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New Data on Minerals. Moscow.: Ocean Pictures, 2005. volume 40, 168 pages, 15 color and 99 b/w drawings, schemes, photos.

The volume 40 includes articles on new mineral species, among which chukhrovite-(Nd), tsepinite-Sr, senkevichite, and kyrgyzstanite are described. The new data on rare minerals - calcurmolite and turanite, easily oxidizable chalcopyrite from black smokers of the Rainbow hydrothermal field (Mid-Atlantic Ridge), vanadium hematite associated with minerals of precious metals, copper, zinc, and iron is given; also there is data on fahlores from the Kvartsitovye Gorki deposit and the nickeline-breithauptite mineral series from the Norilsk ore field. Features of bismuth mineralization of the Djimidon deposit (North Osetia) and rare-metal mineralization connected with bituminous matters from pegmatites of the Khibiny and Lovozero massifs are revealed. The results of study of metacolloidal gold and delhayelite crystals are published.

In the «Mineralogical Museums and collections» part, the minerals named in honour of collaborators of the Fersman Mineralogical Museum, specimens of platinum of the Ugolnyi stream (Norilsk) from the Museum collection are described; interesting historical data on the items of Decorative and Precious Stones collection (PDK) is given.

«Mineralogical Notes» part includes the mineralogical summary of main mineral types of ores of Europe and the article devoted to mineral drawings of Victor Slyotov and Vladimir Makarenko. In new «Discussions» part, the polemics on the theme «What are the mineral and mineral species» is opened. The review of new books is published.

The volume is of interest for mineralogists, geochemists, geologists, and also collaborators of natural-historical museums, collectors and amateur of minerals.

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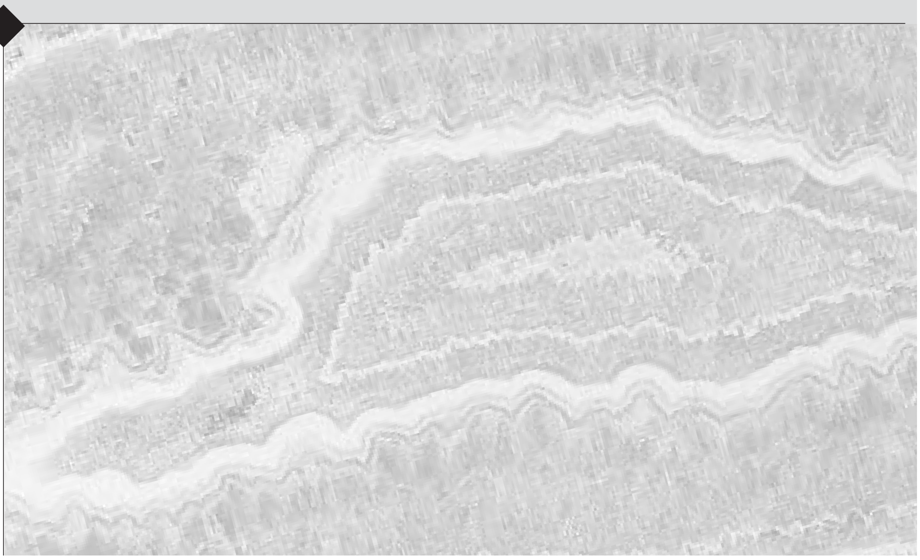
New Minerals and Their Varieties

New Finds of Rare Minerals, Mineral Paragenesis



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CHUKHROVITE–(Nd), $Ca_3(Nd,Y)Al_2(SO_4)F_{13}\cdot12H_2O$, A NEW MINERAL

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In specimens from the oxidized zone of the Kara-Oba deposit (Central Kazakhstan), a new neodymium-dominant analogue of chukhrovite-(Y) and chukhrovite-(Ce) has been found; it has been named chukhrovite-(Nd). The new mineral occurs in the form of isometric grains and small crystals represented by a combination of {100} and {111} faces, with sizes ranging from 0.05 to 0.4 mm; it forms zones within the larger crystals of chukhrovite-(Y) also. Chukhrovite-(Nd) is associated with quartz, fluorite, halloysite, chukhrovite-(Y), anglesite, gearksutite, creedite, and the jarosite group minerals. The mineral is colourless, rarely white. Streak is white. Hardness is 3.5-4 on Mohs' scale. Density (meas.) is 2.42(3) g/cm^3, density (calc.) is 2.42 g/cm^3. The mineral is transparent, and in thin sections it has anomalous grey interference colours, n = 1.443(2) (589 nm). Chemical composition (electron microprobe instrument, wt %) is following: CaO – 20.03; Y_2O_3 – 1.94, La_2O_3 – 2.32; Ce_2O_3 – 1.37; Pr_2O_3 – 1.37; Nd_2O_3 – 6.26; Sm_2O_3 – 1.90; Gd_2O_3 – 1.12; Dy_2O_3 – 0.44; Ho_2O_3 – 0.10; Al_2O_3 – 12.09; SO_3 – 9.38; F – 28.93; H2O (by difference) – 24.93, less O=F 12.18, total 100.00 wt%.Empirical formula is $Ca_{3.06}(Nd_{0.32}Y_{0.15}La_{0.12}Sm_{0.09}Ce_{0.07}Pr_{0.07}Gd_{0.05}Dy_{0.02}Ho_{0.01})_{0.90}Al_{2.03}S_{1.01}O_{3.96}F_{13.06}\cdot11.87H_2O$. Ideal formula is $Ca_3(Nd,Y)Al_2(SO_4)F_{13}\cdot12H_2O$. Cubic, space group Fd3, a = 16.759(3) Å, V = 4707.0(1) Å^3, Z = 8. Strong lines of X-ray pouder pattern are following (d-I(hkl)): 9.7-10(111); 5.92-7(220); 3.22-8(511); 2.555-7(533); 2.240-5(642); 2.180-6(731); 1.827-5(842). The IR spectrum is as follows: 3548, 3423, 1630, 1090, 586, 465 cm^{-1}. The type specimen of the new mineral is at the Fersman Mineralogical Museum, RAS (Moscow). 3 tables, 3 figures, and 11 references.

During the study of samples from the oxidized zone of ore deposits in Kazakhstan, a new neodymium-dominant analogue of chukhrovite-(Y) and chukhrovite-(Ce) has been found; it was named chukhrovite-(Nd)[*] according to the protocol in force for names of rare-earth minerals (Levinson, 1996).

Occurrence and mineral assemblages

Chukhrovite-(Nd) has been found in specimens from the oxidized zone of a molybdenum-tungsten deposit in Kara-Oba (Central Kazakhstan). The Kara-Oba ore field is located on the northeastern flank of the Chu-Iliisk ore belt in the central part of a volcano-tectonic structure. The deposit is connected with the multiphase Late Permian (260±5 Ma) intrusive massif of leucocratic granites breaking the effusive-fragmental series of Lower-Middle Devonian. There are four types of ore veins of different age att the deposit: molybdenite-quartz, wolframite-quartz, huebnerite-sulphide-quartz, and quartz-fluorite. Except for the latter type, the veins are accompanied by the zones of circum-vein greisens. The geology and mineralogy of the deposit have been considered in a number of publications (Shcherba, 1960; Ermilova *et al.*, 1960; Ermilova, 1964; Shcherba *et al.*, 1988; *etc.*). Chukhrovite-(Y) from the oxidized zone of this deposit was described as chukhrovite by L.P. Ermilova with co-authors (1960).

We have found chukhrovite-(Nd) in the specimens formed by columnar milky-white quartz i. Within the quartz there are small (up to 5 mm in length) lamellar grains of huebnerite. In numerous small cavities and interstitions of columnar quartz crystals, are powdery and microcrystalline crusts of jarosite, poorly shaped crystals of anglesite (up to 4 mm in size), druses of small crystals of creedite, massive snowy-white fine-grained aggregations of gearksutite or halloysite are often observed. In these specimens chukhrovite-(Nd) is presented by aggregations of isometric colourless grains and small, often poorly shaped crystals formed seemingly by a combination of cubic and octahedral faces (Fig. 1), with sizes ranging from 0.05 to 0.4 mm. Examining thin sections of chukhrovite-(Nd) grains and crystals from this association in COMPO and AEI modes, it was not possible to reveal any zoning or sectoring of mineral indi-

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[*] It was submitted and recommended for publication by the RMS (Russian Mineralogical Society), Commission on New Minerals and Mineral Names and approved by the IMA Commission on New Minerals and Mineral Names on August 5, 2004.

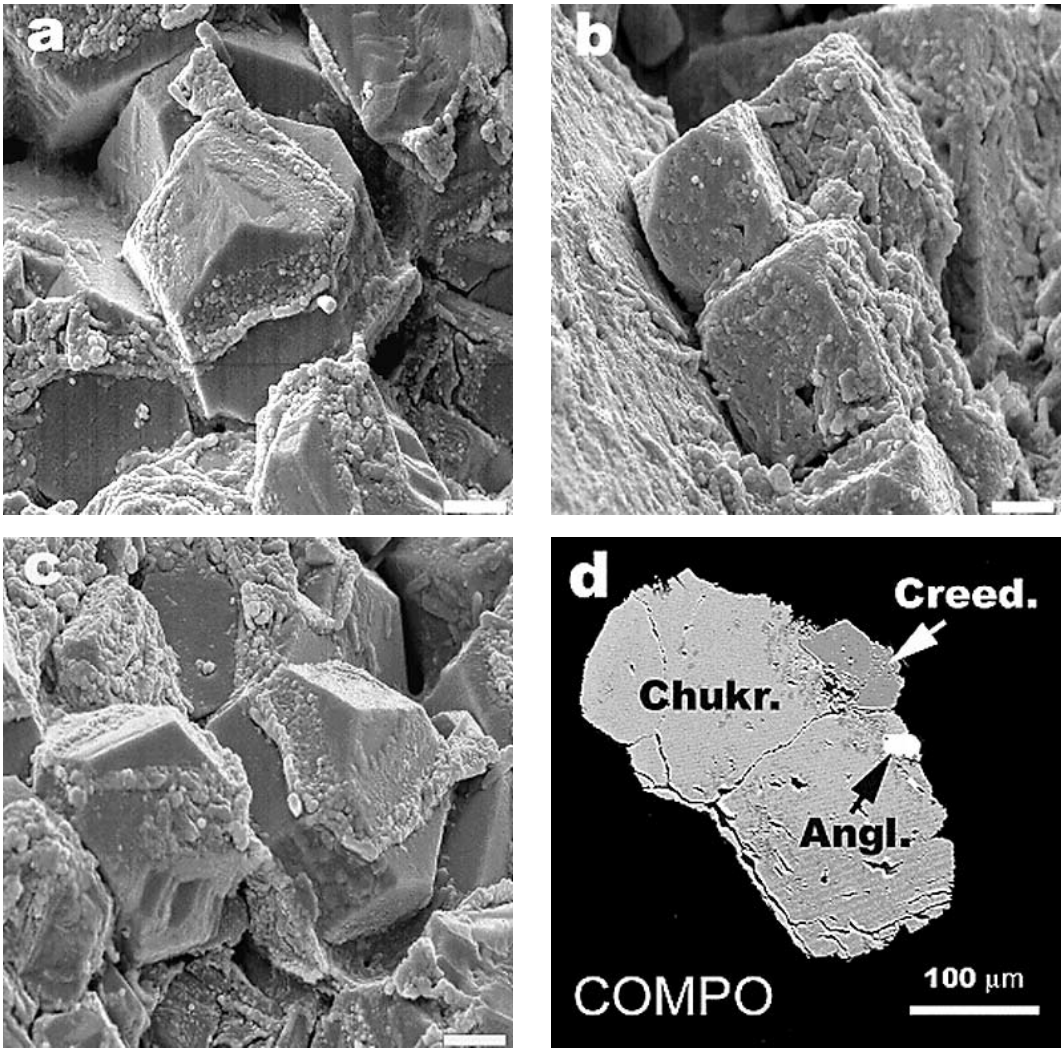

***Fig 1. a, b, c** — general view of chukhrovite-(Nd) crystals. SEM photo. Scale bar length is 10 µm; d — intergrowths of chukhrovite-(Nd) (Chukr) with creedite (Creed) and anglesite (Angl)*

Table 1**. Chemical composition of chukhrovite-(Nd) and chukhrovite-(Y)**

Constituent	1		2	3
	Chukhrovite-(Nd)		Chukhrovite-(Nd)	Chukhrovite-(Y)
	wt %	range	wt %	wt %.
CaO	20.03	19.19 — 20.73	19.89	21.41
Y_2O_3	1.94	1.52 — 2.71	2.37	5.44
La_2O_3	2.32	1.91 — 2.86	2.50	1.04
Ce_2O_3	1.37	1.06 — 1.67	3.36	2.12
Pr_2O_3	1.37	1.22 — 1.59	1.01	0.17
Nd_2O_3	6.26	5.45 — 6.58	5.28	2.31
Sm_2O_3	1.90	1.75 — 2.21	1.35	1.07
Gd_2O_3	1.12	0.67 — 1.47	0.69	0.83
Dy_2O_3	0.44	0.20 — 0.68	0.25	0.89
Ho_2O_3	0.10	0.03 — 0.26	0.07	n.d.
Al_2O_3	12.09	11.74 — 12.42		
SO_3	9.38	9.03 — 9.87		
F	28.93	28.48 — 29.37		
H_2O (by difference)	24.93			
-F=O	-12.18			
Total	**100.00**			

Note:
1 — average value calculated by 8 analyses and fluctuation of values for non-zonal grains of mineral from the first specimen;
2, 3 — incomplete electron microprobe analyses of zoned-sectored grain of chukhrovite from the second specimen (sample # 1208, V.I. Stepanov's collection, FMM). Analyses numbers correspond to points marked on the Figure 2. Analyses by L.A. Pautov.

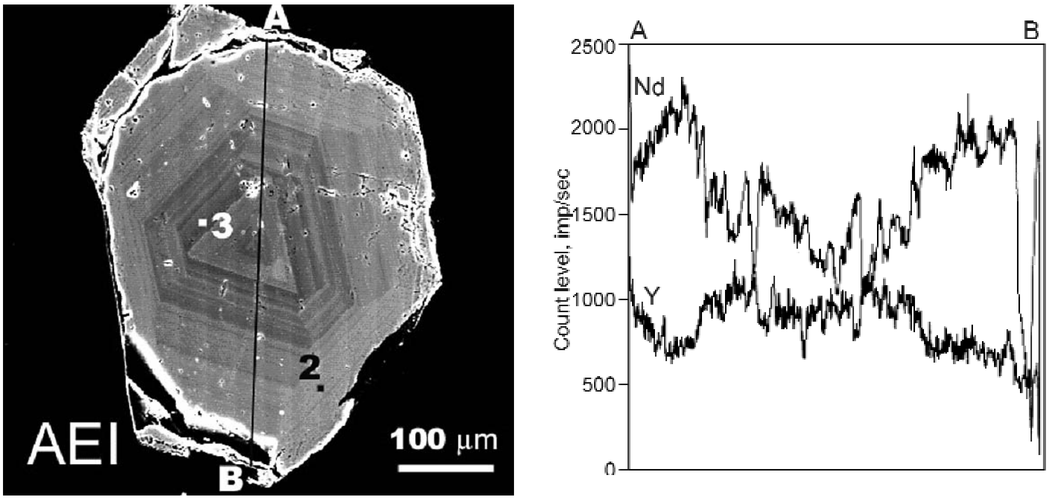

Fig 2. *Zoned-sectored crystal of chukhrovite and concentration profile of Nd and Y. Absorbed electron current image (inversed). Contrast is caused by average atomic number: the lighter parts correspond to heavier matrix. AB — profile line. 2, 3 — points of a local analysis, numbers correspond to analyses numbers in the Table 1*

viduals.

The second finding of the new mineral was made in the sample # 1208 from V.I. Stepanov's collection kept in the Fersman Mineralogical Museum. On the label belonging to this specimen the following is mentioned: «*Chukhrovite. Intergrowths of pinkish cube-octahedrons with white gearksutite. Kara-oba, vein # 8, Djambul quarry, NE Akdala, Central Kazakhstan. Collected in 1950.* V.I. Stepanov». The specimen is represented by a piece of milky-white quartz of columnar constitution (8x6x2 cm in size) with powdery coatings and crusts of ochreous colour and white, chalk-like concretions of gearksutite and halloysite. Rarely in the quartz there are small laths of ferberite and pseudomorphs of goethite after pyrite. The ochreous colour of the powdery coatings on the surface of the quartz is caused by fine-grained aggregates of jarosite, plumbojarosite, beudantite, and as yet undetermined iron hydroxides. In cavities among broken quartz crystals and along cracks there are segregations and individual crystals of the chukhrovite group mineral, up to 1 mm in diameter. Some crystals are water-clear, others are opaque and have a weak pink tint. Separate zones of growth that could be observed in zoned and sectored crystals in COMPO and AEI (Fig. 2) correspond to chukhrovite-(Nd) by chemical composition.

If not mentioned specifically, in all cases below the data on chukhrovite-(Nd) is from the first specimen.

Physical properties

Chukhrovite-(Nd) is a transparent mineral, most often colourless, and rarely, when translucent, white. The lustre is vitreous, slightly greasy. Streak is white. The mineral is brittle.

Cleavage on {111} is not easily visible. Hardness is 3.5-4 on Mohs' scale. Micro-indentation hardness measurements with VHN load of 30 gram gave a mean value 193 kg/mm^2 (from 177 to 213 kg/mm^2). Density determined by suspending of mineral grains in Clerici solution was 2.42(3) g/cm^3; calculated density was 2.421 g/cm^3.

In immersion the sample is colourless, it has anomalous interference colours from dark-grey to grey and undulating running extinction. Refractive index measured in a mixture of glycerine with water at 589 nm is n = 1.443(2).

Infrared spectrum of chukhrovite-(Nd) obtained with Specord-75IR spectrometer (tablet of mineral with KBr) is characterized by following strong absorption bands: 3548, 3423, 1630, 1090, 586, 465 cm^{-1} (Fig. 3). The presence of crystallization water in mineral is confirmed by bands in the ranges 3600-3200 cm^{-1} and 1630 cm^{-1} and sulphate tetrahedra indicated by the strong band at 1090 cm^{-1}.

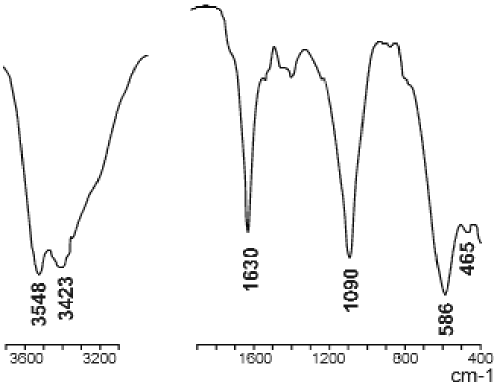

***Fig 3**. Infrared spectrum of chukhrovite-(Nd)*

The compatibility Index of properties and chemical composition, which was calculated by Gladstone and Dale equation, is 1 — (Kp/KC) = 0.012 (excellent).

Chemical composition

Chemical composition of the new mineral was determined with by JXA-50A (JEOL) electron microprobe instrument equipped with three wave spectrometers and an energy-dispersive spectrometer. The energy-dispersive spectrometer analyses were obtained at accelerating voltage U = 20 kV and electron microprobe current I = 2 nA, beam diameter was 2 μm. The etalons were as follows: anorthite USNM 137041 (Ca, Al, Si); Y_2O_3 (Y); LaF_3 (La); CeF_3 (Ce); $NdPO_4$ (Nd); $SmPO_4$ (Sm); $PrPO_4$ (Pr); $GdPO_4$ (Gd); Dy_2O_3 (Dy); Ho_2O_3 (Ho); $BaSO_4$ (S). Fluorine was determined with a wave spectrometer at accelerating voltage U = 15 kV, electron microprobe current I = 25 nA, and beam diameter 5 μm. Calculation of concentrations was made by CARAT program. The homogeneity of the grains was checked by scanning their profiles with wave spectrometers.

Zonal distribution of yttrium and rare-earth elements in the grains of chukhrovite-(Nd) from the first specimen was not revealed. Average chemical composition and fluctuation of component contents by analyses of 8 grains are given in Table 1. Because of the lack of material the water was not determined by the direct method; its content was calculated by difference. Empirical formula (based on the sum of cations, Ca + REE + Al = 6) from these analyses is as follows: $Ca_{3.06}(Nd_{0.32}Y_{0.15}La_{0.12}Sm_{0.09}Ce_{0.07}Pr_{0.07}Gd_{0.05}Dy_{0.02}Ho_{0.01})_{0.90}Al_{2.03}S_{1.01}O_{3.96}F_{13.06}\cdot 11.87H_2O$. The ideal formula is $Ca_3(Nd,Y)Al_2(SO_4)F_{13}\cdot 12H_2O$.

Table 2. **Results of calculation of X-ray powder pattern of chukhrovite-(Nd)**

I	$d_{meas.}$Å	$d_{calc.}$Å	*h k l*
10	**9.7**	**9.676**	**1 1 1**
7	**5.92**	**5.925**	**2 2 0**
3	5.04	5.053	3 1 1
1	4.87	4.838	2 2 2
4	4.20	4.190	4 0 0
3	3.85	3.845	3 3 1
8	**3.22**	**3.225**	**5 1 1**
1	2.957	2.963	4 4 0
3	2.836	2.833	5 3 1
4	2.646	2.650	6 2 0
7	**2.555**	**2.556**	**5 3 3**
3	2.343	2.347	7 1 1
5	**2.240**	**2.239**	**6 4 2**
6	**2.180**	**2.182**	**7 3 1**
1	2.096	2.095	8 0 0
3	1.975	1.975	8 2 2
2	1.936	1.935	7 5 1
5	**1.827**	**1.829**	**8 4 2**
1	1.756	1.757	9 3 1
4	1.681	1.684	7 7 1
1	1.641	1.643	10 2 0
0.5	1.611	1.613	10 2 2
0.5	1.562	1.563	9 5 3
1	1.511	1.511	11 1 1
1	1.461	1.464	9 7 1
0.5	1.418	1.416	10 6 2
0.5	1.358	1.359	10 6 4
1	1.282	1.282	11 7 1
0.5	1.201	1.200	13 5 1
0.5	1.141	1.140	14 4 2
0.5	1.077	1.075	11 11 1
0.5	1.063	1.064	12 10 2
0.5	1.039	1.041	13 9 3
0.5	1.009	1.009	16 4 2

In comparison, the crystals of the mineral from the second specimen have pronounced zoning and sectoring (fig. 2). In the photo the light growth zones and sectors are enriched by neodymium and accordingly depleted by yttrium. In such crystals the separate zones correspond by chemical composition to chukhrovite-(Nd), and the others correspond to chukhrovite-(Y). Incomplete analyses (obtained with energy-dispersive spectrometer at U = 20 kV, I = 2 nA) are given in Table 1. The Y and Nd concentration profiles across the crystal, were obtained with wave spectrometers. They are shown on Figure 2.

Table 3. **Comparison of data on chukhrovite-(Nd), chukhrovite-(Y), chukhrovite-(Ce), and menyailovite**

	Chukhrovite-(Nd) $Ca_3(Nd,Y)Al_2(SO_4)F_{13}\cdot 12H_2O$	Chukhrovite-(Y) $Ca_3(Y,Ce)Al_2(SO_4)F_{13}\cdot 12H_2O$	Chukhrovite-(Ce) $Ca_3(Ce,Nd)Al_2(SO_4)F_{13}\cdot 12H_2O$	Menyailovite $Ca_4AlSi(SO_4)F_{13}\cdot 12H_2O$
Space group	*Fd3*	*Fd3*	*Fd3*	*Fd3*
a,Å	16.759	16.80	16.80	16.722(2)
Z	8	8	8	8
Strong lines on X-ray	9.7(10)		9.75(10)	9.63(10)
powder pattern, d (I)	5.92(7)		5.93(8)	5.91(7)
	4.20(4)	3.261(9)	4.20(5)	4.173(4)
	3.22(8)	2.843(8)	3.22(7)	3.219(7)
	2.555(7)	2.572(9)	2.56(6)	2.551(7)
	2.240(5)	2.193(10)	2.24(5)	2.235(5)
	2.180(6)	1.834(10)	2.17(6)	2.178(8)
	1.827(5)	1.684(8)	1.824(5)	1.824(5)
	1.512(8)			
Density (measured), g/cm^3	2.42	2.274 – 2.398		2.25
n	1.443	1.42 – 1.44	1.443	1.430
Reference	Our data	Ermilova *et al.*, 1960	Walenta, 1978	Vergasova *et al.*, 2004

X–ray data

X-ray study of the mineral was made by powder method. X-ray powder pattern was obtained using RKU-114 mm camera, Mn filtered FeK radiation. Corrections were inserted by separate film with NaCl. Indexing was made by analogy with chukhrovite-(Y). Calculation of X-ray powder pattern is given in Table 2. The mineral has cubic symmetry, space group *Fd3*, a = 16.759(3)Å, V = 4707.0(1)Å^3, Z = 8.

Discussion

At present it is possible to distinguish the chukhrovite group, including three rare-earth silicon-free minerals with general formula $Ca_3REEAl_2(SO_4)F_{13}\cdot 12H_2O$, i.e. chukhrovite-(Y), chukhrovite-(Ce), chukhrovite-(Nd), and the silicon-bearing REE-free mineral, menyailovite, with the formula $Ca_4AlSi(SO_4)F_{13}\cdot 12H_2O$. The scheme of isomorphism among REE-minerals of this group and menyailovite can be represented as: $Al^{3+}_{VI} + REE^{3+}_{VII} => Si^{4+}_{VI} + Ca^{2+}_{VII}$. It is very difficult to judge the scale and borders of such isomorphism in natural specimens of the chukhrovite group minerals, because there are only a limited number of published chemical analyses available. By these few analyses of natural rare-earth chukhrovites the ratio Ca:REE is close to 3:1, in artificial analogues of chukhrovite the significant deviation from this ratio was obtained (Sokolova, Konovalova, 1981). However, there is no strict evidence that the synthetic analogue of chukhrovite chemical analyses obtained by wet chemistry methods reflects the composition of a homogenous phase.

Minerals of the chukhrovite group are studied up to different level. By contemporary nomenclature known as chukhrovite-(Y) with strong predominance of yttrium over lanthanides was the first mineral of this group discovered at the Kara-Oba deposit (Ermilova *et al.*, 1960). In the first description two chemical analyses were given, the rare-earth elements were determined by X-ray spectral method from the sediment precipitated from the mineral. Yttrium was not determined, but calculated by difference. The predominance of yttrium over lanthanides in many samples of chukhrovite from Kara-Oba is also confirmed by our microprobe electron analyses.

Another specimen of Y-dominant chukhrovite was found by M.I. Novikova (1973) in Siberia. Although unsuccessful in obtaining the complete chemical analysis of this mineral, the sum of rare-earth elements was determined, measuring 14.11%; the spectrum of these elements was detected by X-ray method. We shall note that in this work there are the contents of rare-earth oxides expressed in weight percents and relative weight percents of rare-earth elements from the sum of rare-earth oxides, but not atomic or molecular percents. That results in confusion: in reference literature the references on the work of M.I. Novikova (1973) have appeared as descriptions of chukhrovite-(Ce) although the simple re-calculation of weight percents in atomic ones shows the prevalence of yttrium over any other element from the lanthanides group.

S.V. Ryabenko with co-authors (1985) found the chukhrovite group mineral in a totally different occurrence at the Katugin deposit (Transbaikalie). It occured in nest segregations of cryolite with other fluorides. Unfortunately, in the aforementioned work there are no quantitative data about individual rare-earth elements and yttrium; moreover, it is not clear whether yttrium was detected. In this publication there is only a figure, spectrum of rare-earth elements, with not quite clear units on ordinates axis.

For the first time chukhrovite-(Ce) was described at Clara deposit (Oberwolfach, FRG) in barite and fluorite veins (Walenta, 1978). There is no quantitative data on the yttrium content in the mineral in that paper. Apparently, this is the single finding of Ce-dominant chukhrovite up till now. It would be interesting to study Clara deposit chukhrovite-(Ce) again a material of this finding to determine rare-earth elements and yttrium. As it was mentioned before, the mineralogical reference books give wrong information about chukhrovite-(Ce) from Siberia by M.I. Novikova (1973) since that mineral is evidently a chukhrovite-(Y).

The ratio of calcium to the sum of rare-earth elements and yttrium (in atoms per formula unit) is close to 3:1 for all enumerated natural rare-earth minerals from the chukhrovite group that gives the possibility to suppose the ordered distribution of calcium and rare-earth elements in the crystal structure of the mineral. However, at present there is only one work devoted to the study of the crystal structure of rare-earth chukhrovite, which was made by photomethod (R=13%) and which did not confirm this assumption (Bokii, Gorogotskaya, 1965). The crystal structure of menyailovite (Vergasova *et al.*, 2004) was not studied, but the crystal structure of its synthetic analogue (R=2.5%) has been determined (Mathew *et al.*, 1981). Thus, refinement of crystal structure of rare-earth representatives of the chukhrovite group and re-study of chukhrovite-(Ce) are the most important tasks in the study of this group of minerals.

Comparative characteristics of the chukhrovite group minerals are given in Table 3.

The sample with the grain of chukhrovite-(Nd) is kept in the Fersman Mineralogical Museum RAS (Moscow).

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TSEPINITE–Sr*, $(Sr,Ba,K)(Ti,Nb)_2(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$, A NEW MINERAL OF THE LABUNTSOVITE GROUP

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Tsepinite-Sr is a new mineral of the labuntsovite group (the vuoriyarvite subgroup); it is an analogue of tsepinite-Na, tsepinite-K, and tsepinite-Ca, with predominance of Sr among the extra-framework cations. Tsepinite-Sr has been found in hydrothermal paragenesis in cavities of nepheline-syenite pegmatite at the Mt. Eveslogchorr in the Khibiny massif, Kola Peninsula, Russia. It is associated with microcline, albite, natrolite, analcime, aegirine, eudialyte, leifite, vuoriyarvite-K, tsepinite-Ca, kuzmenkoite-Zn, paratsepinite-Ba, takanelite, etc. The mineral forms coarse-prismatic crystals up to 0.2 x 0.4 x 2 mm in size and crusts up to 4 x 5 mm. It is translucent, colourless or white; the streak is white, and the lustre is vitreous. The mineral is brittle, without cleavage; the fracture is uneven. The Mohs' hardness is ~5. The measured density is 2.67(2), and the calculated density is 2.63 g/cm^3. The mineral is optically biaxial, positive; $N_p = 1.649(2)$, $N_m = 1.651(2)$, $N_g = 1.770(4)$; $2V_{meas} = 20(5)°$, $2V_{calc} = 16°$. Chemical composition is as follows (the electron microprobe data, H_2O by TGA, wt %): Na_2O 0.61, K_2O 1.30, CaO 0.92, SrO 5.12, BaO 4.27, MgO 0.01, MnO 0.05, FeO 0.08, ZnO 0.26, Al_2O_3 0.18, SiO_2 41.89, TiO_2 18.49, Nb_2O_5 16.07, H_2O 11.14, total 100.39. The empirical formula calculated on $(Si,Al)_4O_{12}(O,OH)_2$ is as follows: $(Sr_{0.28}Ba_{0.16}K_{0.16}Na_{0.11}Ca_{0.09}Zn_{0.02})_{0.82}(Ti_{1.32}Nb_{0.69}Fe_{0.01})_{2.02}(Si_{3.98}Al_{0.02})_4O_{12}[(OH)_{1.89}O_{0.11}]_2 \cdot 2.59H_2O$. The ideal formula is $(Sr,Ba,K)(Ti,Nb)_2(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$ (Z = 4). The mineral is monoclinic; space group Cm. The unit cell parameters (from the single crystal data) are as follows: a = 14.490(3), b = 14.23(1), c = 7.881(3) Å, β = 117.28(2)°, V = 1444(1) Å^3. The strongest lines on the X-ray powder pattern are as follows (d,Å -I (hkl)): 7.10-90 (020, 001); 6.45-50 (200, 20-1); 5.01-40 (021); 3.230-100 (42-1, 400, 40-2); 3.135-80 (022, 041, 24-1); 2.510-80 (44-1, 401, 40-3, 042), 1.728-50 (461, 46-3, 081, 442, 44-4), 1.570-45 (84-1, 820, 84-3, 190, 82-4). The IR spectrum is given. The type specimen is deposited in the Fersman Mineralogical Museum RAS, Moscow.
3 tables, 1 figure, 12 references..

At present, the labuntsovite group minerals are the most studied natural zeolite-like titano- and niobosilicates. In the recent decade, they were being studied the most actively, that has resulted not only in the discovery of more than 20 new mineral species of this group and the disclosure of the wide distribution of its members in derivatives of alkaline complexes but also the revelation of a number of the important regularities concerning to crystal chemistry, properties, and genesis of microporous silicates with heteropolyhedral (mixed) frameworks in whole. We have established the nomenclature of the labuntsovite group approved by the IMA Commission on New Minerals and Mineral Names (CNMMN) (Chukanov *et al.*, 2002), and slightly later the data on these minerals was summarized in a special monograph (Chukanov *et al.*, 2003b). The members of the labuntsovite group are characterized by wide variations of the framework configuration, symmetry, cation order, and chemical compositions: each of 11 cations, excepting Si, i.e. Ti, Nb, Mn, Fe, Mg, Zn, Na, K, Ba, Sr, Ca, can be practically absent in the mineral composition or play a species-forming role, dominating in the respective structural site. The members of this group significantly excel the most of synthetic titano- and niobosilicates in their own diversity and perfection of crystals; therefore, the study of the crystal structures and properties of these minerals is of a great practical interest today. On the other hand, features of crystal chemistry of the labuntsovite group members are the important typomorphic signs reflecting conditions of mineral formation in alkaline pegmatites and hydrothermalites.

The unique framework of heteropolyhedral type is a basis of all labuntsovite-like structures. It is formed by the infinite chains of the M octahedra occupied by Ti and Nb atoms. In two other directions, the octahedra are connected with each other by the $[Si_4O_{12}]$ rings. Some mon-

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*It was approved by the IMA KNMMN on May 3, 2004.

Table 1**. Comparative characteristic of the vuoriyarvite sub-group minerals**

Mineral	Vuoriyarvite-K	Tsepinite-Na	Tsepinite-K	Tsepinite-Ca	Tsepinite-Sr
Formula	$(K,Na)_2(Nb,Ti)_2$ $(Si_4O_{12})(O,OH)_2 \cdot 4H_2O$	$(Na,H_3O,K)_2(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$	$(K,Ba,Na)_2(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$	$(Ca,K,Na)_{2-x}(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 4H_2O$	$(Sr,Ba,K)(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$
Symmetry	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Cm*	*Cm*	*Cm,*	*C2/m*	*Cm*
a, Å	14.629	14.604	14.327	14.484	14.49
b, Å	14.164	14.274	13.802	14.191	14.216
c, Å	7.859	7.933	7.783	7.907	7.88
β°	117.9	117.40	116.95	117.26	117.1
V, Å^3	1446	1468	1372	1445	1445
Z	4	4	4	4	4
D_{exp}, g/cm^3	2.95	2.74	2.88	2.73	2.67
n_p	1.649	1.655-1.658	1.689	1.666	1.649
n_m	1.655	1.661-1.668	1.700	1.676	1.652
n_g	1.759	1.770	1.7752	1.780	1.770
2V	+20°	+20–30°	+35°	+30°	+20°
Reference	Subbotin *et al.*, 1998	Shlyukova *et al.*, 2001	Chukanov *et al.*, 2003b	Pekov *et al.*, 2003	Present work

oclinic members of the group also contain the additional D octahedra occupied by Mn, Fe, Zn, Mg, rarely Ca, atoms. The bonds between the Si tetrahedra and the M octahedra are realized by the joint O vertices; the M octahedra are connected among themselves by the joint (O,OH) vertices, whereas with the D octahedra they are united by the joint O edges. The framework contains zeolite-like channels, in which are the large alkaline and alkaline-earth cations and the water molecules; the presence of vacancies is typical for the extra-framework sites (A, B, and C). These features and a set of the extra-framework cations (Na, K, Ca, Sr, and Ba), which is equal for the labuntsovite group members and the «true», i.e. aluminosilicate, zeolites, bring together these two groups of minerals.

The labuntsovite group unites the orthorhombic and monoclinic minerals with a general formula $A_4B_4C_{4-2x}[D_x(H_2O)_{2x}][M_8(O,OH)_8][Si_4O_{12}]_4 \cdot 4\text{-}12H_2O$, where x = 0-2. Eight structural types of the labuntsovite-like minerals are known; they differ in topology of the framework, symmetry, and unit cell dimensions; eight subgroups are distinguished in the labuntsovite group respectively. Among monoclinic members of the group, the members of the vuoriyarvite group are characterized by the most disordered and «friable» crystal structures. In them, the «linking» D octahedra are vacant, and the Ti and Nb atoms are strongly displaced from the centres of the M octahedra from the direction of one of the bridge vertices. The characteristic feature of the vuoriyarvite group minerals, which distinguishes them from the most of other members of the labuntsovite group, is the large number of the extra-framework sites of cations and the water molecules; many of them are brought together to the distances excluding their simultaneous occupation; as a result vacancies prevail in most of these sites. Because of that, in the vuoriyarvite subgroup, the mineral species are distinguished like in zeolites: all extra-framework sites (without subdivision into A, B, and C) are united, and the cation, prevailing over each other, is considered as a species-forming cation. This cation is entered in the suffix-modifier. In the vuoriyarvite subgroup, only niobium member, vuoriyarvite-K, and three titanium members: tsepinite-Na, tsepinite-K, and tsepinite-Ca, were known till now (Chukanov *et al.*, 2002, 2003b).

In the present work, a new titanium member of the vuoriyarvite subgroup is described; it belongs to the tsepinite series, in which strontium predominates among extra-framework cations (Table 1). According to accepted nomenclature, it was named tsepinite-Sr. The new mineral and its name were approved by the IMA CNMMN on May 3, 2004. The holotype specimen is deposited in the Fersman Mineralogical Museum RAS, Moscow (the registration number is 3169/1).

Occurrences and general appearance

The holotype of tsepinite-Sr was found in a pegmatite uncovered in the right bank of the Astrofillitovyi (Astrophyllite) stream on the south slope of the Mt. Eveslogchorr in southeast part of the Khibiny alkaline massif, Kola Peninsula, Russia. This pegmatite lens (up to 1 m thick) occurs in gneiss-like nepheline syenite. Like the most of pegmatites connected with nepheline syenites of the Khibiny massif, this pegmatite is composed mainly by microcline and aegirine, with subordinate amounts of nepheline, albite, and eudialyte; astrophyllite, lorenzenite, epididymite, mangan-neptunite, and belovite-(Ce) are usual here. In the pegmatite, especially in its cavernous core, the low-temperature hydrothermal mineralization is widespread. The whole parts are composed by late drusy albite, natrolite, analcime. Eudialyte is intensively replaced by catapleiite; abundant Mn-pectolite (or serandite?) is entirely altered to brown-black aggregates of takanelite. In cavities, leifite, thorite, vinogradovite, ancylite-(Ce), and barite occur; solid bituminous matters exude. The typical feature of this pegmatite is the diversity of late hydrothermal minerals of the labuntsovite group represented by members of the structural types with a low order of the extra-framework cations: vuoriyarvite, paratsepinite, and kuzmenkoite subgroup minerals. The zinc member of the group, kuzmenkoite-Zn, has been found here for the first time beyond the bounds of the Lovozero massif (Pekov *et al.*, 2004), also tsepinite-Na, tsepinite-K, tsepinite-Ca, tsepinite-Sr, and paratsepinite-Ba occur. Vuoriyarvite-K is the most widespread; it mainly composes fine-grained pseudomorphs after the well-shaped lamellar crystals of vuonnemite (up to 1 cm) in the pegmatite core. It forms also individual crystals on the surface of these pseudomorphs and in the cavities near them. Undoubtedly, at this place, vuonnemite was the source of Nb and Ti for vuoriyarvite-K. The other members of the labuntsovite group, indistinguishable from each other by sight here, mainly crystallize later than vuoriyarvite-K on the surface of pseudomorphs after vuonnemite or in the cavities on albite, microcline, and natrolite.

Tsepinite-Sr is one of the most rare minerals of the pegmatite. It occurs as coarse-prismatic, usually split crystals up to 0.2 x 0.4 x 2 mm in size. Sometimes they form crusts up to 4 x 5 mm and up to 0.3 mm thick, on the surface of vuoriyarvite pseudomorphs after vuonnemite. The crystals of new mineral are elongated on [010]. Their prism zone is formed mainly by faces {100} and {001}; these crystals are not well-terminated.

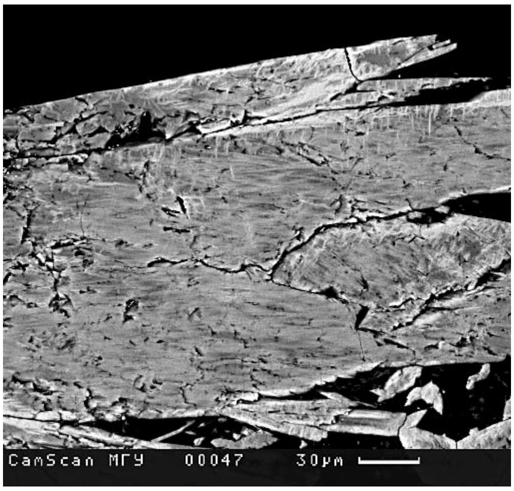

Figure 1*. Crystals of tsepinite-Sr with Ba-enriched (light parts) margin zones. Mt. Eveslogchorr, Khibiny. Image in reflected electrons*

Tsepinite-Sr was found also in two other pegmatites of the Khibiny-Lovozero complex, both remarkable for diversity of the labuntsovite group members (Chukanov *et al.*, 2003b). At the Mt. Khibinpakhkchorr, Khibiny, tsepinite-Sr forms zones in the white short-prismatic crystals of tsepinite-Na up to 1 mm in size (Shlyukova *et al.*, 2001); these crystals epitactially overgrow the orange crystals of labuntsovite in the cavities of khibinite pegmatite. In the cavities of pegmatite No. 45, occurring in poikilitic feldspathoid syenites at the Mt. Lepkhe-Nel'm in the Lovozero massif, tsepinite-Sr forms light beige prismatic crystals (up to 3 mm long) overgrowing on lamprophyllite and eudialyte.

Physical properties

Tsepinite-Sr from the Mt. Eveslogchorr is colourless and white, translucent to transparent, has the white streak and vitreous lustre. It is not fluorescent in ultraviolet light. The Mohs' hardness is ~ 5. The mineral is brittle; the cleavage was not observed; the fracture is uneven. The density measured by heavy liquids is 2.67(2), the calculated density is 2.63(1) g/cm^3.

The new mineral is optically biaxial, positive; $N_p = 1.649(2)$, $N_m = 1.651(2)$, $N_g = 1.770(4)$; $2V_{meas} = 20(5)°$, $2V_{calc} = 16°$. The dispersion is very weak, $r < v$. Tsepinite-Sr is colourless under microscope, no pleochroism. The orientation is $Y = b$.

The Gladstone-Dale compatibility (Mandarino, 1981) is 0.004 for the experimental density and -0.010 for the calculated density,

Таблица 2. **Химический состав цепинита-Sr**

№ an.	1	2	3	4	5	6
			wt.%			
Na_2O	0.61	0.55	0.69	0.77	2.22	1.26
K2O	1.30	1.71	1.65	2.30	1.25	1.81
CaO	0.92	0.85	1.39	1.36	2.11	1.03
SrO	5.12	5.57	4.89	5.67	8.64	4.66
BaO	4.27	0.81	5.25	2.06	1.62	2.15
MgO	0.01	bdl	0.01	0.01	bdl	bdl
MnO	0.05	0.11	bdl	bdl	bdl	0.06
FeO	0.08	0.05	0.05	bdl	bdl	0.16
ZnO	0.26	bdl	0.56	0.95	bdl	0.64
Al_2O_3	0.18	0.03	0.27	0.11	0.17	0.12
SiO_2	41.89	45.46	42.28	43.15	43.24	43.74
TiO_2	18.49	18.85	17.48	20.58	20.71	19.21
Nb_2O_5	16.07	19.27	17.95	14.93	13.50	14.51
H_2O	11.14	n.d.	n.d.	n.d.	n.d	n.d.
Total	100.39	93.26	92.47	91.89	93.46	89.35
Formula coefficients, calculation on (Si + Al) = 4						
Na	0.11	0.09	0.13	0.14	0.40	0.22
K	0.16	0.19	0.20	0.27	0.15	0.21
Ca	0.09	0.08	0.14	0.13	0.21	0.10
Sr	0.28	0.28	0.27	0.30	0.46	0.25
Ba	0.16	0.03	0.19	0.07	0.06	0.08
Mn	–	0.01	–	–	–	–
Zn	0.02	–	0.04	0.06	–	0.04
Σ A	**0.82**	**0.68**	**0.97**	**0.97**	**1.28**	**0.90**
Fe	0.01	–	–	–	–	0.01
Ti	1.32	1.25	1.23	1.43	1.43	1.32
Nb	0.69	0.77	0.76	0.62	0.56	0.60
Σ M	**2.02**	**2.02**	**1.99**	**2.05**	**1.99**	**1.93**
Al	0.02	–	0.03	0.01	0.02	0.01
Si	3.98	4.00	3.97	3.99	3.98	3.99

Note:
1-4 – Mt. Eveslogchorr, Khibiny (including 1 – holotype); 5 – Mt. Khibinpakhkchorr, Khibiny; 6 – Mt. Lepkhe-Nel'm, Lovozero;
bdl – below detection limits of electron microprobe method (contents of REE, Zr, Ta, F are bdl in all analyses);
n.d. – content of water was not detected.
A – extra-framework cations: Na, K, Ca, Sr, Ba, Mn, Zn;
M-cations: Ti, Nb, Fe.

i.e. «superior» in both cases.

The IR spectrum of the new mineral is close to spectra of other members of the vuoriyarvite subgroup. The absorption bands are as follows (cm^{-1}; frequencies of the most intensive bands are underlined; sh – shoulder, w – wide band): 3545, 3475, 3290w, 1665, 1605, 1537, 1135sh, 1120, 949, 935sh, 760sh, 675, 610sh, 450. The low-frequency position of a band corresponding to stretching vibrations (Ti,Nb)-O (675 cm^{-1}) confirms that the D octahedron is significantly vacant (Chukanov *et al.*, 2003b). Tsepinite-Sr is only mineral of the labuntsovite group, in which IR spectrum are more than two well-distinguished bands in the range of bending vibrations of the water molecules, i.e. bands at 1665, 1605, and 1537 cm-1. Undoubtedly, this phenomenon is connected with unusually great amount of non-equivalent sites of H2O in zeolite channels (Rozenberg *et al.*, 2003).

Chemical composition

Chemical composition of the new mineral (Table 2) was studied by the electron microprobe method; the water content was detected by thermogravimetric procedure. The empirical formula of the holotype calculated on $(Si,Al)_4O_{12}(O,OH)_2$ is as follows: $(Sr_{0.28}Ba_{0.16}K_{0.16}Na_{0.11}Ca_{0.09}Zn_{0.02})_{0.82}(Ti_{1.32}Nb_{0.69}Fe_{0.01})_{2.02}(Si_{3.98}Al_{0.02})_4O_{12}[(OH)_{1.89}O_{0.11}]_2 \cdot 2.59H_2O$. The O/OH ratio is calculated by the charge balance. The ideal formula (Z = 4) is: $(Sr,Ba,K)(Ti,Nb)_2(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$.

In minerals of the tsepinite series, the ratios of the extra-framework alkaline and alkaline-earth cations vary widely. It is evident from Table 2 that tsepinite-Sr is represented by the varieties enriched by Ba, Na, or K. At the same time, the samples from different localities are quite close to each other by the Ti/Nb ratio and the low content of the small bivalent cations (Mn, Zn, Fe, Mg).

The significant variations of composition of the extra-framework cations are usual within a single crystal. On the Figure, it is evidence that peripheral parts of the tsepinite-Sr crystals from the Mt. Eveslogchorr are significantly enriched by barium. The «spotted» internal constitution is typical for many crystals from Lovozero: the parts with Na>Sr and Sr>Na are distributed irregular in them. At the same time, in the samples from the Mt. Eveslogchorr, the sharp phase bounds between the individuals of tsepinite-Sr and kuzmenkoite-Zn and also tsepinite-Sr and vuoriyarvite-K were observed. The latter pair of minerals is especially interesting, because its members belong to the same structural type. Probably, the distribution of the extra-framework cations between the niobium and titanium members of the group is caused by the charge restrictions, according to the isomorphous scheme: $Nb^{5+} + K^{+} \quad Ti^{4+} + A^{2+}$, where A^{2+} = Sr, Ba, Ca.

Tsepinite-Sr is the second member of the labuntsovite group, after alsakharovite-Zn, $NaSrKZn(Ti,Nb)_4[Si_4O_{12}]_2(O,OH)_4 \cdot 7H_2O$ (Pekov *et al.*, 2003b), in which strontium plays species-forming role. The highest content of strontium (8.6 wt % SrO) in the minerals of this

Table 3. **Results of calculation of X-ray powder diagram of tsepinite-Sr.**

$I_{meas.}$	$d_{meas.}$ Å	$I_{calc.}$	$d_{calc.}$ Å	*h k l*
90	7.10	100, 88	7.108, 7.015	020, 001
50	6.45	64, 73	6.450, 6.425	200, 20-1
40	5.01	72	4.993	021
5	4.78	6, 10	4.776, 4.766	220, 22-1
10	3.92	12, 10	3.937, 3.921	201, 20-2
100	3.230	45, 34, 33	3.228, 3.225, 3.213	42-1, 400, 40-2
80	3.135	47, 25, 26	3.145, 3.113, 3.110	022, 240, 24-1
3	3.015	2	3.021	311
20	2.945	11, 10	2.937, 2.927	420, 42-2
30	2.643	2, 6, 7, 6, 8	2.673, 2.638, 2.633, 2.621, 2.613	15-1, 241, 24-2, 202, 20-3
80	2.510	19, 11, 13, 37	2.537, 2.526, 2.514, 2.496	44-1, 401, 40-3, 042
5	2.156	4	2.150	600
5	2.091	1, 3	2.104, 2.093	511, 351
20	2.057	7, 4, 7, 2	2.059, 2.058, 2.052, 2.051	441, 620, 44-3, 62-3
10	1.961	8	1.963	062
15	1.813	12	1.811	80-2
10	1.781	13	1.777	080
10	1.755	1, 2, 7	1.755, 1.755, 1.754	82-2, 26-3, 004
50	1.728	7, 6, 3, 9, 10	1.728, 1.724, 1.723, 1.722, 1.717	461, 46-3, 081, 442, 44-4
5	1.675	1, 3	1.680, 1.678	66-1, 66-2
45	1.570	8, 3, 7, 1, 4	1.574, 1.572, 1.571, 1.568, 1.567	84-1, 820, 84-3, 190, 82-4
5	1.468	1, 3, 4	1.469, 1.468, 1.464	28-3, 840, 84-4
10	1.448	6, 6, 6, 1	1.453, 1.451, 1.445, 1.442	481, 48-3, 443, 10.0.-2

Note: *camera RKU-114.6, FeKα radiation, Mn filter. Indexes hkl are selected in accordance with $I_{meas.}$ values obtained from structural data.*

group is detected in tsepinite-Sr from the Mt. Khibinpakhkchorr (an. *5* in Table 2). We should note that Sr as well as Ca is the most typical for members of the vuoriyarvite and gutkovaite subgroups; Sr is a usual minor admixture in minerals of the paratsepinite, organovaite, and kuzmenkoite subgroups; but this element is absolutely untypical for members of the labuntsovite sensu stricto, paralabuntsovite, and lemmleinite subgroups with more ordered distribution of the extra-framework cations.

X-ray data and crystal structure features

The X-ray study of a single crystal of tsepinite-Sr carried out by a diffractometer ENRAF NONIUS has obtained the monoclinic symmetry (space group *Cm*) and the following unit cell parameters: a=14.490(3), b=14.23(1), c=7.881(3) Å, β =117.28(2)°, V=1444(1) Å^3 (Rozenberg *et al.*, 2003). The X-ray powder pattern of the new mineral (Table 3) is close to ones of other members of the tsepinite series. The unit cell parameters obtained from X-ray powder data are as follows: a=14.49(2), b=14.216(6), c=7.88(1) Å,β=117.1(1)°, V=1445(3) Å^3.

