. The idealized form of crystals is shown at Fig. 2.

Mine N 244 was founded in 1977 by E.P. Makagonov on submeridianal ridge of bedrock outcrops of gneisses and amphibolites in the extent of about 250 m of presumably Selyankinsky strata (A-PR*sl*) in a middle part of the Ilmeny reserve, in 3 km to the west from the lake Tatkul`. On the southern end of this ridge rocks are intersected by a vein of granitic graphic pegmatite (1 m thick) with almandine, biotite, zircon, ilmenite, gahnite, and monazite-(Ce). Small crystals of monazite-(Ce) up to 1 mm in size have elongated-tabular shape with prevalence of facets of the following forms: $\{100\}$, $\{110\}$, $\{102\}$, $\{\bar{3}22\}$; other are lesser developed.

Amazonite pegmatites are the latest in the Ilmeny mountains. Radiological age of different minerals according to 40 definitions by various methods accounts for about 240 million years (generalization, see. Popova *et al.*, 1982). Age of minerals belonging to pegmatite of the mine N 244 was not determined earlier.

Methodics of investigation

Chemical dating of radiological age of accessory monazites with the help of electron-sound microanalyzers is applied rather widely (Suzuki *et al.*, 1991; Montel *et al.*, 1996; Williams *et al.*, 1999; Suzuki, Kato, 2008; etc.). The method is based on an assumption that there was no loss of lead during evolution of monazites, and the initial concentration of lead during the formation of radioactive mineral is low and frequently equals to zero; thus simultaneous measurement of U, Th and Pb allows to receive the value of age from electron-sound microanalysis in individual grain (for ages more than 100 million years; probably, a little bit younger).

Images of monazite grains in secondary electrons are made at low force of current (3 nA) due to the fact that grains of the mineral have been mounted in epoxy resin. The analysis was carried out on electron-sound microanalyzer SX 100 of the Cameca firm with five wave spectrometers (Sp1-5). Pressure in the chamber of samples accounted for $8 \cdot 10^{-5}$ Pa, pressure in the field of electron gun accounted for $2.3 \cdot 10^{-6}$ Pa. In order to achieve the high resolution during the analysis of monazites with non-uniform distribution of elements accelerating voltage of 15 kV and force of a current of 250 nA was used. A corner of selection of X-ray radiation by wave spectrometers accounts for 40°, diameter of electron beam focused on a sample accounts for 2 micron. An operating mode of the detector is differential. Measured lines: Th M_α, U M_β, Pb M_α, P K_α, La L_α, Ce L_α, Pr L_β, Nd L_α, Sm L_β, Eu L_α, Gd L_β, Dy L_α, Ho L_β, Y L_α, Si K_α, Ca K_α. For analysis of Th, U, and Pb in monazite *M*-lines were more preferable than *L*-lines as energy of excitation for *L*-shells of thorium and uranium exceeds 15 keV. For the full quantitative analysis of monazites concentrations of uranium, thorium, lead, yttrium (numerous overlapping of lines of rare earth and other elements are taken into account), silicon, calcium, phosphorus and rare earth elements (for the account of numerous imposings of lines and matrix corrections) are determined. For acceleration of carrying out of the analysis determination of elements was produced on different spectrometers: Y and Si — on spectrometer Sp1 with crystal-analyzer TAP; U and Ca — on Sp2 with increased crystal LPET; Pb — on Sp3 with LPET; Th and P — on Sp4 with PET; lanthanides — on Sp5 with crystal-analyzer LIF. Measurements of intensities of peaks of U, Th and Pb were carried out during 300 seconds, other elements — during 10 seconds. For definition of the minimal error of monazites` age, the analysis was carried out during 600 seconds for peaks of U, Th and Pb. The following standard samples are used: for calculation of Th metal thorium and ThO_2 are used; for calculation of Si pyrope is used; for Ca — $Ca_2P_2O_7$; Y — YPO_4; for U — UO_2; for Pb — $Pb_2P_2O_7$; for Ce and P — $CePO_4$; for other rare earth elements monophosphatic glasses are also used.

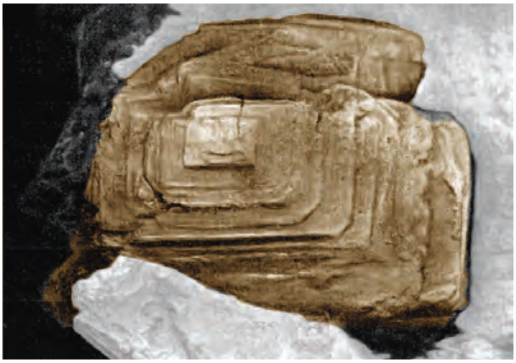

Fig. 1. Crystal of monazite-(Ce) 1.5 sm in size with induction surfaces with biotite (black) and microcline (light grey). Blyumovskaya mine. A.G. Zhabin`s photo (1960).

In this article it is used the earlier suggested formula of dating of mineral age based on the

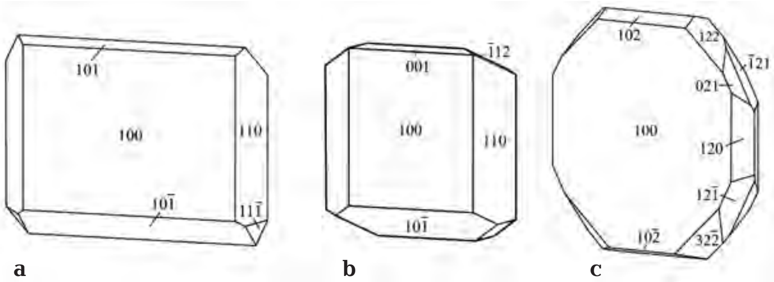

Fig. 2. The idealized form of monazite-(Ce) crystals from the Blyumovskaya mine. Crystals are measured by the authors and drawn according to the program Shape 7.1.

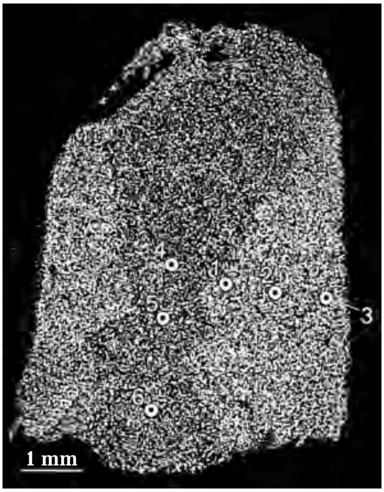

Fig. 3. Sectorial structure of monazite-(Ce) from the Blyumovskaya mine in X-ray characteristic radiation of Th M_{α}. Figures correspond to numbers of analyses in Table 1.

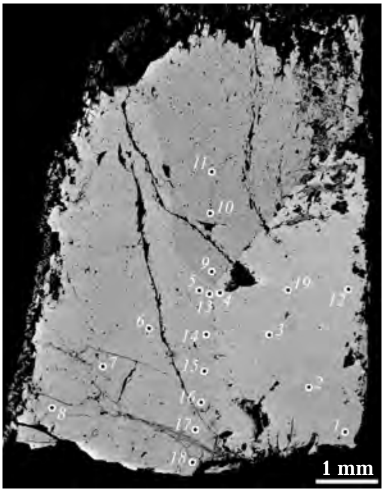

Fig. 4. Picture of sectoriality in secondary electrons in the new section (see the text) of monazite-(Ce) from the Blyumovskaya mine. Figures correspond to numbers of analyses in Table 2.

Table 1. **Chemical composition (wt.%) of monazite (Ce) from the Blyumovskaya mine**

	Prism *m* {110} zones of growth (see Fig. 3)				Pinacoid *x* {$\bar{1}$01} zones of growth			
№ an.	1 *c*	2	3 *e*	Average	4 *c*	5	6 *e*	Average
ThO_2	32.11	32.26	32.79	32.22	24.92	26.47	26.93	26.11
UO_2	*N.d.*	*N.d.*	1.13	1.13	*N.d.*	*N.d.*	1.04	1.04
P_2O_5	18.19	18.60	18.19	18.33	21.39	20.92	20.95	21.09
La_2O_3	5.72	5.70	3.04	4.82	6.26	6.17	5.87	6.10
Ce_2O_3	22.25	22.02	23.48	22.58	24.63	24.20	23.86	24.23
Pr_2O_3	2.66	2.47	2.76	2.63	3.27	3.13	2.89	3.10
Nd_2O_3	7.59	8.20	8.82	8.20	9.35	9.16	9.06	9.19
Sm_2O_3	1.58	1.56	1.52	1.55	1.93	1.55	1.91	1.80
Gd_2O_3	0.43	0.40	0.56	0.46	0.57	0.55	0.54	0.55
Dy_2O_3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Y_2O_3	0.67	0.53	0.64	0.61	0.75	0.95	0.90	0.87
CaO	0.10	0.09	0.08	0.09	0.16	0.15	0.15	0.15
SiO_2	7.13	7.14	7.20	7.16	5.70	5.83	5.79	5.77
Total	98.43	98.97	100.21	99.78	98.93	99.08	99.87	100.0

Empirical formulas based on O = 4 (average data)

Analyses 1 – 3: $(Ce_{0.36}Th_{0.32}Nd_{0.13}La_{0.08}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.01}U_{0.01})_{0.98}(P_{0.68}Si_{0.32})_{1.00}O_4$;

Analyses 4 – 6: $(Ce_{0.38}Th_{0.25}Nd_{0.14}La_{0.10}Pr_{0.05}Sm_{0.03}Gd_{0.01}Y_{0.02}U_{0.01}Ca_{0.01})_{1.00}(P_{0.76}Si_{0.25})_{1.01}O_4$

Notes: Microprobe JXA-733 Superprobe with energy-dispersion spectrometer INCA, accelerating voltage 20 kV, electron beam diameter 5 micron, analyst E.I. Churin. Y_2O_3 and Eu_2O_3 (<0.3 wt. %) contents have been detected with the help of wave spectrometer. N. d. – not detected; c – center of the crystal, e – edge of the crystal.

equation of disintegration of parent isotopes of U and Th and accumulation of radiogenic lead (Montel *et al.*, 1996; Williams *et al.*, 1999). This formula has after transformations at a ratio of isotopes` abundance $^{238}U/^{235}U = 137.88$ the following form: $Pb = Th\{\exp(\lambda^{232}t)-1\} + U[\{\exp(\lambda^{235}t) + 137.88\cdot\exp(\lambda^{238}t)\}/138.88-1]$, where Pb, U, and Th correspond to the contents of elements (in ppm); $\lambda^{232}, \lambda^{235}, \lambda^{238}$ correspond to constants of radioactive disintegration of ^{232}Th, ^{235}U, and ^{238}U; *t* corresponds to radiological age (in years). The decision of the equation relatively to t with the use of the specialized software products gives the age of a mineral determined for grain in a point of the analysis.

Results of investigation and their discussion

Monazite-(Ce) of amazonite pegmatite of the Blyumovskaya mine of the Ilmeny mountains. The first data about contrast sectoriality of monazite-(Ce) composition from pegmatite of this mine have been received during investigation of monazites of different veins of the Urals according to the Task program of interdisciplinary projects between the UrO of the Russian Academy of Sciences and Siberian Branch of the Russian Academy of Sciences (Popova, Churin, 2009). With the help of X-ray spectral energy dispersive analysis in the section along (100) of monazite grains in zones of growth of a prism *m* {110} it is determined about 32 wt.% of ThO_2, and in the zones of pinacoid *x* {$\bar{1}$01} it is determined 25 – 27 wt.% of ThO_2 (Fig. 3; tab. 1). Respectively, pyramids of growth <110> contain higher concentrations of SiO_2 and smaller concentrations of P, La, Ce, and Y oxides. Such sharp differences in composition of the monazite-(Ce) growth pyramids of different simple forms have caused more detailed investigation of this grain.

After additional grinding and polishing of the asymmetric grain it was obtained the new section a little bit distinguishing from the early one. In secondary electrons and in X-ray characteristic radiation of Si, P, Ce and Th it was revealed more complex picture of the grain structure with additional sectors of growth of crystal facets differing in composition (Figs. 4, 5). According to facets occurring on crystals of monazite and pictures of distribution of elements, it is possible to assume display in the analyzed section not only sectors of growth <110> and <$\bar{1}$01>, but also <101>, <100>, <$\bar{1}\bar{2}\bar{2}$>, <32$\bar{2}$> and <1$\bar{2}\bar{1}$> (Table 2). In sectors of growth of different simple forms the greatest contents of ThO_2 are characteristic for <110> (from 33.8 wt.% in the central part of grain up to 31.6 % – on the periphery), and the least – for <101> (22.7 – 22 wt.%); the analysis in <32$\bar{2}$> is similar to average analyses in sector <110>. Concentration of ThO_2 in other sectors – <100>, <$\bar{1}\bar{2}\bar{2}$>, <1$\bar{2}\bar{1}$> accounts for 25.5 – 27 wt.% and are close to the data resulted for <$\bar{1}$01> (Table 1).

Directly proportional connection between the concentrations of ThO_2 with UO_2, PbO, SiO_2 and inversely proportional – between P_2O_5, rare earth elements, Y_2O_3, and CaO (Table 2) is distinctly shown. Concentrations of UO_2 and PbO within the limits of each sector of growth are relatively sustained. The sum of rare earths in different analyses accounts for 39 – 47 wt.% with absolute prevalence of Ce and Nd above La. According to the distribution of elements, it is possible to expect in monazite microinclusion of thorianite, cheralite, huttonite, apatite, and quartz (see Fig. 5, the right top corner) not influencing on the general laws of composition in sec-

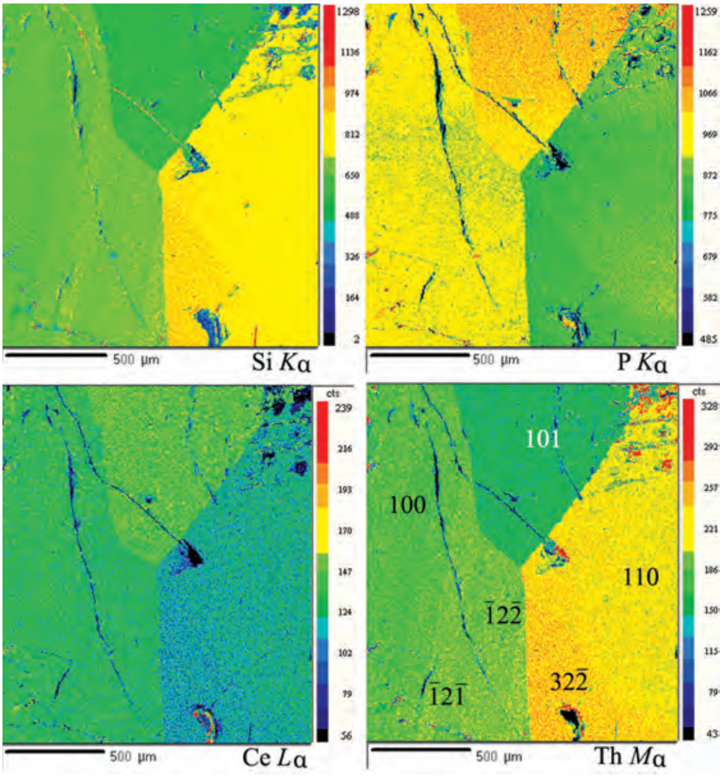

Fig. 5. Sectoriality of monazite-(Ce) composition in the central part of the grain (see Fig. 4) in X-ray characteristic radiation of elements.

Table 2. **Chemical composition wt.%) and radiological age (*t*, million years) of the monazite-(Ce) from the Blyumovskaya mine, new section**

	Composition in spots of analysis (see Fig. 4)																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
ThO_2	32.75	31.84	33.41	33.78	26.87	26.99	25.52	26.16	22.71	22.25	22.04	31.57	27.03	27.09	27.19	27.59	28.64	26.15	32.38
UO_2	0.64	0.63	0.66	0.66	0.58	0.57	0.56	0.54	0.48	0.49	0.48	0.62	0.61	0.62	0.60	0.60	0.65	0.59	0.63
PbO	0.36	0.34	0.37	0.36	0.29	0.30	0.28	0.29	0.25	0.24	0.24	0.34	0.29	0.29	0.30	0.31	0.32	0.28	0.34
P_2O_5	17.59	17.59	17.28	16.98	19.99	19.93	20.69	20.74	21.64	21.94	21.99	18.32	19.39	19.17	19.15	19.11	19.11	19.63	17.15
La_2O_3	7.31	7.50	7.44	7.25	7.80	7.81	8.01	7.94	8.59	8.81	8.91	7.63	7.99	8.20	8.15	7.98	8.10	8.12	7.82
Ce_2O_3	20.92	21.43	21.38	20.81	23.16	22.93	23.61	23.24	24.66	24.85	24.85	21.65	23.20	23.04	23.19	22.55	22.62	23.26	21.20
Pr_2O_3	2.65	2.53	2.51	2.47	2.92	2.83	2.89	2.81	2.95	2.93	2.89	2.48	2.73	2.96	2.87	2.98	2.85	3.04	2.76
Nd_2O_3	7.80	8.02	7.94	7.72	9.13	8.89	9.18	8.87	9.34	9.58	9.63	8.04	8.88	8.81	8.73	8.85	8.45	8.78	7.73
Sm_2O_3	0.40	0.32	0.47	0.37	0.54	0.67	0.61	0.44	0.59	0.57	0.65	0.40	1.22	1.13	0.97	1.01	1.12	0.98	0.87
Eu_2O_3	–	–	0.10	–	–	–	–	–	–	0.01	–	–	–	0.04	–	0.07	–	–	–
Gd_2O_3	0.02	0.10	0.10	0.06	0.10	0.12	0.15	0.16	0.17	0.09	0.13	0.06	0.39	0.33	0.44	0.30	0.41	0.47	0.41
Dy_2O_3	0.03	0.07	0.08	0.08	0.08	0.09	0.07	0.05	0.07	0.05	0.10	0.07	–	0.09	–	–	0.06	0.09	–
Ho_2O_3	0.08	0.05	–	0.05	–	–	–	–	0.03	0.06	–	–	–	–	–	–	–	–	–
Y_2O_3	0.51	0.51	0.53	0.52	0.75	0.73	0.78	0.67	0.74	0.77	0.76	0.57	0.74	0.73	0.74	0.70	0.67	0.71	0.51
CaO	0.15	0.15	0.14	0.14	0.24	0.23	0.25	0.24	0.25	0.26	0.25	0.15	0.22	0.23	0.23	0.21	0.20	0.30	0.14
SiO_2	7.37	7.16	7.54	7.61	5.87	5.93	5.62	5.73	4.88	4.78	4.72	7.08	5.86	5.86	5.90	6.02	6.13	5.83	7.16
Total	98.59	98.26	99.95	98.88	98.32	98.01	98.21	97.88	97.34	97.68	97.66	98.99	98.57	98.58	98.48	98.28	99.31	98.23	99.11
t	**242**	**241**	**245**	**240**	**242**	**245**	**241**	**243**	**239**	**237**	**244**	**238**	**236**	**233**	**240**	**245**	**244**	**237**	**237**
±Δ *t*	11	11	11	11	11	11	11	11	11	11	11	11	12	12	12	12	12	12	12

Empirical formulas for average analyses from different sectors of growth (O = 4)

<110> – an. 2–4, 12, 19 (average of 5 analyses.): $(Ce_{0.35}Th_{0.33}Nd_{0.12}La_{0.12}Pr_{0.04}Sm_{0.01}Y_{0.01}U_{0.01}Ca_{0.01})_{1.00}(P_{0.66}Si_{0.33})_{0.99}O_4$;

<$\bar{1}\bar{2}\bar{2}$> – an. 5, 13–18 (average of 7 analyses): $(Ce_{0.37}Th_{0.27}Nd_{0.14}La_{0.13}Pr_{0.05}Sm_{0.02}Gd_{0.01}Y_{0.02}U_{0.01}Ca_{0.01})_{1.03}(P_{0.72}Si_{0.26})_{0.98}O_4$;

<101> – an. 9–11 (average of 3 analyses): $(Ce_{0.39}Th_{0.22}Nd_{0.15}La_{0.14}Pr_{0.05}Sm_{0.01}Y_{0.02}Ca_{0.01})_{0.99}(P_{0.80}Si_{0.21})_{1.01}O_4$

Note. Analyses in sectors of growth: 1 – <32$\bar{2}$>; 2–4, 12, 19 – <110>; 9–11– <101>; 7–8 – <100>; 5, 13–18 – <$\bar{1}\bar{2}\bar{2}$>; 6 – <1$\bar{2}\bar{1}$>. Microprobe SX 100 Cameca, analyst V.V. Hiller. Dash – not detected (less than detection limit).

tors of crystal growth. Calculated values of radiological age *t* in different points of the analysis make from 233 up to 245 million years (average of 19 definitions accounts for 240 ± 11–12 million years) that is comparable to the available average data obtained by other methods of analysis of minerals from this vein.

Monazite-(Ce) of the granitic pegmatite from the mine N 244 of the Ilmeny mountains is investigated also in section along (100) of elongated-tabular crystal (Fig. 6). In secondary electrons distinct zones of facet growth of simple forms {110}, {$\bar{1}$22}, {$\bar{3}$22}, {$\bar{3}$02}, {102} were revealed; zones are characterized by different thickness at rather same alternation of dark (more "light ") and light-coloured zones; the central part of a crystal, probably, is a zone {100}. Profile of microprobe analysis is passed only through the parts of sectors of forms <$\bar{1}$22>, <100>, <$\bar{1}$0$\bar{2}$> and <32$\bar{2}$> (Table 3). Dark zones of the central part of the crystal contain about 14 wt.% of ThO_2, and light peripheral – up to 19–23%. Comparison of compositions of peripheral zones of growth sectors <$\bar{1}$22> (Table 3, analyses 3, 4, 6) and zones corresponding to them in sector <$\bar{1}$0$\bar{2}$> (Table 3, analyses 11, 12, 13) shows their significant distinction: in <$\bar{1}$22> in analyses 3 and 4 concentration of ThO_2 is lower than in respective zones <$\bar{1}$0$\bar{2}$> (analyses 11, 12), but in analyses 6 and 13 the relationship is reverse; distinctions and contents of P, Si, Ce, and Y oxides are shown that reflects sectoriality of composition of monazite-(Ce) crystal. Coefficients of correlation of oxides in the monazites` composition show (Table 4) strong positive connections between the contents of ThO_2-UO_2-PbO-SiO_2; P_2O_5-La_2O_3-Ce_2O_3-CaO; Y_2O_3-Dy_2O_3 and accordingly inverse relationship between these groups. According to the monazite from the mine N 244 analyses, average value of radiological age accounted for 247 ± 16 million years (on 16 analyses).

Conclusions

Heterovalent isomorphism is revealed in composition of the investigated monazites-(Ce) according to the scheme $[(Th^{4+},U^{4+},Pb^{2+})_{1-x}Ca_x^{2+}] + Si^{4+} \leftrightarrow (REE^{3+},Y^{3+}) + P^{5+}$. Monazite-(Ce) from granitic amazonite pegmatite of the Blyumovskaya mine with a gem stone mineralization is enriched in Th and Pb and is charac-

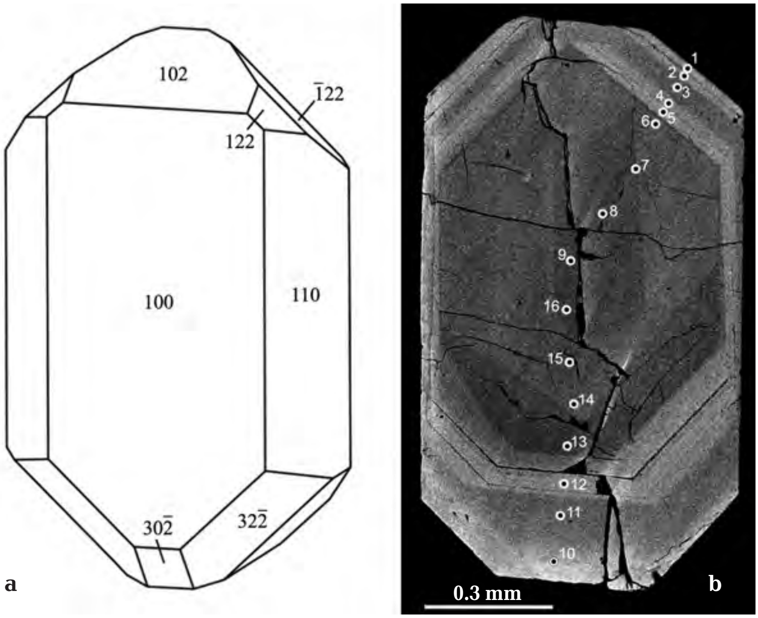

Fig. 6. The ideal form (the crystal is measured by the authors and it is drawn according to the program Shape 7.1): a — zonality in secondary electrons; b — sections of monazite-(Ce) crystal from pegmatite N 244 of the Ilmen mountains. Figures correspond to the numbers of analyses in the Table 3.

Table 3. **Chemical composition (wt.%) and calculated age (*t*, million years) of monazite-(Ce) from pegmatite of the mine N 244**

	Composition in spots of analysis (see Fig. 6)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
ThO_2	22.07	20.99	15.38	19.39	20.41	15.74	13.90	13.92	14.21	18.12	16.32	23.06	12.15	15.57	15.20	14.12
UO_2	1.08	1.09	0.86	1.08	1.09	0.64	0.63	0.62	0.63	0.94	0.90	1.17	0.50	0.64	0.66	0.61
PbO	0.25	0.24	0.19	0.24	0.25	0.19	0.18	0.17	0.17	0.22	0.20	0.28	0.15	0.18	0.18	0.17
P_2O_5	21.38	21.93	24.60	22.15	21.84	24.64	26.41	25.74	25.37	24.17	23.84	20.85	26.09	25.04	25.03	25.57
La_2O_3	10.25	11.44	12.40	11.55	11.30	12.63	13.03	12.84	12.83	11.92	12.24	10.85	13.23	12.42	12.35	13.09
Ce_2O_3	21.90	22.47	25.23	23.74	23.34	24.54	25.26	25.17	25.04	23.68	24.28	22.03	25.80	24.60	24.31	25.08
Pr_2O_3	2.45	2.38	2.78	2.56	2.44	2.57	2.50	2.53	2.78	2.37	2.57	2.42	2.94	2.54	2.64	2.55
Nd_2O_3	9.00	8.25	9.08	9.13	8.93	9.14	8.93	9.06	8.87	8.65	8.94	8.46	9.82	9.34	9.14	8.91
Sm_2O_3	1.39	1.18	1.22	1.14	1.22	1.18	1.28	1.34	1.30	1.16	1.31	1.03	1.34	1.46	1.39	1.34
Eu_2O_3	0.02	0.04	–	0.05	0.03	0.03	0.02	0.13	–	–	0.07	0.05	0.02	0.03	0.05	0.03
Gd_2O_3	1.01	0.97	1.04	0.91	0.89	0.97	0.93	1.10	0.96	0.97	1.06	0.70	1.04	1.07	1.31	1.01
Dy_2O_3	0.21	0.25	0.21	0.17	0.18	0.22	0.27	0.31	0.24	0.35	0.26	0.20	0.24	0.26	0.29	0.25
Y_2O_3	0.65	0.88	0.78	0.56	0.73	0.76	0.84	0.84	0.81	1.02	0.83	0.76	0.78	0.77	0.86	0.82
CaO	0.31	0.55	0.42	0.25	0.27	0.91	1.03	0.99	1.00	0.68	0.46	0.26	0.83	0.87	1.04	0.99
SiO_2	4.75	4.38	3.24	4.35	4.53	2.69	2.19	2.17	2.30	3.32	3.29	5.04	1.94	2.65	2.47	2.25
Total	96.71	97.06	97.43	97.27	97.47	96.85	97.40	96.95	96.50	97.58	96.58	97.16	96.86	97.45	96.94	96.78
***t*±16**	**228**	**234**	**243**	**252**	**246**	**256**	**263**	**250**	**247**	**247**	**247**	**247**	**250**	**247**	**247**	**244**

Empirical formulas of selected analyses (O = 4)

Center <100> – analyses 7–9, 16 (average of 4 analyses): $(Ce_{0.39}La_{0.21}Nd_{0.13}Th_{0.13}Ca_{0.04}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.02}U_{0.01})_{1.00}(P_{0.91}Si_{0.09})_{1.00}O_4$;

earlier zone <$\bar{1}22$> – analyses 6: $(Ce_{0.38}La_{0.20}Nd_{0.14}Th_{0.15}Ca_{0.04}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.02}U_{0.01})_{1.01}(P_{0.88}Si_{0.11})_{0.99}O_4$;

the same zone <$\bar{1}0\bar{2}$> – analyses 13: $(Ce_{0.39}La_{0.20}Nd_{0.15}Th_{0.12}Ca_{0.04}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.02})_{0.99}(P_{0.92}Si_{0.08})_{1.00}O_4$;

later zone <$\bar{1}22$> – analyses 4: $(Ce_{0.38}Th_{0.19}La_{0.18}Nd_{0.14}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.01}Ca_{0.01}U_{0.01})_{0.99}(P_{0.81}Si_{0.19})_{1.00}O_4$;

the same zone <$\bar{1}0\bar{2}$> – analyses 12: $(Ce_{0.35}Th_{0.23}La_{0.18}Nd_{0.13}Pr_{0.04}Sm_{0.02}Gd_{0.01}Y_{0.02}Ca_{0.01}U_{0.01})_{1.00}(P_{0.77}Si_{0.22})_{0.99}O_4$

Note. Analyses in sectors of growth: 1–6 – <$\bar{1}22$>; 7–9, 16 – <100>; 10–13 – <$\bar{1}0\bar{2}$>; 14–15 – <$32\bar{2}$>. Microprobe SX 100 Cameca, analyst V.V. Hiller. Dash – not detected (less than detection limit)).

Table 4. **Correlation matrix of components in the composition of monazite-(Ce) from the mine № 244**

	ThO_2	UO_2	PbO	P_2O_5	Ce_2O_3	La_2O_3	Nd_2O_3	Pr_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Eu_2O_3	SiO_2	CaO
UO_2	**0.95**													
PbO	**0.98**	**0.96**												
P_2O_5	-0.98	-0.95	-0.96											
Ce_2O_3	-0.97	-0.88	-0.93	**0.93**										
La_2O_3	-0.97	-0.91	-0.94	**0.95**	**0.96**									
Nd_2O_3	-0.62	-0.62	-0.62	0.53	0.63	0.48								
Pr_2O_3	-0.69	-0.61	-0.68	0.56	0.71	0.60	**0.72**							
Sm_2O_3	-0.54	-0.61	-0.63	0.53	0.42	0.37	0.56	0.33						
Gd_2O_3	-0.55	-0.54	-0.63	0.53	0.44	0.41	0.45	0.36	**0.75**					
Dy_2O_3	-0.42	-0.43	-0.45	0.55	0.30	0.42	-0.08	-0.13	0.31	0.49				
Eu_2O_3	-0.02	-0.02	-0.01	-0.02	-0.01	0.02	-0.02	-0.21	0.09	0.20	0.17			
SiO_2	**0.98**	**0.98**	**0.98**	-0.99	-0.91	-0.95	-0.54	-0.58	-0.56	- 0.56	- 0.54	- 0.03		
CaO	-0.81	-0.91	-0.84	**0.88**	0.69	**0.82**	0.29	0.32	0.52	0.52	0.62	0.05	- 0.91	
Y_2O_3	-0.30	-0.28	-0.31	0.42	0.21	0.37	-0.33	-0.14	0.03	0.26	**0.86**	-0.06	-0.40	0.49

Note. Strong positive relationships are bold.

terized by sharp sectoriality of composition with higher concentrations of ThO_2, UO_2 and PbO in pyramids of growth <110> and <32$\bar{2}$> and lowerst – in <101>; average age of monazite according to chemical dating accounts for 240 ± 11 – 12 million years.

Monazite-(Ce) from granitic amazoniteless pegmatite from the mine N 244 is zonal in composition with lower concentrations of Th, U and Pb in central zones of the crystal and increased concentrations in peripheral zones alternating with less rich. Monazite from the mine N 244 contains more La than Nd. According to the relashionship in it $La_2O_3 – Nd_2O_3$ (in percentage from the sum of *TR*), this vein is attributed to the late granitic (preamazonite) pegmatites (Popova, etc., 1982). Average radiological age of monazite from this vein is a little bit more ancient than from the Blyumovskaya mine and accounts for 247 ± 16 million years that corresponds to the data on sequence of formation different type pegmatites in the Ilmeny mountains (Popov, Popova, 2006).

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TO MINERALOGY OF TETRAVALENT URANIUM

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On the basis of the author experimental data and analysis of literature, modern state of mineralogy of tetravalent uranium is considered. New and little known results are obtained due to utilization of local methods of analytical electron microscopy (AEM). More thorough mineralogical investigations from optical level to electronic level not only widened range of U^{4+} minerals, showing possibility of existence of U^{4+}-phospho-silicates, but also allowed us to say more definitely about structural relation of Ca and U^{4+} in these minerals.
5 figures, 1 table, 28 references.
Keywords: minerals of tetravalent uranium, U^{4+}-phosphates.

Introduction

In mineralogical data base are noted about 200 mineral species, in which uranium is structure-forming element. From all big quantity of uranium minerals we know less than ten minerals of tetravalent uranium. Among them are wide known: uraninite, coffinite, brannerite. By these three mineral species of U^{4+}, as a rule, the interest of geologist to mineralization of primary (non oxidized) uranium ores is restricted. U^{4+} phosphates – ningyoite and three minerals of lermontovite group are less known. Such approach does not simply "impoverish" mineralogy of uranium ores, but is not always correct. Moreover, incomplete mineralogical study of the ores might result in erroneous interpretation of their genesis, on the one hand, and incorrect assessment of physical – chemical (technological) properties of ore, on the other hand. As far as these problems have very important significance, the necessity arises for consideration of modern status of mineralogy of tetravalent uranium.

Uranium as chemical element has such structure of outer electronic shell ($5f^3 6d7s^2$), which allows him to form ions of different valency – from 2^+ to 6^+. As a result, uranium in each valent state forms definite, corresponding only to this state specific compounds. Under natural conditions compounds of U^{4+} and U^{6+} are stable.

During many years in mineralogy it was considered, that U^{5+} cannot form stable compounds and therefore there are not in nature minerals of pentavalent uranium. At present moment publications about existence of minerals with U^{5+} in their composition are already known, but the problem of definite determination of such valent state of uranium is not solved. The presence of U^{5+} in composition of nature uranium oxides was established due to data of X-ray photoelectronic spectroscopy (XPhES), however taken as standards natural samples, by our opinion, were not sufficiently studied (Teterin *et al.*, 1981). Later the data were published regarding synthesis of stable compound of pentavalent uranium U^{5+}, and then also about finds of natural mineral wyartite (Burns, Finch, 1999), in whose composition enters U^{5+}. Proof of presence of pentavalent uranium in composition of this water-bearing calcium-uranium uranyl-carbonate, obtained during determination of mineral structure, is indirect – crystallochemical. It is based on geometry of polyhedrons and sum of valency bonds of one of uranium positions in structure, requiring presence here of U^{5+} for electrically neutral balance of valencies. The other valence states of uranium are displayed only in laboratory syntheses. Thus, under natural conditions at present are trustworthily known compounds of tetra- and hexavalent uranium.

Speaking about uranium mineralogy, it worths first of all to underline, that behaviour of this element in geological processes is in principle different for its different valence states. Minerals of tetravalent urnium U^{4+} are formed under reduction geochemical environment, and minerals of U^{6+} – under oxidized one.

By their chemical properties ions of U^{4+} and U^{6+} are so different, that each of them forms compounds on principle different type both by crystal structure, morphology and by physical-chemical properties. During mineral formation U^{4+} behaves as typical cation, demonstrating isomorphism with Th and *REE*, more rarely with Ca. Differing from it, cation U^{6+} is not typical and usually is represented in nature as linear ion $(U^{6+}O_2)^{2+}$ – uranyl. It is unique ability of U^{6+} to create specific uranyl-ion that determines individuality of its compounds. As a result it is necessary to consider independently and separately mineralogy of tetravalent and hexavalent uranium.

Mineralogy of uranyl (U^{6+}) differs by very wide spectrum of mineral species (about 170), formed as a result of its contrast and energetic water migration under conditions of hypergenesis. These exogenic (so called secondary) minerals of hexavalent uranium strongly reflect conditions of ore formation (Sidorenko, Doynikova, 2009).

Mineralogy of uranium U^{4+} is rather limited as regards a number of mineral species composing it (until now less than 10, and real number of mineral species of U^{4+} might be greater, but their revealing requires utilization of modern methods of mineralogical analysis). However exactly minerals of tetravalent uranium are practically the most important components of mineral raw material for atomic industry. Therefore just mineralogy of U^{4+} attracts special attention.

Up till now this division of mineralogy was restricted only by three mineral species. They are – oxide *uraninite* and its morphological varieties: collomorphic nasturan (pitchblende) and highly dispersed powder uraninite, silicate *coffinite* and titanate *brannerite*. At the end of 20th century these commercially significant mineral species were added by Ca-U^{4+}-phosphate *ningyoite* (Doynikova, 2007). Besides there were discovered U^{4+}-phosphates (Belova *et al*., 1998) – lermontovite, vyacheslavite, urfoite, later united into mineral group of lermontovite (Doynikova, 2005), they are represented by separate single finds. It is noteworthy to recall also earlier single finds of sedovite and mourite, known as molybdates of U^{4+} (Sidorenko, 1978), which are not still sufficiently studied and represent only scientific interest. Coexisting in their structure simultaneously of reduced (U^{4+}) and oxidized (U^{6+}) uranium forms, as well as the most oxidized form of molybdenum Mo^{6+}, seems to be geochemical groundless. Taking into consideration high dispersion of this formations, at present it is necessary to do their additional study using modern methods.

While considering of mineral species, composing the class of minerals of tetravalent uranium, we shall expose only new or little known information, which adds known handbook data. Such information was obtained during last decades as a result of developing of mineralogical investigations and transferring from the level of optical microscopy to the level of electronic one. Analytical electronic microscopy (AEM) allows us to study both composition of the finest mineral formations and diffraction characteristics of micron particles (microdiffracton of electrons). Study of complex for traditional diagnostics uranium ores with the help of highly local methods of AEM (transmission and scanning), in fact – investigation of micromineralogy, led to accumulation of new knowledge about U^{4+}-minerals, to refinement of their isomorphic transformations.

About well known minerals of tetravalent uranium

Uraninite – a single represantative of uranium oxides in nature. All above mentioned its morphological varieties have the simplest cubic crystal structure of fluorite type with idealized crystallochemical formula UO_2. Some varieties are known with isomorphic admixtures of rare earth elements of cerium group (cleveite) or thorium Th (to uranothorianite).

During study of exogenic (so called black's) ores with the help of transmission AEM it was observed very wide spectrum of degree of uraninite crystallization in them. Finely dispersed character of uranium oxide segregation in composition of uranium blacks facilitates in its quick oxidation. Process of oxidation decreases degree of particles crystallinity at the expense of increase of structure dislocations during oxidation (without uranyl forming). According to patterns of electron microdiffraction (from spot to circle ones) one can observe decreasing of structural perfection of uranium-oxide substance right up to electron amorphous state (Fig. 1a). Electron amorphous segregations of uraninite occur in natural samples rather often. In such case mineral is diagnosed by means of element composition of particles, determined directly under electron microscope. In composition of poorly crystallized dispersed uraninites (with diffused circular refflextions) rather often is present admixture of silicon; alongside with decrease of crystallinity degree quantity of Si increases. Entering of Si in composition of the mineral in this case is caused by high sorption properties of dispersed matter, it should not be related to uraninite structure.