The crystal structure of tsepinite-Sr studied on a single crystal is described in the work of K.A. Rozenberg with co-authors (2003). Its basis is the mixed framework, typical for the labuntsovite group minerals; it consists of the chains of the vertex-linked (Ti,Nb)O$_6$ octahedra and the fourfold rings of the SiO$_4$ tetrahedra, connecting them. The Sr, K, Ca, Na, and Ba atoms and the water molecules occupy 15 sites (instead 7-8 sites in the ordered members of the labuntsovite and lemmleinite groups and 12 sites in tsepinite-Na and vuoriyarvite-K) in the channels parallel to the coordinate axes. Five sites contain the cations, 7 — the water molecules, and 3 — the cations and water molecules together. Thus, tsepinite-Sr is one of the most cation-disordered members of the labuntsovite group. In the new mineral, the vacancies predominate in all extra-framework sites. It differs from tsepinite-Na not only by the prevalence of Sr among the extra-framework cations but also its distribution. In tsepinite-Sr, atoms of strontium is situated in three sites; in tsepinite-Na (Rastsvetaeva *et al.*, 2000), first of these sites is also occupied by Sr, the second site -by Na, and the third site is vacant.

Genetic features

It is experimentally found that members of the vuoriyarvite subgroup, especially titanium ones, tsepinites, have the strongest cation-exchange properties among all labuntsovite-like minerals (Pekov *et al.*, 2002). We conceive it is caused by a combination of four following features: 1) the low content of the extra-framewor inning (especially in tsepinite-Na). It is quite possible that the relative enrichment of the vuoriyarvite subgroup minerals by Ca and Sr, the high degree of site splitting in the zeolite channels, and the «spotted», irregular distribution of parts with different composition of the extra-framework cations in crystals are just a result of the natural ion-exchange processes taking place at late hydrothermal stages. The enrichment of margin parts of crystals by barium can be caused by the same process (see Figure). Perhaps, the origin of tsepinite-Sr, enriched by so untypical for the labuntsovite group members component as strontium, with maximally disordered distribution of zeolite cavities «stuff», is possible only by the ion-exchange way.

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UDC 549.6

SENKEVICHITE, $CsKNaCa_2TiO[Si_7O_{18}(OH)]$, A NEW MINERAL

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Senkevichite is a new cesium mineral, which has been found in the alkaline massif of Darai-Piyoz (Tajikistan). The mineral forms intergrowths of elongated board-like grains up to 1 mm in light in quartz-pectolite aggregates from blocks consisting mainly of granulated massive quartz. When transparent, the mineral is colourless, otherwise, white. The fracture is brittle. The Mohs hardness is 5.5-6. Measured density is 3.12 g/cm^3. The mineral is biaxial, optically positive; $\alpha_p = 1.616(2)$, $\beta_m = 1.645(2)$, $\gamma_g = 1.683(2)$. Triclinic, space group P-1; a = 10.4191(4) Å, b = 12.2408(5) Å, c = 7.0569(3) Å, V = 887.8(1) Å^3, Z = 2. Chemical composition is as follows (electron microprobe analysis; H_2O is calculated, wt %): SiO_2 – 50.48, TiO_2 – 8.94, Nb_2O_5 – 0.64, FeO – 0.50, MnO – 2.59, CaO – 11.09, Na_2O – 3.73, K_2O – 6.13, Cs_2O – 15.28, H_2O (calc) – 1.09, total – 100.47. Empirical formula of the mineral is $Cs_{0.90}K_{1.08}Na_{1.00}(Ca_{1.65}Mn_{0.30}Fe_{0.06})_{2.01}(Ti_{0.93}Nb_{0.04})_{0.97}O_{0.97}[Si_7O_{18}(OH)]$. Ideal formula is $CsKNaCa_2TiO[Si_7O_{18}(OH)]$. Strong lines on X-ray powder diagram are following (d, I): 4.08 (13), 3.33 (11), 3.25(25), 3.14 (21), 3.06 (100), 2.959 (20), 2.038 (17). Crystal structure is solved with R = 4.5%. The type specimen of the new mineral is kept in the Fersman Mineralogical Museum RAS (Moscow, Russia).
3 tables, 4 figures, 7 references

Senkevichite, a new member of the cesium natural silicates with the formula $CsKNaCa_2TiO[Si_7O_{18}(OH)]$, has been found at the Darai-Piyoz glacier (Tajikistan) in a moraine line with the same name as the alkaline massif. The mineral was encountered in a block of granulated quartz in assemblage with aegirine, pectolite, stillwellite-(Ce), polylithionite, leucosphenite, neptunite, baratovite, fluorite, pekovite, zeravshanite, etc. Senkevichite was named in honour of Yurii Alekseevich Senkevich (1937-2003), outstanding Russian traveller, medical officer, researcher of the behaviour of the human organism in extreme conditions, famous TV reporter and journalist. Senkevichite is Cs analogue of tinaksite (Rogov, 1965).

Occurrence and mineral assemblage

Senkevichite has been found in the rocks samples from the Upper Darai-Piyoz alkaline massif, which were collected at the moraine of the Darai-Piyoz glacier (Garm region, Central Tajikistan). A number of publications have been devoted to the geology and mineralogy of the massif (Dusmatov, 1968, 1971; Belakovsky, 1991; etc.). The Darai-Piyoz massif is difficult to access because of complicated mountain relief; therefore the main part of mineralogical studies have been carried out on material collected in moraine deposits of the glacier cutting the massif. Diversity of proper cesium minerals is one of the peculiarities of the Darai-Piyoz alkaline massif. At present, in the rocks of this massif, the following minerals of cesium have been discovered: cesium kupletskite, telyushenkoite, zeravshanite, sokolovaite, and senkevichite. Probably, the list of cesium minerals will be expanded during further study of the mineralogy of the massif.

Senkevichite has been found in so called «quartz block», composed predominantly by granulated quartz. It was written about this unusual rock in detail earlier (Pautov, 2004). The mineral was found in a polymineral brown aggregate, which sometimes occurs in «quartz blocks». The aggregate consists mainly of pectolite with minor amounts of quartz. Besides these minerals there are accessory amounts of aegirine, fluorite, polylithionite, neptunite, hyalotekite, baratovite in the aggregate; extremely rare sokolovaite and pekovite occur in it. Senkevichite intergrows with

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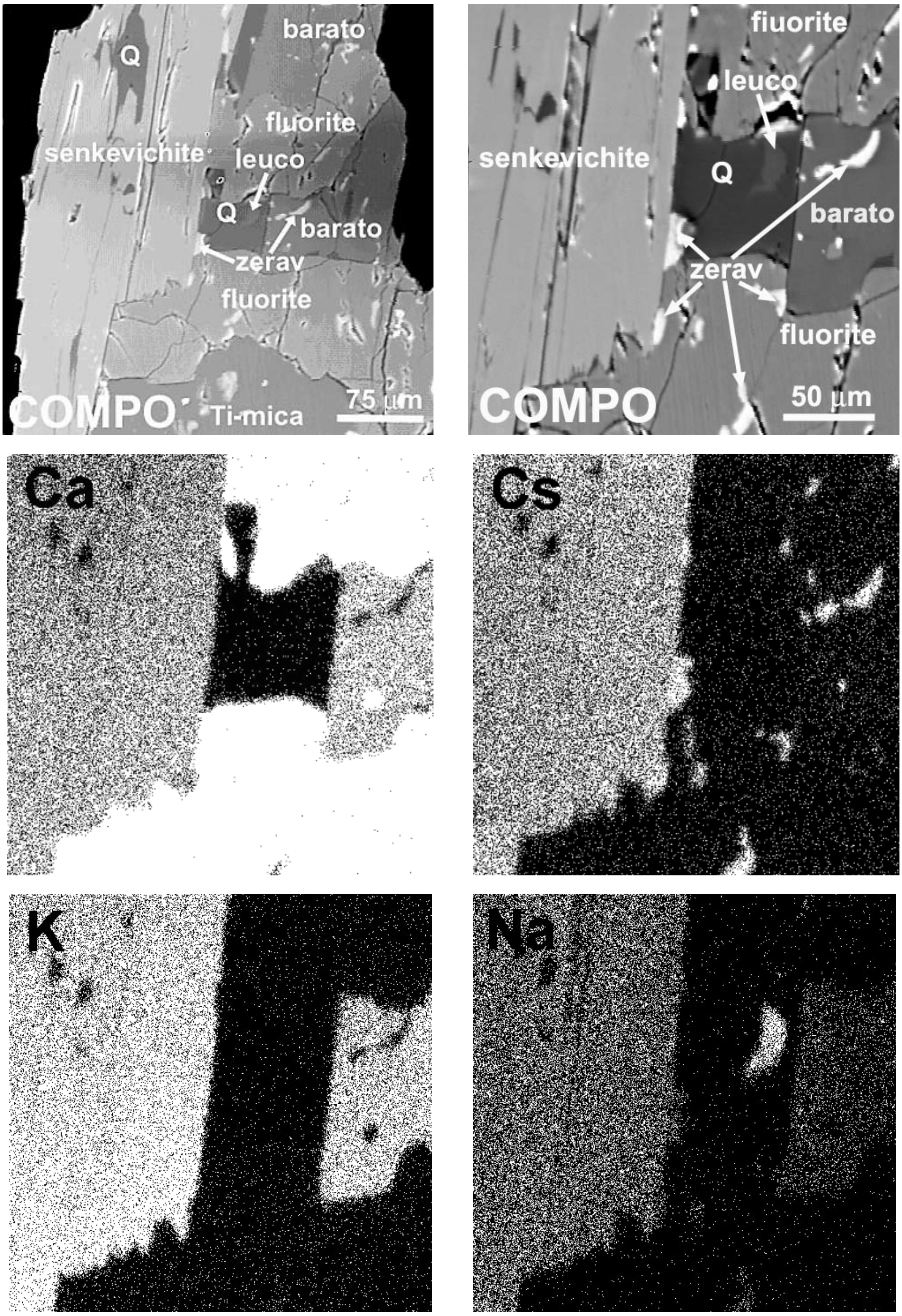
[*] The mineral was considered and recommended for publication by the Russian Mineralogical Society Commission on New Minerals and Mineral Names and approved by the IMA Commission on New Minerals and Mineral Names on July 13, 2004

[**] The name of the gorge, where the alkaline massif of the same name is located, is translated from Tajik as «onion pie» and has the English version «darai-piyoz». In the first publications, the geographic name of the alkaline massif was also Darai-Piyoz. Below the authors will follow the same orthography


Q
barato
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senkevichite
leuco
Q
barato
zerav
fluorite
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Ti-mica
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senkevichite
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barato
zerav
fluorite
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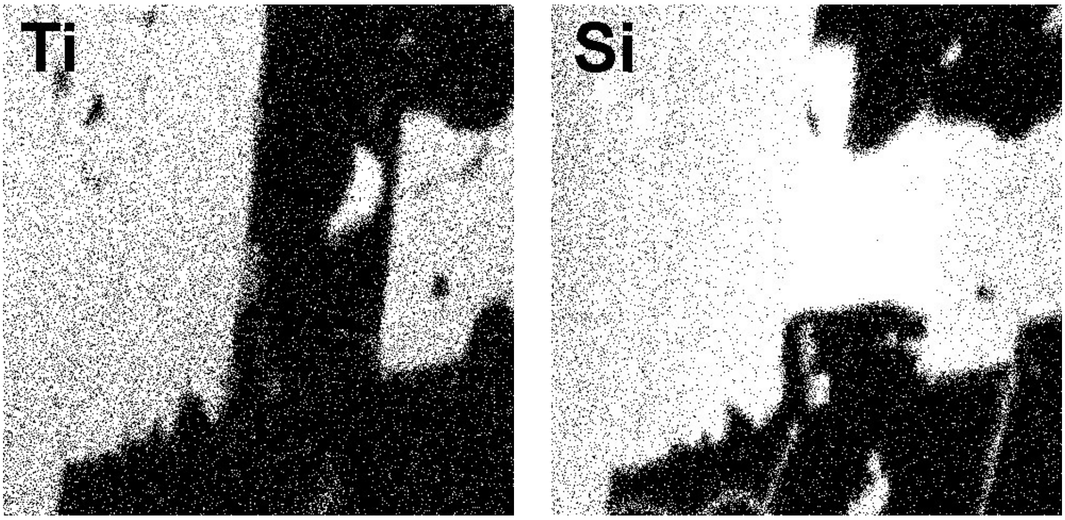

Fig. 1. *Intergrowth of senkevichite with fluorite (fluorite), quartz (Q), zeravshanite (zerav), leucosphenite (leuco), baratovite (barato), and presumably new mineral, titanium mica (Ti-mica). Image in COMPO regime and characteristic emanation of indicated elements*

neptunite, baratovite, quartz, pectolite, leucosphenite, fluorite, and a potentially new titanium mica (Fig. 1).

Physical properties

Senkevichite is a colourless, transparent mineral with strong vitreous lustre. It often looks white because of cracks. The mineral forms intergrowths of elongated board-like grains up to 1 mm in size. The Mohs hardness is 5.5-6. Micro-indentation measurements with a VHN load of 100g gave a mean value of 650 kg/mm^2 (20 measurements with the range from 611 to 708 kg/mm^2). The mineral is brittle. Mineral density was determined by grain balancing in Clerici solution. Measured density of the mineral is 3.12(2) g/cm^3; calculated density is 3.13 g/cm^3. Senkevichite is optically positive, biaxial. Refraction indexes obtained by immersion method (at 589 nm) are as follows: $\alpha_p = 1.616(2)$, $\beta_m = 1.645(2)$, $\gamma_g = 1.683(2)$. Angle measured on Fedorov's stage $2V = 85(2)°$, calculated angle is 84°. Dispersion is strong, $r < v$. The mineral is insoluble in water and HCl (1:1). The IR spectrum of senkevichite obtained with Specord-75IR instrument (the sample is a tablet of mineral with KBr) is close to the IR spectrum of tinaksite (Fig. 2); it is characterized by the following absorption bands (cm^{-1}): 3450, 3380, 1262(sh), 1092, 1065, 1035, 965, 880, 780, 718(sh), 703, 678, 652, 638, 541, 508, 480, 467.

Chemical composition

Chemical composition of senkevichite was analyzed with JCXA-50A (JEOL) electron microprobe instrument equipped with an energy dispersive spectrometer and three wave spectrometers. Analyses were obtained on an energy dispersive spectrometer at accelerating voltage of 20 kV and electron microprobe current of 20 nA. The standards used are as follows: microcline USNM143966 (Si, K), synthetic jadeite $NaAlSi_2O_6$ (Na), synthetic $CsTb(PO_3)_4$ (Cs), ilmenite USNM 96189 (Ti). It was not possible to detect water by direct method because of the small amount of material; its content was calculated. Concentrations were calculated by program of ZAF correction. Homogeneity of grains was checked with wave spectrometers. 6 grains were analysed. The average chemical composition of the analysed grains (Table 1) can be calculated for Si = 7 on empirical formula: $Cs_{0.90}K_{1.08}Na_{1.00}(Ca_{1.65}Mn_{0.30}Fe_{0.06})_{2.01}(Ti_{0.93}Nb_{0.04})_{0.97}O_{0.97}[Si_7O_{18}(OH)]$. Ideal formula of senkevichite is $CsKNaCa_2TiO[Si_7O_{18}(OH)]$. The compatibility index of coincidence of properties is $(1-K_p/K_c) = 0.017$, that is superior category.

X-ray data

X-ray powder diagram of senkevichite was obtained with DRON-2 diffractometer instrument (Table 2); it is individual and well-indicated

Table 1. **Chemical composition senkevichite (wt %)**

	1	2	3	4	5	6	7	8	Average
SiO_2	50.92	49.94	50.36	50.83	50.87	50.51	50.42	50.00	50.48
TiO_2	8.52	8.90	9.41	9.14	8.83	8.73	8.71	9.28	8.94
Nb_2O_5	0.61	0.59	0.39	0.46	0.59	0.89	0.85	0.72	0.64
FeO	0.36	0.73	0.47	0.61	0.48	0.45	0.45	0.43	0.50
MnO	2.47	3.40	2.29	2.60	2.26	2.67	2.66	2.39	2.59
CaO	11.20	9.82	11.04	11.81	11.24	11.62	11.60	10.38	11.09
Na_2O	3.70	3.84	3.56	3.75	3.78	3.90	3.58	3.74	3.73
K_2O	6.12	5.78	6.34	6.22	6.02	6.12	6.15	6.25	6.13
Cs_2O	15.68	15.51	14.77	14.78	14.92	15.56	15.57	15.46	15.28
$H_2O_{calc.}$	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
Total	100.57	100.80	99.83	100.45	100.23	101.05	100.32	100.39	100.47

Note: *analysts A.A. Agakhanov and L.A. Pautov.*

in suggested parameters of unit cell of triclinic system: a = 10.4191(4)Å, b = 12.2408(5)Å, c = 7.0569(3)Å, α = 90.857(1)°, β = 99.193(1)°, γ = 91.895(1)°, V = 887.8(1) $Å^3$, space group P-1, Z = 2.

Crystal structure of senkevichite was refined to an R_1 index of 4.5% for 4872 inique reflexes (Bruker P4 diffractometer with four-circle CCD detector, MoKα -radiation) (Sokolova *et al.*, 2005 in press). General, the crystal structure of senkevichite represents a mixed framework construction formed by silica-oxide chains and bands of Na-polyhedra and octahedra of Ti and Ca; there are Cs and K atoms in the cavities of the framework. There are seven tetrahedral Si sites (<Si-O> = 1.623Å); six of these tetrahedra are surrounded by oxygen atoms, one tetrahedron, Si(7), is surrounded by three oxygen atoms and an (OH) group. Also there are three sites M in sixfold coordination: M(1) is occupied predominantly by Ti with small portion of Nb (<M(1)-O> = 1.985 Å), M(2) is filled up solely by Ca (<M(2)-O> = 2.382Å), and M(3) is occupied by Ca with small portion of Fe^{2+} and Mn^{2+} (<M(3)-O> = 2.317Å sites: there are a site of Na-polyhedron with sevenfold coordination (<Na-O> = 2.504Å) and two A sites. Among them [12]-coordinated A(1) is occupied predominantly by Cs (with a small portion of K) (<A(1)-O> = 3.318Å), [10]-coordinated A(2) is filled up by K (<A(2)-O> = 2.986Å). In senkevichite, silica-oxide chains represent an infinite chain of hybrid clusters $[Si_7O_{18}(OH)]^{9-u}$, composed of two wollastonite-like chains jointed by common oxygen atom and additional Si-tetrahedron (Fig. 3a). M(1) octahedra and Na-polyhedra are connected by common edges and form a band with two polyhedra width; M(2) and M(3) octahedra jointing by common edges form another band with width also in two polyhedra (Fig. 3b). These bands extend along the c axis and, joined by common vertices, form the layers parallel to (011). Hybrid doubled chains $[Si_7O1_8(OH)]^{9-u}$, M(2) and M(3) octahedra, and

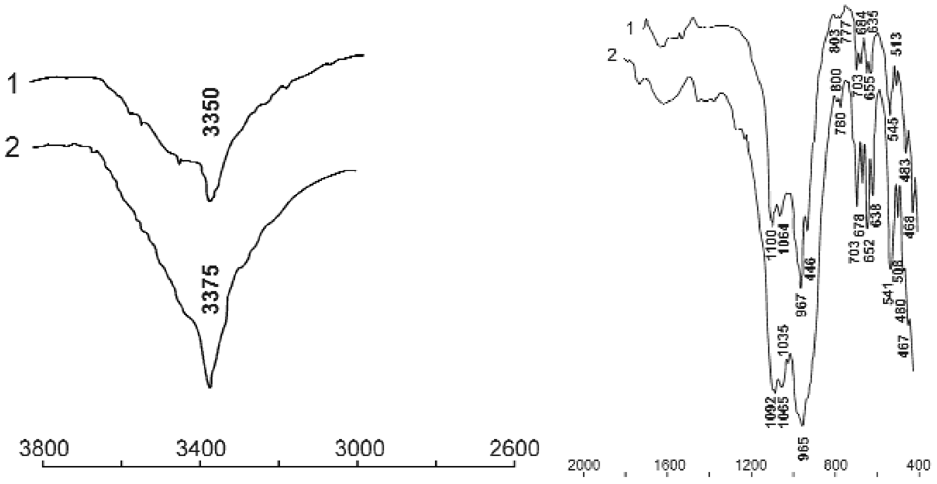

Fig. 2. *The IR-spectra of tinaksite (1) and senkevichite (2). Analysts: N.V. Chukanov, L.A. Pautov*

Table 2. **X-ray powder diffraction data of senkevichite**

I	$d_{meas.}$	$d_{calc.}$	*h k l*
3	10.30	10.28	1 0 0
5	**5.16**	5.17	2 0 0
3	4.97	4.99	1 -1 1
3	4.67	4.68	2 1 0
		4.64	0 2 -1
4	4.49	4.49	2 0 -1
4	4.36	4.38	1 -2 -1
5	4.16	4.19	2 1 -1
13	**4.08**	4.08	0 3 0
7	**4.01**	4.01	2 -2 0
3	3.88	3.87	2 2 0
		3.85	2 0 1
3	3.60	3.63	2 1 1
3	3.54	3.55	0 3 -1
3	3.43	3.43	3 0 0
11	**3.33**	3.35	1 1 -2
		3.33	0 1 2
		3.33	3 -1 0
4	3.28	3.27	3 1 0
16	**3.25**	3.25	2 -3 0
21	**3.14**	3.14	2 3 0
		3.15	1 0 2
100	**3.06**	3.06	0 4 0
		3.07	2 0 -2
		3.05	2 -3 -1
		3.04	3 -2 0
		3.03	2 -1 -2
20	**2.959**	2.96	1 -4 0
7	**2.904**	2.903	1 4 0
5	2.673	2.675	0 3 -2
		2.671	3 -3 0
7	**2.578**	2.579	3 2 1
		2 578	3 3 0
3	2.453	2.454	3 -2 -2
3	2.401	2.406	3 -3 1
4	2.323	2.323	3 -4 0
4	2.241	2.242	3 4 0
17	**2.038**	2.039	0 6 0
7	2.014	2.014	1 -6 0
3	1.985	1.986	2 4 2
3	1.937	1.940	3 5 -1
		1.940	1 -6 -1
5	1.826	1.827	5 -2 1
		1.826	4 -4 -2
6	**1.712**	1713	1 7 0
5	1.673	1.673	2 -7 0
1	1.667	1667	0 5 3
		1.666	2 -2 -4
5	**1.637**	1.637	5 -4 -2
1	1.631	1.629	3 -6 -2
2	1.616	1.616	5 -2 2
3	1.602	1.602	4 4 2
3	1.542	1.542	4 -5 2
		1.542	3 3 -4
	1.520	1.520	1 -8 0
2	1.468	1.468	7 0 0
3	1.439	1.440	7 -2 0
4	1.379	1.380	6 5 0
4	1.358	1.359	0 9 0
2	1.331	1.331	2 3 -5

Note: *DRON-2 diffractometer, Fe anode, graphite monochromator, counter rate is 1 grad/min, the internal standard is quartz. Analyst A.A. Agakhanov The strong lines are marked by semi-bold*

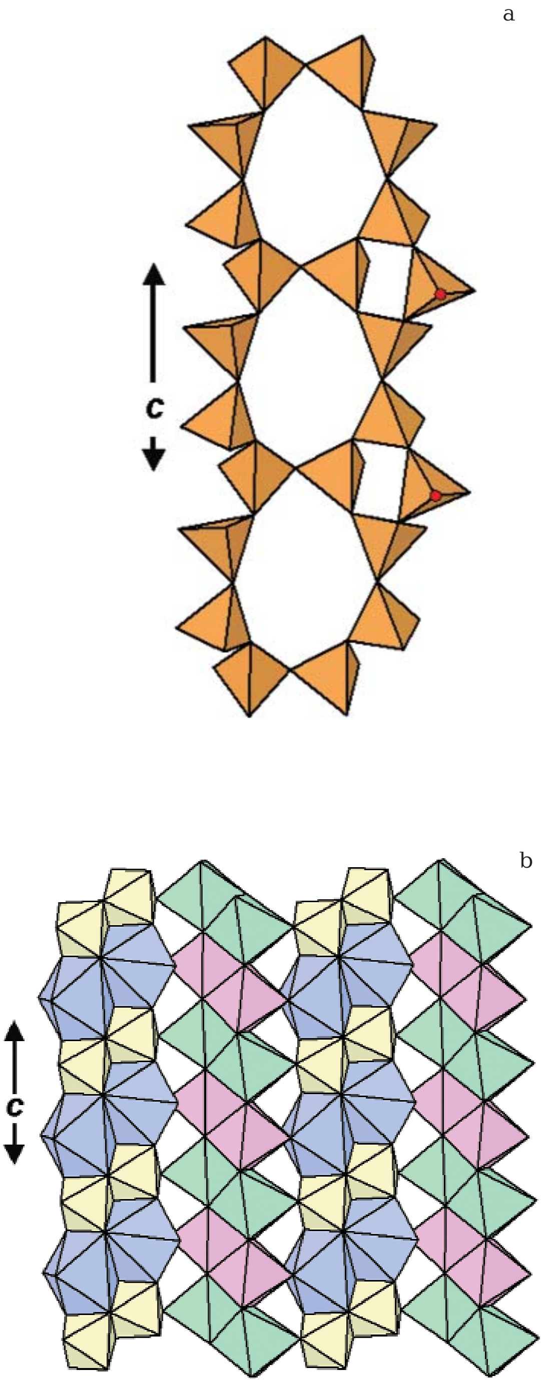

Fig. 3. *a) hybrid doubled chain, $[Si_7O_{18}(OH)]^{9-u}$, one of the main constituent elements of senkevichite crystal structure; (OH)-group is marked by red circle; b) layers composed by M(1), M(2), M(3) octahedra and Na-polyhedra; M(1) octahedra are marked by yellow colour, M(2) - green, M(3) - pink, Na-polyhedra - blue*

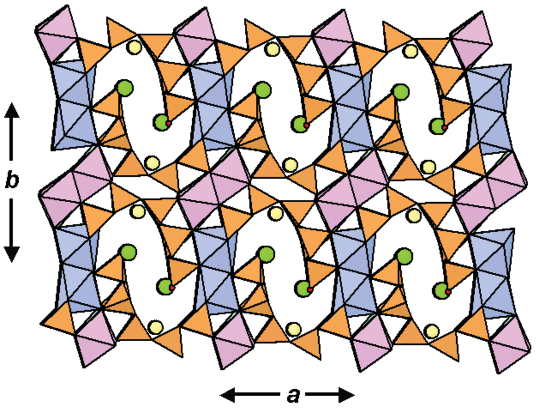

Fig. 4. *Crystal structure of senkevichite in projection on (110). Si-tetrahedra are coloured by orange, Na-polyhedra - by blue, atoms A(1) are marked by green circles, atoms A(2) - by yellow circles, (OH)-groups - by small red circles*

Table 3. **Comparative characteristic of senkevichite and tinaksite**

Chemical	senkevichite	tinaksite
formula	$CsKNa\ Ca_2TiO[Si_7O_{18}(OH)]$	$NaK_2Ca_2TiO[Si_7O_{18}(OH)]$
Space group	*P*-1	*P*1, *P*-1
a, Å	10.4191	10.35
b, Å	12.2408	12.17
c, Å	7.0569	7.05
α, °	90.857	91.00
β , °	99.193	99.20
γ, °	91.895	92.30
Z	2	2
Strong lines of X-ray powder diagram:		
$d_{meas.}$ Å*(I)*	5.16(5)	5.09(30)
	4.08(13)	4.04(30)
	3.33(11)	3.32(30)
	3.25(16)	3.25(80)
	3.14(21)	3.09(50)
	3.06(100)	3.03(100)
	2.959(20)	2.952(50)
	2.904(7)	2.8.65(50)
	2.038(17)	2.002(45)
Density (meas), g/cm^3	3.13	2.82
	biaxial (+)	biaxial (+)
n_p	1.616	1.593
n_m	1.645	1.621
n_g	1.683	1.666

Na-polyhedra, joined by mutual vertices, form mixed framework with mutual cluster $[NaCa_2Ti(Si_7O_{18}(OH)O]^{2-}$. The latter concludes the large cells occupied by A(1) and A(2) atoms (Fig. 4). Senkevichite is a Cs analogue of tinaksite, $K_2NaCa_2Ti(Si_7O_{18})O(OH)$, (Petrunina *et al.*, 1971) and Cs-Na-Ti oxianalogue of tokkoite, $K_2Ca_4Si_7O_{18}(OH)F$, (Rozhdestvenskaya *et. al.*, 1989).

Comparative characteristic of senkevichite and tinaksite is given in Table 3.

The sample of senkevichite is deposited at (the Fersman Mineralogical Museum, Russian Academy of Sciences (Moscow).

Acknowledgements

The authors thank I.V. Pekov and V.D. Dusmatov for valuable notes and advice. The work was supported by the Russian Foundation for Basic Research (No. 04-05-64118).

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UDC 549.6

KYRGYZSTANITE*, $ZnAl_4(SO_4)(OH)_{12}{\cdot}3H_2O$, A NEW MINERAL FROM THE KARA-TANGI DEPOSIT, KIRGIZIA

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Kyrgyzstanite is a new hydrous sulphate of aluminium and zinc with the formula $ZnAl_4(SO_4)(OH)_{12}{\cdot}3H_2O$ (monoclinic, sp. group $P2_1/n$, $a=10.246(9)$ Å, $b=8.873(4)$ Å, $c=17.22(1)$ Å, $\beta=96.41(7)°$, $V=1556(3)$ Å^3, $Z=4$), which has been found in vanadium-bearing slates of the Kara-Tangi deposit (Batken region, Kirgizia) in assemblage with quartz, calcite, alumohydrocalcite, nickelalumite, and allophane. The mineral forms crusts of radiating fibrous aggregates of split crystals. The dominant forms as follows: {001}, {110}, {010}, and {310}. Colour is light blue to greenish. The mineral is transparent; lustre is vitreous. The Mohs' hardness is $2-2.5$; VHN$=70$ kg/mm^2. Cleavage is perfect on (001). Density is 2.25(1) (meas), 2.242 g/cm^3 (calc). Kyrgyzstanite is optically negative, biaxial; $n_p=1.517(1)$, $n_m=1.525(1)$, $n_g=1.527(1)$, $2V_{calc}=53°$. Dispersion is strong, $r<v$. Orientation is $c\wedge Np=6°$. Strong lines on X-ray powder diagram are as follows (d, I): 8.60(100), 7.93(70), 4.83(80), 4.27(100), 2.516(70), 2.292(80), 1.998(95), 1.896(65), 1.720(65). Chemical composition (electron microprobe analysis, wt %, average on 6 measurements) is as follows: ZnO 10.02 , NiO 4.13, CuO 0.58, FeO 0.32, V_2O_5 0.08, Al_2O_3 38.45, SiO_2 0.33, SO_3 15.00, H_2O 31.10 (wet chemistry), total 99.01. The empirical formula is $(Zn_{0.65}Ni_{0.29}\,Cu_{0.04}Fe_{0.02})_{0.99}\,Al_{4.00}Si_{0.03}(SO_4)_{0.99}\,(OH)_{12.12}{\cdot}2.81H_2O$.

Kyrgyzstanite is a structural analogue of nickelalumite. Crystal structure of the latter was solved on a single crystal of zinc-rich variety from the same geological formation; it represents brucite-like octahedral layers along (001) (octahedra Al and M). In the interlayer space the single (SO^4) tetrahedra and H_2O molecules are localized. The IR spectrum is given. Mineral genesis is hydrothermal. Kyrgyzstanite was named in honour of Kirgizia (the Republic of Kyrgyzstan), where it was first discovered. Type material has been deposited in the collection of the Fersman Mineralogical Museum, Moscow.

4 tables, 4 figures, 9 references

While carrying out of field works in the summers of 2002-2003, at the area of distribution of vanadium-bearing carbon-flinty slates in Batken region (Kirgizia) at the Kara-Tangi deposit, a zinc analogue of nickelalumite**, kyrgyzstanite, $(Ni,Zn)Al_4(SO_4)(OH)_{12}{\cdot}3H_2O$, was found; it was named in honour of the Republic of Kyrgyzstan, where this mineral was discovered, and where carbon-flinty slates are distributed. We did not name the mineral «zincalumite» in order to avoid confusion with the already existing mineral «zincaluminite».

Occurrence and assemblage

The uranium deposit Kara-Tangi worked in the 1960's is located in a folded zone of the Turkestan range foothills at the northern slope of the Katran-Tau mountains. It is connected to a zone of strongly folded chlorite-sericite slates of Upper-Silurian age. Within the limits of the deposit, the horizons of boudinated carbon-flinty slates are widespread; uranium-vanadium mineralization is connected to them. The size of the lenses ranges from single meters to several tens of meters. The mineral has been found in the dump and the adit mouth at the right side of Kara-Tangi.

Kyrgyzstanite was encountered in cracks and small cavities in carbon-flinty slates in the form of thin crystal crusts and spherulites composed by radiating-fibrous aggregates, and rarely, separate lamellar split crystals and their intergrowths (Fig. 1) with the size of individuals ranging from 0.2 to 1 mm in assemblage with quartz, calcite, alumohydrocalcite and Zn-rich nickelalumite. One of less split mineral crystals with a well-shaped vertical face band was measured on a two-circle goniometer; however, the

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[*] 'The mineral was considered and recommended for publication by the RMS (Russian Mineralogical Society) and approved by the IMA Commission on New Minerals and Mineral Names on September 1, 2004.

[**] At present, the status of nickelalumite is in an indeterminate situation. Description of this mineral was initially published (Martini, 1980) together with two new minerals, its nitrate analogues: mbobomkulite and hydrombobomkulite. In spite of sufficient complete description of nickelalumite, only the two latter minerals were approved by the IMA CNMMN. Nevertheless, nickelalumite was entered in such recognized handbooks as Fleisher's Glossary of Mineral Species 2004 (The Mineralogical Record *Inc.*, 2004) and Hey's Mineral Index (3^d edition, Chapman and Hall, 1993). Recent studies of nickelalumite from Kirgizia (Karpenko *et al.*, 2004a) and also the refinement of the crystal structure of this mineral (Uvarova *et al.*, 2005) confirmed nickelalumite as a valid mineral species. In this connection, the authors have received some recommendations from E. Burke, chairman of the IMA CNMMN. While using the term «nickelalumite» in this article, the authors realize the mineral did not pass a formal voting and in parallel carry on work on the rehabilitation of nickelalumite as a recognized mineral species.

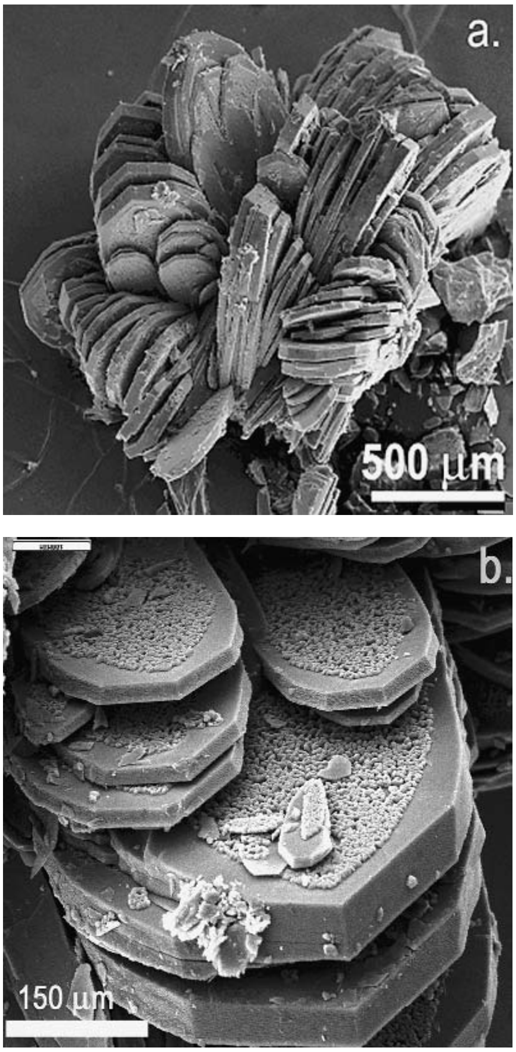

Fig. 1. REM-photo of kyrgyzstanite crystals:
a) intergrowth of split crystals; b) fragment of Figure 1a. Kyrgyzstanite crystals are covered by allophane crust.

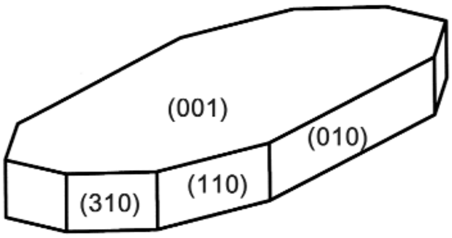

***Fig. 2**. Drawing of ideal kyrgyzstanite crystal.*

Table 1**. Chemical composition of kyrgyzstanite (wt %)**

Constituent	1	2	3	4	5	6	Average composition
ZnO	8.34	9.13	9.45	9.50	10.73	13.02	10.02
NiO	5.51	4.16	4.34	5.37	3.05	2.36	4.13
CuO	1.17	0.97	0.95	0.15	0.19	0.06	0.58
FeO	0.53	0.41	0.41	0.00	0.38	0.20	0.32
V_2O_5	0.03	0.23	0.00	0.00	0.13	0.06	0.08
Al_2O_3	38.01	38.72	37.85	37.72	38.99	39.42	38.45
SO_3	14.84	15.21	14.54	14.80	15.95	14.63	15.00
SiO_2	0.26	0.30	0.42	0.40	0.09	0.52	0.33
H_2O	30.10	30.10	30.10	30.10	30.10	30.10	30.10
Total	98.79	99.23	98.06	98.04	99.61	100.37	99.01
Formula coefficients, calculation on 4 Al atoms							
Zn^{+2}	0.55	0.59	0.63	0.63	0.69	0.83	0.65
Ni^{+2}	0.40	0.29	0.31	0.39	0.21	0.16	0.29
Cu^{+2}	0.08	0.06	0.06	0.01	0.01	0.00	0.04
Fe^{+2}	0.04	0.03	0.03	0.00	0.03	0.01	0.02
V^{+5}	0.00	0.01	0.00	0.00	0.01	0.00	0.00
[8]Me	**1.07**	**0.98**	**1.03**	**1.03**	**0.95**	**1.00**	**1.01**
Al^{+3}	4.00	4.00	4.00	4.00	4.00	4.00	4.00
S^{+6}	0.99	1.00	0.98	1.00	1.04	0.95	0.99
Si^{+4}	0.02	0.03	0.04	0.04	0.01	0.04	0.03
$(OH)^-$	12.24	12.07	12.25	12.22	11.85	12.26	12.12
H_2O	2.85	2.74	2.88	2.93	2.80	2.51	2.81

***Note**. Analysts are A.A. Agakhanov and V.Yu. Karpenko. Coefficients for $(OH)^-$ and H_2O are calculated by charge balance*

fluctuation of readings was from one to two degrees. When the mean values of signal were compared with theoretical values of spherical coordinates with simplest indexes, they corresponded to the {110}, {010}, and {310} forms (Fig. 2). Often spherulites and crusts of kyrgyzstanite are replaced by white allophane and as well as bohmite.

Physical properties

Colour of kyrgyzstanite is light blue, greenish. The mineral is transparent; lustre is vitreous. The Mohs' hardness is 2-2.5. Micro-indentation hardness (VHN) of 70 kg/mm^2 (mean value of 20 measurements between 47 to 87 kg/mm^2). Micro-hardness was obtained with PMT-3 instrument at a load of 20 g, calibrated by NaCl. Cleavage is perfect on (001). The mineral is easily split on to plates. Mineral density was deter-

Table 2. **Coincidence indexes of some sulphates of aluminium**

Mineral	Formula	*k* Al_2O_3		Coincidence index	
		for sulphates	for other minerals	for sulphates	for other minerals
Basaluminite	$Al_4(SO_4)(OH)_{10}(H_2O)_{4-5}$	0.233	0.217	0.078	0.023
Cyanotrichite	$Cu_4A_{l2}(SO_4)(OH)_{12}(H_2O)_2$	0.269	0.253	0.032	0.007
Chalcoalumite	$CuAl_4(SO_4)(OH)_{12}(H_2O)_3$	0.255	0.238	0.088	0.035
Kyrgyzstanite*	$(Zn,Ni)Al_4(SO_4)(OH)_{12}(H_2O)_3$	0.250	0.237	0.067	0.018

Note. *Data for calculation were taken form Handbook of mineralogy (Anthony et al., 2003)*
* — *our data were used for calculation.*

mined by grain balancing in a water solution of Clerici liquid. Experimental density is 2.25(2) g/cm^3, calculated density is 2.242 g/cm^3. Kyrgyzstanite is optically negative, biaxial. Refraction indexes measured by immersion method (at 589 nm) are as follows: $n_p = 1.517(2)$, $n_m = 1.525(2)$, $ng = 1.527(2)$. Calculated angle $2V = -53°$. Dispersion is strong, $r < v$. Orientation is $c \wedge N_p = 6°$. The mineral is insoluble in water; it dissolves during heating in HCl (1:1). The IR spectra of kyrgyzstanite were obtained with the IR Fourier spectrometer Nicolet; mineral sample was pressed into KBr tablet with a weight of 20 mg (Fig. 3). Bands at 600, 935, and 1100 cm^{-1} correspond to stretching vibrations of SO_4-tetrahedra; an intenseive band at 1632 cм$^{-1}$ is connected with bending vibrations δ_{H_2O}; range 3300-3500 cm^{-1} conforms to stretching asymmetrical vibrations of (OH) groups.

Chemical composition

The chemical composition of kyrgyzstanite was studied with electron microprobe instrument JXA-50A equipped with energy-dispersive spectrometer Link (Table 1). Analyses were made on EDS with accelerating voltage to 20 kV, electron microprobe current was 3x10^{-9}Å. The following standards were used: microcline USNM 143966 (Si, Al), ilmenite USNM 96189 (Fe), gahnite USNM 145883 (Zn), metallic V and Cu (V, Cu), NiO (Ni), barite (S). Grains of the new mineral are homogenous and free from intergrowths of other minerals. Calculation of concentrations was made with using ZAF correction.

Water was detected by weight loss during combustion of a 5 mg sample. Ignition was made in a platinum boat in a muffled furnace at 500—550°C.

The empirical formula of the mineral is as follows: $(Zn_{0.65}Ni_{0.29}Cu_{0.04}Fe_{0.02})_{0.99}$ $Al_{4.00}Si_{0.03}(SO_4)_{0.99}$ $(OH)_{12.12}$ $·2.81H_2O$, the ideal formula is $ZnAl_4(SO_4)(OH)_{12}·3H_2O$ (calculation on 4 Al atoms).

Since kyrgyzstanite is a hydroxyl-bearing sulphate of aluminium and zinc, the compatibility index ($1-k_p/k_c$) can be calculated in two ways, using different values of k for Al_2O_3. Depending on the mineral belonging to either mineral class, there are different k values for sulphates and selenates (0.242), for nesosilicates and inosilicates (0.176), and for other mineral classes (0.207) (Mandarino, 1981). If k is used for other mineral classes, the compatibility index is 0.018, which corresponds to «superior» degree; if it uses k for sulphates and selenates, the index is 0.067, which is classed as «fair». We have calculated the compatibility indexes for a number of hydroxyl-bearing sulphates of aluminium with similar chemical compositions (Table 2), using different k for Al_2O_3, and found that the best results can be obtained with a calculation of $k_{Al_2O_3}$ for other classes (0.207).

X-ray data

X-ray powder diagram of kyrgyzstanite was obtained by photomethod using the RKU 114 mm camera, FeKα radiation, Mn filter (Table 3). Quartz was used as internal standard.

Similarity of physical properties, chemical composition, and X-ray powder diffraction data shows that kyrgyzstanite and nickelalumite are, in all probability, the members of an isomorphous series. Recently Yu. Uvarova with co-authors solved the crystal structure of zinc-roch nickelalumite from the same deposit (Uvarova *et al.*, 2005). By virtue of aforesaid, we shall note brief data of this study. Nickelalumite, $(Ni,Zn)Al_4(SO_4)(OH)_{12}·3H_2O$, belongs to the monoclinic system and has the following unit cell parameters: $a = 10.2567(5)$Å, $b = 8.8815(4)$Å, $c = 17.0989(8)$Å, $\beta = 95.548(1)°$, $V = 1550.3(2)$Å^3; space group $P2_1/n$, $Z = 4$. Its crystal structure was solved by direct method and refined with factor $R_1 = 5.7\%$ for 1554 unique reflexes ($F_o > 4\sigma F$)

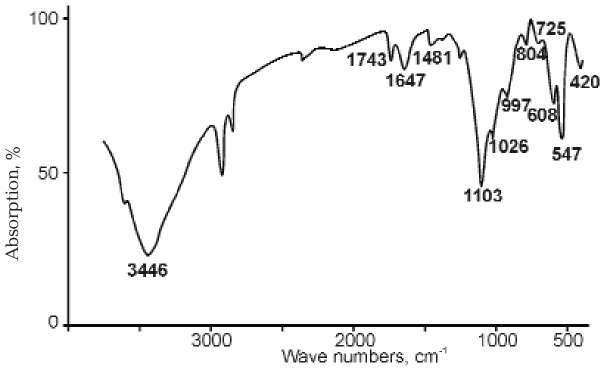

Fig. 3. *The IR spectrum of kyrgyzstanite.*

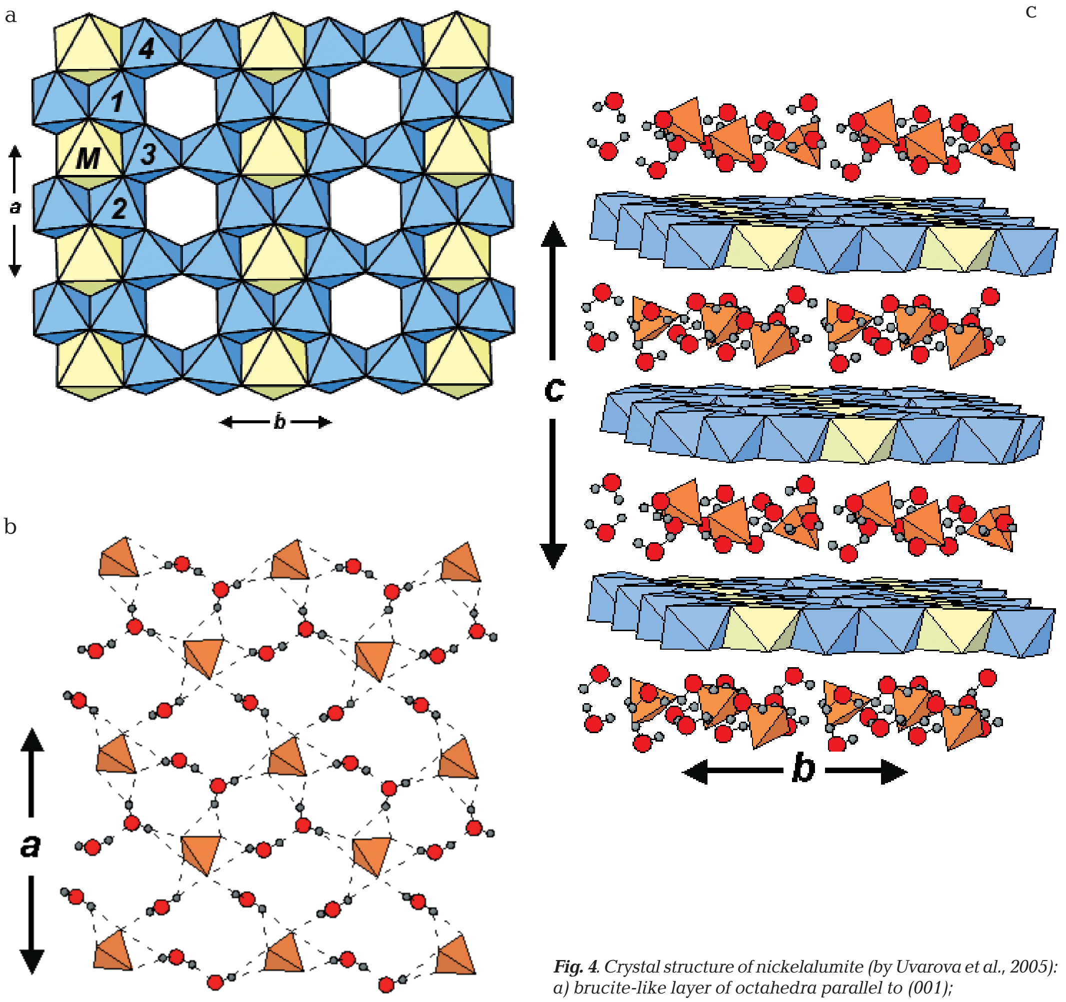

Fig. 4. *Crystal structure of nickelalumite (by Uvarova et al., 2005):*
a) brucite-like layer of octahedra parallel to (001);
b) hydrogenous bonds of (SO_4) tetrahedra and (H_2O) groups;
c) perspective view of crystal structure along (001).
M octahedra are light yellow, Al octahedra are pale blue, S tetrahedra are orange; atoms of oxygen are marked by red circles; atoms of hydrogen are marked by small grey circles

on diffractometer Bruker P4 (MoKα radiation, Smart 4K CCD detector). In the crystal structure there are five octahedral sites. Among them, the M site is occupied predominantly by Ni and Zn with a small amount of V and Fe: $(Ni_{0.55}Zn_{0.39}V_{0.02}Fe_{0.01})_{\Sigma 0.97}$(<M-OH> = 2.079 Å). Four other sites are occupied predominantly by Al (<Al-OH> = 1.900 Å). There is one S site with tetrahedral coordination (<S-O> = 1.468 Å) and also three sites occupied by H_2O molecules, and twelve sites occupied by (OH) groups. Main elements of nickelalumite structure are the octahedral layers along (001) consisting of Al and M octahedra (Fig. 4a, c). Al octahedra are connected by common edges and form six-fold rings with another octahedron in the centre. A half of these octahedra are occupied by Ni and Zn (M site); the remaining half of these octahedra are vacant. This framework is analogous to brucite, in which a sixth part of the octahedral sites is vacant. (SO_4) tetrahedra and H_2O molecules are localized in the interlayer space and connected with each other by hydrogenous bonds (Fig. 4b, c).

Nickelalumite is stoichiometrically close to mbobomkulite, $(Ni,Cu^{2+})Al_4[(NO_3), (SO_4)]_2(OH)_{12}(H_2O)_3$, hydrombobomkulite, $(Ni,Cu^{2+})Al_4[(NO_3),(SO_4)]_2(OH)_{12}(H_2O)_{12}$ (Martini, 1980), and chalcoalumite, $CuAl_4(SO_4)(OH)_{12}(H_2O)_3$ (Larsen, 1925; Williams, BaSaw Khin, 1971). The crystal structures of these minerals are unstudied, but the unit cell parameters are close to the ones of nickelalumite. Octahedral layers in the crystal structure of nickelalumite are topologically close to the same layers of alvanite, $(Zn,Ni)Al_4(VO_3)_2(OH)_{12}(H_2O)_2$ (Pertlik, Dunn, 1990) and ankinovichite, $NiAl_4(VO_3)_2(OH)_{12}(H_2O)_2$ (Karpenko *et al.*, 2004b). The presence of chains composed of doubled tetrahedra $[VO_3]^{1-}_2$ distinguishes the crystal structure of nickelalumite. Comparative characteristics of X-ray data, physical, and crystal structural properties of kyrgyzstanite, chalcoalumite, and nickelalumite are given in Table 4.