At a number of deposits uranium-oxide substance was found as mineraloid, glass-like

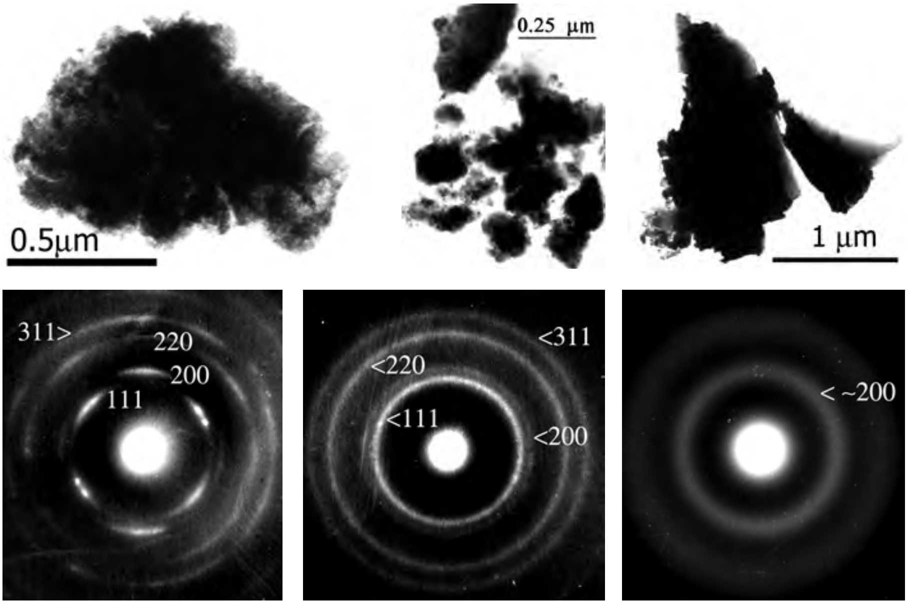
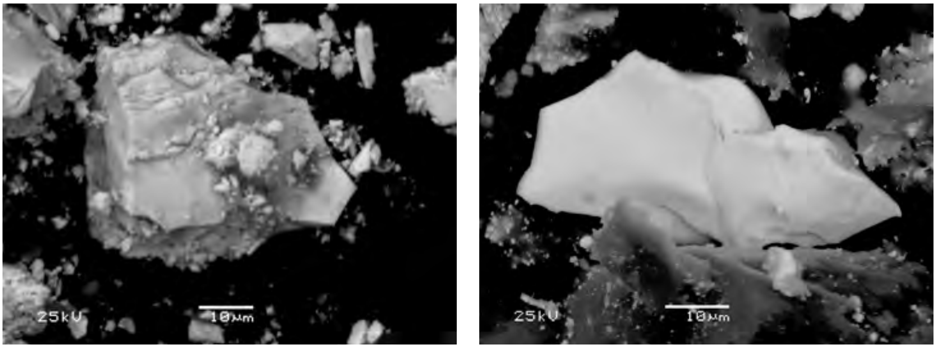
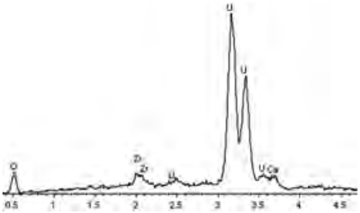


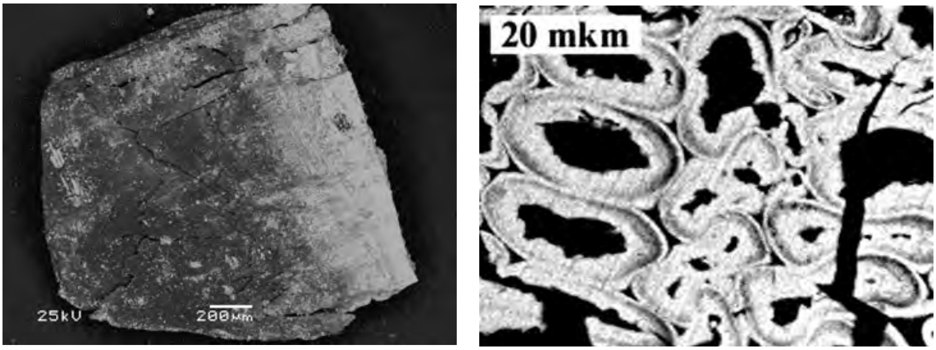
Fig. 1. Uraninite: a — the TEM-image of uraninite particles in suspension preparation; corresponding SAED pictures show fall of degree of crystallinity of particles (from left to right) up to electron-amorphous state;





b — fragments of glassy (vitriform) uranium-oxide matter (with Ca, Zr impurity), the SEM (BSE)- image;

c — a coalificated fragment of lignite (black) with uranium-oxide impregnation (white), with a pyrite (light gray) and quartz (dark gray) — on the left; the uraninite phytomorphous — on the right.



hardened gel. As regarding their composition these glasses are close to uranium dioxide, but besides main mineral-forming component they contain admixtures of Zr, Ti, Si, Fe, S, P. Few finds of similar uranium-bearing glasses are considered in the work (Dymkov *et al.*, 2003); here are discussed possible conditions of their formation at the expense of transformation of nasturan, zircon and brannerite in the process of argillization of uranium ores. At the figure are displayed images of glass-like microfragments of uraninate, resembling hardened gel, with typical conchoidal fracture on a chip (Fig. 1b) and composition spectrum. This is a main ore phase at the hydrogene deposit of paleaovalley type Khokhlovskoye, Southern Transuralian (Khalezov, 2009; Veichkin *et al.*, 2009). In the same ores uranium-oxide "gel" was found as phytomorphs and impregnation in carbonificated fragments of lignites (Fig. 1c).

In exogene ores uranium oxides are often related to carbonificated organic material, but more often dispersed nasturan is confined to cementic material or itself plays a role of cement. By present time, notwithstanding the proved many stage formation, polymineral composition of uranium black, its dominant component, according to statistics, is more often nasturan as oxide UO_{2+x} (Sidorenko, Doynikova, 2008).

Coffinite with ideal crystallochemical formula $USiO_4$ is considered to be a single silicate of U^{4+}, which is formed under natural conditions. Exogene coffinite, as a rule, is well crystallized (Fig. 2). Endogenic (hydrothermal) coffinite is usually metamict, X-ray amorphous. Practically up till the end of 80s coffinite was considered as endogenic uranium mineral, and his presence in composition of exogene ores was regarded as rare specific feature. Modern data show, that this U^{4+}-silicate is rather wide spread as significant component of friable black's ores (powder uraninite ores). In this case sizes of its needle or oval crystals make up 1–10 µm, but more often coffinite is represented by cloddy formations of several microns in size (Fig. 2a, b). Characteristic feature of exogene coffinite – high degree of its crystallinity, ability to preserve structure (dot patterns of microdiffraction) even at considerable loss of uranium. During coffinite study in suspension preparations most often are displayed microdiffraction patterns, corresponding to planes of inverse lattice $(010)^*$ and $(021)^*$, which testifies to predominant development in microcrystals corresponding faces (010) and (052).

In contrast to uraninite in samples of exogene ores electron-amorphous coffinite was never found. As a result appears methodical note important for mineralogical diagnostics. At analysis of finely dispersed black's ores it is possible erroneous diagnostics using only traditional X-ray diffraction method: on the background of X-ray amorphous uranium oxides mineral composition of such ores will be determined as monocoffinitic.

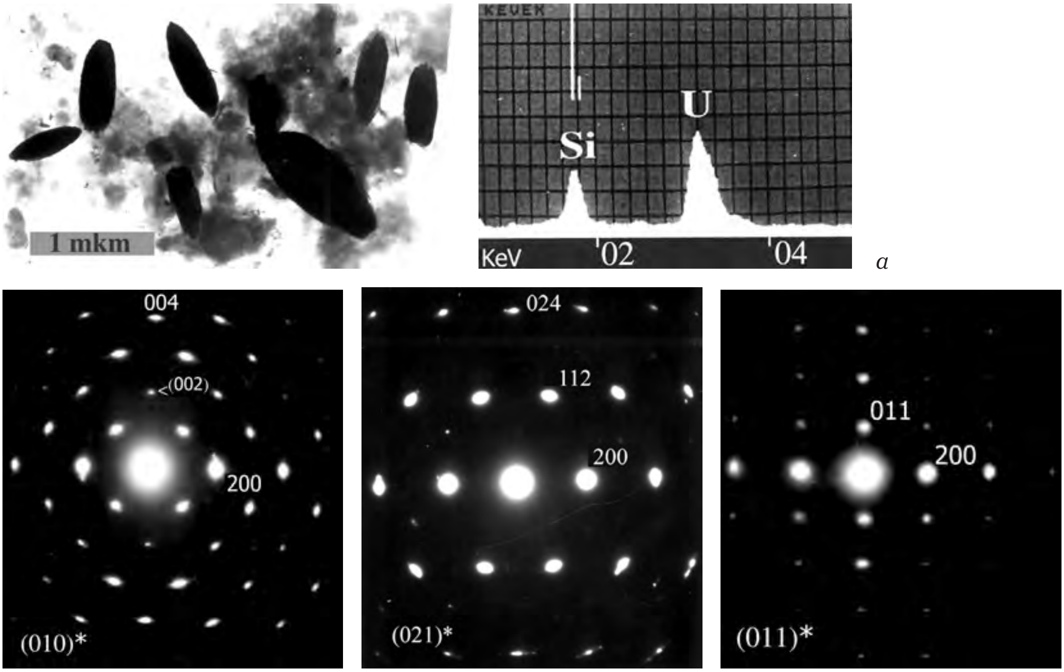
Crystal structure of coffinite relates to zircon type. Thus, coffinite is a member of group of isostructural minerals: zircon – coffinite – thorite – xenotime ($ZrSiO_4 - USiO_4 - ThSiO_4 - YPO_4$), which gives way to isomorphous substitutions of uranium for Th и TR_Y. Under natural conditions isomorphism of U^{4+} and Th in coffinite is limited (although in synthenic specimens one could observe continuous row of solid solutions coffinite – thorite). At substitution of U^{4+} for *TR* preference has yttrium group of *REE*. Entrance of phosphorus in composition of coffinite is supported by many finds of P-bearing coffinites in exogene ores (Belova *et al.*, 1980), which is explained by possible pseudomorphous formation of coffinite after ningyoite.

Investigation of different and numerous samples showed, that coffinite in ores of infiltration deposits is exclusively close related to carbonificated organic material. For example, in microfragment from the ore of the above mentioned Khokhlovskoye deposit were observed alternated accumulations of microcrystals of coffinite between coaly layers.

Coffinite in polished sections might be erroneously diagnosed as ningyoite, while carrying out optic diagnostics (by color, reflecting ability and inner reflexes). Therefore for diagnostics of X-ray amorphous coffinite it is necessary to use AEM methods besides usual optic methods.

Brannerite – practically single mineral species among titanates, in which U^{4+} is mineral-forming element. *Davidite*, often mentioned by geologists as urnium titanate is not properly uranium mineral. It is proved, that practically, from crystallochemical point of view, davidite is rare earth *TR*-titanate, which conventionally is related to ilmenite group; in its composition uranium is not mineral-forming element, but isomorphous admixture (Sidorenko, 1978).

Usually in mineralogical practice for investigation of structural characteristics of metamict brannerite is applied previous ignition of the sample. Using possibility of electron diffraction during study of X-ray amor-



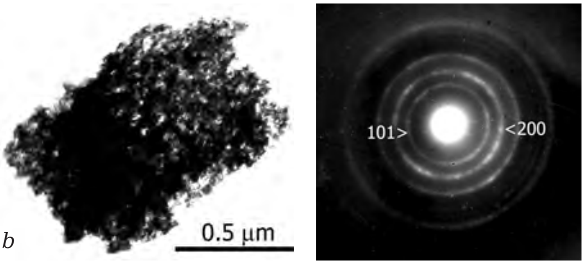


Fig. 2. Coffinite: a — the TEM- image of coffinite microcrystals among of phyllosilicate particles, an EDS-spectrum of composition and typical spot SAED pictures (the 002 reflex is caused by secondary diffraction); b — cloddy particle of badly crystallized coffinite and a corresponding ring-shaped SAED picture.

phous substance, were obtained structural characteristics of brannerite in its natural not heated-up state (Ivanova *et al.*, 1982). Endogene uranium titanate was studied from the Antei deposit of the ore field Strel'tsovskoye, developing as impregnation and nests in metasomatically altered granites (Fig. 3). Determined by SAED (microdiffraction) parameters of the mineral ($a = 9.8$, $b = 3.8$, $c = 6.7$ Å; $\beta \approx 119°$) correspond to monoclinic cell of synthetic brannerite and cell of the thorium titanate isostructural to it. Structural similarity of natural brannerite and synthetic $ThTi_2O_6$ was proved by coincidence of a number of diffraction characteristics (syngony, angle of monoclinic structure, parameter *b*, intensity of *001* reflexes). On this basis in the work (Ivanova *et al.*, 1982) is exposed, that brannerite is uranium titanate $U(TiO_3)_2$, but not a complex oxide of U and Ti, as was considered before. Notion "complex oxide" of U и Ti, widely used in literature at describing of brannerites, is not crystallochemically based and is erroneous.

Here it is worthwhile to make some deviation. Recent discovery of holfertite (Belakovskiy *et al.*, 2006) testifies to existence in nature of Ca-uranyl-titanate. Uranyl (U^{6+}) minerals are not the object of this article. However this fact of appearance of not known previously U-Ti-minerals should attract special attention of geologists. At revealing of positive correlation between uranium and titanium in mineral formations it is necessary to make more thorough, than previously, and detailed diagnostics of mineral with determination of uranium valence.

About phosphates of tetravalent uranium

By the present time at uranium mineralogy are known trustworthily four U^{4+}-phosphates (Belova *et al.*, 1998), related to different mi-

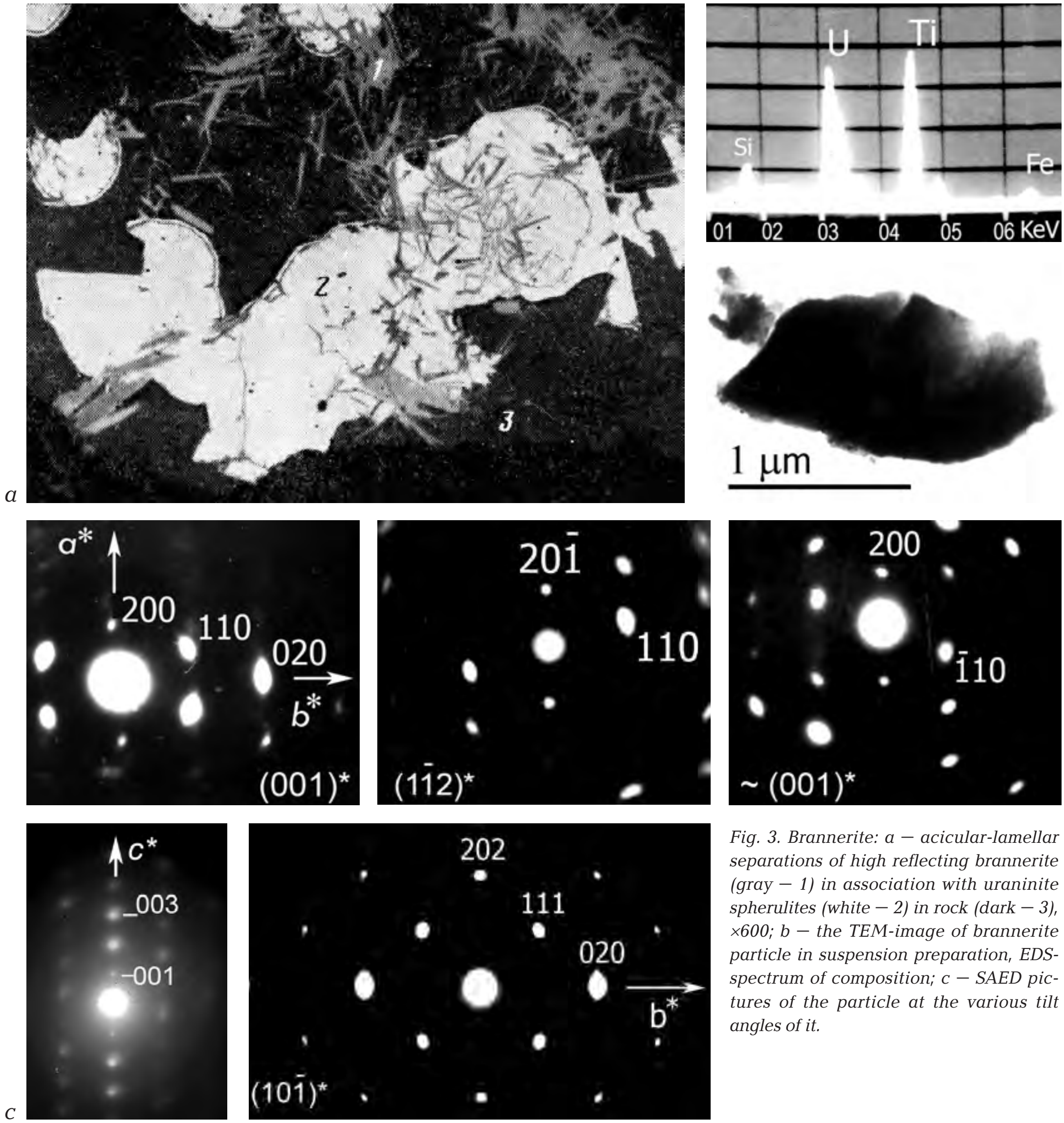


Fig. 3. Brannerite: a — acicular-lamellar separations of high reflecting brannerite (gray — 1) in association with uraninite spherulites (white — 2) in rock (dark — 3), ×600; b — the TEM-image of brannerite particle in suspension preparation, EDS-spectrum of composition; c — SAED pictures of the particle at the various tilt angles of it.

neral groups (Table). Thus, it is evident existence in mineral world of higher, than mineral group, taxon — phosphates of tetravalent uranium (U^{4+}-phosphates). This taxon is lesser than mineral class, which unites all phosphates. For association of U^{4+}-phosphates was selected taxon *family*, which has wide application in mineralogical classification. According to definition of G.B. Bokiy "*this taxon unites mineral species by similarity of their composition, ...independently of mineral structure*" (Bokiy, 1997). This new mineral family (supergroup) of tetravalent uranium was opened as a result of detailed crystallochemical investigations by the method of electron microdiffraction (SAED) in transmission AEM (Doynikova, 2005). The minerals of U^{4+}-phosphate family are united by common conditions of their formation in zone of reduction in hypergene environment.

Lermontovite — one of minerals of this family. Discovery of this new mineral in our country (Melkov, Pukhal'skiy, 1957) gave rise to study of tetravalent uranium phosphates. Its name was given to designation of mineral group, including also two other minerals — **vyacheslavite** and **urfoite** (Doynikova, 2005). Minerals of lermontovite group are formed in

Table 1. **Crystallochemical characteristics of the tetravalent uranium**

Minerals	Chemical formula	Structural parameters (Å) syngony, space group	Colour, density, (g/cm^3)	Optical constants	Reference
Rhabdophane group $CePO_4 \bullet H_2O$					
Ningyoite	$(U,Ca,Ce)_2(PO_4)_2 \bullet 1-2H_2O$	rhombic, pseudohexagonal	brown,	$n_{cp} \approx 1.64$	Muto *et al.*, 1959
	$CaU(PO_4)_2 \bullet nH_2O$ n = 1 − 2	*hexagonal, *P*6$_2$22 *a* 6.86, *c* 6.38, Z 3	green (in slices) 4.74 (calc.)		Belova *et al.*, 1985
"Tristramite"	$(CaU^{4+}Fe^{3+})[(PO_4)(SO_4)(CO_3)] \bullet 1.5H_2O$ Ca>>U>>Fe; PO_4>>SO_4	hexagonal, *P*6$_2$22 *a* 6.913, *c* 6.422, *Z* 3	greenish- yellow 3.8 − 4.2; 4.18 (calc.)	$n_o = 1.644$ $n_e = 1.664$	Atkin *et al.*, 1983 Belova *et al.*, 1987
Lermontovite group, generalised formula: $UPO_4OH \bullet nH_2O$					
Vyacheslavite	$(U_{1.061}Ca_{0.04})_{1.1}(PO_4)(OH)_{1.3} \bullet 2.7H_2O$	*rhombic, *Cmcm*, *Cmc*2$_1$, *C*2*cm*; *a* 6.96, *b* 9.10, *c* 12.38, *Z* 8	dark-green, 4.6 − 5.2; 5.02 (calc.)	$n_g = 1.731-1.729$ $n_m = 1.729-1.726$ $n_p = 1.700$	Belova *et al.*, 1984
Lermontovite	$(U_{0.94}Tl_{0.4}Ca_{0.02})_{1.0}(PO_4)(OH)_{1.2} \bullet 0.4H_2O$	*rhombic, *Ccca*-?, *a* 9.74, *b* 19.0, *c* 10.1; *Z* 8	green, 4 − 4,5; 4,37 (calc.)	$n_g = 1.724-1.726$ $n_m = 1.707$ $n_p = 1.686-1.690$	Melkov *et al.*, 1983
	$(U^{4+}_{0.73}Ca_{0.005})_{0.74}(PO_4)$	monoclinic, *a* 10.00, *b* 19.40, *c* 8.55; γ 96°	______"______	______"______	Sidorenko *et al.*, 1986
Urfoite	$U_{0.85}Ca_{0.004}(PO_4)_{1.0}(OH)_{0.48} \bullet \sim 0.3H_2O$	*rhombic, *Ibca*, *a* 14.06, *b* 13.22, *c* 14.4; *Z* 24	emerald- green 4.29 (calc.)	$n_g{}' \approx n_m{}' \approx 1.734$ $n_p{}' \approx 1.707-1.708$	Belova *et al.*, 1996

*Note. * − electron microdiffration data (SAED).*

reduction zone in hypergenese environment, it is characteristic their association with black uranium ore generations.

All minerals of the group are represented yet by single finds. These minerals are close by composition, have general idealized formula $U(PO_4)(OH) \bullet nH_2O$, but are different by structural parameters. Their unification into the group (Table) at present time is rather conventional. It is not excluded, that in the future, at refinement of cristallochemical data using new finds, each of the minerals might appear representative of independent group.

Ningyoite $CaU(PO_4)_2 \bullet 2H_2O$, discovered at Japan calcium-uranium phosphate (Muto *et al.*, 1959), is related to the group of rhabdophane; later was discovered at various world regions. Till the end of 20th century ningyoite was not related to economic uranium minerals, as far as his presence in composition of uranium blacks "was lost" due to insufficient level of study of the latter. At present ningyoite is considered to be rather common mineral in ores of the infiltration deposits (Doynikova, 2007).

It is worthwhile to underline, that characteristic feature of ningyoite is micron size of its crystals: usually 1 − 2 μm, rarely more than 10 μm (Fig. 4), as well as its specific confinement to areas enriched in organic material. Thus, in samples of uranium ores of one of deposits at Bulgaria was practically absent another mineralization, a sample represented friable mixture of organic matter with ningyoite (Doynikova *et al.*, 2003).

Tristramite (Atkin *et al.*, 1983), mineral of rhabdophan group, is not individual mineral species, its identity with ningyoite was proved erlier (Belova *et al.*, 1987). As far as tristramite is not annulled by the International Commission on New Minerals, Nomenclature and Classificaton, it is displayed in the Table in inverted commas (which reflects doubt in its individuality).

As a result of crystallochemical investigations it is established, that all three phosphates of the lermontovite group, as well as previously studied ningyoite, represent independent mineral species of the family of phosphates of tetravalent uranium. Vyacheslavite

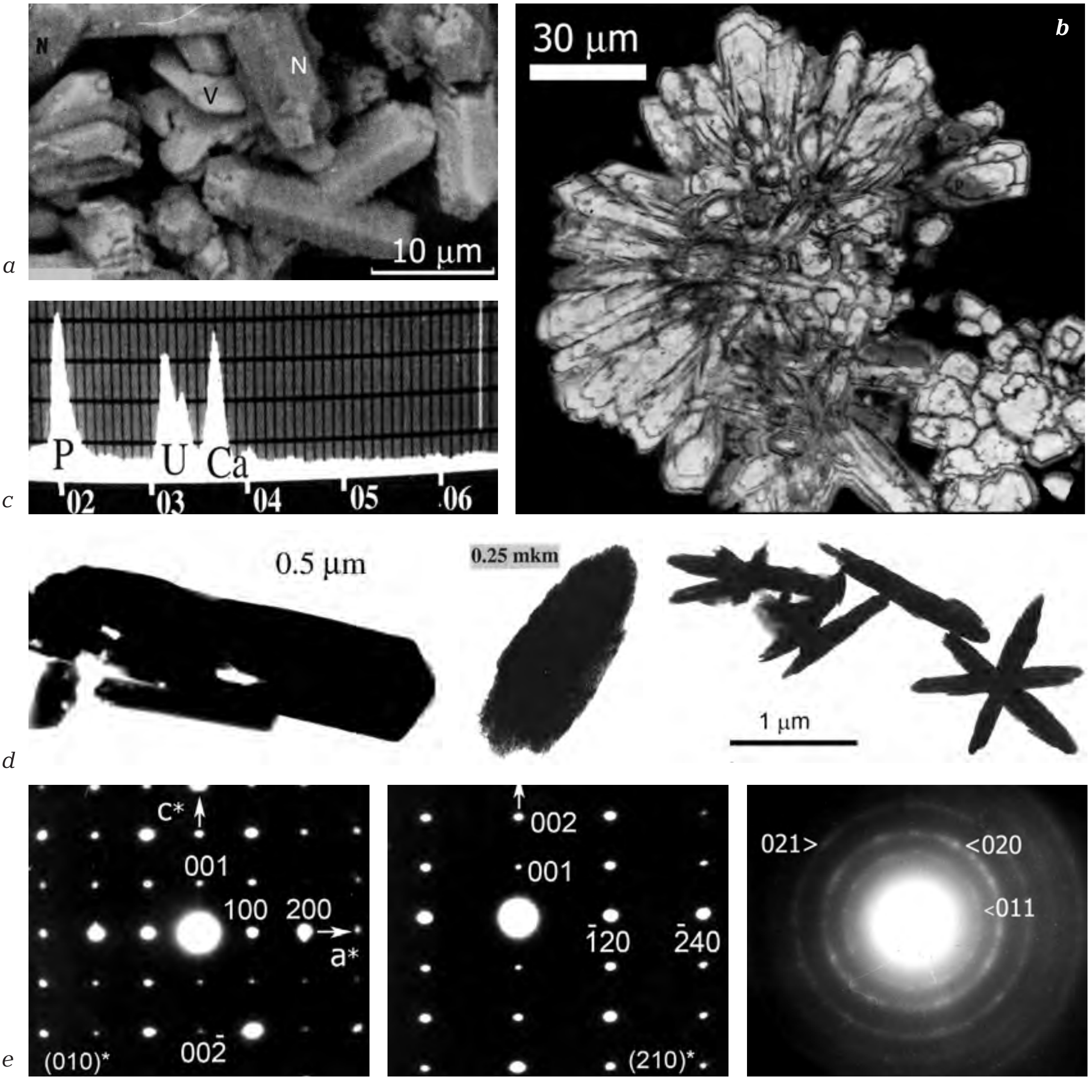


Fig. 4. Ningyoite: a, b. SEM (BSE) image (Scharmova, Scharm, 1994), Stráž-deposit, northen Bohemia, Czech Republic; a — columnar crystals of ningyoite (N) intergrown with plates of vyacheslavite (V); b — rosette-like aggregate of euhedral ningyoite crystals, with thin dark interbeds of a pyrite (P) in growth zones; c — EDS-spectrum of pure ningyoite composition; d — forms of microcrystals, TEM-image; e — typical SAED pictures.

is almost pure uranium phosphate with insignificant quantity of calcium; the ratio U:P = 1:1, but negligible predominance of uranium is always fixed. Lermontovite contains yet less calcium, but about 10% of thallium is present. In urfoite composition is observed deviation towards decreasing of uranium in ratio U:P = 1:1. But in ningyoite quantity of calcium is equal to that of uranium or somewhat predominates it. One might with sufficient confidence suggest, that each from uranium U^{4+} phosphates could afterwards form independent subgroup, which should be added by new, structurely close mineral species. In particular we are sure, that such one will be the lermontovite subgroup with minerals, containing in cation part also alkaline element (thallium) alongside with uranium.

Phospho-silicate phase of uranium U^{4+}. Not known previously uranium silicate was established in association with disperse uranium oxide during study of friable hydrogenic ores of the Dalmatovskoye uranium deposit of paleovalley type (Doynikova *et al.*, 2009) by the methods of scanning AEM. This mineral phase of U^{4+} is predominant in ore intervals of one of studied boreholes, it is confined, as a rule, to altered feldspar and is represented by microcrystals of slightly elongated lenticular form, with unclear side faces. Microcrystal sizes are about of several microns. Aggregates of microcrystals are often found (Fig. 5), colloform segregations occur more seldom. Idealized formula of the studied phase is (U,Ca) [(Si,P)O_4]$_2$, where U:Ca ≈ 3:1 and Si:P ≈ 3:1. Relation between cation and anion components is (U,Ca):(Si,P) = 1:2, that is twice as less than in coffinite, where U:Si = 1:1. As far as relief objects were studied but not polished ones, results of analyses were normalized, the problem was not solved concerning presence of OH-group or water in composition of this phase. Since quantitative EDS-analysis showed (in atomic units) considerable predominance of silicon over phosphorus (three times), the phase might be characterized as uranium silicate, containing phosphorus, or more exactly — uranium phosphor-silicate.

Morphology of segregations of found uranium phase is close to forms of hypergene U^{4+}-minerals: coffinite and ningyoite. In contrast to ningyoite, in composition of this U-phospho-silicate is observed constant predominance of U over Ca. The phase under consideration differs from P-bearing coffinite first of all by constant presence of calcium, as well as by consistent ratio Si/P. Thus, one could probably add one more mineral — phospho-silicate of uranium to already known minerals of tetravalent uranium.

At present this uranium phase is studied only as regarding composition. Data of scanning AEM revealed specific features of composition, which allow us to say about individuality of this mineral phase, but its structure parameters are yet absent. For receiving diffraction characteristics of this U^{4+}-phase, taking into consideration its micron sizes and occurring into polymineral mixture, it is more preferable method SAED, realized in transmissive AEM.

About place of calcium in minerals of tetravalent uranium

The problem of mode of occurrence of Ca in composition of U^{4+}-minerals attracts attention for a long time and remains a subject of discussion. It is interesting the fact, that both phosphates and phosphor-silicate described above contain Ca alongside with U^{4+}. Is it possible to say here about isomorphous substitution?

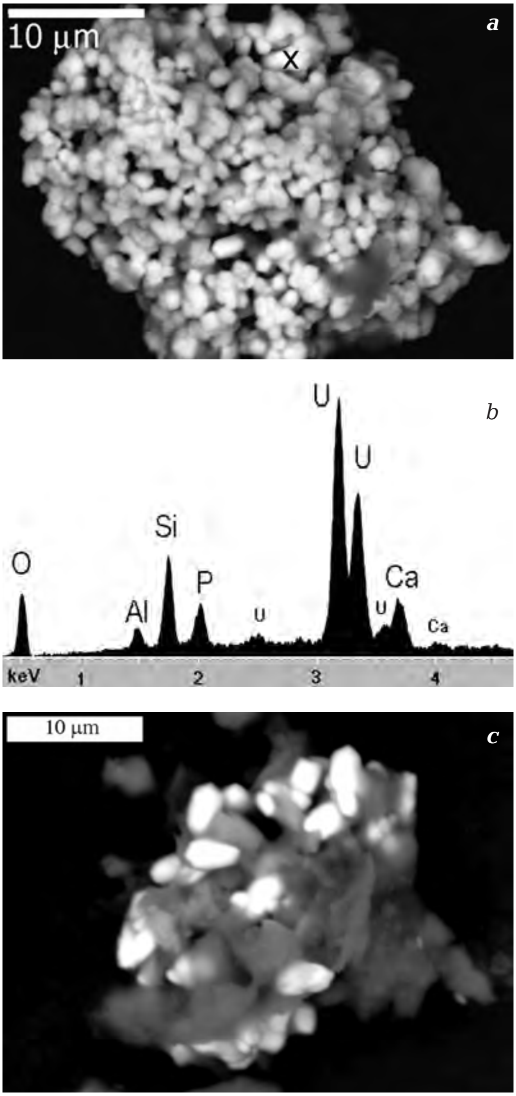


Fig. 5. Ca-phosphosilicate of U^{4+} (white): a — the aggregation of microcrystals; b — EDS-spectrum of composition in marked point (x); c — separations among aluminosilicates.

Isomorphous substitution of U^{4+} for Ca^{2+} at equality of their ionic radii always invoked doubt due to crystallochemical individuality of each of them. For a long time there is a discussion about place of calcium in uranium minerals. At first equality of ionic radii and isostructurness of uraninite and fluorite were taken as foundation of isomorphous substitution of U^{4+} and Ca^{2+}. It was accepted without doubt, that in apatite structure U^{4+} substitutes for Ca^{2+}. Denial of this version came from technologists of treatment of ores, in which U^{4+} is related to apatite. Having extracted pure apatite they did not receive expected concentration of uranium. Therefore, uranium is not structural admixture of apatite.

However, it is known entrance of uranium into pyrochlore structure with formation of uranpyrochlore (Ca,Na,U)(Ti,Nb,Ta)O_6 (F,OH), in which uranium U^{4+} statistically occupies in the structure sites of Ca^{2+}. By X-raying method are revealed also consequences of this event: disordering of the pyrochlore structure, up till destruction (possibly through metamictization), breach of stoichiometry. For preservation of the charge balance at increase of uranium content in structural motive AB_2O_6 (OH,F) there is enrichment of the mineral in Ti in site B (Ta,Nb). As a result breach of stoichiometry in structural motive takes place. Besides, own crystal structure of the mineral breaks up. Taking into consideration widening of bands of diffraction spectra, alongside with enrichment of structure in uranium at first occurs decreasing of elementary cell sizes (twofold), then breach of three-dimensional order, further – complete metamictization.

At ordered setting of U^{4+} and Ca^{2+} in structural positions mineral obtains individual crystalline structure, that, probably takes place in the structure of ningyoite. The second example, as we suggest, will be the structure of the new found U^{4+}-phase of phosphor-silicate composition.

The phase under consideration (Ca-U^{4+}-phospho-silicate) is interesting due not only to mixed anion composition, but also by high content of Ca, which alongside with uranium becomes mineral-forming element.

We should note that rather clearly fixed relation of uranium and calcium in idealized composition of ningyoite (CaU)PO_4 (U:Ca = 1:1) and in composition of phosphor-silicate (U,Ca) $[(Si,P)O_4]_2$ (U:Ca = 3:1) testifies to ordering of setting of U^{4+} and Ca^{2+} in structural sites of cations.

Isomorphism SiO_4 – PO_4 was shown at study of P-bearing coffinites: Si and P coexisted in single structure, responsible for electron diffraction (Belova *et al.*, 1980).

From crystallochemical point of view, change of chemical composition from coffinite $USiO_4$ to ningyoite (Ca,U)PO_4, that is complete replacement of Si for P, is accompanied by appearance of calcium in cation part. Crystal structure is cardinally changed from tetragonal to hexagonal one. Therefore, here takes place not isomorphism U^{4+} – Ca, but formation of cation part of composition by two elements. Characteristic for ningyoite some predominance of Ca over U (variable value, max 2:1), might be considered as one of variants of filling of Ca in the structure. However, as a whole a general regularity of ningyoite composition U:Ca = 1:1 is preserved (Doynikova, 2003).

Then we shall consider change of composition from silicate coffinite $USiO_4$ to the found U^{4+}-pospho-silicate (U,Ca)$[(Si,P)O_4]_2$. In comparison with ningyoite relative further predominance of U over Ca in cation part, where U:Ca = 3:1, is accompanied by isomorphism (Si – P) also in anion part of composition. Thus, combination of silicate SiO_4 and phosphate PO_4 groups in structure of U^{4+}-mineral results in obligatory appearance here of Ca ion. In composition of the phospho-silicate balance of valency is achieved by equivalent, with the same ratio 3:1, replacement of U for Ca and Si for P.

According to existing at present data, we have in view predominantly structural, individual, but not isomorphous position of Ca in minerals of tetravalent uranium. "Pair" substitution of such kind practically takes place into crystallochemical group apatite – britholite (apatite – typical phosphate, and britholite – its silicate structural analogue). It is worthwhile to underline, that exactly silicate analogue with constant presence of phosphorous has U^{4+} in its composition.

Thus one could see development of U^{4+}-phosphate family at the expense of appearance of phosphor-silicate branch. Transformation of anion part of compositions takes place, while in this case in cation part U^{4+} obligatorily "cooperates" with Ca.

We suggest, that calcium (up to 3.3% CaO), which according to data of A.B. Khalezov (2009), instrumentally is fixed in composition of uraninites simultaneously with phosphorus (up to 2% P_2O_5), is not related to uraninite structure. Its presence is probably related to origin of phase heterogeneity (formation of new microphase?).

And nonstructural Ca? Evidently, it is present as admixture in composition of unstructural hardened gels of uranium-oxide composition, so called uranium-bearing glasses (~ 2% Ca).

Conclusion

Already available experimental data testify to increasing of number of U-minerals, in which mineral-forming element is represented by tetravalent uranium. Considerable progress in cognition of U^{4+}-minerals is provided by transition of mineralogical investigations to local levels of "electron" micromineralogy. Utilization of AEM did not only expand spectrum of natural U^{4+} phosphates, but allowed us, at last, to say more definitely about structural relation of Ca to U^{4+}, it also opened a new page in mineralogy of tetravalent uranium, showing possibility of existence of U^{4+}-phospho-silicates.

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SULFIDE–OXIDE MINERAL ASSEMBLAGES AS INDICATOR OF SULFUR AND OXYGEN REGIME IN MODERN SUBMARINE MASSIVE SULFIDE DEPOSITS

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During ore-forming hydrothermal processes at the oceanic bottom, the behavior of sulfur and oxygen varies like at the continents. These variations are illustrated by the sulfide-oxide mineral assemblages from the modern submarine massive sulfide deposits in hydrothermal ore areas of the Eastern Pacific Rise (occurrence 6° N and massive sulfide deposits in the range of 18°5′ to 21°8′ S) and two hydrothermal fields of Mid Atlantic Ridge (active section Irina-2 14°5′ N in Logachev field and Rainbow field 36°14′ N). Probable causes of these variations are discussed.

7 figures, 1 table, 10 references.
Keywords: hydrothermal ores at the oceanic bottom, sulfide-oxide mineral assemblages, sulfur and oxygen regime during modern submarine ore-formation.

According to the study of continental deposits, S and O regimes are important for ore-formation and depend on geological and physicochemical factors. These regimes are opposite that is exhibited with juxtaposition of different stages or with facial changes of mineral assemblages during a single stage. As illustrated by the Fe-S-O and Fe-Cu-S-O systems (Betekhtin, 1953), the "fight" between sulfur and oxygen regimes determines many common features in mineral assemblages and distribution of metals at deposits.

Let us discuss this problem as applied to the modern submarine hydrothermal ores. By the elements of variable valence, the major minerals of oceanic massive sulfide deposits are extremely sensitive to the change of geochemical parameters. Four hydrothermal ore areas in different geodynamic environment were selected to be investigated:

- occurrence 6° N, Eastern Pacific Rise (EPR);
- hydrothermal complex of massive sulfide deposits in the range of 18°5′ to 21°8′ S, EPR;
- active location Irina-2 14°5′ N, Logatchev field, Mid Atlantic Ridge (MAR);
- Rainbow field 36°4′ MAR.

Major ore minerals in the sulfide-oxide assemblages are pyrrhotite $Fe_{1-x}S$, pyrite FeS_2, marcasite FeS_2, chalcopyrite $CuFeS_2$, isocubanite $CuFe_2S_3$, bornite Cu_5FeS_4, chalcocite Cu_2S, sphalerite (Zn,Fe)S, and hematite Fe_2O_3.

Brief description of selected areas

Occurrence 6° N, EPR was discovered in 1990 in the northern near-equatorial zone of EPR during Cruise 9 the R/V *Geologist Fersman*. Significantly eroded flattened and isometric sulfide mounds are at the western flank of axial graben. They are located on the even surface of basalt flow and slightly covered by sediments. The largest mounds are 0.8 m in diameter and height. Total weight of collected sulfides was 112 kg. According to structural and mineralogical features, the following major varieties of sulfide ore are distinguished: zoned fragments of chimneys, complex breccia ore, and porous ore. Pyrite, chalcopyrite-pyrite, and sphalerite-pyrite-marcasite assemblages with abundant shells of vestinmentifera were identified in the latter. Coloform and/or gel sulfides are widespread.

Massive sulfide hydrothermal complex (18°5′ 21°8′ S, EPR) occurs on the basalt flow (Tufar, 1993). Groups of black smokers up to few meters high are characteristic. Like occurrence 6° N, numerous inclusions of vestinmentifera relicts were identified in the fragments of black smokers. Iron, copper, and zinc sulfides are the major ore minerals. Coloform segregations of sulfides are intergrown frequently with high-temperature sulfides (for example, isocubanite and chalcopyrite) indicating disequilibrium conditions of mineralization (Tufar, 1993).

Section Irina-2 located within the Logatchev hydrothermal field was discovered during Cruise 7 (1993 – 1994) of the R/V *Professor Logatchev* and was studied by many researchers with both shipborne devices and submersible. This field located at the junction zone of small rift step and large step at a depth of 2970 – 3000 m. The step is a top surface of ridging serpentinite massif. This structure is confined to the large zone of transverse tectonic dislocations. More than 10 ore hills (the largest one is 200×100 m) were found within the field. Main part of the field is inactive. The active areas are located in linear structure passing through its center from NW to SE (Mozgova *et al.*, 1999).

As a result of the detailed study of the hydrothermal field with the submersible, separate active locations were marked. For example, in 1995, as a result of four submerges of submersible from French R/V Nadir locations Irina-1 and Irina-2 were found; these locations were named in honor of I.M. Poroshina, a researcher of All-Russia Research Institute for Geology and Mineral Resources of the World Ocean, who participated in the cruise. The samples studied here were collected from the Irina-2 active chimney complex in 2001 during cruise of R/V Atlantis with the Alvin submersible.

Like the Logatchev field, the **Rainbow hydrothermal field** (36°4′ N, MAR) related to ultramafic rocks was discovered in 1997 (Fouquet *et al.*, 1997). This field located at a depth of 2270 – 2329 m is confined to the western slope of axial rise of the MAR rift composed of serpentinite. The field extends in latitudinal direction for 250 m with 60 m wide. Numerous active and varied relict sulfide mounds were found within it: single chimneys of 2 – 3 m to few cm high, groups of intergrown chimneys, mounds composed of large fragments of massive sulfides, and hills consisting of their oxidizing products. The detailed study of young zoned active chimneys (samples were collected during Cruise 47 of the R/V Academician Mstislav Keldysh in 2002) allowed us to discuss of mechanism of their formation and to develop the known models of formation of sulfide chimneys of black smokers (Borodaev *et al.*, 2004). This article is focused only relationship between sulfide and oxide paragenetic assemblages.