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Table 3. **X-ray powder diagram of kyrgyzstanite**

I_0	$d_{meas.}$	$d_{meas.}$	*h k l*
100	8.60	8.557	0 0 2
70	7.93	7.877	0 1 1
80	4.83	4.798	0 1 3
30	4.71	4.755	1 0 3
20	4.61	4.607	2 0-2
100	4.27	4.278	0 0 4
30	3.85	3.854	0 1 4
20	3.50	3.502	0 2 3
30	**3.355**	**3.360**	**1 0 -5**
50	**3.193**	**3.193**	**0 1 5**
50	**3.056**	**3.060**	**3 1 1**
10	2.796	2.797	2 2 3
		2.795	0 3 2
50	**2.723**	**2.721**	**1 3 -2**
70	**2.516**	**2.518**	**4 0 -2**
30	**2.489**	**2.489**	**2 3 -2**
20	**2.442**	**2.440**	**1 0 -7**
80	**2.292**	**2.288**	**4 1 2**
30w	2.230	2.230	4 1 -4
		2.230	3 3 0
30w	**2.210**	**2.208**	**4 2 0**
20w	2.099	2.100	4 1 -5
		2.098	3 0 -7
95	**1.998**	**1.999**	**2 4 -2**
65w	1.896	1.897	3 2 -7
		1.897	4 1 5
30	1.849	1.849	4 3 2
40	1.807	1.806	2 4 4
65	1.720	1.720	2 3 7
20	**1.697**	**1.697**	**3 3 6**
50w	1.558	1.558	1 3 9
40w	1.480	1.480	2 2 10
30	**1.469**	**1.469**	**2 5 -6**
30	1.457	1.457	5 4 2
		1.457	0 6 2
20	1.144	1.444	3 1 10
		1.444	7 1 -1
		1.444	0 4 9
30w	1.395	1.396	7 0-5
		1.394	2 6 2
20	1.372	1.372	5 1-10
		1.372	4 5 -5
40	1.355	1.355	3 5-7
		1.355	0 4 10
30	1.311	1.311	7 3 -1
		1.311	1 6-6
30	1.296	1.296	2 5 8
10	1.274	1.274	0 4 11

Conditions: *URS-50IM, FeKα radiation, Mn filter, sample — rubber post (d=0.15 mm), camera RKD-114; w — widening of line; data used for calculation of unite cell parameters are marked by semi-bold. Analyst V.Yu. Karpenko*

Table 4**. Comparative characteristic of kyrgyzstanite, chalcoalumite, and nickelalumite**

	Kyrgyzstanite	Chalcoalumite, Bisbee, Arizona (Williams and Khin, 1971)	Nickelalumite, Mbobomkulu (Martini, 1980)
Formula	$ZnAl_4(SO_4)(OH)_{12}{\cdot}3H_2O$	$Cu^{+2}\ Al_4\ (SO_4)(OH)_{12}{\cdot}3H_2O$	$(Ni,Cu^{+2})Al_4[SO_4,(NO_3)_2](OH)_{12}{\cdot}3H_2O$
Space group, system.	P21/n	P21	Mon. s.
a, Å	10.246	17.090	10.175
b, Å	8.873	8.915	8.860
c, Å	17.220	10.221	17.174
β,°	96.41°	95.88°	95.95°
Z	4	4	4
Strong lines on X-ray powder diagram $d_{meas.}$(I)	8.60(100)	8.502(100)	8.543(100)
	7.93(70)	7.898(22)	7.877(20)
	4.83(80)	4.786(22)	
	4.27(100)	4.250(91)	4.267(10)
		4.178(23)	
		3.287(45)	
	2.516(70)	2.520(11)	2.507(15)
	2.292(80)		2.289(15)
	1.998(95)		1.997(20)
	1.896(65)		
	1.720(65)		
Colour	Bluish, turquoise	Turquoise-green, pale grey	Pale blue
D, g/cm^3 (meas./calc.)	2.25/2.227	2.29/2.25	2.24/2.28
	Biaxial (-)	Biaxial (+)	Biaxial (+)
n_p	1.517	1.523	1.532
n_m	1.525	1.525	–
n_g	1.527	1.532	1.543

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CARCURMOLITE: NEW DATA ON CHEMICAL COMPOSITION AND CONSTITUTION THE MINERAL

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The revised crystallochemical formula of calcurmolite, $(Ca,Na)_2(UO_2)_3Mo_2(O,OH)_{11}$ nH_2O, is given on the basis of electron microprobe analyses of the samples from Kazakhstan (Kyzyl-Sai) and Armenia (Kadjaran). Parameters of the monoclinic unit cell: a = 16.30 0.03 Å, b = 25.49 0.05 Å, c = 19.50 0.06 Å, $\beta = 90°07'$, are estimated by X-ray diffraction method. The IR spectra and spectra of laser luminescence of two mentioned findings of the mineral have been obtained for the first time; they show the identity, stability, and diagnostic value of both methods. Micro-textural and structural peculiarities of calcurmolite prevent from the research of a crystal structure of the mineral. Calcurmolite was formed as a pseudomorph after uranophane.
2 tables, 8 figures, 14 references.

Steady progress in methodology of mineralogical investigations makes it possible to obtain chemical and physical data, as well as structural characteristics with better reliability, precision and resolution. In some cases it can lead to revision of accepted notion about mineral species, varieties and series of solid solutions. Uranium minerals give bright examples of this tendency (Sidorenko *et al.*, 2003).

One of such examples is calcurmolite, which is considered either as a mineral with fixed chemical composition, or as an isomorphous series named «calcium-sodium uranyl molybdates» (Skvortsova *et al.*, 1969). Judging by previous publications, calcurmolites are morphologically extremely diverse and do not practically have even more or less reliable crystallochemical formula. Calcurmolite as a mineral species did not have the usual procedure of approbation in the IMA Commission on New Minerals and Mineral Names. The name **calcurmolite** was not suggested by discoverers of this mineral and has appeared in literature for the first time in the appendices on the group of calcium-sodium uranyl molybdates made by A.S. Povarennykh to the Russian version of the Mineralogical Tables of H. Strunz (1962).

For the first time, the considered mineral was described by L.S. Rudnitskaya in 1955 in the oxidized zone of the Kadjaran ore field (the Kafan region, Armenia) under the previous name **kadjaranite** (Pekov, 1998; Chernikov, 1971), however, so as not to disclose geography of the deposit, in the publication in Proceedings of the Geneva Conference on Peace Use of Atomic Energy (1959, p. 161) the mineral has appeared as **«calcium molybdate of uranium»**. According to the first data of microchemical analysis, L.S. Rudnitskaya characterised the chemical composition of this mineral by a formula $Ca(UO_2)_3(MoO_4)_3(OH)_2$ $8H_2O$.

The second finding of the calcium uranyl molybdate from the oxidized zone of the uranium deposit in Kazakhstan was briefly described by O.V. Fedorov in 1963, giving a formula $Ca(UO_2)_3(MoO_4)_3(OH)_2$ $11H_2O$, that differs from the formula of L.S. Rudnitskaya only by amount of the water molecules per formula unit.

The first full summary of data on calcurmolite under the name «calcium-sodium uranomolybdates» from deposits of the USSR was published in 1969 (Skvortsova *et al.*, 1969), after that the new data on these minerals did not appear for a long time. However, in the article about tengchongite (Chen Zhangru *et al.*, 1986), the close assemblage of the latter with calcurmolite was noted. In 1992, calcurmolite was found in Rabejac (France) and its «comparison with calcurmolite from the Soviet Union» was made (Deliens, 1992). However, it was concluded that a sample from France is a worse material for study.

K.V. Skvortsova and E.V. Kopchenova (Skvortsova *et al.*, 1969) have studied a series of calcium-sodium uranyl molybdates connected with oxidized zones of Kyzyl-Sai, adding to the summary the data of L.S. Rudnitskaya and O.V. Fedorov.

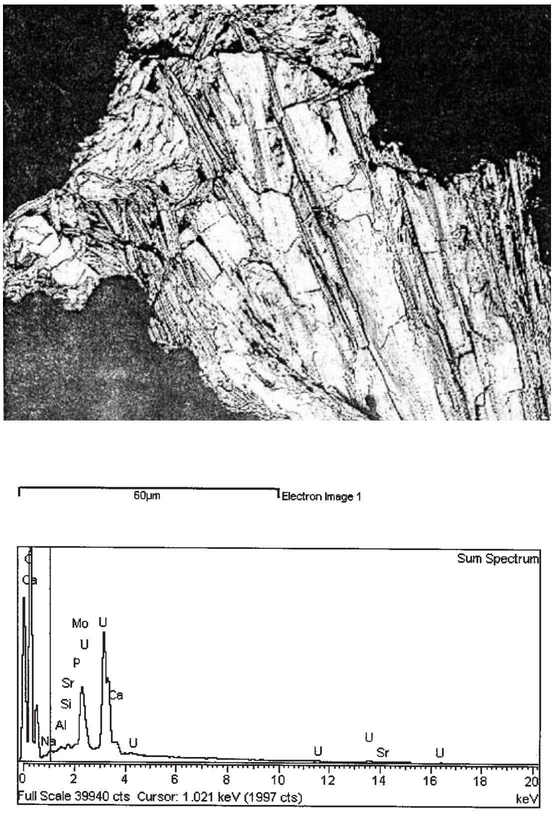

***Fig. 1**. Inner bunch-shaped texture of outwardly monocrystal (massive, compact) calcurmolite and its total spectrum of the element composition, revealing U and Mo as a dominative elements.*

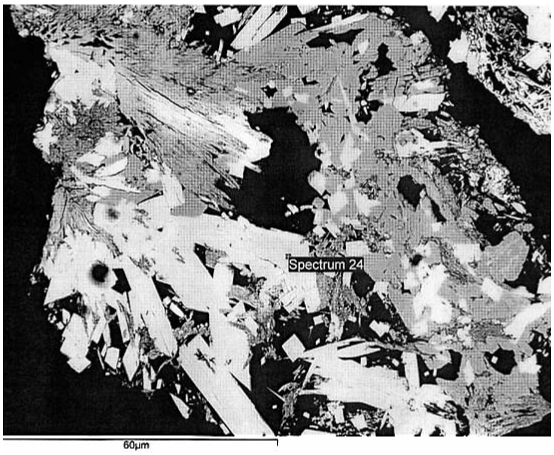

***Fig. 2**. Bunch-like form of segregation of calcurmolite, similar to one presented at Fig. 1, in closest assemblage with uranophane (white crystals) and phosphate of strontium (uranocircite).*

Quite full description of genetic conditions, paragenetic assemblages, morphological diversity, chemical composition, optical properties, X-ray characteristics with adduction of results of methods of study, accessible at that time, is presented in the work of K. Skvortsova with co-authors (1969). At that, the authors noted the closest assemblage of uranyl molybdates with other minerals of uranyl and took that into account during calculation of data of the microchemical analysis of practically phase heterogeneous matter on crystallochemical formulae.

The formula suggested in the article are extremely diverse and not charge-balanced and can evoke neither satisfaction no the least certainty in their correspondence to the true chemical composition of calcurmolites.

Because of remoteness of the summary publication, it is expedient to remind the crystallochemical formulae calculated in the work (Skvortsova *et al.*, 1969) by data of microchemical analyses of calcurmolites (in authors' determination, «calcium-sodium uranomolybdates») with the regard of admixtures of uranophane or « -uranotil»; without a suggestion of the general crystallochemical formula for calcurmolite as a mineral species, as follows:

sample 1 –
$(Ca_{0.95}Na_{0.19})_{1.14}(UO_2)_{3.99}(MoO_4)_{4.02}(OH)_2\ 14.5H_2O$;
sample 2 –
$Na_{1.95}(UO_2)_{4.98}(MoO_4)_{5.03}(OH)_2\ 8.6H_2O$;
sample 3 –
$(Ca_{0.44}Na_{0.66})_{1.10}(UO_2)_{4.3}(MoO_4)_{3.7}(OH)_2\ 13H_2O$;
sample 4 –
$(Ca_{0.38}Na_{0.62})_{1.0}(UO_2)_{4.52}(MoO_4)_{3.57}(OH)_2\ 10H_2O$;
sample 5 –
$Na_{1.14}(UO_2)_{4.18}(MoO_4)_{3.96}(OH)_2\ 12H_2O$;
sample of L.S. Rudnitskaya –
$Ca(UO_2)_{2.97}(MoO_4)_{2.73}(OH)_2\ 7H_2O$.

It follows from these formulae that a value of the ratio U:Mo in them lays within the limits from 0.99 to 1.27 and an amount of sodium, calcium and water varies widely. Some inconstancy of the U:Mo value seems to be the most considerable, since just the ratios of [UO_2] and anion-forming complex are determinative in the crystal structures of uranyl minerals formed by them (Sidorenko, 1978). Just this fact was a basis for revision of chemical composition and simultaneously carrying out of additional studies of calcurmolite both from Kadjaran and Kyzyl-Sai, with use of new methodical, technical, and apparatus means.

In the present work the samples from collections of minerals and rocks, containing uranyl molybdates, which have been studied earlier by K.V. Skvortsova and E.V. Kopchenova and kept to one of the authors of this work, were studied. The study of chemical composition of sodium-calcium uranyl molybdates and ratios of the main mineral-forming elements (uranium, molybdenum, calcium, sodium) and also the research or crystal structure of calcurmolite were the main objective. Implementation of this goal was complicated by the absence of perfect crystals and synthetic analogues of uranyl molybdates of calcium and sodium. It is necessary to note that during study of the R-U-Mo system, where R is a cation (alkaline and alkaline-earth elements), one failed to synthesize the analogue of calcurmolite (Spitsyn *et al.*, 1981).

Methods of study

Study of element composition and morphological peculiarities of the mineral was made with the electron microprobe instrument JXA-8100 (JEON, Japan) equipped with the energy-dispersive system Inca Energy 400 (Oxford Instruments, Great Britain). Chemical composition was obtained by the crystal-diffraction method at accelerating voltage 20 kV and electron microprobe current 10 nA. The standards were as follows: UO_2, MoO_3, diopside (Ca), and albite (Na).

The X-ray powder patterns of the samples were performed with the ADP-1 diffractometer (monochromatic $CuK\alpha_1$ radiation).

The IR spectra of calcurmolite were registered by a standard method with use of pellets with KBr with the spectrophotometer Specord 75 in a range of frequencies 400-4000 cm^{-1}. Polystyrene and gaseous ammonia were used as standards.

Measurement of luminescence properties was made with a complex assembled on a basis of microscope, single-beam spectrophotometer MSFU-312 equipped with a computer, a counter board for use of a method of photons counting and a module of control of step engine of diffraction lattice drive. The source of generation of luminescence was a laser on molecular nitrogen ($\lambda rad = 337.1$ nm).

The complex is intended to registration of luminescence spectra of different microobjects approximately of 50 μm in size and also microparts of macroobjects in polarized and depolarised light in a spectral interval of 250-1200 nm at a room temperature and a temperature of liquid nitrogen.

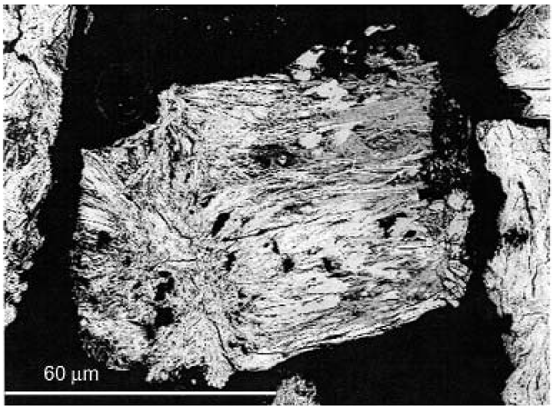

Fig. 3. *«Crystallite» of calcurmolite, entirely composed by fibres and laths of the mineral, between which there are grains of uranophane (light).*

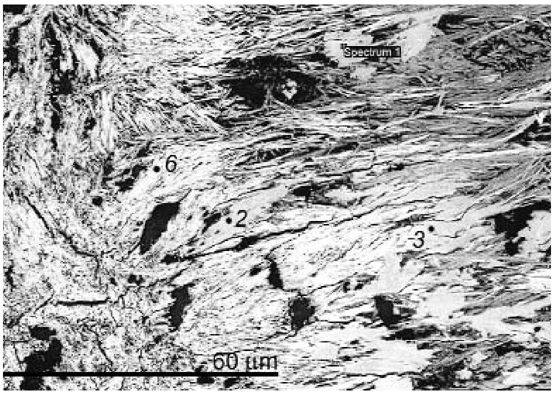

Fig. 4. *A fragment of Fig. 3 with some more magnificence, interfiber inclusions of uranophane are more clear and confirmed by element analysis.*

Fig. 5. *Heterogeneous structure of a grain of calcurmolite, in which the crystals of uranophane with different degree of alteration prevail (the most perfect are white (1), less perfect are light grey (2), and still more altered are grey (3)); at the periphery of a grain the fibrous calcurmolite grow.*

Table 1. **Results of electron microprobe analyses of calcurmolite (wt %) from Kazakhstan and Armenia and its calculation on ratios of main mineral-forming elements**

Deposit-	No. of analysis	Na_2O	CaO	MoO_3	UO_3	Total	Atomic quantities				Formula coefficients*			
							Na	Ca	Mo	U	Na	Ca	Mo	U
Kazakhstan (Kyzyl-Sai)	1	0.6	6.1	20.9	64.4	92.0	0.0194	0.1088	0.1453	0.2252	0.13	0.75	1	1.55
	2	0.6	5.8	21.5	63.9	91.8	0.0194	0.1034	0.1493	0.2233	0.13	0.69	1	1.50
	3	0.9	5.6	20.9	64.1	91.5	0.0290	0.0999	0.1454	0.2240	0.20	0.69	1	1.54
Armenia (Kadjaran)	4	0.7	5.8	20.6	62.2	89.3	0.0225	0.1034	0.1430	0.2173	0.16	0.72	1	1.52
	5	0.5	5.4	20.4	61.3	87.6	0.0161	0.0962	0.1415	0.2144	0.11	0.68	1	1.52
	6	1.0	5.5	20.7	61.2	88.4	0.03223	0.0981	0.1438	0.2152	0.22	0.68	1	1.50
Average value		0.72	5.7	20.8	62.85	90.07	0.0231	0.1016	0.1447	0.2199	0.16	0.70	1	1.52

**Basis of calculation: Mo=1*

Results of study of calcurmolite

Up to now calcurmolite was characterized by a set of interplanar distances obtained by the clear X-ray diffraction patterns and not quite convincing unit cell parameters, approximately monoclinic. The examination under binocular of the monomineral fractions of calcurmolite from Kazakhstan and Armenia revealed the transparent yellow crystals in a fractions of a millimetre in size, which looked as single crystals (though far from crystallographic perfection in comparison with the needle-shaped crystals of uranophane associated with them). However, all crystals of calcurmolite were not suitable for structural investigations: one failed to obtain a point diffraction pattern even at use of synchrotron radiation.

An explanation of this fact was given by studies in reflected electrons and in characteristic radiation, which have revealed a real constitution of the crystallites, being microheterogeneous system, in which there are bunches or laths tangled in ball and small crystals both needle-shaped, orthogonal and without crystallographic contours. For outwardly homogeneous transparent segregations, such textural-structural constitution is so unusual and diverse that it deserves a number of illustration. Figures 1-4 present the inner bunch-like texture of the outwardly monocrystal (massive, compact) calcurmolite and its total spectrum of element composition, revealing both dominating elements, U and Mo, and very low contents of admixture elements (As, Si, P, Sr). In the same crystallite of calcurmolite, in closest assemblage, there are uranophane and strontium phosphate (uranocircite). Some crystals of calcurmolite entirely consist of the tangled fibres and laths of the mineral, between which are uranophane grains. Possibly, this is a pseudomorph of calcurmolite after the uranium silicate.

In some grains of calcurmolite, the inclusions of uranophane crystals with different degree of alteration prevail; their difference by reflected ability is an evidence of that; fibrous calcurmolite grows at the periphery of the grain (Fig. 5). A process of substitution of uranophane by calcurmolite, above-mentioned as a suggestion, is clearly shown within the limits of a crystallite in reflected electrons and in characteristic radiation (Fig. 6).

Chemical composition of calcurmolite from Kyzyl-Sai and Kadjaran was studied by a method of the local X-ray spectral analysis. The results of quantitative analysis on mineral-forming elements with taking into account of uranophane inclusions are given in Table 1. In the same Table are the atomic quantities of contained elements calculated by the results of analysis and their ratios (at the calculation the quantity of Mo was accepted as a unit). The total of oxides was less than 90% that is connected with high hydration of the mineral, which (by difference from total 100) contains more than 10% of water, including the water in the form of hydroxide (see below).

From the data given in Table 1, it follows that in the chemical composition of calcurmolite:

1) the ratio $[UO_2]^{2+}$:$(MoO_4)^{2-}$=3:2, that creates the $[U\text{-}Mo]^{2+}$ complexes, for which binding together in a three-dimensional structure the additional ions are required;
2) the presence of additional ions of Ca and Na requires the compensation of valency, that can be achieved by the entry of hydroxyl ions in the mineral, their amount is determined by a sum of additional cations and their charge;
3) the additional cations are represented predominantly by Ca at constant presents of sodium, with relatively constant ratio, which is close (but not equal) to 3:1.

On the basis of data on chemical composition for the samples from Kyzyl-Sai and Kadjaran, the

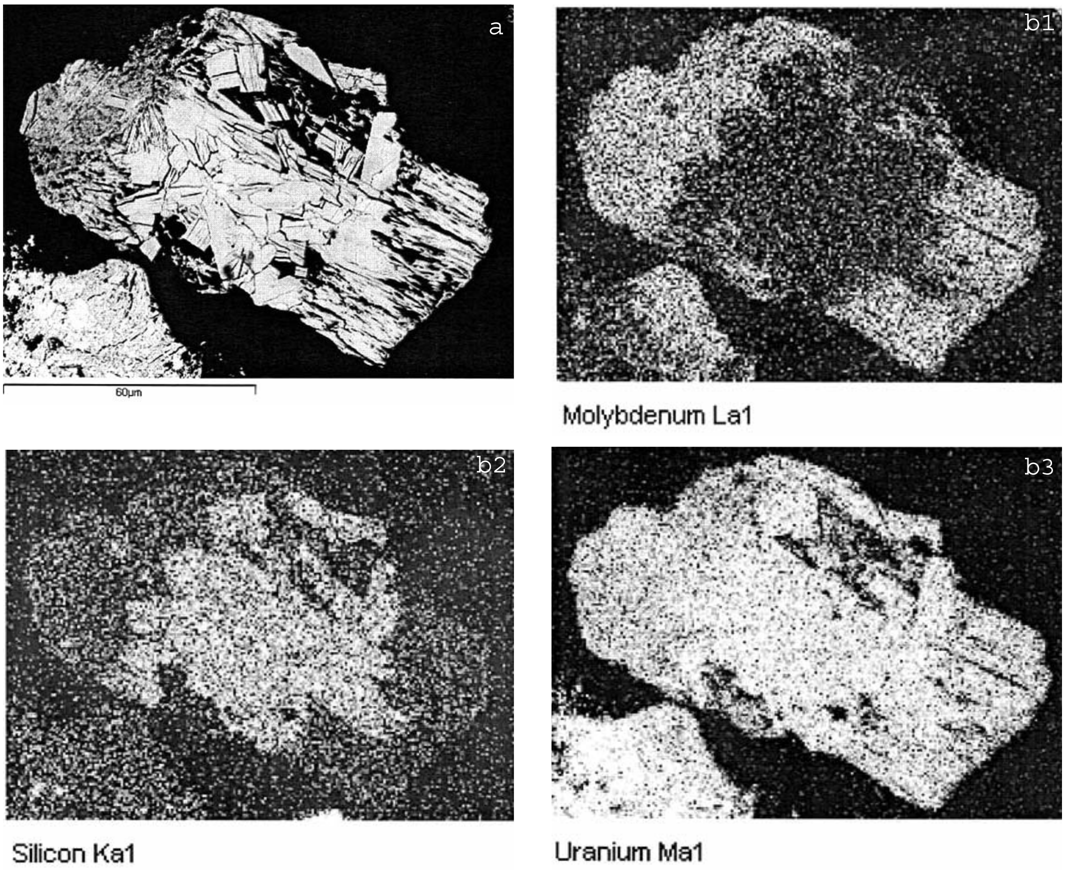

***Fig. 6**. Pseudocrystallite of calcurmolite, showing the process of substitution of uranophane by uranyl molybdate: a - in reflected electrons; b - in characteristic radiation.*

formula of calcurmolite can be presented as follows: $(Ca_{1-x}Nax)_2(UO_2)_3(MoO_4)_2(OH)_{6-x}\ nH_2O$, where x does not exceed 0.3. The content of water is high, but difficultly determined at microprobe analysis of microheterogeneous «crystallites».

The X-ray powder patterns of calcurmolite in different morphological aggregations (from the thin «crystallites» to massive, solid formations) are analogous and characterized by the peaks of two types: sharp and rather wider at the medium values of 2 to indistinct ones at the angles more than 50°, that can be an evidence of disturbance of the three-dimensional order of crystal structure (Tab. 2). The consequence of that are the some fluctuation of the interplanar distances values, which is revealed during comparison of data on two morphological varieties of calcurmolite from Kazakhstan and samples from Armenia, and the deviation of these data from calculated ones. The calculated data were obtained with use of a size of the monoclinic unit cell; their values are practically identical (within the limits of precision of the reflection angles measurements) for three presented mineral samples. In some samples, an admixture of uranophane is present. One failed to obtain the X-ray diffraction patterns from the crystals.

The IR spectra of absorption, obtained for the first time for calcurmolites from Kyzyl-Sai and Kadjaran, are identical both on bands position and their relative intensity (Fig. 7). In the range of the O-H stretching vibrations, the strong wide band with a maximum at 3390-3450 cm^{-1} and a shoulder at 3225-3250 cm^{-1} is present, which is predominantly caused by vibrations of the water molecules. Belonging of a large part of the O-H bonds to the molecular water, but not to hydroxyl groups, is confirmed by a presence in the spectrum the quite strong band of the HOH bending vibrations at 1622 cm^{-1} with a shoulder at 1570 cm^{-1} (a presence of the latter is an evidence that the water is diverse in the structure of calcurmolite). Free OH groups, which usually

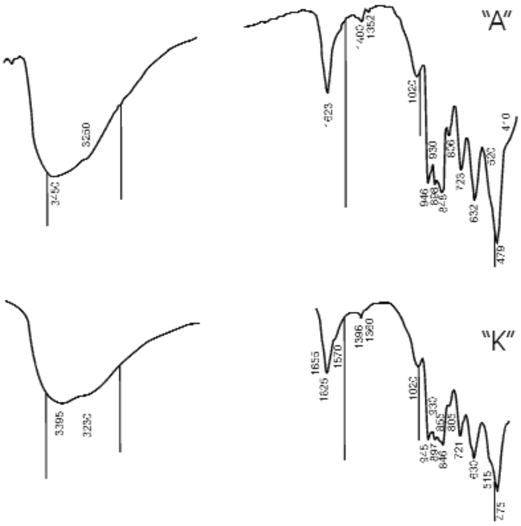

Fig. 7. The IR spectra of calcurmolite for Kazakhstan («K») and Armenia («A»).

Table 2. **Values of interplanar distances (in A) for calcurmolite**

	Kazakhstan				Armenia		$D_{calc.}$
	Sample I		Sample II				
h k l	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	
0 1 2			9.156	5	9.099	10	9.12
1 0 2	8.377	50	8.393	12			8.43
2 0 1	7.762	100	7.775	100	7.762	100	7.76
0 6 0					4.25	3	4.25
0 6 1, 2 0 4	4.179	16	4.183	6			4.183
1 3 4, -2 1 4	4.125	13					4.129
0 0 5, -2 2 4	3.965	34	3.974	14	3.994	8	3.976
1 5 3, 4 2 0	3.87	32	3.883	34	3.883	29	3.883
4 1 2, -3 3 3	3.745	8					3.745
0 6 3, 1 7 0	3.562	3	3.551	7	3.556	6	3.556
6 1 3, -1 6 3	3.474	5	3.485	6	3.490	2	3.477
3 4 6, 5 0 0	3.264	10	3.264	11	3.260	8	3.26
0 8 0, 0 6 4	3.202	20	3.202	24	3.202	17	3.205
0 8 1, 0 7 3	3.138	6	3.119	8	3.121	5	3.119
2 2 6, 1 2 0	2.953	5					2.957
5 4 0, -2 8 2	2.84	7	2.836	5	2.844	4	2.84
5 4 2	2.78	10					2.781
3 6 4, -5 5 1	2.725	8			2.722	3	2.72
1 3 7, 6 2 0	2.644	11	2.663	3	2.666	3	2.658
6 3 0	2.581	5	2.594	5	2.591	5	2.588
3 8 3, 6 0 -3	2.509	3					2.507
4 -7 2, 1 8 5	2.439	8					2.44
-7 0 1	2.315	3					2.313
4 9 3, 0 5 8	2.209	3	2.203	4	2.189	3	2.199
-1 1 2 2	2.059	12					2.06
7 1 5, 3 2 9			1.998	5	1.993	3	1.988
3 12 0, 6 6 5, 8 3 2	1.987	8	1.970	6	1.966	3	1.979
-7 3 -5					1.946	3	1.946
1 12 5, -3 11 5	1.869	5	1.870	4	1.872	3	1.871
1 9 8	1.834	3	1.837	5	1.838	3	1.836
8 2 5					1.789	3	1.788
8 9 0	1.652	6	1.654	5			1.654
4 13 5	1.609	3	1.591	4			1.609
	(+ additional weak diffusive peaks)						
a	16.3±0 0.03		16.30±0.003		16.31±0.03		16.3
b	25.49±0.05		25.47±0.05		25.50±0.06		25.5
c	19.506±0.06		19.50±0.05		19.50±0.06		19.5
β	90 .17		90 .06		90		90
V	8104		8095		8110		8105

have the narrow bands in the IR spectrum in a range of 3500-3700 cm^{-1}, are absent in calcurmolite, although one cannot exclude the presence of small amount of hydroxyl groups, forming quite strong hydrogen bonds (of the water-water bond type).

In the IR spectrum of calcurmolite, there are two weak narrow bands at 1396-1400 cm^{-1} and 1352-1360 cm^{-1}. In all studied samples these bands have the identical intensities that excludes their belonging to an admixture of carbonate mineral. It is more probable that these bands are caused by the vibrations of the H^+ ion, which does not form strong covalent bonds with oxygen.

The group of strong bands at 946 cm^{-1} (with a shoulder at 930), 898, and 848 cm^{-1} belongs to the anti-symmetrical stretching vibrations of the UO_2^{2-} ion, occupying different sites in the crystal structure of the mineral. The bands at 723, 632, and 479 cm^{-1} belong to the stretching vibrations of the molybdenum-oxygen bonds in the MoO_6 octahedra; the latter band is the strongest in the spectrum of calcurmolite.

It is important to note that, according to the data of the IR spectroscopy, there are no the MoO_4^{2-} tetrahedral anions in the crystal structure of calcurmolite. It is known that a maximum of the most intensive band of the Mo-O stretching vibrations in the IR spectra of monomolybdates lay in the range ν_{max}=770-820 cm^{-1}. For example, powellite (ν_{max}=805 cm^{-1}), wulfenite (ν_{max}=778 cm^{-1}), scenicksite (ν_{max}=797 cm^{-1}),

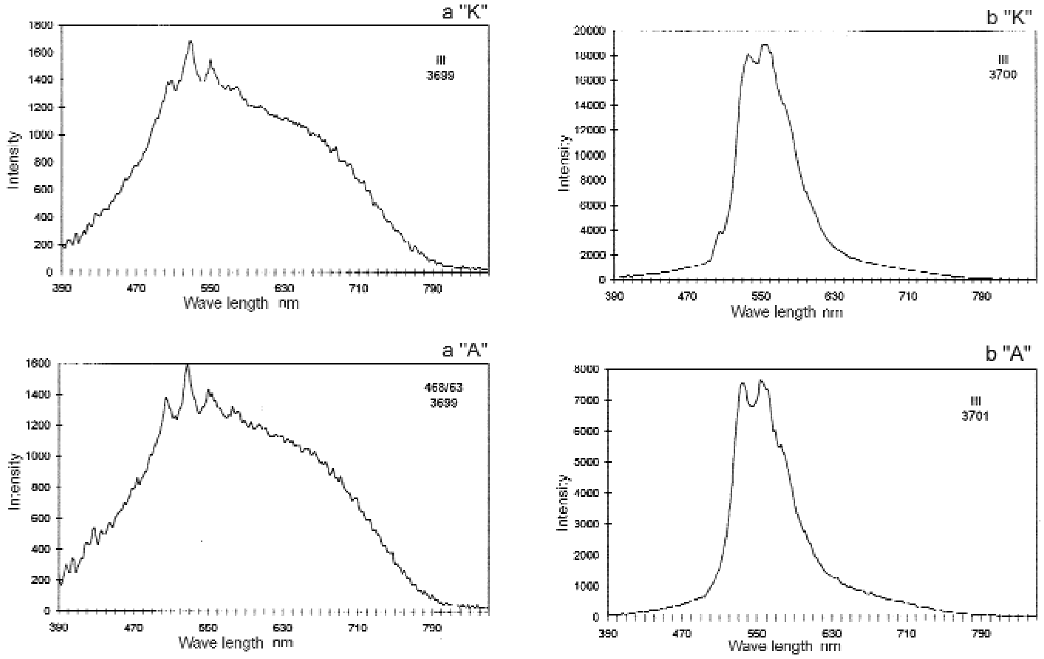

Fig. 8. *The spectra of laser luminescence of calcurmolite from Kazakhstan («K») and Armenia («A»):*
a - at the room temperature; b - at the temperature of liquid nitrogen

etc. The condensation of tetrahedra always results in still more low frequencies of the Mo-O stretching vibrations. So, for umohoite, in which structure the chains of the MoO_6 vertex-joined octahedra are present, the value $\nu_{max} = 593$ cm^{-1}. For iriginite, in which the pairs of the MoO_6 edge-joined octahedra form the chains , connected via common vertexes of octahedra belonging to neighbouring pairs, the value $\nu_{max} = 539$ cm^{-1}. In the case of calcurmolite, $\nu_{max} = 479$ cm^{-1}, that allows with certainty to attribute this mineral to the class of aqueous oxides of hydroxides, but not to the class of molybdates.

On the basis of the IRS data, the general crystallochemical formula of calcurmolite, which does not conflict with the results of study of chemical composition and requirements of the valence balance, can be suggested: $(Ca_{2-x}Na(UO_2)_3Mo_2O_{11-x}(OH)_x$ nH_2O. Taking into account the real chemical compositions of the samples from two deposits, $x = 0.3$, and the formula becomes as follows: $(Ca_{1.7}Na_{0.3})(UO_2)_3Mo_2O_{10.7}OH_{0.3}$ nH_2O; however, it requires a confirmation by the solution of the mineral crystal structure.

The results of study of the luminescence spectra of calcurmolite give the additional information about this mineral. In the publication (Gorobets, Rogozhin, 2001), it is noted that at a room temperature under ultraviolet beam generated by a fluorescent tube, calcurmolite does not give luminescence. Only placed in liquid nitrogen, the crystals of calcurmolite show a yellow luminescence under ultraviolet radiation. However, use of the LGI-505 laser as a source of generation has allowed to register a luminescence spectrum of calcurmolite at a room temperature.

At a room temperature under influence of high-intensive radiation of the laser, the crystals of calcurmolite give luminescence extremely unevenly: the main part has a green colour with bright green zones, which are typical for uranyl, that is connected with phase microheterogeneity of the object. At that, photodestruction of the centres of luminescence is observed: in 10-20 seconds the colour of luminescence becomes dirty-green, bright green zones of uranophane fade less intensively, the zones with yellow luminescence of proper calcurmolite appear.

At a temperature of liquid nitrogen, the spectra are more clear, a splitting of lines on a green one (λ~530 nm), belonging to uranophane, and a yellow one (λ~550 nm), belonging to calcurmolite, is noted that is shown on Figure 8.

Conclusion

The studies of calcurmolite (a mineral, earlier attributed to the calcium-sodium uranyl molybdates) by a complex of contemporary methods on the samples from Kadjaran (Armenia) and Kyzyl-Sai (Kazakhstan) have shown:

1. At seeming homogeneity of transparent grains of the mineral, both visually and under optic microscope, they are practically represented by an aggregate of, as a rule, lath-like or tangled fibrous crystallites formed as a result of pseudomorphous substitutions of uranophane by molybdate.
2. By results of the microprobe electron analyses and data of the IR spectroscopy, the chemical composition of calcurmolites can be expressed by a formula $(Ca,Na)_2(UO_2)_3Mo_2(O,OH)_{11}$ nH_2O, where a value n can reach 10-15, i.e. the mineral is highly hydrated, and the content of Na does not exceed a value of 0.6 *apfu*.
3. Purely calcium or purely sodium members were not found.
4. The sizes of the unit cells, the IR spectra, the spectra of laser-induced luminescence of calcurmolite from Armenia and Kazakhstan are very similar that is an evidence of stability of properties and chemical composition of a mineral species calcurmolite, excepting, probably, some variations of the water content, which does not influence on parameters of the monoclinic unit cell and is caused by relatively weakly bonded molecular water.

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TURANITE FROM TYUYA-MUIUN, KIRGIZIA: NEW DATA ON MINERAL

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The new data has been obtained for turanite described in the beginning of the last century at the Tyuya-Muyun deposit; there are the results of study of the holotype specimen from the Fersman Mineralogical Museum RAS (Moscow) and new field collections. Turanite forms spherulite aggregates in assemblage with tangeite, malachite, barite, quartz, calcite; also turanite forms the cavernous aggregations with tangeite. Turanite is olive-green, transparent, often it is represented by polysynthetic twins; the mineral is brittle. The Mohs hardness is 4.5-5, VHN = 436 (354-570 kg/mm^2). The cleavage is perfect on (011). Density (calc) = 4.452 g/cm^3. The unit cell parameters calculated by the X-ray powder pattern are as follows: $a = 5.377(6)$ Å, $b = 6.276(7)$ Å, $c = 6.833(7)$ Å, $\alpha = 86.28(2)$, $\beta = 91.71(3)$, $\gamma = 92.35(2)°$, $V = 229.8(1)$ Å^3. Chemical composition is as follows (the holotype specimene/new collections; wt %): CuO 62.94/64.81, V_2O_5 28.90/29.86, H_2O 5.85 (calculation by the crystal structural data)/5.81 (calculation by the charge balance), total 97.69/100.52. The empirical formula is $Cu_{4.97}(VO_4)_{2.00}(OH)_{4.08}$.
The IR spectra of turanite and tangeite are given. The mineral genesis is hydrothermal. The turanite study results along with the earlier determined crystal structure confirm its status as the original mineral species. At the same time, a revision of information about findings of turanite in Nevada, USA, is necessary.
3 tables, 4 figures, and 12 references.

Studying minerals of vanadium from South Fergana, the authors have realised that the data on turanite, $Cu_5(VO_4)_2(OH)_4$, at present, is scanty and scarcely satisfactory. In the beginning of the last century, K.A. Nenadkevich described two new vanadium minerals from the radium deposit Tyuya-Muyun, alaite and turanite, named them by location of the Tyuya-Muyun pass, «...proper in the limits of north-eastern part of Alai foothills representing the south border of the Turan basin...» (Nenadkevich, 1909). The article probably had a preliminary character, since there were only a brief description of occurrences of two minerals and also their formulas without chemical analyses. In that article, basing on stoichiometry, the author concluded its closeness to mottramite. At the end K.A. Nenadkevich noted, «...analyses and more detailed description of chemical and physical properties of these minerals will be published in Proceedings of Geological Museum of Academy». But in «Proceedings...» this work was not published for any reasons. A.E. Fersman in his review on geochemistry and mineralogy of Tyuya-Muyun (Fersman, 1928) mentioned turanite together with other vanadates: tangeite, vanadinite, and Turkestanian volborthite*. He noted turanite as the most usual vanadate in the upper horizons, in particular, in the Yellow cave. Larsen and Berman (1937) gave optical properties of turanite, which they obtained on material from Tyuya-Muyun. The interplanar spaces (without the hkl indexes) were published for the first time by Guillemin (Guillemin, 1956).

In addition to Tyuya-Muyun, turanite was found in Nevada, USA: application Van-Nav-Sand, Fish Creek region, Eureka district (Pullman and Thomssen, 1999), the Gold Querry mine, Maggie Creek region (Castor and Ferdock, 2004). These works have a character of reports, and turanite is mentioned here only in reviews of occurrences of Nevada, without some analytical data or references on articles, instrumentally confirming the mineral diagnostic. We have examined by the X-ray method two specimens from the Fish Creek region, Eureka district but both are volborthite.

Absence of the reliable instrumental data on chemical composition and crystal structure of the mineral has resulted in that turanite has got the mark «?» in reference books. Therefore, our goal was to check turanite specimens of the Fersman Mineralogical Museum collections. Determination of the crystal structure of turanite (Sokolova et al., 2004) has clarified a question of its status. Our additional study of the turanite properties has finally confirmed the mineral individuality. In this work the data on chemical composition of turanite, more high-quality X-ray powder data, and the IR spectrum of turanite are published for the first time. More information on assemblage and morphology of mineral aggregations is given also.

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*Turkestanian volborthite, $2V_2O_5 \cdot 2H_2O \cdot 3CaO \cdot 3CuO$ (Fersman, 1928), is tangeite.

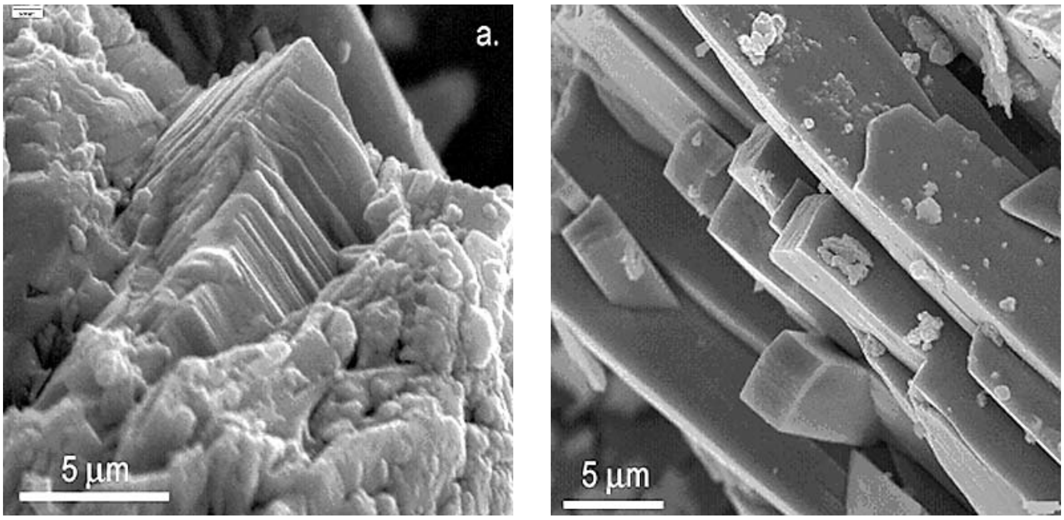

***Fig. 1**. Crystals of turanite and tangeite: a) crystals of turanite; b) aggregate of tangeite crystals from assemblage with turanite. REM-photo*

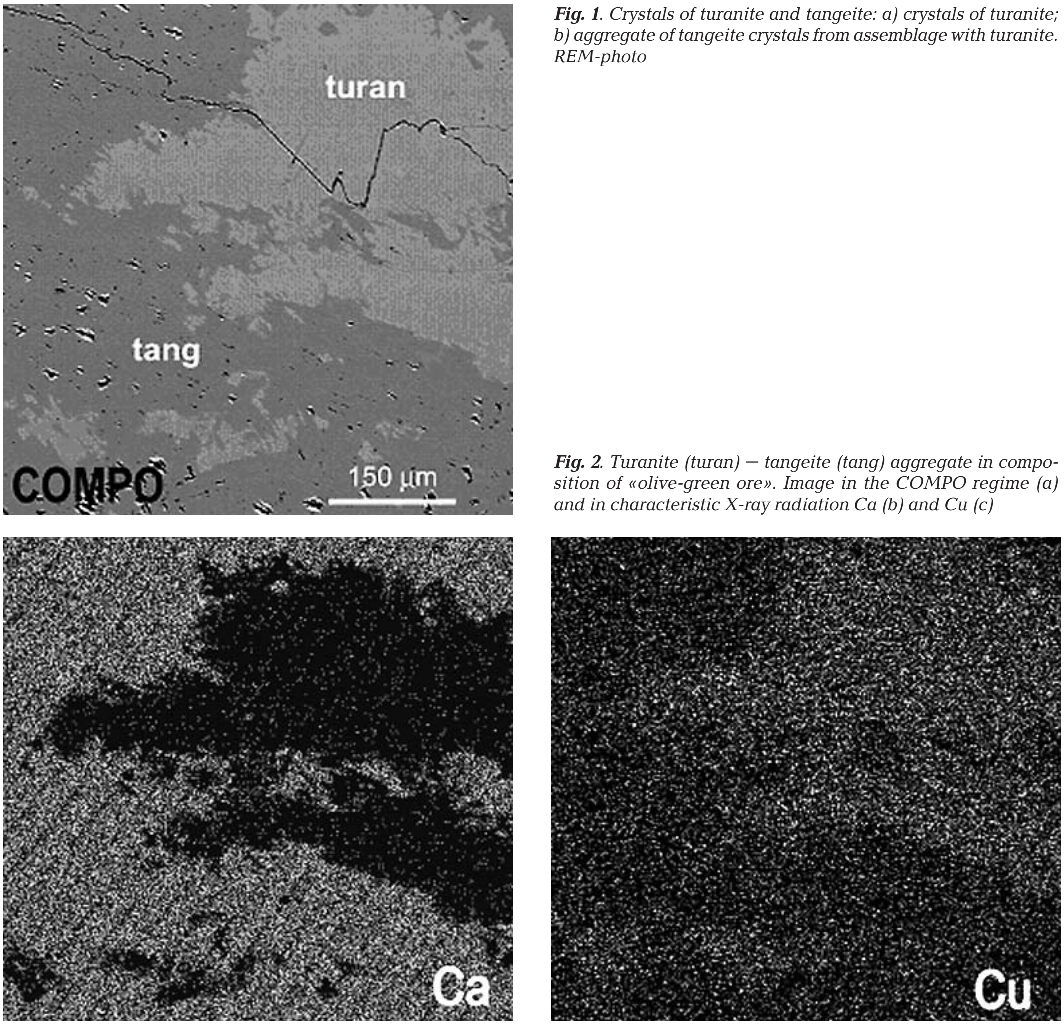

***Fig. 2**. Turanite (turan) — tangeite (tang) aggregate in composition of «olive-green ore». Image in the COMPO regime (a) and in characteristic X-ray radiation Ca (b) and Cu (c)*

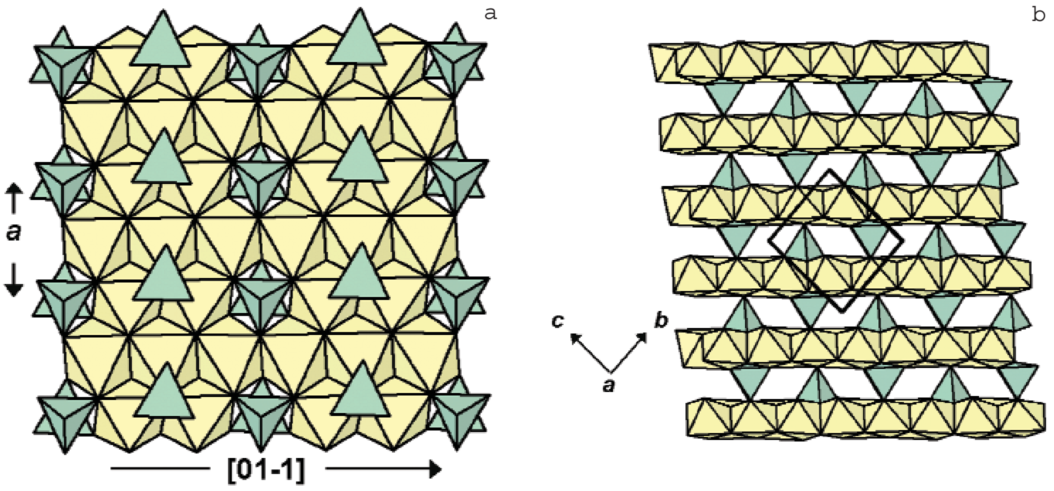

Fig. 3. Crystal structure of turanite (by Sokolova et. al., 2004): a) layers of the Cu octahedra and the V tetrahedra in a projection along {001}; b) mixed octahedral-tetrahedral interlayer, view along [100]. The Cu octahedra are yellow; the V tetrahedra are green

Geology of the deposit

The radium-uranium Tyuya-Muyun deposit has been discovered in 1902; it is located in 30 km to the southeast from the city Osh (Kirgizia), at the left side of middle stream of the Aravan River. It is localized within the bounds of a small range, which was characterized very picturesquely and at the same time exactly by D.P. Mushketov, «...from a distance it appears in the form of sharply outlined, gloomy, long monolith dipped in some extraneous to it, surrounding shapeless mass» (Mushketov, 1926). In the beginning of the last century, the deposit has attracted attention of many researchers, fist of all V.I. Vernadsky, K.A. Nenadkevich, A.E. Fersman, D.I. Shcherbakov. That was connected not only with increased interest to radium at that time, but also unique morphology and genesis of pipe-like ore bodies of the deposit. V.I. Kazanskii (1970) has summarized a history of study of Tyuya-Muyun and also its geological structure. The ore bodies confined to old karst cavities are located in Lower-Carboniferous steeply dipping limestones of sublatitudinal strike, which are penetrated by a grate number of crack dislocations and pressed with both sides by Middle-Upper Paleozoic flinty, coaly-clay shales with intercalations of sandstones and limestones, and also porphyritic tuffs (in the south). The peculiarity of genesis of the Tyuya-Muyun deposit is that «morphology of cavities filled up by ore series is not determined by its active formation during brining of ore elements, but the latter have used in considerable degree the already prepared cavity... of karst character» (Fersman, 1928). The age of karst, according to the data of V.I. Kazanskii (1970), is Paleozoic, i.e. much older than it was supposed by the earlier researchers.

Description of the mineral and assemblage

K.A. Nenadkevich first of all has played a great role in study of material composition of ore bodies of Tyuya-Muyun; he has discovered four new minerals: turanite, alaite, tangeite, and tyuyamunite there. N.N. Smol'yaninova (1970) has made a review on history of mineralogical studies and mineralogy of the deposit. Calcite and barite are the most widespread minerals composing bodies of the karst cavities. Among vanadium minerals, tangeite, including its high-arsenic variety, and tyuyamunite are the most widely distributed; mottramite, descloizite, as well as the vanadium-bearing conichalcite occur in small amounts (Belova *et al.*, 1985). The findings of turanite and alaite are noted only with a reference on the above-mentioned work (Nenadkevich, 1909). Apropos, alaite is not formally approved for some reason by the IMA CNMMN, although its status does not raise doubts thanks to sufficient detailed study of holotype that was conducting by G.A. Annenkova with co-authors (1976).

Table 1. **Unit cell parameters of turanite**

	From data of the crystal structure refinement (Sokolova *et al.*, 2004).	Calculated from the X-ray powder data
a(Å)	5.3834(2)	5.377(6)
b(Å)	6.2736(3)	6.276(7)
c(Å)	6.8454(3)	6.833(7)
α (°)	86.169(1)	86.28(2)
β (°)	91.681(1)	91.71(3)
γ (°)	92.425(1)	92.35(2)
V(Å^3)	230.38(2)	229.8(1)
Space group	P (-1)	
Z	1	

Table 2**. X-ray powder diffraction data for turanite, Tyuya-Muyun.**

No. 3578		Guillemin (1956)		Calculated values		
$I_{meas.}$	*d/n*, Å $_{meas.}$	$I_{meas.}$	*d/n*, Å $_{meas.}$	*I.*	*d/n*, Å.	*hkl*
		80	7.25			
<1w	5.26		5	5.377	001	
10	4.79	100	4.76	100	4.771	011
4	3.67		12	3.659	-111	
7	3.47	20	3.45	30	3.484	111
3	**3.41**		15	3.414	002	
2	**3.14**		11	3.127	020	
3	3.07		18	3.083	012	
3	2.91		9	2.9173	-102	
			9	2.9166	021	
2	**2.84**	20	2.88	9	2.8479	102
9	**2.69**	40	2.70	38	2.6883	200
9	**2.568**	60	2.56	39	2.5682	-1-12
8	**2.491**	30	2.47	39	2.4916	1-21
2w	2.387	10	2.37	7	2.3853	022
7	**2.289**	30	2.29	28	2.2941	211
6	**2.113**	30	2.11	24	2.1162	-103
2	**2.070**		10	2.0761	103	
5	**1.971**	30	1.97	22	1.9709	-130
1	**1.918**	10	1.91	7	1.9178	130
1w	1.829		7	1.8297	-222	
4w	1.741		14	1.7420	222	
3w	1.615	10	1.61	11	1.6161	-114
3w	1.582	10	1.57	15	1.5826	114
5	**1.529**	20	1.53	14	1.5297	-3-12
5	**1.521**			15	1.5231	3-21
2	**1.504**			9	1.5047	-141
4	**1.490**			13	1.4894	0-33
3	**1.469**			12	1.4683	141
3	**1.397**	10	1.40	10	1.3993	-233
2	**1.309**			5	1.3108	-411
				4	1.3092	2-33
<1	1.295			3	1.2965	-2-33
				1	1.2937	-2-41
1w	1.200			3	1.2018	314
				1	1.2003	052
				1	1.1984	-341
1w	1.175			1	1.1767	-144
				3	1.1742	2-15
1w	1.146			4	1.1470	422
				1	1.1463	-431
				2	1.1450	341
1w	1.094			3	1.0941	-2-51
				1	1.0930	153
1w	1.064			2	1.0642	-325
2w	1.059			3	1.0581	-206
1w	1.053			3	1.0581	-206
				2	1.0525	-433
3w	0.986			3	0.9854	-260

Notes. *URS-50IM, FeK radiation, Mn filter, the specimen is a rubber cylinder (d=0.15 mm); RKU-114M camera; w — wide lines; reflexes used for calculation of unit cell parameters are marked by bold (analyst V.Yu. Karpenko)*

The holotype turanite specimen of systematic collection of the Fersman Mineralogical Museum (No. 3578) and also turanite specimen of our field collections (August, 2003) were studied.

The specimen No. 3578 (4.5 x 7.5 x 5 cm in size) was collected by K.A. Nenadkevich in 1910 and recorded in the Museum in 1912. The aggregations of this type were described him as the «radiate fibrous olive-green globular concretions and kidney-shaped crusts almost exceptionally inside cavities in malachite and strongly mineralised limestone». The specimen represents a fragment of crystal crust formed predominantly by fibrous aggregates of malachite (length of needle-shaped crystals is 0.5-3 mm). In the central part of the specimen there is a cavity filled by large, up to 10 mm in diameter, spherulites of turanite, which have the characteristic saturated volborthite tint. At careful examination of the specimen, the constitution of the turanite spherulites is not radiate fibrous, but radiate lamellar; along the biggest side the length of plates is up to 5 mm. The turanite spherulites are covered by thin crust of swamp-green tangeite. This mineral is represented by thin needle-shaped crystals up to 0.1-0.2 mm in size. Apparently, the overgrowth of tangeite on turanite has the epitaxial character. Moreover, tangeite forms the separate crusts of the matted-fibrous and spherulite aggregates (1-2 mm in diameter) with a light grass green, whitish colour, overgrowing on malachite. Sometimes, in cavities one can see the transparent double-headed quartz crystals (up to 1 mm long), containing abundant inclusions of the tangeite needles. Material for the study of the crystal structure (Sokolova *et al.*, 2004) and obtaining of other properties and given below characteristics was collected from this specimen.

Among specimens collected by us on August, 2003, in dumps of the Tyuya-Muyun mine in the west part of the Mt. Radievaya, turanite was found as a part of spongy masses noted by K.A. Nenadkevich (1909) and A.E. Fersman (1928) and named «olive ore» by them.

In the compact tangeite-turanite masses, these two minerals are hardly distinguished from each other, but in cavities, turanite can be recognized at once by the tabular morphology of crystals (Fig. 1a), whereas the rod-like crystals are characteristic for tangeite (Fig. 1b). These two minerals are well distinguished in polished sections by reflectivity, which is bigger for turanite in comparison with that of tangeite. Moreover, turanite is polished much better than tangeite. The cavities in turanite-tangeite aggregates are often completely or partly filled up by calcite, rarely by the honey-yellow, brown crystals of barite. A fragment of this tangeite-turanite aggregate is shown of Figure 2.

Physical properties

Turanite has a rich olive-green colour and a vitreous lustre; it is very similar to volborthite. The mineral is transparent in thin fragments. In immersion preparations it shows a polysynthetic twinning. The width of separate individuals in twins is 0.005-0.03 mm that has complicated the selection of material for the crystal structure study (Sokolova *et al.*, 2004). In the concentrated Clerici solution (density is 4.25 g/cm^3), the mineral grains slowly submerge. The calculated density of turanite is 4.452 g/cm^3. Cleavage is perfect on (011); the mineral is brittle. The Mohs hardness is 4.5-5. The micro-indentation hardness measured with the PMT-3 instrument in a section perpendicular to (011) is VHN = 436 kg/mm^2 (10 measurements, fluctuation of values is 354-570 kg/mm^2, load 50 g, calibrated by NaCl). The hardness of turanite is the additional diagnostic characteristic distinguishing it from volborthite, which is close by surface properties, but has the lower Mohs hardness — 3.5-4, VHN = 150-220 kg/mm^2).

X-ray study

The study of crystal structure of the mineral was made on a four-circle diffractometer Bruker P4 with CCD detector APEX 4K, MoKα radiation (Sokolova *et al.*, 2004). The crystal structure was determined by a direct method and refined with the R factor equal to 2.2% for 1332 unique reflexes; space group is P(-1), the unit cell parameters are given in Table 1. The layers of the Cu octahedra are parallel to (001) and make a basis of crystal structure (Fig. 3a); they cause a perfect cleavage of the mineral. There are three Cu sites, first of which is coordinated by four (OH) groups and two O atoms; the Cu(2) and Cu(3) sites are coordinated by two (OH) groups and four O atoms respectively. Also there is a single four-coordinated V site surrounded by the O atoms. Each of the (VO$_4$) tetrahedra leans by three of four its vertices on the vertices of the vacant octahedra. Being located between the Cu octahedra layers, the tetrahedra form a structure of «sandwich» (Fig. 3b). The same motives are known for crystal structures of simonkolleite, cianciullite, gordaite, cornubite, and ramsbeckite (Sokolova *et al.*, 2004).

We obtained the X-ray powder pattern for

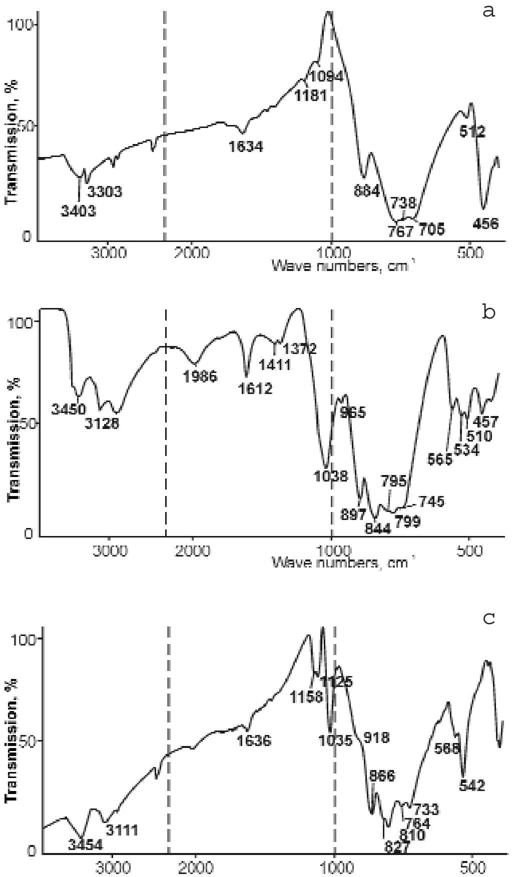

Fig. 4. The IR spectra: a) turanite, the specimen No. 3578 (FMM); b) volborthite (Upper Khodja Akhmet, Uzbekistan); c) tangeite (lab. No. 744)

Table 3. Chemical composition of turanite and tangeite, Tyuya-Muyun (wt %).

Components	Turanite			Tangeite	
	(mean from 2 analisys)	(mean from 2 analisys)			
	1	2	3	4	5
CaO				22.59	11.29
CuO	62.94	64.81	64.60	34.32	23.65
PbO					27.96
V_2O_5	28.90	29.86	29.54	36.35	18.89
SO_3				2.49	0.67
As_2O_5					10.40
H_2O	5.85*	5.81**	5.85	3.66**	3.13**
Total	97.69	100.48	100.00	99.41	95.99

***Note**. Amount of water was calculated: * by results of the crystal structure refinement; ** by the charge balance. 1-3 turanite (calculation on 2 atoms of V): 1 — large spherulites (specimen No. 3578, systematic collection of the FMM), $Cu_{4.97}(VO_4)_{2.00}(OH)_{4.08}$; 2 — a part of the spongy tangeite-turanite aggregates (lab. No. 744, 2003), $Cu_{4.96}(VO_4)_{2.00}(OH)_{4.08}$; 3 — ideal chemical composition, $Cu_5(VO_4)_2(OH)_4$; 4-5 tangeite (calculation on the base of 1 atom (V+As+S): 4 — a part of the spongy aggregates with turanite (lab. No. 744), $Ca_{0.94}Cu_{1.00}(VO_4)_{0.93}(SO_4)_{0.07}(OH)_{0.95}$; 5 — lead-arsenic tangeite the zoned-concentric kidney-shaped concretion, $(Ca_{0.66}Pb_{0.40})_{1.06}Cu_{0.97}[(VO_4)_{0.68}(AsO_4)_{0.29}(SO_4)_{0.03}]_{1.00}(OH)_{1.09}$. Analyses 1, 2, 4 — analyst A.A. Agakhanov; 5 — analyst P.E. Kotel'nikov*

the specimen No. 3578. The unit cell parameters calculated by the X-ray powder pattern and the interplanar distances and are given in the Tables 1 and 2 respectively. The X-ray data given by C. Guillemin (1956) correspond in whole to our data, excepting an interplanar distance d/n = 7.25 Å, which is possibly an artifact or connected with some admixture.

The turanite crystals have a tabular habit determined by a pinacoid {011}. The large crystals of turanite is not well-shaped; unfortunately, it was not possible to measure the small crystals (up to 0.05 mm) because of their size.

Chemical composition

Turanite is the second hydrous vanadate of copper after volborthite, which has been found in nature. Chemical composition of the mineral was studied with a JCXA-50A JEOL electron microprobe instrument, equipped with a LINK energy-dispersive spectrometer, at accelerating voltage 20 kV and electron microprobe current 3 nA. Standards were as follows: metallic Cu and V (Cu, V), diopside USNM 117733 (Ca), barite (S). The arsenic-lead tangeite (an. 5) was analysed with an Superprobe 733 instrument equipped with a INKA ENERGY energy-dispersive spectrometer, 20 kV, electron microprobe current 2.5 nA; standards were as follows: metallic Cu and V (Cu, V), $CaSiO_3$ (Ca), SiO_2 (Si), PbS (Pb), GaAs (As).

The calculated data was accepted for H_2O. Chemical composition of the mineral is given in Table 3. Moreover, tangeite, forming a part of the cavernous aggregates together with turanite, was analysed. A small amount of sulphur, stably presenting in different parts of the analysed tangeite, attracts attention. Arsenic tangeite with unusually high content of lead was found in one of the specimens formed by the zoned kidney-shaped aggregate. Although, in this specimen turanite was not detected, we give chemical composition of tangeite, which more completely characterizes an assemblage of vanadium minerals of Tyuya-Muyun.

IR spectra

The IR spectra of turanite and tangeite were obtained with a Nicolet IR Fourier spectrometer; a mineral specimen was pressed in the KBr tablet (Fig. 4). For comparison, the IR spectrum of volborthite obtained in identical conditions is given. On the spectra of turanite and volborthite one can see the characteristic absorption bands in a range of 450-460 cm^{-1} and 730-1100 cm^{-1}; they are connected with the stretching vibrations of the VO_4 tetrahedra. The main distinctions among them are in a range of 510-600 cm^{-1}. Probably, these distinctions are connected with a presence of the VO_4 tetrahedra jointed in diorthogroups in volborthite. In addition to the characteristic absorption bands connected with the VO_4 tetrahedra, tangeite has a small band in a range of 1120-1160 cm^{-1} that is caused by a sulphate group included in the structure. These data is quite conformed to data of the electron microprobe analysis. In volborthite, the presence of the molecular water is fixed by an intensive band of the bending vibrations δ_{H_2O} at 1612 cm^{-1}, whereas this band is not enough expressed in the tangeite and turanite spectra. A range of 3000-3500 cm^{-1} corresponds to the stretching asymmetric vibrations of the (OH) groups.

Genesis and discussion

The results of study of the holotype specimen and an examination of the additionally collected material show that turanite is indeed a quite individual mineral with the original crystal structure and chemical composition.

According to data of A.E. Fersman (1928), turanite was formed from thermal waters, which extracted vanadium from the Mesozoic coaly shales located to the south. Quartz porphyries cutting the shales were a source of copper. For all specimens we have observed the more late formation of tangeite with respect to turanite. That seems connected with solutions enrichment by calcium. It is interesting, that at the deposit is no volborthite in spite of abundance of vanadium and copper. Formation of turanite instead of volborthite is an evidence of the specific genetic conditions, which cannot occur realized in nature frequently. Since volborthite was found in the specimens from Nevada, USA, the authenticity of the turanite findings here raises doubts and necessarily demands the instrumental confirmation.

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EASILY OXIDIZABLE CHALCOPYRITE FROM BLACK SMOKERS OF THE RAINBOW HIDROTHERMAL FIELD (MID–ATLANTIC RIDGE, 36°14'N)

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Anomalous chalcopyrite from newly discovered sulphide tubes of deep sea hydrothermal vents known as black smokers in the Rainbow field has been studied by a series of methods (X-ray spectral microprobe analysis, mineragraphy, scanning electron microscopy, and X-ray micro-diffraction method). In contrast to common chalcopyrite, the mineral quickly tarnishes in polished sections (high-copper sulphides of chalcocite-digenite series were detected in the oxidized film). The newly polished surface is isotropic in reflected light; the reflectance spectra belongs to chalcopyrite type, but R coefficients are much lower than standard ones (by 10-15%). The interval of values of micro-indentation VHN significantly exceeds those in common chalcopyrite (114-235 to 181-203 kgs/mm^2). These characteristics indicate that the mineral is similar to two easily oxidizable cubic sulphides of the chalcopyrite group, talnakhite and putoranite. In the chemical composition, more copper than iron was noted in the limits expressed by the empirical formula $Cu_{1-x}(Fe,Co,Ni)_{1+x}S_2$, where x changes from 0 to 0.09 at a constant ratio Me/S = 1. The mineral is identified as standard chalcopyrite by X-ray powder diffraction. There are two different reflection parts. The first ones are sharp and correspond to cubic cell with a = 5.25 Å. The second ones are wide that means disorder in chalcopyrite structure. Thus, X-ray diffraction data also confirms the similarity of easily oxidizable chalcopyrite to talnakhite and putoranite.
3 tables, 4 figures, 24 references.

In recent decades of the last century in high-temperature deposits of the Norilsk type and in dunite pegmatites of Bushveld, four sulphides have been found. They are close to chalcopyrite, but are distinguished from it by a deficiency of sulphur: their ratio Me/S>1, whereas in chalcopyrite it is equal to 1. Two of these minerals, talnakhite and putoranite, belong to the cubic system. They can be oxidized easily in the open air in polished sections. Both minerals were originally described as cubic chalcopyrite (Bud'ko, Kulagov, 1963; Genkin *et al.*, 1966; Filimonova *et al.*, 1974).

In sulphide silts of the Red Sea in the Atlantis II deep, isotropic chalcopyrite was discovered and described; the proposed name was isochalcopyrite (Missack *et al.*, 1989). This name appears in the Mineralogy Database on the Internet as a mineral species that was not registered in the IMA Commission on New Minerals and Mineral Names (CNMMN).

During study of oceanic sulphide ores from black smokers of the Rainbow hydrothermal field (Mid-Atlantic Ridge, 36°14'N), an isotropic chalcopyrite, that oxidized easily in polished sections in the open air, was encountered; similar to the above-mentioned cubic minerals by properties. The results of its detailed study are given below.

General characteristic of studied mineral

The samples of ores were picked up from a depth of nearly 2300 m by deep-water inhabited apparatus (DIA) «Mir-1» during run 47 of the scientific-research ship «Academician Mstislav Keldysh» in 2002. They represent the small tubes, branches of larger tubes. Their age, when studied, was not more than two years, since during the preceding run in 2000, the intense activity of black smokers was not yet fixed in this section of the ore field.

Studied tubes belong to the copper type represented mainly by minerals of the Cu-Fe-S and Cu-S systems in contrast to the zinc type, in which sphalerite and iron sulphides predominate. The tubes were small in sizes: their length was 5—12 cm, diameter was from 2 up to 8 cm, the thickness of the walls of the largest specimens was 30 mm. In the centre of the tubes there were one or more channels (Fig. 1).

Minerals and their structural-textural correlations in tubes were studied in polished sections made without heating, in reflected light under ore microscope and scanning electron microscope JEM-100C (IGEM). The results have shown that the tube walls had a distinct zoned structure that was described in detail in the special article (Borodaev *et al.*, 2004). All copper tubes have a similar scheme of zoning; only the width of the zones varies. From the channel to the tube surface are the following zones: I — a zone composed of recently discovered Y phase, that is close to isocubanite (Mozgova *et al.*, 2002); II — chalcopyrite zone represented by an easily oxidizable variety of this mineral, which is described in this work; III — bornite zone, and IV — a zone formed by an assemblage of copper sulphides (chalcocite, digenite, *etc.*).

The chalcopyrite zone that is of interest to us in comparison with other zones has a significantly larger width reaching 5-8 mm in some tubes. The structure of this zone (as well as the first one) is radiate-fibrous with the size of separate elongated grains up to 400 mμ. In newly polished sections in reflected light, a mineral composing this zone has a yellow colour and looks like common chalcopyrite, and is not easily distinguished by reflection and colour from the Y phase in contact with it. Because of quick oxidation in the open air, chalcopyrite looks pinkish-brown, and a border with the Y phase becomes clearly visible (Fig. 2a). At the contact between them, the lattice structure formed by lamellas of tarnished chalcopyrite in the matrix of Y phase is observed (Fig. 2b).

During the study of easily oxidizable chalcopyrite in newly polished sections it was determined that in reflected light the mineral behaves like an isotropic one: anisotropy was not observed even in immersion. Reflection was measured with automatic spectrophotometer MSFU-3121; Si was the standard; objective was 20x0.40. The results have shown (Table 1, Fig. 3a) that the reflectance spectrum of chalcopyrite from the Rainbow is very close to the same spectrum of chalcopyrite and cubic minerals of this group. At the same time, the values of reflection of studied mineral are much lower (on average 10-15%) than the corresponding values of common chalcopyrite and slightly less than the reflection coefficients of talnakhite (on average 2-3%) and putoranite (on average 1-2%). Measurement of reflection values of chalcopyrite covered by an oxidation film has shown the

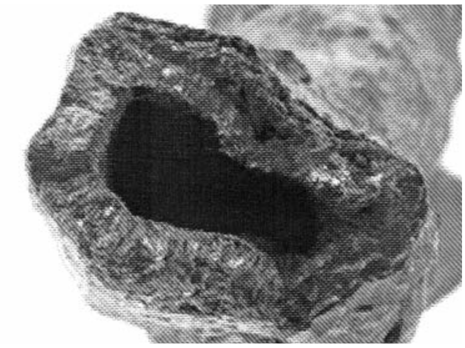

Fig. 1. *Cross-section of zoned cooper tube with easily oxidizable chalcopyrite (specimen FMM No. 4412-M1-6). 1.5x*

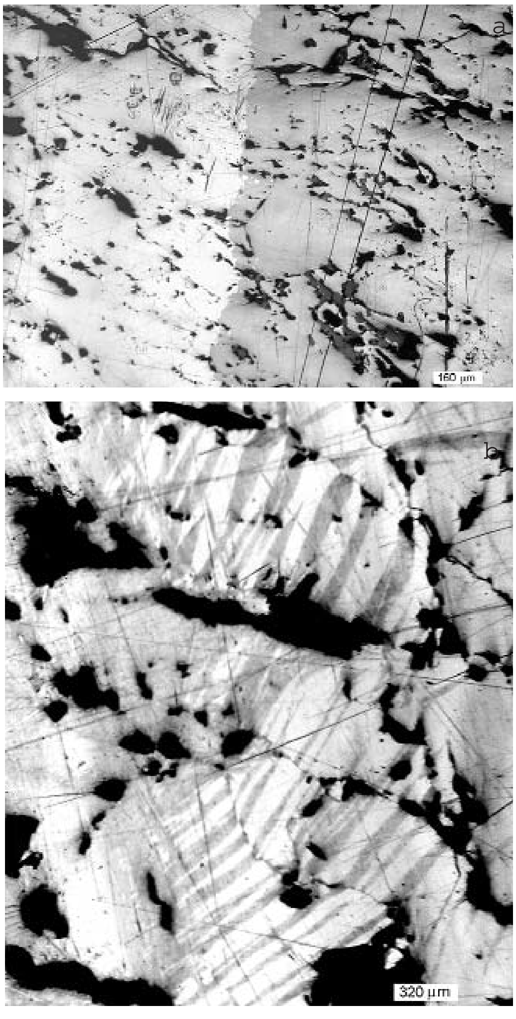

Fig. 2. *Contact of a zone of easily oxidizable chalcopyrite with a zone of Y phase. Polished section in reflected light: a — zone of Y phase (white), zone of easily oxidizable chalcopyrite (grey); b — lattice structure of an aggregate directly on the contact of both zones: lamellae are easily oxidizable chalcopyrite (grey), matrix is Y phase (white)*

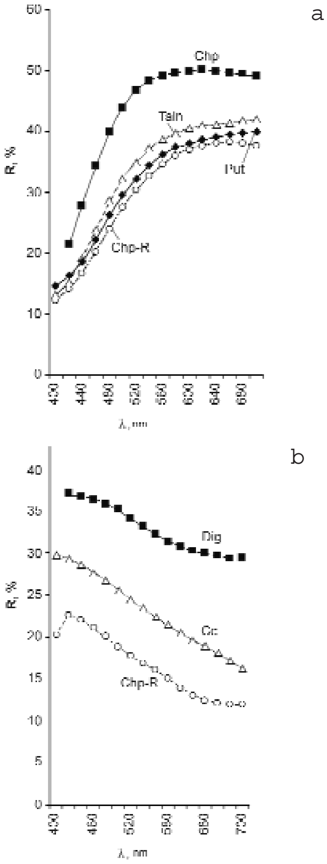

Fig. 3. *eflectance spectra for easily oxidizable chalcopyrite in comparison with published data (Chvileva et al., 1988):*
a) newly polished easily oxidizable chalcopyrite from Rainbow (Chp-R), putoranite (Put), talnakhite (Taln), and common chalcopyrite (Chp);
b) reflectance spectra for chalkopyrite covered by oxidation film from Rainbow (Chp-R), digenite (Dig), and chalcosine (Cc)

Table 1**. Reflectances of newly polished chalcopyrite from Rainbow (1), putoranite (2)*, talnakhite (3)*, and common chalcopyrite (4)***

λ, nm	1	2	3	4
400	12.3	14.6	13.0	–
420	14.1	16.1	15.2	21.3
440	16.6	18.7	19.2	27.9
460	20.2	22.3	23.9	34.2
480	23.9	26.1	28.6	39.8
500	27.4	29.4	32.1	43.8
520	30.3	32.2	34.9	46.7
540	32.5	34.4	37.1	48.3
560	34.5	36.1	38.7	49.1
580	36.0	37.3	39.7	49.7
600	36.9	38.0	40.4	49.9
620	37.5	38.6	40.8	50.0
640	38.0	39.0	41.2	49.9
660	38.2	39.4	41.4	49.7
680	38.0	39.6	41.8	49.4
700	37.5	39.8	42.0	49.1

Note: *analysis marked by * done after Chvileva et al., 1988*

strong decrease of R coefficients in comparison with a newly polished surface (on an average of 20-25% in the long-wave part of the spectrum) and opposite inclination of reflectance spectrum, which is similar to spectra of digenite and chalcocite by configuration (Table 1, Fig. 3b).

Micro-indentation VHN of the studied chalcopyrite, which was obtained with PMT-3 instrument at load 30 g, is was within the limits 114-235 kgs/mm^2; according to reference data (Anthony *et al.*, 1990), it is lower than corresponding values of talnakhite (261-277 kgs/mm^2) and putoranite (263 kgs/mm^2) and significantly exceeds the fluctuation of values of chalcopyrite (181-203 kgs/mm^2).

Thus, easy oxidizability in the open air as well as optical characteristics indicate a considerable distinction of described chalcopyrite from Rainbow from common chalcopyrite and its similarity to cubic minerals of the chalcopyrite group.

Chemical composition

Chemical analyses were performed with X-ray spectral microprobe instrument CAMEBAX-SX-50 and energy-dispersive spectrometer Link ISIS on electron microscope JEM-100C. Conditions of mesurements on CAMEBAX-SX-50 were: 20 kV, 30 nA; standards (element, line) were: CuS (CuKα), FeS (FeKα, SKα).

Results obtained in comparison with data on isochalcopyrite and theoretical chemical compositions of the chalcopyrite group minerals are given in Table 2. Chemical composition of the studied mineral varied within small limits (wt %): Cu 31.23-34.75; Fe 27.87-32.26; S 34.98-36.03. Admixtures of Co (to 0.34, in one analysis up to 3.56 wt %) and Ni (0.25-1.49 wt %) were noted in insignificant amounts. In single instances Au (to 0.4 wt %) and Ag (0.1 wt %) were detected. Analyses were calculated on the formula of chalcopyrite, $CuFeS_2$. Intervals of fluctuation of formula coefficients are as follows: Cu from 0.90 to 1.01, (Fe+Co+Ni) from 0.99 to 1.08, which allows the presenting of the general empirical formula as $Cu_{1-x}(Fe,Co,Ni)_{1+x}S_2$, where x changes approximately within the limits of 0 to 0.09. At the maximum value of x =(0.09) the composition of the end-member in atomic percents is as follows: Cu – 22.75, Fe – 27.25, S – 50; which deviates from the ideal one (Cu – 25, Fe – 25, S – 50 at %) by 2.25 at % in metal contents. The ratio Me/S remains close to 1 in contrast to isochalcopyrite and the chalcopyrite group minerals, where it is always more than 1. On the triangle diagram Cu-Fe-S (Fig. 4), chem-

Table 2. **Chemical composition (wt %) of easily oxidizable chalcopyrite from Rainbow (data of electron microprobe analysis in comparison with reference data)**

№ of sample.	№ an	Cu	Au	Ag	Fe	Co	Ni	Zn	S	Total
Homogeneous chalcopyrite										
4-10	8	31.23	0.37	–	27.87	3.56	1.49	–	35.06	99.58
4-10	6	32.39	0.24	0.10	32.36	0.34	0.20	0.02	35.53	101.18
4412-9	6	33.35	–	0.03	31.45	n.d.	n.d.	–	35.77	100.60
4412-9	5	33.56	–	–	32.16	n.d.	n.d.	–	35.68	101.40
4412-9	32*	34.09	–	–	31.22	n.d.	n.d..	–	36.03	101.34
4-10	9	34.17	0.09	–	30.07	0.11	0.25	0.12	35.38	100.19
4412-6	15*	34.75	–	–	30.25	n.d.	n.d.	–	34.56	99.56
Average		33.36	0.10	0.02	30.77	0.57	0.28	0.02	35.43	100.55
Lamellae from disintegration structures										
4412-9	3L	32.63	0.40	–	31.85	n.d.	n.d.	0.02	35.55	100.45
4412-6	7L	33.01	–	0.03	31.75	n.d.	n.d.	0.15	35.64	100.58
4412-6	10L	33.21	–	–	31.42	n.d.	n.d.	0.02	34.98	99.63
Average		32.63	0.13	0.01	31.42	0.06			35.39	100.22
Isochalcopyrite (Atlantis II, the Red Sea) (Missack *et al.*, 1989)										
Homogeneous		34.04	–	–	32.20	–	–	0.15	33.87	100.26
Lamellae (grain centre)**(L-1)		31.69	–	–	34.51	–	–	0.20	33.85	100.25
Lamellae (grain edge)*** (L-2)		33.08	–	–	32.81	–	–	0.26	33.88	100.03
Theoretical chemical composition of the chalcopyrite group minerals (Anthony *et al.*, 1990)										
Chalcopyrite $CuFeS_2$		34.56			30.52				34.92	100.00
Putoranite 4* $Cu_{18}(Fe,Ni)_{18}S_{32}$		35.68			31.22		0.51		32.49	99.9
Putoranite 5* $Cu_{16}(Fe,Ni)_{19}S_{32}$		32.99			32.11		1.63		33.14	99.87
Talnakhite $Cu_9(Fe,Ni)_8S_{16}$		37.15			29.10		0.75		33.31	100.31
Mooihoekite $Cu_9Fe_9S_{16}$		36.02			31.66				32.32	100.00
Haycockite $Cu_4Fe_9S_8$		32.18			35.35				32.47	100.00

Formula coefficients (calculation on 4 atoms in formula).

N	Cu	Fe	Co	Ni	Zn	Σ Fe, Co,Ni	S	ΣMe	Me/S	Cu/Fe
Homogeneous chalcopyrite										
8	0.90	0.92	0.11	0.05		1.08	2.01	1.99	0.99	0.83
6	0.92	1.05	0.01	0.01		1.07	2.01	1.99	0.99	0.86
6a	0.95	1.02				0.95	2.02	1.98	0.98	0.93
5	0.95	1.04				1.04	2.01	1.99	0.99	0.91
32*	0.97	1.01				1.01	2.03	1.97	0.97	0.96
9	0.98	0.98		0.01		0.99	2.02	1.98	0.98	0.99
15*	1.01	1.00				1.00	1.99	2.01	1.01	1.01
Average	0.96	1.00	0.02	0.01		1.03	2.01	1.99	0.98	0.93
Lamellae from disintegration structures										
3L	0.94	1.04				1.04	2.02	1.98	0.98	0.90
7L	0.94	1.03				1.03	2.02	1.98	0.98	0.91
10L	0.96	1.03				1.03	2.00	1.99	1.00	0.93
Average	0.95	1.04				1.04	2.02	1.99	0.99	0.91
Isochalcopyrite (Atlantis II, the Red Sea) (Missack *et al.*, 1989)										
Homogeneous	0.99	1.06					1.95	2.05	1.05	0.93
L-1	0.92	1.14			0.01		1.94	2.07	1.07	0.80
L-2	0.96	1.08			0.01		1.95	2.05	1.05	0.88

Chemical composition of the chalcopyrite group minerals

	Cu	Fe	Ni	S	ΣMe	Me/S	Cu/Fe	
Chalcopyrite	1	1		2	2	1	1	
Putoranite 4*	18		18	32	36	1.12	1	
Putoranite 5*	16		19	32	35	1.09	0.84	
Talnakhite	9		8	16	17	1.06	1.12	
Mooihoekite		9	9		16	18	1.12	1
Haycockite	4	5		8	9	1.12	0.8	

Note. *Analysts: I.A. Bryzgalov (CAMEBAX, MSU); *N.V. Trubkin (Link, IGEM RAS); ** – average from 5 analyses; *** – average from 3 analyses; 4* – average from 7 analyses; 5* – average from 12 analyses; n.d. -not detected; dash – not determined*

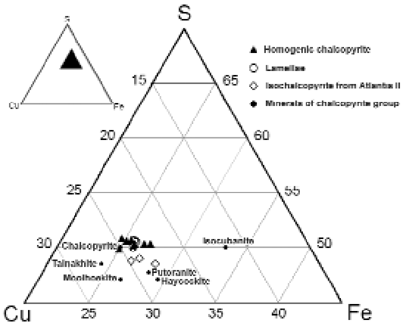

***Fig. 4**. Distribution of chemical compositions of easily oxidizable chalcopyrite (homogenous and lamellae in structures of decomposition of solid solution) from Rainbow, isochalcopyrite from Atlantis II (Missack et al., 1989), and the chalcopyrite group minerals (Anthony et al., 1990) on the triangle Cu-Fe-S-diagram (at %)*

ical compositions of analysed chalcopyrite from Rainbow lies on intersection answering to a ratio of Me/S = 1. From the theoretical composition of chalcopyrite they moved slightly towards an increase of Fe content, towards isocubanite. Points of theoretical compositions of all other minerals of the group are below this intersection on the diagram.

X-ray data

Material extracted from the part of the chalcopyrite zone of a tube analysed with an electron microprobe instrument was used for X-ray study. Registration of the spectrum was carried out by an automatic diffractometer Rigaku D/Max-2000/PC, Cu-K_α radiation, at continuous scanning with a rate of 0.1° (2θ)/s. Correction by means of the Si standard was used in the calculation.

The results of the X-ray study in comparison with standard data for tetrahedral chalcopyrite and cubic chalcopyrite are given in Table 3. Comparison with the chalcopyrite standard gives satisfactory coincidence of X-ray powder patterns and calculated sizes of unit cells.

At the same time, the X-ray diffraction pattern of the studied sample had a number of peculiarities (Table. 3). Some of its reflexes are visibly widened. It is obvious from the third column, where the full width at the half of maximum (FWHM) is given for each reflection; FWHM grows with increase of reflection angle. There are the mainly weak ones that belongs to chalcopyrite tetragonal system (reflections No. 4, 6, 10). As it is evident from the table, sharp and strong reflections correspond to reflections of cubic chalcopyrite.

In addition, X-ray powder patterns were made by Debye-Scherrer method (diameter of camera is 114) with Si standard. The results obtained on material extracted from previously analysed samples on a newly polished section correspond to tetragonal chalcopyrite. On the X-ray powder pattern obtained from microamounts of oxidized chalcopyrite covered by a grey film there are several additional weak lines (intensity of 1-2) in small angle region. Among them the lines with interplanar distances 2.558 and 2.193 are similar to reflexes (2.54, 2.59, and 2.16) of standard X-ray powder pattern of anilite, Cu_7S_4, which belongs to high-copper sulphides of the chalcocite-digenite series: chalcocite, djurleite, anilite, digenite, with Cu/S from 2 to 1.125 (Gablina *et al.*, 2000).

Discussion

As was mentioned above, in studied chalcopyrite the maximum deviation from the stoichiometric ideal formula is 2.25 at % for metals. This is within the limits (2.4 at %) of the chemical composition of chalcopyrite from continental deposits, obtained by processing of the publilshed reference data (Lafitte, Maury, 1982). As is known from experimental data, the close limits (from $CuFeS_2$ to $Cu_{0.9}Fe_{1.1}S_2$) were detected in hydrothermal conditions for a very narrow range of chalcopyrite solid solution at 350 °C and 300 °C in the Cu-Fe-S (Sugaki *et al.*, 1975) and Cu-Fe-Zn-S (Ueno *et al.*, 1980) systems. Consequently, chalcopyrite from Rainbow does not differ by chemical composition from common natural and synthetic chalcopyrites in spite of isotropy, easy oxidizability, low values of reflectance and micro-indentation hardness.

In putoranite and talnakhite the same change of properties was presumably connected with the filling of vacancies in chalcopyrite crystal structure by additional metal atoms (Filimonova *et al.*, 1974; 1980), since these minerals are distinguished from chalcopyrite by a surplus of metals (Me/S>1). The explanation of the unusual characteristics of chalcopyrite from Rainbow are evidently also explained by peculiarities of crystal structure. It is most probably the widening of some reflexes on X-ray diffraction patterns is caused by the defects in crystal structure. Judging by the above-mentioned similarity of strong and sharp peaks of obtained X-ray powder pattern to reflections of cubic chalcopyrite, the distribution of cations by sulphur tetrahedra differs slightly from the cubic one. It means a tendency for statistic distribution of different cations

Table 3. **X-ray diffraction data for easily oxidizable chalcopyrite in comparison with standards**

Studied sample № 4412-6				Standard of chalcopyrite (83-0983 JCPDS)			Standard of cubic chalcopyrite (75-0253 JCPDS)		
№	I	d	FWHM*	*I*	*d*	*hkl*	*I*	*d*	*hkl*
1	100	3.04	0.169	100	3.036	112	999	3.0183	111
2	4	2.65	0.474	4.3	2.643	200	66	2.614	200
3	20	1.871	0.258	16.8	1.869	220	487	1.8483	220
4	32	1.857	0.275	32.5	1.854	204			
5	17	1.593	0.301	18.2	1.5916	312	269	1.5763	311
6	9	1.576	0.339	4.8	1.5712	116			
7	1.5	1.520	0.726	1	1.5181	224	11	1.5091	222
8	2.5	1.3578	0.502	1	1.3506	323			
9	4	1.3225	0.438	3.5	1.3216	400	52	1.3070	400
10	1.8	1.3033	0.567	1.8	1.3013	008			
11	3.2	1.2132	0.488	2.6	1.2118	332	76	1.1993	331
12	5	1.2052	0.423	5.1	1.2038	316			
13	1.4	1.1601	0.715	0.2	1.1687	208	7	1.1687	420
		$I\bar{4}2d$			$I\bar{4}2d$			$F\bar{4}3m$	
		$a = 5.289(2)$			$a = 5.2864(1)$			$a = 5.228$	
		$c = 10.422(6)$			$c = 10.4102(1)$			$V = 142.89$	
		$V = 291.56$			$V = 290.9$				

Note: **FWHM — full width at half maximum*

in tetrahedra. In common tetragonal chalcopyrite, copper and iron atoms have strictly ordered distribution, but in cubic chalcopyrite they are completely disordered. The indistinct character of peaks on X-ray diffraction pattern determines with a high degree of probability is determined by the incomplete order of different cations between different positions.

A question about details of this phenomenon demands an additional study with use of microdiffraction methods and high-precision electron microscopy. Since chalcopyrite belongs to semi-conductors and has antiferromagnetic properties (Vaugan, Kreig, 1978), the study of magnetic and electromagnetic characteristics is also perspective.

Obtained data allow the consideration of some peculiarities of the oxidation process of described chalcopyrite. It is known, that a question about the valency of copper and iron in chalcopyrite was disputed for a long time, and results from the Messbauer spectra of this mineral are discrepant. Nevertheless, recently the formula of chalcopyrite was presented in the form of $Cu^+Fe^{3+}S_2$, where iron is in higher oxidation degree and copper is univalent (Vaugan, Kreig, 1978). If this formula is used as the basis, then in chalcopyrite from Rainbow only copper atoms can be exposed to oxidation: $Cu^+ \rightarrow Cu^{2+}$. Possibly, the process is not complete. A surplus of Cu^+ atoms formed during this process diffuses on the surface of a polished section for maintenance of charge balance; where it forms a film of high-copper sulphides of the chalcocite-digenite series, in which univalent copper dominates.

Thus, the process of copper oxidation is accompanied by copper diffusion. In this connection, it is essential to emphasize that copper in the crystal structures of Cu-bearing minerals often has high mobility. So, in high-copper fahlores, according to X-ray data (Makovicky, Skinner, 1976), part of the copper ions is in motion, without fixing on definite sites; this in many respects determines the nonstoichiometry of these minerals (Mozgova, Tsepin, 1983). It is also known that on the surface of polished sections of Cu-bearing minerals during their exposure to the open atmosphere, new formations of copper sulphides in the form of bushy aggregates and films appear (Mozgova *et al.*, 1994).

Previously published studies show that the Cu-Fe-S system, which was intensively studied during the last century (Merwin, Lombard, 1937; Schlegel, Schuller, 1952; Hiller, Probsthain, 1956; Yund, Kullerud, 1966; Cabri, 1973; Likhachev, 1973, *etc.*), still holds many riddles demanding further study with a variety of methods.

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MINERALS OF THE NICKELINE-BREITHAUPTITE SERIES FROM METAMORPHOGENIC-HYDROTERMAL VEINS OF THE NORILSK ORE FIELD

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The antimonide-arsenide mineralization of the Norilsk ore field, which was considered by previous researchers as a derivative of the P_2-T_1 trap formation, is connected with the post-trap regional metamorphism in conditions of zeolite facies with age 164-122 MA. The antimonide-arsenide mineralization is younger than a trap formation for more than 80 MA. Arsenides and antimonides of Ni (Co, Fe) occur among the metamorphosed Ni-Cu sulphide ores and in the nearest periphery of their deposit, mainly in the calcite and anhydrite-calcite veins. Parameters of vein formation are as follows: P = 0.9-0.1 kbar, T = 216-127°C, solutions NaCl-$MgCl_2$ of low salinity (0.2-1.4% equiv. NaCl). History of formation of metamorphogenic-hydrothermal aggregations is complicated. Three cycles of the antimonide-arsenide mineralization are revealed. The first cycle includes ten mineral complexes with significantly arsenide composition; presence of nickeline with high content of Co, diarsenides, and triarsenides of Ni-Co is characteristic. The second cycle includes two mineral complexes with significantly antimonide composition; presence of silver minerals is characteristic. The third cycle is represented by the sulphoarsenide-sulphoantimonide mineral complex.

The minerals of the nickeline-breithauptite continuous series form a considerable part of the antimonide-arsenide mineralization. The end-members of the series, nickeline and breithauptite, are the most widespread; antimony nickeline is quite wide distributed. The Norilsk nickeline contains up to 12 wt % of Co, up to 3 wt % of Fe and S. Breithauptite is poor by Co, Fe, S, Se. In concentrates of nickeline, Pd, Pt, and Au were not detected. The zones of geometrical selection are present in the aggregates of arsenides and antimonides; that is an evident of crystallization of arsenides and antimonides from the normal solutions in open space.

9 tables, 9 figures, 24 references.

Introduction

The arsenide mineralization is not characteristic for the magmatic Ni-Cu ores. Such mineralization occurs in the metamorphosed types of these ores (Schneiderhohn, 1953a; Yakovlev *et al.*, 1981; Leblanc *et al.*, 1990; Hytonen, 1999).

Nickeline, NiAs, and breithauptite, NiSb, are distributed in different types of hydrothermal deposits, especially they are characteristic for deposits of the five-element formation and close to them nickel-cobalt-arsenide deposits (Krutov, 1959; Ramdohr, 1962; Dymkov, 1985; Chvileva *et al.*, 1988). In these deposits, nickeline usually predominates (Bou-Azzer, Morocco; Khovu-Aksy, Tuva, etc.). Breithauptite prevails significantly rarely (Wittichen, German). In single deposits of the five-element formation (Belorechenskoe, Northern Caucasus), the intermediate members of the nickeline-breithauptite isomorphous series are also widespread (Pekov, 1993). Our observations have shown that minerals in the limits of a whole series of nickeline-breithauptite occur at the Norilsk ore field.

The Ni-Co-arsenide mineralization in the Norilsk sulphide Cu-Ni ores is known nearly 50 years (Godlevskii, 1959, etc.). Maucherite was exactly detected by E.A. Kulagov (Kulagov, 1968; Kulagov, Evstigneeva, 1971); nickeline, gersdorffite, and breithauptite were determined by L.N. Vyal'sov and V.M. Izoitko (Izoitko, Vyal'sov, 1973; Genkin *et al.*, 1981). V.V. Distler with co-authors characterized nickeline, maucherite, safflorite, loellingite, rammelsbergite, gersdorffite, breithauptite, and native arsenic (Distler *et al.*, 1975). A.I. Ponomarenko has found palladium-bearing breithauptite among nests of the initial Pt-Pd intermetallides of the Norilsk ores (Ponomarenko, Malov, 1991). Later, S.F. Sluzhenikin has described cobaltite in assemblage with the Ni arsenides, native bismuth, minerals of silver, and uraninite (Sluzhenikin, Mokhov, 2002). In the mentioned works are the single chemical analyses of arsenides and antimonides, images of distribution of elements in their aggregates.

Arsenide mineralization of the Norilsk ore field have been studied by us on materials of our expedition collections of 1998-2003 (Talnakhskoe and Oktyabr'skoe deposits), more earlier collections of E.A. Kulagov (Noril'skoe deposit), on collections of geologists of the Norilsk industrial complex, E.V. Sereda, S.N. Belyakov, A.N. Glotov, V.N. Serenko. Several hundreds samples have been studied, including the large lumps of ore. Size of most aggregations of arsenides and antimonides of Ni and Co is less than 3 mm. For their exposure the samples was cut up, including cutting up along the little-thick carbonate veins. Some details of three-dimensional correlations of arsenides were studied with the X-ray microtomograph instrument VT50-1 DIATOM. In 60 polished sections and polished lumps of ore, nearly 700 microprobe analyses of ore and vein minerals, nearly 150 photos in reflected electrons and images of distribution of chemical elements in characteristic radiation were made (X-ray microprobe instrument CAMECA SX-50; electron microscope Link 10000, analyst N.N. Korotaeva). Contents of Pd, Pt, and Au in arsenides from the calcite veins were detected in the laboratory of G.M. Varshall in GEOKHI RAS under the guidance of I.Ya. Koshcheeva. Thermobarogeochemical study of fluid inclusions in carbonates of arsenide veins was made in IGEM RAS under the guidance of V.Yu. Prokof'ev.

Geological position and parameters of formation of the antimonide–arsenide mineralization of the Norilsk ore field

The Norilsk region is located in the zone of the edge dislocations on the northwest of the East-Siberian platform. This area has a maximal thickness of platform mantle, formed by several structural stages (Malich, 1975). The first stage consists of the V-C_1 sea deposits with thickness 3-8 km; these are terrigenous-carbonate rocks and evaporites, including anhydrite rocks with lenses of halite and aggregations of naphthides. The second stage is composed by the coal-bearing rocks of the C_2-P_1 Tungus series with thickness up to 1 km. The third stage is formed by the P_2-T_1 trap formation (245±5 MA). This is a lava series of basalts with subordinate tuffs and other volcano-sedimentary rocks with thickness up to 4 km, which is accompanied by numerous intrusions of dolerites and gabbro-dolerites, including ore-bearing ones. Terrigenous sediments of J, K, and KZ lie on the rocks of trap formation in the form of separate spots.

The ore-bearing ultrabasite-basite intrusions are the ribbon-shaped bodies with thickness up to 300 m, which are controlled by a zone of the Norilsk-Kharaelakh fault. They has crossed and metamorphized the sedimentary series of Silurian and Devonian, coal-bearing rocks of the Tungus series, the lower parts of trap formation. The magmatic sulphide Ni-Cu ores (compact deposits, lenses, veins, zones of impregnation) has age 245±3 MA (Zolotukhin, 1997, etc.). They lie at the near bottom parts of intrusions and below intrusions within the bounds of aureole of contact metamorphism (Godlevskii, 1959; Stepanov, Turovtsev, 1988).

Formations of 1st, 2nd, and 3rd stages of platform mantle of northwest of the East-Siberian platform, including gabbroides of the ore-free and ore-bearing intrusions and magmatic sulphide ores, underwent post-trap regional metamorphism (Spiridonov *et. al.*, 2000). Trend of metamorphism is as follows: the 1st stage in conditions of the low-temperature part of zeolite facies (232-196 MA); the 2nd stage in conditions of high-temperature part of zeolite facies to prehnite-pumpellyite facies (184-164 MA); and the 3rd stage in conditions from the high-temperature to the most low-temperature part of zeolite facies (164-122 MA) (Spiridonov *et al.*, 2000). The zeolite, agate, and datolite mineralizations are connected with the first stage; they were significantly changed during metamorphism of the second stage. The copper-zeolite formation, aggregations of the Zn, Pb, Cu, Mn, Cd sulphides, datolite, zeolite, arsenide mineralizations, deposits of Iceland spar are connected with the third stage of regional metamorphism. At that, magmatic sulphide and the low-sulphide Ni-Cu ores underwent visible, in separate parts considerable, changes. In these parts, the initial Fe-Cu-Ni sulphides are substituted by magnetite, valleriite, heazlewoodite, bornite, pyrite, marcasite, mackinawite, millerite, chalcosine, polydymite, tochilinite, Co-pentlandite, godlevskite, hematite in assemblage with anhydrite, carbonates, chlorite, serpentine, hydrogarnets, talc, prehnite, vermiculite, apophyllite, corrensite, xonotlite, muscovite, and quartz. At earlier stages of metamorphism the mineral assemblages enriched by chalcopyrite and millerite have appeared. The later formations are enriched by bornite, still more late formations – by chalcosine, and the latest formations are enriched by pyrite, marcasite, and the Ni-Fe-Co thiospinels.

Metamorphogenic-hydrothermal mineralization intensively occur in the zones of jointing, near any tectonic dislocations, especially in the zone of the Norilsk-Kharaelakh fault, and also among sedimentary rocks enriched by anhydrite and clay minerals. Combination of these two factors is characteristic for that part of the Talnakh deposit, which is worked by the Komsomol'skii mine. Arsenide mineralization of the same type occurs at all deposits of the Norilsk ore field and the most intensively in the mine Komsomol'skii.

The Rb-Sr age of apophyllite from arsenide-carbonate veins of the Norilsk ore field is 164 MA (Spiridonov *et al.*, 2001). Thus, arsenide mineralization, which was considered as a derivative of the trap formation (Godlevskii, 1959, *etc.*), is younger than trap formation for more than 80 MA.

The antimonide-arsenide mineralization occurs within the bounds of the Ni-Cu ores deposit and outside it in the form of separate spots, nests, veins, impregnation, cement of breccias. The main mass of the Fe-Ni-Co arsenides and the Ni antimonides, native arsenic is in the carbonate, calcite-anhydrite, calcite-apophyllite veins and veinlets, often also containing sphalerite, wurtzite, chalcprite, galena, pyrrhotite, magnetite, alabandite, greenockite. Morphology of the carbonate-arsenide veins is complicated, strike is predominantly NNW, bedding is usually steep to vertical, rarely flat; length is from share of meters to 30 m, thickness is to 60 cm. Size of the arsenides nests in the carbonate veins is to 20 cm. The calcite and calcite-anhydrite veins with native arsenic and loellingite occur within the limits of the sulphide ore deposits and beyond their bounds. Carbonate veins with the Ni-Co-Fe arsenides and the Ni antimonides occur among the sulphide Ni-Cu ores and in near periphery of their deposits. Impregnation of the Ni arsenides occurs in the metamorphosed Ni-Cu ores with the millerite-chalcopyrite and pyrite-bornite-millerite composition. It is evidently, the surrounding sulphide Ni-Cu ores was a source of Ni and Co for antimonide-arsenide mineralization. Possibly, the Ni-Cu ores were also a source of As; in them, content of As is to 47 g/t (Czamanske *et al.*, 1992). In veins enriched by arsenides, calcite usually predominates, dolomite and anhydrite occur in a subordinate amount. Along contacts of these veins in the Ni-Cu ores, in the zone of 1-2 cm, pyrrhotite and chalcopyrite are partly replaced by calcite and sphalerite.

Calcite in veins with arsenides and antimonides contains the initial nests of the gas-liquid inclusions with low salinity, 0.2-1.4% equiv. NaCl; NaCl and $MgCl_2$ are predominant components in the inclusions solution. Pressure, from 0.9-0.5 to 0.1 kbar, and temperature 216-203-181-175-172-147-127 °C were detected by these inclusions. Our estimations of temperatures are close to the results given in the work of V.V. Distler with co-authors (1975). The P and T parameters of arsenide mineralization correspond to parameters of formation of zeolite facies.

New actual data show that hydrothermal antimonide-arsenide mineralization of the Norilsk ore field is connected with the post-trap regional metamorphism in conditions of zeolite facies.

Stages of antimonide–arsenide mineralization of the Norilsk ore field

Antimonide-arsenide mineralization of the Norilsk ore field has a number of stages. Occasionally, the crossings of the arsenide-carbonate veins with different mineral composition are observed. More often the brecciated early mineral aggregates are overgrown and/or partly replaced by the younger mineral complexes. Arsenide-carbonate veins are often zoned. Gouges of veins are usually composed by the earlier mineral assemblages; and central parts of veins consist of the later mineral assemblages. Taking into account these observations and the results of detailed mineral studies, three cycles of antimonide-arsenide mineralization were distinguished; each of them is represented by several mineral complexes. Mineral complex can include several generations of arsenides and antimonides. Mineral aggregates of arsenides and antimonides are often represented by spherocrystals and their intergrowths, which are usually named «pisolites», or «nodules», or «peas».

Antimonide-arsenide mineralization of the first cycle is closely associated with bornite-bearing ores. The general trend is from the Ni monoarsenide to diarsenides and triarsenides of Ni and Co. The first cycle is finished by the formation of native arsenic. Antimonide-arsenide mineralization of the second cycle is closely associated with chalcosine-bearing ores. The general trend is from diarsenides to antimonide and monoarsenide of Ni. The presence of native silver, silver sulphides, mercurial silver is characteristic. Mineralization of the third sulphoantimonide-sulphoarsenide cycle is associated with pyrite-bearing ores.