Description of sulfide–oxide mineral assemblages studied

As aforementioned, three major varieties of porous sulfide ore are distinguished in picked up material from the occurrence of near-equatorial part of EPR (6° N): pyrite, chalcopyrite-pyrite, and sphalerite-pyrite-marcasite. In places, they are overprinted by magnetite-hematite assemblage. The samples, where hematite, magnetite and pyrite are the major minerals, are the most attractive. Microscopically, these minerals display frequently controversial relationship. Small polished banded ore sample of 2×2 cm in size (Fig. 1), in which oxides concentrate in darker bands, whereas light bands consist mainly of pyrite with the lightest and coarse-grained zone (Fig. 1, bottom) composed of its branching intergrowths, exemplifies this. As a result of detailed microscopic study in reflected light, variable relationships of these minerals were revealed.

The replacement of hematite crystals by magnetite up to complete pseudomorphs as a result mushketovite formation is the earliest (Fig. 2a). Microcoloform aggregates of pyrite occur as veinlets (Fig. 2b) or areas (Fig. 2c) after these pseudomorphs. Hereafter, small crystals of hematite-II overgrow both magnetite pseudomorphs (Fig. 3a) and branching aggregates of pyrite from the outer part of the sample (Fig. 3b). At the same time, coloform zoned pyrite with separate small inclusions of hematite along boundaries between zones is observable (Fig. 3c). Shape of these inclusions is governed by the morphology of boundaries of coloform zones allowing attribution this hematite also to the second generation. Hematite crystals with inclusions of pyrite fragments among pyrite breccia exemplify hematite later than pyrite (Fig. 3d).

It is apparent that the data obtained testify to oscillation and facial variability of oxide-

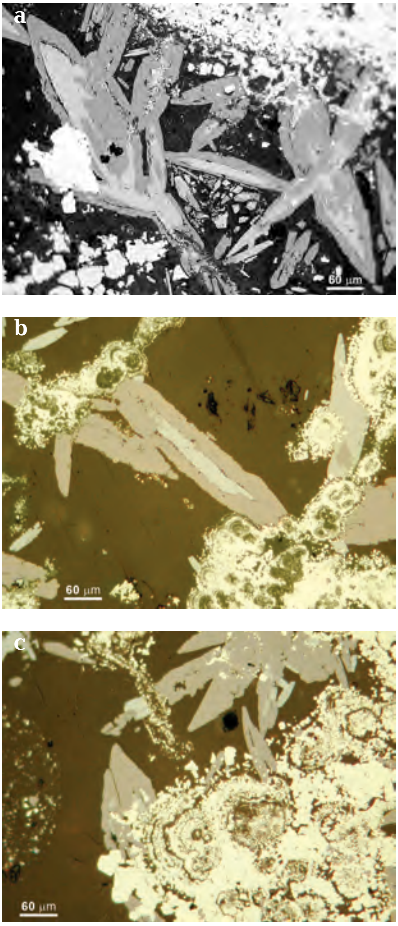

Fig. 1. Polished ore specimen with banded (zoned) structure from submarine massive sulfides (6° N, EPR). Oxides concentrate in the darker zone, pyrite is in the lighter zones, and branching intergrowths of pyrite occur in the lower marginal coarse-grained zone. Size of the specimen is 2×2 cm. Photo in reflected light.

Fig. 2. Relationship of hematite, magnetite, and pyrite in the dark ore zone shown in Fig. 1. Polished sections. Photo in reflected light. Hematite crystals are light grey; magnetite is dark grey; and pyrite is wite:
a — pseudomorphs of magnetite after hematite (mushketovitization);
b, c — microcoloform segregations of pyrite: cutting (b) and replacing (c) pseudomorphs of magnetite.

sulfide conditions with microspace and time during the formation of submarine massive sulfides in the near-equatorial areas of EPR.

Mineralogy of massive sulfides in the range of 18°5′ − 21°8′ S of EPR studied in detail by Tufar (1993) is similar to that reported in the northern part of the same rise. According to Tufar (1993), hematite occurred as aggregates of euhedral crystals intergrown with chalcopyrite, pyrite, melnikovite-pyrite, marcasite, and isocubanite (Tufar uses outdated name chalcopyrrhotite) is abundant in some fragments of black smokers and zone enriched in copper. Together with pyrite and melnikovite-pyrite, hematite is present in rhythmic concentric-coloform layered crusts and colloidal masses.

Despite the absence of special discussion concerning age relationship between hematite and sulfide in the cited paper, the description of assemblage of the mineral and wonderful illustrations given in it suggest that sulfide-oxide relationship in the southern massive sulfide complex (18°5′ − 21°8′ S, EPR) are similar to those described from near-equatorial areas of EPR (6° N). In the southern complex, the quantitative relationship of oxides and sulfides is highly variable. Hematite corrodes and overgrows relicts of sulfide minerals (pyrite, chalcopyrite), contains fragments of pyrite, and in some zones is replaced by magnetite occasionally up to complete pseudomorphs like the northern occurrence of EPR. Small rounded flakes and clusters of small crystals of later hematite overgrow large hematite crystals in numerous cavities in pyrite-hematite ore.

Thus, in spite of long distance between these two massive sulfide complexes in EPR, they are characterized by similar mineral assemblages indicating similar variations in sulfur and oxygen regime.

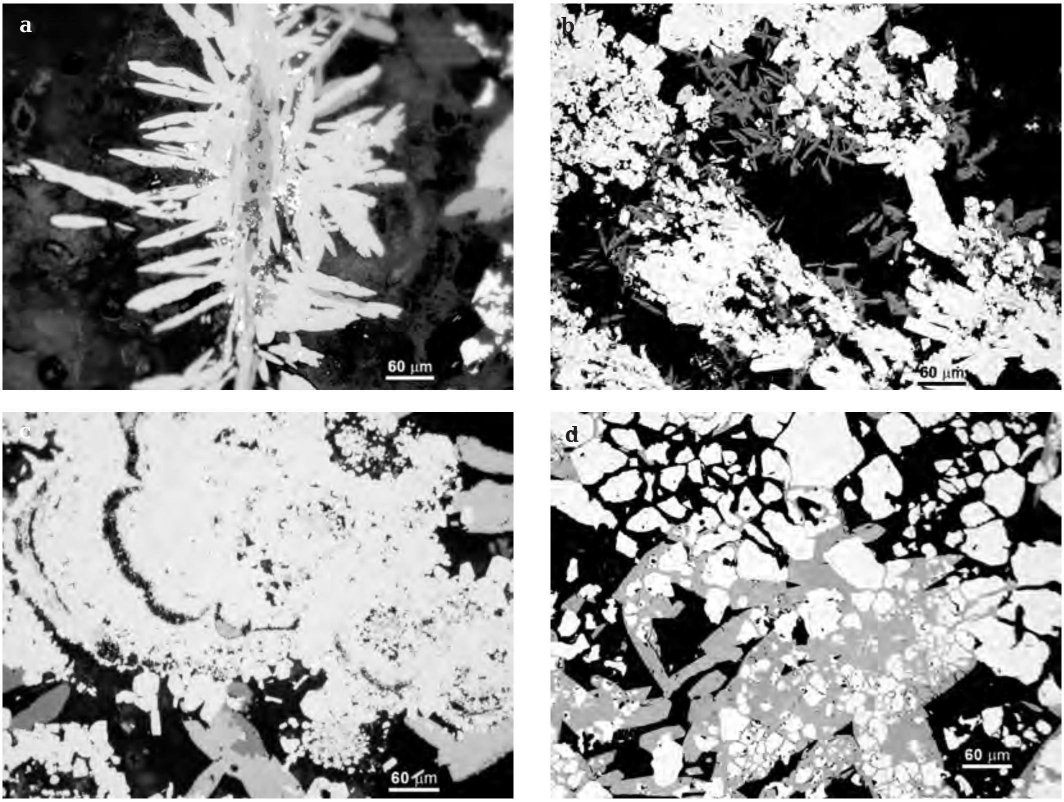

Fig. 3. Relationship between hematite-II and relicts of magnetite pseudomorphs after early hematite and aggregates of pyrite in submarine massive sulfides (6°N, EPR). Polished sections. Photo in reflected light:
a — small crystals of hematite on magnetite (grey) pseudomorph after early hematite; b — aggregate of pyrite grains overgrown by crystals of hematite-II; c — small inclusions of hematite on the boundaries of zones in coloform pyrite; these inclusions are governed by zone boundaries; d — crystals of hematite with inclusions of pyrite fragments enclosed in pyrite breccia.

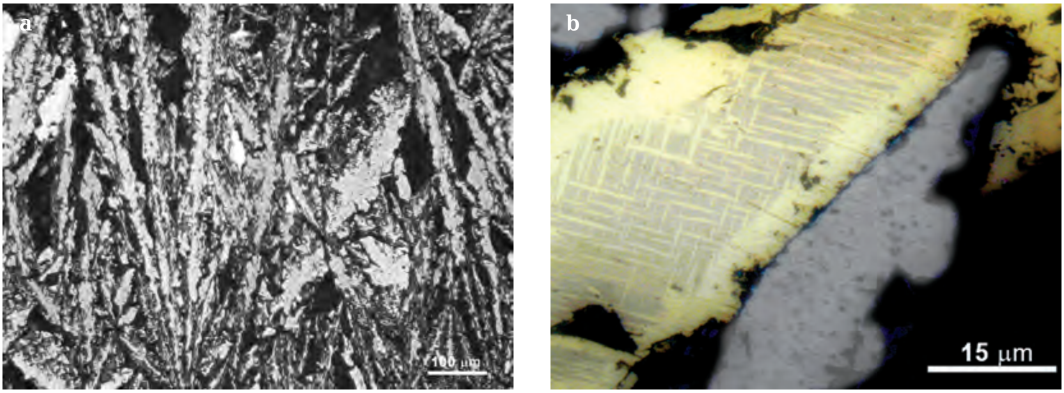

Fig. 4. The first type of relationships between sulfides and oxides at the Irina-2 location, Logatchev field, MAR. Polished sections. Photo in reflected light:
a — radiated aggregate of hematite with single small lanse-shaped grains of isocubanite between elongate hematite crystals;
b — detail; structure of separate lense (upper left) in hematite aggregate: lattice texture of exsolved isocubanite — blades of chalcopyrite (light yellow) in isocubanite matrix (light grey) rimmed by chalcopyrite.

In the ore samples of the Irina-2 active location, Logatchev field, MAR, we have found: hematite, bornite, chalcocite, and iron hydroxides. Three types of relationships were revealed between them.

Relationship between hematite and isocubanite and chalcopyrite is attributed to the first type. Fine isolated lenses of exsolved isocobanite fill interstices between coarse-grained radiated hematite (Fig. 4a). Cores of the lenses are lattice exsolution texture (Fig. 4b), where lattice formed by fine blades is in the cubanite matrix and whole lattice aggregate is rimmed by chalcopyrite. It should be emphasized that the shape of lenses and chalcopyrite rims are subject to morphology of hematite aggregates. It suggests that high-temperature ($T > 300^{\circ}$) homogeneous isocobanite (or chalcopyrite) solid solution enriched in copper crystallized initially, then this solid solution was exsolved to liberate copper as chalcopyrite blades and rims.

The second-type relationships are between hematite and chalcopyrite, bornite, and chalcocite (Fig. 5). Microscopically in reflected light, veinlets of chalcopyrite cut and corrode hematite and contain its relicts (Fig. 5a). At the same time, a narrow zone of bornite with relict chalcopyrite occurs after chalcopyrite close to contact with hematite. Chalcocite rim is seen occasionally immediately at the contact with hematite (Fig. 5b). Bornite develops in place after chalcopyrite that corroded and replaced hematite in outer part of its radiated aggregates. Small irregular-shaped relicts of chalcopyrite and chalcocite strings on the continuation of hematite rays are observed in bornite (Fig. 5c). In these cases, it is evident that bornite and chalcocite in chalcopyrite close to hematite are resulted from oxygen released from the hematite replaced.

The third-type relationships are characteristic of the iron oxides and hydroxides + chalcopyrite + bornite + chalcocite assemblage (Fig. 6). In these assemblages, relicts of hematite are replaced by iron hydroxides[1] nearly to complete pseudomorphs with reddish inner reflections (Fig. 6a).

Zoning described in the second-type relationships is occasional around large pseudo-

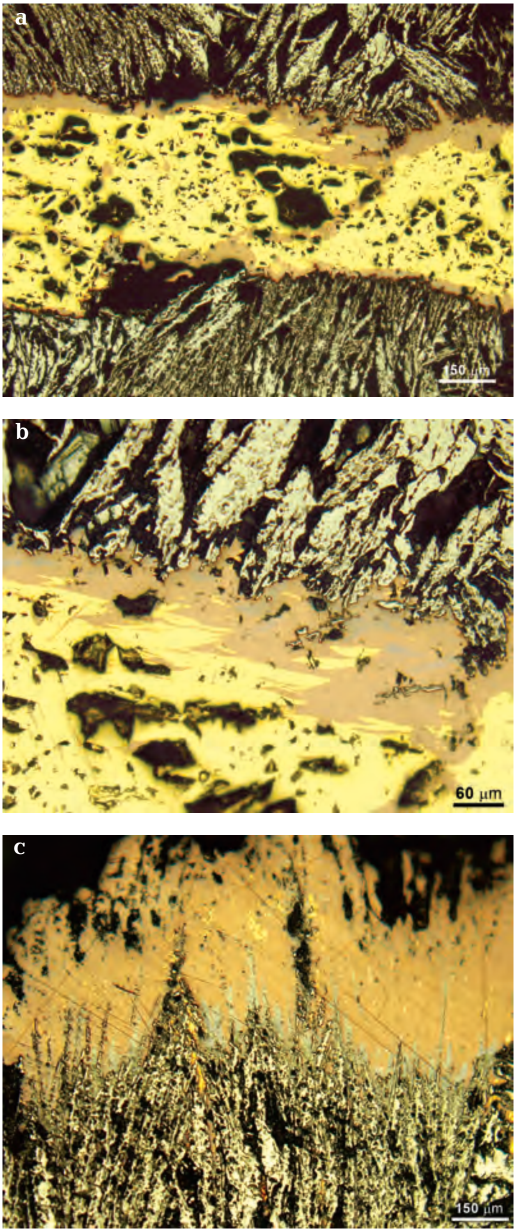

Fig. 5. The second type of relationships between ore minerals at the Irina-2 location. Reaction transformation at the contact between coarse-radiate hematite and cut veinlet of chalcopyrite. Polished sections. Photo in reflected light:
a — general view of chalcopyrite veinlet cutting hematite with reaction rim of bornite (brown) at contacts;
b — near-contact area with remarkable bluish grey spots of copper sulfide (chalcocite) at high magnification;
c — metasomatic bornite zone (light brown) after chalcopyrite at the outer part of radiated aggregates of hematite; bornite contains small relicts of chalcopyrite and string-shaped chalcocite segregations (bluish green) on the continuation of hematite rays.

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[1] — Exact identification of the minerals is impossible because of fine-grained texture and microheterogeneity of the pseudomorphs.

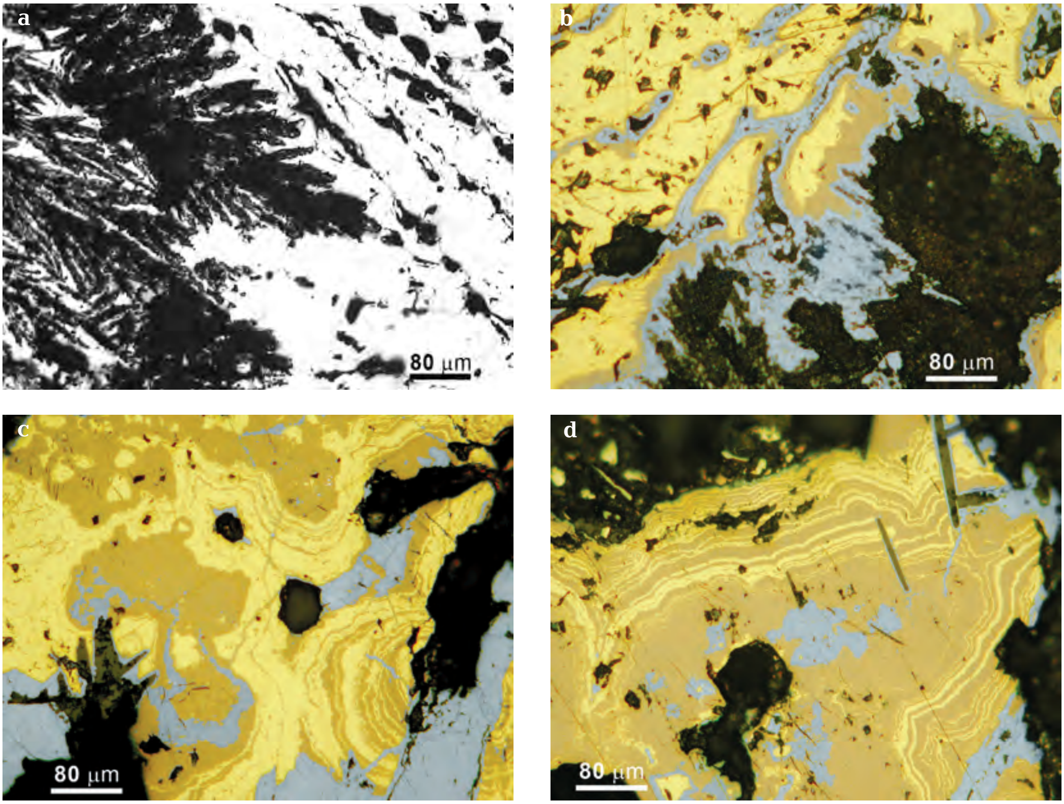

Fig. 6. The third type of relationships between iron hydroxides, chalcopyrite, bornite, and chalcocite, Irina-2 location. Polished sections. Photo in reflected light:
a — complete pseudomorph of iron hydroxides (black) after branching hematite segregation enclosed in pyrite (white);
b — two reaction metasomatic zones, chalcocite (bluish green) and bornite (brownish) alternating each other from pseudomorph of iron hydroxides after hematite to hosting chalcopyrite (yellow); the same zoning exhibits in thin veinlets cutting chalcopyrite;
c, d — chalcopyrite-bornite coloform-zoned aggregates with inclusions of relicts of iron hydroxide pseudomorph after hematite; the character of intergrowths and relation of component are variable.

morphs (Fig. 6b): chalcocite zone adjacent to pseudomorph is followed by zone of bornite that contacts with relicts of chalcopyrite replaced. Alongside, chalcopyrite is cut by net of thin symmetrically zoned veinlets, where similar sequence of thin zones is observable: bornite zone extended along contact with chalcopyrite is followed by chalcocite zone toward central part of veinlet and discontinuous very thin black band (probably, cavities with iron hydroxides) is in the central part immediately. In the other adjacent places (Figs. 6c, 6d), zoned coloform bornite-chalcopyrite aggregates with variable width of zones and quantitative relationship of bornite and chalcopyrite are abundant. Relicts of pseudomorphs of iron hydroxides after hematite are observed also in them, but zoning shown in Fig. 6b is absent. Therein, chalcocite occurs mainly as spots and veinlets.

In the Rainbow hydrothermal field (36°4′ N, MAR), different authors have reported more than 30 minerals including native metals, sulfides, sulfates, oxides, hydroxides, and carbonates. Therein, relationships differ from described above (Fig. 7). On the one hand, these are interaction of iron hydroxides with high-temperature assemblage consisting of pyrrhotite, sphalerite, and isocubanite, on the other hand, these are relationships between iron hydroxides and lower-temperature assemblage of coloform aggregates composed of pyrite, marcasite, and sphalerite. In the former case, iron hydroxides replace intensively lamellar crystals of pyrrhotite nearly up to complete pseudomorphs. Relicts of pyrrhotite crystals are included occasionally into sphalerite-isocubanite aggregate and then, iron hydroxides rim the whole aggregate (Fig. 7a). In the other places, the hydroxides replace nearly completely fine-acicular part at the bottom of radiated aggregate of tabular pyrrhotite crystals and occur as crust on this aggregate on the side of fresh tabular crystals (Figs. 7b, 7c). According to chemical data (Table), relict of lamellar pyrrhotite contains more Fe ($x = 0.06$ in formula $Fe_{1-x}S$), than tabular pyrrhotite in radiated aggregate ($x = 0.12$). As is known, symmetry of the pyrrhotite lattice depends of deficiency of Fe and at $x \sim 0.11$ to 0.20, hexagonal pyrrhotite transforms to monoclinic (Minerals..., 1960). Based on these data, the early relict of pyrrhotite (Fig. 7a) may be considered as hexagonal and pyrrhotite in radiated aggregate (Fig. 7b), as monoclinic.

In the lowest-temperature assemblage composed of coloform grains, pyrite is in the cores of these grains and columnar radiated marcasite, in margins (Fig. 7c). These aggregates are surrounded by zoned rim with discontinuous chains of small crystal of Fe-rich sphalerite enclosed in thin zones of iron hydroxides with bright red inner reflections. The chemical composition of sulfide minerals is given in the Table. In similar rims, separate inclusions of small barite crystals close to

Fig. 7. Relationships between pyrite, sphalerite, and isocubanite and iron hydroxides, Rainbow field, MAR. Polished sections. Back-scattered electron images:
a — tabular crystal of pyrrhotite is replaced by iron hydroxides to form pseudomorph. The crystal is surrounded by sphalerite (light grey) with crenate segregation of isocubanite (slightly darker). All aggregate is rimmed by columnar hydroxides;
b — radiated aggregate of tabular pyrrhotite crystals transiting to fine-acicular segregation that is nearly completely replaced by iron hydroxides. Another side of fresh crystals of pyrrhotite is rimmed by iron hydroxides;
c — coloform pyrite-marcasite aggregate (pyrite in the center; columnar radiated marcasite in margins) is rimmed by discontinuous chain of fine crystals of Fe-rich sphalerite (white) surrounded by thin zones of iron hydroxides with bright red inner reflections;
d — detail of (c).

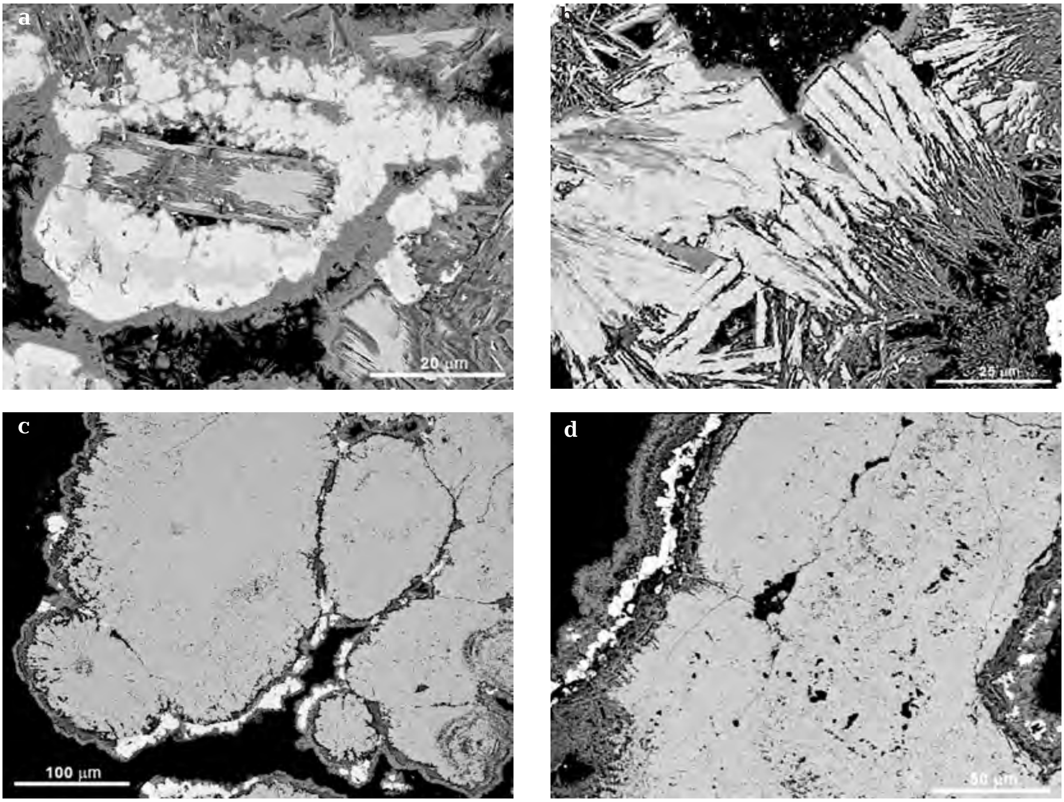

Table 1. **Electron microprobe data of sulfide minerals from submarine massive sulfides of the Rainbow, wt.%**

Mineral	Fe	Cu	Zn	Co	S	Total	Formula	Figure
Pyrrhotite	60.83	–	–	–	37.30	98.13	$Fe_{0.94}S$	7a
–"–	59.69	–	–	0.21	38.77	98.67	$Fe_{0.88}S$	7b
–"–	60.56	0.64	–	–	39.53	100.73	$Fe_{0.88}S$	7b
Pyrite	46.71	–	–	–	53.14	99.85	$Fe_{1.01}S_{1.99}$	7c, d
Marcasite	45.92	–	–	–	54.54	100.46	$Fe_{0.98}S_{2.02}$	7c, d
Sphalerite	21.96	0.07	42.27	–	34.21	98.51	$(Zn_{0.62}Fe_{0.37})_{0.99}S_{1.01}$	7c, d
–"–	23.75	0.17	41.28	–	35.20	100.40	$(Zn_{0.58}Fe_{0.39})_{0.98}S_{1.02}$	7c, d

Notes. Formula of pyrrhotite is calculated on the basis of 1 atom S; formula of pyrite and marcasite, on the basis of 3 atoms per formula; and formula of sphalerite, on the basis of 2 atoms per formula.

sphalerite chains and growth direction of zones of columnar hydroxides are seen at high magnification; these zones grow from central chains of sphalerite crystals both outward and to marcasite replacing it (Fig. 7d).

Thus, on the one hand, iron hydroxides replace sulfides; on the other hand, they cover them by thin crusts containing interlayers of newly formed sulfides.

Discussion

Mineral assemblages of iron sulfides and oxides are abundant in varied types of continental deposits. Betekhtin (1953) discussed numerous examples of these assemblages with emphasis on change of mineral assemblages testifying to change of sulfur and oxygen regime during deposition.

We have studied this problem with application to modern sulfide-oxide mineral assemblages in massive sulfides for the last decade; some our results were reported at the international mineralogical conferences (Mozgova *et al*., 2004_1; 2004_2). The aforementioned data indicate that the assemblages studied in submarine massive sulfides are variable in both quantitative and age relationships of sulfide and oxide constituents, which frequently change in microspace and time. Therefore, they reflect corresponding change of sulfur and oxygen regime and suggest causes of such changes. Microscopic observations in reflected light are important for such studies. We dwell on two most dramatic examples from described above.

One of them is relationships in sulfide-oxide assemblages in massive sulfide samples from occurrence 6° N, EPR. Microscopically, in places, where mineralogy of ore is relatively simple (ore assemblage consists of hematite of different generations, magnetite, and pyrite), clear sequence of mineral formation indicating change of sulfur and oxygen fluid regime is observed. Initially formed hematite lamellas (mineral with the highest oxidation level) are mushketovitized, i.e., are replaced by magnetite (the mineral depleted in oxygen). The process starts from the formation of rims and finishes by the formation of complete pseudomorphs (Fig. 2). At the same time, coloform zoned aggregates of pyrite are formed. These relationships correspond to known reaction of mushketovitization under effect of H_2S that is strong reducing agent: $2Fe_2O_3 + 2H_2S = Fe_3O_4 + FeS_2 + H_2O$ (Betekhtin, 1953). Hereafter, the inverse process occurs: both relicts of magnetite pseudomorphs and accompanying pyrite are overgrown by small euhedral hematite-II crystals. On the one hand, this may indicate to the change of sulfur and oxygen regime determining the damping of sulfide deposition and, on the other hand, to introducing new portions of sea water, that according to some studies (for example, Constantinou, 1975) is good oxidizing agent. For example, according to the same author, pyrite converses to goethite even at the lowest concentration of oxygen in sea water (0.1 ml per liter).

Ore assemblages of the Irina-2 active location, Logatchev field, MAR provide another example. Therein, early coarse-grained radiated hematite with rare small inclusions of exsolved high-temperature (> 300°C) isocubanite has been described. It appears to testify to nearly simultaneous precipitation of hematite and high-temperature isocubanite solid solution during its homogeneous stage (Fig. 4). In another sample, veinlet of chalcopyrite cuts and corrodes similar hematite (Fig. 5). Along margins of the veinlet, reaction rim of bornite, copper sulfide depleted in Fe in comparison with chalcopyrite and containing Fe-free chalcocite, is formed at the contact with hematite. It is obvious that the transformation is due to oxygen released as a result of replacement of hematite. Under these conditions, iron from near-contact chalcopyrite removes and chalcopyrite close to the boundary with hematite converses to bornite initially and then, to chalcocite. The similar removal of iron from chalcopyrite to form reaction rims under oxidative conditions was described multiple at the continental deposits. For example, in massive sulfides of Cyprus, as a result of oxidative leaching of chalcopyrite, the formation of reaction zones of Cu-richer idaite (Cu_3FeS_4) is followed by precipitation of covellite (CuS) (Constantinou, 1975). Betekhtin described removal of iron from chalcopyrite under oxidative conditions, similar to those, which we reported, to form reaction rims of bornite and chalcocite. This phenomenon is caused by capacity of iron to release from chalcopyrite, "whereas copper having high affinity to sulfur can be preserved as sulfides depleted in Fe or Fe-free under the same conditions" (Betekhtin, 1953).

Thereafter, in submarine massive sulfides, hematite aggregates are replaced by amorphous iron hydrosulfides up to complete pseudomorphs (Fig. 6). Relicts of such pseudomorphs surround chalcopyrite and chalcopyrite-bornite coloform zoned aggregates. This process is accompanied in places by strong releasing iron not only from chalcopyrite but bornite also that results in the formation of thin zone of chalcocite immediately at the contact with relicts of hydroxide pseudomorphs after hematite; this zone replaces bornite that in turn develops after chalcopyrite (Fig. 6b).

Restricted by these examples, it can be concluded that sulfur and oxygen regime is widely variable in the modern submarine massive sulfides like continental hydrothermal deposits. It is reflected in change of iron sulfide and oxide assemblages. As hydrothermal process dies out, mineral assemblages change to lower-temperature depleted in sulfide sulfur (up to its complete disappearance) ones. At the same time, in accordance with varied state of fluids or oxidizing capacity of replaced minerals, relationships of sulfide-oxide mineral assemblages may alternate in microspace and time during mineralizing process. It is consistent with thermochemical theoretical calculations, according to which, iron oxides converse to sulfides and reverse within narrow range of pH ans Eh (Garrels and Christ, 1965). The results obtained support the conclusion by Betekhtin that this regime multiple alternates during ore deposition including microscale.

Acknowledgements

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MINERALOGICAL AND GEOCHEMICAL FEATURES OF THE URANIUM ORE COMPOSITION: SCIENTIFIC AND PRACTICAL IMPORTANCE

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Currently, more than 150 uranium and uranium-bearing minerals are known. Most of them pertain to the uranyl group formed under oxidative conditions reflecting physicochemical parameters in the mineral compositions or mineral assemblages. The uranyl minerals compose the following economic ores: (1) uranophane-beta – zeolites (Berezovyi and Gornyi deposits, Transbaikalia), (2) the uranyl minerals associated with zeolites (Severnyi deposit, NE Russia, granite in Bulgaria), (3) parsonsite (La Chaux deposit, France), and (4) uranyl phosphates in argillic granite (Durulgui deposit, Transbaikalia). In addition, large uranium deposits as carnotite calcretes and calcretes with the other uranyl minerals are known from Australia and Namibia, respectively. Cut off ore (up to 0.01% U) and blocks with low uranium grade (up to 0.005% and lower) are economic at the deposits with the uranyl minerals in the case of geotechnological mining or heap-leaching processing, for example schrö ckingerite deposits in Mongolia and Kazakhstan. Such deposits can be large and superlarge.

In the fresh economic ore, uranium (IV) minerals are oxides (nasturan, uraninite, sooty pitchblende), titanates (brannerite and its transition varieties), silicates (coffinite and silicates of variable composition), and less frequent uranium (IV) phosphates and molybdates. Uranium-bearing minerals are apatite, Ti, Zr, and Th oxides and silicates, and zeolites. The ore deposition is significantly affected by the near-surface and deep-seated supergene alteration. The additional exploration and estimation criteria for uranium deposits are proposed. These criteria allow discovery of uranium deposits in: (1) north of the Strel'tsovsk structure, South-East Transbaikalia, (2) Akitkan district and Chara-Olekma block, northern Baikal Region, and (3) Western Siberian Plate.

1 table, 7 figures, 56 references.
Keywords: uranium (IV) minerals, uranyl minerals, uranium-bearing minerals, large and superlarge uranium deposits, prediction of uranium deposits

According to the expression by V.I. Vernadsky on ubiquity of uranium, currently, more than 150 uranium and uranium-bearing mineral species are known. Most them belonging to the uranyl group are formed under oxidative conditions; in this case, the composition of separate mineral species and mineral assemblages reflect physicochemical parameters of mineral-forming medium. The uranyl minerals are hydroxides, silicates, phosphates, arsenates, vanadates, carbonates, sulfates, molybdates, selenites, tellurites, and minerals of the more complex anion and cation composition. Iron and manganese oxides and hydroxides, apatite, zeolites, powellite, wulfenite, clay minerals, and other uranyl-bearing minerals are attributed to the U-bearing minerals.

In addition, amorphous phases and poor-crystallized uranyl hydroxides, as well as Fe, Si, Ti, Zr, Th, and more complex uranyl hydroxides and uranyl-bearing hydroxides are known. All these minerals are formed in the oxidizing zone of uranium deposits whose fresh ores are below oxidizing zone. Recently, such fresh ore was the major object of mining. Mineralogy of oxidizing zone of uranium deposits was multiple reported in geological literature (Frondel, 1958; Heinrich, 1958; Gritsaenko *et al*., 1959; Konstantinov and Kulikova, 1960; Evseeva and Perel'man, 1962; Supergene..., 1965; Formation..., 1976; Chernikov, 1981, 1982, 1996, 2001, 2008, 2009; Mineralogy..., 1983; Large..., 1984; Typomorphic features..., 1989; Kulish and Mikhailov, 2004; Chernikov and Dorfman, 2004; Chernikov *et al*., 2009_1, 2009_2 and other). Redistribution of uranium in oxidizing zone of uranium deposits is important to be described.

Types of oxidizing zones formed after economic fresh uranium ores

According to distribution of uranium, the following types of oxidizing zone of uranium deposits are distinguished: (1) leached or significantly depleted in uranium oxidizing zone in comparison with fresh ore; (2) oxidizing zone with uranium grade like fresh ore; (3) oxidizing zone with ore enriched in uranium in comparison with fresh ore. The first type is divided into three subtypes. Subtype 1a includes oxidizing zones without uranyl minerals or they are insignificant (Byk deposit, Caucuses Mineral Waters, Russia; Adrasman deposit, Kara-Mazar, Tajikistan).

Roll and similar deposits in Southern Kazakhstan, Central Asia, Siberia, Transbaikalia, and sedimentary basins in Bulgaria and other countries may be attributed to this subtype. Oxidizing zones with the uranyl minerals, which are economic ore only on the separate levels (Druzhnyi, Elkon, and Plato deposits, Elkon district, Aldan, Russia), pertain to the 1b subtype. Subtype 1c includes oxidizing zones with the uranyl minerals in ores depleted in uranium in comparison with replaced fresh ores (Strel'tsovsk, Luchistyi, and Tulukuevo deposits, Southeastern Transbaikalia, Russia).

In the second-type oxidizing zones, subtypes 2a and 2b are distinguished. In subtype 2a, uranium grade in oxidized and fresh ore is approximately identical (Chasovoi deposit, Transbaikalia; Cherkasar deposit, Kurama Ridge, Uzbekistan). In subtype 2b, uranium grade at separate levels of oxidizing zone is lesser than in the fresh ore. Most oxidizing zones of the 1c subtype are similar to those of the 2b subtype. The major difference is that in subtype 1c, all oxidizing zone is depleted in uranium, whereas in subtype 2b, only separate levels are depleted in uranium. The Major Zone of the Tabashary deposit, Kara-Mazar, Tajikistan exemplifies this subtype (Chernikov, 1981_1). Geochemical and mineralogical features of both type oxidizing zones are applied for ore prediction below oxidizing zone. The composition of the uranyl minerals and associated minerals of the other elements and their zoned distribution determine the formation type of deposit and its economic importance.

The third-type oxidizing zones are divided into two subtypes: (3a) deposits with rich ore in all oxidizing zone and (3b) deposits with enriched oxidized ore at the near-surface level that gives way to oxidized leached zone. The Sernyi deposit located ~200 km east of Turkmenbashi (former Krasnovodsk), Turkmenistan exemplifies subtype 3a. In the oxidizing zone of this deposit, hydroxides, phosphates and other uranyl minerals were identified. However, silicates (mainly uranophane) and uranyl vanadates (strelkinite, carnotite, and tyuyamunite) are more abundant. Completely oxidized ore of this deposit in which only uranyl minerals were identified contains three times more uranium and mixed ore (with uranyl minerals, sooty pitchblende and relict nasturan), — 2.8 times more uranium to 1 m depth in comparison with sooty pitchblende-nasturan ore. Oxidizing zone enriched in uranium in comparison with fresh ore is formed in U-V deposits, for example, Shakoptar and Maili Sai, Kirgizstan and Pap, Uzbekistan.

It is evidently that elevated uranium grade in oxidized coal whose fresh variety has a background concentration of this element should be attributed to subtype 3a. Uranium frequently concentrates with rare and noble metals in grade of $0.0n - 0.n\%$ in ash of oxidized coal of many coal basins in Siberia, Transbaikalia, Russian Far East, Mongolia, Kazakhstan, and Bulgaria. For example, ash of oxidized coal from the Adun-Chulun deposit, Mongolia contains 0.11 – 0.33% U, up to 0.45% *REE*, 0.36 – 2.1 g/t Au, up to 350 g/t Co, and elevated concentrations of other important chemical elements (Arbuzov *et al.*, 2008). The processing of ash of power-station utilizing such coal will favorable for environment in the districts of its storage because recovery of uranium will decide a problem of radioactive environmental pollution.

The oxidizing zone of the Komsomolsk rare metal-uranium deposit, western outer contact and near-contact igneous rocks of the Kuu granite pluton, Central Kazakhstan (Chernikov, 1981_2; Chernikov and Dorfman, 2004) exemplify subtype 3b. In the uppermost part of the oxidizing zone of this deposit, shrökingerite (Fig. 1) and small amount of uranophane were identified. The clusters of shrökingerite form near-surface subzone (vertical extension from 2 to 5 m) significantly enriched in uranium. The mineral identified along tectonic fractures far from orebodies occurs as large clusters in the Quaternary loose sediments and at the upper levels of tectonic zones, which are not associated with major ore-bearing structures.

Subzone of leached uranium with small number of uranophane and autunite (probably, also uranospinite) is below the shrökingerite subzone down to tens to hundred meters. This subzone is followed by the zone enriched in uranium (vertical extension to several dozen meters) with sooty pitchblende and clay matter absorbing uranium; in turn this zone gives way to the zone depleted in uranium and low-grade zone. Nasturan, uraninite, and brannerite were identified in the low-grade zone.

Lead isotopic composition and radioactive isotopes in minerals and mineral assemblages clearly record intensity of supergene redistribution of uranium in geological section of the Komsomolsk deposit. The distribution of mineral assemblages and lead isotopic ratio and relationship of radioactive isotopes in these assemblages allowed hematitization of rocks before Early Triassic, when the main stage of erosion of Paleozoic sediments took place. Hematitization was strong at the Komsomolsk deposit. After that, during Jurassic, Tertiary, and Quaternary, at the deposits and occurrences located in near-contact igneous rocks and outer contact of the Kuu pluton to which this deposit is related, supergene minerals with highly redistributed uranium and other ore minerals were formed. The strong leached U and Mo lead to the limited formation of their minerals in the oxidizing zone and newly formed minerals precipitated in the cementation zone. Only during late Quaternary, gypsum and shrökingerite started to precipitate in soil, Quaternary sediments, and upper level of weathering profile, including upper level of previously leached oxidizing zone. Since shrökingerite accumulated during Upper Quaternary at different distance from source and leached zones are poor documented, the probability of finding of uranium economic concentration at deep level of the Komsomolsk deposit is high. In this case, near-surface clusters of shrökingerite are of economic interest for heap leaching.

Deposits of uranium minerals of oxidizing zone without evident relation to fresh economic ore

In addition to the deposits with aforementioned types of oxidizing zone, there are deposits, where the uranyl minerals are the major constituents of economic ore formed without evident relation to any fresh economic concentrations of uranium. At first place, these are uranophane-beta — zeolite ore of the Berezovyi and Gornyi deposits (Chernikov, 1981_1, 2001; Chernikov *et al.*, 1983), many occurrences of southern Central Transbaikalia, and some border occurrences in Mongolia. The ores with the uranyl minerals hosted in granite of the Severnyi deposit and some occurrences of NE Russia, and zones of zeolite altered granite in Bulgaria belong to this type.