The first cycle includes nine mineral complexes of different age. The fist complex is cobaltite-gersdorffite-maucherite-nickeline; it is represented by nodules in veins of white calcite and chlorite-calcite veins, by impregnation and nodules in the metamorphosed Ni-Cu ores. The second complex is maucherite-gersdorffite-nickeline; it is represented by the zoned nodules, which overgrow on aggregates of the first complex and partly substitute them. Combination of the low-antimony and high-antimony nickeline is characteristic. The third complex is represented by intergrowths of maucherite and breithauptite, which form separate aggregations and overgrow on aggregates of the second complex; they are edged by Sb-nickeline and rammelsbergite. Aggregates of the fourth, rammelsbergite-nickeline-breithauptite, complex overgrow on aggregates of the first and second complexes, partly substitute them. The fourth complex includes the members the whole nickeline-breithauptite series. The fifth complex is cobaltite-breithauptite-maucherite-nickeline; it is represented by the zoned nodules in veins of pink calcite; absence of intermediate members of the nickeline-breithauptite series is characteristic. Maucherite, breithauptite, and Co-nickeline of the sixth mineral complex overgrow on aggregates of the fifth complex. In seventh complex diarsenides (rammelsbergite, loellingite) alternating with nickeline prevail. Calcite-dolomite veins with the Ni-Co triarsenides of the eighth mineral complex cut arsenide-calcite veins. Triarsenides of the eighth complex overgrow on rammelsbergite of the seventh complex. Even more late and relatively widespread calcite-anhydrite and calcite-apophyllite veins with nests and spherulite aggregates of native arsenic and loellingite are distinguished as the ninth complex. Minerals of the ninth mineral complex often compose central parts of veins, which gouges are formed by aggregates of arsenides of the seventh complex.

The second cycle is characterized by predominance of the Ni antimonide, with trend from diarsenides to antimonide and monoarsenide of Ni; presence of parkerite, native silver, bismuth, and lead, mercurial silver, pyrargyrite, clausthalite, uraninite is characteristic. The second cycle includes two mineral complexes. Nickeline, breithauptite, diarsenides of Ni and Fe, and maucherite of the tenth mineral complex compose the complex-zoned nodules. Sb-nickeline and breithauptite of the eleventh complex form intergrowths with native silver, mercurial silver, pyrargyrite.

The third cycle includes only one, the twelfth, mineral complex, which is significantly sulphoarsenide-sulphoantimonide. Among arsenide nodules of the first two cycles the twelfth mineral complex is represented by the borders of substitution and the cutting veinlets of sulphoarsenides; among arsenide-antimonide nodules of the second cycle it is represented by the borders of substitution and the cutting veinlets of ullmannite.

Minerals of the nickeline–breithauptite series of the Norilsk ore field

It is represented expedient to give the description of these minerals separately for the concrete mineral complexes. The eighth, ninth, and twelfth mineral complexes do not contain the nickeline-breithauptite series minerals.

In the work, the through numeration of mineral analyses for all samples is used. The numbers of analyses in Tables and on Figures are the same.

The first mineral complex. The first mineral complex is represented by the large lamellar crystals of antimony-free nickeline, nodules composed by split crystals of nickeline, Sb-nickeline, maucherite overgrowing of sphalerite and wurtzite, by the Sb-nickeline borders on sphalerite and chalcopyrite, and by the maucherite borders on bornite and millerite.

The borders of Sb-nickeline around crystals of sphalerite and chalcopyrite (Fig. 1a) are the earliest from these formations. The content of antimony in this nickeline varies from 3 to 20 wt % (Tabl. 1, an. 443, 495). Central parts of nodules are composed by aggregates of high-antimony nickeline in intergrowth with separate nodules of maucherite (Fig. 1b); content of antimony in nickeline is to 22 wt % (an. 458, 556). Thin-split aggregates of the low-antimony and antimony-free nickeline overgrow on them, then are the long (1-15 mm) thin (0.01-0.05 mm) lamellar crystals of antimony-free nickeline (an. 544, 558). Typical formations of the first complex are the long lamellae of nickeline framed by the aggregate of Fe-Co-gersdorffite and Ni-cobaltite (Fig. 1c, d).

Content of antimony in nickeline I is from 1 to 22 wt%, it is reduced from the centre of nodules to the edge. Lamellar crystals of nickeline I is poor by antimony (an. 20. 544). Content of sulphur, cobalt, and iron in nickeline I is to 2 wt %.

The X-ray diffraction pattern of lamellar crystals of antimony-free nickeline is as follows: 2.65 Å(10) (101); 2.348 (2) (202); 1.960 (10) (102); 1.810 (5) (110); 1.479 (3) (103); the unit cell parameters, ao 3.58 (1) Å and c_o 5.02 (6) Å, corresponds to standard nickeline.

The second mineral complex. The second complex includes aggregates of thin-split crystals of the low-antimony and Sb-nickeline, gersdorffite, maucherite, cobaltite, i.e. complex-zoned nodules with diameter 0.5-5 mm.

The early formations of the second complex are the most widespread: a) nickeline II from metamorphic ingrowths in aggregates of nickeline I, cobaltite, and gersdorffite. Nickeline II cuts off their borders and a picture of their zoning (Fig. 1c); b) nickeline II of «caps» on lamel-

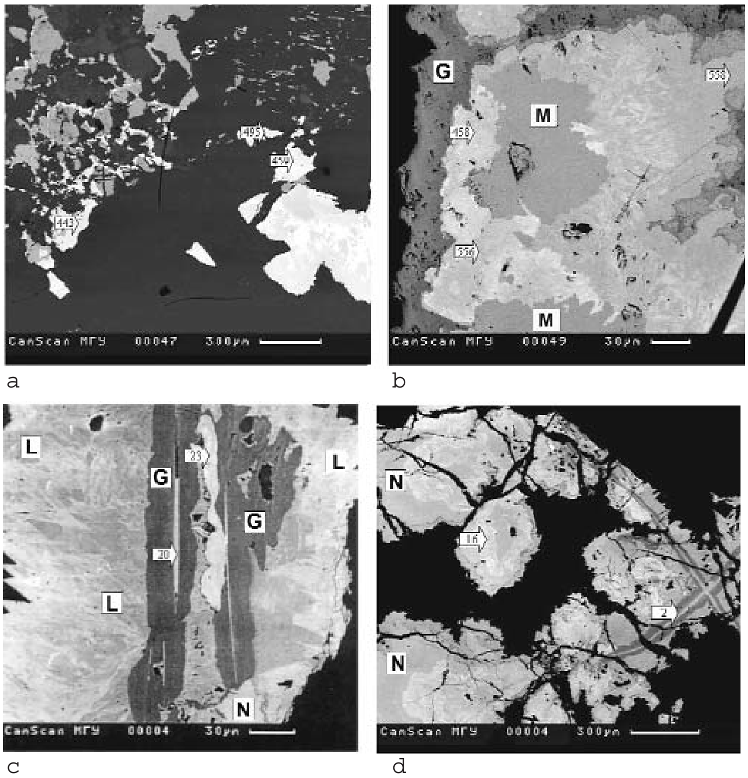


***Fig. 1**. Arsenides of the first and second mineral complexes. Matrix is calcite (black). Talnakh, the Komsomol'skii mine.*
a — Sb-nickeline I (white, an. 443, 459, 495) overgrowing on chalcopyrite and sphalerite (grey);
b — Aggregate of arsenides of the first mineral complex. Intergrowth of high-antimony nickeline (white, an. 458, 556) and maucherite (grey, «M»), overgrown by low-antimony and Sb-nickeline (light grey) with a picture of geometrical selection zone; then low-antimony nickeline (grey, an. 558); then rammelsbergite and gersdorffite (dark grey, «G»);
c — Correlations of the first and second mineral complexes. The first mineral complex: lamellar crystals of antimony-free nickeline I (light grey, an. 20) surrounded by the aggregate of gersdorffite and cobaltite (dark grey, «G»), on which are split crystals of loellingite with a picture of geometrical selection zone (light grey to white, «L»). The second mineral complex: metasomes of Sb-nickeline II (white, an. 23, «N»). Nickeline II cuts off the borders of the first complex minerals.
d — Cruciform intergrowth of lamellar crystals of antimony-free nickeline I (an. 2) bordered by gersdorffite and cobaltite (dark grey), loellingite (grey) of the first mineral complex. On them are zoned nodules of Sb-nickeline II («N», an. 16) of the second mineral complex.
Photos in reflected electrons (BSE image).

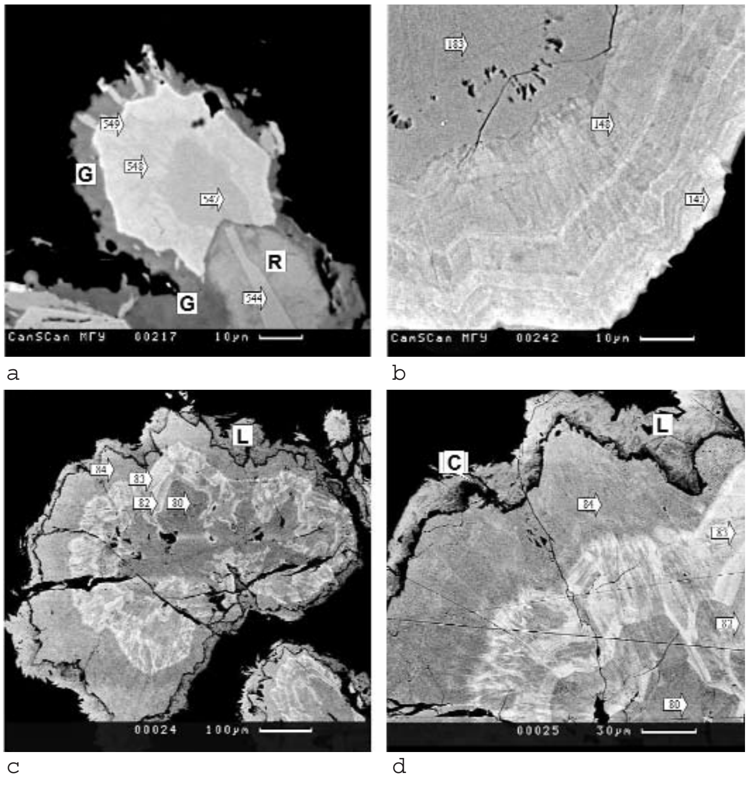


***Fig. 2.** Nodules of arsenides of the second mineral complex. Matrix is calcite (black). Talnakh, the Komsomol'skii mine.*
a — «Cap» of overgrowth, zoned nodule of nickeline II (an. 547) and Sb-nickeline II (an. 548, 549) on the lamellar crystal of nickeline I (an. 544) and on rammelsbergite («R»). Around «cap» is a border of gersdorffite («G»);
b — Fragment of a «cap» of nickeline II: in the centre is low-antimony nickeline (an. 183), outside zone is the thin-zoned Sb-nickeline (an. 142, 148);
c — Pisolite of nickeline II with a border of loellingite («L») and veinlets of calcite (black). Nickeline (an. 80, 84), Sb-nickeline (an. 82, 83);
d — Fragment of the Figure 2c. Nickeline is bordered by cobaltite («C») and loellingite («L»).
BSE image.

Table 1. **Chemical composition of nickeline and Sb-nickeline of the first mineral complex (Fig. 1, 2a).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
20	43.56	1.50	0.22	–	55.13	1.40	0.06	0.19	102.04	0.973	0.033	0.005	–	1.012	0.967	0.015	0.002	0.003	0.988
544	41.12	1.64	1.67	–	53.58	1.96	1.45	–	101.22	0.913	0.036	0.039	–	0.988	0.932	0.021	0.059	–	1.012
443	42.16	0.14	1.33	0.05	48.98	4.96	1.53	0.29	99.44	0.963	0.003	0.032	0.001	0.999	0.877	0.055	0.064	0.005	1.001
558	41.24	1.19	0.01	–	51.76	6.88	0.18	–	101.26	0.952	0.027	–	–	0.979	0.936	0.077	0.008	–	1.021
495	42.65	0.47	0.25	–	45.99	11.71	0.01	0.21	101.29	1.001	0.011	0.006	–	1.018	0.846	0.132	0.001	0.004	0.982
556	40.93	0.35	0.22	–	43.57	14.71	1.13	–	100.91	0.965	0.008	0.006	–	0.979	0.805	0.167	0.049	–	1.021
459	39.83	0.11	0.37	0.05	37.23	20.36	1.22	0.30	99.47	0.974	0.003	0.009	0.001	0.987	0.713	0.240	0.055	0.005	1.013
458	39.17	0.14	0.19	–	35.79	22.26	0.14	0.29	98.18	0.997	0.003	0.005	–	1.006	0.710	0.272	0.007	0.005	0.994

Note. *In Tables 1-9 analyses are performed with X-ray microprobe instrument Cameca SX-50. Conditions: accelerating voltage 20 kV, electron current 20 nA. Analysts are N.N. Kononkova, I.A. Bryzgalov. Dash in table is the content of element is below detection limits and/or element is not detected. Numbers of analyses in the tables and on the figures are the same.*

Table 2. **Chemical composition of nickeline and Sb-nickeline of the second mineral complex (Fig. 1c, d, 2a, b, 3b).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
547	42.30	0.41	1.36	55.17	1.34	1.47	–	–	102.05	0.933	0.009	0.032	0.973	0.953	0.014	0.059	–	–	1.027
183	43.56	1.50	0.22	55.13	1.40	0.06	–	–	101.87	0.971	0.033	0.005	1.009	0.974	0.015	0.002	–	–	0.991
531	41.84	0.62	0.73	51.22	2.99	1.46	–	–	98.86	0.957	0.014	0.017	0.988	0.918	0.033	0.061	–	–	1.012
548	43.02	0.38	1.51	49.26	5.05	1.79	–	–	101.01	0.964	0.009	0.035	1.008	0.865	0.055	0.073	–	–	0.992
148	42.05	0.38	2.40	47.38	6.18	2.19	0.27	0.06	100.85	0.943	0.008	0.056	1.007	0.833	0.066	0.089	0.004	0.001	0.993
532	41.02	0.53	1.16	47.08	8.80	2.16	–	–	100.74	0.934	0.012	0.028	0.974	0.84	0.097	0.09	–	–	1.026
16	40.45	1.01	0.06	46.26	8.97	0.20	0.17	0.04	97.15	0.98	0.024	0.001	1.005	0.878	0.105	0.009	0.003	–	0.995
549	41.25	0.13	1.25	47.14	10.87	1.41	–	–	102.06	0.943	0.003	0.03	0.976	0.845	0.12	0.059	–	–	1.024
23	38.63	2.35	0.71	50.57	5.16	0.53	–	–	97.96	0.965	0.029	0.003	0.997	0.844	0.128	0.031	–	–	1.003
142	42.81	0.11	0.02	41.47	17.30	0.17	0.19	0.11	102.07	1.015	0.003	–	1.018	0.773	0.198	0.007	0.003	0.001	0.982

Table 3. **Chemical composition of nickeline and Sb-nickeline of separate nodules of the second mineral complex (Fig. 2c, d).)**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
80	42.37	1.69	0.15	51.58	2.01	0.49	0.22	0.07	98.51	0.954	0.040	0.004	0.997	0.955	0.023	0.021	0.004	0.001	1.003
71	41.92	0.81	0.11	52.31	2.45	0.13	0.22	0.10	98.05	0.981	0.018	0.003	1.002	0.959	0.028	0.006	0.004	0.001	0.998
63	47.94	1.50	0.11	46.39	3.51	0.55	–	–	100.00	0.959	0.030	0.002	0.991	0.928	0.070	0.011	–	–	1.009
84	40.31	1.68	0.19	49.86	6.52	0.37	–	–	98.93	0.947	0.039	0.005	0.991	0.919	0.074	0.016	–	–	1.009
82	40.58	1.04	–	46.13	9.32	0.32	0.15	0.06	97.54	0.978	0.025	–	1.003	0.871	0.108	0.014	0.003	0.001	0.997
75	40.26	0.79	–	45.88	9.73	0.18	0.20	0.10	97.14	0.979	0.019	–	0.998	0.874	0.115	0.008	0.004	0.001	1.002
83	41.56	1.00	–	44.05	12.60	0.60	0.23	0.11	100.04	0.971	0.024	–	0.995	0.825	0.148	0.027	0.004	0.001	1.005
69	41.10	0.42	0.11	42.11	14.09	0.77	0.23	0.11	98.94	0.990	0.010	0.002	1.002	0.795	0.164	0.034	0.004	0.001	0.998

lae of nickeline I with the cobaltite-gersdorffite border and without it (Fig. 1d, 2a, b, 3a). Nickeline of «caps» is thin-zoned by chemical composition. Content of antimony increases to 20 wt % to edges of «caps» (Tabl. 2, an. 142, 148, 183, 547-549); c) nickeline II of the isolated nodules: in the centre, nickeline is usually low-antimony (Tabl. 3, an. 63, 80), in other volume of nodules the content of antimony is from traces to 15 wt % (Tabl. 3, an. 69, 71, 75, 82, 83). The width of zones with different concentration of antimony is from 10 to 100 μm (Fig. 2c, d); number of such zones reaches 15. Some nodules are bordered by cobaltite.

The late formations of the second complex are less widespread: the lamellae of nickeline in the gersdorffite mass (Fig. 3b) and maucherite with broken basis and thin border of Sb-nickeline III(Fig. 3b, c).

The concentration of cobalt in nickeline II is to 1.5 wt % and iron to 2.5 wt %. Coefficients of pair correlation of contents are as follows: Ni-Co = -0.95; Ni-Fe = -0.77 (selection contains 47 analyses) is an evidence of isomorphous substitution of nickel by cobalt and iron. The high-antimony nickeline is usually less cobaltous than low-antimony nickeline; a coefficient of pare correlation is Sb-Co = -0.45. In nickeline of lamellar crystals and separate nodules is Co>Fe, in nickeline of «caps» is Fe>Co.

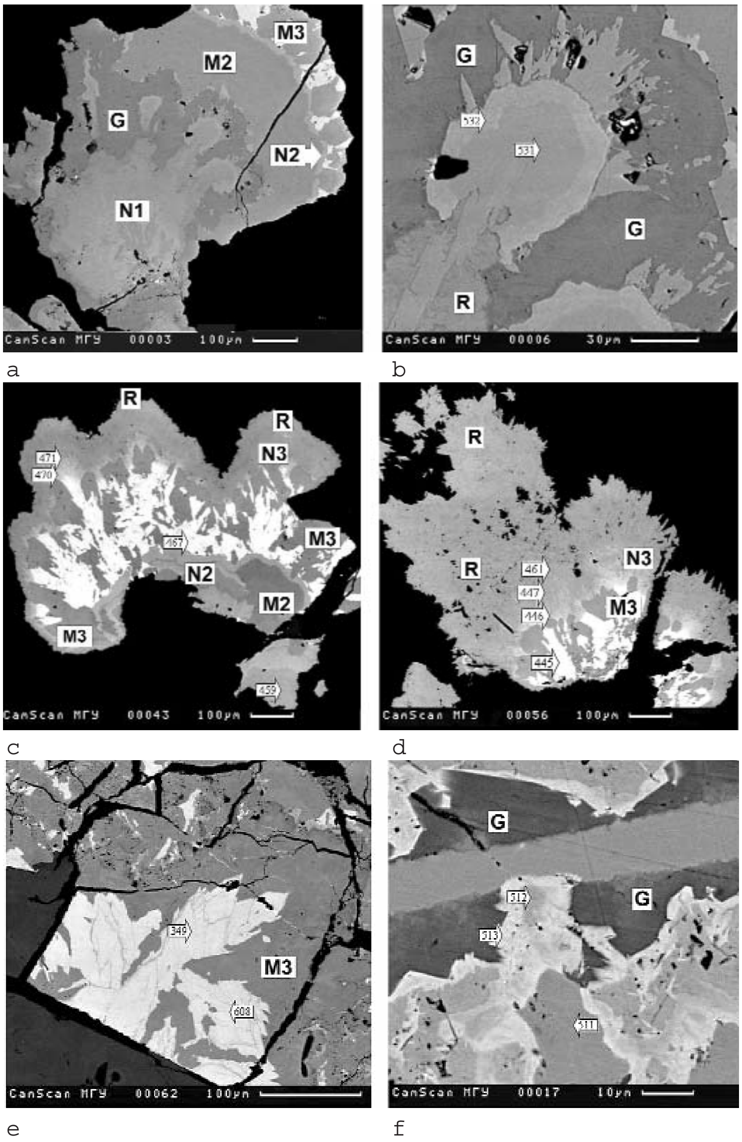


***Fig. 3**. Correlations of the first, second, third, and fourth mineral complexes. a-d, f — the Komsomol'skii mine, Talnakh. e — the Oktyabr'skii mine, Talnakh.*
a — Pisolite of arsenides of the first, second, and third mineral complexes. The first complex: in the basis is the aggregate of low-antimony nickeline I («N1») with projecting crystals, on them is rammelsbergite (dark grey). The second complex: «caps» of nickeline II (on the basis of the first complex), then are the lamellae of nickeline on gersdorffite mass («G») (better seen on the Fig. 3b), then is maucherite («M2») with a thin border of Sb-nickeline («N2»). The third complex: intergrowth of breithauptite (white) and maucherite (grey, «M2»);
b — Fragment of the Figure 3a. Nickeline II (an. 531, 532). Rammelsbergite («R»), gersdorffite («G»);
c — Pisolite of the second and third complexes. The second complex: aggregate of maucherite («M2»), nickeline, and Sb-nickeline («N2»). The third complex: intergrowth of breithauptite (white, an. 467) and maucherite («M3»), the border is Sb-nickeline («N3», an. 470, 471), the edge is rammelsbergite («R»);
d — Pisolite of the full-shown third complex. Early breithauptite (an. 445) and maucherite (dark grey, «M3»), later is Sb-nickeline («N3», an. 446, 447, 461), the latest is Fe-rammelsbergite («R»);
e — Isolated aggregation of early minerals of the third complex. Intergrowth of breithauptite (an. 349, 608) and maucherite («M») on the basis of wurtzite (dark grey);
f — Lamellar crystal of nickeline with a border of gersdorffite («G») of the first complex is partly substituted by arsenides of the fourth complex, low-antimony nickeline (an. 511) and Sb-nickeline (an. 512, 513);
BSE image.

The third mineral complex. The early formations of the third complex, intergrowths of maucherite and breithauptite I, compose the complex-zoned nodules; they are overgrowing on the aggregates of the second complex; in their basis there is the zone of geometrical selection (Fig. 3a, c). Moreover, they form central parts of the isolated nodules of the third complex (Fig. 3d) and the isoletad kidney-shaped aggregates overgrowing on wurtzite (Fig. 3e). Closer to the edge of nodules, breithauptite give place to As-breithauptite, then Sb-nickeline III, and then the antimony-free nickeline with border of Fe-rammelsbergite (Fig. 3d).

The third complex includes minerals of the continuous breithauptite-nickeline series (Tabl. 4). In nickeline III and intermediate members of the nickeline-breithauptite series, the content of sulphur, cobalt, and iron is higher than in breithauptite I: S to 2.6 wt %, Co and Fe to 2.5-3 wt %.

The fourth mineral complex. The aggregates of the fourth complex minerals overgrow on the aggregates of the first and third complexes and partly substitute them (Fig. 3f). In the most cases, they form the isolated nodules (Fig. 4a, b). The intensively split crystals of the low-antimony nickeline (the first generation) form the central parts of nodules, which are surrounded by a narrow zone of nickeline with

Table 4. **Chemical composition of the nickeline-breithauptite series minerals of the third mineral complex (Fig. 3c-e).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
461	42.65	0.09	2.69	0.09	46.89	5.27	2.64	0.27	100.59	0.948	0.002	0.063	0.002	1.015	0.817	0.056	0.108	0.005	0.985
471	38.96	0.87	0.88	0.07	49.85	9.70	0.21	0.26	100.78	0.915	0.020	0.022	0.001	0.959	0.918	0.110	0.009	0.005	1.041
470	40.96	0.53	0.10	0.03	44.54	14.31	–	0.29	100.75	0.979	0.013	0.003	0.001	0.995	0.835	0.165	–	0.005	1.005
460	42.38	0.11	0.29	–	37.41	17.53	2.45	0.31	100.47	0.994	0.002	0.007	–	1.004	0.688	0.198	0.105	0.005	0.996
447	40.58	0.48	0.17	0.04	41.46	17.47	0.06	0.22	100.47	0.984	0.011	0.004	0.001	1.001	0.788	0.204	0.003	0.004	0.999
446	40.43	0.15	0.03	0.08	32.87	27.37	0.02	0.19	101.14	1.013	0.004	0.001	0.002	1.019	0.645	0.331	0.001	0.004	0.981
349	33.10	–	–	–	5.27	63.81	0.31	0.16	102.66	0.964	–	–	–	0.964	0.120	0.896	0.016	0.003	1.036
467	33.31	–	0.04	–	2.21	64.00	0.61	0.17	100.35	0.991	–	0.001	–	0.993	0.052	0.919	0.033	0.004	1.007
608	32.92	–	–	0.26	2.61	64.52	0.53	0.16	100.95	0.980	–	–	0.007	0.987	0.061	0.921	0.029	0.002	1.013
445	32.45	–	–	0.18	2.62	64.19	0.38	0.26	100.07	0.976	–	–	0.005	0.981	0.062	0.931	0.021	0.006	1.019

Table 5. **Chemical composition of the nickeline-breithauptite series minerals of the fourth mineral complex (Fig. 3f, 4).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
496	44.08	0.56	0.58	0.03	52.72	0.96	1.16	0.23	100.32	0.987	0.012	0.014	0.001	1.014	0.925	0.010	0.047	0.004	0.986
511	44.70	0.47	0.08	0.13	52.62	2.85	0.41	0.35	101.61	1.005	0.011	0.002	0.003	1.019	0.927	0.031	0.017	0.006	0.981
512	43.69	0.86	0.01	0.05	52.89	3.08	0.09	0.37	101.04	0.993	0.019	–	0.001	1.014	0.942	0.034	0.004	0.006	0.986
497	42.08	0.75	0.74	0.11	46.83	6.54	2.42	0.31	99.79	0.954	0.017	0.018	0.002	0.991	0.832	0.071	0.101	0.005	1.009
503	42.06	0.52	0.21	–	47.91	8.66	0.01	0.24	99.60	0.993	0.012	0.005	–	1.010	0.886	0.099	–	0.004	0.990
513	41.92	0.08	0.12	0.08	39.38	19.60	0.14	0.26	101.58	1.011	0.002	0.003	0.002	1.017	0.744	0.228	0.006	0.005	0.983
502	39.69	0.20	0.06	0.07	33.82	26.85	0.03	0.21	100.93	0.996	0.005	0.002	0.002	1.004	0.665	0.325	0.001	0.004	0.996
500	37.16	0.05	0.01	0.02	21.99	41.06	0.02	0.19	100.51	0.998	0.001	–	0.001	1.000	0.463	0.532	0.001	0.004	1.000
499	36.82	0.14	0.03	–	16.14	49.73	0.03	0.12	103.00	0.998	0.004	0.001	–	1.003	0.343	0.650	0.002	0.002	0.997
501	34.28	0.05	–	0.08	9.15	57.34	0.05	0.16	101.11	0.987	0.002	–	0.002	0.991	0.207	0.796	0.003	0.003	1.009
498	33.59	0.07	0.05	0.05	4.41	63.25	0.14	0.23	101.78	0.986	0.002	0.001	0.001	0.991	0.101	0.895	0.007	0.005	1.009

Table 6. **Chemical composition of breithauptite and nickeline of the fifth mineral complex (Fig. 6).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Cu	As	Sb	S	Se	Total	Ni	Co	Fe	Cu	Total	As	Sb	S	Se	Total
226	33.28	0.02	0.01	0.03	2.52	65.24	0.02	0.13	101.24	0.995	0.001	–	0.001	0.997	0.059	0.941	0.001	0.002	1.003
230	33.39	0.04	0.06	0.08	2.10	65.93	0.05	0.15	101.80	0.994	0.001	0.002	0.002	0.999	0.049	0.946	0.003	0.003	1.001
243	33.26	0.08	0.00	0.16	1.79	67.05	0.08	0.31	102.73	0.985	0.002	–	0.004	0.991	0.042	0.957	0.004	0.005	1.009
242	34.54	9.99	0.22	–	50.74	3.87	0.07	0.29	99.72	0.797	0.230	0.005	–	1.032	0.918	0.043	0.003	0.005	0.968
239	40.79	2.96	0.11	0.05	52.21	3.39	0.03	0.42	99.96	0.940	0.068	0.003	0.001	1.012	0.943	0.038	0.001	0.007	0.988
225	42.75	2.21	0.04	0.10	52.50	3.93	0.03	0.28	101.80	0.968	0.050	0.001	0.002	1.020	0.931	0.043	0.001	0.005	0.980

5-7 wt % of Sb (Tabl. 5, an. 497) (the second generation). The thin-alternating As-breithauptite and Sb-nickeline (the third generation), rammelsbergite overgrow on nickeline of the second generation. The content of cobalt and iron in nickeline IV and breithauptite II is less than 1 wt %. The content of sulphur in nickeline of the first generation is 1-2.5 wt %. Nickeline of the second and third generations and breithauptite contain less than 0.5 wt % of sulphur.

The fifth mineral complex. The fifth mineral complex is represented by complex-zoned nodules of the antimony-free, cobalt-free and Co-nickeline V, breithauptite III, maucherite, cobaltite (Fig. 5, 6). Central parts of the nodules are usually composed by intergrowths of small crystals of breithauptite and Co-nickeline (Tabl. 6, an. 239) with borders of cobaltite (Fig. 6a, b). On them there are aggregates of the Co-nickeline crystals (an. 242), which growth zones are marked by Ni-cobaltite (Fig. 6a, b). They are surrounded by nickeline with ingrowths of breithauptite and with a border of microcrystalline breithauptite (Fib. 6b). The latter form the central parts of some nodules (Fig. 6c), where the aggregates of maucherite with small inclusions of breithauptite and with a border of the fine-grained breithauptite overgrow on them (Fig. 6c).

Minerals of the nickeline-breithauptite series of the fifth complex are represented by the end-members. The content of cobalt in nickeline V is to 10 wt %, sulphur is <0.1 wt %.

The sixth mineral complex. The sixth complex is formed by maucherite, breithauptite IV,

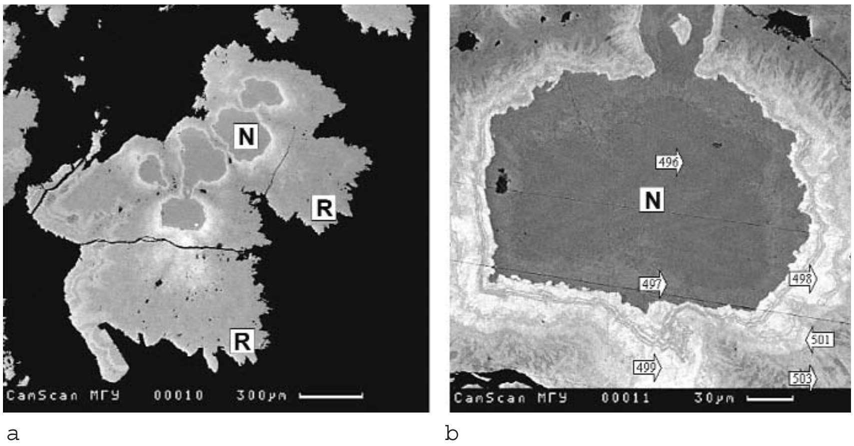


***Fig. 4**. Nodules of the fourth mineral complex in calcite (black). Talnakh, the Komsomol'skii mine. On low-antimony nickeline («N», an. 496, 497) are breithauptite (an. 498-500), Sb-nickeline (an. 501, 503), rammelsbergite (grey, «R»). BSE image.*

***Fig. 5**. Arsenides (white) of the fifth and sixth mineral complexes in carbonate vein. The Oktyabr'skii mine, Talnakh. Polished section. Width of image is 35 mm.*

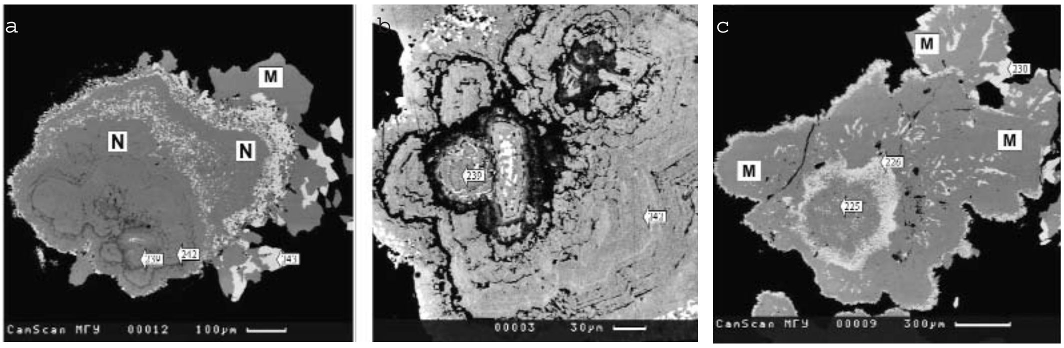


***Fig. 6**. Fragments of the Figure 5. The fifth and sixth mineral complexes.*
a — The fifth complex: early breithauptite (white) and Co-nickeline (an. 239) with a border of cobaltite (black); later Co-nickeline (an. 242) with thin zones of cobaltite (black); even more later nickeline («N») with ingrowths of breithauptite (white); the latest small crystals of breithauptite. The sixth complex: intergrowth of large crystals of maucherite («M») and breithauptite (an. 243), a border around arsenides of the fifth complex; b — The detail of the Figure 6a; c — The fifth complex: nickeline (an. 225) surrounded by the small-grained breithauptite (an. 226). The sixth complex: maucherite («M») with inclusions of breithauptite (white) and surrounded by a border of breithauptite (an. 230). BSE image.

Table 7. **Chemical composition of Co-nickeline and breithauptite of the sixth mineral complex (Fig. 7).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
305	36.40	2.00	0.10	32.28	29.83	0.06	0.14	–	100.80	0.974	0.028	0.002	1.004	0.855	0.134	0.002	0.004	0.001	0.996
309	40.92	1.17	0.06	45.89	11.64	0.04	0.22	0.05	99.97	0.928	0.051	0.003	0.981	0.646	0.367	0.003	0.003	–	1.019
213	41.49	2.79	0.07	52.85	2.58	0.02	0.22	0.06	100.07	0.951	0.064	0.002	1.017	0.949	0.028	0.001	0.004	0.001	0.983
222	38.43	4.81	0.06	51.31	6.45	0.02	0.27	0.07	101.40	0.885	0.11	0.001	0.996	0.925	0.072	0.001	0.005	0.001	1.004
248	37.55	6.62	0.19	50.33	5.96	0.10	0.15	0.03	100.92	0.863	0.152	0.005	1.020	0.907	0.066	0.004	0.003	–	0.98
223	34.95	9.35	0.25	51.66	4.85	0.04	0.20	0.01	101.30	0.798	0.213	0.006	1.017	0.925	0.053	0.002	0.003	–	0.983
242	34.54	9.99	0.22	50.74	3.87	0.07	0.24	0.05	99.72	0.797	0.23	0.005	1.032	0.917	0.043	0.003	0.004	0.001	0.968
249	33.36	10.04	0.32	50.95	3.40	0.99	0.30	0.05	99.40	0.764	0.229	0.008	1.001	0.913	0.038	0.042	0.005	0.001	0.999
214	30.74	12.98	0.29	52.76	2.44	0.06	0.26	–	99.52	0.708	0.298	0.007	1.013	0.954	0.027	0.002	0.004	–	0.987
220	33.35	0.27	0.03	5.21	62.08	0.03	0.12	0.08	101.17	0.983	0.008	0.001	0.992	0.120	0.882	0.002	0.003	0.001	1.008
304	32.21	0.12	0.10	0.63	67.85	0.08	0.12	–	101.10	0.977	0.004	0.003	0.984	0.015	0.994	0.004	0.003	–	1.016

Table 8. **Chemical composition of the nickeline-breithauptite series minerals of the tenth mineral complex (Fig. 8a-c).)**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Te	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Te	Total
679	44.02	0.09	1.71	50.02	1.54	2.16	0.19	0.01	99.75	0.979	0.002	0.040	1.021	0.871	0.017	0.088	0.003	–	0.979
677	42.77	0.13	–	51.44	6.78	0.02	0.21	0.04	101.40	0.987	0.003	–	0.990	0.930	0.075	0.001	0.004	–	1.010
639	41.33	0.31	0.34	44.42	15.54	0.00	0.13	0.03	102.09	0.979	0.007	0.009	0.995	0.825	0.178	–	0.002	–	1.005
644	40.54	0.06	0.32	36.13	24.23	0.08	0.18	0.08	101.61	0.998	0.001	0.008	1.008	0.697	0.288	0.003	0.003	0.001	0.992
641	38.90	0.09	0.10	28.64	31.91	0.05	0.10	–	99.79	1.009	0.002	0.003	1.014	0.582	0.399	0.002	0.002	–	0.986
661	37.36	0.08	0.03	29.06	35.45	0.05	0.12	0.04	102.18	0.964	0.002	0.001	0.966	0.588	0.441	0.003	0.002	–	1.034
633	37.28	0.17	0.05	27.07	36.43	0.11	0.17	0.01	101.29	0.973	0.004	0.001	0.979	0.554	0.459	0.005	0.003	–	1.021
634	32.77	0.19	–	3.30	65.24	0.29	0.16	–	101.95	0.969	0.006	–	0.974	0.076	0.930	0.016	0.004	–	1.026
678	33.02	–	–	3.86	65.51	0.22	0.08	0.04	102.74	0.969	–	–	0.969	0.089	0.928	0.012	0.002	0.001	1.031
675	31.66	–	0.08	2.68	65.82	0.24	0.18	–	100.66	0.957	–	0.003	0.960	0.063	0.960	0.013	0.004	–	1.040
638	33.31	–	0.02	3.19	65.91	0.01	0.11	0.09	102.63	0.983	–	0.001	0.984	0.074	0.938	–	0.002	0.001	1.016
630	32.85	–	–	2.10	66.81	0.76	0.17	–	102.69	0.963	–	–	0.963	0.048	0.944	0.041	0.004	–	1.037

Table 9**. Chemical composition of the nickeline-breithauptite series minerals of the eleventh mineral complex (Fig. 8d).**

№	Element wt %									Formula coefficients calculated on 2 atoms									
	Ni	Co	Fe	Hg	As	Sb	S	Se	Total	Ni	Co	Fe	Hg	Total	As	Sb	S	Se	Total
575	45.00	0.25	0.04	–	49.00	6.82	1.19	0.19	102.49	1.007	0.006	0.001	–	1.014	0.860	0.074	0.049	0.003	0.986
576	44.44	0.32	–	–	50.02	3.87	2.08	0.23	100.96	0.991	0.007	–	–	0.998	0.871	0.042	0.085	0.004	1.002
579	43.50	0.20	0.06	1.01	42.47	14.30	1.27	0.18	102.99	1.005	0.004	0.001	0.007	1.017	0.768	0.159	0.053	0.003	0.983
580	35.18	0.03	0.03	0.15	11.65	52.00	0.68	0.10	99.82	0.995	0.001	0.001	0.001	0.998	0.257	0.708	0.035	0.002	1.002
581	34.30	0.11	–	0.50	7.81	59.38	0.38	0.08	102.56	0.979	0.003	–	0.004	0.986	0.175	0.817	0.020	0.002	1.014
582	41.26	0.05	0.06	0.32	34.20	24.25	1.45	0.16	101.75	0.998	0.001	0.002	0.002	1.003	0.647	0.283	0.064	0.003	0.997
583	40.62	0.08	–	–	32.99	27.27	1.01	0.20	102.17	0.994	0.002	–	–	0.996	0.633	0.322	0.045	0.004	1.004
584	33.10	–	–	2.09	1.02	67.16	0.15	0.02	103.54	0.987	–	–	0.018	1.005	0.024	0.963	0.008	–	0.995
585	34.16	–	–	–	5.01	60.43	0.42	0.08	100.10	1.004	–	–	–	1.004	0.115	0.857	0.022	0.002	0.996
586	38.59	0.12	0.01	–	24.46	38.89	0.24	0.11	102.42	1.000	0.003	–	–	1.003	0.498	0.486	0.011	0.002	0.997
587	33.23	0.03	–	–	1.90	66.93	0.27	–	102.36	0.985	0.001	–	–	0.986	0.044	0.956	0.014	–	1.014

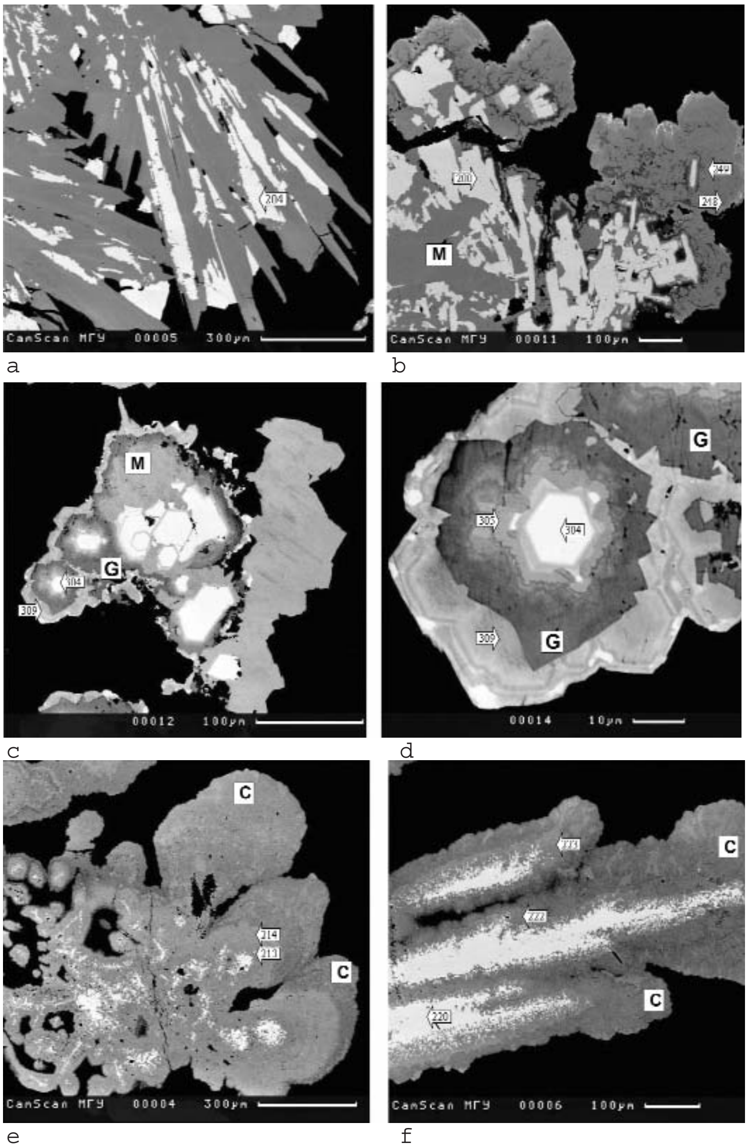


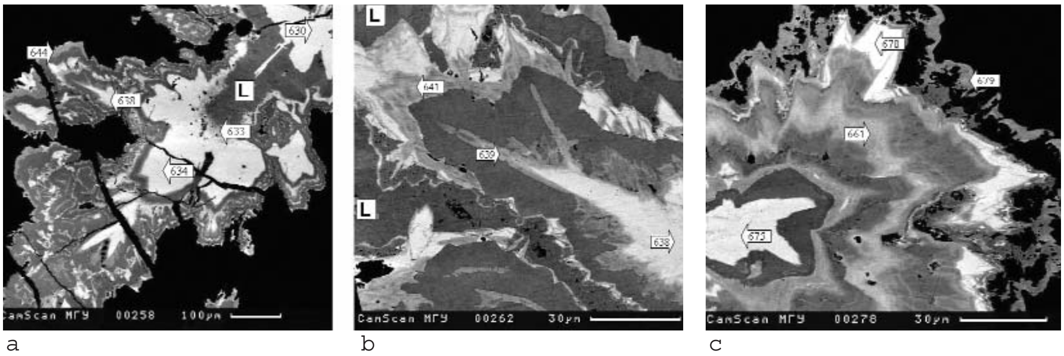
***Fig. 7**. Fragments of the Figure 5. Aggregates of the sixth mineral complex. Talnakh, the Oktyabr'skii mine.*
a — Lamellar crystals of maucherite, interstices between them are filled up by breithauptite (an. 204);
b — Intergrowths of tabular crystals of breithauptite (an. 200) and maucherite («M»), on them is Co-nickeline (an. 248, 249);
c — Crystals of breithauptite (an. 304) and Sb-nickeline are surrounded and partly substituted by maucherite («M»). On them is a border of Co-gersdorffite (dark grey, «G»). Around are Sb-nickeline (an. 309), maucherite, and breithauptite;
d — In the centre is breithauptite crystal (an. 304) with a border of Sb-nickeline (an. 305). Around is Co-gersdorffite («G»), then is zoned aggregations of Sb-nickeline (an. 309);
e — Zoned nodules of Co-nickeline (an. 213, 214) with inclusions of breithauptite (white). Border is sulphur safflorite;
f — Intergrowths of the split crystals of breithauptite (an. 220) and Co-nickeline (an. 222, 223). Border is high-sulphur safflorite («C»).
BSE image.

nickeline VI; split crystals of nickeline enriched by cobalt are typical. The early formations are intergrowths of maucherite and breithauptite (Fig. 7a, b), sometimes with a border of Sb-nickeline. They are surrounded by maucherite with a border of Co-gersdorffite. On the described aggregations are Sb-nickeline (Tabl. 7, an. 309) and breithauptite (Fig. 7c, d). In a number of cases, these minerals form the central parts of nodules (Fig. 7e, f), which outsides are formed by the split crystals of Co-nickeline surrounded by aggregates of the split crystals of the high-sulphur Fe-safflorite (Fig. 7e, f).

The content of cobalt in nickeline VI increases from the centre of nodules to outsides to 15 wt%. Nickeline VI contains to 30 wt% of Sb, breithauptite does not practically contain As (Tabl. 7, an. 243, 304). The X-ray diffraction pattern of breithauptite IV is as follows: 2.83 Å (8) (101); 2.565 (2) (002); 2.047 (7) (102); 1.965 (10) (110); 1.537 (6) (103). The unit cell parameters are as follows: a_0 3.926(6) Å; c_0 5.143(6) Å.

The seventh mineral complex. Nodules of the seventh complex are composed by diarsenides of the rammelsbergite-loellingite series with the separate thin (10—30 m) zones of nickeline VII. This nickeline contains 2—5 wt % of Sb.

The tenth mineral complex. The tenth mineral complex is represented by the com-



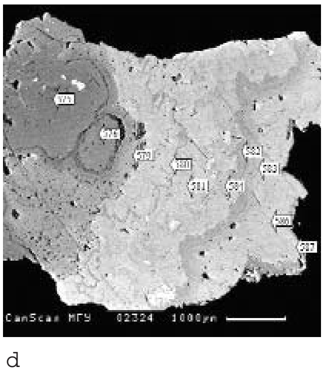


***Fig. 8**. The complex-zoned aggregates of arsenides and antimonides. Talnakh, the Komsomol'skii mine. a — The tenth mineral complex. Early breithauptite (an. 630, 634), Ni-bearing loellingite («L»), Sb-nickeline (an. 633) with a border of diarsenides of Ni-Fe (dark grey). The later crystals of breithauptite (an. 638) and Sb-nickeline, border is diarsenides of Ni-Fe. Outside zones are Sb-nickeline (an. 644); b — Fragment of the Figure 8a. Crystals of breithauptite (an. 638) with a border of Sb-nickeline (an. 639). On them are diarsenides of Ni-Fe (dark grey), then are Sb-nickeline (an. 641) and in different degree arsenious breithauptite (white to light grey), loellingite (dark grey, «L»); c — The tenth mineral complex. Earlier breithauptite (an. 675) with a border of diarsenides of Ni-Fe. Around is a wide zone of in different degree antimonian nickeline (an. 661) and later breithauptite (an. 678). Outside zone is aggregate of calcite (black) and nickeline (an. 679); d — The eleventh mineral complex. Earlier spherulite aggregates of nickeline (an. 575, 576), around is Sb-nickeline (an. 579). The later aggregates of breithauptite (in different degree arsenious, an. 580-587). In breithauptite are inclusions of native silver (white).*
BSE image.

plex-zoned nodules from a great number of generations of breithauptite V, nickeline VIII, rammelsbergite, and loellingite.

The lamellar crystals of arsenic-free breithauptite V of the first generation and their cruciform intergrowths frame the aggregate of Ni-bearing loellingite, on which the high-antimony nickeline VIII of the first generation overgrow (Fig. 8a). On that nickeline are the large short-prismatic crystals of low-arsenic breithauptite V of the second generation (Tabl. 8) with a thin border of diarsenides of Ni and Fe (Fig. 8a).

These formations are a basis for the aggregates of long-prismatic crystals of low-arsenic breithauptite V of the third generation with a picture of the geometrical selection zone (Fig. 8a) and high-antimony nickeline VIII of the second generation with a border of diarsenides of Ni and Fe (Fig. 8b).

On them are the complex-zoned aggregates of the split crystals of the high-antimony, antimony-free, Sb-nickeline VIII of the third generation and breithauptite V of the fourth generation (Fig. 8b, c). In a number of cases, these aggregates are surrounded by a border of nickeline VIII of the fourth generation with calcite (Fig. 8c) or loellingite. On them are Sb-nickeline VIII of the fifth generation (Tabl. 8, an. 644) and breithauptite V of the fifth generation; the breithauptite crystals are to 1 mm in size. Some nodules of the tenth complex are surrounded by a border (10-20 μm) of maucherite.

The eleventh mineral complex. The eleventh complex is represented by the zoned thin-split nodules of antimonides and arsenides with inclusions of native silver, mercurial silver, pyrargyrite (Fig. 8d).

Central parts of the nodules are composed by the thin-split aggregates of Sb-nickeline IX with inclusions of silver. This nickeline contains 5-7 wt % of Sb (Tabl. 9, an. 575, 576). Nickeline containing 15 wt % of Sb (an. 579) overgrow on it; then there is As-breithauptite with inclusions of pyrargyrite. The content of As in breithauptite wavy changes from 1 to 15 wt % (an. 580, 581). The outside zone of nodules is composed by the intermediate members of the nickeline-breithauptite isomorphous series and breithauptite (an. 582-587).

Nodules of the eleventh mineral complex are surrounded by the substitution border and/or cut by the veinlets of ullmannite of the twelfth mineral complex.

Peculiarities of the nicke-

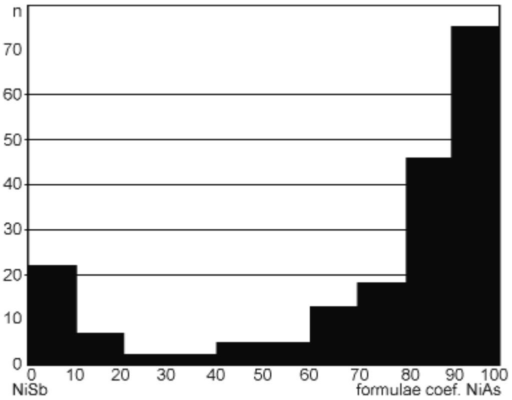


***Fig. 9**. Frequency of encountering of the nickeline-breithauptite series minerals in the Norilsk ore field.*

line–breithauptite series minerals of the Norilsk ore field

Minerals of the whole nickeline-breithauptite series occur in the veins of the first and second cycles of the antimonide-arsenide mineralization of the Norilsk ore field. Nickeline and breithauptite are the most widespread; Sb-nickeline spread quite wide. The Sb-bearing nickeline is more widespread than As-bearing breithauptite (Fig. 9). The coefficient of pair correlation of contents is As-Sb = -1.00 for all selection of analyses of the nickeline-breithauptite series minerals (n = 189 analyses). The Sb-nickeline and As-breithauptite are the most typical for the first four mineral complexes of the first cycle and in the second cycle. The high-cobalt nickeline is characteristic for the arsenide veins of the first cycle. To the end of the first cycle, the content of Fe, S, and Se in nickeline decreases, the content of Co increases up to 12 wt %.

The intermediate members of the nickeline-breithauptite series is usually contain fewer admixtures than low-antimony nickeline. Breithauptite is poor by Co, Fe, S, and Se. For all selection of analyses of the nickeline-breithauptite series minerals (n = 189), the coefficients of pair correlation of contents are as follows: Ni-Co = -0.80, Ni-Fe = -0.40, Sb-Co = -0.40, Sb-Fe = -0.30, Sb-S = -0.30. The coefficients of correlation express the above-mentioned peculiarities of the mineral chemical composition and are an evidence of isomorphous substitutions of nickel by cobalt and iron.

In three concentrates of nickeline from carbonate veins, Pd, Pt, Au were not found (sensitivity of method for Pt and Au is 100 mg/t, for Pd is 30 mg/t; analyst I.Ya. Koshcheeva).

The split and thin-split crystals of nickeline and breithauptite forming nodules are widespread. The split aggregations are the most characteristic for Sb-nickeline and As-breithauptite. The bad-split and non-split crystals are typical for «pure» nickeline and breithauptite.

Conclusions

The antimonide-arsenide mineralization of the Norilsk ore field, which was considered by the previous researchers as a derivative of the P_2-T_1 trap formation, is connected with the post-trap regional metamorphism in conditions of zeolite facies. It is younger than the trap formation for more than 80 MA. At that, the partial mobilization of Ni, Co, As, Sb, and Ag, but not Pd, Pt, and Au, from initial ores took place. The Described Co-Ni antimonide-arsenide mineralization can be considered as the regenerated mineralization, in the interpretation of H. Schneiderhohn (1953b).

Three cycles of antimonide-arsenide mineralization occur. The first cycle is significantly arsenide, the presence of high-cobalt nickeline is characteristic. The second cycle is considerably antimonide. The third cycle is sulphoantimonide-sulphoarsenide.

The minerals of the continuous nickeline-breithauptite series form the significant part of antimonide-arsenide mineralization of the first and second cycles. Nickeline and breithauptite are the most widespread; Sb-nickeline is spread quite wide. The Norilsk nickeline contains up to 12 wt % of Co, to 3 wt % of Fe and S. In nickeline from carbonate veins, Pd, Pt, and Au were not detected. Breithauptite is poor by Co, Fe, and S.

In aggregates of arsenides and antimonides are the geometrical selection zones; that is an evident of crystallization of arsenides and antimonides from the normal solutions in open space.

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NEW DATA ON VANADIUM HEMATITE ASSOCIATED WITH MICRO– AND NANOCRYSTALS OF NOBLE METALS, COPPER, ZINC, AND IRON MINERALS

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The dispersed hematite of bed zone of oxidation, isometric aggregations and veinlets of lamellar hematite from ore and the circum-ore space of a fissure deep-seated zone of oxidation contain more than 1% (to 10.96%) of vanadium. It is detected for the first time that vanadium hematite has the characteristic unit cell parameters: $a_{rh} = 5.44$ Å, $\alpha = 54°73'$; $a_{hex} = 5.03$ Å, $c = 13.84$ Å, space group R-3c). Vanadium hematite often contains carbonaceous aggregations, on which or near which are powdery aggregates of gold-bearing copper, auricupride, native gold, froodite, isoferroplatinum, intermetal compound CuZn, crystallochemical group of Fe, and a new native phase of the Cu_3Pd type, the palladium analogue of auricupride. Size of nanocrystals of these powdery aggregates varies from 1-5 nm to 300-500 nm. The X-ray characteristic spectra of the Cu_3Pd phase show the visible fluctuations of a ratio of palladium to copper in different particles of this phase, whereas the unit cell parameters of these particles are practically identical, $a_0 = 3.68 \pm 0.03$ Å. The ircalculated formulae can be represented as follows: $Cu_{3.3}Pd_{0.6}$, $Cu_{3.3}Pd_{0.7}$, $Cu_3Pd_{1.18}$. A space group of the new phase, Pm3m, is also evidence that it is an analogue of auricupride. In hematized dolomite, a grain of carbonate mineral with diffusive reflections of the AuO(OH) phase, $a_0 = 4.18 + 0.03$ Å, with sizes of nanocrystals 100-150 nm, was found.

Presence of carbonaceous matter, on which nanocrystals of noble metals and other intermetal compounds grow, is an evidence that analytical data on content of the noble metals in ores and in the zone of hematization of ores can be understated in connection with their evaporation together with carbon during analysis. Therefore, the previous forecasts (Chernikov, 1997, 2001; Chernikov *et al.*, 2000) about large reserves of the noble metals in the region of Onezhskaya depression have one more indirect confirmation.

7 tables, 9 figures, 11 references.

Vanadium hematite is widespread in uranium-vanadium deposits of the Onezhskii type. This type of deposits with noble metals (Pb, Pt, Au, Ag), molybdenum, copper, bismuth etc. is the large ore object on reserves of vanadium and, possibly, accompanying elements, in particular, noble metals. The uranium-vanadium deposits, Srednyaya Padma, Tsarevskoe, Kosmozero etc., are located in the Onezhskaya riftogenetic depression in South Kareliya. The gently dipping disseminated ore bodies of these deposits are confined to grey-colour terrigenous rocks at their contact with red-brown (hematized) dolomites (PR_1) of the old deep-seated bed zone of oxidation (Poluektov *et al.*, 1998; Chernikov, 1997, 2001). From the surface up to a depth of 30 m, rarely 150 m, in all deposits, the near-surface contemporary zone of oxidation occur, in which brown and dark brown oxides of iron and manganese are widespread, they limit uranium-vanadium ores from the top. Moreover, in the ore bodies and in circum-ore space are the isometric aggregations and veinlets of hematite with dark red — brown to black colour, they are obliged to activity of fissure deep-seated zone of oxidation and cut ore bodies and hematized dolomites. Dolomites with dispersed hematite at the contact with grey-colour rocks, isometric aggregations and veinlets of hematite in ore bodies are enriched by the redeposited noble metals, sometimes uranium; the nature of their separation was not detected by common mineralogical methods. Therefore, a complex of high-precision methods was used: the raster electron microscopy with the X-ray spectrometer and the transmission electron microscopy with microdiffraction analysis, and also the microprobe electron analysis for detection of ultramicroscopic centres of concentration of noble metals, their chemical composition, structure and form of aggregations. Nano- and microcrystals of gold, platinum, palladium, their compounds and uranium oxides in vanadium hematite was studied the most minutely.

This data is important for solution of a number of practical questions, which are considered

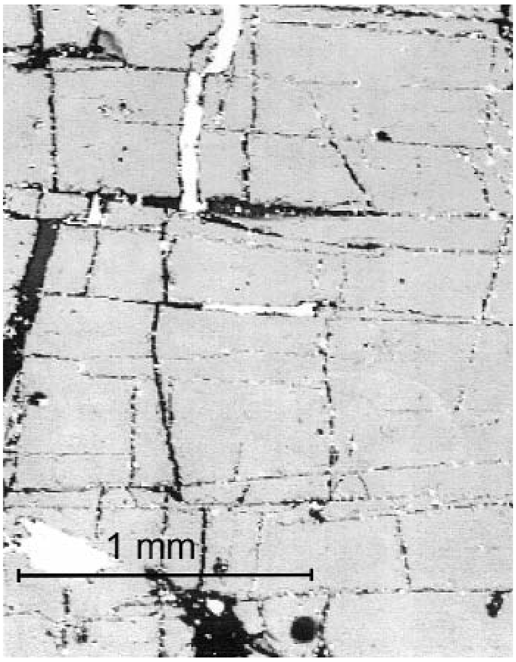
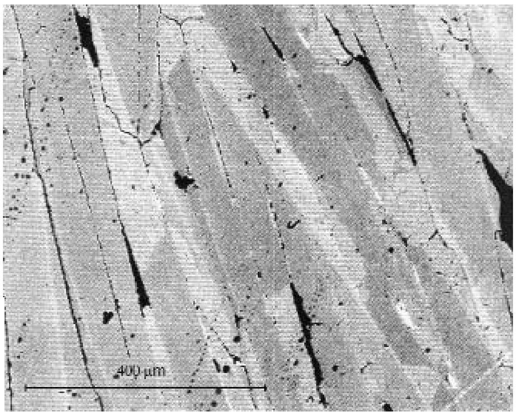
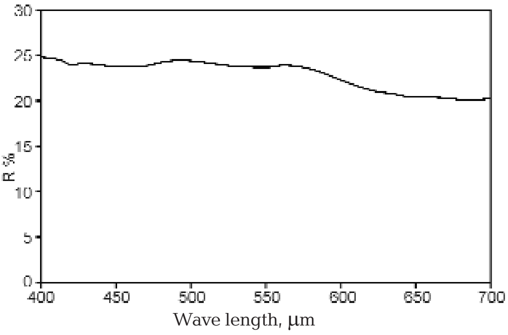


Fig. 1. *Lamellae of vanadium hematite (grey), broken in longitudinal and transversal directions by cracks filled up by clausthalite (light), carbonate (dark grey). Rarely, quartz and clay minerals having the same dark grey colour as carbonate in reflected light crystallize along cracks.*

Fig. 2. *Lamellae of vanadium hematite with different contrast of image in back-scattered electrons. Lines of hematite with grey contrast contain up to 10.96 % of vanadium; lamellae with light grey contrast contain up to 5 % vanadium. Light aggregations is clausthalite, black is carbonate.*





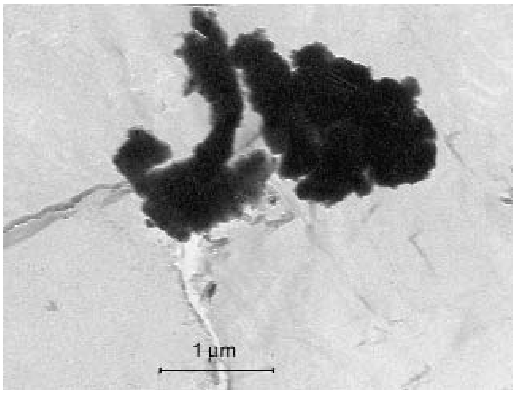


Fig. 3. *Refraction coefficient of vanadium hematite.*

Fig. 4. *Dendrite aggregations of isoferroplatinum, Pt_3Fe.*

Fig. 5. *Dendrite aggregates of native gold.*

Table 1. **Chemical composition of vanadium-bearing hematite, %, data of electron microprobe analysis.**

№	Ti	V	Cr	Mn	Fe	Ni	O	Total
1	0.53	5.21	0.06	0.04	68.48	0.04	24.11	98.47
2	0.36	4.52	0.90	0.02	65.55	0.10	23.01	94.45
3	0.08	9.44	0.05	0.02	64.38	0.17	25.83	99.71
4	0.05	10.96	0.12	0.08	62.87	0.03	26.51	100.11
5	0.07	8.23	0.05	0.05	65.90	0.05	25.41	99.66
6	0.82	5.53		0.03	67.90	0.07	24.37	98.73
7	0.48	3.83			68.94		23.08	96.32
8	0.34	6.07			62.27		22.83	91.51
9	1.02	6.79			85.05		24.65	97. 51
10	0.03	10.52			63.01		26.29	99.79
11	0.45	3.59			69.08		22.90	96.02

below. The study was carried out mainly on the samples from the Srednyaya Padma deposit, the largest and the most minutely prospected object in the region.

The study of vanadium-bearing hematite, ore mineral of uranium-vanadium ores, under the raster electron microscope has shown that in all its spectra is a line of vanadium. The content of vanadium does not exceed 1-3% in dispersed hematite and is visibly higher in the compact variety of the mineral, forming isometric aggregations and veinlets. The concentration of vanadium in this hematite fluctuates from 3.59% to 10.96% (Tabl. 1). In polished sections under the microscope, hematite from veinlets and aggregations are represented by the lamellae broken by cracks in longitudinal and transversal directions (Fig. 1). In the cracks more often are clausthalite and carbonate, rarely quartz, clay and other minerals. Under the electron microscope, the lamellar form of hematite aggregations is detected; it is also broken by microcracks on microblocks, in which aggregations of carbonaceous matter with different powdery aggregates often occur, however, in them are no the proper vanadium phases.

The electron microprobe analysis of hematite has shown that the parts of mineral, which are the most enriched by vanadium, look dark grey in back-scattered electrons (Fig. 2); they contain up to 10.98% of vanadium. Significantly less amount of this element (nearly 3-5%) was detected in the hematite lamellae, which look light grey in back-scattered electrons. In reflected light, by measurements of V.A. Rassulov (VIMS) and O.M. Uvarkina (The Fersman Mineralogical Museum), in 15 points noted varieties of hematite are not distinguished. Intensity of reflectance (R) is 25-21% (Fig. 3). Size of unit cell parameters of hematite with increased content of vanadium is following: $a_{rh} = 5.44$ Å, $\alpha = 54°73'$; $a_{hex} = 5{,}03$, $c = 13.84$ 'Å, space group $R\bar{3}c$; in contrast to common hematite with low content of vanadium (less than 1%), for which unit cell parameters are: $a_{rh} = 5.42$ 'Å, $\alpha = 55°17'$; $a_{hex} = 5.04$ 'Å, $c = 13.76$ Å. By analogy with varieties named titanohematite or alumohematite, for vanadium-enriched hematite one can offer the name vanadiohematite with a formula $(Fe_{1.6-1.9}V_{0.4-0.1})_2O_3$, that was earlier determined (Ryzhev *et al.*, 1991). However, then a distinction of the unit cell parameters of vanadium-bearing and common hematite was not found.

Vanadium-bearing hematite from a fissure zone of oxidation also contains the redeposited uranium and noble metals in high concentrations; they often form powdery aggregates on carbonaceous matter and near it. Among them, the present studies have shown the thin-dispersed aggregations of uranium oxides, isoferroplatinum, Pt_3Fe, native gold, froodite, and auricupride, Cu_3Au. The thin-dispersed well-shaped uranium oxides form the isometric aggregations about 100 μm, sometimes crossed by the hematite microveinlets and microstringers. Moreover, in hematite are the complex uranium iron-vanadium-siliceous compounds. By data of the electron microprobe analyses of single grains, in them, the content of uranium fluctuates from 39.63 to 48.88%; silicon — from 6.73 to 9.79; iron — from 3.62 to 9.96; vanadium — from 4.59 to 4.85; calcium — from 2.26 to 2.56%. In smaller concentrations are the following elements: aluminium — from 0.78 to 1.87; magnesium — from 0.83 to 1.48; sodium — from 0.13 to 0.38; titanium — from 0.08 to 0.18, and phosphorus — from 0.00 to 0.51%. The calculated total of oxides fluctuates from 92.88 to 98.19%. Since the small size of grains, the additional studies of the mineral were not carried out, therefore, its belonging to some mineral species was not determined.

The dendrite aggregations of Pt_3Fe (Fig. 4), 15-3 μm in size, are formed by nanocrystals with a size of 10-15 nm (calculated by data of microd-

Table 2. **Calculation of microdiffraction pattern of Pt_3Fe**

Standard data for Pt_3Fe (Sel. P. Data, 1974)		Calculated data for studied sample of Pt_3Fe		*hkl*
d	*I*	*d*	*I*	
3.85	25	3.90	3	012
2.74	40	2.78	5	104
2.22	100	2.19	10	110
1.93	90	1.82	9	113
1.73	40	1.66	5	024
1.57	40	1.58	5	116
1.36	90			214
1.28	25	1.25	3	300
1.22	25			208
1.16	25	1.13	3	119

Table 3. **Calculation of microdiffraction pattern of Cu_3Au**

hkl	Standard data for Cu_3Au (Bokii, 1954; Garelik *et al.*, 1970)		Calculated data for studied sample of Cu_3Au	
	d	*I*	*d*	*I*
100	3.75	20	3.66	3
110	2.65	5		9
111	2.17	100		10
200	1.88	60		
210	1.67	15	1.69	9

Table 4. **Calculation of microdiffraction pattern of Cu_3Pd**

	Calculated data		Standard data (Garelik *et al.*, 1970)	
hkl	*d*	*I*	*d*	*I*
110	2.57	80	2.59	weak
111	2.12	80	2.13	middle
200	1.84	100	1.84	strong
210	1.64	20	1.63	weak
211	1.47	70	1.49	middle
220	1.28	80	1.30	middle
300	1.20	10	1.227	weak
310	1.16	10	1.173	very weak
311	1.08	40	1.100	middle
322	1.04	40	1.062	weak

iffraction by the Selyakov's equation (Kitaigorodskii, 1952)). Their identification was made on the basis of comparison of microdiffraction pattern of the studied aggregations to standard data (Tabl. 2). Native gold with size of nanocrystals nearly 300-500 nm forms the dendrite aggregates with a size of 800 μm (Fig. 5). The lamellar aggregations of native gold among the prisms of froodite and the small powdery aggregates of gold with a weak microdiffraction pattern were also found (Fig. 6). The size of nanocrystals of auricupride, Cu_3Au, forming the roundish aggregates to 1 m in size (Fig. 7), is nearly 1-5 nm. Comparison of the microdiffraction patterns of Cu_3Au with standard data is given in Table 3.

Besides auricupride, in hematized dolomite of the bed zone of oxidation, a new mineral phase, the palladium analogue of auricupride, has been found. In the studied sample of dolomite, the carbon-bearing matter was found, which melt under the influence of thermal and radiation electron beam and form the thing films.

The microdiffraction pattern of this film corresponds to the compound Cu_3Pd with a space group Pm_3m and the interplanar distances (Tabl. 4), being characteristic for this compound, $a_0 = 3{,}68 \pm 0{,}03$ Å.

A particle (Fig. 8) with a size of 1.5 m was also found; it was located near a pore in dolomite and overgrown by hematite from the side of this pore, near there was the same particle with size nearly 1.0 m, overgrown by hematite from every side. The lamellar and hexagonal crystals of palladium analogue of auricupride are marked (Fig. 9). The X-ray characteristic spectra were obtained from a film and several particles of this phase. The results of calculation of quantitative ratios of all presenting chemical elements by four spectra are given in Table 5.

The obtained results show that a ratio of atom amounts of Cu'Pd in them fluctuates from 2.55 to 5.8. At the same time, all studied particles are practically identical by the unit cell parameters in the detection limits. By virtue of that, one can suppose that studied crystals are imperfect, or in them are isomorphous admixtures, which do not significantly influence on the unit cell parameters. Calculated formulae for analysed samples are close to each other. They can be represented as follows: $Cu_{3.32}Pd_{0.6}$ (an. 1); $Cu_{3.3}Pd_{0.7}$ (an. 2, 3); $Cu_3Pd_{1.18}$ (an. 4). The aggregation (an. 2) practically without admixture and the grain (an. 3) containing significant amount of iron and lead have the identical calculated formulae. The differences in measured limits of detection of palladium and copper in the analy-

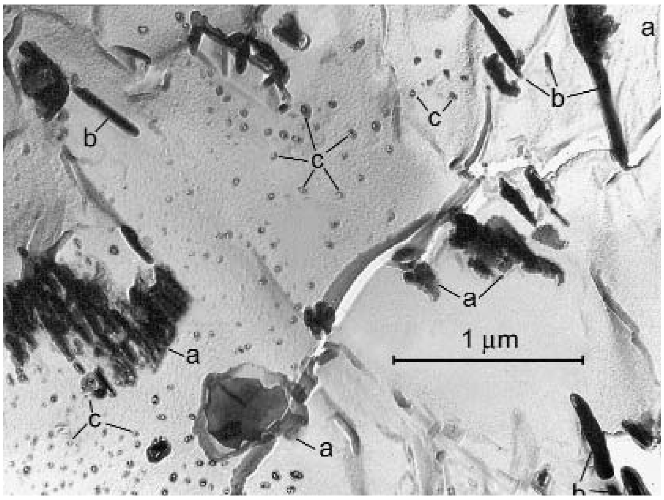


Fig. 6. *Lamellar aggregations of native gold (a), prisms of froodite (b). Small powdery aggregates (c) of native gold with weak microdiffraction pattern.*

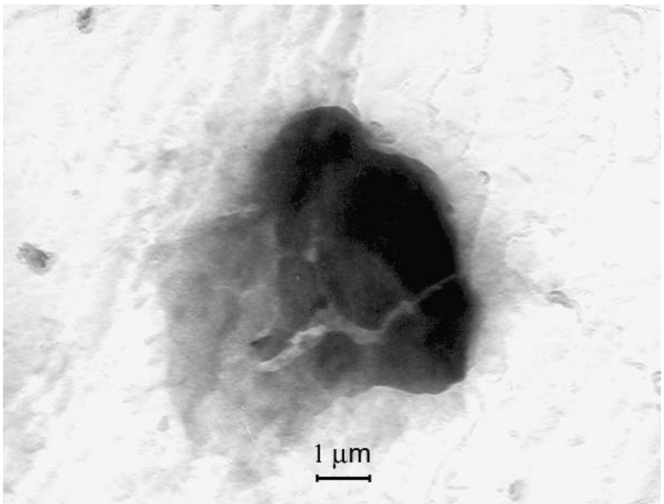


Fig. 7*. Roundish aggregates of auricupride broken by cracks.*

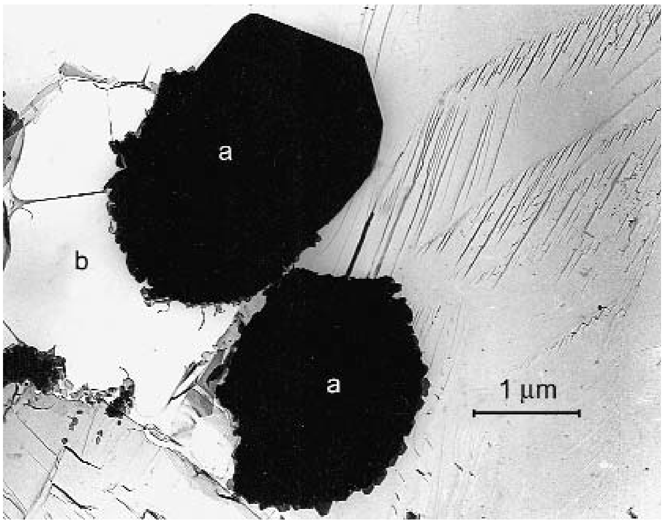


Fig. 8. *Aggregations of* Cu_3Pd *(black, a) near pore (b) in dolomite. Crystal of palladium analogue of auricupride (a) is overgrown by hematite from the side of the pore. The second crystal of palladium analogue of auricupride (a) is overgrown by hematite from every side.*

Table 5. **Results of calculation of quantitative ratios of chemical elements of palladium analogue of auricupride**

No.	Chemic. of analyses elements	E(keV)	Intensity	Content,%	Atom amount, Cu/Pd
1	Pd	2.84	217.365	12.99	
	Mn	5.90	1.575	0.60	
	Fe	6.40	66.198	37.12	5.8
	Cu	8.95	35.299	44.96	
	Pb	10.55	0.342	4.32	
2	Pd	2.84	192.791	26.45	4,7
	Cu	8.05	32.860	73.55	
3	Pd	2.84	245.171	14.84	4.7
	Fe	6.40	68.352	37.48	
	Cu	8.05	36.018	41.81	
	Pb	10.55	0.806	5.87	
4	Pd	2.84	238.087	39.70	2.55
	Cu	8.05	18.990	60.30	

Table 6. **Interplanar space of intermetal phase CuZn and crystallochemical group of iron**

	Standard data for CuZn (Garelik *et al.*, 1970)		Standard data for Fe group. (Mikheev, 1957)		Расчетные данные CuZn	
hkl	*d*	*I*	*d*	*I*	*d*	*I*
110	2.09	very weak	2.02	9	2.12	10
200	1.47	weak	1.43	7	1.50	9
211	1.21	weak	1.16	10	1.22	5
220	1.04	middle	1.02	7	0.94	3
310	0.93	middle				
222	0.85	middle				

Table 7. **Interplanar space of phase AuO(OH)**

Calculated data		Standard data (Novgorodova *et al.*, 1995)		
d	*I*		*d*	*hkl*
3.45	1	hematite		
2.82	4	hematite		
2.47	8		2.47	111
2.09	9		2.02	200
1.72	7		1.75	220
1.55	7		1.43	311

ses 1, 2, and 3, do not also considerably affect on formulae. Consequently, one can admit that analysed samples are represented by imperfect crystals.

In carbonaceous matter, which quite often occurs in hematite, during its study under the raster electron microscope the powdery aggregates of native copper are also observed; they have the increased unit cell parameters that can be connected with a presence of gold in copper. Moreover, on quartz from the hematized dolomite, the powdery aggregates decorating splits were noted; they give the microdiffraction pattern of the iron crystallochemical group and intermetal compound with chemical composition CuZn (Tabl. 6). The size of nanocrystals, used for obtaining of a microdiffraction pattern, is 100-200 nm. The interplanar distances of the CuZn phase are slightly higher than standard ones; that can be connected with a presence of isomorphous iron in this aggregation.

At last, in hematized dolomite, the crushed grain of carbonate mineral was found; it contains an inclusion, on which microdiffraction pattern are the diffusive reflections of the AuO(OH) phase. One failed to measure these reflections earlier; because of that the value «I» in Table 7 in the column «standard data» is absent. The first two lines in the column «calculated data» belong to hematite, with which this phase forms intergrowths; the other four lines belong to the AuO(OH) phase, $a_0 = 4.18 \pm 0.03$ Å. The size of separate particles forming the AuO(OH) grain fluctuates from 100 to 400 nm. The size of nanocrystals is of 100-150 nm.

Conclusion

The studies have shown that dispersed hematite of dolomites from the old deep-seated zone of oxidation, the isometric aggregations and veinlets of lamellar hematite, occurring in the circum-ore space and in uranium-vanadium ores, always contain the increased (more than 1%) concentrations of vanadium. At that, the lamellae of hematite, which look dark grey in back-scattered electrons, are much enriched (in our cases up to 10.96%) by vanadium. It is detected for the first time, that vanadium hematite has the characteristic unit cell parameters distinguishing from the unit cell parameters of hematite with low (less than 1%) concentrations of vanadium.

Vanadium hematite often contains carbonaceous aggregations, on which or near which the redeposited powdery aggregates of gold-bearing copper, auricupride, native gold, froodite, isoferroplatinum, intermetal compound with chemical composition CuZn, the Fe group and new natural phase of Cu_3Pd type, palladium analogue of auricupride, are noted. The size of nanocrystals of these phases fluctuates from 1-5 nm to 300-500 nm.

In hematized dolomite, a grain of carbonate mineral with diffusive reflections of the AuO(OH) phase was found (the second finding in nature, for the first time definite $a_0 = 4.18 + 0.03$ Å), sizes of its nanocrystals are 100-150 nm.

The presence of carbonaceous matter with powdery aggregates of nanocrystals of gold-bearing native copper, auricupride, intermetal compounds of CuZn type, crystallochemical group of iron, Pt_3Fe, Cu_3Pd in hematite is important for the working of technological processes of extraction of noble metals from ores, understanding of their genesis and reasons of frequent discrepancy in analytical data on noble metals. The joint occurrence of carbonaceous matter and noble metals and also other intermetal compounds is an evident that in process of their transportation and sedimentation the carbonaceous matter played a significant, unless decisive, role. The separation of noble metals on carbonaceous matter and near it is also an evident that analytical data on content of noble metals in ores and in the zone of hematization of rocks can be understate since during analysis process they evaporate together with carbon. Therefore, the previous forecasts (Chernikov, 1997, 2001, Chernikov *et al.*, 2000) about large reserves of noble metals in the region of the Onezhskaya depression have one more indirect confirmation.

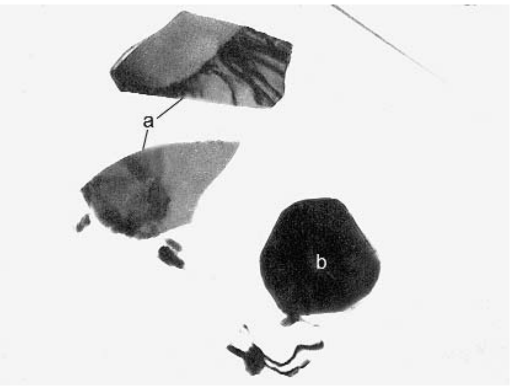


Fig. 9. *Lamellar (a) and hexagonal (b) aggregations of Cu_3Pd*

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Selected Powder Data for Mineral (first edi-

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BISMUTH MINERALIZATION OF Pb–Zn ORES AT THE DJIMIDON DEPOSIT (NORTH OSETIA)

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The Djimidon deposit is a new object in the Sadon ore district (Northern Osetia — Alania). Bismuth mineralization represented by a wide spectrum of Pb-Bi-Ag-S-bearing minerals has been found in the deposit and studied in detail. Its relationships with other mineral assemblages are shown in general sequence of consecution of ore deposition. The spatial regularities in distribution of bismuth mineralization in ores of the deposits are revealed.
1 table, 5 figures, 13 references.

The Djimidon deposit discovered in the end of the 1970s belongs to the group of the wide-known Pb-Zn deposits of the Sadon ore destrict (Northern Osetia — Alania). It is located in the Ardon River basin.

Deposits of lead and zinc in North Osetia are wide known. Their study and working began since 1853. Many geologists (Azhgirei, 1958; Vardanyants, 1935; Gurbanov, Zembatov, 1978; Davydov, Granovskii, 1985; Dobrovol'skaya, 1987, 1989; Nekrasov, 1980; Chernitsyn, 1985; Khetagurov, Katova, 1972; Konstantinov *et al.*, 2003, 2004, *etc.*) carried out the detailed studies of geological-structural position of the deposits, their mineral composition and geochemical peculiarities of ores, and also genesis conditions. The interest to these deposits has again arisen since the moment of discovery of the Djimidon deposit in the end of the 1970s and the following prospecting and working of its ores; it is represented by the Bozang and East Djimidon ore zones (Fig. 1).

Geological position of the deposit

The Sadon ore region is an area between horst-anticlinorium of the Main Caucasus Range and the Darial-Bogos uplift, which part is the Sadon-Unal horst-anticline controlling allocation of the main industrial deposits of the region. The Djimidon ore field is located within the bounds of the same name uplift, which is the eastern block-segment of the Sadon-Unal horst-anticline. Rock complexes with different age form the structure of the Djimidon deposit; they compose two structural stages divided by the regional unconformity. The lower structural stage is formed by the deep metamorphosed complex of rocks of the Buron suite (Upper Proterozoic — Lower Paleozoic), which are broken by the Upper Paleozoic granitoids. The Buron suite has the distinctly pronounced binary structure conditioned by the predominant distribution of hornblende amphibolites in its basis, which up-section are gradually changed by crystalline schists of different composition. On the rocks of the crystalline substratum with basal conglomerates in the sole the Lower Jurassic terrigenous sediments of the upper structural stage are superposed. Considerable role in the structure of deposit belongs to magmatic formations of the Jurassic volcano-plutonic assemblage represented by the consecutive series: from effusive facies of covering andesites (Osetinian volcanogene complex) to subvolcanic and hypabyssal facieses of diorites, granite-porphyries, and trachyandesites (Ardon-Nogkau complex).

In structural respect, the Djimidon ore field is confined to the Djimidon uplift represented by simple anticline structure, in which core the metamorphous rocks of basement are exposed, and on the limbs the formations of the upper structural stage are represented. Along the series of transversal dislocations, the uplift is divided into separate blocks.

The Djimidon deposit is a representative of the «blind» type of mineralization (Konstantinov *et al.*, 2003); main volume of its industrial ores is concentrated in ore bodies localized in the rocks of the Pre-Jurassic basement. The ores of metamorphic complex of the Buron suite are the most propitious (Fig. 1). At transition in rocks of the upper structural stage, the ore bodies are transformed to the zones of dispersed silicification and chloritization accompanied by dispersed sulphide mineralization. Detected vertical interval of mineralization is not less than 300-350 m. Morphology of ore bodies is determined by the composition of pre-ore structure and competence of host rocks. The veined platy ore bodies prevail; quite often they are accompanied by the aureole of vein-impregnated mineralization. Morphology of ore bodies is constant up the dip.

***Fig. 1**. Schematic geological map of the Djimidon ore field.(After K.V. Davydov with some changes).*
1 — limestones, dolomites (J_1ox); 2 — sandstones, aleurolites, clays, limestones (J_2); 3 — argillites, intercalations of sandstones (J_1t_{1-2}-J_2a); 4 — clay shales, aleurolites, intercalations of sandstones (J_1t_{1-2}); 5 — sandstones, aleurolites (J_1p_{2m}); 6 — conglomerates (J_1^1). The Buron suite: 7 — crystalline schists, amphibolites (PR_3 — PZ_1br); 8 — coarse-grained granites (γPZ_3). The Jurassic volcano-plutonic assemblage: 9 — lavas of andesites and their tuffs (νJ_1os); 10 — trachyandesites ($\tau\alpha J_2$); 11 — ore zones: 1 — Bozang, 2 — Zagarsar, 3 — East Djimidon; 12 — dislocations with a break in continuity: upthrow faults (a), faults (b), fractures (c): I — Fist transversal fault, II — Second transversal fault, III — East Djimidon fault, IV — West Djimidon fault, V — Agshartyrag upthrow fault, VI — Sadon-Unal fault, VII — Latitudinal fracture, VIII — Zamadon upthrow fault, IX — Zagadon fault, X — Dagom fault; 13 — supposed geological boundaries; 14 — thrusts

Post-ore dislocations significantly influence on position of ore bodies; their amplitude varies from 1 cm to 30-40 m.

Mineral assemblages and sequence of ore formation

The macroscopic and microscopic study of representative samples from the Djimidon deposit from the Bozang (adit 47, North, South, and Main drifts; adit 3, South drift; and adit 8) and East Djimidon (holes 045, 047, 061, 061A, *etc.*) ore zones allow to distinguish main mineral assemblages and make a scheme of mineral formation. Textural and structural features, variations of chemical composition of the mineral individual, in particular, sphalerite from different assemblages, and fluid regime of ore-forming system were the basis for detection of age correlations of mineral aggregates.

In the result of summarizing of obtained data, four stages of ore formation were distinguished: 1) quartz-pyrite-arsenopyrite; 2) quartz-carbonate-pyrite-pyrrhotite-chalcopyrite-sphalerite; 3) quartz-calcite-arsenopyrite-sphalerite-galena; 4) quartz-fluorite-calcite-barite. Each of these stages is represented by one or several mineral assemblages (Fig. 2).

The pre-ore stage preceded the ore deposition; quartz, potash feldspar, chlorite, sericite

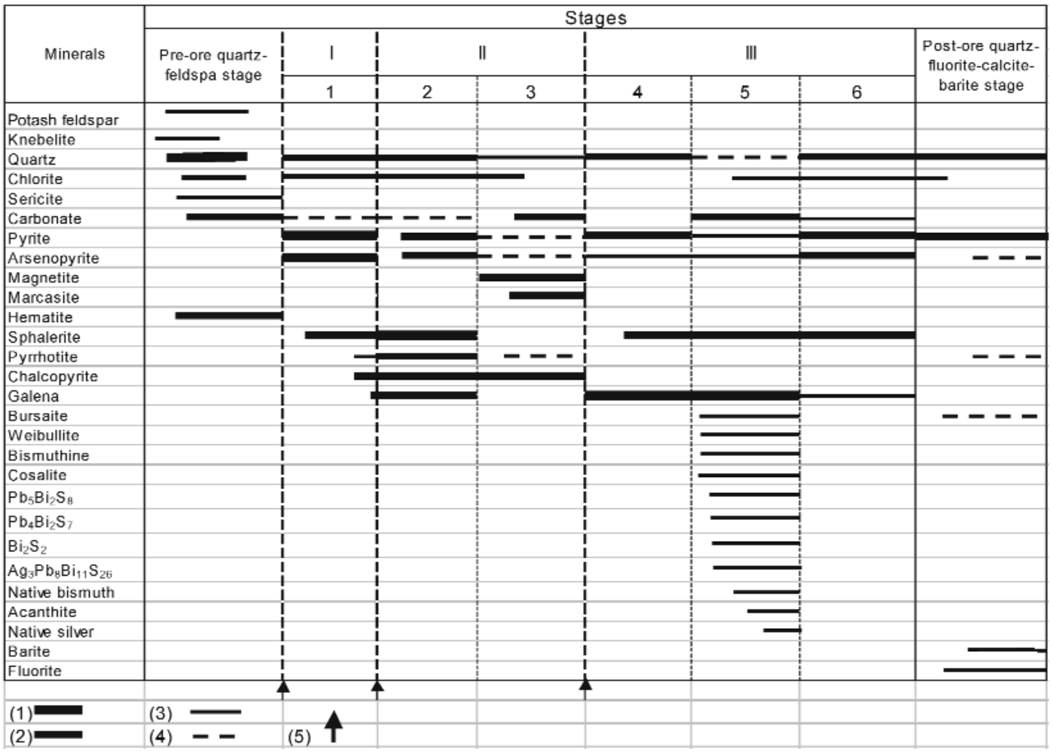


Fig. 2. Scheme of sequence of ore formation of the Djimidon deposit. Stages: I — quartz-pyrite-arsenopyrite; II — quartz-carbonate-pyrite-pyrrhotite-chalcopyrite-sphalerite; III — quartz-calcite-arsenopyrite-sphalerite-galena, assemblages: 1 — quartz-pyrite-arsenopyrite, 2 — quartz-galena-pyrrhotite-chalcopyrite-sphalerite, 3 — quartz-carbonate-pyrite-marcasite-magnetite, 4 — quartz-chalcopyrite-galena-sphalerite, 5 — acanthite-bismuthine-cosalite-galena, 6 — quartz-pyrite-arsenopyrite. Minerals: (1) — main, (2) — accessory, (3) — rare, (4) — redeposited; (5) — dislocations with a break in continuity

were mainly deposited during pre-ore stage. Crystallization of knebelite, occurring in the form of xenoliths in ores, can also be related to this stage. Mineral aggregates of the pre-ore stage were here and there broken, brecciated as a result of tectonic movements that took place in the beginning of the ore deposition.

The quartz-pyrite-arsenopyrite assemblage, here and there with sphalerite I, was deposited during the fist stage in the disturbed tectonic conditions. The mineral aggregates of this assemblage form veinlets, spot-veinlet aggregations, rarely they occur in the form of compact ores. The quartz-pyrite-arsenopyrite assemblage with predominance of either pyrite or arsenopyrite occurs in the ore bodies irregularly, but its correlations with the later minerals are simple. Quartz, pyrite, and arsenopyrite are brecciated, broken down, fractured; the fractures are filled up by sphalerite, chalcopyrite, pyrrhotite, galena, and quartz, forming the next by time of deposition assemblage belonging to the second stage. The assemblage is not observed everywhere. In separate parts, the amounts of minerals forming it are changed. In some parts, pyrite and chalcopyrite prevail in the assemblage, they form intergrowths; in other parts are chalcopyrite and sphalerite, and also pyrite of the second generation. Sphalerite in this assemblage contains the abundant inclusions of chalcopyrite and pyrrhotite, which are characteristic for sphalerite II.

The quartz-galena-pyrrhotite-chalcopyrite-sphalerite assemblage of the second stage is the main assemblage in the ores. After its formation, the deformations in mineral aggregates of this assemblage (the local fragmentation and boudinage of aggregates, the curved and removed twins in pyrrhotite and sphalerite, etc.) have appeared as a result of the disturbed tectonic conditions. We should note galena was not undergone deformations; that indicates its later crystallization.

Galena, pyrrhotite, chalcopyrite, and sphalerite form intergrowths, sometimes with features of earlier deposition of sphalerite. A peculiarity of this assemblage is in unsteady ratios of quartz and sulphides; sometimes, it is represented only by quartz with rosettes of chlorite and by sphalerite II without other sulphides. The quartz-sphalerite aggregates form veinlets or aggregations in the gouges of ore bodies.

In the end of the second stage, the conditions were strongly changed; the sulphur and oxygen activity has increased, as a result, the disulphidization of pyrrhotite and formation of carbonate-pyrite-marcasite-magnetite assemblage has happened; this assemblage is probably reactionary, arising at the border of two stages of ore deposition. Pyrite and marcasite intensively substituted pyrrhotite, sometimes together with magnetite and siderite. In the separate parts magnetite (muschketowite) replaced hematite.

The third stage, quartz-calcite-arsenopyrite-sphalerite-galena, is represented by three mineral assemblages: quartz-chalcopyrite-galena-sphalerite, here and there with pyrrhotite; acanthite-bismuthine-cosalite-galena; and quartz-pyrite-arsenopyrite. The quartz-chalcopyrite-galena-sphalerite assemblage, sometimes with calcite and pyrrhotite, occurs everywhere and mainly in the central parts of ore bodies. In contrast to early assemblage with the similar name, pyrrhotite in the late assemblage is not disulphidized. Sphalerite III, dominating in the assemblage, contains the irregularly distributed inclusions of chalcopyrite, but in significantly smaller amounts. Crystallization of low-iron sphalerite associated with galena, quartz, and calcite is connected with the third stage.

The acanthite-bismuthine-cosalite-galena assemblage occurs in the ores locally. It was found in the adit 47 and in a number of holes: 045, 047, 061, 061A, 076. The facies distinctions are typical for it. In some parts, the Ag-Pb-Bi assemblage with galena, native bismuth, sulphides, and sulphosalts of Pb and Bi occurs; in other parts are native silver, acanthite, and galena. Bismuth minerals substitute earlier sulphides: pyrite, arsenopyrite, pyrrhotite, chalcopyrite, sphalerite; they are associated with quartz and calcite.

Mineral aggregates of the quartz-pyrite-arsenopyrite assemblage of the third stage fill up the veinlets; minerals of this assemblage form metacrystals. Pyrite and arsenopyrite overgrow quartz in the form of cockades, cut up mineral aggregates of earlier stages, form metacrystals in sphalerite, chalcopyrite, and galena. Quartz metacrystals are often observed among sulphides.

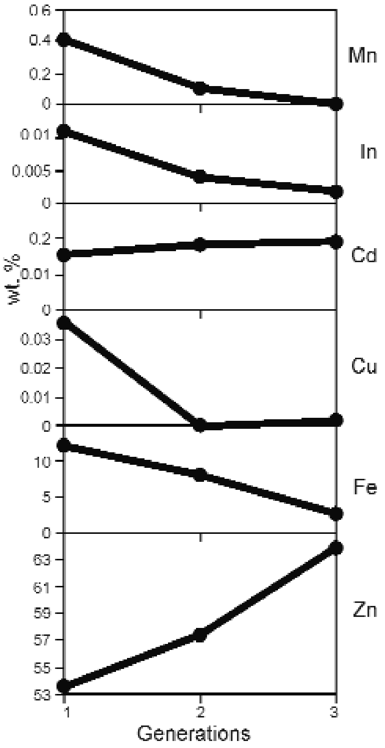


Fig. 3. *Graphs showing average contents of elements-admixtures in sphalerite of different generations. Generation I (24 analyses), generation II (9 analyses), genera-*

The fourth stage, quartz-fluorite-calcite-barite, finishes a process of minerogenesis. In this stage, the quartz-calcite veinlets were deposited, which cut the mineral aggregates of earlier stages. In some veinlets, quartz prevails, in other ones, calcite does so; sometimes there are barite and fluorite. These minerals form also individual veins with thickness of 20-30 cm, beyond the bounds of main ore bodies. Some veins are composed by microcline and calcite.

The distinguished mineral assemblages, textural and structural analysis of ores indicate the interrupted-continuous process of coming of hydrothermal solution, that resulted in crystallization of identical minerals (quartz, pyrite, arsenopyrite, sphalerite, pyrrhotite, chalcopyrite, galena) in mineral assemblages, differing by time of formation, and within the limits of different stages. The periodicity in formation of early and late assemblages, in particular, quartz-pyrite-arsenopyrite assemblage, is an

Table 1. **Chemical composition of bismuth minerals from ores of the Djimidon deposit (wt %)**

№ п/п	№ sample	Occurrence	Pb	Bi	S	Fe	Ag	Sb	Se	Zn	Cu	Total	Mineral
1	3-8a	Bozang, adit 3	84.43	1.35	13.37	–	0.46	0.00	0.47	–	0.02	100.10	galena
2	1.8	East Djimidon, hole 061A-220.5	70.24	14.09	13.91	0.06	0.30	0.00	0.28	0.00	0.07	98.95	Bi-galena
3	3-8a	East Djimidon, hole 061A-220.5	68.42	15.10	14.80	–	0.48	0.04	0.57	–	0.11	99.52	Bi-galena
4	1.3	East Djimidon, hole 061A-219.6	63.60	21.03	13.50	1.02	0.25	0.00	0.26	0.03	0.08	99.77	beegerite
5	1.3	East Djimidon, hole 061A-219.6	59.06	26.89	11.05	0.34	2.00	0.09	0.26	0.05	0.00	99.74	hoongarrite
6	1.1	East Djimidon, hole 061A-220.5	50.86	34.84	13.50	0.09	0.43	0.00	0.23	0.04	0.00	99.99	lillianite
7	3-8a	Bozang, adit 3	44.19	37.36	15.78	–	1.48	0.01	0.50	–	0.11	99.43	bursaite
8	3-8a	Bozang, adit 3	39.33	42.22	16.60	–	0.62	0.00	0.23	–	0.81	99.81	cosalite
9	1.6	East Djimidon, hole 061A-219.6	37.86	44.91	15.42	0.09	0.25	0.04	0.20	0.04	0.00	98.81	cosalite
10	47-43	Bozang, adit 47	37.58	44.74	15.28	–	2.63	–	–	–	–	100.24	cosalite
11	47-43	Bozang, adit 47	34.68	47.61	15.58	–	1.90	0.00	0.10	–	0.30	99.35	weibullite
12	47-43	Bozang, adit 47	33.78	48.04	16.70	–	1.30	0.00	0.10	–	0.00	100.16	weibullite
13	47-43	Bozang, adit 47	32.31	47.76	15.97	–	5.60	0.00	0.10	–	0.40	98.24	$Ag_3Pb_8Bi_{11}S_{26}$
14	1.9	East Djimidon, hole 061A-220.5	22.18	61.14	15.75	0.03	0.18	0.10	0.11	0.04	0.04	99.57	galenobismutite
15	5	East Djimidon, hole 061A-220.5	5.56	75.72	18.26	0.20	0.02	0.10	0.00	0.04	0.00	99.96	bismuthine
16	8.2	East Djimidon, hole 061A-219.6	0.00	81.06	18.51	0.11	0.00	0.00	0.11	0.00	0.00	99.81	bismuthine
17	1.7	East Djimidon, hole 061A-219.6	7.93	89.19	1.43	1.11	0.02	0.00	0.07	0.04	0.06	99.89	native Bi
18	47-43	Bozang, adit 47	0.86	96.08	0.15	–	0.00	0.00	0.00	–	0.80	98.49	native Bi
19	2.4	East Djimidon, hole 061A-219.6	0.00	99.56	0.07	0.03	0.00	0.00	0.00	0.02	0.03	99.71	native Bi
20	47-43	Bozang, adit 47	0.70	83.24	12.81	–	0.10	0.00	0.10	–	0.60	98.96	Bi_2S_2

Note: *Desh – element was not detected. Analyses were performed in the laboratory of IGEM RAS, electron microprobe instrument SX-50, analyst A.I. Tsepin.*

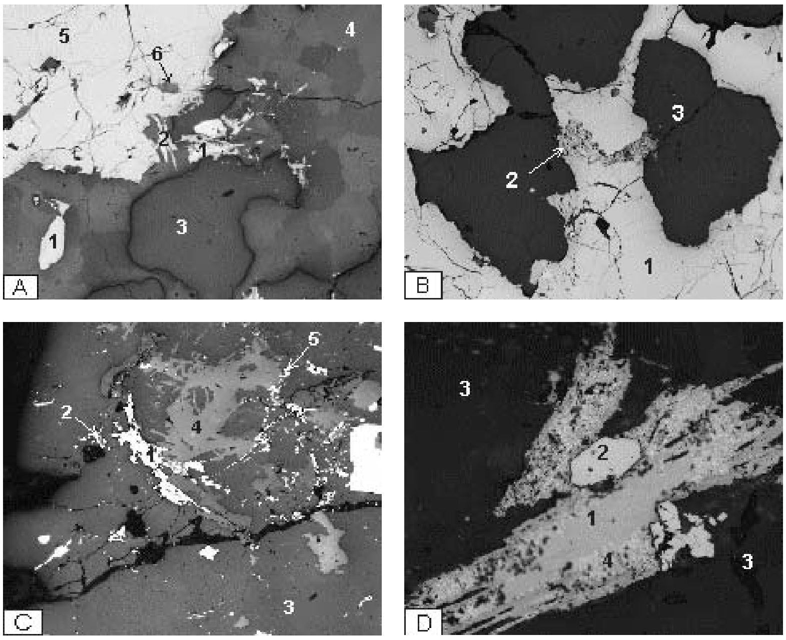
indication of the stage formation of ore bodies (Dobrovol'skaya, 1989). The consecution of ore deposition is also confirmed by the change of chemical composition of sphalerite. The analytical data has shown that sphalerite I is enriched by iron (9.55-15.48 wt %) and manganese, in sphalerite II, the content of iron varies from 5.8 to 9.96 wt %, the third generation of sphalerite is represented by the low-iron (0.73-3.88 wt %) cleiophane with content of cadmium up to 0.3 wt % (Fig. 3).

The results of the thermo-cryometric study of fluid inclusions in sphalerite, quartz, and carbonate from ore bodies also allow realizing the main features of fluid regime of formation of mineral assemblages of the Djimidon deposit. Ores were deposited from hydrothermal solutions with predominantly sodium-chloride composition with admixtures of other components in a wide range of concentrations from 18 to 0.5 wt % equiv. NaCl under the pressure not less than 400-300 bar. In each ore stage, the process of minerogenesis began from higher temperatures (250-350 °C); to the end, the temperature has reduced to 120-150 °C. This data also emphasizes the pulsatile character of the process.

Chemical composition of the Bi-minerals

The bismuth mineralization is represented by a wide spectrum of Bi-bearing minerals (Tabl. 1).

tion III (14 analyses)



The analytical data allowed identifying bismuthine (Bi_2S_3), bursaite ($Pb_3Bi_4S_{11}$), weibullite ($Pb_3Bi_4S_9$), cosalite ($Pb_2Bi_2S_5$). In the same assemblage, the phases $Pb_5Bi_2S_8$ and $Pb_4Bi_2S_7$ were found, and also there are a phase, containing silver ($Ag_3 Pb_8Bi_{11}S_{26}$), acanthite (Ag_2S) and native silver and bismuth. Chemical composition of Bi-bearing minerals is studied quite minutely, 94 phases were analysed; in Table 1 are the analyses, which are correctly calculated on mineral formulas and correspond by chemical composition to sulphosalts of lead and bismuth described by N.N. Mozgova (1985).

The distribution of bismuth mineralization in ores has some peculiarities. One of them is in occurrence of the bismuth minerals containing up to 5.6 wt % of silver in the upper parts of the ore bodies. In the lower parts, the amount of silver in them is reduced up to 1.7 wt %. The other peculiarity is the change of mineral composition according to depth of the ore body uncovering. Bismuthine is the most widespread mineral in the deep parts; above is cosalite. It is evidence that amount of bismuth increases with depth. The third peculiarity is in regular occurrence of bismuth mineralization only in determined parts, in particular, within the interval of depths of 180-220 m and only where pyrite, arsenopyrite, and pyrrhotite are present in ores; pyrrhotite was partly or sometimes entirely disulphidized. The single findings of the bismuth minerals were made at a depth of 100 m.

Native bismuth, sulphides, and the bismuth sulphosalts have been found in the adit 47 and in the holes 045, 047, and 061A. These minerals are mainly associated with quartz (Fig. 4). Their occurrence among calcite is explained by that quartz in alkaline conditions were dissolved and partly redeposited in the form of metacrystals; the bismuth minerals associating with quartz were kept in calcite (Fig. 4a). In a number of cases, the bismuth minerals occur among sulphides: pyrrhotite (Fig. 4b), arsenopyrite, sphalerite, and chalcopyrite. The sizes of single grains of the Bi minerals and their intergrowths are units of microns, sometimes up to 30 μm. The forms of aggregations are diverse: irregular, lamellar, needle-shaped, aggregated (Fig. 4).

Galena, presenting in the composition of Bi-bearing assemblage, differs by chemical composition according to depth of its occurrence. In 9 samples collected at the Djimidon deposit, galena contains a small amount of silver (0.09-0.48 wt %) and bismuth (0.24-15.1 wt %). At a depth of 186-220 m (holes 047, 061A), galena is enriched by bismuth (Tabl. 1, an. 3).

Native bismuth is distributed considerably wide than other Bi minerals. Especially often it occurs in samples from the holes of underground drilling, 045, 047, 061A, in the intervals of depths of 180-220 m. Native bismuth usually substitutes Bi-bearing minerals and also forms separate small aggregations among quartz (Fig. 4c). Chemical composition of 8 grains of native bismuth has shown the significant contents of admixtures of iron, copper,

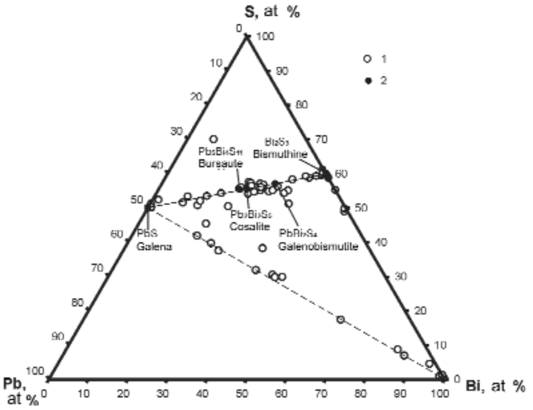


Fig. 4. *Forms of aggregations of Bi-bearing minerals. Polished sections. Magnification 160 (a, c), 200 (b), 250 (d).*
a — thin-lamellar aggregates of bismuthine (1) (Tabl. 1, an. 15), galenobismutite (2) (Tabl. 1, an. 14) in quartz (3) and calcite (4)

and sulphur in it. In one of analyses are silver (0.28 wt %) and lead (1.58 wt %). These admixtures are probably connected with surrounding sulphides, since grains of native bismuth are extremely small. The most representative analyses (an. 17 — 19) are given in Table 1.