Fig. 1. Schröckingerite in clay of the Komsomol'sk deposit, Central Kazakhstan. Size of segregation is 6.5×7 mm.

In the zones of zeolite altered granite of the southern Central Transbaikalia (Chikoi-Ingoda structural zone), uranophane-beta is one or predominant uranium mineral of ore at deep level (from 150—300 to >700 m below surface). Small number of apatite, quartz-apatite, and silica veinlets were found, where the finest segregations of nasturan and coffinite with electron microscope had been established. Nasturan was identified with electron microscope in the core of radiated segregations of uranophane-beta (Fig. 2). However, the contribution of U-bearing apatite and silica veinlets and nasturan from uranophane-beta segregations to total uranium reserves at the deposits does not exceed 0.0*n* and 0.00*n*%. Uranophane-beta precipi-

Fig. 2. Radiated segregations of uranophane-beta with nasturan (N) located in the cores of these segregations, Gornyi deposit, Central Transbaikalia. ×7500.

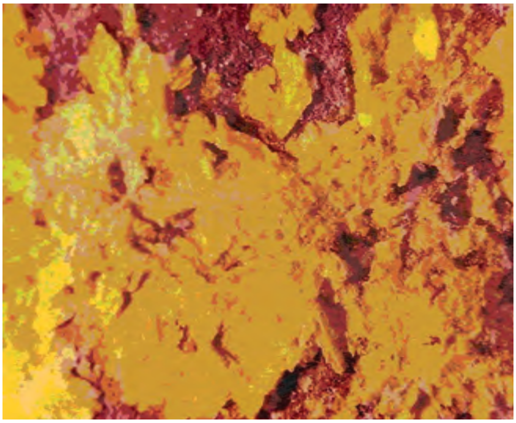

Fig. 3. Plates of yellow autunite on limonitized granite, Berezovyi deposit, Central Transbaikalia. ×10.

Fig. 4. Plates of dark green autunite, Durulgui deposit, Central Transbaikalia. ×10.

tated in alkaline environment is the major ore mineral at the Berezovyi and Gornyi deposits (Chernikov, 1981_1, 2001; Typomorphic features..., 1989). This mineral is replaced by uranophane upward due to pH increasing under effect of penetrated meteoric water, and at the depth of 50 – 150 m under weakly acidic conditions, by yellow autunite (Fig. 3). Upward, in weakly reductive acidic environment, yellow autunite, uranophane, and uranophane-beta are replaced by dark green autunite (Fig. 4) containing U^{4+}. In this case, near surface, the rare phenomenon is observable. Therein, the uranium (VI) contained in uranyl is reduced partly to tetravalent state because of introducing organic matter removed from soil and swamped places, rather than oxidation level of ore increases.

At the Gornyi deposit, insignificant amount of kasolite was observed and at the Berezovyi deposit, among listed varieties of autunite, single grains of sabugalite were indentified. At the Severnyi deposit and occurrences of the Shumilovo pluton, where the greisen mineralization is abundant, in addition to uranophane-beta, uranophane, and autunite, torbernite and uranyl arsenates (zeunerite and uranospinite) are abundant.

Autunite is the most abundant in the ore of the Durulgui deposit, southern East Transbaikalia, where only uranyl mineral were found. Just at this deposit, dark green autunite, containing tetravalent uranium was found for the first time in Russia in 1958 (Chernikov *et al.*, 1964). Therein, torbernite (Fig. 5) and sabugalite are less frequent. Uranyl minerals are associated with clay minerals, limonite, and manganese oxides. At the La Chaux deposit, France, parsonsite is the major ore mineral (Branche *et al.*, 1951). It fills fractures and cavities in smoky quartz associating with opal-like quartz, cerussite, pyromorphite, limonite, and manganese oxides. Other uranyl minerals, torbernite, autunite, dewindite, and kasolite are rare in this assemblage. Only autunite was described from occurrences at the Sila Plateau, Calabria, South Italy (The Formation..., 1976).

Carnotite is one ore mineral identified in the Yeelirrie calcrete deposit, Western Australia forming large uranium reservs (Sofoulis, 1962; Premoli, 1976; The Formation..., 1976; Laverov *et al.*, 1983). This mineral occurs as film along horizontal stratification of waterpenetrating carbonate or carbonate-rich rocks. In the other U-bearing calcretes of Western Australia, tyuyamunite is dominant over carnotite. Calcretes in Namibia and probably in Somali, Africa, are similar to the Yeelirrie calcretes, but in Namibia, uranyl minerals are closely associated with U-free gypsum. Like Yeelirrie, the films of carnotite in Somali fill interstices, fractures, and cavities in calctere, marble, clay, and broken carbonate at depth down to 8 m below surface only over ground-water level.

Australian or African-type near-surface calcrete-type orebodies with different uranyl minerals were identified in the northern part of Uch-Kuduk deposit adjacent to the Paleozoic granite pluton, Uzbekistan. Orebodies occurred at the depth of 1 – 3 m below surface in the Quaternary loam are concentrated at the talus and proluvium bottom partly involving upper carbonatized sediments (calcretes). The Quaternary loam is strongly gypsinate and uranium minerals in it occur as eyes and small lenses ranging from few mm to 3 cm in size. These eyes and lenses are fine-grained loose clusters saturated by earthy uranyl silicates and carbonates. They are weakly gypsinate in the places of the thickest mineralized loam (3 m). Bands of strongly gypsinate are over uranium mineralization. As thickness of the Quaternary sediments decreases, ore band gradually joins to the bands of gypsinate loam. In this case, gypsification is accompanied with removal of uranium. According to bulk analysis of samples taken through the section of the Quaternary sediments, there is no clear relationship between uranium grade and concentration of Ca, Mg, Mn, and Fe. The samples enriched in SO_4^{2-} are dramatically depleted in uranium. Microscopically, the replacement of uranium minerals by gypsum is observable. In the places of the most abundant gypsum, uranium is leached down to 0.02 – 0.03%.

In the district of the Uch-Kuduk ore field, lenses of gravelite with carbonate cement are frequently identified, but they are mineralized only at the contact with granite, where relicts of uranium minerals are frequently observed. Uranium minerals, haiweeitwe, weeksite, and liebigite-type uranyl carbonate fill fractures and cavities in the upper calcrete. However, their largest clusters are established in loam, where they occur as yellow band ranging from few cm to 10 – 15 cm thick following along rough of calcrete. Hence, uranium mineralization in the Quaternary loam was formed previously gypsinate rocks, but after carbonation. According to relationship of radioactive isotopes in the ore samples (Table 1), the rocks were carbonatized before 230 ky and gypsification, later 40 ky. These data are satisfactory consistent with previously results (Chernikov, 1981_2, 1982) concerning intensity of formation of uranium minerals during periods transited from warming to cold spell (Fig. 6).

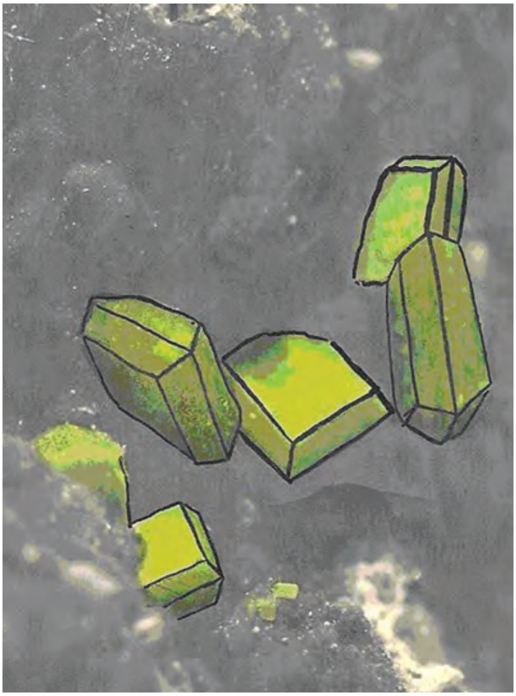

Fig. 5. Crystals of torbernite in leached cavity, Durulgui deposit, Central Transbaikalia. ×15.

Mineral assemblages and their zoned distribution determine the formation type of deposits and their economic importance. The deposits with uranyl minerals can be mined by underground leaching or heap leaching. In the case of such exploitation of orebodies, both rich and cut off (up to 0.01% U) ores are economic. Taking into account easy solubility of mineral, the rocks with 0.005% U and probably lower in the near-surface shrökingerite clusters of Kazakhstan, Mongolia,

Table 1. **Age of uranium mineralization in calcrete and loam**

Characteristic of sample	U^{234}/U^{238}	Io/U^{238}	Ra/U^{238}	Age, ky
Calcretes with the uranyl minerals	2.18	1.09	–	230
Lower loam enriched in the uranyl minerals	1.46	1.18	1.06	190
The same	1.68	1.25	1.18	185
Gypsinate loam with the uranyl minerals	1.45	1.27	–	180
Liebigite with gypsum	1.45	0.89	–	120
Weeksite and haiweeite with gypsum	1.46	0.39	–	40

and possibly the United States (Frondel, 1958; Sheridan *et al.*, 1961) and other arid areas are applied to exploit. The reserves of uranium in such deposits can be significantly increased to large and superlarge. For example, at the Nars deposit, Mongolia (Minerals of Mongolia, 2006), the shrökingerite clusters are followed by workings for 11 km along striking of ore-bearing beds. Broad areas of the shrökingerite mineralization were found in the other districts of Mongolia, Southern and Central Kazakhstan, and Kirgizstan.

Uranium minerals of fresh economic ore

In fresh economic ores, uranium minerals present lesser number of mineral species: oxides (uraninite, sooty pitchblende and nasturan), titanates (brannerite and its transitional varieties), silicates (coffinite and uranium silicates of variable composition), less frequent uranium (IV) phosphates and molybdates. In addition, at the Radium Hill deposit, where uranium ore is related to the high-temperature hydrothermal veins, ore minerals is davidite poor studied, in which Fe is partly substituted by *REE* and U. At the deposits of the Former Soviet Union, this mineral was not established. Many researches describe it as ilmenite with inclusions of uraninite.

Uranium-bearing minerals are apatite, titanium oxides and silicates, oxides and hydroxides of Nb, Zr, and Th, clay minerals, and zeolite. Mineral assemblages of uranium and uranium-bearing species and uranium-free minerals are widely variable (Laverov *et al.*, 1992); composition of uranium minerals and their properties are also significantly variable. The author described 11 ore types in Russia and neighbor countries (Chernikov *et al.*, 1997; Chernikov, 1996, 1998, 2006/2007). Among these types, there is no bornite and chalcopyrite ore with nasturan (very rare barannerite), native gold, and silver minerals in hematite breccia, which are described from the Olympic Dam largest deposit, Southern Australia. Ores with uraninite (less frequent nasturan, brannerite, coffinite, and U-bearing carbonaceous matter) and native gold characteristic of the Witwatersrand Precambrian System, South Africa were also not found in Russia and neighbor countries. Brannerite ore type with native gold hosted in potassic feldspar alteration is original and infrequently described worldwide. All these ore types are characterized completely. Therefore, concrete change of ore composition allows estimating physicochemical parameters of ore deposition, formation type of mineral deposit and its age, and erosion level. For example, change of mineral composition and size of mineral segregations in the ore of the Strel'tsovsk deposit, southeastern Transbaikalia as groundwater penetrating downward (Chernikov *et al.*, 2008) is a feature of formation of minerals that is identified in wildlife. At the border between air and land, higher organisms having the greatest size habit together with protozoa, whereas at the depth of hundred meters to few km, there are only protozoa. At the upper level of the Strel'tsovsk structure, frequently well crystallized uranium minerals (Fig. 7) occur as large crystals. Downward, they decrese in size and from 1500 to 2600 m, they are poor crystallized or amorphous occurred as nanoscaled segregations of uranium silicates, U-Ti compounds, and less frequent uranium oxides. Usually, they are hydrated compositionally ranging from coffinite to brannerite or to uranium oxides and titanates of the anatase-, ilmenite- and titanomagnetite-type. PbO content in most these segregations is below 0.0*n*% indicating their young geological age and formation from meteoric water infiltrated from sur-

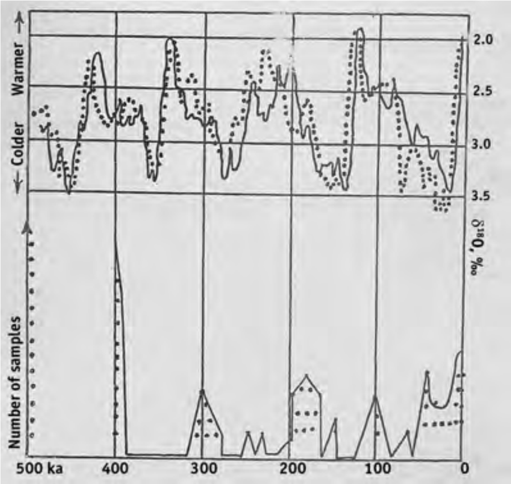

Fig. 6. Oxygen isotopic composition (upper curves) and intensity of mineral formation in oxidized uranium ore (lower curve) during 500 ky. Solid line was derived by Emiliani (1978); dot curve, by Kowi (1984), and lower curve, by Chernikov (1981, 1982).

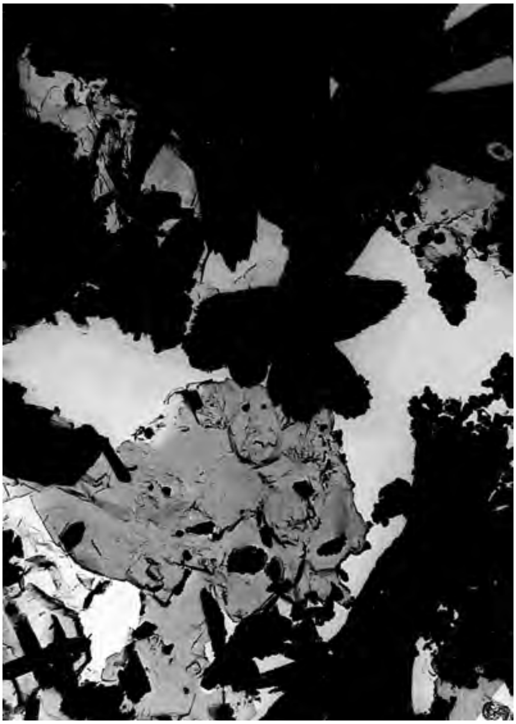

Fig. 7. Crystals of coffinite (dark), Strel'tsovsk deposit, Southeastern Transbaikalia. ×2000. Photo by V.T. Dubinchuk.

face to the deep level of the deposit. The conclusion of meteoric origin of mineralizing fluids is consistent with the previous results (Andreeva *et al.*, 1996, 1998; Chernikov *et al.*, 2008, 2009_2). Community of the formation of minerals and living being in vertical section at near-surface level of the Earth is basic feature.

Conclusions

The significant effect of near-surface and deep-seated supergene processes upon mineralization at the Strel'tsovsk deposit and some other districts appreciably changes prospecting and exploration guides, which were previously reported by Chernikov *et al.* (2009_1) for the main types of uranium deposits. Several districts fully corresponded to these criteria may be proposed. (1) North of the Strel'tsovsk structure: (a) sediments of the Eastern Urulyungui depression; (b) along the Urulyungui faults and in the basement structures; (c) in the rocks of basement of the northern side of the Eastern Urulyungui depression, first of all, along NNE-trending faults from Kislyi spring with U grade in water of $1-2{\bullet}10^{-4}$ g/l and North of known Yamkun radon spring. Further north, in the Eastern Transbaikalia, the Olovskii deposit with stratiform and polygenic ore is poor-explored. In the first place, ores in the granite of basement should be estimated both along veins and zones, and to the depth. (2) Akitkan district, North Baikal Region (Golubev *et al.*, 2008; Tolkachev, 2008; Bavlov and Mashkovtsev, 2009; Shashorin, 2009) and Chara-Olyokma block completely correspond to these conditions. (3) West Siberian Plate, where combination of deep transformation of clay rocks enriched in uranium and discharge of ore-forming gley stratal water of oil-and-gas basins allow probable large uranium-multimetall deposit in the Chulim-Enisei depression, infiltration deposit related to Altai-Sayan and Enisei Ridge, and different type deposits within the West Siberian Plate (Vorob'ev *et al.*, 2008; Domarenko *et al.*, 2008). At the southwestern margin of the West Siberian Plate (frequently reported as Ural region) infiltration uranium deposits, whose ore is located in sediments of paleovalleys cut rocks of basement are known (Kondrat'eva and Nesterova, 1997; Khalezov, 2000). Northeastern margin of the plate and regions related to the Altai-Sayan and Enisei Ridges are promised for this ore type. Finding of sufficiently long stratal oxidation zones or paleovalleys cut rocks of basement is important for these regions.

In addition to the complex U-V ore (Chernikov, 1997, 2001; Chernikov *et al.*, 2000, 2005, 2007, 2009_1), rare metal ore, especially carbonatite deposits taking into account complex nature of their ores (economic grade of U, Nb, P, and Zr) should be industrially used. Uranium as by-product produces from the Palabora apatite-bearing carbonatite, South Africa (The geology..., 1976; Laverov *et al.*, 1983) along with gold, silver, and PGE. Large copper deposit containing 0.001 – 0.001% U was found in this carbonatite. Copper ore occurred as stock-shaped body of 1.4×0.8 km in area in the centre of carbonatite pluton is followed downward more than 1000 m. Chalcopyrite, bornite, cubanite, chalcosite, pyrrhotite, pentlandite, millerite, bravoite, linneite, apatite, magnetite, titanomagnetite, U-bearing thorite, baddeleyite and vermiculite were identified in this ore. Uranium-richer carbonatite ore was explored at the Newman deposit, Manitou Islands, Nipissing Lake, Ontario Province, Canada.

Betafite (uranpyrochlore), uranium tantaloniobate of the pyrochlore-microlite group, is the major mineral of this ore. Its composition $(Ca, Na,U)_2(Ti,Nb,Ta)_2O_6(O,OH,F)$ differs from pyrochlore and microlite in higher U (up to 30% U_3O_8 with Nb_2O_5 ranging from 25 to 45%) and approximately identical content of Ta_2O_5. In addition, few percents of Th and from 0.0n to few percents of *REE* also introduce in this mineral. Such complex ore frequently contains P, economic U, Ta, or Nb. For example, 5431 t of such ore with ~0.53% Nb_2O_5 and ~0.039% U_3O_8 were identified at the Newman deposit before 1955 (Rowe, 1954; Gill and Owens, 1956; Heinrich, 1958). Further exploration of uraniferous complex carbonatite deposits for uranium ore was terminated because of discovery in this region rich uranium deposits. Nevertheless, as a result of exploration only for complex Ta-Nb ore, about 50 uraniferous carbonatite deposits with one third in Russia were identified. Some complex carbonatite deposits contain 0.05%, occasionally up to 0.12% U_3O_8. However, more frequently, uranium grade ranges from 0.01 to 0.03% and reserves of uranium reaches are medium to large with significant concentration of the other elements. For example, in certain zones of the Belaya Zima and Srednya Zima deposits, the demonstrated and inferred reserves of betafite ore are 10 kt of Ta_2O_5 and U_3O_8 with approximately identical grade in the ore, 0.012 – 0.028%. In the weathering profile of the Belaya Zima deposits, the demonstrated and inferred reserves are 1 mt Nb_2O_5 with grade of 0.5%, about 40 kt Ta_2O_5 and approximately identical U_3O_8 (with 0.014% of these oxides in ores); 3 mt *REE* with 1.8% REE_2O_3, and 15 mt P_2O_5 with grade of 13.6% in ores (Belov *et al.*, 2008). There are other examples illustrating the presence of complex betafite ore with grade of 0.01 – 0.05% U_3O_8 forming great uranium reserves. Therefore, the exploitation of large carbonatite deposits in Russia is very promised taking into account imported niobium and tantalum and deficiency of phosphorous and uranium in our country.

In the nearest future, complex sulfide U-P deposits with rare metals from deposits in Kalmykia (Stolyarov and Ivleva, 2008; Sharkov, 2008) and similar ore objects in other regions will be exploited.

Thus, the great diversity of uranium and U-bearing mineral species and their assembleges allows determination of: (1) physicochemical parameters of formation of mineral segregations based on certain changes; (2) age of mineral species; (3) formation type of uranium ore; (4) intensity of supergene leaching or enrichment in uranium of certain levels of endogenic occurrences and deposits. In this case, increasing deficiency of energy resources (Laverov, 2009) can be compensated in the nearest future by exploitation of rich ores including newly discovered ores and poor complex and uranyl-bearing ores. Reserves of such ores can be large and superlarge with decreasing cut-off grade of uranium to 0.005% and lower. We have no alternative so far.

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Crystal Chemistry, Minerals as Prototypes of New Materials, Physical and Chemical Properties of Minerals

ORICKITE FROM THE KHIBINY ALKALINE COMPLEX (KOLA PENINSULA) AND ITS STRUCTURE FEATURES

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The hydrous sulfide of Fe and Cu, orickite, was found for the second time in the world at the Khibiny alkaline massif (Kola Peninsula, Russia). It was discovered at the Koashva mountain, in cavities of hydrothermally altered peralkaline pegmatite with natrolite, aegirine, astrophyllite, lorenzenite, fluorapatite, fluorite, burbankite, sphalerite, chlorbartonite, amicite, vishnevite, elpasolite and other minerals. Orickite forms hexagonal laminar crystals (up to 1.5 mm) of bronze-yellow color with metallic luster. Chemical composition of the mineral (wt.%, electron microprobe data) is: Na 0.0 – 0.2, K 0.1 – 0.2, Ca 0.05 – 0.2, Tl 0.0 – 0.3, Fe 27.7 – 31.7, Cu 29.9 – 33.8, Zn 0.2 – 0.9, S 28.8 – 34.0, O 5.2 – 8.6. The average empirical formula of the best studied sample is: $Ca_{0.01}Cu_{1.01}Fe_{1.03}Zn_{0.01}S_{1.95}\bullet0.83H_2O$. The simplified formula of orickite is: $CuFeS_2(H_2O)_{1-x}$, where $0 \le x \le 0.8$. According to X-ray powder diffraction patterns, for orickite is suggested, as the most probable, hexagonal symmetry, space group $P6_3mc$ and structure model corresponding to wurtzite with disordered distribution of H_2O molecules that form layers (or their "fragments"), statistically substituting pairs of layers [(Fe,Cu)-S]. The Khibiny orickite represents intergrowth of two polytypic modifications, one of which (predominant) corresponds to wurtzite-2*H* ($a = 3.71(4)$, $c = 6.16(3)$ Å – according to single-crystal data; $a = 3.700(2)$, $c = 6.137(6)$ Å – according to X-ray powder data), and the second one – to wurtzite-4*H* (according to X-ray powder data: $a = 3.700(2)$, $c = 12.267(12)$ Å).
3 tables, 2 figures, 17 references.

Keywords: orickite, hydrous sulfides, wurtzite structure type, alkaline pegmatites, Khibiny massif, Kola Peninsula.

Orickite, a hudrous sulfide of iron and copper, discovered by R. Erd and J. Czamanske (Erd, Czamanske, 1983), was known up till now only in high-alkaline pegmatoids of small diatreme of Coyote Peak (California, USA), composed mainly of phlogopite, schorlomite, aegirine, sodalite, pectolite and natrolite. Interesting feature of these rocks is unique variety of sulfides containing as species-forming components alkaline metals and/or H_2O molecules: these are djerfisherite, bartonite, chlorbartonite, rasvumite, erdite, coyoteite and orickite. The latter was studied very insufficiently: absence of individuals suitable for single-crystal X-ray investigation allowed us to judge about structural features only by X-ray powder-diffraction pattern. Even, inspite of its bad quality (diffused lines), it was revealed undoubted relationship of orickite with wurtzite-2*H* that made it possible to characterize a new mineral as hexagonal one with parameters of unit cell $a = 3.695(10)$, $c = 6.16(1)$ Å, $V = 72.8$ Å^3. However, the authors did not exclude for it also ortho rhombic pseudohexagonal symmetry. On the basis of electron microprobe data (Table 1, an. 1) for orickite it was established the formula $Na_xK_yCu_{0.95}Fe_{1.06}S_2\bullet zH_2O$ ($x, y < 0.03$, $z < 0.5$) (Erd, Czamanske, 1983), which is often written in simplified form: $CuFeS_2\bullet0.5H_2O$.

We made the second find of orickite – on the Koashva mountain in the Khibiny alkaline massive (Kola Peninsula, Russia). The mineral was found in 2007 by I.V. Pekov and A.S. Podlesnyi in peralkaline pegmatite uncovered in a quarry operating for the apatite deposit Koashva. By the present time this pegmatite, located at the level +100 m at south-western part of the quarry, is destructed by mining workings.

The pegmatite body was represented by a lens with about 3 m in length, situated in urtite near the contact with nepheline-apatite rock. Its marginal zone was composed mainly of microcline and aegirine with minor amounts of nepheline, sodalite, alkali amphibole, eudialyte, titanite, lamprophyllite, lorenzenite, and fluorapatite. The major part of pegmatite volume is its cavernous core, formed by hydrothermal minerals, among which substantially predominated natrolite and green thin needle-shaped, aegirine, and subordinate components were represented by astro-

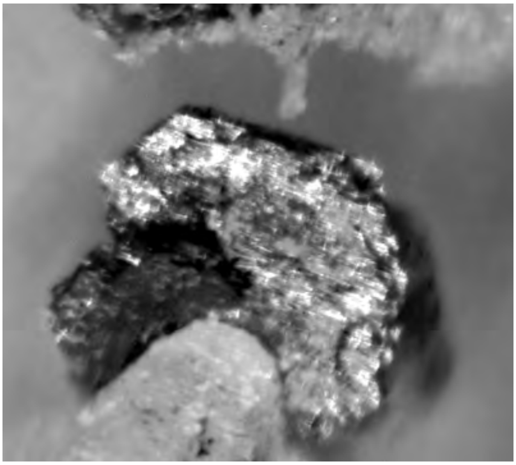

Fig. 1. Orickite crystal (0.4 mm across) on natrolite. Koashva Mountain, Khibiny massif, Kola Peninsula, Russia. Photo: I.V. Pekov and A.V. Kasatkin.

phyllite, fluorapatite, intermediate members of ilmenite-pyrophanite series, titanite, lorenzenite, fluorite, burbankite, and sphalerite, as well as solid bitumen in the form of spherical aggregations. In small amounts were present pectolite, chlorbartonite, tainiolite, lamprophyllite, barytolamprophyllite, vinogradovite, leucophanite, amicite, vishnevite, elpasolite, labuntsovite-Mn, catapleiite, zircon, pyrochlore, galena, orickite, and Na-bearing Fe-rich chlorite-like mineral.

Orickite occurs in caverns of aegirine-natrolite aggregates. It forms lamellar hexagonal crystals (Fig. 1) typically, not perfect, bended and split in different degree with uneven surface, and their intergrowths, including fan-like or similar to open book. Size of its crystals is typically up to 0.5 mm, and intergrowths – up to 2 mm. Well-shaped crystals of orickite are found for the first time. Their main habit form is pinacoid {001}, we did not manage to determine indexes of side faces. Mineral individuals are soft, flexible, easily split along plane of perfect, mica-like cleavage {001}, giving thin flakes. The orickite color is bronze-yellow, luster is metallic. Under the influence of air the mineral gradually darkens and becomes dull.

Chemical composition of the Khibiny orickite was determined by means of electron microprobe method for several crystals in two laboratories.

At the chair of petrology of Moscow State University (analyst V.O. Yapaskurt) the mineral was studied using scanning electron microscope Jeol JSM-6480LV with combined system microanalysis (Table 1, an. 2). Analysis was carried out in conjugated regime: contents of metals and sulfur were measured using energy-dispersive spectrometer INCA-Energy 350 (window ATW-2), oxygen – by wave dispersive four-crystal spectrometer INCA-Wave 500. Conditions of analysis: accelerating voltage 15 kV, beam current 45.8 nA, beam area from 12 to 100 μm^2, duration of accumulation of energy-dispersive spectrum – 100 sec. (dead time 32%), duration of accumulation of signal at measurement of oxygen concentration at peak – 20 sec., at background – 10 sec. Standards: Cu, Fe, S – CuFeS2; Zn – ZnS; Ca, O – $CaWO_4$.

At the chair of mineralogy of Moscow State University (analyst I.A. Bryzgalov) the mineral was studied by wos method using a Camebax SX 50 microanalyzer (Table 1, an. 3). Accelerating voltage 15 kV, beam current 30 nA, duration of accumulation of signal at peak is 10 sec, at background – 5 sec at each side. Analyses were carried out by defocused beam at the area of 10 × 10 μm. Standards: Cu – covellite; Fe, S – FeS; Na – albite; K – $KTiPO_5$; Tl – lorandite.

Contents of the main components – Cu, Fe and S, obtained for the Khibiny orickite in two laboratories, are very close to each other and differ slightly from corresponding data for the specimen from Coyote Peak (Table 1). Concentrations of Na and K vary, but are low, in the Khibiny mineral are discovered also small admixtures of Ca and Tl. Content of oxygen in orickite from Khibiny is considerably higher, than in Californian one: calculated on its content average amount of H_2O in our specimen is $0.83H_2O$ per formula (unit $Cu+Fe+Zn+S = 4$), while in the mineral from Coyote Peak it varies in the limits of $(0.18-0.61)H_2O$. Thus, the simplified orickite formula can be modified as follows: $CuFeS_2(H_2O)_{1-x}$, where the value x ranges, according to empiric data, from 0.0 to 0.8.

We tried to study single-crystal of Khibiny orickite using a Xcalibur S CCD diffractometer, MoKα-radiation. Unfortunately, all tested crystals proved to be useless for structural analysis due to curring and/or splitting. However, for the first time we determine parameters of orickite unit cell by the single-crystal method: the mineral is hexagonal, $a = 3.71(4)$, $c = 6.16(3)$ Å.

Powder X-ray diffraction study of the Khibiny orickite was carried out by Gandolfi

Table 1. **Chemical composition of orickite from Coyote Peak, California, USA (1), and Khibiny, Kola Peninsula, Russia (2–3)**

Component	1	2	3
wt.%			
Na	0.4 (0.2–0.5)	bdl	0.08 (0.00–0.2)
K	0.2 (0.05–0.25)	bdl	0.14 (0.1–0.2)
Ca		0.15 (0.05–0.2)	non determ.
Fe	31.0 (30.0–32.2)	28.90 (27.7–31.7)	29.45 (28.1–29.9)
Cu	31.7 (30.8–32.7)	32.01 (29.9–33.8)	30.91 (30.3–31.7)
Zn	0.49 (0.2–0.9)	non determ.	
S	33.6 (33.1–34.4)	31.30 (28.8–34.0)	31.41 (30.2–32.4)
O	1.5–5.1	6.60 (5.2–8.6)	non determ.
[H_2O calc]	[1.7–5.7]	[7.43]	
Total	96.9 *(without oxygen)*	99.45 [100.28]*	92.10**
number of atoms per formula, calculation for (Cu+Fe+Zn+S) = 4			
Na	0.03	–	0.01
K	0.01	–	0.01
Ca		0.01	
Fe	1.06	1.03	1.06
Cu	0.95	1.01	0.98
Zn		0.01	
S	1.99	1.95	1.96
H_2O	0.18–0.61	0.83	

Note: 1 – Erd, Czamanske, 1983, 2, 3 – our data for two different crystals (average for 6 analyses in each case).

** – value of analytical total in square brackets includes not O but H_2O; ** – total includes also 0.11% Tl (average for 6 analysis with range: 0.0–0.3%); bdl – below detection limit by electron microprobe method; non determ. – component was not determined.*

metod using single-crystal diffractometer STOE IPDS II (the chair of crystallography St. Petersburg State University), equipped by IP detector. MoKα-radiation was used. Our powder diffraction pattern in its strongest reflections is very close to the X-ray powder pattern of the Californian orickite, but additionally includes 7 more reflections (Table 2). All its reflections, excluding one with d = 1.938 Å, are well indexed in the hexagonal cell suggested in (Erd, Czamanske, 1983) and based upon the cell of wurtzite-2*H*. Refined by 17 lines from 18 ones (excluding the above mentioned with d = 1.938 Å) parameters of unit cell of orickite from Khibiny are: a = 3.700(2), c = 6.137(6) Å, V = 72.8(2) Å^3. Lines of X-ray powder pattern of our specimen, as well as Californian one, are brooden and diffuse.

With support on new X-ray data, we tried to analyze in more details, than authors of the first description, the specific features of orickite structure.

In 1988 was described a new mineral chvilevaite, $Na(Cu,Fe,Zn)_2S_2$, trigonal, a = 3.873, c = 6.848 Å (Kachalovskaya *et al.*, 1988), and then it was characterized its crystal structure, which proved to be derivative from wurtzite structure, but with another law of alternating of layers of three types: S, transition metals (Cu, Fe, Zn) and Na; this induced lowering of symmetry from $P6_3mc$ for wurtzite to $P3m1$ for chvilevaite (Kaplunnik *et al.*, 1990; Fig. 2). Very close structure, although other space groups, has the whole family of chvilevaite-like synthetic sulfides and selenides: $Na(CuFe)S_2$, $Li(CuFe)S_2$, $Li(CuFe)Se_2$ – $P\text{-}3m1$ (Ramirez *et al.*, 2001), $Na(Cu_{1.54}V_{0.46})S_2$ – $P\text{-}3$ (Mujica *et al.*, 1996). It is interesting that change of layers of Na or Li atoms for the layers of more large K, Cs or Tl results in transition from the structural type of trigonal chvilevaite to the structural type of tetragonal bukovite (Ramirez *et al.*, 2001), to which is related murunskite $K(CuFe)S_2$, also occurring at the Koashva mountain (Pekov *et al.*, 2009) in pegmatites of the same type that orickite does, but only less altered by late hydrothermal processes.

Based on chemical composition, stoichiometry, dimensions of unit cells, and structural similarity to wurtzite, one of the authors of the present article in 2006 suggested that orickite could be an analogue of chvilevaite with layers of molecules H_2O instead of

Table 2. **X-ray powder data for orickite, wurtzite-2*H* and wurtzite-4*H***

hkl(2*H*)	Orickite					Wurtzite-2*H*				Wurtzite-4*H*		*hkl* (4*H*)
	Koashva Mount, Khibiny massif (our data)			Coyote Peak (Erd, Czamanske, 1983)		synthetic (Swanson, Fuyat, 1953)		calculated ac-cord. to (Kisi, Elcombe, 1989)		calculated ac-cord. to(Chao, Gault, 1989)		
	$I_{meas.}$	$d_{meas.}$, Å	$d_{calc.}$, Å	$I_{meas.}$	$d_{meas.}$, Å	$I_{meas.}$	$d_{meas.}$, Å	$I_{calc.}$	$d_{calc.}$, Å	$I_{calc.}$	$d_{calc.}$, Å	
100	100	3.199	3.204	90	3.20	100	3.309	100	3.311	25	3.311	100
–			3.100*					–	–	100	3.200	101
002	85	3.078	3.069	100	3.08	86	3.128	62	3.130	64	3.130	004
101	41	2.853	2.840	60	2.84	84	2.925	98	2.927	75	2.927	102
–			2.522*					–	–	11	2.594	103
102	15	2.224	2.216	15	2.20	29	2.273	36	2.275	9	2.274	104
–	27	1.938*	1.948*					–	–	33	1.997	105
110	40	1.854	1.850	70	1.85	74	1.911	71	1.911	78	1.911	110
103	19	1.736	1.724	55	1.73	52	1.764	69	1.765	58	1.765	106
200			1.602			10	1.654	10	1.655	3	1.655	200
–			1.589*					–	–	13	1.641	201
112	13	1.593	1.584	30	1.583	45	1.630	44	1.631	50	1.631	114
201	8	1.550	1.550	3	1.543**	12	1.599	13	1.600	12	1.600	202
004			1.534			2	1.564	1	1.565	2	1.565	008
202	4	1.417	1.420			5	1.462	7	1.463	2	1.463	204
104	5	1.370	1.384			1	1.414	1	1.415	0.4	1.415	108
203	7	1.265	1.261	10	1.261	14	1.296	21	1.297	19	1.297	206
210	3	1.213	1.211			6	1.251	7	1.251	2	1.251	210
211	4	1.187	1.188			3	1.226	9	1.227	8	1.227	212
105	4	1.149	1.146	5	1.146	4	1.170	14	1.171	14	1.171	1.0.10
212	4	1.119	1.127			8	1.161	6	1.162	2	1.162	214
204			1.108			<1	1.136	0.4	1.137	0.2	1.137	208
300	5	1.070	1.068			13	1.103	9	1.104	12	1.104	300
213	12	1.042	1.042	5	1.043	6	1.072	20	1.073	21	1.073	216
symmetry and parameters of unit cell, Å												
	hex., $P6_3mc$ (?) *a* 3.700 *c* 6.137			hex., $P6_3mc$ (?) *a* 3.695 *c* 6.16		hex., $P6_3mc$ *a* 3.820 *c* 6.254		hex., $P6_3mc$ *a* 3.8227 *c* 6.2607		hex., $P6_3mc$ *a* 3.8227 *c* 12.52		

Note. The Table does not include reflexes of theoretical X-ray powder patterns of wurtzite with intensites <10, which are not observed upon experimental X-ray powder patterns. For wurtzite-2H they are (hkl–d, Å) 114–1.211 and 301–1.087, and for wurtzite-4H: 002–6.260, 006–2.087, 112–1.828, 107–1.574, 203–1.539, 116–1.409, 205–1.381, 109–1.282, 0.0.10–1.251, 211–1.245, 207–1.215, 118–1.211, 213–1.199, 215–1.119, 301–1.094, 302–1.087 ana 1.0.11–1.076. Strike line means that reflex is impossible by symmetry ($P6_3mc$) for wurtzite-2H.

** – reflexes possible for modification of orickite corresponding in unit cell dimensions to wurtzite-4H, but not to wurtzite-2H;*

*** – reflex with d = 1.543 Å is considered in original work as 004 (Erd, Czamanske, 1983) but, basing upon relationships of intensities in calculated X-ray powder patterns of wurtzite, this is most probably 201.*

Na atoms, which could arise as a result of leaching from the latter of Na and hydration: $Na(Cu,Fe)_2S_2 \rightarrow (Cu,Fe)_2S_2 \cdot 0.nH_2O$ (Pekov, 2006).

However, investigation of orickite, found in 2007 at the Khibiny massif, shows, that this mineral and chvilevaite most probably are not direct structural analogues. Thus, at X-ray powder pattern of chvilevaite are present strong reflexes 001 and 111, as well as weaker lines 003 and 113 (Kachalovskaya *et al.*, 1988), impossible according to symmetry for wurtzite ($P6_3mc$, $a = 3.823$, $c = 6.261$ Å; Kisi, Elcombe, 1989). These reflections are absent for orickite (Table 2), if we ignore weak reflex with $d = 1.370$ Å at the X-ray powder pattern of the Khibiny specimen, which one could interpret as 113. However, it could be considered most probably as 104: appearance of the weak line 113 with simultaneous absence of

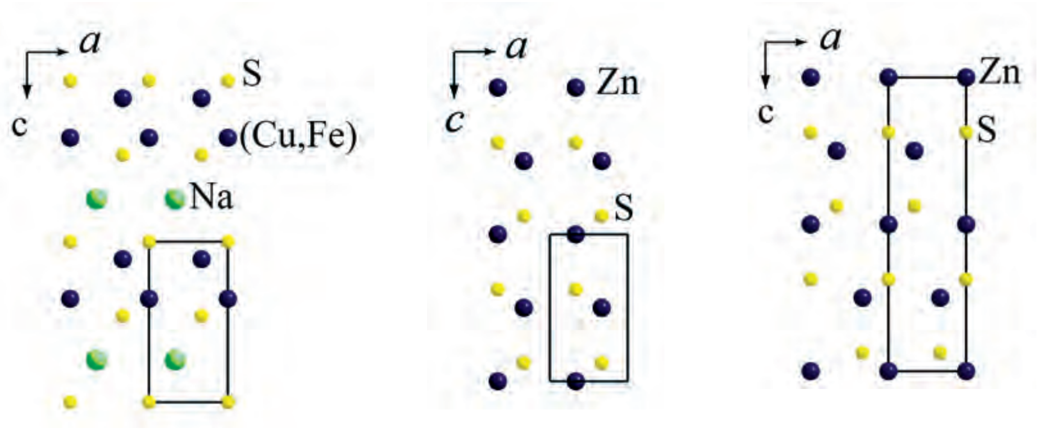

Fig. 2. Crystal structures of chvilevaite (a), wurtzite-2H (b) and wurtzite-4H (c) in the ac projection. Parameters of the unit cell are shown. Drawn using data from: a — Kaplunnik et al., 1990; b — Kisi, Elcombe, 1989; c — Chao, Gault, 1989.

strong reflex 111 seems to be hardly probable. We simulated with the help of program LAZY PULVERIX (Yvon *et al*., 1977) X-ray powder patern of $CuFeS_2(H_2O)_{0.83}$ — hypothetical analogue of chvilevaite, at which Na is replaced for H_2O with preserving symmetry *P*3*m*1, and parameters of unit cell (as well as occupancy of H_2O position) correspond to the Khibiny orickite. Comparison of this theoretical X-ray powder pattern with experimental one of the Khibiny orickite (Table 3) shows essential differences which have systematic character. At the first place they are represented by absence at orickite a reflex 001 (d = 6.14 Å) and very high intensity of reflex 002 (d = 3.078 Å), whereas at hypothetical chvilevaite-like $CuFeS_2(H_2O)_{0.83}$ reflection 001 should be very strong, and reflection 002 — weak. We should also note an absence at the experimental X-ray powder pattern of orickite reflexes 003 and 111, impossible according to symmetry of wurtzite ($P6_3mc$), but rather intensive for its derivatives, crystallized in space groups *P*-3*m*1, *P*3*m*1 and *P*-3 (X-ray powder patterns of the mentioned above synthetic chvilevaite-like phases were also simulated by us).

Set of reflexes and their intensities for orickite are the most similar with ones for wurtzite-2*H*. It was noted by R. Erd and J. Czamanske (Erd, Czamanske, 1983), and now it is confirmed by us at the X-ray powder pattern of higher quality (Table 2).

In contrast to the Californian orickite, the Khibiny one has rather strong reflex with d = 1.938 Å, which violates the pattern corresponding to unit cells of both wurtzite-2*H* type and chvilevaite (Table 2 and 3). However it is well indexed as 105 while doubling the parameter *c* (Table 2). Appearance of this reflex might serve as indication for the fact, that the Khibiny orickite according to unit cell dimensions is an analogue of wutzite-4*H*, but the latter has relative intensities of reflexes 100 and 101 substantially another than for wurtzite-2*H* (Table 2). If an absence of reflex 111 ($d_{calc.}$ = 3.100 Å) yet could be explained in the frame of the model "4*H*" by its merge with the reflex 004 ($d_{calc.}$ = 3.069 Å) into single broad line with d ≈ 3.08 Å, the high intensity of the reflex 100 (the strongest reflection at all X-ray powder patterns of orickite) clearly indicate to better correspondence to the model of wurtzite-2*H*. Thus, it is possible to assume with considerable probability, that orickite as well as wurtzite are characterized by polytypism, and the Californian specimen by dimensions of its unit cell corresponds to wurtzite-2*H*, and the Khibiny one is represented by intergrowths of the same polytype, having the minimum possible by volume unit cell, with another one, with the doubled *c* parameter is in correspondence with the model of wurtzite-4*H* (Fig. 2). Calculation of parameters of its unit cell by 18 lines, including reflex with d = 1.938 Å, results in: a = 3.700(2), c = 12.267(12) Å, V = 145.5(3) Å^3. Judging from relations of reflex intensities at the X-ray powder pattern of the Khibiny specimen, the polytype with small unit cell predominates.

Due to absence at the orickute X-ray powder pattern of other reflexes, first at the low-angle area (d > 3.25 Å), it is possible to con-

Table 3. **Comparison of experimental X-ray powder data of orickite from Khibiny and calculated data of hypothetical analogue of chvilevaite with composition $CuFeS_2(H_2O)_{0.83}$, space group $P3m1$ and parameters of unit cell $a = 3.700$, $c = 6.137$ Å**

Orickite		$CuFeS_2(H_2O)_{0.83}$		*hkl*
$I_{meas.}$	$d_{meas.}$, Å	$I_{calc.}$	$d_{calc.}$, Å	
		80	6.137**	001**
100	3.199	100	3.204	100
85	3.078	9	3.069	002
41	2.853	56, 27	2.840	011, 101
15	2.224	57, 14	2.216	102, 012
		18	2.046**	003**
27	1.938*			
40	1.854	69	1.850	110
		9, 9	1.771**	111**, 11-1**
19	1.736	16, 35	1.724	013, 103
		11	1.602	200
13	1.593	4, 4	1.584	112, 11-2
8	1.550	3, 8	1.550	021, 201
		1	1.534	004
4	1.417	3, 12	1.420	202, 022
5	1.370	4, 1	1.384	104, 014
		13, 13	1.372**	113**, 11-3**
7	1.265	5, 11	1.261	203, 023
		1	1.227**	005**
3	1.213	4, 4	1.211	210, 120
4	1.187	2, 1, 2, 1	1.188	21-1, 12-1, 121, 211
		1, 1	1.181	114, 11-4
4	1.149	4, 4	1.146	105, 015
4	1.119	1, 4, 1, 4	1.127	21-2, 12-2, 122, 212
		0.5, 1	1.108	204, 024
5	1.070	8	1.068	300
		1, 1	1.052	301, 031
12	1.042	2, 2, 5, 5	1.042	123, 21-3, 12-3, 213

*Note. * — reflex impossible for crystals corresponding unit cell dimensions to wurtzite-2H;*
*** — reflexes impossible by symmetry in space group $P6_3mc$.*

clude, that there are no or slightingly little polytypes with greater value of the parameter *c* (correspoanding to wurtzite-6*H*, -8*H*, etc.) in studied specimens. By analogy with all above mentioned natural and synthetic compounds with studied structures, as well as in terms of parameters of orickite unit cell, it is possible with great possibility to assume, that Cu and Fe in it are disordered.

From systematic extinction of reflexes of X-ray powder pattern (even values of l in the series 00*l* and *hhl*) and in terms of structural archetype of orickite is most probably represented by the wurtzite-2*H* type, one might assume, that the most possible space group for orickite is the same: $P6_3mc$. Corresponding to the same rule of special extinction the space groups $P6_3/mmc$, $P\text{-}62c$, $P\text{-}31c$ and $P31c$ are not confirmed in structural models based upon wurtzite-2*H*. Transition to other lower-symmetry variants (first attention was attracted by space groups $P\text{-}3m1$, $P3m1$ and $P\text{-}3$, corresponding to chvilevaite and related synthetic phases — see above) invariably leads to appearance at the theoretical X-ray powder patterns of additional strong reflexes that are absent for orickite.

In nature are known also other hexagonal and trigonal sulfides of copper and iron with stoichiometry of (Cu,Fe):S = 1:1 — they are nukundamite, $(Cu,Fe)_4S_4$ ($P\text{-}3m1$, $a = 3.783$, $c = 11.195$ Å; Rice *et al.*, 1979; Sugaki *et al.*, 1981), and idaite, Cu_3FeS_4 (?) (hexagonal, $a = 3.90$, $c = 16.95$ Å; Frenzel, 1959; Rice *et al.*, 1979). However the first one is close by its structure not to wurtzite but to covellite (Sugaki *et al.*, 1981), and the second one is studied insufficiently and its structural features are not known. According to X-ray powder patterns nukundamite and idaite differ strongly from orickite.

Where is H_2O in orickite? We tried to simulate crystal structures of the compound $CuFeS_2(H_2O)_{1\text{-}x}$ (with $x < 0.5$) with ordered distribution of H_2O molecules, which would have metrics of wurtzite-2*H* unit cell. It proved to be, that this is possible only at lowering of symmetry with disappearance of the *c* plane. This inevitably results in disappearance of systematic extinctions and, correspondingly, in appearance at theoretical X-ray powder patterns of strong reflexes that are absent for orickite (the examples are represented by structures of chvilevaite and related synthetic compounds; see Table 3, Fig. 2). Another way — multiple increase of one or of both parameters of the unit cell — also leads to appearance of additional reflections, which are absent at the X-ray powder patterns of orickite. Thus, experimental X-ray powder patterns of this mineral are satisfied only by structure of wurtzite itself. From this, as well as from diffusivity of reflexes, observed by the authors of first description of orickite (Erd, Czamanske, 1983) and by us, follows the conclusion, that distribution of H_2O molecules in its structure, which in the whole analogous to wurtzite structure (in the first place to polytype 2*H*), is most probably disordered. Presumably, they form layers (or their "fragments"), statistically replacing pairs of layers [(Fe,Cu)-S]. Exactly such disorde can be a cause of wide variations of oxygen content, revealed as a result of electron microprobe investigation.

It is not excluded, that just presence of H_2O molecules makes more stable wurtzite structure of sulfide of iron and copper: no data found in literature on compounds with wurtzite structure and compositions close to $(CuFe)S_2$.

We should note that we have no reasons to assume presence of oxygen in orickite not in the form of neutral H_2O molecules, but in some other form (O^{2-}, OH^-). Stoichiometry of (Cu,Fe):S = 1:1 is distinctly preserved and is in accordance with wurtzite type of X-ray powder pattern, that implies charge-balanced sulfide part of the structure. Appearance in this layered mineral of the charged O-bearing component (anion) would require existence of compensator in the form of additional cation, as, for example, in mixed-layered hydroxide-sulfides of the valleriite family (Organova, 1989), which in orickite, judging from electron-microprobe data, is absent.

The hudrous sulfides are generally typical for late stages of mineral formation just in high-alkaline systems (Pekov, 2006). At the Khibiny massif they are represented by two layered sulfides of Cu and Fe found in hydrothermally altered hyperagpaitic pegmatites at the Koashva mountain – these are wilhelmramsayite, $Cu_3FeS_3 \cdot 2H_2O$ (Pekov *et al.*, 2006), and orickite. Presumably, such minerals could form in nature by two ways: as products of alteration of an hydrous sulfides with alkaline metals – as result of leachihg of the latters accompanied by hydration, or as a result of direct crystallization from aqueous solution (fluid). The first mechanism is well illustrated at the example of the evolution series of layered sulfides caswellsilvertite $NaCrS_2$ → schöllhornite $Na_{0.3}CrS_2 \cdot H_2O$ → cronosite $Ca_{0.2}CrS_2 \cdot 2H_2O$, in which the first stage is represented by the process of leaching of 70% Na with replacing it by H_2O molecule, and the second one – by exchange of the remaining Na for Ca and introduction between Cr,S-layers (with their moving apart) one more H_2O molecule (Britvin *et al.*, 2001). For orickite both direct crystallization from hydrothermal solution and transformation (leaching of Na with hydration) under the influence of this solution upon the hypothetical phase $Na_{1-x}(CuFe)S_2$ seem possible. In the last case small amount of Na found in orickite from Coyote Peak and Khibiny could be relict, and K, Ca, Tl – products of natural ion exchange.

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Mineralogical Museums and Collections

FERSMAN MINERALOGICAL MUSEUM EXHIBIT DEVOTED TO THE 125th ANNIVERSARY OF A.N. LABUNTSOV

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In 2009, Fersman Mineralogical Museum of Russian Academy of Sciences celebrated the 125th anniversary of Alexander Nikolaevich Labuntsov, a remarkable mineralogist, the discoverer of the huge Khibiny apatite deposits. Being a great expert and collector of minerals, Labuntsov had worked in the Museum for about 35 years, organized field expeditions of wide geographic scope, and contributed to various museum collections with more than two thousand objects. The exhibit organized at the Museum by this date presents specimens collected by A.N. Labuntsov, his working materials, personal items, photographs, published works, and documents (including those found in the Archive of Russian Academy of Sciences).
13 figures, 7 references.

Keywords: mineralogical collection, A.N. Labuntsov, Khibiny apatite deposits, labuntsovite, fersmanite

On September 25th, 2009, Fersman Mineralogical Museum of Russian Academy of Sciences celebrated 125th birthday of a remarkable person and scientist — Alexander Nikolaevich Labuntsov (1884—1963). Labuntsov (Fig. 1), who had worked in the Museum for about 35 years, was the outstanding mineralogist with an incredibly wide scope of scientific interests, co-worker of A.E. Fersman, and the discoverer of the gigantic Khibiny apatite deposits (Kornetova, 1986). The Museum held a seminar and a special opening ceremony for the exhibit. Among the presenters there was Marina Alexandrovna Labuntsova, the scientist's daughter, Ph.D. in Biological Sciences, a Member of the Friends of Mineralogy Club. Labuntsova maintained long-lasting friendship with the Museum staff members and took active part in the preparation of the jubilee celebration. Being the keeper of the family archive, she handed over very interesting materials for the exhibit, including documents and some personal things that belonged to her father. The speach of Gleb Borisovich Udintsev, corresponding member of RAS, dodicated to a several pages of the White Army history, has caused a great interest of audience.

The jubilee exhibit includes a showcase with the mineral and rock specimens collected by Alexander Nikolaevich and his coworkers of the Khibiny and other expeditions, his working materials, personal items, and two stands with Labuntsov's published works and documents (including those found in the Archive of Russian Academy of Sciences). The exhibit is supplemented by the photographs from A.N. Labuntsov's and A.E. Fersman's archives.

Alexander Nikolaevich Labuntsov had an unusual destiny (Labuntsova, 2001). When he came to work in the Mineralogical Museum of the Academy of Sciences in 1922 being 38 years old, his life took a completely new turn. By that time, Labuntsov, following his family tradition, had already built a brilliant military career, had a title of Georgiy Cavalier, went through battles and wounds of three wars, miraculously surviving in the last one — Civil War.

At the same time, Labuntsov was interested in minerals since early years. He managed to find time for college mineralogy classes and for stone collecting during the years of his military service. In 1924, he graduated from the Natural Science Division of the Department of Physics and Mathematics of Leningrad State University.

Since the first years of his employment as a geologist-mineralogist at the Museum, Alexander Nikolaevich showed exceptional scientific intuition and special talent in organizing and leading the field expeditions. The geography of his trips is extremely wide: Labuntsov explored the alkaline massifs of Khibiny and Lovozero (Kola Peninsula), pegmatites of the Northern Karelia, Ilmen Mountains (South Urals), Western Pamir, Badakhshan (Afghanistan), South and Central Urals, Vaigach Island, Baikal Region, Central Asia (Kyrgyzia, Kazakhstan), and Donetsk Basin (Ukraine). In those cruel years of Russian history, frequent travel and life away from the capital cities were beneficial for Labuntsov, who had a "dark spot" on his biography as a participant of White movement, colonel of Kolchak's Division. At that time, he supplied more than 2000 specimens to the Museum collections.

The mineralogical material collected by A.N. Labuntsov reflects the wide geographic spread of his scientific work, and it is the main content of the exhibit. The specimens are placed in territorial and chronological order.

More than two thirds of Labuntsov's field stock is represented by minerals from Northern Karelia and Khibiny, the regions he studied mostly.

After Labuntsov joined the Museum staff, he was involved by academician A.E. Fersman into exploration of the Kola Peninsula. The contribution that Alexander Nikolaevich made to the study and development of the Khibiny area is hard to overestimate. As early as in 1923, he was the first who had realized the extraordinary importance of the apatite-nepheline rocks as a new type of natural resource, investigated the deposits, and pushed for the acknowledgment of his discovery. This story is told by the documents presented at the exhibit stands, in particular, recently published Transactions of the First Polar Conference on Complex Utilization of Khibiny Apatite-Nepheline Rock (1932), where Labuntsov was one of the main speakers (First Polar... 2009, p. 20), as well as the minutes protocol of the Leningrad District Council of National Economy of 23rd of May, 1930, in which it was emphasized that: "the survey, which was carried on in very hard conditions of the arctic circle, resulted in the brilliant discovery of the richest apatite-nepheline deposit by geologist A.N. Labuntsov". There are also photographs of the first stacks of apatite ore, quarried from Khibiny (1928), and the first construction site at the place of today's city of Kirovsk (1931).

Also there is exhibited the copy of the map of the apatite-nepheline deposits in Khibiny of 1926 — 1927, which was made by Alexander Nikolaevich by eye survey. Among the Khibiny photographs, there is also his picture of the Tietta Research Mining Station of the Academy of Sciences. By assignment from academician A.E. Fersman, Labuntsov chose the site for the station, prepared the sketches for the construction project. The opening of the station was held in conjunction with the aforementioned First Polar Conference — the second-day sessions, April 10, 1932, were hosted there (First Polar... 2009, p. 120 — 124).

Fig. 1. Alexander N. Labuntsov is the 1st Moscow Cadet Corps graduate. 1901. Moscow.

A.N. Labuntsov worked at Kola Peninsula for many years. He is one of the authors of the fundamental mineralogical study of the Khibiny and Lovozero (1937). In Khibiny, Alexander Nikolaevich discovered a new mineral — fersmanite

Fig. 2. Labuntsovite. Khibiny, Kola Peninsula, Russia. Anonymous presenter. 9 cm. FMM No 88495. Photo: Elena N. Matvienko.

Fig. 3. Fersmanite. Khibiny, Kola Peninsula. 7 cm. FMM No 41088.
Fig. 4. Eudialyte. Khibiny, Kola Peninsula. 11 cm, up to 4 cm. FMM No 25963, 36859.

Fig. 5. Lamprophyllite with aegirine. Lovozero, Kola Peninsula. 11 cm. FMM No 25962.
Fig. 6. Lorenzenite (ramsayite) with author`s label. Lovozero, Kola Peninsula. Crystal size up to 2 cm. FMM No K2249, K2236.

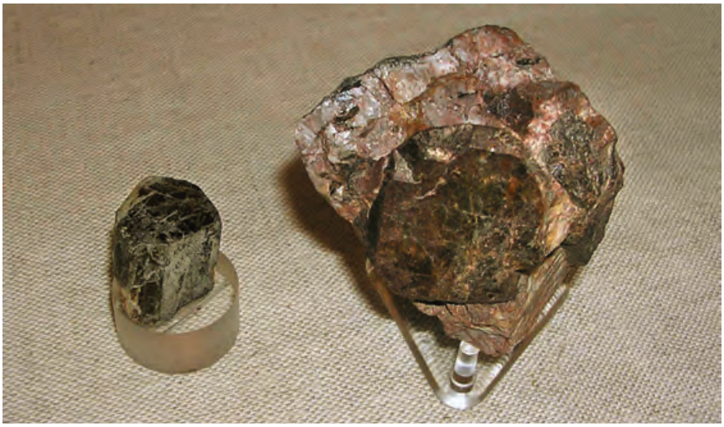

Fig. 8. Monazite-(Ce). Chornaya Salma Vein, Northern Karelia. FMM No K3584.

Fig. 7. Oligoclase (belomorite). Northern Karelia, Russia. 11 cm. FMM No 25946.

Photo: Elena N. Matvienko

Fig. 9. Lazurite. Lazorevaya-river, Baikal region. 10 cm. FMM No 20999. Photo: Elena N. Matvienko.
Fig. 10. Graphite. Botogol Massif, East Sayan. 12 cm. FMM No 41982. Photo: Elena N. Matvienko.

(1929) — and also was the first who described the titanium elpidite as a mineral variety (1926). The copies of the published articles on those subjects are presented at the exhibit. Later, titanium elpidite was identified as a new mineral (Semenov and Burova, 1955) and named *labuntsovite* (Fig. 2). Labuntsov's specimens displayed at the Museum, both rock-forming minerals and rare species, thoroughly characterize the mineralogy of the Khibiny alkaline massif. In addition to apatite, the exhibit includes fersmanite (Fig. 3), manganoneptunite, large crystals of eudialyte (Fig. 4), and well cut pseudooctahedral crystals of zircon up to 2 cm in size, and astrophyllite. Among the demonstrated Lovozero specimens, one can observe lamprophyllite (Fig. 5) and beautiful crystals of lorenzenite (Fig. 6) and zircon.

From 1924 to 1947, Alexander Nikolaevich repeatedly visited Northern Karelia and studied about 200 pegmatite bodies, in which he described in detail 60 minerals (Labuntsov, 1939). The Karelian specimens make up almost a half of all of them that he brought to the Museum. Some rock-forming minerals presented at the exhibit include crystals of mica (biotite and muscovite), oligoclase, and apatite. The famous oligoclase variety — belomorite — with irization on cleavage planes (Fig. 7) is especially attractive. Labuntsov's trip to the Sinyaya Pala vein was shared with Fersman, who described that "lunar mysterious flickering stone" in his story "Belomorite" (Fersman, 1940). The exhibit also includes minerals of rare and radioactive elements: monacite (Fig. 8), xenotime-(Y), and uraninite with rutherfordine. Labuntsov was very interested in such minerals, and there are many of them in his collections. The scientist also studied more complex polymineral radioactive substances (e.g. gummite, carbocer, etc.), which are rich in rare earth elements. A piece of paper from Labuntsov's notebook shows his neat small handwriting of the results of the chemical analysis of uraninite and gummite from several North Karelian pegmatite veins. The Karelian ores explored by Labuntsov in 1925 were the first uranium ores discovered in the USSR.

Alexander Nikolaevich took many trips to the South Urals. In 1938, he explored the Akhmatovskaya and Eremeevskaya mines in the Nazyam Mountains and, in 1940s, he studied pegmatites in the Ilmen Mountains. This work of him is illustrated by the specimens of Nazyam clinochlore and Ilmen crystals of corundum, columbite, and samarskite-(Y), malacon, and a pseudomorph of limonite after pyrite crystal. The geological map of Atlyan-Miass region (scale 1:50000, 1949) drawn by Labuntsov's hand is also exhibited here.

In 1920s, (1924, 1926), A.N. Labntsov was a participant of Sayan expeditions of the Mineralogical Museum. At the exhibit, one's attention is captured by a bright piece of lazurite from the classical domestic deposit of this mineral in the vicinity of the Malaya Bystraya River (Fig. 9). Beside it, pages of Labuntsov's field journal show his pencil-written descriptions of the character of lazurite occurrence and the parent rocks. The materials from Botogol Golets feature a remarkable selection of graphite of various morphology (Fig. 10).

After these expeditions, in 1928, A.N. Labuntsov as an expert in domestic lazurite was sent to Afghanistan for studying the famous Badakhshan deposit. Because of the tense political situation in that region, he could not reach his destination, but along the way, was able to study the Kukhi-Lal deposit in the Western Pamir and brought some specimens (namely, gummite and spinel) from there.

In 1939, Labuntsov traveled in Ukraine: visited Donets Basin's salt mines and Esaul deposit, collecting there some beautiful specimens of

Fig. 11. Boulangerite, sphalerite, quartz upon ankerite. Nagol`nyi Kryazh, Donbas, Ukraine. 25 cm. FMM No 42598. Photo: Elena N. Matvienko.
Fig. 12. Evansite. Karatau Range, Kazakhstan. 3 cm. FMM No 43924, 43926. Photo: Elena N. Matvienko.

boulangerite and sphalerite (Fig. 11), quartz crystals with boulangerite inclusions, and other minerals.

The activities of A.N. Labuntsov at a number of Central Asian deposits of rare elements are reflected in his specimens of evansite (Fig. 12) and a signed by him photocopy of his paper "Colloid Minerals from Northern Karatau". From his trip to Karatau (Kazakhstan), Labuntsov brought a whole collection of phosphate silica gels – semitransparent, sometimes brightly colored, previously unknown formations. He began studying colloid minerals, and that material was later used by academician F.V. Chukhrov in his work.

At last, the gold washed by A.N. Labuntsov from the glacier deposits in Moscow region, also presented at the exhibit, is the result of his later work, already after his retirement. In those years, Labuntsov arranged the new exhibit in the Mineralogical Museum entitled "Minerals of Moscow Region" using material of his own collections. He was really good at dredging, studied the Jurassic placers with diamonds and platinoids in the Central Urals in 1940.

Crystals and crystallography were the subjects of special attention and passion for Alexander Nikolaevich. Well-shaped crystals of different minerals take an honorable place among his materials. In one of the photographs, Labuntsov is pictured with an improved by him goniometer, which he used for measuring and indexing faces of numerous crystal specimens. A.N. Labuntsov created a special exhibit "Crystals", which is mainly preserved in its original order and still attracts attention of Museum visitors. The anniversary exhibit also contains boxes with home collections of small crystals (Fig. 13). Taking care of his mineral collection was Labuntsov's favorite hobby during his free time.

In addition to documents, field journals, the exhibit includes some scientific instruments and tools that belonged to A.N. Labuntsov: welding torch, small hammer, magnifying glass.

At stands there are also the photographs of A.N. Labutsov's parents, grandfather, and wife – Ekaterina Evtikhievna Kostyleva-Labuntsova, who was his all-time companion, a participant of the Khibiny expeditions, also a remarkable mineralogist and scientist of the Mineralogical Museum. Young Alexander Labuntsov is pictured with his family at the time when he studied at the 1st Moscow Cadet Corps. There are also photographs of the award list attached to the complete works of Russian poet A.N. Maikov, which was presented to A.N. Labuntsov "for excellent discipline and high achievements in sciences" after his graduation. Another image shows the Emperor's IV Degree Saint Georgiy Military Orden that Alexander Nikolaevich was awarded for the battle of August 15, 1914.

The documents from the Archive of Russian Academy of Sciences, first made available to the public at this exhibit, tell us about the hardships and obstacles that awaited the White Army officer Labuntsov on his way to become a scientist in Soviet Russia. These are the letters of Alexander Nikolaevich to academician V.I. Vernadsky written during the period of 1935–1939. Apart from purely scientific matters, there is an appeal from Labuntsov on his re-employment, a request to support the approval by the Qualifying Com-

Fig. 13. Labuntsov`s home collection.
Box size 16×18 cm.
Photo: Elena N. Matvienko.

mittee of his science degree (1938). The stand also contains an excerpt from the minutes protocol of the meeting of the Presidium of Gosplan of the RSFSR (the Russian Federation) of October 4th, 1929. The decision was taken at this meeting to honor the merits of the scientists doing research on Khibiny apatites and especially to acknowledge the roles of geologist Labuntsov and academician Fersman. A list of scientific works of A.N. Labuntsov is presented. The letters and related documents are published for the first time in this magazine issue in the rubric "Personalities".

On a final note, the above-reviewed anniversary exhibit was the first public show that nicely illustrated all sides of life and scientific career of the outstanding geologist and mineralogist A.N. Labuntsov, who made significant contributions to the collections of Fersman Mineralogical Museum and to the development of the national mineral resources.

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Personalities

TO A.N. LABUNTSOV'S 125TH ANNIVERSARY: A.N. LABUNTSOV'S LETTERS TO ACADEMICIAN V.I. VERNADSKY (from the Archive of Russian Academy of Sciences)

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To the 125th anniversary of A.N. Labuntsov, the discoverer of the Khibiny apatite deposits, his letters to the academician V.I. Vernadsky of years 1935 – 1939 as well as referred documents are published for the first time, both having been found in the Archive of Russian Academy of Sciences (RAS Archive).
4 figures, 9 references.

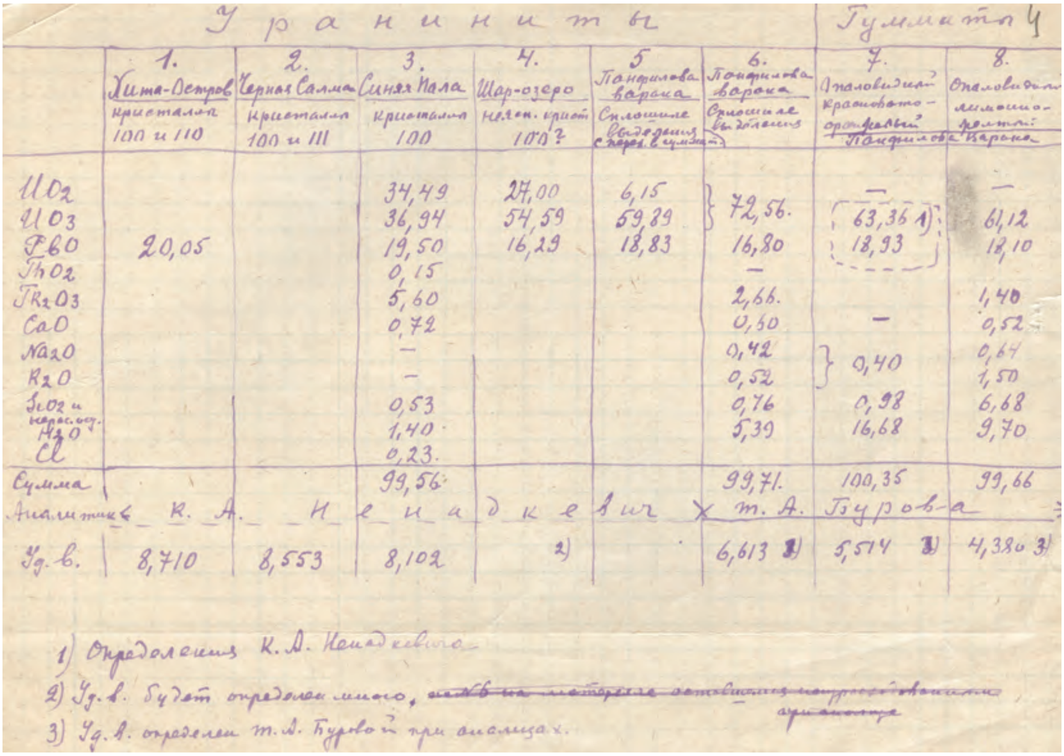
Keywords: A.N. Labuntsov, V.I. Vernadsky, Khibiny apatite deposits, Khibiny expeditions.

In September 2009, the exhibition devoted to the 125th anniversary of Alexander Nikolaevich Labuntsov (Fig. 1, see also the article in this issue) was opened in Fersman Mineralogical Museum. A.N. Labuntsov was a disciple and a team-mate of his two prominent contemporaries, academicians V.I. Vernadsky and A.E. Fersman. In the process of the exhibition creation, we found, in the academician V.I. Vernadsky Archive (of RAS Archive), some letters from A.N. Labuntsov and documents that refer to the latter's scientific activities and have never been published before. With courteous permission of V.Yu. Afiani, the RAS Archive director, and with the assistance of I.G. Tarakanova, the head of the Archive reference room, we present these documents as the evidences of the heroic and tragic epoch that was fully reflected in the Alexander Nikolaevich's fate.

The letters to Vladimir Ivanovich Vernadsky refer to the period since 1935 to 1939. The two first letters are of purely scientific character. In them, the problem of the age of Karelian radioactive minerals as well as publication of an article on this topic is discussed. In the letter of 10 May 1935 the table with chemical analyses of some of these minerals (Fig. 2) is enclosed. It should be taken into account that A.N. Labuntsov as a mineralogist was supervising the works to determine absolute age in the Radium Institute of Academy of Sciences; the Karelian uraninite age was determined just on his materials (Shcherbina, Bonshtedt-Kupletskaya, 1963).

The letter of 26 November 1935 was apparently written as a reply to the V.I. Vernadsky's request. This letter contains a detailed description of the Khibiny apatite discovery and the Labuntsov's role in it (Fig. 3). He sets the facts rather modestly withholding these first expeditions' difficulties. For example, the narration of field work in the summer 1926 contains only few words about "the apatite rock distribution area on the Rasvumchorr Mountain was extended up to 34000 square meters and the stratification depth was determined as over 20 meters". However, real events, as described by other participants (Kornetova, 1986) were much more dramatic. For example, the employed four bearers abandoned the party. So the three remaining expedition members, A.A. Saukov, a student (later the known geochemist, Academy of Science corresponding member), V.V. Lepishin, borer and firer, and A.N. Labuntsov had alone to carry 5 puds (80 kg) of apatite. To determine the stratification depth, A.N. Labuntsov makes a

Fig. 1. Alexander Nikolaevich Labuntsov. 24 January 1964. Photograph from the Museum archive.



	Ураниниты						Гуммиты 4	
	1. Хита-Остров кристаллы 100 и 110	2. Черная Салма кристаллы 100 и 111	3. Синяя Пала кристаллы 100	4. Шар-озеро неясн. крист 100?	5 Панфилова варака Сплошные выделения с перех. в гуммит	6. Панфилова варака Сплошные выделения	7. Опаловидный красновато-оранжевый Панфилова варака	8. Опаловидный лимонно-желтый
UO_2			34,49	27,00	6,15	72,56.	—	—
UO_3			36,94	54,59	59,89		63,36 1)	61,12
PbO	20,05		19,50	16,29	18,83	16,80	18,93	18,10
ThO_2			0,15			—		
TR_2O_3			5,60			2,66.		1,40
CaO			0,72			0,60	—	0,52
Na_2O			—			0,42	0,40	0,64
K_2O			—			0,52		1,50
SiO_2 и нераств. ост.			0,53			0,76	0,98	6,68
H_2O			1,40			5,39	16,68	9,70
Cl			0,23.					
Сумма			99,56			99,71.	100,35	99,66
Аналитики	К. А. Ненадкевич					т. А. Бурова		
Уд. в.	8,710	8,553	8,102	2)		6,613 3)	5,514 3)	4,380 3)

1) Определения К. А. Ненадкевича

2) Уд. в. будет определен много, ~~[illegible]~~

3) Уд. в. определен т. А. Буровой при анализах.

Fig. 2. The table with chemical analyses of uraninite and gummite from pegmatite veins of Northern Karelia. Attachment to the A.N. Labuntsov's letter of 10 May 1935.

Fig. 3. A.N. Labuntsov (front row, third from the left), B.M. Kupletsky (front row, first from the left), A.E. Fersman (stands in the center of second row) and other workers of the Kola Base. Photograph from the family archive. Published for the first time.

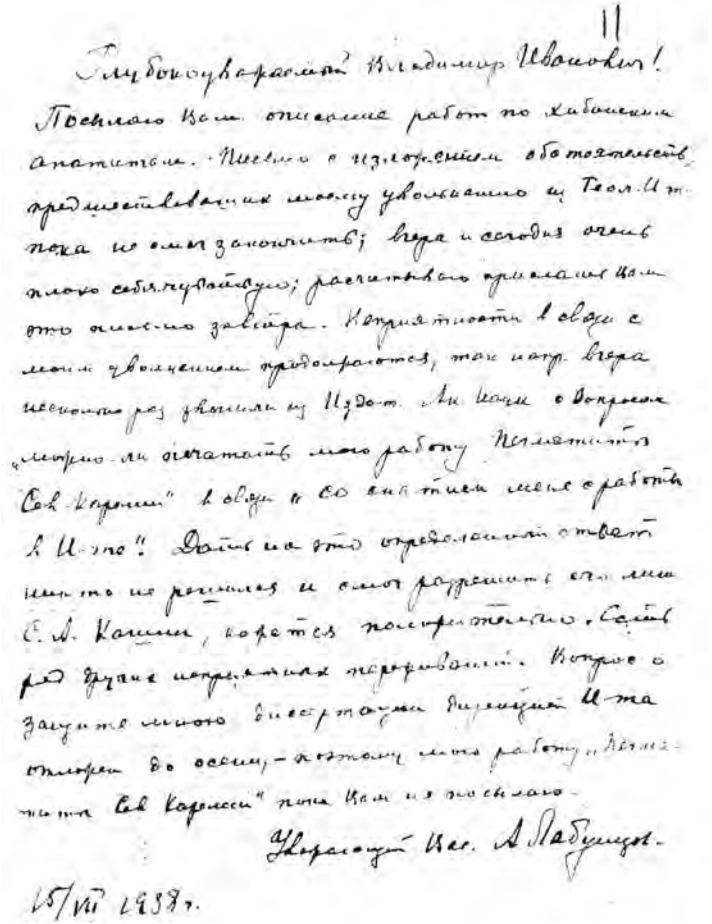


Fig. 4. A.N. Labuntsov's letter to academician V.I. Vernadsky of 15 July 1938.

11

Глубокоуважаемый Владимир Иванович!

Посылаю Вам описание работ по хибинским апатитам. Письмо с изложением обстоятельств, предшествовавших моему увольнению из Геол. Ин-та пока не смог закончить; вчера и сегодня очень плохо себя чувствую; рассчитываю прислать Вам это письмо завтра. Неприятности в связи с моим увольнением продолжаются, так напр. вчера несколько раз звонили из Изд-ва Ак Наук о вопросе „можно ли печатать мою работу Пегматиты Сев. Карелии" в связи и со снятием меня с работы в Ин-те". Дать на это определенный ответ никто не решился и смог разрешить его лишь С.А. Кашин, кажется положительно. Целый ряд других неприятных переживаний. Вопрос о защите мною диссертации дирекцией Ин-та отложен до осени, – поэтому мою работу „Пегматиты Сев. Карелии" пока Вам не посылаю.

Уважающий Вас. А Лабунцов.

15/VII 1938 г.

risky decision to descend by the cord with meter marks down the Rasvumchorr Mountain steep. He could not descend below 20 meters as this was the cord length; however, he made sure that apatite was even farther along the steep. And this is not mentioning the difficulties to obtain money for this and other Khibiny expeditions. One can read more about them in his letter of 15 July 1938 (see also Labuntsova, 2001; Schpachenko, 2009; Makarova, 2009).

Labuntsov indicates at the end of his November letter that he participated, besides Khibiny, in numerous other expeditions: in the Sayan Mountains, Baikal Area, Northern Karelia, Pamir, Afghanistan, Vaigach Island etc. He has, everywhere, a series of scientific as well as practical achievements. He is preparing now a monograph on the minerals of the North Karelia pegmatites and should like, by the A.E. Fersman advice, to present it as his doctoral dissertation. Unfortunately, this was not to be.

The point is that after the death of S.M. Kirov who supported the Khibiny development works, and after, accoding to the USSR Government decision, the Academy of Sciences movement to Moscow in 1934 – 1935, a hard time came for Labuntsov. From this period on, his name disappears from the publications related to the Khibiny expeditions; his merits in discovering, studying, and developing the Khibiny apatites being hushed up. Enemies appear to him and even to academician A.E. Fersman. Some problems arise in the "Apatit" trust that has been established on the Kola Peninsula as well as in the Kola Base (so was called the Fersman's "Tietta", the Khibiny Research Mining Station, renamed in 1934; Khalezova, 2001; see also the paper by Matvienko *et al.* in this issue) and in the Institute of Geological Sciences (Vernadsky, 2006_1, pp. 185, 385, 386; A.N. Labuntsov's letter of 21.03.1939). An elucidation should be made here. This Institute also included then the Mineralogical Museum as one of its sections, since the Institute itself (primary Lomonosovsky or Lomonosov Institute) has been established, in 1930, on the base of the Museum's analytical laboratories organized due to the V.I. Vernadsky and A.E. Fersman's efforts. Academician A.E. Fersman who was the director of the Mineralogical Museum, became also the director of the new Institute. V.I. Kryzhanovsky was charged to direct the museum section (see the letter of 21.03.1939). Therefore, all the workers of the Mineralogical Museum were officially itemized in the Institute of Geological Sciences (IGN) staff. Perhaps, this circumstance along with political atmosphere played certain role in the A.N. Labuntsov's troubles.

Anyway, the things proceeded as yet, in May of 1935, in their usual order. The Lomonosov Institute (LIGEM) and its Scientific Council under the chairmanship of A.E. Fersman asks the Qualifications Commission of the Academy of Sciences Geological Group to consider awarding the science-degree of candidate to Labuntsov due to the totality of his works (Extract of 26.05.1935), and the Commission accedes to this request (Extract of 22.12.1935). This is small wonder as the Labuntsov's merits and achievements are evident and doubtless (see Extract of 26.05.1935; Honorary Comment of 30.05.1925; Protocol of the Lenigrad District Council Meeting of 23.05.1930; Extract of the protocol of RSFSR Gosplan Presidium Meeting of 04.10.1929; List of works No. 1; List of articles No 2). Seemingly, the things finished well. However, this Qualifications Commission decision had to be upheld by the Presidium of the Academy of Sciences; but LIGEM did not do this, and its deadline elapsed (see the letter of 21.03.1939). When in May 1937 the item of awarding science-degree to Labuntsov was at last introduced for consideration by the Presidium of the Academy of Sciences, the decision was not reached again, and the matter was returned to LIGEM to be re-considered. It is clear now from the Alexander Nikolaevich's letters of 1938 – 1939 that the things might be still more tragic in 1937 since it was mentioned at the Presidium session that he was former White Army officer and he was even named a "Kolchak's adjutant". Indeed, he was not one. In 1918, he was a student of the Ural Mining Institute in Ekaterinburg and entered the Kolchak army by force of circumstances (Labuntsova, 2001). As the result of that session, A.N. Labuntsov had to give up on his work at the Kola Base, and in June 1938 he was suddenly dismissed from the IGN on "reduction of personnel". His endeavors to get a job anywhere else were not successful; he only could work for a short time in the Academy Publishing House and, then, in the "Zolotorazvedka" (gold prospecting) Trust.

All the rest A.N. Labuntsov's letters of this period (July 1938 – March 1939) that are stored in the RAS Archive as well as the enclosed documents tell us about his hard struggle for his right to work in the Academy on the same position that he occupied last 8 years (since October 1930) – senior researcher with scientific degree (Fig. 4). Alexander Nikolaevich knows no fault of his own and boldly refers to every instance able to decide the question, up to prosecution office, and asks help and support from V.I. Vernadsky. At the moment of writing his last letter dated 21 March 1939, Labuntsov is still unemployed. However soon, yet in April 1939, he gets the possibility to return to his work in the IGN and Mineralogical Museum. Even now we do not know exactly what a fortune was the cause of this. A.N. Labuntsov's Personnel Action File was not found in the archives of the Museum and Institute (now Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS). Academician V.I. Vernadsky alone elucidates a little this story. Here is what he writes on 7 April 1939: "The position of A.E. {Fersman} took a twist. The head of the Khibiny Combine (assistant to Kondrikov {former director of the "Apatit" Combine}...) in charge of the Council {apparently Murmansk District Executive Committee} came to him and indicated that it was now decided to increase and expand the North. A.E. said, of course, that he is always ready. This – {a place was left for the name; perhaps, for V.A. Prokopenko, director of the "Apatit" Combine} said that the A.E.'s forecasts acknowledged right. There are enormous possibilities there. When he {A.E. Fersman} said that the {scientific} workers have been dispersed, the other said that everything can be {settled} through him. Labuntsov gets the possibility to return to his job" (Vernadsky, 2006_2, p. 52; ibid, see comments on pp. 48 – 49).

However, the A.N. Labuntsov's scientific degree was never upheld. His monograph "The North Karelia Pegmatites and Their Minerals", which he mentioned in his letters and designed as the doctoral dissertation, was, though behind time, published in 1939 and became, according V.A. Kornetova, a model not only to emulate descriptions of pegmatite deposits but mineralogical monographs in general (Kornetova, 1986).