Bismuthine occurs in the form of prismatic and needle-shaped crystals, sometimes thin-crystal intergrowths among quartz (Fig. 4a). Chemical composition of bismuthine is relatively constant. Content of bismuth fluctuates from 75.7 to 83.2 wt %, sulphur — from 15.8 to 18.4 wt %. Some decrease of the bismuth content is caused by the lead admixtures. Results of analyses are well calculated on the bismuthine formula (Tabl. 1).

Cosalite is similar to bismuthine by forms of aggregations (Fig. 4c, d). The thin needle-shaped crystals, sometimes intergrowths and small-grained aggregates are also typical for it. Cosalite is optically heterogeneous; it forms intergrowths with other Bi-bearing minerals. The most constant by chemical composition cosalite was found in samples from the adit 47. The bismuth content in it increases with depth. 17 phases of cosalite were analysed; selected analyses calculated on mineral formula (an. 8-10) are given in Table 1. The summarized data has shown the fluctuations of Bi from 41.5 to 50.8 wt %, lead — from 36.6 to 41.2 wt %, sulphur — from 15.1 to 16.7 wt %.

Galenobismutite is not practically distinguished from cosalite by the optical properties. By chemical composition, these minerals are close to each other; in the single analyses of galenobismutite (Tabl. 1, an. 14), the higher, in comparison with cosalite, contents of bismuth and smaller amounts of lead, 61.14 and 22.18 wt % respectively, were obtained.

Weibullite, bursaite, Pb–Bi phases, and Ag–Pb–Bi–bearing phases occur usually in thin intergrowths with each other, these minerals and mineral phases are relatively rare in ores; their description is difficult because of sub-microscopic sizes of their grains. They were detected only on the basis of chemical analyses, distinguishing from analyses of cosalite and bismuthine (Tabl. 1), and calculated mineral formulas.

The variations in the chemical composition of the Pb-Bi-S minerals are shown on the diagram of phase correlations in the system (Fig. 5), which shows the regular continuous series of mineral phases, PbS — Bi_2S_3 (Minerals, 1974). The diagram is made on the basis of cosalite, experimentally grown as a stable phase at the temperature 400 °C (Craig, 1967), and chemical compositions of minerals from the Djimidon deposit. On the diagram, the filled circles correspond to theoretical chemical compositions of galena, bursaite, galenobismutite; the unfilled circles correspond to Bi-bearing minerals from the deposit. Some fluctuations of chemical compositions from the PbS-Bi_2S_3 system (Fig. 5) are probably connected with formation of phases in the same series at lower temperatures (Craig, 1967). Once more series, PbS-Bi, corresponding to the analysed samples, was found during the diagram making. This series, galena — native bismuth, corresponds to the unsteady ratios of lead, bismuth, and sulphur in the studied phases; it is apparently connected with their heterogeneity because of small-grained intergrowths.

By data of microthermometry of fluid inclusions (by quartz and carbonate from acanthite-bismuthine-cosalite-galena assemblage), it is obvious that solutions had both sodium-chloride and magnesium-chloride chemical composition and high concentrations up to 17 wt % equiv. NaCl; the highest temperatures of minerogenesis to 300-350°C were here.

Conclusion

Mineral composition of ore bodies of the Djimidon deposit is quite simple and similar to ore composition of other lead-zinc deposits of the Sadon ore region. The quite wide occurrence of arsenopyrite and presence of the diverse Pb-Bi-Ag-S mineralization found at the deposit for the first time are the distinctive peculiarity of ores of the Djimidon deposit.

Ores of the Djimidon deposit are characterized by the presence of facies distinctions in the mineral composition of main assemblages, local distribution of the Pb-Bi-Ag-S mineralization, and presence of two to three-four generations of main ore-forming minerals.

Geochemical peculiarities of ores, in particular typomorphism of sphalerite and galena, have shown the increased concentrations of indium in early stages of mineralization and cadmium, silver, and bismuth in later stages.

Acknowledgements

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RARE–METAL MINERALIZATION CONNECTED WITH BITUMINOUS MATTERS IN LATE ASSEMBLAGES OF PEGMATITES OF THE KHIBINY AND LOVOZERO MASSIFS

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The mineral composition and structure of microheterogeneous aggregates from the low-temperature assemblages, containing solid bituminous matters (SBM), from the Khibiny and Lovozero massifs have been studied. It is shown that thin intergrowths of SBM with the rare elements minerals are the typomorphic formations of hydrothermal zones of agpaitic pegmatites of these massifs. 4 types of such intergrowths are distinguished, which are characterized by different mineralogical composition, high content of rare elements, and extremely high degree of separation of Ce, La, Nd, Y, Sr, Th, U, Ti, Nb, and Ba between different phases, right up to the formation of proper minerals of these elements. Not only new mineral species for Khibiny and Lovozero but also a whole number of phases that do not have analogues among known minerals were found. The possible mechanisms of formation of microheterogeneous aggregates containing SBM and a role of complexes with organic compounds in the transportation of rare elements at low temperatures are discussed.

4 tables, 9 figures, 28 references.

Located at the Kola Peninsula, the Khibiny and Lovozero massifs of agpaitic alkaline rocks are characterized by a unique diversity of the rare-metal mineralization (Kostyleva-Labuntsova *et al.*, 1978; Semenov, 1972, 1997; Khomyakov, 1990; Yakovenchuk *et al.*, 1999, Pekov, 2001a). At present, within the bounds of these two massifs more than 570 mineral species are found, most of them contain rare elements (with clarks 0.1%) as the species-forming or important secondary components. The diversity of the Th, *REE*, U, Ti, Nb, Zr, Be, and Li minerals increases in the following series of stages: magmatic early pegmatite late pegmatite. This fact, which is in the obvious contradiction with the low mobility of many of mentioned elements at the low temperature (Dement'ev, Syromyatnikov, 1965; Semenov, 1972; Syromyatnikov *et al.*, 1976; Pekov *et al.*, 1997; Pekov, 1998, 2001b; Chukanov, 2002; Azarova *et al.*, 2002), in many cases can be explained by the formation of pseudomorphs after early minerals as a result of introduction or carrying-out of mobile components, whereas the less mobile components form the new phases. So-called transformation mineral species are a special case of such pseudomorphs (Khomyakov, 1990). However, as we noted elsewhere (Chukanov *et al.*, 2006, in press; Ermolaeva *et al.*, in press), there is another, possibly, the not less important way of formation of the rare-metal mineralization in the late derivatives of alkaline rocks. This way is caused by increase of mobility of a number of high-valence elements (Th, *REE*, U, Ti, Nb, Zr) in presence of such water-soluble organic complexing agents as the oxygen-bearing aromatic compounds.

The microscopic aggregations of organic compounds, represented, as a rule, by the solid bituminous matters (SBM), are widespread in pegmatites of the Khibiny and Lovozero massifs (Antonov *et al.*, 1933; Labuntsov, 1937; Petersil'e, 1959, 1960, 1964; Linde, 1961; Sokolova, 1965; Zezin, Sokolova, 1967; Florovskaya *et al.*, 1968; Loskutov, Polezhaeva, 1968). One can observe the stable and clear connection of SBM with the regions, having the increased contents of zeolites and especially zeolite-like microporous hydrous titano-, niobo-, and zirconosilicates (elpidite, catapleiite, umbite, paraumbite, vinogradovite, minerals of labuntsovite, hilairite, lovozerite groups, etc.; Fig. 1), and directly with the aggregations of minerals of lanthanides, yttrium, and thorium, and also with the occurrences of carbonate and sulphide mineralization. In the previous work (Chukanov *et al.*, 2006, in press), we have discussed the possible catalysis role of microporous zeolite-like Ti, Nb, and Zr silicates in the formation of SBM from the low-molecular organic compounds in alkaline pegmatites.

In the Khibiny massif, the largest aggregations (to 5 mm in size) and abundant gatherings of SBM were observed in the feldspar-sodalite-natrolite pegmatite vein of the Kukisvumchorr deposit in close assemblage with natrolite, murmanite, nenadkevichite, etc. (Sokolova, 1965). The considerable aggregations of SBM were found in the mineralised cavities of pegmatite veins with villiaumite-carbonate mineralization, occurring among Khibinian ristschorrites and uncovered by the working of the Kirovskii underground mine at the Mt. Kukisvumchorr (Chukanov *et al.*, 2006, in press).

In the Lovozero massive, the Shomiokitovoe pegmatite body should be mentioned as the most outstanding object, containing organic matters. The rich yttrium and oxalate mineralization, being unique for agpaitic rocks and accompanied by the abundant aggregations of SBM (numerous spherules up to some millimetres in size and films) and the microporous Ti, Nb, and Zr silicates (korobitsynite, nenadkevichite, elpidite, etc.), occurs here. Also in the Lovozero massif is the Elpiditovoe pegmatite body, in which black drop-like aggregations of SBM are associated with elpidite and the insignificantly studied hydrous silicate of Fe and Ti. The «oxalate mechanism» is seemed to be the most effective way of accumulation of Y and heavy Ln at the Shomiokitovoe pegmatite body (Pekov, 1998). The oxalate ions are able to form very strong complex compounds with yttrium and lanthanides, keeping these elements in the movable state to the latest stages. At a final stage of minerogenesis, the $C_2O_4^{2-}$ ions are removed from solution, they enter in the composition of oxalate minerals, natroxalate and whewellite.

Characteristic of studied samples

In pegmatites of the Khibiny and Lovozero massifs, at least four types of the microheterogeneous formations, containing organic matters, are known. Formations of the first type are the most characteristic for the hydrothermal paragenesis of the Khibinian pegmatites. These are **macroaggregations of SBM** with a high content of the oxygen-bearing aromatic compounds.

Fig. 1. *Aggregations of SBM on the aggregate of paraumbite crystals (Mt. Koashva, Khibiny). Specimen max size is 8 5 mm*

Fig. 2. *Typical structure of decomposition of SBM (sample Kh3): black is organic phase without metals, grey is significantly organic phase with metals, white is mineral phase (thorite). Image in back-scattered electrons.*

Almost always they include the abundant microscopic ingrowths of minerals, containing Th, REE, Ca, rarely U, Y, Nb, Ti, Ba, Sr. Formation of these microheterogeneous systems is connected with decomposition of the initially homogeneous phase into the purely organic (with predominance of hydrocarbons), mineral and organic phases with heavy elements (Ermolaeva *et al.*, in press; Fig. 2). The bituminous matters, in which the content the aliphatic hydrocarbons prevail, are usually poorly mineralised. Such formations are characteristic for hydrothermalites of the Lovozero massif.

The minerals of rare elements (most often Th and REE) belong to the second type, **they contain dispersed impregnation of SBM** and are easily detected by the IR spectroscopy method. Thus, in many cases, in the aggregations of thorium minerals from late assemblages in pegmatites of Lovozero, the large amounts of the oxidized aromatic compounds are found (Ermolaeva *et al.*, in press); obviously, they were captivated during crystallization.

The third type of heterogeneous aggregates with organic matters in alkaline pegmatites are represented by the **microheterogeneous crusts enriched by SBM** around large crystals of the Th and REE minerals: belovite-(Ce), karnasurtite-(Ce), Na-Th silicate (Fig. 3).

The predominance of the second and third types formations is depended on the peculiarities of crystallization. During crystallization, either the capture of metalloorganic complex by a growing crystal or the decomposition of this complex, being synchronic to the process of crystal growth, and the displacement of organic part to the periphery of a forming mineral individual can be the limiting stages. The second type formations are the most characteristic for the hydrothermal assemblages of the thorium minerals. An example of the «through» minerals (thorite, Na-Th silicate, minerals of the steacyite-turkestanite series), which are stable in a wide interval of temperatures, is especially characteristic in this respect. By our numerous observations, the samples of these minerals from the hydrothermal assemblages almost always contain the SBM ingrowths, detected by the IR spectroscopy method; whereas in the same minerals from the earlier parageneses in alkaline rocks and pegmatites, the organic matter is absent.

At least, the fourth type is represented by the **polymictic pseudomorphs after steenstrupine,** which contain SBM. Such pseudomorphs are known in a whole number of pegmatites of the Lovozero massif, containing ussingite or apoussingite natrolite.

The samples studied in the present work are given in Table 1. All them, according to data of the IR spectroscopy, are characterized by high contents of the dispersed bituminous matters.

The IR spectroscopic studies

The IR spectra were obtained with the two-ray spectrophotometer Specord 75 IR in the range of wave numbers 400-4000 cm^{-1}. The samples were prepared by a standard method in pellets with KBr; the analogous pellet of pure KBr was placed in a reference beam.

The presence of numerous absorption bands in a range of 1210-1740 cm^{-1} is a characteristic feature of the presence of **aromatic** compounds **with oxygen-bearing groups**. In particular, a series of bands in the frequency range of 1370-1600 cm^{-1} belongs to the C-C stretching

Fig. 3. *Crusts (black margins) enriched by SBM around aggregation of karnasurtite-(Ce) in natrolite, Mt. Karnasurt, Lovozero (a) and around the belovite-(Ce) crystal in albite, Mt. Alluaiv, Lovozero (b). Image size is 6 cm.*

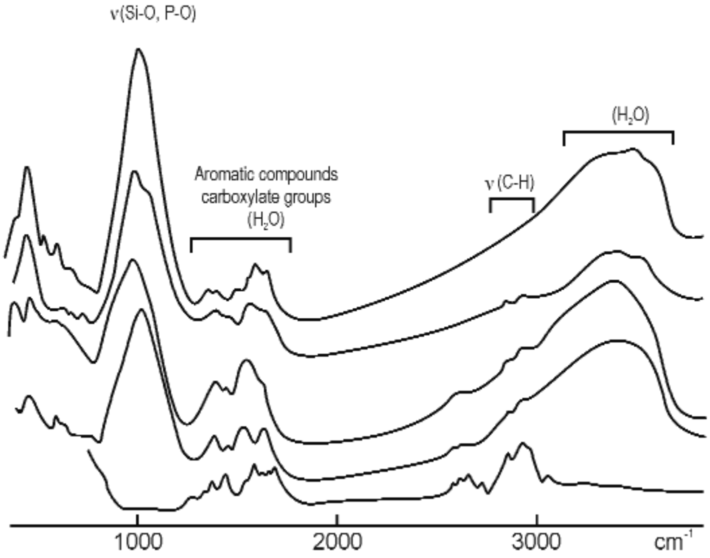


Fig. 4. *The IR spectra of minerals of thorium from hydrothermalites of the Lovozero massif (1 — the Na-Ti-Th silicate with admixture of rhabdophane-(Ce), Mt. Alluaiv; 2 — the Na-Th silicate, Mt. Kedykverpakhk; 3 — thorite, Suluai River; 4 — the thorium phosphate, Mt. Malyi Punkaruaiv; 5 — villiaumite from late-pegmatite assemblage, the Palitra pegmatite, Mt.*

vibrations in aromatic rings. The CO_2^- carboxylate groups absorb in the ranges of 1550-1670 cm^{-1} (antisymmetric stretching vibrations) and 1280-1430 cm^{-1} (symmetric stretching vibrations). The bands in these ranges are present in the IR spectra of the most SBM macroaggregations from Khibiny and, as a rule, in the IR spectra of samples with the dispersed SBM from Lovozero. Thus, one can conclude that salt (carboxylate) complexes are one of the main forms of occurrence of metals (mainly, alkaline-earth and rare-earth elements) in bituminous matters from agpaitic pegmatites.

The C=O bonds (carbonyl and carboxyl groups, including two-dimensional forms of carbonic acids) have characteristic bands at 1690-1740 cm^{-1}; aromatic ethers have these bands in the range of 1210-1310 cm^{-1} (antisymmetric stretching vibrations of the C-O-C bridges). In the mentioned range (1210-1740 cm-1) also the bands of bending vibrations of the water molecules are present; they are characterized by a single or slightly split band in the relatively narrow range (usually 1600-1650 cm^{-1}).

For aromatic compounds, the bands of the C-H stretching vibrations in a range of 3000-3100 cm^{-1} are characteristic, but at presence of a large amount of substitutes, especially for polycyclic aromatic compounds, these bands can be absent in the IR spectrum. A band with maximum of absorption nearly 2835 cm^{-1} is characteristic for the O-CH_3 methoxy group connected with aromatic ring.

The bands in the range of 2843-2972 cm^{-1} in the spectrum (often there is a doublet belonging to CH_2 or CH_3 groups) are the most effective characteristic of the presence of aliphatic hydrocarbons or **aliphatic** hydrocarbon groups. The large aggregations of bituminous matters, in which composition the aliphatic components prevail, are especially characteristic for alkaline hydrothermalites of Lovozero. As a rule, SBM of this type are characterized by very low contents of the oxygen-bearing groups.

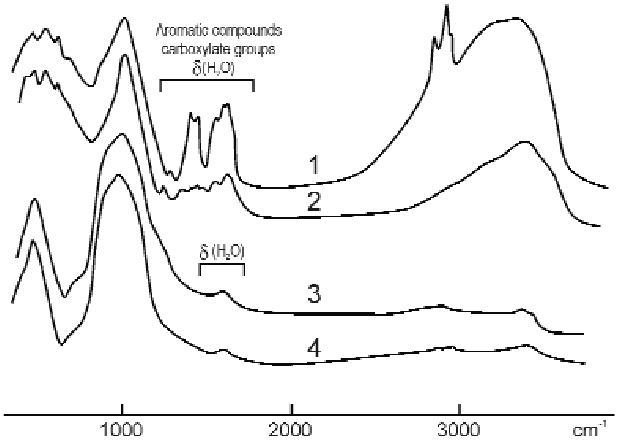
As a result of systematic study of the low-temperature minerals of thorium from hydrothermalites of the Lovozero massif, it has been ascertained that all studied samples contain the dispersed admixture of organic matters, which can be easily detected by the IR spectroscopy method. Some examples are given on Figure 4. Also the IR spectrum of villiaumite of the third generation (late pegmatite stage), enriched by dispersed organic matter, is given at the same figure; this mineral is associated with the Na-Th silicate in the Palitra pegmatite (Lovozero).

The dispersed organic matter is quite often found also in the REE minerals from hydrothermal zones of alkaline massifs. Both in accompanying minerals without Th and REE (for example, in zeolites) and in earlier minerals of Th and REE (for example, in umbozerite or unaltered steenstrupine from paragenesis with ussingite), organic matter is contained in significantly lower concentrations and, as a rule, is not observed in the IR spectra obtained by a standard method. In the IR spectra of steenstrupine from the association with natrolite weak bands of the C-H stretching vibrations in a range of 2800-3000 cm^{-1} are present (curves 3 and 4 on

Table 1**. The studied samples**

Sample	Occurrence	Description
Minerals of Th and *REE* with high contents of the dispersed SBM (by the IRS data)		
Na-Th silicate, $Na_5Th_3Si_8O_{24}(OH)\ nH_2O$	The Palitra pegmatite (Mt. Kedykverpakhk, Lovozero)	Colourless and grey grains up to 5 mm in size, ingrowing in manaksite, sometimes with margins of SBM; crystals in cavities filled up by late villiaumite (Pekov, in press). It is associated with ussingite, natrosilite, serandite, the nordite group minerals, bario-olgite, chkalovite,phosinaite-(Ce),vitusite-(Ce), belovite-(Ce), steenstrupine-(Ce), thoros teenstrupine, etc
Thorite, $ThSiO_4$	Valley of the Suluai River, Mt. Kuamdespakhk, Lovozero	Brown-black tetragonal-dipyramidal crystals ingrown in natrolite; crystals size is 0.5-3 mm; fracture is conchoidal; lustre is pitchy
Na-Ti-Th silicate, $Na_{6-x}ThTiSi_8(O,OH)_{24}\ nH_2O$	The Shkatulka pegmatite, Mt. Alluaiv, Lovozero	Metamictic; it forms pseudomorphs with reddish-brown colour (up to 1 cmin size) after steenstrupine grains, in ussingite (Ermolaeva *et al.*, in press)
Thorium , phosphate $(Th,Na)(P,Si)O_4\ nH_2O$	Ussingite pegmatite # 71 $(Th,Na)(P,Si)O_4{\cdot}nH_2O$ Malyi Punkaruaiv, Lovozero	Grains with hexagonal section, size is nearly 2 mm. Empirical formula (by data of electron microprobe analysis) is $(Th_{0.88}Na_{0.07}K_{0.02}Ca_{0.02}U_{0.01}Ba_{0.01}Sr_{0.01})_{\sum 1.01}(P_{0.71}Si_{0.15}Al_{0.14})_{\sum 1.00}O_{4.15}{\cdot}nH_2O$. It is associated with mangan-neptunite and belovite-(Ce)
High-thorium or ussingite (formula is after Pekov *et al*., 1997)	Natrolite and natrolite-ussingite veins, Mt. Kedykverpakhk, Lovozero	Isometric grains up to 1 cm in size, in natrolite steenstrupine, $Na_{0\text{-}5}Ca_{1\text{-}3}(REE,Th)_6(Mn,Fe,Al,Ti)_{4\text{-}5}[Si_6O_{18}]_2[(Si,P)O_4]_6(OH,F,O)_x{\cdot}nH_2O$
Karnasurtite-(Ce), $(Ce,La,Th)(Ti,Nb)Al,Fe^{3+})(Si,P)_2O_7(OH)_4{\cdot}3H_2O$	Pegmatite # 62 (Semenov, 1972), Mt. Karnasurt, Lovozero	Yellow fine-grained aggregations up to 10 cm in size, in coarse-grained natrolite; rarely isometric grains up to 2 cm in size, with orange-brown colour, coarse jointing in one direction, and black margin enriched by the SBM inclusions (Fig. 3a).
Belovite-(Ce), $Sr_3NaCe(PO_4)_3F$	The Shomiokitovoe pegmatite body, Mt. Alluaiv, Lovozero	Large crystals with black margin composed by burbankite and remondite-(Ce) and containing abundant small inclusions of bituminous matters (see Fig. 3b). It is associated with albite, korobitsynite, elpidite, sidorenkite, etc.
Microaggregations of SBM		
Kh1	Lovchorrite-apatite vein, Mt. Apatitovaya, Khibiny	Aggregations of irregular and spherical form, size up to 4-5 mm, brittle, black, with lustreless surface of fracture. They contain abundant inclusions of thorite (detected by chemical composition and the X-ray powder pattern). Collection of A.N. Labuntsov (Antonov *et al*., 1933; Labuntsov, 1937; Loskutov, Polezhaeva, 1968). Sample # 40749 from the Fersman Mineralogical Museum RAS («carbocere»).
Kh2	The same	The same; sample # 41156 from the Fersman Mineralogical Museum RAS.
Kh3	The same	The same; sample # 44322 from the Fersman Mineralogical Museum RAS.
Kh4	The Kirovskii mine, Khibiny	Roundish aggregations of SBM with dark brown colour, up to 3 mm in diameter, from cavity of rinkite-nepheline-aegirine-microcline pegmatite. It contains abundant microingrowths of steacyite (detected by chemical composition and the IRS). It is associated with crystals of microporous titanocilicate pyatenkoite-(Y), $Na_5(Y,HREE)TiSi_6O_{18}{\cdot}6H_2O$.

Kh5	Pegmatite at the contact of urtites with apatite ore, Mt. Koashva, Khibiny	Abundant roundish aggregations of SBM with black colour (up to 5 mm in diameter), included in natrolite. They are associated with Sr-*REE* phosphates (belovite-(Ce), fluorcaphite), microporous Zr, Ti, and Nb silicates (sazykinaite-(Y), catapleiite, sitinakite, lemmleinite-K).
Kh6	Natrolite vein, cutting ijolite-urtites, Mt. Kukisvumchorr, Khibiny	Roundish brown-black aggregations of SBM (up 1.5 mm in size) from cavity in natrolite.
Kh7	Feldspar-sodalite-natrolite vein, laying in melteigites of the Kukisvumchorr apatite deposit	Drop-like aggregation of SBM with shining surface (in fracture it is lustreless, black), size is 2.4x1.4 mm, it was extracted from aggregate of altered nenadkevichite. Detailed description see in following articles: Sokolova, 1965; Zezin, Sokolova, 1967.
Kh8	The Natrolite vein, Mt. Eveslogchorr, Khibiny	Spherical aggregation of SBM with diameter 5 mm (in fracture it is lustreless with dark grey colour), included in coarse-tabular aggregate ofnatrolite. It is associated with thorite and the labuntsovite group minerals(vuoriyarvite-K, kuzmenkoite-Zn, paratsepinite-Ba, tsepinite-Ca).
Kh9	The Ileritovoe pegmatite body, Mt. Kukisvumchorr, Khibiny.	Dark brown roundish aggregations up to 1 mm in size among cavernous natrolite. Aggregations of SBM are accompanied by exceptional diversity of rare-metal mineralization, connected mainly with hydrothermal stage.
L1	The Shkatulka pegmatite, Mt. Alluaiv, Lovozero	Nests (up to 1 mm in size) of black SBM in ussingite and serandite.
	Polymictic pseudomorphs after steenstrupine, containing SBM	
L2	The Shkatulka pegmatite, Mt. Alluaiv, Lovozero	Friable polimictic margins with grey-brown colour, replacing isometric and tabular grains of steenstrupine (up to 2 cm in size), composing by silicates and phosphates of *REE*, Th, U, Ti, and containing dispersed microscopic ingrowths of SBM (detected by the IR spectra).
L3	The same	The same
L4	The same	The same
L5	The same	Incomplete polymictic pseudomorphs after steenstrupine, mainly composed by rhabdophane-(Nd), in which mass the ingrowths of SBM, Na-Th silicate, Na-Mn-Y silicate, and high-barium variety of belovite-(Ce) are dispersed. After some grains the X-ray amorphous phase with grey-brown colour is developed, it corresponds by chemical composition to Nd-dominated analogue of abenakiite-(Ce), it is closely associated with sodium-uranium silicates. In edge zones of these pseudomorphs, the aggregations (up to 2-3 mm in size) of Na-U silicates are noted.
L6	The same	Compact polymictic pseudomorph after steenstrupine

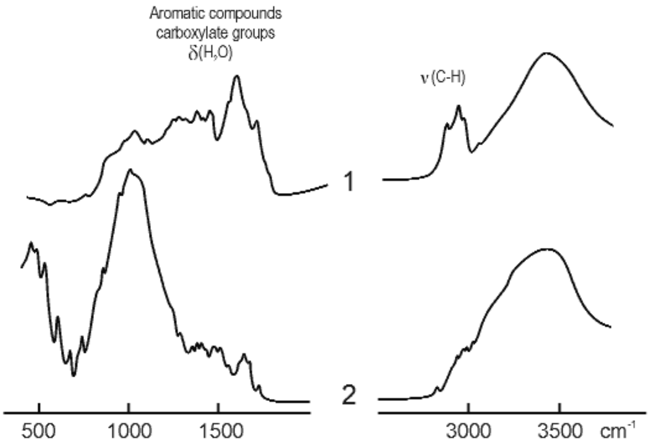


Kedykverpakhk.

Fig. 5. *The IR spectra of karnasurtite-(Ce) from the Mt. Karnasurt, Lovozero (1 — orange-brown compact variety, see Fig. 3a; 2 — yellow powdery variety) and steenstrupine-(Ce) from assemblage with natrolite from the Mt. Kedykverpakhk, Lovozero (3 — the Kedykverpakhk-21 vein; 4 — the*

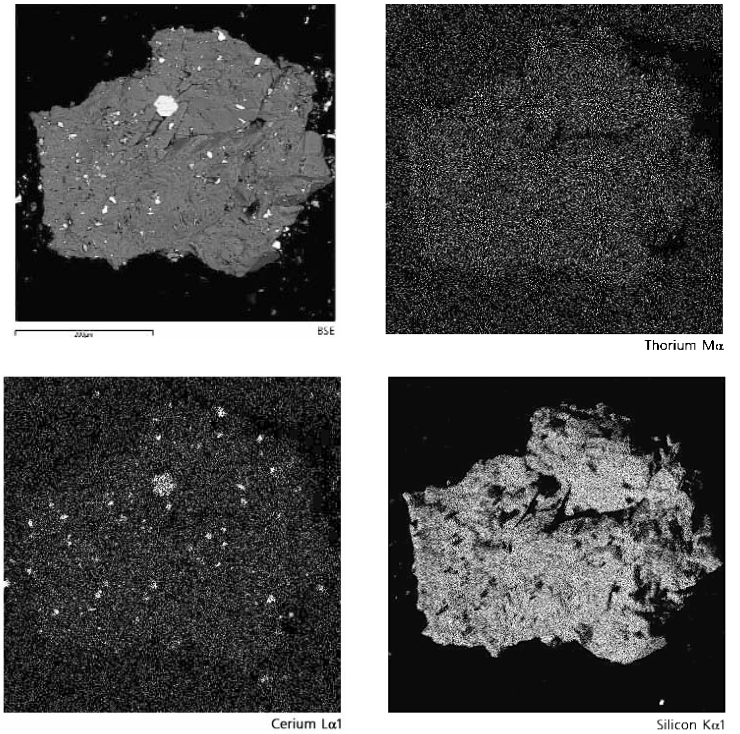
Fig. 5). The hydrothermal alteration of steenstrupine leading to the formation of polymictic pseudomorphs after it (see below) is accompanied by introduction of thorium, titanium, and also a large amount of organic matter (curve 2 on Fig. 6). Another phosphatosilicate of Th and REE, karnasurtite from paragenesis with natrolite, is characterized by high contents of aromatic compounds, both in combination with aliphatic hydrocarbon groups (curve 1 on Fig. 5) and purely aromatic compounds (curve 2 on Fig. 5).

E. Makovicky and S. Karup-Moller (1981) have described steenstrupine from sodalite-natrolite-aegirine veins in naujaites of the Ilimaussaq massif in Greenland. In the IR spectra of the mineral is a series of bands in a range of 1270-1780 cm^{-1}, the most part of which is concerned by the authors of the cited work to the bending vibrations of the water molecules, although these bands (to the exclusion of a wide band at 1655 cm^{-1}) are more typical for combination C-H of bending and C=C stretching vibrations of aromatic organic matters. A band at 1740 cm^{-1} is characteristic for stretching vibrations of C=O (carbonyl groups in composition of organic matters). The wide structured bands in the range of 2500-3700 cm^{-1} are interpreted as the stretching vibrations of the water molecules (Makovicky, Karup-Moller, 1981). The most intensive and broad band within the limits of this range (3380-3400 cm^{-1}) really corresponds to vibrations of the weakly joined water molecules, but rather narrow bands at 2830 and 2950 cm^{-1}, obviously, correspond to the C-H stretching vibrations of aliphatic hydrocarbons. A doublet in the range of 2800-3000 cm^{-1} is so characteristic for aliphatic hydrocarbons that it is a test on their presence; for assignment of these bands to other types of vibrations the weighty reasons are necessary, but they are absent in the cited work.



Kedykverpakhk-19 vein, see (Pekov, 2001)).

Fig. 6. *The IR spectra: 1 — SBM, containing aromatic and aliphatic components (sample Kh5); 2 —*



polymictic pseudomorph after steenstrupine (sample L2).

Study of samples by the X-ray analysis method

The electron microscopy study, including the obtaining of image of studied object in secondary electrons, back-scattered and reflected electrons, and also the local X-ray spectral (electron microprobe) analysis were made on a digital electron scanning microscope instrument CamScan MV2300 (Tescan Vega TS5130MM), equipped with the YAG detectors of secondary and reflected electrons and the energy-dispersed X-ray microanalysis instrument with a semi-conductor Si(Li) detector instrument Link INCA Energy. The calculations of results of the X-ray spectral microanalysis were made with a program INCA Energy 200 with subsequent recalculation of the obtained data by a packet of programs elaborated in the IEM RAS.

The studies were made at accelerating voltage of 20 kV. The absorbed electrons current was 540 pA on a standard sample of cobalt (Co) and 565-615 pA on the studied silicate samples. A size of the electron microprobe beam on the surface of a sample was 0.2 μm.

The spatial distribution of SBM in microaggregations of organic matters from pegmatites of the Khibiny massif has quite often a form of typical structures of decomposition: in purely organic matrix there are the lamellar ingrowths of essentially organic matter with total contents of heavy elements (with atomic numbers above 10) from 3 to 11 wt %. Mainly these are the alkaline-earth and rare-earth elements, lead and thorium. Judging by the IR spectra, heavy elements are here predominantly in the form of carboxylate salts (see above). These phases in their turn contain microingrowths of inorganic phases. The latter are usually represented by minerals of rare elements and also calcite. The typical sizes of the mineral inclusions in SBM are from several units to several tens of microns. As a rule, they do not form well-shaped crystals. Only carbonates, including carbonates of rare-earth elements (Fig. 7) and calcite, sometimes form perfect crystals in the SBM mass.

In detail the microheterogeneous formations of this type are described in a separate publication (Chukanov *et al.*, 2006, in press), an example of their typical structure is given on Figure 2. In present work, the main attention is paid to their mineral components. Chemical compositions of some mineral microphases from SBM are given in Table 2. In a number of cases, diagnostics of minerals can be made exactly on the basis of chemical composition. Steacyite was also identified by the IR spectrum, and thorite was also confirmed by the X-ray powder pattern. At the same time, in SBM the inclusions of the rare-metal microphases with a stable chemical composition are often

Table 2**. Chemical composition of minerals, forming inclusions in SBM**

Mineral	Thorite	Thorite	Steacyite	Silicate of Th and *REE*		Silicate of Ti and Th		Silicate of Na and U
No. of sample	Kh2	Kh3	Kh4	Kh5		Kh6		L1
No. of analysis	1	2	3	4	5	6	7	8
				Contents of components, wt %				
Na_2O	bdl	bdl	4.41	bdl	bdl	bdl	bdl	2.20
K_2O	bdl	bdl	3.93	0.60	0.71	bdl	bdl	bdl
CaO	2.85	3.60	5.41	1.94	1.77	2.08	2.21	0.18
SrO	bdl	bdl	bdl	bdl	bdl	0.95	1.52	bdl
FeO	bdl	bdl	0.77	bdl	bdl	0.54	0.71	bdl
MnO	bdl	bdl	bdl	0.81	bdl	0.87	0.96	bdl
ZnO	bdl	bdl	bdl	2.08	0.64	bdl	bdl	bdl
Al_2O_3	bdl	bdl	bdl	1.32	0.79	0.96	0.80	bdl
La_2O_3	bdl	bdl	bdl	1.04	bdl	2.86	2.11	bdl
Ce_2O_3	0.95	1.99	bdl	5.41	2.55	3.37	2.12	bdl
Pr_2O_3	bdl	bdl	bdl	1.46	1.13	bdl	bdl	bdl
Nd_2O_3	0.85	1.76	bdl	2.36	3.06	bdl	bdl	bdl
ThO_2	66.00	59.72	30.69	48.15	57.18	38.31	41.01	0.46
UO_2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	27.83
TiO_2	bdl	bdl	bdl	bdl	bdl	12.20	12.25	bdl
SiO_2	15.45	15.79	53.62	24.16	21.59	13.57	14.84	34.78
Nb_2O_5	bdl	bdl	bdl	bdl	bdl	7.16	7.06	bdl
P_2O_5	bdl	bdl	bdl	1.36	0.91	0.75	0.57	bdl
SO_3	2.15	2.07	bdl	bdl	bdl	bdl	bdl	bdl
Total	88.25	84.93	99.79	96.40	95.29	88.12	90.64	66.21
				Formula coefficients				
Na	–	–	1.28	–	–	–	–	0.73
K	–	–	0.74	0.03	0.04	–	–	–
Ca	0.20	0.24	0.86	0.08	0.09	0.16	0.15	–
Sr	–	–	–	–	–	0.04	0.06	–
Fe	–	–	0.09	–	–	0.03	0.04	–
Mn	–	–	–	0.03	–	0.05	0.05	–
Zn	–	–	–	0.06	0.02	–	–	–
Al	–	–	–	0.06	0.04	0.08	0.06	–
La	–	–	–	0.02	–	0.08	0.05	–
Ce	0.02	0.05	–	0.08	0.04	0.09	0.05	–
Pr	–	–	–	0.02	0.02	–	–	–
Nd	0.02	0.04	–	0.03	0.05	–	–	–
Th	0.97	0.92	1.04	0.43	0.58	0.61	0.61	0.02
U	–	–	–	–	–	–	–	1.07
Ti	–	–	–	–	–	0.65	0.60	–
Si	1.00	1.00	8.00	0.96	0.97	0.96	0.97	6.00
Nb	–	–	–	–	–	0.23	0.21	–
P	–	–	–	0.04	0.03	0.04	0.03	–
S	0.10	0.10	–	–	–	–	–	–
Method of calculation, f. c.	Si=1.00	Si=1.00	Si=8.00	(Si+P) =1.00	(Si+P) =1.00	(Si+P) =1.00	(Si+P) =1.00	Si=6.00

Table 2 **(end).**

Mineral	Nb silicate		Thin intergrowths of Sr-barite, thorite, and calcite		*REE* carbonate
No. of sample	Kh7		Kh8		Kh9
No. of analysis	9	10	11	12	13
			wt %		
Na_2O	3.68	3.71	bdl	bdl	11.57
K_2O	1.89	1.34	bdl	bdl	0.28
CaO	9.57	12.40	5.64	6.47	1.56
SrO	1.16	0.33	5.83	9.61	3.05
BaO	bdl	bdl	15.45	16.09	10.61
FeO	1.09	0.39	bdl	bdl	0.96
MnO	1.81	1.69	bdl	bdl	bdl
Al_2O_3	1.66	1.00	bdl	bdl	bdl
La_2O_3	bdl	bdl	bdl	bdl	5.95
Ce_2O_3	0.47	bdl	bdl	bdl	9.75
Nd_2O_3	bdl	bdl	1.06	bdl	1.84
ThO_2	0.63	0.74	36.12	27.27	1.45
UO_2	0.96	0.26	bdl	bdl	bdl
TiO_2	10.78	11.07	bdl	bdl	bdl
SiO_2	13.95	15.57	10.63	6.69	1.12
Nb_2O_5	30.68	40.17	bdl	bdl	bdl
SO_3	2.12	0.90	12.69	15.92	1.27
Total	81.82	91.18	87.42	82.05	49.95

***Note:** bdl means that content of this component is below detection limits.*
The total also includes (numbers of analyses, wt %): 3 – Y_2O_3 0.96; 4 – PbO 1.97, Sm_2O_3 1.49, Gd_2O_3 0.83, Y_2O_3 0.56, Lu_2O_3 0.86; 5 – Y_2O_3 0.82, Sm_2O_3 0.88, Eu_2O_3 1.32, Gd_2O_3 1.00, Tb_2O_3 0.94; 6 – PbO 2.42, Y_2O_3 2.08; 7 – PbO 1.77, Y_2O_3 2.71; 8 – Y_2O_3 0.76; 9 – F 2.37, $-O{=}F_2$ 1.00; 10 – F 2.78, $-O{=}F_2$ 1.17; 13 – Cl 0.7, $-O{=}Cl_2$ 0.16. All these correspond to following formula coefficients: 3 – Y 0.08; 4 – Pb 0.02, Sm 0.02, Gd 0.01, Y 0.01, Lu 0.01; 5 – Y 0.02, Sm 0.01, Eu 0.02, Gd 0.01, Tb 0.01; 6 – Pb 0.05, Y 0.08; 7 – Pb 0.03, Y 0.09; 8 – Y 0.06.
Low totals of analyses of thorium and uranium minerals are connected with submicron inclusions of organic matter in them and also with their metamict (in case of thorite, semi-metamict) state (Ermolaeva et al., in press). By data of the IRS, only steacyite has perfect crystal structure. For analyses 9-13 the formula coefficients is not given, since the method of their calculation, resulting in integer coefficients in ideal formulas, was not found.

present, that do not have analogues among known in nature mineral species. Chemical compositions of these phases are specific and characterized by wide set of rare elements. These are the minerals with following hypothetic ideal formulas: $(Th,REE,Ca)_{1-x}Si(O,OH)_4 \cdot nH_2O$ (analyses 4 and 5); $(Th,REE,Ca)(Ti,Nb)SiO_6 \cdot nH_2O$ (analyses 6 and 7); $NaUSi_6O_{14}(OH) \cdot nH_2O$ (analysis 8), etc.

In some analyses there are small amounts of accessory components, which nature is not clear. Some of accessory components could be captured by an electron beam from phases intergrowing with the analysed minerals. Thus, in chemical composition of thorite, forming inclusions in «carbocer» (analyses 1 and 2 in Table 2), there are Ca and S. Possibly, the increased content of calcium in thorite is caused by the ingrowths of calcite, and sulphur can be included in the chemical composition of organic compounds.

On Figure 8 there is an BSE image of a peripheral part of the belovite crystal from the Shomiokitovoe pegmatite body (Fig. 3b). Around the grain of belovite there is a crust, consisting of intimately intergrowing grains of the Sr-REE carbonates (burbankite and remondite-(Ce)), in the interstices between them there are microscopic inclusions of SBM (see chemical compositions in Table 3). The presence of SBM in this sample (the black parts with roundish faces on Fig. 8) was confirmed by the IR spectroscopy method. Nearing to the peripheral zone of a margin, which is enriched by bitumens, the relative impoverish of carbonates by Sr and enrichment by Ca, *REE*, and Th take place.

From the above data, it is evident that some group of rare elements (above all Th, but also U, *REE*, and a number of other elements) in hydrothermal parageneses of Khibiny and Lovozero are constantly closely connected, often at a level of microintergrowths, with organic matter. The diversity of mineral phases in these intergrowths is astonishing, including phases, which do not have analogues by chemical composition in nature. We should note that above-described steacyite is the first finding of this mineral in the Khibiny massif, and findings of remondite-(Ce) and belovite-(La) are the first in the Lovozero massif. These minerals were detected by the IR spectra and by chemical composition.

On Figure 9 one can see an example of the fourth type of microheterogeneous formations, containing SBM, a fragment of polymictic pseudomorph after steenstrupine. Such pseudomorphs are widespread in the Shkatulka pegmatite. The spatial distribution of different minerals in them has irregular, mosaic character. In

Table 3. **Chemical compositions of minerals from margin around belovite-(Ce) crystal (the Shomiokitovoe pegmatite body, the Lovozero massif), Fig. 3b**

No. of analysis	1	2	3	4	5	6	7	8
Mineral	Belovite-(La)	Belovite-(Ce)	Belovite-(Ce)	Burbankite	Burbankite-	Burbankite-	Remondite-(Ce)	Remondite-(Ce)
				Contents of components, wt %				
Na_2O	5.08	5.20	4.90	9.27	10.29	12.96	13.33	13.88
CaO	bdl	bdl	bdl	bdl	bdl	2.95	4.47	5.49
SrO	37.31	38.90	39.40	32.33	32.97	19.30	16.07	11.02
BaO	3.87	3.93	3.88	2.51	3.14	1.20	2.11	2.38
Y_2O_3	bdl	bdl	bdl	1.53	2.06	1.23	1.39	2.47
La_2O_3	9.10	9.58	10.04	8.56	8.75	11.87	10.73	11.12
Ce_2O_3	8.89	10.87	10.76	9.10	8.99	11.92	12.70	13.24
Pr_2O_3	0.29	0.60	0.66	0.50	bdl	bdl	1.34	0.92
Nd_2O_3	1.15	1.64	2.06	1.51	1.64	2.06	2.12	2.40
ThO_2	bdl	bdl	bdl	bdl	bdl	0.89	0.63	0.79
SiO_2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P_2O_5	28.22	28.89	29.22	bdl	bdl	bdl	bdl	bdl
F	2.83	2.79	2.53	bdl	bdl	bdl	bdl	bdl
$-O=F_2$	1.19	1.17	1.07	bdl	bdl	bdl	bdl	bdl
Total	95.55	101.23	102.38	65.31	67.84	64.38	64.89	63.71
				Formula coefficients				
Na	1.24	1.24	1.15	2.22	2.41	2.93	2.92	3.04
Ca	–	–	–	–	–	0.37	0.54	0.66
Sr	2.72	2.77	2.77	2.32	2.30	1.32	1.06	0.72
Ba	0.19	0.19	0.18	0.12	0.13	0.05	0.10	0.11
Y	–	–	–	0.10	0.12	0.08	0.09	0.15
La	0.42	0.43	0.45	0.38	0.36	0.50	0.44	0.47
Ce	0.41	0.49	0.48	0.40	0.36	0.50	0.52	0.54
Pr	0.01	0.03	0.03	0.02	–	–	0.06	0.04
Nd	0.05	0.07	0.09	0.07	0.07	0.09	0.09	0.10
Th	–	–	–	–	–	0.02	0.02	0.02
Si	–	–	–	–	–	–	–	–
P	3.00	3.00	3.00	–	–	–	–	–
F	1.12	1.08	0.97	–	–	–	–	–
Method of calculation, f. c..	$PO_4=3$	$PO_4=3$	$PO_4=3$	$CO_3=5$	$CO_3=5$	$CO_3=5$	$CO_3=5$	$CO_3=5$

Note: *bdl means that content of the component is below detection limits*

the Shkatulka pegmatite, at hydrothermal stage, during formation of pseudomorphs after steenstrupine-(Ce), i.e. mineral with «average» cerium-dominated composition of the *REE* and containing the Th and U admixtures, the deep separation of components, close to each other by their chemical characteristics, took place. We can observe not only a separation of Th and U (with formation of their proper phases) and their separation from rare-earth elements but also the fractionating of the *REE* among themselves; as a result, the minerals with strongly pronounced maximums of La, Ce, Nd, and Y in the *REE* spectra are formed. It is most possible that these processes, proceeding in so small objects, are be caused by formation of the metalloorganic complex compounds, in which Th, U, and individual *REE* show the maximally contrast properties. Origin of the late proper minerals of Ti, Y, Ce, La, Nd, Sr, Th, and U was partly accompanied by the introduction of a number of elements. In particular, some pseudomorphs are significantly enriched by titanium and thorium in comparison with unaltered steenstrupine.

The typical chemical compositions of new-formed minerals in such pseudomorphs are given in the Table 4. Among them, together with known mineral species (including rhabdophane-(Ce), rhabdophane-(Nd), monazite-(La), and belovite-(Ce), which presence is confirmed also by the IR spectroscopy data), the minerals are widespread that have been not earlier described. Their chemical compositions correspond to the lanthanum analogue of vitusite-(Ce) (analysis 7), the neodymium analogue of abenakiite-(Ce) (analysis 16), the minerals with following hypothetic ideal formulas: $Na_{2-5}ThTiSi_8(O,OH)_{24}{\cdot}nH_2O$ (analysis 1); $Na_2U_2Si_3O_{11}{\cdot}nH_2O$ (analysis 3); $Na_2USi_4O_{11}{\cdot}nH_2O$ (analyses 4, 5); $Na(U,Th)Si_3O_8\ (OH){\cdot}nH_2O$ (analysis 6); $Na_2Th_3\ Si_8O_{23}{\cdot}nH_2O$ (analysis 11); $Na_5REE_2(Si,P)_6O_{18}{\cdot}\ nH_2O$ (analysis 12); and $(Na,Ca)_4(Mn,Fe)\ (Y,HREE,Th,U)_2\ Si_{12}O_{30}{\cdot}\ nH_2O$ (analysis 15). During calculation of the formulae, the valency 4 was assumed for uranium, taking into account its joint entry in some phases together with thorium, and also paragenesis with SBM, which formation demands the reducing medium. In the Shkatulka pegmatite, the dispersed organic matter is present in most pseudomorphs after steenstrupine (see the IR spectrum 2 on Fig. 6). To all appearances, the reduced total sums of analyses of mineral phases are connected with that (Table 4).

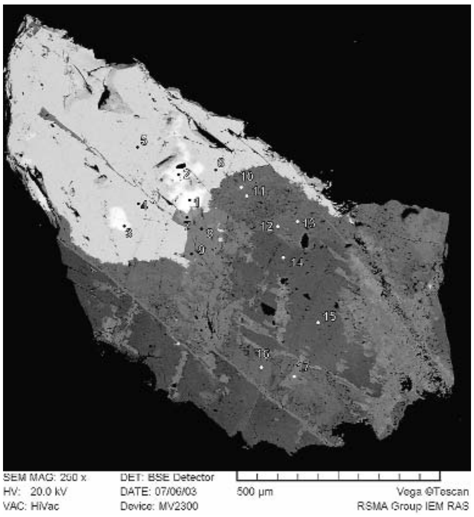


Fig. 7. *Crystal of the REE carbonate (analysis 13 in Table 1) in SBM (sample Kh9). Image in back-scattered electrons and in characteristic radiations of different elements.*

Fig. 8. *Contact zone of belovite with carbonate margin, containing SBM (black parts). Image in back-scattered electrons. Points corresponds to following minerals: 1, 6 — belovite-(La); 2,*

Conclusions

1. Thin intergrowths of SBM with the rare elements minerals are the typical formations of the hydrothermal zones of agpaitic pegmatites of the Khibiny and Lovozero massifs.

2. For all studied minerals of Th and *REE* from the late assemblages in pegmatites, the high contents of the oxidized aromatic compounds, captured during crystallization, are characteristic. Rarely around crystals, of these minerals the crusts enriched by organic matter are observed. Neither early minerals of Th and *REE* no minerals of hydrothermal stage, which do not contain Th and *REE*, as a rule, have this peculiarity.

3. The aggregations of the oxygen-bearing bitumen matters, enriched by aromatic components and formed in alkaline pegmatites at the low-temperature stages, almost always contain the abundant microscopic ingrowths of minerals, in which composition Th, Ln, and Ca, and sometimes also U, Y, Sr, Ba, Nb, and Ti are the main components.

4. In the Shkatulka pegmatite, the substitution of steenstrupine by the late minerals is accompanied by the introduction of organic matter and rare elements and the high degree of separation of Ti, Ce, La, Nd, Y, Sr, Th, U among different phases, right up to formation of the proper minerals of all these elements. As a result, mineralogy of the heterophase formations, containing SBM, is extremely diverse. Here, not only minerals species, new for Khibiny (steacyite) and Lovozero (remondite-(Ce), belovite-(La)), but also a number of phases, which do not have analogues among the known minerals, were found.

5. The high activity of rare elements and titanium in alkaline hydrothermalites is mainly caused by the presence of complexes with organic compounds, taking part in transportation of these elements.