The A.N. Labuntsov's merits in discovery and mastering the Khibiny apatites were only acknowledged after his death. To his 100th anniversary, a street in the Kirovsk city was named in honor of geologist Labuntsov and memorial plaque was erected with his bas-relief and inscription: "Alexander Nikolaevich Labuntsov

(1884 – 1963), participant of the Academy of Sciences of the USSR Khibiny expeditions, the discoverer of apatite deposits in Khibiny". Unfortunately, this plaque disappeared from the wall of former cinema, which was turned to a trade center (Shpachenko, 2009).

In the offered letters and documents, the author's and original spelling and punctuation are saved except for features of the A.N. Labuntsov's handwriting (hyphen after the end of some sentences) and small details of dates and names. In all cases, the initials from the family names were separated with gaps. Insertion in letters from above are not marked as they are rare and fitted in the text. Authentic signatures in documents are marked italics accompanied with in parenthesis – (signature). Explanations and additions inserted by the authors of this work are enclosed in square brackets. In citations of academician V.I. Vernadsky's diaries, the comments and additions of the compiler (V.P. Volkov) and the editors of mentioned publication were separated from the author's text with curly braces.

The A.N. Labuntsov's letters to V.I. Vernadsky and enclosed documents from the Archive of RAS

Dear Vladimir Ivanovich!

I handed over to you, for the "doklady Ak. Nauk", my paper on the age of radioactive minerals of Karelia, there was not in it a reference to the printed work by Konst. Avtonom. [Nenadkevich] and something else, therefore I send you the new exemplar whose title I have changed. I ask you, if possible, to set the paper last exemplar to printing. In order you would not worry, I send the paper second copy into the publishing house to M. Eizen, the editor, with the instruction, if there will be your confirmation, to publish in the "doklady" under the title "On the age of uraninite and monazite from the pegmatite veins of Northern Karelia".

Yours faithfully A. Labuntsov

3/I 35
Moscow.

RAS Archive. F. 518. Op. 3. D. 916. L. 1.

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10/V. 35 Moscow

Dear Vladimir Ivanovich!

The report on "the age of uraninite and monazite from the N. Karelia pegmatite veins" was printed in the A.S. Contributions for March of this year, No. 9; I send you 3 copies.

As to the Karelian uraninite which you need to obtain uranic lead from it, I can say as follows: I have just a small quantity, about 30 g, of uraninite from the "Sinyaya Pala" veins, which I can send you.

As to the other veins, uraninite larger quantities are available, so I'm able to send you: from the "Khita-ostrov" and "Chernaya Salma" up to 100 g from each of them.

I send you, on the separate piece of paper, the available analyses of uraninite and gummite [see Fig. 2]. I should like to have else the uraninite analyses from the "Khita-ostrov" and "Chernaya Salma" veins which I told, in due time, to K.A. Nenadkevich who 2 1/2 years [ago] has promised to carry them out and took from me good and large pieces of pure uraninite from the "Chernaya Salma" but did not begin this uraninite analysis up to now. As judged by the paragenetic conditions of bedding and the crystal shapes, I expect that in the "Khita-ostrov" uraninite UO_2 would prevail over UO_3 as it gives fine crystals, namely cubes in combination with rhombic dodecahedron faces and has, according to my determinations, the highest density; after it, as expected, the "Chernaya Salma" uraninite that forms cubes with octahedral faces seems to be on the second place by the UO_2 content; and the "Sinyaya Pala" uraninite (cubes) is expected to be on the 3rd place.

I recently spoke with Konst. Avtonom. [K.A. Nenadkevich] and he promised to make the "Chernaya Salma" uraninite analysis in a short time; it would be good if you, too, ask him not to delay this; as to the "Khita-ostrov" uraninite, perhaps somebody else, in the Radium Institute, will take it to carry out its analysis.

At the moment, I only have remainders of carburan from the "Tedino" vein as a piece about 10 g; the same quantity may be scraped as a ground trifle mixed with muscovite and feldspar; I suppose, carburan can be easily separated due to its low density about 1.7.

I desire you to write me whether the denoted quantities of available uraninite and carburan are sufficient and should they be sent to you.

As to the organization of carburan mining this summer, I cannot answer you at the moment because it is not yet determined, through the unclarity of the housing question and other conditions of life, what a time would I be able to have this summer. It has been planned now that I will study, this summer, minerals of the River Tuloma area in the NW part of the Kola Peninsula and molybdenite in the Khibiny; probably I also ought to go once or twice to Karelia, to the NW of Kovdozero, for mineralogical consultation of the O.A. Vorobyeva team. In any case, I'll try to visit one or two of the main and richest *in carburan Karelian veins ("Tedino", 8 km to the East of Polarnyi Krug Station and "Yelovyi Navolok" at the Loukhi Lake in 25 km to the East of the Murmansk Railway "Loukhi" station) and take carburan as much as possible.*

Yours faithfully A. Labuntsov

RAS Archive. F. 518. Op. 3. D. 916. L. 2–4.

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Dear Vladimir Ivanovich!

As to the discovery and study of the Khibiny I can inform you as follows:

The blocks of apatite-nepheline rock found by me together with other colleagues in 1923 in placers on the Rasvumchorr plateau in the Khibiny Tundras have intrigued me very much. When I worked again in the summer of 1925 in the Khibiny Tundras, I undertook a special investigation of the Rasvumchorr Mountain and managed to trace the apatite bedrock on the area over 10000 square meters. Attaching great [importance] to that, in January of 1926, I gave a talk about this deposit in the Institute of the North. However, as such rock was never fixed by geologists wherever in the world, my report, though it attracted some interest, at the same time arose doubts in possibility of such rock to exist anywhere and its distribution within a large area. None the less I raised the question of money assignment for the study of the apatite deposits to be continued; as the result of these efforts with acad. A.E. Fersman's support, the Colonization Department of the Murmansk Railway promised to dispense 8000 roubles for this aim; then, however, because of the money deficit I only has got, through the Institute of the North, 700 roubles, which were only sufficient for me to work in the Khibiny Tundras in summer 1926 for one month. As the result of this work, the apatite rock distribution area on the Rasvumchorr Mountain was extended up to 34000 square meters and the bedrock depth fixed at over 20 meters; besides, another two deposits were found, one of them on the "Apatitovyi Otrog" measuring 16875 square meters and another one, an enormous deposit on the Mount Kukisvumchorr (which is mining now). These results have been reported to acad. A.E. Fersman at the end of summer, and prof. R.L. Samoylovich, D.I. Shcherbakov and P.A. Borisov visited the Khibiny Tundras; unfortunately, snow came down in the mountains and did not let them examine the deposits in detail, so they could only visit the Mount Rasvumchorr.

My talk on 14th October 1926 in the Mineralog. Museum of the Acad. of Sciences in your presence, as you remember, arouse a great interest and, at the same time, again arouse doubts in dimensions and apatite reserves in the deposits as well as miners' doubts in possibility to organize a mining enterprise in such a remote region. Nevertheless, it was possible, due acad. A.E. Fersman's support, to organize a high-quality study of the apatite ore and determination of its preparation characteristics in the Institute "Mekhanobr" and to send the ore samples, through the Murmansk Railway Colonization Department, to German company "Humboldt" to be tested in dressing by the flotation method, that we could not yet do here then. Both tests gave propitious results.

The question of organization of larger prospecting works on apatite that I raised in spring of 1927 was not settled, despite of the acad. A.E. Fersman's support, as neither Geol. Committee nor any other department believed in this matter; and, again, the Murmansk Railway Colonization Department alone promised 8000 roubles but then could not allocate more than 1000 roubles which was transferred to me through the Inst. of North. For this money, I could work, together with two students, in the Khibiny Tundras for one and a half month. The Kukisvumchorr deposit was investigated in detail and its continuation found on the Mount Yukspor; besides, the apatite rock new Western stripe on the Poachvumchorr Mountain was traced. I already have determined the apatite expected reserves as tens of million tons being based on the outcrops alone, which should be much increased after prospecting; at the same time, in my opinion, the Kukusvumchorr deposit is the largest, richest, and easiest to mine.

The later prospecting works in 1928 and, especially, in 1929, when Leningrad Region Ispolkom [Executive Committee] assigned 250000 roubles, and the Institute of Fertilizers was engaged, increased the apatite reserves still more, and the tests confirmed the apatite full applicability to produce superphosphate.

Therefore, there was dead certainty in autumn of 1929 about industrial meaning of the Khibiny apatites, and A.E. Fersman, who was very persistent and energetic in the promotion of the apatite problem (a series of his works of 1929) went to Moscow at the beginning of October, and there, as the result of his reports for the Committee for Chemization of National Economy and Gosplan, the government came to the decision to establish the "Apatit" Trust for the Khibiny apatites mining and exploitation. The "Apatit" Trust began to be organized in December 1929, and comrade V.I. Kondrikov, *the director, invited me to organize prospecting. I was working in the "Apatit" Trust from 15/XII 1929 until VIII 1934, as the head of the geological survey department at first, and then, after some mining engineers were engaged, as a consultant in scientific geology. While working in the Khibiny Tundras, I was lucky to find the new rare earth mineral "lovchorrite", which was named after the Mount Lovchorr; then the lovchorrite similar deposits were discovered by N.I. Gudkova, a researcher, on the Yukspor Mountain near the apatite deposits; these deposits are in operation now; then I found and studied deposits of pyrrhotite as a source of sulfur acid raw material; the deposits of sphene and molybdenite were found and investigated by me too. All the foregoing is highlighted in detail in the "Khibinskie Apatity", vol. I, 1930, as well as in the next volumes. My role and merits in the discovery and study of the Khibiny apatites were marked in 1929 in the Gosplan presidium (prot. of 4/X 1929), and in 1930 I was awarded a commendation and 2000 roubles of testimonial from Leningrad Council of Nat. Economy (prot. of 23/V 1930 No. 4239).*

My scientific works concerning minerals and other investigations in the Khibiny Tundras were distinguished by the Rus. Mineralogical Society, and I was awarded with the "honorary comment" substituting for a golden medal.

Besides the works in Khibiny and the Kola Peninsula other parts I participated since 1922 every year as a team head in expeditions to various other regions of the Soviet Union, the main of which are: Sayan Moumtains, Baikal Area, Northern Karelia, Pamirs, and Afghanistan (sending from Sovnarkom), Vaigach Island etc. There is a series of scientific and practical achievements of all these expeditions, therefore my printed works have the two areas of focus. In the recent years, I was mostly engaged in the studies of new minerals, radioactive and rare-earth ones, among which the Khibiny and Northern Karelia ones are the most interesting. In this year, I finish and prepare for publishing my monograph "The Minerals from Pegmatite Veins of North. Karelia". I should like, on acad. A.E. Fersman's advice, to present this work, in the beginning of 1936, as a doctoral geological dissertation.

Yours faithfully A. Labuntsov

26 November 1935.

Concerning the radioactive and rare-earth minerals of N. Karelia, I can report that, after my discovery, in 1925, of the radioactive uranium ore and gummite, these minerals were in the sequent years found out in a series of veins together with other radioactive and rare-earth ones like carburan, orthite, cyrtolite, monazite etc., which are the materials for your and special studies of the State Radium Institute in the recent years.

RAS Archive. F. 518. Op. 3. D. 916. L. 5—6.

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11/VII 38.

Dear Vladimir Ivanovich!

Having remembered your sensitive attitude and support that you rendered me in hard moments of life, I decided now to address you again with the great request to help me to settle difficult problems: 1) to get the scientific degree and 2) to continue my scientific work as I was suddenly discharged (without any explanation of cause) from the Institute of Geological Sciences "on grounds of staff reduction". I pray, if you will soon visit Moscow, please assign me time to accept me or permit me to come to Uzkoe on some of these days. Tomorrow on 12th I'm going to call on my family at the dacha near the Istra town and will be back on 13th about 1 p.m. I beg you to send your reply through Alexander Pavlovich Vinogradov. I tried a few times to phone on you or Natalia Yegorovna but this was no-go; I beg your pardon for the disturbance.

Yours faithfully A. Labuntsov

RAS Archive. F. 518. Op. 3. D. 916. L. 7.

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Dear Vladimir Ivanovich!

I send you the description of works on the Khibiny apatites. I could not yet finish my letter with the circumstance summary that preceded my dismissal from the Geological Institute; I feel very bad yesterday and today; hope to send it tomorrow. The troubles related to my dismissal go on; e.g., one phoned yesterday several times from the Academy of Sciences Publishing House with the question "whether is it possible to print my work on the pegmatites of Northern Karelia" in connection with "my dismissal from the Institute". Nobody ventured to make a definite reply, and S.A. Kashin alone could settle it, seemingly, positively. There is a series of other disagreeable stresses. The question of the defense of my thesis is postponed by the Institute administration till autumn; therefore I don't send you my work "The Pegmatites of Northern Karelia" for the moment.

Yours faithfully A. Labuntsov

15/VII 1938

RAS Archive. F. 518. Op. 3. D. 916. L. 11.

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Dear Vladimir Ivanovich!

Concerning the discovery and studying the Khibiny Tundras apatite deposits I can tell you the following: Before 1923, apatite pieces have been found more than once in taluses of various locations during field prospecting; a few veinlets up to 10 cm thick were known as well. All those finds were of mineralogical and geochemical interest only.

In 1923, I together with E.E. Kostyleva, E.M. Bonshtedt, and B.M. Kupletsky, during our passing the Mount Rasvumchorr plateau, in the rain, found large pieces of the apatite-nepheline rock; some days later I made a special climb onto Rasvumchorr and could trace significant primary outcrops of this rock on the plateau steep in the 2nd Western Rasvumchorr Cirque. 1) At that moment, this find was not attached with great importance and even the possibility itself of such type of rock to exist was contravened. This find was only mentioned in the general review and in the report about field trip in 1923 as one in the list of various mineral deposits. 2) As far as the field mineralogical and petrographic investigation of the Khibiny Tundras was considered as finished, generally, in 1923, no further works were undertaken in 1924 and 1925. In the summer 1925, while working in North. Karelia, I made a short trip to the Khibiny Tundras to take, by the Mineral. Museum and Mineral Exchange Bureau of the Inst. Appl. Miner. order, about 10 puds [160 kg] of the new mineral lovchorrite that I found in 1923 on the Mount Lovchorr. During this trip, I visited the Rasvumchorr Plateau again and, having some tools and a demolitions expert, made a series of strippings of taluses and placers and was lucky to fix the primary outcrops [here the footnote placed in the letter end] to enlarge upon the area over 10000 m^2.

In January of 1926, in spite of the critical relation to the existence possibility of such a rock and its bedding upon a vast area, I gave a special talk in the Institute of the North, where I had to defend the reality of the apatite deposit. After fruitless attempts to contest money allotment in the Academy of Sciences and Geol. Committee, I managed, with A.E. Fersman's aid, to get the consent from the Colonization Department of Murmansk (now Kirov) Railway to finance further investigations and searches. However, instead of promised 8000 roubles, the Coloniz. Dep. could only allot 1000 roubles of which only 700 roubles were allotted by the Inst. of the North for works, both in Karelia and Khibiny. In the second half of summer I worked in Khibiny together with A.A. Saukov, a student, and Lepishin, a borer and a demolitions expert. As a result of works of 1926, the outcrop area of apatite rock on the Mount Rasvumchorr was broadened up to 34000 m^2 and bedding depth was traced up to over 20 m. Besides, two new deposits were found: one was on the Rasvumchorr Apatitovyi Branch and the other, the larger one, was on the Kukisvumchorr Mountain. The results of these successful works were reported in a letter to acad. A.E. Fersman; a special session was held in the Inst. of the North, and the Commission, which included R.L. Samoilovich, D.I. Shcherbakov and P.A. Borisov, went to Khibiny; unfortunately, they could not examine all the deposits in detail because of the first snowfall at the beginning of September, so they only visited the Mount Rasvumchorr and could stay there not longer than half an hour.

My talk about apatites in the Mineralogical Museum of the Academy of Sciences on 14th of October 1926 in your presence, as you remember, arose a great interest, though, but raised a doubt of many geologists both in the ore reserves quality that I indicated and, generally, possibility to organize mining beyond the Arctic Circle. Despite this, we were able, with the aid of acad. A.E. Fersman and Coloniz. Dep., to make analyses and investigations of benefication of the mined apatite rock; the results of benefication in the Mekhanobr and, especially, flotation in the "Humboldt" Company, Germany, gave good results.

Despite the Khibiny Apatite popularization in a series of magazines and the acad. A.E. Fersman's support, the question of organization of greater prospecting works and technologic tests that I raised at the beginning of 1927 got a favorable decision neither in the Geol. Committee nor in other agencies; nobody believed in this, and Coloniz. Department of the Murmansk Railways alone promised to give 8000 roubles; however, it could only allot 1000 roubles at the beginning of summer which I cashed through the Institute of the North. In 1927, this money let me and three students, Solovyev, Ryabov and Rozhentsev, work for 11/2 month. The large Kukisvumchorr Deposit, which was found in 1926, was surveyed in detail; a deposit was found on the Mount Yukspor as well as the new Western stripe (narrow) of deposits on Poachvumchorr. The apatite rock reserves were then estimated by me already as tens of millions tons. The Kukisvumchorr Deposit was the largest, richest in the apatite content and most accessible for exploitation. Generally, the results of the year 1927 were so *evident that no doubt was left in the great industrial value of the deposits. Nevertheless, it was not possible in 1928 to obtain money for industrial exploration and ore mining for the factory tests, and, again, the Coloniz. Department alone promised 8000 roubles instead of the necessary 200000. These 8000 were allotted by the Coloniz. Department for the Inst. of the North. At the beginning of 1928, the Acad. of Sciences sent me to the Pamirs as the head of the Mineralogical crew of the Soviet-Germany expedition and then to Afghanistan; as to Khibiny, the geologist V.I. Vlodavets, an Inst. of the North worker, was ordered there instead of me. The V.I. Vlodavets' field works and detailed testing fully confirmed my data on the ore reserves and high quality. However, these works were insufficient for industrial exploration and construction of a mine. After a series of reports in Moscow and Leningrad, acad. A.E. Fersman managed to gain recognition of great industrial significance of apatites. In 1929, the "Apatite and Nepheline Commission" was established at Leningr. District Executive Committee where the workers of Acad. of Sciences, Geol. Committee, Inst. of Fertilizers, GIPKh [State Institute of Applied Chemistry], Mekhanobr and other research institutes were invited. 250.000 roubles were allotted and industrial prospecting was organized as well as a series of technologic works. I took most active part in this work. At the beginning of October 1929, after the reports in the Commt. for Chemization and Gosplan, the decision was taken to establish the state trust "Apatit". I was invited (holding this job with the work in the Acad. of Sciences) to organize and direct the trust's prospecting section. In the "Apatit" I worked until 1933; then, having created a mighty enough section prospecting not only apatites but also other minerals of the Kola Peninsula, including pyrrhotite, sphene ores, and molybdenite that were found by me, I remained the trust consultant since 1933 till autumn of 1934 (untill the movement to Moscow). — This is, in short, the history of my participation in the apatite business. — For my scientific works in the study of the Khibiny Tundras, the Russ. Mineralogical Society awarded me with the "Honorary Comment equivalent to the gold medal". Appendix 1. My participation and role in the discovery of the Khibiny Apatites have been marked by the Gosplan. Appendix No. 2. For the work energy and discovery of the apatite deposits I was awarded by Leningr. District Council of Nat. Economy a commendation and a bonus. Appen. No. 3. You will realize, Vladimir Ivanovich, how is it hurtful and offensive for me that the accusation is now circulating of hardly not sabotage by mine at the apatite discovery, and I had to suffer both in getting a scientific degree and in my work in the Institute of Geol. Sciences; whereas all the circumstances of discovery, study and development of the apatite business could be checked easily. With the tr. "Apatit" former administrator Kondrikov, I had no commerce since 1934 (June), and he himself was already not in the "Apatit" but in the "Kolstroi". I enclose for you a copy of the "Karelo-Murmanskii Krai" magazine, 1929, No. 11—12, with my article "How Khibiny Apatite Was Discovered" and the book by acad. A.E. Fersman "The Apatite-Nepheline Problem of the Khibiny Tundras". Materials for the Chemization of the USSR Nat. Economy. 1929, where A.E. Fersman represents, in general terms, the gradual development of the Khibiny apatite investigation. About the discovery itself of apatite is written by A.E. Fersman more detailed in the "Khimiya i Khozyastvo" magazine No. 2—3, 1929 — "The Lessons of A Discovery", but I could not obtain this issue to the moment.*

I wrote the following articles on apatites in 1926—1929

Apatite Deposits on the Kola Peninsula.

Osved. Byull. Akad. Nauk, 1926. No 8.

The Apatite Deposits in the Khibiny Tundras and the Possibility of Their Practical Usage. Gorn. Zhurn. 1926, No. 12.

The Report on the Business Trip into the Khibiny Tundras in the Summer of 1926.

Doklady Akad. Nauk SSSR. 1927. p.3.

Natural Resources of Khibiny Tundras and Kola Peninsula.

"Karelo-Murmanskii krai" 1927. No 5—6.

The Studies in the Khibiny Tundras in 1927.

Osvedom. Byull. Akad. Nauk 1927. No 19.

Khibiny Apatites. "Karelo-Murm. Krai" 1927. No 10—11.

On the Usage of Khibiny Apatite in Our Phosphate Industry. Gorn. Zhurn. 1928. No 1.

And a series of articles in the Geolkom Publ., "Apatity" collections of scientific papers and other magazines of 1929 and ensuing years.

Yours faithfully A. Labuntsov

15/VII 1938.

[1] — "Khibiny and Lovozero Tundras", a monograph. Vol. I Routs. P. 150. [2] — Ibidem, p. 24.

RAS Archive. F. 518. Op. 3. D. 916. L. 8—10.

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Dear Vladimir Ivanovich!

Here is the information concerning my dismissal from the Inst. of Geologic. Sciences and *awarding a scientific degree. All the mentioned information and data can be confirmed with according documents or attested copies. I do not mention the circumstances of my repudation of the combined job at the Kola Base of the Acad. of Sciences as, according the statement of S.D. Popov, the [Communist] Party organizer at the Inst. of Geologic. Sciences, and S.A. Kashin, the vice director of the Institute, the dealing with the Kola Base did not matter in my dismissal from the Institute. Though, this possibly should be included, too, for the purpose of the general analysis of the entire matter since the Kola Base Scientific secretary T.T. Baryshev (formerly member of the Acad. of Sciences personnel department), when he joined the Kola Base stuff as the Scientific secretary, immediately took a spiteful position towards me as well as the majority of the Base old workers and got intention of their amotion.*

I enclose my statement of 22/II of this year to the Committee of Bases that protests against my dismissal from the Base. I received no reply or decision for this statement and met no desire for the part of the Scientific Secretary P.I. Kolesnikov to clear up the mess; as to my ensuing appeals, I only got a reply that comr. T.T. Baryshev considered correct the formulation of my dismissal; when I said that I would contest this, P.I. Kolesnikov answered that "this is your right; however, you should have in mind that we will deal shortly with you if anything crops up". I know that after this a dishonoring me message was sent in May or June to the Inst. of Geologic. Sciences; its exact contents is unknown for me.

I beg of you, Vladimir Ivanovich, for helping me in explanation of all these complicated questions that evidently root mostly, on the one hand, in the desire to get rid of a worker with bad past (a kind of insurance), though this should not be because yet in 1922, when I was entering the Acad. of Sciences, the Security bodies GPU which knew my past in detail – my military service in the Kolchak's Corps and voluntary surrender in Krasnoyarsk – confirmed that there was no obstacle for my job in the Acad. of Sciences from the Security's side. Besides, the same was confirmed by the Securities in October 1925, when they called me and put forward to ask "to strike off the register of former White officers, since, according to their information, I work honestly and conscientiously and there are good reports of me". On 12th of September 1925 I was stricken off the register of former White officers. After this, I twice underwent the purge and was allowed to work and occupy the same position.

Therefore, it was confirmed every time that my "past" cannot be an obstacle for my job in the Acad. of Sciences and for limitation or persecution for my past or limitation of my right for the scientific work and getting a scientific degree and title. It seemes to me that with my honest work I'm atoning, to a significant extent, "my past", which I never forgot and try to atone it by the yielded benefit highly appreciating the credit that is rendered me by the access to the work in the USSR Academy of Sciences. What has changed? I do not feel any guilt of mine, I have reeducated myself, I take an active part in the social duty, I have grown in the scientific respect, and nevertheless I'm apparently not taken into confidence or, may be, this is an excess of caution which is explicable and well understood by me in view of those malicious sabotages that were elicited in the recent years. On the other hand, a certain point of my problem is, as well, the attitude towards me of some colleagues in the former Lomonosov Inst., in connection with their misunderstanding with acad. A.E. Fersman whose disciple I am. A series of cases made me sure that when I was charged by the A.E. Fersman or encouraged by A.E. Fersman's initiative or idea, I met no support, often an unfriendly relation, and for the part of the former vice-director I.F. Stashinsky [possibly I.K. Stashinsky, see Vernadsky, 2006$_1$, p. 71 and 2006$_2$, p. 111] even a hostile attitude. I hope very much that, thanks to a support of yours and higher Party officials, I will be able to rehabilitate myself in order to get a possibility to continue my scientific work and get the candidate scientific degree.

Faithfully yours and thankful for your countenance and assistance

A. Labuntsov

21/VII 1938

RAS Archive. F. 518. Op. 3. D. 916. L. 12–14.

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Dear Vladimir Ivanivich!

Acad. G.M. Krzhizhanovsky received me, took great interest in the apatite matter, and asked me about the Alexander Evgenyevich's role; did not hear me out and directed me with a note to the comrade Ivanov, the head of the staff department, with the request: to investigate thoroughly my problem and take down in a shorthand my report of apatites. The latter was done: comr. Ivanov inquired me in detail about my past and my job in the Inst. As to the job, he offered me to come to Stalinabad as the Scientific Secretary of the Ac. of Sciences Base, which I refused; then he said that he would negotiate in the Inst. of Geol. Sciences and *would call me about the job in general. As to the Acad. of Sciences support [in] the Institute in soliciting to consider my affair by the Higher Attestation Commission, he stated categorically that the Acad. of Sciences would do nothing and I have myself to appeal there everything having indicated that the materials are in the Acad. of Sciences Staff Department. After this, the statement for G.M. Krzhizhanovsky was left by me with the detailed summary of the problem and requests. However, there is nothing up to now since V.M. Kryzhanovsky [likely G.M. Krzhizhanovsky, see Vernadsky, 2006$_1$, p. 81] is on the Supr. Soviet session.*

Faithfully yours A. Labuntsov

11/VIII 1938.

P.S. Pray to return 2 books that I took in the library and the "Karelo-Murmanskii Krai" magazine.

RAS Archive. F. 518. Op. 3. D. 916. L. 15.

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Dear Vladimir Ivanovich!

In addition to available materials, I send you the documents on "the awarding me "the scientific degree of candidate of sciences". With these documents I was in the "VAK" (Higher Attestation Commission for Academic Degrees and Titles under the Committee on Higher School and Scientific Research Institutions); — the scientific secretary is now absent, I spoke with the secretary assistant who admonished me that there is a lot of obscurities and term and rule violations.

1) It is not clear for whatever reason the Institute submission and the decision of the Qualification Commission of 22/XII 1935 were not considered and not confirmed by the Presidium of the Acad. of Sciences during the year 1936 and up to 15/V 1937.

2) The resolution of 15/V 1937 of the Presidium of the Acad. of Sciences is, virtually, a refusal to confirm the Qualification Commission resolution of 22/XII 1935, but refusal with no reasoning: "proposition for the Institute to organize the defense [thesis presentation] and to solve, at the defense, the question of awarding the candidate either doctor degree" — is wrong, because there are different demands and defense conditions for candidate and doctor.

3) It cannot be understood why the Institute, with the Presidium of the Acad. of Sciences permission, did not use its right to confirm me in the candidate degree (at the Inst. Scientific Council) without the thesis defense before 1/VII 1938 (according to the "Directive instruction of the Committee on Higher School confirmed by the Higher Attestation Commission 29/I 1938 § 27a.)

4) The reply of A.L. Bonkvitser, the OMEN [Section of mathematic and natural sciences] Scientific Secretary, though does not answer to the point of the matter that was taken up with the presidium of the Acad. of Sciences by the Institute, however correctly, from the official point of view, explains my situation, as the state in the capacity of the senior scientific researcher even during 8 years does not give the right to the scientific title of senior scientific researcher, which, according to the "Instruction on Scientific degrees and titles" of 20/III 1937, should be confirmed by the VAK for a person who has the "candidate of science" degree, and for those who does not — could be, by the Institute presentation, confirmed by the presidium of the Acad. of Sciences before 1/VII 1938 (on the ground of the Directive Decree of 29/I 1938). It is odd, why the Institute did not do this? But now, officially, not having the confirmed scientific title of "Senior Scientific Researcher", I have no right to defend both doctoral and candidate thesis without examinations.

As the way out of the situation, I was proposed in the VAK to do as follows:

1) The Institute's appeal to the VAK with the request to confirm me in the title of "senior scientific researcher" as an exceptional case with the reasoning of the passed term (until 1/VII 1938).

2) Also appeal to the VAK with the request to consider, as an exceptional case, the question of awarding the candidate title without thesis defense of as this question was raised before 1/I 1936; preferably, the presid. of the Acad. of Sciences would support the Institute presentation (since Presid. made [some — striken out] its resolution on this in 1937, 15/V); as soon as this question was solved again positively, but the term 1/VII 1938 was missed.

3) For the defense then, by me, the doctoral thesis, it is necessary that the Institute asks the VAK's permission in the case I am not an Institute worker.

Therefore, some possibilities seem to be available to get [title — striken out] candidate degree and [degree — stricken out] title of senior scientific researcher, if the Institute would "desire" this and the Acad. of Sciences presid. would support the Institute's presentation. However, I do not know if all this could be done as the vice-director A.S. Kashin went to the Urals for 2 months, and would the Institute administration undertake this without him?

I will speak today with the vice-director I.F. Grigoryev.

Yours faithfully A. Labuntsov

P.S. The vice-director of the Institute I.F. Grigoryev avowed the Institute's error and is willing to raise the questions of awarding me: scientific title of senior scientific researcher and scientific degree of candidate of science without thesis defense.

A. Labuntsov

[No date; probably 1939]

RAS Archive. F. 518. Op. 3. D. 916. L. 16–17.

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A.N. Labuntsov

I have been working at the Acad. of Sciences as a scientific researcher since 1922, besides I have been occupying senior scientific researcher position since October 1930.

13 XII 1935 Qualification Commission of the Acad. of Sciences on Geol. Sciences awarded me the scientific degree "candidate of sciences", which should be confirmed by the Acad. of Sciences Presidium. However, the Acad. of Sciences staff department, under the influence of Stashinsky, the Lomonosov Institute vice-director, consistently delayed and did not present this question for the confirmation by the Acad. of Sciences Presidium. No sooner than May 1937 (when the confirmation term was already missed) this question was presented to the Acad. of Sciences presidium; besides, academician Gorbunov (apparently based on the Stashinsky's reports through the staff department) probably negatively but not positively elucidated this question of the discovery by me of the Khibiny apatites, and I was named "the Kolchak's adjutant". In view of all this, the Acad. of Sciences Presidium proposed the Lomonosov Institute to clear out my role in the discovery of the Khibiny apatites and promotion the problem of their use and, correspondingly, to organize my thesis defense where to solve the question of awarding me the candidate or... doctor scientific degree! The "information" of me presented by academician Gorbunov became known, still more distorted at the oral reproduction, in the Lomonosov Institute and the Acad. of Sciences Kola Base, where I worked in summer 1937 (doing two jobs at a time), and this created very difficult work conditions. At the end of 1937, because of obstruction for work for the part of the Kola Base vice-director comr. Baryshev, I was impelled to refuse to work at the Kola Base, and when I tried to reveal to the Base director, acad. Fersman, as well as to the Base Committee, shortcomings of the comr. Baryshev's "guidance". The latter began to lay the blame on me, and after two months since my voluntary termination, issued a new order of my dismissal [from work – striken out] for the "work derange". My appeals to the Base Committee lead nowhere. Nothing was undertaken in 1937 in the Lomonosov Institute concerning my scientific degree, and the relation to me of the former vice-director Stashinsky deteriorated still more at the same time, and, under his influence, the relation [for his part – striken out] to me changed also for the part of comr. Kashin, the Institute former Party organizer, and comr. Malyshev, the Geogroup former secretary. Moreover, the relationship of acad. Fersman (whose disciple I am) with these persons became strained uncommonly and acad. Fersman practically stopped his participation in the Institute management. Only due to my honest and persistent job and support of comr. Popov, the Party committee secretary, at the end of 1937 and at the beginning of 1938, I could remain in the Institute during the amalgamation of geological institutes of the Academy of Sciences. However, the problem of the scientific degree was left unsolved. In April 1938, the wholesome for me resolution was announced of the Committee on Higher School and Scientific Research Institutions. Accoding this resolution the right was given to the Geologic. Institute of the Acad. of Sciences to settle, until 1/VII 1938 [the date is double underlined], the questions of scientific degrees for the time gone, if these questions arose before 1936 and were not still solved. However, despite of this and my statements, the problem of the scientific degree remained unsolved, and on 27th of June 1938 I was suddenly discharged "on grounds of staff reduction", and I was refused not only to work temporarily or in expedition at least but even the possibility was not given to finish (which needed about a month) the work that I did on "The Mineralogy of the USSR". My dismissal, inexplicable both for me and many others, created an impression that there was some special cause for this dismissal, so the latter became to be considered as "a displacement", this could be seen from the fact that everyone "was afraid" to bother about me; and even the printing of my work "The Pegmatites of Northern Karelia" was delayed in the Acad. of Sciences Publishing House. [Nevertheless – striken out] Only for the party of the Party secretary comr. Popov alone I met support, and thanks to him there were a good comment and a neutral characterization of my work, and the scientific degree question was promoted. At his insistence, on 27th of June the sitting of the bureau of the scientific workers' section was held, and there the positive *resolution to award me the candidate of sciences degree was accepted. However, in spite of certain instruction of the Higher School Committee, the Institute administration did not solve the question of confirming the degree itself, but appealed on 28th of June to the Acad. of Sciences presidium with the request to confirm me in the candidate degree having indicated: "that I am a highly qualified specialist — mineralogist who always can combine the questions of science and practice, and also my recent work "The Pegmatites of North. Karelia and Their Minerals" exceeds the demands to the candidate thesis. The entire folder of the documents on my scientific degree was received on 28th of June 1938 in the Acad. of Sciences secretariat; however, it was impeded by the Personnel Department and not admitted to the Acad. of Sciences presidium sitting until 1/VII. Thus the term 1/VII was missed; so the documents were returned, on 12th of July, to the Geol. Institute. My appeal to acad. Komarov at the beginning of July 1938 on the question of reconsideration of my dismissal from the Geol. Institute or the possibility of my job in the SOPS [Council for the Study of Productive Forces], where I was at first invited, led nowhere despite good recommendations of mine as well as acad. Komarov's (who was going to leave for the South on vacation) resolution; according to his secretary's report, "the attempt to come to an agreement with the Personnel Department on the question of reconsideration failed", and in eight days the SOPS denied me employment. My appeal to acad. Krzhizhanovsky, with your letter, led nowhere too. At the suggestion of acad. Krzhyzhanovsky [G.M. Krzhizhanovsky] I presented a note that enlightened the question of discovery of the Khibiny apatites; however, the both questions of reemployment and of the scientific degree, the latter in spite of the Geol. Institute's repeated solicitation, were nowhere considered but passed to the Personnel Department to be settled. I received neither reply nor resolution for my statement, except of (after numerous appeals) oral "explanation" of comr. Ivanov, the personnel department head assistant, that "I bother acad. Krzhizhanovsky in vain, that the question of dismissal is the Institute's business, whereas the question of the degree, as far as the legal term is missed (1/VII), so it can be considered no more in the Academy, just the same, there is no reason to raise it the Higher Attestat. Commission [VAK] (as the Geologic. Institute asks).*

Having lost any hope to continue my work in the Acad. of Sciences, I 1) presented on 22nd of August a statement on the question of the degree in the Higher Attestat. Commission concerning which you, Vladimir Ivanovich, wrote then to Kaftanov, while 2) began to look for a job myself. — I had a temporary job in the Acad. of Sciences Publishing House, but soon I was given to understand that the question and the vagueness of my dismissal from the Geol. Inst. arouse excessive talks, and my job continuation in the Publishing House is "inconvenient".

As I raised yet at the beginning of 1937 the question of necessity to search diamonds, resting upon the possibility to use the newest methods (luminescence and fat benefication), which I presented a message in the Lomonosov Institute about. In 1938 "Zolotorazvedka" trust was engaged in this problem, so I related to the Trust in September 1938 and got an offer to work on diamonds. On 27th of September, I was employed in the "Zolotorazvedka" Trust and, at its suggestion, urgently left for the Urals. I replaced there the head of the diamond party, who turned sick, and worked for two months having given a boost to all the works and finishing them (with finding diamonds) as well as fulfilling also a series of additional jobs. On December 1st, 1938 I returned to Moscow and started the cameral treatment of materials. To the end of December I put together the estimating reports of the summer work, which were tested by the trust's production and planning departments, on which ground, in the Trust document, the work was acknowledged to be completed up to 102% with about 10% saving of expense. Despite this, I could make sure yet in December 1938 that the Trust Director was reported of "certain information of me" as I was declared a temporary worker, though was promised to give the possibility to finish the material treatment. However, I was dismissed on 8th after the 5th of January 1939, when the former party head returned from the sanatorium after three months of absence (after my protest, the dismissal term was delayed up to 24/I, thanks to which I managed to process, though in a shortened version, the main data for the report, the diamond crystals alone were left not described and not measured; this work is now doing in the Inst. of Geol. Sciences of the Acad. of Sciences by the contract with "Zolotorazvedka"). The protests of the production department head, chief engineer and engineer-dispatcher against my dismissal led nowhere. — As you know, my appeal then in the Geologic. Institute (of Glavgeologiya) to acad. Usov with your letter about my employment, in spite of acad. Usov's consent as well as, seemingly, comr. Kostrov's, the vice-director, then under the influence of the telephone chats with comr.

Malyshev (in Glavgeologiya) and comr. Kashin from the Geol. Inst. (of the Acad. of Sciences) also led to the refusal of employment.

On 2nd of February 1939 I made a complaint to the Committee of Soviet Control concerning unjust dismissal and deny of employment in the Acad. of Sciences and, in connection with this, also in other institutions, and concerning not solving the question of the scientific degree. In the middle of February, the question of job was passed, at the suggestion of Committee of Soviet Contol, to the Office of the Prosecutor of the Soviet Union. During this time, I tried to get job in the Moscow Geological Survey Institute, a contract job for the Ilmeny Reserve, in the Mineralogical Institute of the Acad. of Sciences [Mineralogical Museum] where V.I. Kryzhanovsky would take me with great relish (he said me so); however, the Museum is subordinate of the same comr. Kashin and I could not manage even to get a temporary paid work in the Museum to look over, order and constrict the Khibiny collections — at last my appeal for a job for me on the "Soviet Union Mineralogy" [reference book] to the head of the mineral-geochemical sector of the Geol. Institute D.I. Shcherbakov and N.A. Smolyaninov, though was met compassionately by them and was supported by comr. Popov, the Partkom [Party Committee] secretary, was nevertheless declined categorically by comr. Kashin, the Institute vice-director, who said that "this will be a disguised work in the Institute", so comr. Kashin confirmed once more his opinion of "impossibility" of my job in the Inst., even a temporal one and by contract. In the Commission of Soviet Control (after making any kind of inquiries about my pleas on "job" and "scientific degree") I was informed that on 19 March all my documents were transfered for solving to academician O.Yu. Schmidt in the Acad. of Sciences; the same I was also told in the prosecutor's office, that through acad. Vyshinsky my documents were transfered to acad. O.Yu. Schmidt. In the prosecutor's office, my documents were firstly in the special section (apparently for checking data on my past), and then under general supervision.

Therefore, all materials of my matter are now with acad. O.Yu. Schmidt.

A. Labuntsov 21/III 1939.

I ask you very much, dear Vladimir Ivanovich, to help me and clarify the true situation to O.Yu. Schmidt, and to confirm what you heard on 15th of May 1937 at the sitting of the Presidium of the Acad. of Sciences, when acad. Gorbunov was reporting my matter of the scientific degree, and, also, if you consider this possible, portray that abnormal condition which occurred in the former Lomonosov Institute by the intrigues of Stashinsky, former vice-director, concerning acad. A.E. Fersman as well as, in connection with this, a group of his old colleagues. This situation, properly, owing to Stashinsky, continues to be in the Inst. of Geol. Sci. of the Acad. of Sciences. Having felt deeply for the recent half a year quite undeserved and unfair dismissal of me from the Academy of Sciences, and deprivation of the senior researcher title (that I had for 8 years), as this title is now bond with the scientific degree of candidate of science, and, as well, after the dismissal from the Acad. of Sciences, feeling constantly that some slander follows me, whereupon I am related everywhere with suspicion, and they denies me of employment, <u>I hope that now at last they</u>, from the Academy of Sciences, would examine my question carefully and justly and give me a job in accordance with my avocation. I repeat once more that I always worked honestly and conscientiously, do not know any guilt of mine for the whole period of work under Soviet Power; therefore, it is <u>unjust</u>, after 19 years of honest work — to persecute me and deprive me of the right for job. I ask you, Vladimir Ivanovich, once more, to help me.

Yours faithfully and truly yours
21/III 1939 A. Labuntsov

RAS Archive. F. 518. Op. 5. D. 84. L. 1 — 4.

Copy

RUSSIAN
MINERALOGICAL SOCIETY

Leningrad HONORARY COMMENT
"30" May 1925 named after A.I. Antipov
№ 833

By this comment, equivalent of the gold medal, Russian Mineralogical Society awards ALEXANDER NIKOLAEVICH LABUNTSOV for his studies in crystallography, mineralogy and petrography of the Khibiny Tundras, Kola Peninsula.

SOCIETY DIRECTOR, ACADEMICIAN — A. KARPINSKY
SOCIETY SECRETARY — A. GERASIMOV

the copy is true: Arkhipova (signature)
10/VII — 38 .
Seal: ACADEMY OF SCIENCES OF THE USSR. Institute of Geological Sciences

RAS Archive. F. 518. Op. 3. D. 916. L. 20.

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EXTRACT

From the protocol No. 88 of the Meeting of the RSFSR Gosplan Presidium on 4 October 1929.

"The Gosplan Presidium considers necessary to mark the merits of scientific workers who are engaged in the study of the Khibiny apatites, especially marking the role in this of geologist Labuntsov and academician Fersman as the head of these works.

Chairman R. Levin
Secretary Gorbunova
The copy is true. A. Labuntsov
The copy is true. Petrov
[Handwritten by A.N. Labuntsov]

RAS Archive. F. 518. Op. 3. D. 916. L. 18.

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To comr. LABUNTSOV
copy of copy

PROTOCOL No. 4239-c
of the meeting of the Leningrad District Council of National Economy (LOSNKh)
23 May 1930

<u>HEARD</u>:

About the results of prospecting works in the Khibiny Tundras, Kola Peninsula (Murmansk region), organized by the Leningrad District Sovnarkhoz (LOSNKh), in order of revelation of the apatite deposit capacity, and possibility of apatite use for the industry and export.

<u>RESOLVED</u>:
Noting that:

1/the studies of the Khibiny Tundras, first began by the geolkom [apparently, geologist] Ramsay, were continued highly successfully and widely developed by the expeditions organized by the Academy of Sciences of the USSR in the person of acad. A.E. Fersman;

2/these studies undertaken in extremely difficult conditions of polar region were crowned with brilliant discovery by geologist A.N. LABUNTSOV and, then, V.I. VLODAVETS of the wealthiest apatite and nepheline deposit;

3/the mentioned deposit is now of tremendous industrial value for the whole USSR economy thanks to the energy shown by the LOSNKh in the deed of organization of realization of all the necessary arrangements related to the prospecting the deposit and determination of its capacity.

4/All works that resulted in determination of the deposit capacity as one of largest world sources of phosphorous and other ores have been completed within utterly short terms — less than half a year.

<u>Consider necessary</u>:

a/For the exclusive energy in the mentioned hot job that let us, yet in the current year, organize the export of the apatite rock and start its use at our factories in the production of superphosphate and phosphorus, instead of imported Moroccan phosphorite.

TO AWARD A COMMENDATION TO:
1/ Acad. A.E. Fersman
2/ Geologist A.N. Labuntsov
3/ " V.I. Vlodavets
4/ Member of the scient. inst. of fertilizers eng. M.P. Fiveg
5/ " " " " prof. S.I. Volfkovich
6/ " of Mekhanobr eng. Sheblovinsky.

<u>To award prizes to the following persons</u>:
1/ Acad. A.E. Fersman 3.000 roubles
2/ Geologist A.N. Labuntsov 2.000 roubles
3/ " V.I. Vlodavets 1.000 roubles
4/ Prof. S.I. Volfkovich 1.000 roubles
5/ Eng. M.P. Fiveg 1.000 roubles
6/ eng. N.I. Sheblovinsky 1.000 roubles.

Signed S. Afanasyev.
(Place of Seal) "certified true copy":
On behalf of Chief of secret section LOSNKh (signature)
It is true (Petrov)
This is a true copy: Arkhipova (signature)
10/VII 38. Seal: USSR ACADEMY OF SCIENCES. Institute of Geological Sciences

RAS Archive. F. 518. Op. 3. D. 916. L. 19.

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<u>COPY</u>
<u>26/V-1935.</u>

TO QUALIFICATION COMMISSION
OF GEOLOGICAL GROUP OF
THE ACADEMY OF SCIENCES OF THE USSR.

The scientific specialist of the Lomonosov Institute A.N. LABUNTSOV has the 13 — [the figures are several times recorrected with pencil, in the document of RAS Archive the figures on the margins in brackets handwritten 13 years once more, corrected for 16, however, Labuntsov could not enter the Academy for job earlier than 1921, see Labuntsova, 2001] year period of scientific work in the system of the Academy of Sciences.

The A.N. Labuntsov's scientific work, mostly mineralogical, proceeded in two fields:

1. <u>Scientific theoretical work</u> for the study of minerals and mineralogy of the Soviet Union various regions, connected with wide expeditionary activities. Since 1922, LABUNTSOV participated, year over year, in expeditions to the Sayan and Baikal Area, Khibiny Tundras and other parts of Kola Peninsula, Karelia, Pamirs, Afghanistan, Vaigach Island etc. As the result of materials treatment and more fundamental comprehensive study of minerals, <u>[crossed] 25 [numerals handwritten on mar-</u>

gins] scientific works /see the List of works/ No. 1 [No. 1 is written by ink, blurred] were written by LABUNTSOV, of which the main ones refer to the study of minerals and their deposits: the Botogolsky Golets, Khibiny Tundras where new minerals fersmanite and titanoelnodite [titanoelpidite] were found and researched; North. Karelia that gave the first mineralogical description of the pegmatite veins of this area with their uranium and rare-earth minerals; Western part of Pamirs, Badakhshan Province in Afghanistan; Vaigach Island etc.

For his scientific activity, LABUNTSOV was bestowed in 1925 of the Honorary Comment, equivalent of the gold medal, by Rus. Mineralogical Society for the works on study of the crystallography and mineralogy of the Khibiny Tundras; in 1925, he was elected as a member of the Scientific Council of the State Radium Institute; in 1927, he was the scientific secretary of the 1st All-Union congress of mineralogists.

2. The mineralogical work of applied character, related to industrial exploration of mineral raw materials: the study of the graphite deposit on the Botogolsky Golets, the discovery and study of apatite, molybdenite, pyrrhotite, sphene and other deposits of the Khibiny Tundras, sulfide ores of Vaigach etc. Due to these works, A.N. LABUNTSOV in various times was elected in the Academy of Sciences as a member and consultant of various commissions. In [corrected by pencil] 1929 the Gosplan marked special merits of LABUNTSOV in the discovery and study of the Khibiny apatite deposits, and Lenoblispolkom [Leningrad District Executive Committee] and LOSNKh awarded him the commendation and the money prize. Since 1929 until moving to Moscow, A.N. LABUNTSOV was a consultant of the State Mining-Chemical Trust Apatit by scientific and prospecting questions; in 1931, he was elected, from the Academy of Sciences, a member of the Leningrad Bureau of NIS NKTP; in 1932, he was elected member of the Karelo-Myrmansk Committee at Lenoblispolkom and consultant in mineral raw materials; in 1932 he was elected member of Len. District Committee for Chemiz[ation] of Nat[ional] eco[omy] and the Chairman assistant of the Raw Materials section.

LABUNTSOV wrote [crossed] 36 [the number is written by ink] articles in various scientific, industrial and other journals, collection of scientific articles, handbooks etc., where [where – written by pencil] the questions of industrial importance and utility of mineral raw materials using are discussed /see list of articles/ No. 2 [No. 2 is written by ink].

On the ground of the foresaid, the Scientific Council of the Lomonosov Institute asks to consider the question of awarding the scientific degree of candidate of science to A.N. LABUNTSOV, considering for its own part that by the assemblage of his works he deserves thoroughly this degree without a thesis defense.

Chairman
of Scientific Council LIGEM
academician A.E. Fersman.
Scientific secretary: A.V. Pek.

It is true:
26/V 1935 [the date is written by ink, by A.N. Labuntsov handwriting]

RAS Archive. F. 518. Op. 5. D. 84. L. 7.

***

Draft No. 1
[It is written by A.N. Labuntsov with ink]

LIST
[MAIN – crossed] SCIENTIFIC WORKS
[BY SCIENTIFIC SPECIALIST – crossed]
by senior researcher [insert with ink] of the
LOMONOSOV INSTITUTE of THE USSR
ACADEMY OF SCIENCES –
A.N. LABUNTSOV.

1. Khibiny and Lovozero Tundras /description of traverses/. Acad. A.E. Fersman, Ed. Vol. 1, 1925.

2. In association with E.E. Kostyleva. On the mineralogy of the Botogol Golets. Coll. Materials for study of Russian graphite. Mat. KEPS, 1925, No. 52, p. 93.

3. Natrolite from the Khibiny and Lovozero Tundras. Trudy GMM. 1925, v. V, issue 2.

4. In association with V.I. Kryzhanovsky – The report of a scientific trip to Altai in 1921. DAN. 1926. p. 69.

5. Ilmenite from the Khibiny Tundras. Trudy MM. 1926. Vol. 1 p. 35.

6. On titanium elpidite from Khibiny Tundras and its paragenesis. DAN. 1926. p. 39.

7. Zeolites of Khibiny and Lovozero Tundras. Trudy MM.1927. Vol .II. p. 91.

8. Apatite. – In "Fosfor" ("Phosphorus"), a monograph. Geol. Com. publishing. 1927.

9. Apatite. – In "Nerudnye Iskopaemye" ("Nonmetallic minerals"), Vol. III, KEPS, 1927. p. 491.

10. [Khibiny and Lovozero Tundras. Vol. II] /description of deposits/. Acad. A.E. Fersman, Ed. 1927.

11. For the mineralogy of Northern Karelia. IAN. 1927. P. 609.

12. Fersmanite, new mineral from Khibiny Tundras. DAN. 1929. P. 297.

13. Apatite. — In "Nerudnye Iskopaemye" ("Nonmetallic minerals"), Vol. IV, KEPS, 1929.

14. Geological and mineralogical studies in the Western Pamirs and the Badakhshan Province, Afghanistan, in 1928. Proc. Pamir. Expedition, AN, 1929.

15. The molybdenite deposits in Khibiny Tundras. DAN. 1929. P. 455.

16. Apatite prospecting in the Khibiny Tundras, up to 1929. — In "Khibinskie apatity", Vol.1. Committee of Chemization by Sovnarkom of the USSR, 1930.

17. Geochemical and prospecting investigations in the Takhtarvumchorr area in Khibiny Tundras and other regions of Kola Peninsula in 1930. — In "Khibinskie apatity", Vol. II. Com. Chem. Nat. Econ. VSNKh SSSR, 1932.

18. The mineral resources of the Khibiny Tundras and their practical importance. A guide to the Khibiny Tundras. 2nd edition. Akad. Nauk. 1932.

19. The works of the Central geochemical party of the Kola Expedition of the Academy of Scienties. 1931. — In Materials for petrography and geochemistry of the Kola Peninsula, part. II, p. 5. SOPS Akad. Nauk. 1933.

20. Pyrrhotite from the Khibiny Tundras. — In "Rare elements and pyrrhotites from Khibiny". Leningrad, NKTP, p. 180.

21. Mineralogical survey in the Khibiny Tundras central part. — In "Khibinskie apatity". Vol. VI. NKTP, 1933.

22. Apatite and its world deposits. — In "Khibinskie apatity" Vol. VII. NKTP, 1934.

23. The molybdenite deposits in the Khibiny Tundras. Proc. Kola Base of the Academy of Sciences, 1935.

24. On the age of uraninite and monazite from pegmatite veins of North. Karelia. Doklady Ak. Nauk. 1935 [written by ink]. No. 9, 646.

25. "Apatit" — Encyclopedia. "Nemetallicheskie iskopaemye SSSR" (Nonmetallic ores of the USSR). Akad. Nauk, 1936.

26. The minerals of the Khibiny Tundras. Collective work. A monograph. In English 1937 and in Russian 1937. (22 minerals are described).

ALabuntsov (signature) A. Labuntsov.

27. "The pegmatite veins of North. Karelia and their minerals". In print. "Pegmatity Soyuza". Vol. II. 1938.

28. "Anatase". <u>Prepared for printing</u> in "Mineraly SSSR" (Minerals of the USSR). — 1938.

29. "Brookite" — <u>Prepared for printing</u> in "Mineraly SSSR" — 1938.

30. "Rutile" — <u>Prepared for printing</u> in "Mineraly SSSR". — 1938.

[To the left of Nos. 25, 26 and, probably, 27 (the edge of the paper sheet is failed) there are checks written by ink. The entries beginning from No. 26 were also made by A.N. Labuntsov with ink and, apparently, later, as the text of No. 26 was over the Labuntsov's signature.]

RAS Archive. F. 518. Op. 5. D. 84. L. 9.

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<u>No. 2</u>
[the number is written with ink,
A.N. Labuntsov's handwriting]

<u>LIST</u>
<u>OF ARTICLES IN VARIOUS SCIENTIFIC, INDUSTRIAL AND OTHER JOURNALS, COLLECTED BOOKS, HANDBOOKS etc. BY A.N. LABUNTSOV</u>

1. The results of the expedition in the Eastern Sayan. DAN. 1924, p. 192.

2. A description of the Aliber Mine. Materials for studying Russian graphite. Mat. KEPS 1925, No. 52, p. 38.

3. The deposits of uranium compounds in the Karelian Republic. DAN 1925, p. 113.

4. In association with A.E. Fersman — The report of scientific trip to the uranium deposits of Karelia. DAN — 1925, p. 147.

5. The deposits of uraninite/pitchblende/ in North. Karelia. Gornyi Zhurnal, 1925, No. 10, p. 846.

6. The results of the errand to the Khibiny Tundras in summer 1925. DAN, 1926, p. 15.

7. The Mineralogical museum of the Academy of Sciences — "Priroda" (Nature). 1926. Nos. 1—2. p. 119.

8. The apatite deposits in the Khibiny Tundras and the possibility of their practical use. Gorn. zhurn. 1926. No. 12, p. 796.

9. The apatite deposits of the Khibiny Tundras. Osvedomit. Byulleten' Osob. Komit. po issl. soyuzn. i avt. resp. /OKISAR/. 1926. No. 8.

10. The report of the errand to the Khibiny Tundras in summer 1926. DAN. 1927. p. 5

11. The mineral resources of the Khibiny Tundras, Kola Peninsula. "Karelo-Murmanskii Krai" 1927. Nos. 5—7, p. 7.

12. The Mineralogical Museum. Nauchnye uchrezhdeniya Akademii Nauk (The scientific institutions of the Academy of Sciences), 1917—27. p. 54

13. The pegmatite veins of North. Karelia. — Osvedom.Byullet.OKISAR. 1927. Nos. 15—16.

14. The mineralogical studies in Khibiny Tundras in 1927. Osvedom. Byullet. "OKISAR" 1927. No. 19.

15. The Khibiny apatite. "Karelo-Murmanskii Krai" 1927. No. 11, p. 34.

16. On the use of Khibiny apatite in our phosphate industry. Gornyi Zhurnal. 1928. No. 1. p. 32.

17. The conference on the feldspar raw materials, 5–7 Dec.1927. Gornyi Zhurnal. 1927. No. 2. p. 126.

18. Materials of the second conference on the feldspar. I.I. Ginzburg and A.N. Labuntsov, Eds. Mat.KEPS, 1927. No. 71.

19. First All-Union congress of mineralogists in 1927. A Repot about scientific and technical works. Republ. Scien. Chemic. Techn. Publish. Hause, issue XXIII. 1928.

20. On the zirconium industry. "Mineral'noe syr'e" (Mineral raw materials). 1929. No. 3.

21. The works of the Pamir Expedition mineralogical party. Osvedom.byulleten' KEI. 1929. No. 7.

22. The journey to Afghanistan at the end of 1928. Priroda 1929. No. 4, p. 346.

23. The mineralogical trip to North. Karelia. Osved.byul. KEI 1929. No. 20.

24. The prospecting works in the Khibiny Tundras. Osved.byullet. KEI 1929. No. 21.

25. The Khibiny nepheline-apatite deposits. zhur. "Khochu vse znat'" ("To know everything" magazine) 1929. No. 10.

26. How the Khibiny apatite was discovered "Karelo-Murm. Krai" 1930. No. 11–12.

27. The mineral resources of the Khibiny Tundras. Gornyi Zhurnal 1930. Nos. 7–8.

28. The materials on the apatite-nepheline deposits of Khibiny Tundras as the base of raw materials for producing phosphorous fertilizers and the comparison of apatite-nepheline rock with the phosphorites of the Union. The manuscript in materials for the technical and economic feasibility of investigation, mining and processing the Khibiny apatite-nepheline rock. Leningrad section of Khimtrest Vsekhimprom. July 1930.

29. The mineral resources of the Khibiny Tundras and their use in industry. A Guide to the Khibiny Tundras. Izd. AN 1931.

30. The routes of the Khibinogorsk station. Nefelin, Apatitovyi mine, Loparskii pass. Umbozero. A Guide to the Khibiny Tundras. Izd. AN 1931.

31. "Apatite". Collected book of raw and combustive resources of Leningrad district. Izd. Lenkhimsektor. 1932. p. 1.

32. Titanite /sphene/. Ibidem p. 97.

33. Titanomagnetite. Ibidem p. 99.

34. Titanium raw materials. Proc. of the 1st All-Union conference of Paint and coatings industry. 1932.

35. The journey to the Kildin Island. Vestn.Akad.Nauk. Special No. 1932.

36. The Arctic outpost of the socialist construction /to five years developing of the Kola Peninsula resources/. Zhurn. Nauka i Tekhnika ("Science and Technics" magazine) 1934. No. 23.

Labuntsov (signature) A. Labuntsov.

RAS Archive. F. 518. Op. 5. D. 84. L. 8.

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EXTRACT FROM THE PROTOCOL OF THE QUALIFICATION COMMISSION ON GEOLOGICAL SCIENCES OF THE USSR ACADEMY OF SCIENCES

22/XII–35.

There were the chairman acad. A.A. BORISYAK; commission member acad. A.D. Arkhangelsky and scientific secretary P.I. LUNIN
<u>HEARD</u>:

Awarding scientific degrees without thesis presentation in geological sciences.
RESOLVED:

Award a scientific degree of candidate of geological sciences without thesis presentation to the following scientists:

45. LABUNTSOV A.N. Award the scientific degree of candidate of geological sciences in the geochemistry section without thesis presentation, on the basis of all his works.

signature, seal. Chairman of Qualification
Commission on geol. sciences of the USSR
Academy of Sciences
(ac.Borisyak)
member of commission: acad. Arkhangelsky
Scientific Secretary (Lunin)
true (signature)
certified copy: respons. offic. on staff
(signature)

Seal: USSR ACADEMY OF SCIENCES. Institute of Geological Sciences

RAS Archive. F. 518. Op. 5. D. 84. L. 6.

***

Labuntsov [signed with pencil]

HIGHER ATTESTATION COMMISSION FOR ACADEMIC DEGREES AND TITLES OF THE ALL-UNION COMMITTEE ON HIGHER SCHOOL UNDER THE COUNCIL OF PEOPLE'S COMMISSARS (SNK) OF THE USSR

<u>Moscow, Kuibyshev str. 21 Telegraphic address: Moskva, KOMSHKOL.</u>

EXTRACT

from protocol <u>No. 4 of "29" January 1939.</u>

(The original resides in the Higher Attestation Commission)
<u>HEARD</u>:

§ 73. The solicitation of the Moscow Institute of Geological sciences of the USSR

Academy of Sciences for revision of resolution concerning LABUNTSOV A.N.

By the resolution of the Presidium of the USSR Academy of Sciences of 15/V-37 the solicitation for confirmation of LABUNTSOV Alexander Nikolaevich in the scientific degree of candidate of geological-mineralogical sciences without thesis presentation was denied.

RESOLVED:

Confirm the resolution of the Presidium of the USSR Academy of Sciences of 15/V-37.

CHAIRMAN OF THE HIGHER ATTESTATION COMMISSION
FOR ACADEMIC DEGREES AND TITLES — S. Kaftanov
SCIENTIFIC SECRETARY — A. Platonov
True: Scientific Secretary of the Higher Attestation Commission
(signature)
/A. Platonov/

Seal: All-Union Committee on Higher School under the SNK of the USSR
27 February 1939

RAS Archive. F. 518. Op. 5. D. 84. L. 5.

***

In conclusion, the authors and the directorate of Fersman Mineralogical Museum thank the RAS Archive, its director Vitaly Yuryevich Afiani, and the head of the reference room of RAS Archive Irina Georgievna Tarakanova for their assistance in preparing of the A.N. Labuntsov's letters to academician V.I. Vernadsky for publication. We also appreciate Vladislav Pavlovich Volkov, who has found these letters in RAS Archive.

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Kornetova V.A. In memoriam of Alexander Nikolaevich Labuntsov (To 100 years from his birthday) // Novye dannye o mineralakh. **1986**. Issue 33. P. 158—162. (in Russian).

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Makarova E.I. The story from the archive documents: Report about summer work in the Khibiny Tundras by the scientific specialist of the Lomonosov Institute of the Academy of Sciences (LIGEM) A.N. Labuntsov, who worked here in 1934 accoding to the the Khibiny Research Mining Station of the Academy of Sciences (KhIGS) regulation // Tietta. **2009**. No 3(9). P. 81—85. (in Russian)

Shcherbina V.V., Bonshtedt-Kupletskaya E.M. Alexander Nikolaevich Labuntsov // ZVMO. **1963**. Part XCII. Issue 6. P. 751—752. (in Russian).

Spachenko A.K. Alexander Nikolaevich Labuntsov — the Khibiny legend // Tietta. **2009**. No 3(9). P. 75—80. (in Russian).

Vernadsky V.I. The Diaries, 1935—1941 / The Library of academician V.I. Vernadsky's Works / Complier V.P. Volkov. M.: Nauka, **2006**$_1$. Book 1: 1935—1938. 444 p. (in Russian).

Vernadsky V.I. The Diaries, 1935—1941 / The Library of academician V.I. Vernadsky's Works / Complier V.P. Volkov. M.: Nauka, **2006**$_2$. Book 2: 1939—1941. 295 p. (in Russian).

Mineralogical Notes

INTERGROWTH TWINS OF MAGNETITE IN ORES OF KURZHUNKUL DEPOSIT, KAZAKHSTAN

Vladimir A. Popov, Sergey G. Epanchintsev
Institute of Mineralogy, UB of RAS, Miass, popov@mineralogy.ru

Rare intergrowth twin crystals of magnetite from Kurzhunkul deposit were described along with composition of magnetite and chlorite in zoned botryoidal aggregate.
1 table, 1 figure, 3 references.

Keywords: rare intergrowth twin crystals of magnetite.

Magnetite twin crystals on {111} usually occur as a flattened contact twins. Intergrowth twins are rarely found in natural magnetite (Minerals, 1967). The find of a druse of magnetite interpenetration twins in the open pit of Kurzhunkul deposit can be considered as a unique discovery.

Kurzhunkul deposit is located 120 km South-Southwest from Kustonay in the limits of Tyumen'-Kustonay paleo rift valley in Valerianovsky iron ore belt (Ovchinnikov, 1998). Iron ore forms stockworks composed of complex veins and veinlets hosted in Visean volcanics and limestone. Ores have variable structures including brecciated. Breccia cement is formed by fine grained botryoidal magnetite (Dymkin, Permyakov, 1984).

The found hand specimens have reniform chlorite-magnetite aggregate with terminations of medium-coarse grained magnetite and chlorite crystal druses on the top of fine pyrite-magnetite aggregates. Some parts of the druse were formed with magnetite crystals with well developed faces of rhomb dodecahedron {110} and small ones of octahedron {111}. Another parts of the druse were composed of twin magnetite crystals (see the figure). Chlorite forms tabular crystals and thick plates and has compromise surfaces with magnetite. Later spherulitic chlorite grew on the top of some magnetite crystals.

Reniform aggregate has zoning noticeable in section and stressed with sporadic chlorite inclusions. Composition of magnetite from different zones is shown in the table. Some admixture of Al, Si and Mg appear in magnetite due to fine chlorite inclusions as well as from its own composition. Calculated formulae of magnetite from consequent zones show that the composition of magnetite in latter zones in reniform aggregate had been cleared from the impurities.

Chlorite of high aluminous chlynochlore composition grew together with magnetite in early zones. It has a trygonal habit, higher magnesium and low Cr and Ni content. Pyrite from the association has up to 0.1% of Ni. Late chlorite has even higher aluminum content and its composition corresponds to high iron sudoite.

It is hard to prove that the change in magnetite composition caused appearance of intergrowth twin crystals. Nevertheless, up to 5 and more mol.% of magnesiofferrite content in magnetite could possibly influence growth mechanisms of the crystals.

Magnetite intergrowth twins were found in similar mineralogical environment on Teyskoye and Korshunovskoye iron deposits (Dymkin, Permyakov, 1984). Their occurrence was explained as a result of initially skeletal crys-

Table 1. **Composition of magnetite and chlorite from the reniform aggregate**

Components, wt.%	1	2	3	4
FeO	93.18	94.50	4.07	9.30
MnO	–	0.16	0.39	0.08
MgO	0.82	0.25	29.18	22.93
TiO_2	0.25	0.74	0.95	–
SiO_2	0.44	–	23.81	22.36
Al_2O_3	0.29	0.42	32.18	32.89
Total	94.98	95.97	90.58	87.56

Calculated formulae

Grain 1 – $(Fe_{0.95}Mg_{0.05})_{1.00}(Fe_{1.98}Al_{0.01}Ti_{0.01})_{2.00}O_4$;

Grain 2 – $(Fe_{0.98}Mg_{0.02}Mn_{0.01})_{1.01}(Fe_{1.93}Al_{0.02}Ti_{0.03}Cr_{0.01})_{1.99}O_4$;

Grain 3 – $(Mg_{3.95}Al_{0.68}Fe_{0.31}Mn_{0.03}Cr_{0.02})_{4.99}Al(Si_{2.17}Al_{1.77}Ti_{0.06})_{4.00}O_{10}(OH)_8$;

Grain 4 – $(Mg_{3.31}Al_{0.93}Fe_{0.75}Mn_{0.01})_{5.00}Al(Si_{2.17}Al_{1.83})_{4.00}O_{10}(OH)_8$

Note: 1, 2 – magnetite from early to latter zones of the aggregate, 3 – aluminous clinochlore from early zone, 4 – sudoite of late zone. JXA-733 microprobe, operator E.I. Churin (grains 1, 2, 3) and REMMA-202M microprobe, operator V.A. Kotlyarov. Grains 2 and 3 have also 0.11 and 0.24 wt.% of Cr_2O_3 correspondingly. Dash – component was not detected.

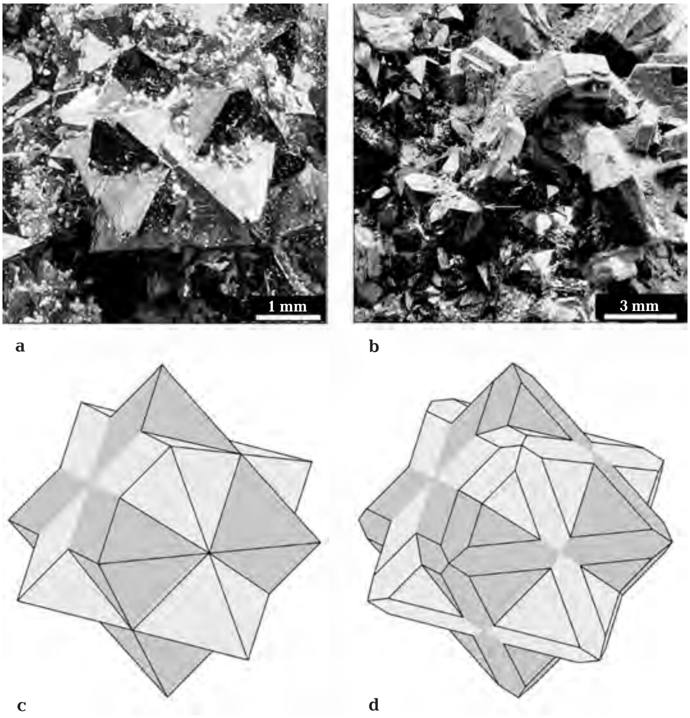

Fig. 1. Magnetite twin crystals from Kurzhunkul deposit: a — octahedral crystals, b — combination of rhomb dodecahedron and octahedron shapes (shown with arrow), c, d — idealized shape of twin crystals.

tal growth. There were no signs of initial skeletal growth observed in the samples we studied. We found only multiple changes of dominate crystal shape from octahedron to rhomb dodecahedron. The nature of preferential formation of intergrowth or contact twin crystals is not clear.

The authours are grateful to E.I. Churin, V.A. Kotlyarov and V.I. Popova for collaboration in the study.

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Ovchinnikov L.N. Mineral deposits and metallogeny of the Urals. Moscow: ZAO "Geoinformmark". **1998**. 412 p.

OLD MISTAKES IN DETERMINATION OF MINERAL COMPOSITION

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Some cases of mistakes in determination of minerals content are described.
9 references.

Keywords: mineral, mineral name.

History of mineralogy shows numerous cases of essential change of mineral chemical formulae. It is related to their subsequent additional studies, structural or chemical ones, using more sophisticated methods.

Earlier, at the epoch of domination of "wet" chemistry, mistakes in determination of content of related isomorphous ions were rather usual. Thus, in lamprophyllite ("molengraphite") of Pilansberg (RSA) and belovite from the Lovozero massif strontium was considered as calcium (Minerals..., 1937; Semenov, 1981). Division of titanium and zirconium was erroneous in lorenzenite from Greenland, which proved to be a complete analogue of ramsayite from the Khibiny massif.

Similar mistake was made on analysis of Ceylon and Brazil zirkelite, which proved to be analogues of zirconolite from the Kola Peninsula (isovalent isomorphism Zr-Ti and Sr-Ca) (Semenov, 1981, 1991). Commercial elements of the Lovozero massif loparite — niobium and tantalum — at first were taken as titanium (heterovalent isomorphism TiCa-NbNa) (Kuznetsov, 1926).

Tantalum in columbite (USA) at first was considered as part of isovalent niobium. Many false rare-earth "minerals" and "elements" were distinguished in 18th and 19th centuries during separation of complex isomorphic mixture of 14 lanthanoids and yttrium. Rare earths were sometimes taken as aluminium (ashcroftine from Greenland) and often as isomorphic thorium: thorotungstite proved to be yttrotungstite not containing thorium (Bredshaw, 1950).

Yet in recent times a great problem was separation of amphoteric elements beryllium and aluminium. Thus, beryllosilicates bavenite (Kutukova, 1946) and roggianite (Passaglia, 1969, Rassaglia, Vezzaline, 1989), equivalent to ginzburgite (Voloshin, 1986), were described as alumosilicates. So called "loss on ignition" included sometimes, besides water, also carbon dioxide (initially not discovered in tundrite).

Sometimes chemical analyses of minerals were carried out without previous complete qualitative spectral (energy-dispersed and other) analyses. Thus, in nordite from the Lovozero massif during long time zinc (about 10%) was not reported (Semenov, 1981). Electron microprobe analysis at first attempts of study of enriched in sodium phosphate of rare earths vitusite yielded low content of Na (evaporated at strong heating) in it. It is usually far from 100% the sum for microprobe analyses of minerals of weathering crust of carbonatites (pyrochlore, monazite, ilmenorutile) due to their nano-sizes (and water adsorption). "Lost" rare elements cadmium, gallium, indium were firstly extracted from sphalerite, and thallium and selenium — from pyrite.

Besides mistakes in mineralogy are known cases of direct adulteration. Thus, as new mineral — texasite — was suggested chemical preparation — oxisulphate of praseodymium (Crook, 1980).

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Discussion

THE ESSAYS ON FUNDAMENTAL AND GENETIC MINERALOGY:
5. MINERAL SPECIES AND THE METASTABLE MINERALIZATION

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The problems of the valid mineral species definition are discussed: in case of the metastable and convergence mineralization.

4 figures, 41 references.
Keywords: fundamental and genetic mineralogy, mineral species, metastable mineralization, convergence.

In the previous articles (Borutzky, 2005; 2006; 2008; 2009) the author made an attempt to convince the readers that mineralogy is in need of systematization of the *real objects* of investigation (minerals), and not their conceptual abstract character (*minerals concept*). Secondly, as far as mineralogy studies mineral matter within *geology*, the *mineral species* should be determined and systematized according to the laws of geology — *natural-history* science unlike that of chemical or crystallochemical approaches implanted nowadays. Since minerals are geological bodies which are formed in *nature*, i.e. independent, conditions and later occur in specific physical-chemical conditions, the totality of individuals with variations in chemical composition and structure should be merged into species according to the *natural* criteria discovered during investigation of geological objects and processes, and not to the *formal* features accepted in chemistry and crystallochemistry and dissimilar to *real* correlations, complicated and diverse, observed in nature.

In the first essay (Borutzky, 2005), using correlation between another natural-history science — biology, the author indicated, that despite the importance of such fundamental characteristics as chemical composition and crystal structure, the basic *species-forming* criterion for mineral species, by analogy with biology, should be their *genetic* characteristic, which defines the possibility of forming and the existance of certain chemical compound and crystal structure in certain physical-chemical parameters in certain geological conditions. The author believes that such a criterion for instance should be *confidence* that the candidate that is to become a valid mineral species has its *own stability field*, separated from the others' by *natural bounds*. In this field the chemical composition and some structural features can vary *continuously* within this or another limits. The bounds of the stability field (and hence — this mineral species) are determined as the phase boundaries — solidus, phase transformations, solvus, where the features and composition of the mineral matter change dramatically: the individuals of the mineral species get destroyed, transformed or replaced by another mineral species.

The application of these ideas was developed in the second essay (Borutzky, 2006) on the example of "*natural-genetic*" nomenclature and systematization of alkali feldspars. It was indicated that the term "mineral species" is not set in a rigid convention and constant; the composition and features of its individuals vary according to the changes in character of mineral-forming conditions. Thus, the high-temperature sanidine and anorthoclase are the members of the practically *complete* isomorphic series between potassium and sodium feldspars. These species are separated by the boundary of reconstructive phase transformation with the change in symmetry $C2/m \rightarrow C\overline{1}$ in $Ab_{63}Or_{37}$ (room temperature) and nearly $Ab_{80}Or_{20}$ (on the solvus curve, at approximately 650°C) respectively; and not in $Ab_{50}Or_{50}$ according to the "chemically" proven "50% rule", recommended by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA). The low-grade feldspars — microcline and "low" albite, on the contrary, are divided by a field of solvus, and sodium admixture in microcline is under 10 relative %, and potassium admixture in albite — under 5 relative % (there is no question of applying the "50% rule"). The fundamentally important issues here are: evidence by mineralogists-geologists and improvement of some common misunderstandings. Thus, I totally agree with Evgeny K. Lazarenko (Lazarenko, 1963) that *continuous* isomorphic series should not be divided into formal species, corresponding to its end-members, exactly due to this continuity – this is one (single) valid mineral species. In alkali feldspars the isomorphic series between $KAlSi_3O_8$ and $NaAlSi_3O_8$ becomes not only complete, but continuous – above the point of phase transformation at temperatures greater than 980°C and water pressure 1 kbar; the feldspars in this series remain monoclinic. On the other hand we cannot disagree with Andrey G. Bulakh (Bulakh, 2004), that both microcline and sanidine are one and the same mineral species, because they differ only by a degree of Si and Al ordering in tetrahedral framework (minerals which are formed due to orderings are not approved by the CNMNC IMA as mineral species). This is misunderstanding, because the process of Si/Al ordering in this case is followed by the phase transformation $C2/m \rightarrow C\bar{1}$, resulting in two separate stability fields: the microcline and the sanidine one. Taking into account genetic information – considerable differences in formation conditions, one has no doubt that these are different mineral species.

The correlation of mineral species and *varieties* were thoroughly discussed earlier (Borutzky, Urusov, 2008). Their differences are in estimation of *importance* of the features observed in totality of the mineral species compared. According to the principle of "Ockam's razor" one should not proliferate terms as happens in the modern mineralogy, unless there is an urgent necessity. It is obvious to everyone that amethyst or morion are varieties of quartz. In more complicated cases, for example, in eudialyte or labuntsovite "groups" we should be more careful in formal application of the "rule of dominance" ("50% rule") implanted by CNMNC IMA, but use more considerable criteria. Formal statement of change in symmetry (space group) without reasoned explanation for change is of concern. Reasons can be various. Quite often this is slight, insignificant displacement of atoms, as observed, for example, in anorthite. In other cases, the differences in symmetry are "set" by the scientific researcher during the crystal structure refinement, according to a number of reflexes involved in the analysis, especially the weak ones from "loose" weakly fixed atoms. It is common that the scientists do not understand this and it leads to further speculation around space groups and the discovery of "new" mineral species. Finally, for appropriate comparison of the minerals the scientists deliberately diverge from the strict analysis and choose the largest unit or the high-symmetry space group. The example, again, can be feldspars, in which the primitive units of triclinic albite or microcline are compared with the primitive unit of monoclinic sanidine and doubled body-centered unit of anorthite. Considering the above-said, Vadim S. Urusov believes that the most important, i.e. species-forming, structural feature should be *structural type*, which reflects the structural identity of the mineral crystal lattice and not its space group.

It is noticeable that in the time of pandemia of "proliferation" of mineral species in mineralogy, the imaginary pseudo-isomorphic series are also considered. The glaring example is eudialyte, considered in detail earlier (Borutzky, 2007; 2008; 2009). Thus, aggressively implanted "*eudialyte-kentbrooksite*" (instead of traditional classic *eudialyte-eucolite*) isomorphic series (Johnsen *et al.*, 1998; Johnsen, Grice, 1999; Johnsen *et al.*, 2003) is based on substitution of an *additional* Si atom for an additional Nb atom in the silicon-oxygen frame of *kentbrooksite*. The substitution occurs in one of 22 additional positions of the crystal structure (oxygen and frame silicon sites are not considered); it is substituted for only 55% of 1 formula unit, but it did not stop the authors "deduced" the formula of a hypothetical end-member with Nb = 1.00. However, even conceding total substitution (although in all known structural analyses it is below Nb = 0.80), which corresponds to Nb_2O_5 3.60–3.80 wt.%, and does not exceed 1 at.% from the total chemical composition of a mineral, I could agree with Andrey G. Bulakh (Bulakh, 2004) saying that this micro-impurity has no effect on the structural topology and features of the mineral. It should be noted that this additional position also usually shows simultaneous substitution by titanium and zirconium, i.e. the supposed isomorphic series is not binary but complex: Si ← Nb, Ti, Zr. An identical situation occurs with new eudialyte mineral – *khomyakovite*, in which silicon in this position is substituted by tungsten for 56%. In general, eudialyte is a complex analogue of zeolites, ion-exchanger, where up to one third of the Periodic Table can be involved in the composition as micro-impurities at any one time. However this is not followed by the formation of individual pure isomorphic series. The complex simultaneous substitution of various components in one and the same sites leads to distortion of the structure, transformation of co-ordination polyhedra, displacement of atoms and therefore lowering of symmetry, doubling of c parameter in a cell and change in physical and spectroscopic features of the mineral. However all these changes could be considered within the single stability field of one mineral – eudialyte. Unlike the decisions of CNMNC IMA, the character of these chemical and crystallochemical features of eudialyte does not qualify as significant characteristics for a discovery of individual valid mineral species. Eudialyte and minerals similar to it are considered here as *minerals of variable composition with variable structure (MVCVS)* – i.e. one (single) mineral species.

It well may be so, that some of these compounds (which are considered as chemical and structural varieties of eudialyte) with time will "deserve" the status of mineral species but in order to be so, the general basic condition should be fulfilled – their individual stability field should be proven to exist in a certain mineral-forming processes. We believe, that investigation of typomorphism of eudialyte varieties are the most perspective in this respect (Borutzky, 2009).

Metastable state and metastable crystallization of minerals

> *"The mighty nature is full of wonders!"*
> Alexander N. Ostrovsky

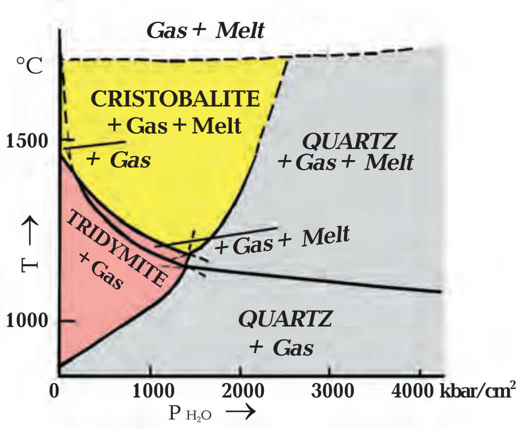
As we saw above, the presence of a stability field is in general a compulsory condition for the separation of the mineral species. But a stability field is inherent in only *equilibrium* crystallization of a mineral, and mineral-forming processes in nature are not always in equilibrium. Does this mean that we have to "sustain a defeat", refuse the *genetic species-forming* criteria and return to the chemists' "formality"? By no means. Mineralogy should investigate real natural minerals, and not their "made-up" images. One should take into account all the peculiarities of mineral formation in nature and try and find their place in mineralogical nomenclature and systematization.

Generally speaking, the *metastable state* – is not an exception, but the *usual* form of existence in nature. Almost everything we are able to observe at present (possibly despite the products of the modern mineral-forming process) does not correspond to the primary equilibrium conditions that existed when the mineral was formed. It did not achieve equilibrium with its present environment so far, hence is in a metastable state.

The typical and most simple example of such correlations are polymorphs of SiO_2 (Putnis, McConnell, 1980; Putnis, McConnell, 1983). A priori, the position of atoms at a high temperature has a higher thermodynamic probability, than at a low temperature; the internal energy decreases during cooling and any transformations. That is, in order to achieve equilibrium with the new low-temperature conditions, the structure should attain reconstructive change with commensurate internal energy decrease. However, this reconstruction happens differently: in one cases – with considerable re-organizing of the structure (*structural-reconstructive*, "spasmodic" transitions), in other cases – only with the minor atom displacements and structure distortions (*gradual* transitions). The first type is comparable with thermodynamic transformations of the first type – when at the temperature of transformation we observe the gap between the change in the first-order derivative of the free energy function: entropy, volume and enthalpy (a hidden heat effect of transformation) at the temperature of transformation. The second type corresponds to *thermodynamic transformations of the second type* – all the above-mentioned functions are continuous, and the gaps are typical only for second-order derivatives of the free energy function (this, for instance, specific transformation heat). The structural-reconstructive transitions are more energy-intensive; in order for such a transition to take place the matter should be supplemented by additional *energy of activation*, some *energy barrier* should be overcome – therefore the real processes are strongly dependant on the *kinetics* of the mineral-forming process. When the energy barrier is not overcome, the matter can remain in the other's stability field, i.e. be in metastable state.

Silica polymorphs

The polymorphs of SiO_2 depend both on temperature and pressure (Fig. 1, 2). We will not describe here the high-pressure modifications: coesite (monoclinic, $C2/c$ or Cc) and stishovite (tetragonal, $P4_2/mnm$) with their



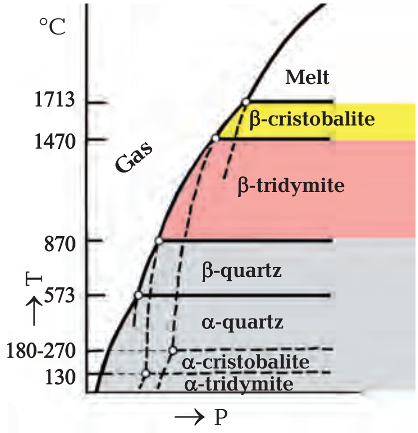


Fig. 1. $SiO_2 - H_2O$ system by increased pressure. After I.A. Ostrovskiy et al., 1959.
Fig. 2. The scheme of polymorphic transformation of SiO_2 in dry conditions, by normal pressure. After K.N. Fenner (Classic works..., 1937).

dense structures, probably typical only for abyssal zones of the Earth. Quartz occurs in the wide area of temperatures and pressures: at P = 40 kbar and T = 1300°C, P = 40 – 80 kbar and 1000 – 700°C, at 100 kbar and T = 1200°C it transforms into coesite, at 100 – 140 kbar and 1000°C it transforms into stishovite. Cristobalite and tridymite are unstable at the high pressures. High-temperature β-cristobalite at normal pressure exists within the temperatures 1710 – 1470°C. Under cooling till 1470° it transforms into high-temperature β-tridymite, stable to 870°, which at this temperature transforms into high-temperature β-quartz.

The structure of cubic β-cristobalite ($Fd3m$ or $P2_13$; $a = 7.11$ Å) (Wyckoff, 1925) can be presented as succession of two-dimensional tetrahedral layers, parallel to (111). The tetrahedra are tilted to different sides from this plane; the atoms of oxygen form closest packing *ABCABC...* The structure of hexagonal β-tridymite ($P6_3/mmc$ or $P\bar{6}2c$; $a = 5.04$, $c = 8.24$ Å) is a three-dimensional frame with the hexagonal rings of SiO_4 tetrahedra. The baselines of tetrahedra in all these rings are parallel to (0001), and the apexes are oriented alternately up and down. Thus they form a two-layered structure *ABAB...* parallel to (0001). The structure of hexagonal β-quartz ($P6_222$ – right and $P6_422$ – left; $a = 4.999$, $c = 5.457$ Å) is also presented by a frame, but SiO_4-tetrahedra are located on different layers and are twisted right or left along hexagonal two-way spiral axis. The transitions between the high-temperature modifications are structural-reconstructive, because considerable additional energy is required. For instance, the heat of transformation of β-cristobalite into β-quartz is 29 cal/g – slightly less than the heat of melting of β-quartz (39 cal/g). Metastable crystallization of the high-temperature forms of SiO_2 outside their stability fields has been observed. The further partial transitions β-cristobalite → β-tridymite and β-cristobalite → β-quartz are activated by the presence of different mineralisers. However, under reverse dry annealing at 1000 – 1200°C (i.e. in the stability field of tridymite), metacristobalite was formed, and then partially transformed into tridymite.

Besides the high-temperature modifications of these minerals, there are the low-temperature ones. The most abundant and well-known is trigonal low-temperature α-quartz ($P3_121$ – right and $P3_221$ – left; $a = 4.913$, $c = 5.405$ Å). At normal pressure the transformation $\beta \rightarrow \alpha$ quartz occurs at 573°C. The temperature of transformation rises with increasing pressure: to 599°C (1000 bar) and 704°C (5000 bar). This $\beta \rightarrow \alpha$ transition is reversible and extended in the temperature range 555 – 574°C depending on the type of quartz-bearing rocks and impurities in quartz: germanium increases the temperature of transition, aluminium and lithium – decrease it. Atoms of Si misplace insignificantly, i.e. this is the transformation that could be characterized as of the second type. On the other hand, this transition is evidently not gradual: the thermal capacity of quartz increases (with peak in interval 550 – 577°C and maximum at 574.1°), and then gradually decreases. The temperature of transition in this interval is 9.2 cal/g, although it is only 1.5 cal/g at $\beta \rightarrow \alpha$ transition. The unit cell parameters also change unevenly (at 575 – 570°: $a = 4.993 \rightarrow 4.983$, $c = 5.430 \rightarrow 5.400$ in β-quartz; $a = 5.027 \rightarrow 4.983$, $c = 5.580 \rightarrow 5.400$ in α-quartz). Taking into account the aforesaid and the importance of the low-temperature quartz for the analysis of geological objects, it is reasonable to consider it as a valid mineral species of a silica group.

The low-temperature modifications of cristobalite and tridymite are more problematic; as they are an example of *an alternative behavior* of silica minerals (Putnis, McConnell, 1980; Putnis, McConnell, 1983). β-cristobalite can transform into β-tridymite, but alternatively can transform into the low-temperature α-cristobalite (tetragonal $P4_12_12$ or $P4_32_12$; $a = 4.9709$, $c = 6.9278$ Å, see Pluth *et al.*, 1985). The transition $\beta \rightarrow \alpha$ cristobalite is also reversible, at temperatures of 180 – 270°C with maximum at nearly 220°C, depending on crystallinity. Microimpurities, stabilizing the high-temperature β-phase, also affect the character of transition resulting in: $SiO_2 \rightarrow Si_{1-x}Al_xM^{n+}_{x/n}O_2$, where M = Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} and La^{3+} (Perrotta *et al.*, 1989; Saltzberg *et al.*, 1992; Thomas *et al.*, 1994). This transition is also characterized by significant hysteresis, i.e. difference between the temperatures of transformation at heating ($\alpha \rightarrow \beta$) and cooling ($\beta \rightarrow \alpha$). Thus, for instance, in the vanadium-containing system ($Si_{0.85}V_{0.15}Na_{0.15}O_2$) the $\alpha \rightarrow \beta$ transition was observed at T = 246°C, and $\beta \rightarrow \alpha$ – at 231°C (Bruhns, Fischer, 2000), although it is unclear whether vanadium is occupies a site in the cristobalite structure or only acts as a catalyst. The heat of $\alpha \rightarrow \beta$ transformation of cristobalite is even less than that of quartz (4.4 cal/g). But the most alerting fact is that α-cristobalite has no stability field of its own, more precisely – it is within the stability field of α-quartz. i.e. both β- and α-cristobalite can be metastably formed within the stability field of α-quartz.

The crystal structures of α- and β-cristobalite and their $\beta \rightarrow \alpha$ transformation were studied in detail by Wyckoff, 1925; Nieuwenkamp, 1937; Peacor, 1973; Wright, Leadbetter, 1975; Hatch, Ghose, 1991. The scientists were not satisfied with the *ideal* cubic model of "C9-type" β-cristobalite (Wyckoff, 1925). It was later designated as $Fd\bar{3}m$, because otherwise it could not be interpreted in detail compression of the structure with rigid angle Si-O-Si = 180° along [111] axis and interatomic distance Si-O = 1.540 Å under its transformation into the structure of α-cristobalite with Si-O-Si = 146° and Si-O = 1.609 Å. In the new hexagonal model (Nieuwenkamp, 1937; Peacor, 1973; Wright, Leadbetter, 1975) the 16 atoms of oxygen occupy a 96(h) system with 1/6 occupancy in each sixth site, which is related to a rotation of 60° around the Si-Si axis along a small circle with radius 0.45 Å, resulting in Si-O = 1.609 Å and an Si-O-Si angle = 146°. The structure of β-cristobalite is interpreted as the average of 6 domains around [111] axes of the cubic phase "C9". The total symmetry of these twins was presumed to decrease from $Fd\bar{3}m$ to $I\bar{4}2d$, which is not a super-group $P4_32_12$ or $P4_12_12$ (Wright, Leadbetter, 1975; O'Keefe, Hyde, 1976). The transition into α-phase ($I\bar{4}2d \rightarrow P4_12_12$) is a further rotation of the SiO4-tetrahedra. Finally, Dorian M. Hatch and Subrata Ghose (Hatch, Ghose, 1991) noted that the a parameter in β-cristobalite at 205°C (7.195 Å) is slightly less that in the initial cubic structure $Fd\bar{3}m$ (7.432 Å), and although the Si-O-Si angle is still 180°, the distance Si-O is 1.609 Å, i.e. corresponding to α-cristobalite. Applying formalization of Landau, they showed the possibility of formation of 12 domes during $\beta \rightarrow \alpha$ transition: 1) transformation twins, with loss of L_3 along [111], 2) enantiomorphous twins, with loss of symmetry centre, and 3) antiphase domains, with loss of translation vector $^1/_2$[110] ($F \rightarrow P$). This structural model correlates with the X-ray model by Donald R. Peacor (Peacor, 1973), although the true inner symmetry of these domes in the high-temperature β-phase is $P4_32_12$ (or in enantiomorphous group – $P4_12_12$) and not $I\bar{4}2d$, as the other researchers assumed (Wright, Leadbetter, 1975; O'Keefe, Hyde, 1976). In a β-phase these P-domains are both microscopic and dynamic, imitating higher symmetry, and in α-phase they are macroscopic and static.

Thus such a complicated mechanism of $\beta \rightarrow \alpha$ transformation is interpreted as fluctuating-caused transition of the first type. During transformation into α-cristobalite, SiO_4-tetrahedra rotate simultaneously and translate along x and y axes, which is related to a gradual Si-O-Si angle divergence from 180° in an ideal structure (Pluth *et al.*, 1985).

However, the displacement leap is strictly limited by temperature (~220°C), whereas fluctuations and ordering are observed in a larger range, entailed by changes in such features as, for instance, elastic parameters C_{11}-C_{12}. Thus, we have a combination of thermodynamic transitions of the first and second type.

Similar effects are typical for the transition $\beta \rightarrow \alpha$ tridymite, in the interval 117 – 163°C. Three phases of α-tridymite, stable at the room temperature, were discovered: orthorhombic (or triclinic, but with $\alpha = \beta = \gamma = 90°$) with a = 9.932, b = 17.216, c = 81.854 Å (Konnert, Appleman, 1978), monoclinic *Cc* (Dollase, Baur, 1976) and monoclinic with unrequited superstructure MX-1 (Graetsch, Topalovich-Dierdorf, 1996). Besides, two "intermediate" structures were established (Wennemer, Thompson, 1984; Pryde, Dove, 1998). The heat of transformation $\beta \rightarrow \alpha$, calculated in total ($\alpha \rightarrow \beta_1$ 0.43 cal/g; $\beta \rightarrow \beta_1$ 0.23 cal/g) does not exceed 0.66 cal/g. Similar to α-cristobalite, α-tridymite has no stability field of its own and is formed in the stability field of α-quartz.

The low-temperature forms of cristobalite and tridymite are typical for the opal, chalcedony, agate deposits among volcanic rocks. They occur as overgrowths on zeolite crystals in cavities in basalts, in sedimentary rocks – opokas, tripoli, diatomites. α-cristobalite often occurs along with opal globules and micro-globules (Fig. 3). Sometimes α-cristobalite is observed together with β-cristobalite, which indicates the metastable crystallization of a high-temperature form outside its stability field, with a further partial transformation into a low-temperature form. The attempt to classify opals in mineralogical terms was made by Jones and Segnit (1971, 1972). They highlight three main types: 1) "*opal-C*" – with an ordered α-cristobalite forming horizontal layers in the bottom parts of agates and geodes of Uruguay type, 2) "*opal-CT*" – with a disordered α-cristobalite and tridymite as flaky-spherulitic aggregates and cristobalite as pencil aggregates of lussatite, and 3) "*opal-A*" – as an amorphous non-crystallized hyalite. In "opals CT", V.G. Balakirev *et al*. (Balakirev *et al*., 1977) determined three types of particles: (1) hexagonal or pseudo-hexagonal platelets 100 – 200 Å forming tracery aggregates, (2) flattened fibers 100 – 200 Å thick (in transparent opals), and (3) large fibers 300 – 1000 Å across (in milky opals). Using micro-diffraction cristobalite and tridymite were determined in the samples. The experiments on hydrothermal sedimentation of cristobalite (Flörke *et al*., 1990) showed, that various forms of SiO_2 (hyalite, quartz, cristobalite) form together, although tridymite crystallized only at high temperature (750°C) as β-modification. Cristobalite also crystallized at the temperatures over 250° and later transformed into the α-modification at various times depending on the level of ordering in specimens.

Considering the above said, one should admit that the nomenclature of low-temperature cristobalite and tridymite is unclear. The

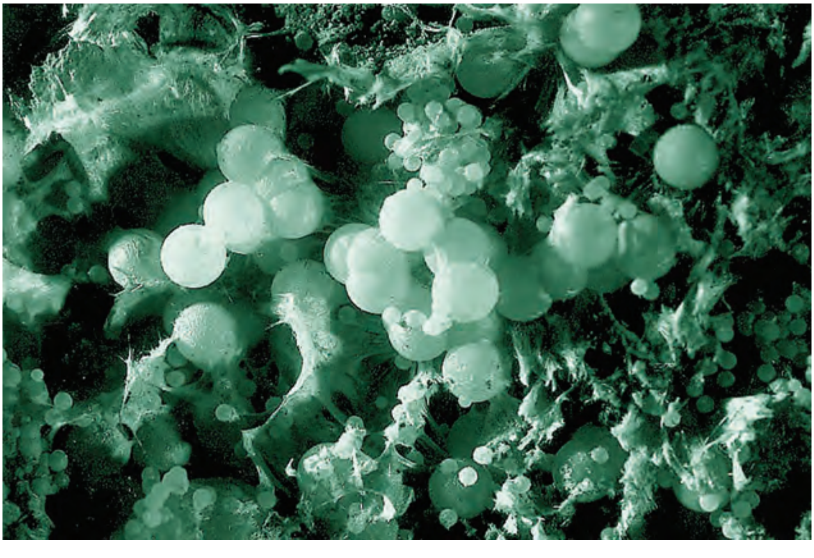


Fig. 3. Globular and micro-globular opal with cristobalite at Pomachskoye agate deposit, Georgia. ×30. After L.M. Lebedev, 1965.

absence of individual stability fields, uncertain character of complicated "uneven-extended" transitions which cannot be classified as thermodynamic ones of the first or second types, weak energy effects — leads us to consider them as *varieties*, depending on gradual changes, and not as individual *mineral species*. However, the situation might change with further investigation, as happened with α-quartz which is obviously more stable and abundant in nature.

Alkali feldspars

Restoring the conditions of crystallization and post-crystallization transformation using physical-chemical simulation, we face the totality of kinetically different parallel processes. The case with SiO_2 polymorphs was relatively simple as only structure was subject to change with constant chemical composition. In the minerals with variable composition both can change.

As an example I will use well-studied alkali feldspars (Fig. 4), which for I suggested natural-genetic nomenclature of minerals (Borutzky, 2006). Under lava quenching their relic state, which is close to their initial state, remains. Whereas under slow crystallization of a melt, both the structural state and chemical composition of a feldspar change, attaining equilibrium with the later low-temperature stages of a rock. In the latter case the components can re-distribute and order in the feldspar framework, as a result of diffusion. The diffusion of Na and K in the hollows is more rapid than Si and Al in the frame. In the next stage the ordering of alkali reaches the first stages of "exsolution": first — spinodal, then — coherent. The phase exsolution was deliberately mentioned in quotes, because these phases are rather peculiar. The spinodal exsolution results in undulating fluctuations of a composition, from K- to Na-feldspar without phase interfaces. Coherent "phases" are essentially potassic and essentially sodium within a single Si/Al framework, they are detectable in X-ray diagrams as cells with a different a parameter, equal *b* and *c* parameters, and angles distinctly different from the angles of albite and K-feldspar cells. Such morphology of the cells enables them to adapt to each other whilst still within the single crystal space, as a result the lattice is tensed, i.e. has surplus internal energy. Si/Al ordering has the same results. For instance, in K-feldspar (i.e. without influence of a sodium component) a pseudo-microcline lattice appears that is visible under SEM — *tweed* structure of *orthoclase*; it is both monoclinic and triclinic with gradual transformations in between, i.e. even without phase interfaces.

The general principles of the behavior of feldspars are written in the fundamental work (Putnis, McConnell, 1980; Putnis, McConnell, 1983). We know that the stable low-temperature forms of alkali feldspars are *microcline* (below 500±50°C) and low albite (680±20°C). However, according to kinetic limitations, the direct transition of sanidine and anorthoclase (or analbite) into these modifications is not always possible as the activation energy of transformation into the stable form cannot be overcome as one or another temperature conditions. Thus, the mineral matter will remain as metastable or will transform into the stable form gradually, via a number of intermediate close states, according to the "Ostwald Step Rule". An equilibrium can be reached for kinetically faster processes but not for the slower, therefore the exsolution of K- and Na- phases outstrips the process of exsolution of Si/Al-ordering in exsolved phases, and the Na-phase will always be better ordered and purer than the potassic one. If we use the equilibrium phase diagrams insufficiently critically, for, say, the estimation of the temperature conditions of postcrystallizing history of the feldspars, then we will get lower temperatures "by sodium" than "by potassium".

The stable low-temperature forms of alkali feldspar are nevertheless formed, due to the relatively high temperatures required for the heat fluctuations to overcome the energy barriers. It is known, that depending on geological history, either homogeneous microcline and low albite, or their conforming co-growths as crypto-, micro- or macro-perthites form. They are formed not only under the process of phase exsolution, but under their *collective re-crystallization*, which takes place with an increased role of water — post-magmatic solutions in the primary-magmatic system. In the range of stability fields of microcline and albite, variations in chemical composition keep on changing in response to changes in the physical-chemical parameters until almost pure $KAlSi_3O_8$ with impurity of Na-component under 10 relative %, and $NaAlSi_3O_8$ with impurity of K-component under 3—5 relative %, with distinct phase interfaces and change in the internal morphology of the exsolved phases: from peri-

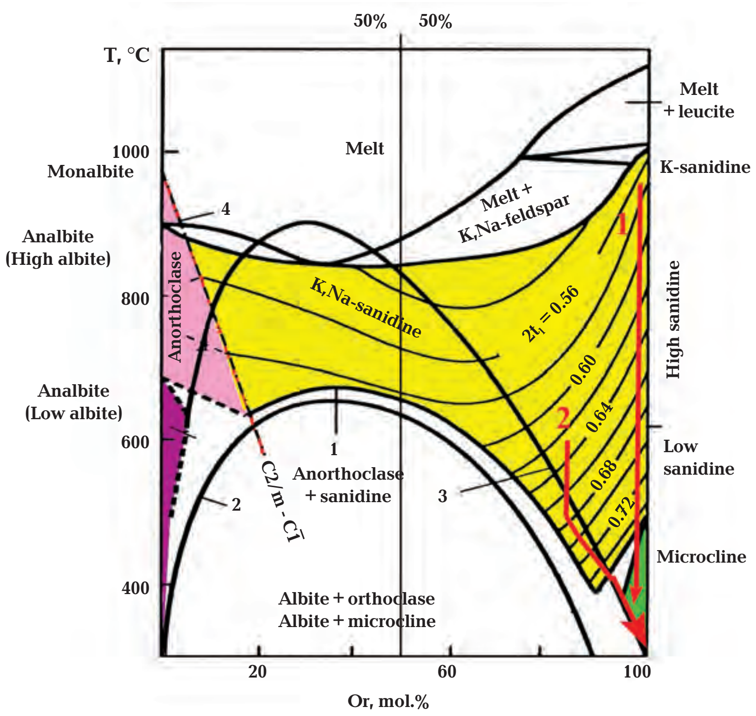


Fig. 4. Diagram "T-x" by E.E. Senderov (1990), composed for P = P(H_2O) = 1 kbar, considering degree of Si/Al-ordering of the phases; for explanation the natural-genetic nomenclature of alkali feldspars (Borutzky, 2006).
The explanation the natural-genetic nomenclature of alkali feldspars: 1 — the true-equilibrium coexistence curve (after Senderov), 2 — analbite (high albite)-sanidine solvus, 3 — albite (low albite)-microcline solvus, 4 — non-tempering phase transition between monoclinic and triclinic feldspars.
Red arrows indicate: 1 — metastable crystallization of adularia, 2 — metastable formation of a "tweed" orthoclase.

cline to albite twins in Na-phase and to albite-pericline (*twin lattice*) in K-phase.

Thus, along with "alkali K,Na-feldspar", "sanidine", "anorthoclase", "microcline" and "albite" having their own stability fields with natural boundaries — there are minerals which we can specify as valid mineral species which in nature include a number of metastable states of feldspar matter that cannot be ignored but whose status in mineralogical nomenclature and classifications is less determined.

These, first of all, are *adularia* and *orthoclase*.

It is well-known, that adularia forms under low-temperature hydrothermal conditions — in the "alpine" veins, deposits of gold, during zeolite stage of pegmatite-forming process etc. Judging by the character of mineral associations and immediate co-occurrence with low albite and microcline, it crystallizes metastably within the stability field of microcline. Its sterility regarding micro-impurities and specific crystal morphology is confirmed. Nevertheless, the structural state of adularia corresponds to sanidine, even "high sanidine". This fact even amazed scientists, because "high sanidines" (the most Si/Al-disordered potassic feldspars) were described not from volcanic rocks, but from adularia-bearing veins. It also should be noted, that "sanidine", being formed during diagenesis of marine sediments, strictly speaking should be identified as adularia and not as sanidine. Thus, we again face the well-known problem of crystallization of the high-temperature modification outside its stability field, or rather — its absence. At the same time, genetically, adularia is a fully determined mineral with distinctive typomorphic features and is important for geological investigation. So, can one determine adularia as a valid mineral species? We believe not: it is only a variety of feldspar. Genetically important variety! In this connection we have to remind once again we previously wrote (Borutzky, 2005; 2006): the term *variety* is no less important a category for mineral systematization, than *mineral species*, and it is time to stop the mass action for transforming known mineral varieties into individual species.

Orthoclase was mentioned before. Orthoclase is not a synonym of potassic feldspar, but its specific modification, which is optically (and sometimes X-ray) monoclinic but built of triclinic blocks, i.e. intermediate between sanidine and microcline. Apparently, orthoclase should not be determined as a valid mineral species, but, strictly speaking it is neither variety, nor mineral aggregate — mineralogists did not conceive how to systematize such a natural mineral objects.

On convergence of the mineral–forming processes and "convergent" minerals

In view of the problem examined, one should dwell on convergence of mineral-forming processes, i.e. forming one and the same minerals or mineral associations under different geological conditions. The detailed overview of such a convergence and convergence of typomorphic features of minerals, was made by Fedor V. Chukhrov in the book "Typomorphism of minerals and its application" (1972). According to academician Chukhrov, the "convergence of the first order" can be determined when the minerals of one and the same species (or association) occur both in endogenic and supergene processes; and the "convergence of the second order" — when they occur either in endogenic or supergene processes. The convergent minerals can also differ by a range of thermodynamic conditions of formation — the wider or narrower. The convergence of the 1st type is more typical for quartz. Pyrite and chalcopyrite are formed from the early magmatic crystallization stage ending with the supergene processes. Titanium oxides — rutile, brookite and anatase crystallize both at high temperatures and under supergene conditions by leucoxenisation of the primary titanium-bearing minerals. Minerals with complex chemical composition can also be convergent, such as alkali feldspars, aegirine, riebeckite, reedmergnerite, elpidite, labuntsovite etc. Although they are typical of alkaline granites, syenites and pegmatites, they were discovered in association with authigenic minerals in the limnic sediments of the Tertiary formation Green-River in the USA. In the book mentioned above there are multiple examples of minerals from different classes, with a smaller range of conditions of formation. There are also examples of convergent minerals of the 2nd-type given, but in my opinion, they are less convincing because they are not mineral species but varieties, which obviously occur at narrower variations of temperature, pressure and chemism of a mineral-forming environment. Comparison of convergence of supergene and hypogene mineral-forming processes is presented in the later papers by Fedor V. Chukhrov (Chukhrov, 1979; 1980). He analyses not so much the differences in physical-chemical conditions, as in the sources of solutions: "the same minerals, typical for supergene processes, can be formed from cooled thermal solutions; it enables one to talk about convergence of mineral formation from both ascending thermal solutions and solutions of supergene zone, which were not affected by hypogene heat" (Chukhrov, 1980, p. 102).

Analysing the data on convergence of typomorphic features of minerals (introduction to the book "Typomorphism..., 1972"), Fedor V. Chukhrov precisely defined the problem (p. 14): "The important question is similarity or coincidence of the features of minerals, which were formed in different conditions. This phenomenon can be named the convergence of typomorphic features". In fact, there are no "convergent minerals" — there are *convergent* (coincident) features, whose nature should be understood prior to naming them typomorphic — i.e. being typical for a certain geological conditions. Fedor V. Chukhrov cites literature examples of colloform aggregates of cassiterite and framboidal aggregates of pyrite that were crystallized from gels — both in near-surface zones and hydrothermal deposits of abyssal zones, when solutions entered open fissures and cavities. It was shown that the isotopic composition of sulphur, oxygen and carbon can be one and the same in minerals from igneous, sedimentary, metamorphic and some diagenetic rocks; the same can be applied to polytypism of micas, molybdenite etc. However, it does not mean that the minerals are identical, convergent by other features too.

Trying not to be persistent, we will discuss this fact using the example of alkali feldspars, which, as is known, occur under various combinations of temperature and pressure. Initially, at high temperature, monoclinic sanidine with maximum disordered distribution of Si and Al within four tetrahedral positions of a crystal structure: 0.25:0.25:0.25:0.25 (% Al per unit) crystallizes from a melt; this is the "high sanidine" with stoichiometry Si:Al = 3:1. Upon cooling, Al is re-distributed in the feldspar framework and predominantly segregated in two tetrahedral positions (T_1) out of four: 0.50:0.50:0:0; this is "low sanidine". This is the reason that we do not observe high sanidine in nature — it does not remain even in quenched volcanic rocks, and was only grown experimentally. However, as it was mentioned above, K-feldspars with such a high grade of Si/Al-disorder were discovered in alpine veins and diagenetically altered sediments, often in association with maximum ordered K-feldspar – triclinic *microcline*, where all Al is concentrated in only one position (T_10). As we clarified such "sanidines" are metastable, formed within the stability field of microcline. Their convergent feature is Si/Al-disorder. They fundamentally differ from "real" sanidine by other features: their pure, almost sodium-free chemical composition and dissimilar crystal morphology with dominant (110) prism. These feldspars are known as *adularia*. Genetically it is clearly an individual mineral with a specific combination of the main features – chemical composition, structure and morphology, which are typomorphic for a certain geological conditions. It would be incorrect to equate adularia with such mineral species of the K-feldspar group, as sanidine or microcline.

A similar example was described by Fedor V. Chukhrov (Typomorphism..., 1972). Thus, he gave an example of the similarity of "dipyramidal" quartz – high-temperature hexagonal-dipyramidal from some effusive rocks, and falsely-dipyramidal (with two equally developed rhomboherda) – from low-temperature deposits, as *false* convergence. It is possible to consider this feature as false or true, but it is obvious that their other features differ; in particular, these minerals belong to different structure modifications: α- and β-quartz. Partial convergence, the convergence of separate features, i.e. actually *false* regarding to a term mineral species, gives individual names for such a minerals. For example, fibrous low-temperature quartz is *chalcedony*, colloidal-amorphous molybdenite is *jordisite*, sedimentary fluorite – *ratofkite*, supergene cassiterite – *varlamoffite*.

Mineral or mineral aggregate?

Discussing my suggestion to consider an individual *stability field* as a major species-forming criterion for a potentially new mineral species, Vadim S. Urusov suggested substituting the term *stability field* for the term existence *field* (Urusov, 2009). In principle we agree with this, although in general it makes the term mineral species undesirably less specific. The Russian equivalent for "stability" is "steadiness". Substitution of "steadiness" for "existence" unwittingly support our opponents criticism, who substantiate the approved by CNMNC IMA multiple *cloned* "new" mineral species by their real *existence* in nature (and who never wonder whether they are new species or varieties of the known species). On the other hand, this suggestion enables one to consider in the scientific systematization of mineralogical objects both stable and metastable minerals, and also some minerals which have lost stability with geological time (having in mind that mineralogy is a natural-historical science). We discussed unstable and metastable minerals above. Examples of minerals which have lost stability are perthites and their plagioclase analogues that were mentioned casually above.

In the previous papers (Borutzky, 2006), it was shown, that the diagrams $NaAlSi_3O_8$-$KAlSi_3O_8$-T has an area of immiscibility (solvus) between anorthoclase and sanidine and (at a lower temperature) between albite and microcline. It seems that there is nothing to speak about: in this field there are two coexisting minerals (two mineral species) with distinct phase interfaces, i.e. mineral aggregate. Yes, but this concerns only macro- and micro-perthites – the co-growth of low albite and microcline, with appropriate chemical compositions and cell parameters. However, in crypto-perthites the inter-grain boundaries are absent: perthitic "aggregate" is represented by the integrated alumosilicic framework with identical b and c unit cell parameters for Na- and K-phases and variable a parameter, which reflects the site occupancy by these alkaline metals. The inter-axis angles distort in order that the cell volume has a minimum deviation from the volume of unexsolved K,Na-feldspar. For this case, within the field surrounded by equilibrium solvus, one could draw an area limited by coherent solvus. Finally, at the earlier stage of exsolution in a homogenous K,Na-feldspar there occurs undulatory fluctuations of composition – coherent spinodal; the X-ray data is not dissimilar to homogenous, i.e. we have all the reasons to identify this "aggregate" as a monomineral and refer it to a certain mineral species.

A similar situation is observed in plagioclases. In the so-called, intermediate plagioclases (from oligoclase to bytownite) the crystal structure is built from co-existing domains of albite and anorthite, which can be detected only by additional ("over-structural") reflexes. In practical mineralogical-petrological research such plagioclases are considered as homogenous and described by the summary X-ray diagrams. Even their heterogeneity can be detected on the electron-microscopic level using SEM/EMPA. When the intermediate plagioclases reveal iridescence ("moonstones" — peristerites, labradorites), i.e. exsolution becomes obvious, they still are considered as homogeneous, corresponding to relevant minerals species or (according to some scientists) — varieties. In this respect how can we not reconcile it with similar structural effects seen in more complicated mineralogical objects, such as eudialyte or labuntsovite, which are used for speculative multiplication of new mineral species.

Conclusions

1. It is normally believed that the reason for all terminology and classification misunderstandings in mineralogy is the absence, carelessness or artificiality (formality) of species-determing criteria. They are discussed by various commissions, where different opinions, approaches and scholarships conflict, and where the majority approve decisions, obscure to the scientists who deal with the natural matter, or suit only the minority who use them to speculative purposes. We suppose, that one of the important reasons for such misunderstanding is "disregard" for the objects of mineralogical research — the minerals, which are considered only "snatched out" of a certain geological environment. Therefore one classifies not certain objects, but ideas about them. The objects themselves are more complicated and diverse, and their chemical composition, structural features and other characteristics depend directly on variations in formation conditions, that should be considered in systematization.

2. In the previous papers on the subject we indicated that, in general, for determination of a new mineral species proof is required of its individual stability field. Within this field, the chemical composition, structural peculiarities and features of the mineral might change gradually, depending on conditions of formation (and retaining), without abrupt changes resulting in formation of a new mineral species.

3. However, under certain conditions in nature there occur unstable phases, metastable phases, minerals which have lost equilibrium relationship with the mineral-forming (or mineral-retaining) environment, "mineralogical hybrids" — several mineral species "mixed", "quenched" "intermediate" states etc. On one hand, we cannot recognise them as non-minerals, and on the other — cannot properly equate them with the known species.

4. The question about approval of such minerals as valid species is open, and apparently should be solved individually. In one cases, the crystallization of a mineral outside its stability field can be described by one or another existence area, in another cases — the stability field can be determined for this certain modification, and thirdly — there is insufficient experimental data and observation in nature. The term "spasmodic" transition itself is not quite determined: besides distinct transformations of the "first" and "second" types, for which energy difference is not a strong criterion, there evidently are more complex transformations inheriting features of the first and second transition types.

5. The term convergence of minerals is not fully determined. Probably, it is more correct to speak about convergent features of minerals and not about convergent minerals, because either similar structures of compositions are repeated. But at the same time the compared objects differ essentially by their morphology and other features, which can be considered as typomorphic for their recognition and understanding of their relation with geological environment.

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ON 90th ANNIVERSARY OF ILMENY STATE RESERVE

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Ilmeny State Reserve of the Urals Branch of Russian Academy of Sciences was found 90 years ago, on May 14, 1920. At first it was formed as a mineralogical Reserve and later it received a status of a complex Reserve and became a nucleus of the research center of the Academy of Sciences in the South Urals. It is the only mineralogical Reserve in Russia. The International Meeting "Science, Nature and the Society" was dedicated to the anniversary and took place in Miass on May 10 – 13, 2010. It gathered geologists and biologists in a friendly and creative atmosphere. P.M. Valizer, the director of the Ilmeny Reserve, opened the meeting with the speech on the state of the reserve area and its meaning to the Urals. Academician N.P. Yushkin (Institute of Geology, Komi Science Centre of the Urals Branch of the RAS, Syktyvkar) was among those who congratulated the staff of the Reserve. He presented very interesting report named "Bio-mineral Evolution". Academician V.A. Koroteyev from the Institute of Geology and Geochemistry of the Urals Branch of the RAS (Ekaterinburg) highly esteemed the fundamental mineralogical research carried out in the Ilmeny Reserve. Ten new minerals out of the eighteen were discovered there during the period 1965 – 2005 by the local scientists. Models of mineral formation, theories of pegmatite formation and metamorphism and other hypotheses were developed on the material obtained in the Ilmeny Reserve. Contemporary world-class studies on mineral classification among individual mineral groups and creation of mineral registers are carried out in the Reserve. V.G. Korinevskiy, E.P. Makagonov, S.N. Nikandrov, V.A. Popov, V.I. Popova, the well known mineralogists from the Ilmeny and other scientists participated in the section "Precambrian Polimetamorphic Complexes of the Southern Urals". Excursions on the territory of the Ilmeny mineralogical Reserve and at the Museum of Natural Science were organized for the conference participants. The Museum is one of the five biggest geological-mineralogical museums in Russia and represents a large education center receiving 60 thousands of visitors annually. Exposition dedicated to the history of studies of the Ilmeny Reserve was remodeled to the anniversary and gained a special attention as well as new exhibitions of crystals, technogenic minerals and new minerals found in the Ilmeny during 20th and the beginning of 21st centuries. Separate division of the new mineral exhibition was dedicated to their discoverers, the well known mineralogists from the Ilmeny: B.A. Makarochkin, A.G. Bazhenov, V.O. Polyakov, B.V. Chesnokov and other mineralogists from the Ilmeny, who carry on the studies today. Museum community found interesting the work of the section "Science and Education: Ways of Interaction".

E.N. Matvienko, PhD in Geosciences and Mineralogy congratulated the colleagues from the Ilmeny on the anniversary from the name of the staff of the Fersman Mineralogical Museum of the RAS. Her presentation was dedicated to minerals from the Ilmeny in the collection of the Fersman Mineralogical Museum and to their discoverers. The history of the Mineralogical Museum of the RAS was tightly connected with the studies of the Ilmeny starting from the visit of academician P.S. Pallas, who was the head of the Mineralogical Cabinet in the Kunstkamera. He was the first to publish data on the Ilmeny Mountains. Academician V.M. Severgin, one of the founders of the Russian mineralogical science and another head of the Cabinet, was first to publish materials on minerals from the Ilmeny in his fundamental works in Russian. Academicians V.I. Vernadsky and A.E. Fersman directed the recreation of mineralogical collection of the Academy of Sciences and were originators of the idea of creation of the Ilmeny Reserve and research center of the Academy of Sciences in the Southern Urals. Joined activities of radium and complex expeditions of the Academy of Sciences and the Museum during many years pulled together the staff of the Mineralogical Museum and the one of the Ilmeny Reserve. The Ilmeny had its special place in the work of V.I. Kryzhanovsky who organized extensive exploration of the Ural Mountains mine after mine and delivering of specimens of minerals he discovered to the Museum. He lead evacuation of the Museum from Moscow to the Ilmeny during the World War II when the most valuable specimens were moved to the Urals. Professor G.P. Barsanov, the director of the Mineralogical Museum of the USSR Academy of Sciences, recovered from his battle injury in the Ilmeny and actively participated in studies of mineralogy of the area. Barsanov made the studies a subject for many of his publications including his degree thesis. The list of people from the Mineralogical Museum of the Academy of Sciences who studied the Ilmeny and its minerals as well as scientists from the Ilmeny itself is very long. Strong scientific ties between the institutions are still well maintained. Fersman Mineralogical Museum of the RAS has more than 5000 samples from the Ilmeny.

Efforts of the scientists on keeping mineral and biological diversity of the Reserve intact and scientific work are well known and esteemed. The Reserve is popular within a wide public that brings to it a cultural significance along with the scientific.

We wish a fruitful work to the colleagues in the Ilmeny. V.I. Kryzhanovsky, an authoritative investigator of the Ilmeny, stated: “Has study of the Ilmeny accomplished? Of course not... It is to be continued".

THE NEW APPROACH TO THE SCIENTIFIC MUSEUMS: THE "MUSEUM ORIENTEERING"

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The Fersman Mineralogical museum RAS due to its scientific and educational profile together with the academician status is considered as "difficult" and therefore it is less known to the general public. However each year it becomes more and more popular. The one of the world-class largest mineralogical collections with 300-years history attracts the visitors with the beauty of natural stone, masterpieces of famous lapidaries, laboratory-grown crystals and meteorites.

We always would like to make our museum closer to the public without changing the scientific concept of the exhibition, and to show our visitors the world of stone – economically significant and aesthetically attractive part of Nature, to make their visit captivating and informative.

The project "Museum puzzles" comprehending 7 natural history museums in Moscow and supported by ICOM Russia and Moscow government was launched in 2010, October 9–10, within the "5th Science Festival in Moscow". The project aimed to attract the visitors with the gaming guidebooks which enable people (mostly children) to plan the visit themselves and to make it more sensible.

Two types of the guidebooks were developed: for the youngest visitors and for the schoolchildren. The former guidebook or the "stickers" game, named the "Fersman Rainbow", is represented by a sketch map of the museum with the certain display cases numbered – on the one side, and a field with 18 questions on the other. The number of a question corresponds to the number of the case marked. The player has to navigate himself to the destined display case, using the map, find an answer to the appropriate question and put the sticker in the answer field. The final task of the game is to compile a "rainbow" of the minerals been seen. The latter, "big" guidebook, the "Fersman Rebus", combines together a mini-tour in the museum, questions for quick wits and attention, and also impart orienting skills. Using the compass and the map, along with the guidebook itself, every visitor would feel himself a real naturalist, a researcher, even in the museum interiors; and at the end of the game will have his own guidebook – the compiled mineral handbook – as a gift. There are five different routes in the game. En route the players have to solve puzzles using tips & signs, and navigate himself from stop to stop in order to obtain 7 letters for the rebus: 1–2 from each route. The final task is to compile a word from 7 letters collected. Also, there is a crossword game at the end of all the guidebooks, where the players have to fill the template with the mineral names they collected en route; it is a team game to be played in schools.

The games "Museum puzzles" were held at the museum since October 2010 and will continue till May 2011. During the 3 months period (October–December 2010) the number of visitors to the museum increased significantly: more than 400 people chose the sticker game and over 50 groups of 20–30 people signed in to play the "Fersman Rebus" game.

We do hope that the Moscow project "Museum puzzles" started with the Fersman Mineralogical Museum would stimulate the population of all ages to learn more about different aspects of nature. With such an application a visit to the museum will no longer be a boring trip to the "storehouse of dusty exhibits", but an opportunity to come closer to a real science.