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Table 4. **Chemical composition of minerals from microheterogeneous pseudomorphs after steenstrupine (the Shkatulka pegmatite, Lovozero).**

No. of sample	L2							
Mineral	Na,Ti,Th silicate	Sazhinite (Ce)?	Na,U-silicate	Na,U-silicate	Na,U-silicate	Na,U,Th-silicate	«Vitusite-(La)»?	Steenstrupine (Ce) (relic)
No. of analysis	1	2	3	4	5	6	7	8
	Content of components, wt %							
Na_2O	6.05	4.49	5.38	8.40	7.6	4.92	21.11	5.41
K_2O	0.22	1.12	bdl	bdl	bdl	bdl	bdl	bdl
CaO	0.43	0.21	bdl	bdl	bdl	bdl	bdl	0.76
SrO	0.47	0.37	0.40	bdl	bdl	bdl	bdl	1.22
BaO	bdl	0.36	bdl	bdl	bdl	bdl	0.74	0.46
PbO	0.49	bdl	bdl	1.67	0.06	1.76	bdl	0.42
MnO	0.79	bdl	bdl	bdl	bdl	bdl	bdl	5.40
FeO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.68
La_2O_3	bdl	4.60	bdl	bdl	0.55	0.46	26.73	6.06
Ce_2O_3	0.84	11.63	bdl	bdl	0.81	0.45	8.09	8.41
Pr_2O_3	0.30	1.53	bdl	bdl	bdl	bdl	bdl	0.84
Nd_2O_3	0.31	3.29	bdl	bdl	bdl	bdl	0.90	2.03
Sm_2O_3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ThO_2	23.17	2.03	1.92	4.25	3.77	14.46	bdl	11.29
UO_2	bdl	bdl	54.12	34.79	36.12	27.62	0.53	0.95
TiO_2	6.54	bdl	bdl	bdl	bdl	bdl	bdl	0.55
SiO_2	40.67	51.86	18.68	30.26	30.81	31.03	bdl	29.32
Nb_2O_5	0.50	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P_2O_5	bdl	bdl	bdl	bdl	bdl	bdl	32.35	5.79
Total	80.78	81.49	80.50	79.37	80.77	80.70	90.55	79.59
	Formula coefficients							
Na	2.31	1.01	1.68	2.15	1.78	0.92	2.99	5.52
K	0.06	0.16	–	–	–	–	–	–
Ca	0.09	0.02	–	–	–	–	–	0.42
Sr	0.05	0.02	0.04	–	–	–	–	0.38
Ba	–	0.02	–	–	–	–	0.02	0.09
Pb	0.03	–	–	0.06	0.06	0.05	–	0.06
Mn	0.13	–	–	–	–	–	–	2.40
Fe	–	–	–	–	–	–	–	0.31
La	–	0.20	–	–	0.02	0.02	0.72	1.17
Ce	0.06	0.49	–	–	0.04	0.01	0.22	1.61
Pr	0.02	0.07	–	–	–	–	–	0.17
Nd	0.02	0.14	–	–	–	–	0.02	0.38
Sm	–	–	–	–	–	–	–	–
Th	1.04	0.05	0.07	0.13	0.11	0.32	–	1.35
U	–	–	1.94	1.02	1.05	0.60	0.01	0.11
Ti	0.97	–	–	–	–	–	–	0.22
Si	8.00	6.00	3.00	4.00	4.00	3.00	–	15.42
Nb	0.04	–	–	–	–	–	–	–
P	–	–	–	–	–	–	2.00	2.58
Method of calculation, f. c..	Si = 8.00	Si = 6.00	Si = 3.00	Si = 4.00	Si = 4.00	Si = 3.00	P = 2.00	Si + P = 18.00

Table 4. **(end)**

No. of sample	L3		L4		L5			
Mineral	Monazite-(La)?	Rhabdophane -(Ce)?	Na,Th-silicate	Na,*REE* -silicate	Rhabdophane-Nd	Belovite-(Ce)	Na-Y-Mn silicate	«Abenakeite-(Nd)»?
№ of analysis	9	10	11	12	13	14	15	16
Na_2O	1.28	1.62	2.63	15.09	bdl	4.61	8.0	27.14
K_2O	bdl	bdl	0.35	bdl	bdl	bdl	0.2	0.02
CaO	1.43	1.19	bdl	bdl	0.69	0.09	1.7	0.22
SrO	4.47	3.69	bdl	bdl	0.98	24.67	bdl	bdl
BaO	1.32	0.87	bdl	bdl	bdl	20.51	bdl	0.37
PbO	bdl	bdl	bdl	bdl	0.73	bdl	bdl	bdl
MnO	0.42	0.68	bdl	bdl	bdl	bdl	2.9	0.17
FeO	bdl	bdl	bdl	bdl	bdl	bdl	1.9	bdl
La_2O_3	26.00	11.32	bdl	2.98	4.20	4.13	bdl	1.05
Ce_2O_3	25.34	25.29	bdl	13.78	19.83	9.40	0.4	8.83
Pr_2O_3	2.33	3.41	bdl	2.61	4.04	1.20	bdl	2.03
Nd_2O_3	3.52	11.48	bdl	11.45	22.48	5.39	1.0	13.40
Sm_2O_3	bdl	bdl	bdl	3.16	7.53	1.08	1.0	4.79
ThO_2	1.02	bdl	51.19	1.70	0.11	bdl	3.2	0.19
UO_2	bdl	bdl	bdl	bdl	1.01	bdl	2.8	bdl
TiO_2	bdl	bdl	bdl	bdl	bdl	bdl	0.6	bdl
SiO_2	3.10	2.66	31.24	33.21	bdl	bdl	53.4	12.51
Nb_2O_5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P_2O_5	23.89	23.37	bdl	1.72	27.99	27.25	bdl	15.44
Total	94.12	85.58	85.41	87.23*	89.59	98.33	89.5**	90.11***
					Formula coefficients			
Na	0.11	0.14	1.30	5.06	–	1.16	3.48	24.70
K	–	–	0.11	–	–	–	0.06	0.01
Ca	0.07	0.06	–	–	0.03	0.01	0.41	0.11
Sr	0.11	0.10	–	–	0.02	1.86	–	–
Ba	0.02	0.02	–	–	–	1.04	–	0.07
Pb	–	–	–	–	0.01	–	–	–
Mn	0.02	0.03	–	–	–	–	0.55	0.07
Fe	–	–	–	–	–	–	0.36	–
La	0.41	0.19	–	0.19	0.07	0.195	–	0.18
Ce	0.40	0.41	–	0.87	0.31	0.45	0.03	1.52
Pr	0.04	0.06	–	0.16	0.06	0.06	–	0.35
Nd	0.05	0.18	–	0.71	0.34	0.25	0.08	2.25
Sm	–	–	–	0.19	0.11	0.05	0.08	0.77
Th	0.01	–	2.98	0.07	–	–	0.16	0.02
U	–	–	–	–	0.01	–	0.14	–
Ti	–	–	–	–	–	–	0.10	–
Si	0.07	0.12	8.00	5.75	–	–	12.00	5.87
Nb	–	–	–	–	–	–	–	–
P	0.93	0.88	–	0.25	1.00	3.00	–	6.13
Method of calculation, f. c. .	P+Si=1.00	P+Si=1.00	Si=8.00	Si+P=6.00	P=1.00	P=3.00	Si=12.00	Si+P=12.00

Note*: bdl means that content of the component is below detection limits.*

Method of calculation of formula coefficients for steenstrupine was selected in accordance with general formula for minerals of the steenstrupine-(Ce) – thorosteenstrupine series (Pekov et al., 1997).

*Totals of analyses include: *1.53 % Gd_2O_3 (respectively Gd0.09); **12.4 % Y_2O_3 (respectively Y1.48); ***0.12 % Y_2O_3, 0.70 % Eu_2O_3, 1.82 % Gd_2O_3, 1.31 % SO_2 (respectively $Y_{0.03}$, $Eu_{0.11}$, $Gd_{0.28}$, $S_{0.54}$).*

Understated totals of some analyses are caused by dispersed inclusions of SBM.

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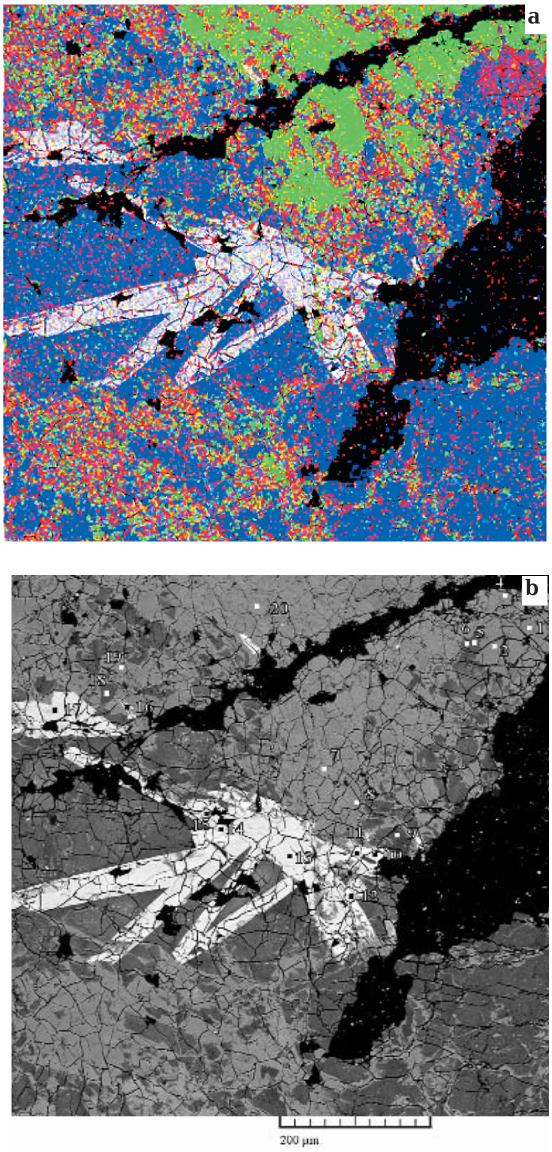

5 — belovite-(Ce); 7-11, 17 — burbankite; 12-16 — remondite-(Ce)

Fig. 9. *Fragment of polymictic pseudomorph after steenstrupine (sample L2): a — image in imposed characteristic radiation Th M 2 (red colour), P* $K_{\alpha}1$ *(green), and Si* $K_{\alpha}1$ *(blue); b — points of analyses, corresponding to the Na-Ti-Th silicate (1, 2), vitusite-(La) (3, 4, 7, 20), sazhinite-(Ce) (5, 6, 9, 18), steenstrupine-(Ce) (8, 19), phase* $Na_2U_2Si_3O_{11}{\cdot}nH_2O$ *(10, 12), the*

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FAHLORES FROM THE KVARTSITOVYE GORKI HYPABYSSAL GOLD–ANTIMONITE DEPOSIT (NORTH OF CENTRAL KAZAKHSTAN)

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The new data on mineral assemblages, evolution, macro- and microelement composition of fahlores of the Kvartsitovye Gorki plutonogene hydrothermal gold deposit, the less deep one in the North Kazakhstan gold-ore province, is given.

Studied fahlores are stoichiometric by chemical composition, their crystals are often zoned; the smooth change of chemical composition form zone to zone is characteristic. Fahlores are poor by Bi, Te, Se, Tl, Cd, Sn; contents of Au, Pb, Ni, Co, Ge, and In in them are below detection limits of analysis.

Fahlores of the productive assemblage are the most diverse. The earlier fahlores are enriched by mercury, especially in the less deep ore body IV (to 7 wt %). In fahlores of late generations of productive assemblage the contents of mercury is low in tens times. Evolution of fahlores of the productive assemblage in the industrial ore bodies I and IV is different: in the ore body IV, from early to late generations the contents of silver and antimony increase; in deep-penetrating ore body I, from early to late generations the relative content of antimony decreases and the silver contents increase. Just among the late generation of fahlores, in ore body I, argentotennantite occurs.

8 tables, 2 figures, 8 references.

Fahlores, $(Cu^{1+},Ag,_{Tl,Au})_{10}$ $(Zn,Fe,Cu^{2+},Hg,Cd,Pb,Mn,_{Ni,Co})_2$ $(As,Sb,Bi,Te,_{Ge,In})_4(S,Se)_{13}$, are widespread minerals of many plutonogene and volcanic hydrothermal gold deposits (Spiridonov, 1987; Chvileva *et al.*, 1988; *etc.*). Because of the widespread isomorphism, the content of fahlores reflects the conditions and evolution of the ore-forming processes (Charlat, Levy, 1974; Mozgova, Tsepin, 1983; Spiridonov, 1985). Fahlores are widespread in the hydrothermal gold deposits of North Kazakhstan.

The North Kazakhstan gold-ore province (NKGP) is the largest in caledonides of Central Kazakhstan, it includes the same type deposits of the Late Ordovician plutonogene gold-quartz formation of different facies of deepness: hyp-, meso-, and abyssal (Spiridonov, 1995). In the present work are the new data on mineral assemblages, evolution, macro- and microelement composition of fahlores of the least deep in this province large deposit Kvartsitovye Gorki.

Geology of the Kvartsitovye Gorki deposit

The deposit is located in the east part of the Stepnyakskii synclinorium, in knot of intersection of the Tselinogradskii deep fault and regional Atansorskii strike-slip fault, in its footwall (Spiridonov *et al.*, 1986). This is a cause of safety of Kvartsitovye Gorki from erosion. The most part of the deposit volume is composed by volcanites with the basalt, picrite, andesite, and dacite composition of the $Є_3$-O_1 Aksui series and covering them greywackes of the Ushtogan suite of upper O_1. In zone of the Tselinogradskii fault are numerous tectonic wedges of gneisses, crystalline schists, and amphibolites of PR, phtanites and carbonaceous siliceous, terrigenous, and carbonate rocks of V-$Є_2$. The small intrusions belong to the Aksui and Krykkuduk complexes. The Aksui O_1 complex is represented by stocks of gabbro-dolerites with a size from tens of meters to first kilometers; they cover volcanites. The Krykkuduk O_3 complex (440-450 MA) is represented by the multiphase bodies of quartz gabbro-diorites, tonalites, granodiorites of the dike and tube-like form and with a square up to 0.3 km^2, and the post-intrusive dikes of granitoid-porphyries, microdiorites, and spessartites. A thickness of dikes is from first meters; their length is to first hundreds meters. The dikes are widespread in ore bodies of the deposit, where the most part of them is pre-ore, another part is intra-ore, and the small part is post-ore. Formation of the Krykkuduk complex was finished by hydrothermalites of the propylite and beresite-listvenite formations. Propylites of the small-deep epidote-chlorite facies are distributed in all area of Kvartsitovye Gorki. The fields of younger beresites and listvenites (445-450 MA), including the gold-bearing metasomatites with streaky-impregnated mineralization, are controlled by a system of large ruptures, branches of zone of the Tselinogradskii deep fault. The deposit includes 9 stockwork ore bodies. The industrial ore bodies (Kvartsitovye Gorki I and IV) are confined to tectonic blocks of molybde-

Table 1. **Chemical composition (wt %) of tennantite (an. 1-6) and tetrahedrite (an. 7) of the first generation of early carbonate-polysulphide assemblage of Gvartsitovye Gorki**

Analyses	1	2	3	4	5	6	7
Elements							
Cu	44.92	44.98	42.19	42.89	40.83	39.43	39.86
Ag	0.18	–	0.04	0.39	0.05	0.11	0.22
Tl	–	–	0.13	–	0.20	0.08	–
Zn	2.53	2.02	5.34	3.11	5.21	3.86	4.67
Fe	4.59	5.41	2.84	4.08	2.79	3.40	2.44
Hg	–	0.20	–	0.31	0.09	0.04	0.71
Cd	–	–	0.02	–	0.04	–	–
As	17.29	16.63	14.19	13.20	12.11	11.08	3.46
Sb	4.37	4.39	7.78	9.94	11.90	13.20	23.95
Bi	–	–	0.09	–	0.06	0.05	–
Te	–	–	0.01	–	–	0.08	–
Sn	–	–	0.02	–	0.10	0.03	–
S	28.35	28.49	28.42	27.61	26.77	26.80	26.03
Se	–	–	0.06	–	0.10	0.04	–
Total	102.23	102.12	101.10	101.53	100.24	98.19	101.34
Formula units at calculation on 29 atoms							
Cu^{1+}	9.98	10.00	9.94	9.95	9.95	9.80	9.97
Ag	0.02	–	–	0.05	0.01	0.02	0.03
Tl	–	–	0.01	–	0.02	–	–
Total	10.00	10.00	9.95	10.00	9.98	9.82	10.00
Zn	0.57	0.45	1.22	0.72	1.23	0.93	1.15
Fe	1.20	1.42	0.76	1.10	0.77	0.97	0.70
Cu^{2+}	0.38	0.35	–	0.25	–	–	0.12
Hg	–	0.01	–	0.03	0.01	–	0.06
Cd	–	–	–	–	0.01	–	–
Total	2.15	2.23	1.98	2.10	2.02	1.90	2.03
As	3.38	3.25	2.83	2.66	2.50	2.34	0.75
Sb	0.53	0.53	0.96	1.24	1.53	1.72	3.16
Bi	–	–	0.01	–	–	–	–
Te	–	–	–	–	–	0.01	–
Sn	–	–	–	–	0.01	–	–
Total	3.91	3.78	3.80	3.90	4.04	4.07	3.91
S	12.95	12.99	13.26	13.01	12.94	13.20	13.06
Se	–	–	0.01	–	0.02	0.01	–
Total	12.95	12.99	13.27	13.01	12.96	13.21	13.06
Sb#	13	14	25	32	38	42	81
Cu#	18	16	0	12	0	0	6

Note: *dash means the element was not detected. Au, Pb, Ni, Co, In, Ge were not detected. Sb#=Sb/(As+Sb), %, Cu#=*$Cu^{2+}/(Zn+Fe+Cu^{2+}+Hg+Cd)$*, %. Numeration of analyses in tables is through*

num-vanadium-bearing phtanites-radiolarites, phtanites-spongiolites, pyrite-carbonaceous-siliceous schists of $\mathrm{Є}_2$. During processes of beresitization these rocks were transformed in beresites, i.e. microquartzites, which clearly stand out in relief: it was a reason for the deposit name.

Deposit was not practically affected by epigenetic metamorphism.

Mineral assemblages of ore bodies

The process of ore formation had a multiphase character. The following mineral assemblages occur: 1) assemblage of relic minerals; 2) assemblage of beresites, listvenites, and connected quartz and ankerite-quartz veinlets (quartz, ankerite, muscovite, phengite, fuchsite, chlorites, pyrophyllite, rutile); 3) assemblage of early sulphides (pyrite, arsenopyrite, kaolinite, anatase); 4) early calcite-polysulphide assemblage (main minerals are pyrrhotite, cubanite, chalcopyrite, bornite, pyrite, graphitoid; accessory minerals are Fe-sphalerite, arsenopyrite, galena, gersdorffite, Ni-Co-pyrite, fahlores); 5) late calcite-polysulphide assemblage (Sb-As-pyrite, Sb-arsenopyrite, sphalerite); 6) productive gold-antimonite assemblage (antimonite, berthierite, jamesonite, zinkenite, bournonite, chalcostibite, fahlores, Hg-gold, andorite, roshchinite, miargirite, *etc.*) (Naz'mova *et al.*, 1971; Spiridonov *et al.*, 1986; Spiridonov, 1995). First four assemblages are the same type within the bounds of the whole deposit. Pyrrhotite, cubanite, chalcopyrite, bornite, and galena of the early calcite-polysulphide assemblage are kept mainly at the periphery of Kvartsitovye Gorki. Within the bounds of ore columns, mineral aggregates of the first four assemblages are brecciated and partly or completely substituted by intergrowths of spherocrystals (ore body IV) and/or small cubes (ore body I) of Sb-As-pyrite, short-prismatic Sb-arsenopyrite, low-iron sphalerite, antimonite. Here, the reactionary minerals are widespread, the products of influence of the Au-Sb solutions on early sulphides: berthierite (after pyrrhotite), zinkenite and jamesonite (after galena), chalcostibite and tetrahedrite (after chalcopyrite, bornite, cubanite). The productive assemblages of Kvartsitovye Gorki I and IV are different: andorite, roshchinite, and miargyrite are absent in the ore body I, but there is argentotennantite (Spiridonov *et al.*, 1986) in assemblage with Hg-gold and galena.

Genesis of the deposit

By geological data (Spiridonov *et al.*, 1986), the deposit was formed at the depths of 1-2 km in conditions of pressure. The ore body IV was formed in less deep conditions, the industrial mineralization in it is found at a depth up to 600 m. The ore body I was formed in less deep conditions, the industrial mineralization in it is traced to the depth more than 1300 m, without evident features of the vertical mineral-geochemical zoning. By the results of study of fluid inclusions with liquid carbon dioxide in early quartz, the temperature of its formation

Table 2. **Chemical composition (wt %) of tennantite (an. 8-10) and tetrahedrite (an. 11-19) of the second generation of early carbonate-polysulphide assemblage of Gvartsitovye Gorki**

Elements	8	9	10	11	12	13	14	15	16	17	18	19
Cu	40.37	38.88	39.49	39.42	38.60	39.05	37.38	36.59	36.79	35.50	35.60	36.30
Ag	2.03	2.13	2.15	2.21	1.87	2.44	1.46	1.60	1.75	2.59	2.45	2.36
Tl	–	–	–	–	–	–	0.18	0.09	0.02	0.08	–	0.08
Zn	3.89	4.09	4.24	5.43	3.30	4.84	6.87	5.57	5.40	4.13	4.31	5.08
Fe	2.98	3.45	3.46	2.54	4.15	2.97	1.12	1.60	1.95	2.53	2.31	2.39
Hg	–	–	0.02	–	–	–	0.20	0.11	–	0.36	0.89	0.32
Cd	–	–	–	–	–	–	–	0.01	–	–	–	0.03
As	14.07	11.70	11.03	9.58	8.54	7.00	3.63	2.60	2.39	1.09	1.06	0.04
Sb	8.01	11.72	13.03	15.69	16.58	19.10	23.97	25.80	26.36	27.88	27.75	29.12
Bi	–	–	–	–	–	–	0.04	0.06	–	0.08	0.17	0.06
Te	–	–	–	–	–	–	–	0.08	–	0.02	–	0.07
Sn	–	–	–	–	–	–	0.14	0.12	0.12	0.17	0.20	0.16
S	26.39	26.30	26.46	26.18	26.13	26.59	25.68	25.26	25.13	24.95	24.49	24.73
Se	–	–	–	–	–	–	0.06	0.06	–	0.05	0.02	–
Total	97.74	98.27	99.88	101.05	99.17	101.99	100.73	99.56	99.92	99.44	99.24	100.74
Formula units at calculation on 29 atoms												
Cu^{1+}	9.70	9.69	9.69	9.68	9.71	9.64	9.60	9.58	9.61	9.43	9.54	9.58
Ag	0.30	0.31	0.31	0.32	0.28	0.36	0.22	0.25	0.28	0.40	0.39	0.36
Tl	–	–	–	–	–	–	0.01	0.01	–	0.01	–	0.01
Total	10.00	10.00	10.00	10.00	9.99	10.00	9.83	9.84	9.89	9.84	9.93	9.95
Zn	0.94	0.99	1.02	1.31	0.81	1.16	1.71	1.42	1.37	1.07	1.12	1.30
Fe	0.84	0.98	0.97	0.71	1.18	0.84	0.33	0.48	0.58	0.76	0.70	0.71
Cu^{2+}	0.28	0.02	0.07	0.09	–	0.02	–	–	–	–	–	–
Hg	–	–	–	–	–	–	0.02	0.01	–	0.03	0.08	0.03
Cd	–	–	–	–	–	–	–	–	–	–	–	0.01
Total	2.06	1.99	2.06	2.11	1.99	2.02	2.06	1.91	1.95	1.86	1.90	2.05
As	2.95	2.48	2.31	2.01	1.82	1.47	0.79	0.58	0.52	0.25	0.24	0.01
Sb	1.02	1.52	1.68	2.03	2.18	2.47	3.21	3.53	3.60	3.87	3.88	4.02
Bi	–	–	–	–	–	–	–	–	–	0.01	0.01	–
Te	–	–	–	–	–	–	–	0.01	–	–	–	0.01
Sn	–	–	–	–	–	–	0.02	0.02	0.02	0.02	0.03	0.02
Total	3.99	4.00	3.99	4.04	4.00	3.94	4.02	4.14	4.14	4.15	4.16	4.06
S	12.95	13.01	12.95	12.85	13.02	13.04	13.07	13.11	13.02	13.14	13.00	12.94
Se	–	–	–	–	–	–	0.01	0.01	–	0.01	–	–
Total	12.95	13.01	12.95	12.85	13.02	13.04	13.08	13.12	13.02	13.15	13.01	12.94
Sb #	26	38	42	50	54	63	80	86	87	94	94	100
Cu #	14	1	3	4	0	1	0	0	0	0	0	0

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

was 310-290° C, pressure was 0.3 kbar for Kvartsitovye Gorki IV and 0.5-0.6 kbar for Kvartsitovye Gorki I, salinity of the KCl-NaCl-$MgCl_2$ solutions was 3-8% of NaCl equivalent. The productive mineral assemblage formed from solutions of the close chemical composition, without liquid carbon dioxide, at the temperature 195-160° C (Spiridonov, 1995).

Fahlores of the Kvartsitovye Gorki deposit

Chemical composition of fahlores was studied with the electron microprobe instruments with the wave analyzer CAMECA SX-50 (analyst N.N. Kononkova) and Camebax (analyst E.M. Spiridonov). The analysis conditions were as follows: accelerating voltage – 20 kV, electron current – 30 nA. The analysis on all chemical elements was made with two programs, without change of the electron beam position (in one point). Standards were as follows: Cu (Kα) – $CuSbS_2$, Ag (Lα) – Ag, Tl (Mα) – $TlAsS_2$, Au (Lα) – Au, Fe (Kα) – FeS_2, Zn (Kα) – ZnS, Pb (Mα) – PbS, Hg (Lα) – HgS, Cd (Lα) – Cd, Mn (Kα) – $MnTiO_3$, Ni (Kα) – Ni, Co (Kα) – Co, As (Lα) – AsGa, Sb (Lα) – $CuSbS_2$, Te (Lα) – Te, Bi (Mα) – Bi, Sn (Lα) – SnO_2, Ge (L) – Ge, S (Kα) – $CuSbS_2$, Se (Lα) – Se. The lower detection limit of detected elements by the K line was 0.02 wt %, by the L line was 0.1 wt %, and by the M line was 0.3 wt %.

The nomenclature of fahlores is given after the article (Spiridonov, 1985).

Fahlores of the early carbonate-polysulphide assemblage. These fahlores do not have the wide diversity of a set of

Table 3. **Chemical composition (wt %) of mercury-zinc tennantite (an. 20-27) and tetrahedrite (an. 28-31) of the first generation of productive assemblage in intergrowth with antimonite, jamesonite, zinkenite, low-silver Hg-gold, Kvartsitovaya Gorka IV**

Elements	20	21	22	23	24	25	26	27	28	29	30	31
Cu	38.53	35.98	34.34	35.09	38.03	35.87	34.78	36.09	35.21	34.56	35.74	35.37
Ag	2.82	4.83	4.79	5.24	3.39	4.83	5.07	4.78	5.50	5.74	4.13	3.02
Tl	–	–	–	–	–	0.12	0.09	–	–	–	–	–
Zn	6.44	4.97	5.39	5.10	6.64	5.89	5.19	5.56	5.25	5.43	4.89	3.51
Fe	1.13	1.15	1.07	1.61	0.87	0.58	0.65	1.50	1.64	1.45	1.92	2.69
Hg	2.40	5.79	6.80	4.68	2.23	3.76	4.77	2.97	3.43	4.49	3.12	3.50
Cd	–	–	–	–	–	0.06	0.04	–	–	–	–	–
As	12.45	11.24	11.00	10.81	10.98	10.37	10.08	9.34	8.36	7.55	6.19	2.66
Sb	10.98	11.52	11.40	11.91	12.51	12.90	12.94	14.16	15.79	17.18	19.29	24.14
Bi	–	–	–	–	–	0.05	0.07	–	–	–	0.22	0.22
Te	–	–	–	–	–	–	0.08	–	–	–	–	–
Sn	–	–	–	–	–	0.04	0.15	–	–	–	–	–
S	26.64	25.47	25.20	24.94	26.46	25.48	24.80	25.40	25.26	24.86	25.12	24.55
Se	–	–	–	–	–	–	0.07	–	–	–	–	–
Total	101.39	100.95	99.99	99.38	101.11	99.94	98.79	99.80	100.44	101.26	100.62	99.66
Formula units at calculation on 29 atoms												
Cu^{1+}	9.50	9.25	8.97	9.15	9.47	9.25	9.19	9.27	9.13	9.04	9.32	9.47
Ag	0.41	0.73	0.74	0.80	0.50	0.73	0.78	0.73	0.84	0.88	0.63	0.48
Tl	–	–	–	–	–	0.01	0.01	–	–	–	–	–
Total	9.91	9.98	9.71	9.95	9.97	10.00	9.98	10.00	9.97	9.92	9.95	9.95
Zn	1.54	1.24	1.37	1.29	1.61	1.48	1.33	1.39	1.32	1.38	1.24	0.91
Fe	0.32	0.34	0.32	0.48	0.25	0.17	0.20	0.44	0.48	0.43	0.57	0.81
Cu^{2+}	–	–	–	–	–	–	–	0.02	–	–	–	–
Hg	0.19	0.47	0.56	0.39	0.17	0.31	0.40	0.24	0.28	0.37	0.26	0.30
Cd	–	–	–	–	–	0.01	0.01	–	–	–	–	–
Total	2.05	2.05	2.25	2.16	2.03	1.96	1.94	2.09	2.09	2.18	2.07	2.02
As	2.60	2.45	2.44	2.39	2.32	2.27	2.26	2.04	1.84	1.67	1.37	0.61
Sb	1.41	1.55	1.55	1.62	1.63	1.74	1.78	1.90	2.15	2.35	2.62	3.37
Bi	–	–	–	–	–	–	0.01	–	–	–	0.02	0.02
Te	–	–	–	–	–	–	0.01	–	–	–	–	–
Sn	–	–	–	–	–	0.01	0.02	–	–	–	–	–
Total	4.02	4.00	3.99	4.01	3.95	4.01	4.08	3.94	3.97	4.02	4.01	4.00
S	13.02	12.97	13.05	12.88	13.05	13.03	12.98	12.96	12.97	12.88	12.97	13.03
Se	–	–	–	–	–	–	0.02	–	–	–	–	–
Total	13.02	12.97	13.05	12.88	13.05	13.03	13.00	12.96	12.97	12.88	12.97	13.03
Sb#	35	39	39	40	41	43	44	48	54	58	66	85
Cu#	0	0	0	0	0	0	0	1	0	0	0	0

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

microadmixtures within the bounds of the whole deposit. The earliest of falhores (the first generation) are associated with cubanite, Ni-Co-pyrite, chalcopyrite; fahlores overgrow and substitute chalcopyrite, form vienlets in it. By chemical composition, this is zinc- and iron-bearing tennantite, rarely tetrahedrite, with average relative content of copper (Cu^{2+}/Me^{2+},%) from 0 to 18%, with low contents of Ag (less than 0.4 wt %), Hg, and Tl, poor by Cd, Bi, Sn, Te, Se (Tabl. 1). The later of them are zinc-bearing tennantite and predominating tetrahedrite of the second generation form microveinlets in chalcopyrite and early tennantite. Fahlores of the second generation is rather rich by Ag (1.5-2.6 wt %) and Sn (0.1-0.2 wt %), poor by Hg, Tl, Cd, Bi, Te, Se (Tabl. 2), they have low relative content of copper.

Fahlores of the productive assemblage are remarkably different in the ore bodies IV and I.

Kvartsitovaya Gorka IV. Fahlores form the xenomorphic aggregations up to 20-40 mm, usually 0.05-3 mm in size, in the calcite nests together with antimonite, sulphosalts of Pb-Sb, Pb-Fe-Sb, Pb-Cu-Sb, and Ag-Pb-Sb, mercurous gold.

Fahlores of the first generation are the most widespread and form the largest aggregations; they are associated with antimonite, zinkenite, jamesonite, chalcostibite, the low-silver Hg-gold. They contain relics of chalcopyrite, arsenopyrite, and ferriferous sphalerite. The contacts of crystals of fahlores and antimonite are the inductive surfaces of joint growth. By chemical composition, fahlores correspond to mercury-zinc tennantite and tetrahedrite with a moderate content of Ag (3-6 wt %) (Tabl. 3). Outside zones of crystals are more antimonial.

Table 4. **Chemical composition (wt %) of zinc- and iron-bearing tetrahedrite of the second generation of productive assemblage in intergrowth with antimonite, famatinite, high-silver mercury-enriched gold, Kvartsitovaya Gorka IV.**

Elements	32	33	34	35	36	37	38	39	40	41
Cu	33.69	32.54	30.75	32.82	32.10	32.32	32.89	33.72	31.06	31.27
Ag	6.44	7.05	9.75	7.26	8.28	8.30	5.07	4.90	7.80	7.83
Tl	–	–	0.02	–	–	–	0.01	0.04	–	–
Zn	5.74	5.67	2.71	5.23	4.38	4.17	3.48	3.65	3.23	3.23
Fe	2.71	2.67	3.91	2.86	3.21	3.20	3.23	2.96	3.52	3.35
Hg	1.22	2.03	0.36	1.61	1.47	1.66	0.12	–	0.06	0.20
Cd	–	–	0.07	–	–	–	–	–	–	–
As	4.97	4.91	3.50	3.09	2.97	2.94	0.89	0.69	0.45	0.44
Sb	21.62	22.23	23.40	22.56	23.53	24.12	27.65	28.81	28.28	28.52
Bi	–	–	0.14	–	–	–	0.27	0.09	–	0.14
Te	–	–	0.04	–	–	–	0.05	0.03	0.04	0.06
Sn	–	–	0.16	–	–	–	0.16	0.11	0.17	0.16
S	25.21	25.19	24.40	24.93	23.89	24.87	24.64	24.69	23.88	23.72
Se	–	–	0.03	–	–	–	0.02	0.03	–	0.03
Total	101.60	102.29	99.23	100.36	99.83	101.58	98.46	99.71	98.50	98.94
Formula units at calculation on 29 atoms										
Cu^{1+}	8.72	8.46	8.30	8.67	8.66	8.54	8.90	9.04	8.54	8.61
Ag	0.98	1.08	1.55	1.13	1.32	1.29	0.81	0.77	1.26	1.27
Tl	–	–	–	–	–	–	–	–	–	–
Total	9.71	9.54	9.85	9.80	9.98	9.83	9.71	9.81	9.81	9.88
Zn	1.44	1.43	0.71	1.34	1.15	1.07	0.91	0.95	0.86	0.86
Fe	0.80	0.79	1.20	0.86	0.99	0.96	0.99	0.90	1.10	1.05
Cu^{2+}	–	–	–	–	–	–	–	–	–	–
Hg	0.10	0.17	0.03	0.13	0.13	0.14	0.01	–	0.01	0.02
Cd	–	–	0.01	–	–	–	–	–	–	–
Total	2.34	2.39	1.95	2.34	2.26	2.17	1.92	1.85	1.97	1.93
As	1.09	1.08	0.80	0.69	0.68	0.66	0.20	0.16	0.11	0.10
Sb	2.92	3.02	3.30	3.11	3.31	3.33	3.91	4.03	4.06	4.10
Bi	–	–	0.01	–	–	–	0.02	0.01	–	0.01
Te	–	–	0.01	–	–	–	0.01	–	0.01	0.01
Sn	–	–	0.02	–	–	–	0.02	0.02	0.02	0.02
Total	4.01	4.10	4.14	3.80	3.99	3.98	4.16	4.21	4.20	4.24
S	12.94	12.98	13.05	13.06	12.77	13.02	13.21	13.11	13.02	12.94
Se	–	–	0.01	–	–	–	–	0.01	–	0.01
Total	12.94	12.98	13.06	13.06	12.77	13.02	13.21	13.12	13.02	12.95
Sb#	73	74	80	82	83	83	95	96	97	98
Cu#	0	0	0	0	0	0	0	0	0	0

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

Fahlores of the second generation, associating with antimonite, famatinite, and the silver-enriched Hg-gold, are represented by the zinc- and iron-enriched high-antimonial tetrahedrite, containing 5-10 wt % of Ag, up to 2 wt % of Hg, poor by Bi (Tabl. 4). Outside zones of the fahlores crystals do not practically contain As.

Fahlore of the third generation is the ferriferous high-antimony tetrahedrite enriched by Ag (9-15 wt %), containing up to 2 wt % Hg (Tabl. 5); it are associated with antimonite, andorite, roshchinite, mercury-enriched gold and electrum. Outside zones of the fahlore crystals do not practically contain As.

The positive correlation of the Fe and Ag contents is characteristic for fahlores of the ore body IV.

Kvartsitovaya Gorka I. Size of fahlores of productive assemblage is microscopic. The fahlores of the first generation occur in assemblage with antimonite and the low-silver Hg-gold; they are represented by the zinc- and iron-enriched arsenic tetrahedrite, containing 3-8 wt % of Ag, up to 2 wt % of Hg (Tabl. 6).

In assemblage with the high-silver Hg-gold are fahlores of the second generation, they are enriched by the silver zinc tetrahedrite and argentotetrahedrite, containing up to 31 wt % of Ag and 0.4 wt % Cd (Tabl. 7). The low contents of Hg (0.1-0.3 wt %) are characteristic for these fahlores. Argentotennantite forms outside zones of the fahlores crystals.

In the richest ore columns of the ore body I is the assemblage of fahlores of the third generation with galena and late Hg-gold and Hg-electrum. Intergrowths of these minerals

Table 5. **Chemical composition (wt %) of ferriferous tetrahedrite of the third generation of productive assemblage in intergrowth with andorite, roschinite, high-mercury gold, Kvartsitovaya Gorka IV**

Elements	42	43	44	45	46	47	48	49	50	51	52	53
Cu	29.42	31.77	27.43	28.58	28.52	30.28	27.81	28.55	27.99	28.37	28.39	27.78
Ag	11.32	9.41	13.36	14.51	13.20	11.46	11.81	11.79	14.12	12.55	13.81	13.53
Tl	–	–	–	–	–	–	0.19	0.17	–	0.02	–	–
Zn	2.68	2.67	2.97	3.1	2.49	2.78	2.60	3.46	2.65	2.58	2.72	2.94
Fe	4.39	4.04	3.91	3.25	4.33	3.86	3.68	3.03	3.81	3.62	3.95	3.38
Hg	1.73	0.67	1.85	0.91	1.22	0.74	0.15	0.43	0.58	0.53	0.49	0.79
Cd	–	0.01	–	–	–	0.06	0.05	0.06	–	0.06	–	0.13
As	4.92	4.66	3.12	2.55	2.37	2.09	0.77	0.67	0.64	0.65	0.22	0.07
Sb	20.94	21.15	23.13	24.13	24.41	24.87	27.24	27.66	26.81	27.58	27.78	26.94
Bi	–	–	–	–	–	–	0.08	0.03	–	–	–	–
Te	–	–	–	–	–	–	0.01	0.06	–	0.05	–	–
Sn	–	–	–	–	–	–	0.16	0.11	–	0.15	–	–
S	24.42	24.56	23.87	24.43	24.08	24.17	23.76	23.37	23.76	23.82	23.82	23.39
Se	–	–	–	–	–	–	–	0.05	–	–	–	–
Total	99.82	98.94	99.64	101.46	100.62	100.31	98.30	99.43	100.36	99.98	101.18	98.95
Formula units at calculation on 29 atoms												
Cu^{1+}	7.92	8.50	7.56	7.69	7.77	8.17	7.78	7.96	7.70	7.85	7.77	7.76
Ag	1.80	1.48	2.17	2.31	2.12	1.83	1.95	1.94	2.30	2.04	2.23	2.24
Tl	–	–	–	–	–	–	0.02	0.01	–	–	–	–
Total	9.71	9.98	9.73	10.00	9.88	10.00	9.74	9.91	10.00	9.89	10.00	10.00
Zn	0.70	0.69	0.80	0.81	0.66	0.73	0.71	0.94	0.71	0.69	0.73	0.80
Fe	1.34	1.23	1.23	1.00	1.34	1.19	1.17	0.96	1.20	1.14	1.23	1.08
Cu^{2+}	–	–	–	0.03	–	0.03	–	–	0.03	–	0.02	0.04
Hg	0.15	0.06	0.16	0.08	0.11	0.06	0.01	0.04	0.05	0.05	0.04	0.07
Cd	–	–	–	–	–	0.01	0.01	0.01	–	0.01	–	0.02
Total	2.19	1.98	2.18	1.93	2.11	2.03	1.90	1.95	1.98	1.89	2.02	2.01
As	1.12	1.06	0.73	0.58	0.55	0.48	0.18	0.16	0.15	0.15	0.05	0.02
Sb	2.94	2.95	3.33	3.40	3.47	3.52	3.98	4.03	3.86	3.98	3.98	3.95
Bi	–	–	–	–	–	–	0.01	–	–	–	–	–
Te	–	–	–	–	–	–	–	0.01	–	0.01	–	–
Sn	–	–	–	–	–	–	0.02	0.02	–	0.02	–	–
Total	4.07	4.01	4.06	3.99	4.02	4.00	4.19	4.21	4.01	4.16	4.03	3.97
S	13.03	13.02	13.03	13.09	12.99	12.98	13.17	12.92	13.00	13.06	12.95	13.02
Se	–	–	–	–	–	–	–	0.01	–	–	–	–
Total	13.03	13.02	13.03	13.09	12.99	12.98	13.17	12.93	13.00	13.06	12.95	13.02
Sb#	72	74	82	85	86	88	96	96	96	96	99	100
Cu#	0	0	0	2	0	2	0	0	1	0	1	2

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

form small (60-100 microns) metasomatic ingrowths in pyrite. Fahlores are presented by the zinc antimony argentotennantite (to 34 wt % of Ag) and arsenic argentotetrahedrite (to 39 wt % of Ag) (Tabl. 8). Argentotetrahedrite forms the isolated aggregations and margins around crystals of argentotennantite. The stable admixture of Cd (0.10-0.12 wt %), extremely low contents of Hg, and also remarkable relative content of copper are characteristic for late fahlores, that distinguishes them among other fahlores of the productive assemblage.

The late productive mineralization with high-silver fahlores is found at different levels of the ore body I: from surface to a depth of 950 m.

Evolution of chemical composition of fahlores

Fahlores of pre-productive assemblage, tennantite and, in smaller degree, tetrahedrite, are poor by Ag, Hg, Cd and have a moderate content of copper. Fahlores of the productive assemblage are enriched by Ag, often Hg, and with extremely low content of copper. That is an evidence of the low oxidizing potential of ore-bearing solutions.

Fahlores of productive assemblage of the ore body IV are enriched by silver tetrahedrite, rarely tennantite. Fahlores of productive assemblage of the ore body I are tetrahedrite, rarely argentotennantite and argentotetrahedrite. During ore formation from the first to third generation, the concentrations of silver in fahlores increased (Fig. 1b-d).

The largest concentration of mercury was

Table 6. **Chemical composition (wt %) of zinc- and iron-bearing tetrahedrite of the first generation of productive assemblage, Kvartsitovaya Gorka I**

Elements	54	55	56	57	58	59
Cu	35.89	35.21	34.59	34.80	35.24	31.95
Ag	3.96	5.23	4.34	3.54	3.33	8.27
Tl	0.06	–	0.14	–	–	–
Zn	6.75	5.64	6.67	3.52	3.44	6.03
Fe	0.58	2.36	0.89	3.80	3.49	1.13
Hg	1.76	0.49	0.52	1.72	1.73	0.05
Cd	0.04	–	0.06	–	–	–
As	8.33	4.41	2.06	2.04	1.37	0.58
Sb	16.53	22.25	26.11	26.18	27.38	27.36
Bi	0.05	–	0.11	–	–	–
Te	0.05	–	0.06	–	–	–
Sn	0.06	–	0.13	–	–	–
S	25.99	24.67	24.93	24.64	25.18	23.87
Se	0.05	–	0.03	–	–	–
Total	100.08	100.26	100.65	100.24	101.16	99.24
Formula units at calculation on 29 atoms						
Cu^{1+}	9.18	9.19	9.13	9.22	9.26	8.67
Ag	0.60	0.81	0.68	0.56	0.52	1.33
Tl	–	–	0.01	–	–	–
Total	9.78	10.00	9.82	9.78	9.78	10.00
Zn	1.68	1.43	1.71	0.91	0.88	1.60
Fe	0.17	0.70	0.27	1.15	1.04	0.36
Cu^{2+}	–	0.02	–	–	–	0.07
Hg	0.14	0.04	0.04	0.14	0.14	–
Cd	0.01	–	0.01	–	–	–
Total	2.00	2.19	2.03	2.20	2.06	2.03
As	1.81	0.98	0.46	0.46	0.31	0.13
Sb	2.20	3.04	3.60	3.62	3.75	3.91
Bi	–	–	0.01	–	–	–
Te	0.01	–	0.01	–	–	–
Sn	0.01	–	0.02	–	–	–
Total	4.03	4.02	4.10	4.08	4.06	4.04
S	13.18	12.79	13.04	12.94	13.11	12.93
Se	0.01	–	0.01	–	–	–
Total	13.19	12.79	13.05	12.94	13.11	12.93
Sb#	55	76	89	89	92	97
Cu#	0	1	0	0	0	3

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

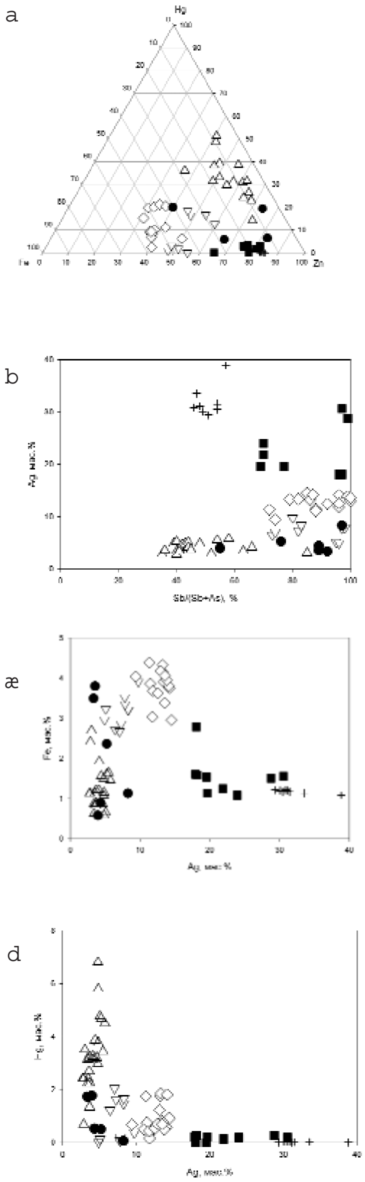

Fig. 1. *Chemical composition of fahlores of productive assemblage of the ore body I (l— first, n — second, and* + *— third generations) and ore body IV (△ — first, ▽ — second, and ◇ — third generations) of the Kvartsitovye Gorki deposit*

detected in fahlores of productive assemblage of the less deep ore body IV. During ore formation from the first to second and third generation, the concentration of mercury in fahlores decreased (Fig. 1a, d). Mercury was redistributed in native gold.

The relative content of antimony in fahlores of productive assemblage of the ore body IV increased from the first to third generation. This is a standard trend of evolution of the fahlores chemical composition (Charlat, Levy, 1974; Mozgova, Tsepin, 1983; Spiridonov, 1987; Chvileva *et al.*, 1988; etc.). The relative content of antimony in fahlores of productive assemblage of the ore body I from the first and second to third generation considerably decreased, just here argentotennantite occurs.

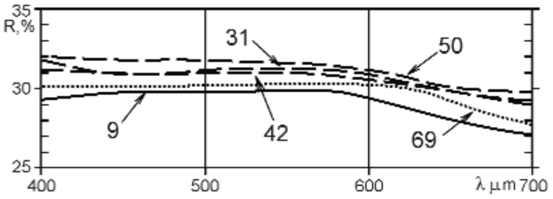

Fig. 2. *Reflectance spectra of tennantite (N. 9), tetrahedrite (N. 31, 42, 50), and argentotennantite (N. 69) of the Kvartsitovye Gorki deposit*

Table 7. **Chemical composition (wt %) of zinc-bearing tetrahedrite (an. 60-66) and argentotetrahedrite (an. 67-68) of the second generation of productive assemblage, Kvartsitovaya Gorka I**

Elements	60	61	62	63	64	65	66	67	68
Cu	24.51	21.15	22.72	24.40	23.45	23.97	23.15	14.83	16.35
Ag	19.52	23.93	21.87	19.65	18.18	17.93	18.06	30.57	28.79
Tl	–	–	–	–	0.09	0.18	0.12	–	0.10
Zn	5.62	5.67	5.67	5.86	5.24	5.51	5.25	5.37	5.74
Fe	1.53	1.08	1.25	1.13	1.59	1.60	2.78	1.56	1.50
Hg	–	0.18	0.12	0.20	0.27	0.22	–	0.18	0.26
Cd	–	0.41	0.25	0.24	0.25	0.18	0.18	0.31	0.24
As	5.31	4.94	4.94	3.85	0.61	0.60	0.61	0.41	0.24
Sb	19.05	18.93	19.18	20.72	26.93	26.59	27.30	25.66	26.07
Bi	–	–	–	–	0.12	0.07	0.06	0.13	0.15
Te	–	–	–	–	–	0.11	0.06	0.05	0.06
Sn	–	–	–	–	0.15	0.16	0.14	0.11	0.13
S	23.45	23.12	23.50	23.53	23.25	23.61	23.17	22.52	22.19
Se	0.08	–	0.02	0.01	0.02	–	0.02	–	0.03
Total	99.07	99.41	99.52	99.59	100.11	100.74	100.89	101.69	101.85
Formula units at calculation on 29 atoms									
Cu^{1+}	6.80	6.00	6.37	6.77	6.66	6.73	6.52	4.36	4.80
Ag	3.20	4.00	3.61	3.23	3.04	2.96	2.99	5.30	4.98
Tl	–	–	–	–	0.01	0.02	0.01	–	0.01
Total	10.00	10.00	9.98	10.00	9.71	9.71	9.52	9.66	9.79
Zn	1.52	1.56	1.54	1.59	1.45	1.50	1.44	1.54	1.64
Fe	0.49	0.34	0.40	0.36	0.51	0.51	0.88	0.53	0.50
Cu^{2+}	0.02	0.01	–	0.04	–	–	–	–	–
Hg	–	0.02	0.01	0.02	0.02	0.02	–	0.02	0.02
Cd	–	0.07	0.04	0.04	0.04	0.03	0.03	0.05	0.04
Total	2.03	2.00	1.99	2.05	2.02	2.06	2.35	2.12	2.20
As	1.25	1.19	1.17	0.91	0.15	0.14	0.14	0.10	0.07
Sb	2.77	2.80	2.81	3.02	3.99	3.90	4.02	3.94	3.99
Bi	–	–	–	–	0.01	0.01	–	0.01	0.01
Te	–	–	–	–	–	0.02	0.01	0.01	0.01
Sn	–	–	–	–	0.02	0.02	0.02	0.02	0.02
Total	4.02	3.99	3.98	3.93	4.17	4.09	4.19	4.08	4.10
S	12.93	13.01	13.05	13.02	13.09	13.14	12.92	13.13	12.90
Se	0.02	–	–	–	–	–	0.01	–	0.01
Total	12.95	13.01	13.05	13.02	13.09	13.14	12.93	13.13	12.91
Sb#	69	70	70	77	96	96	97	97	99
Cu#	1	0	0	2	0	0	0	0	0

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

Possibly, such trend of evolution of fahlores is characteristic for such relatively developed to the depth deposits as Kvartsitovaya Gorka I.

Physical properties of fahlores

The reflectance spectra of tennantites, containing antimony and practically non-containing Ag and Hg, are characterized by the presence of a gentle maximum in the yellow-green range and the significant decrease of peaks in the red range (Fig. 2, sample an. 9), this is a reason of a greenish tint of the mineral in reflected light. The reflectance spectra of mercurous tennantite, independently from its relative content of antimony, are distinguished by a noticeable maximum in a yellow range, a sag in green and a decrease of reflection in the red range. Such peculiarities of the reflectance spectrum are shown already in fahlores with 3-4 wt % of Hg (sample an. 31). The reflectance spectrum of argentotennantite is different, in the blue and yellow-green ranges, it has a straight profile, analogous to tetrahedrite enriched by silver, in a red range, reflection of argentotennantite strongly decreases (sample an. 69), a blue tint of mineral is caused by that. In tetrahedrites, with increase of the silver content up to 30%, reflection significantly increases, a form of spectrum changes slightly (samples an. 42 and 50).

The unit cell parameters of the studied fahlores increase from tennantite (10.294(2) Å, sample an. 9) to tetrahedrite (10.401(2) Å, sample an. 31); diffractometer DRON-4.5; Co anticathode; inner standard α-quartz; the unit cell parameters were calculated by method of the least squares. During entry of the silver large cation in fahlores, the unit cell parameter increases to 10.417(1) Å (8% of Ag, sample an. 36), 10.452(2) Å (11% of Ag, sample an. 42), and 10.518(2) Å (14% Ag, sample an. 50) in tetrahedrite and to 10.583(2) Å (argentotennantite,

Table 8. **Chemical composition (wt %) of zinc-bearing argentotennantite (an. 69-72) and argentotetrahedrite (an. 73--75) of the third generation of productive assemblage, Kvartsitovaya Gorka I.**

Elements	69	70	71	72	73	74	75
Cu	17.21	15.60	16.76	17.11	17.78	17.78	11.64
Ag	30.87	33.54	31.13	30.07	30.48	31.48	38.86
Zn	5.93	5.44	5.81	5.98	6.23	6.23	5.81
Fe	1.21	1.13	1.19	1.19	1.17	1.17	1.08
Hg	0.02	0.02	–	0.02	0.02	0.01	–
Cd	0.11	0.10	0.10	0.12	0.12	0.12	0.12
As	9.02	8.80	8.72	8.52	7.66	7.66	6.89
Sb	12.64	12.59	12.98	13.34	14.74	14.74	14.83
S	22.87	22.66	22.82	22.90	23.08	23.08	21.92
Se	–	–	–	0.02	0.02	0.01	–
Total	99.88	99.88	99.51	99.27	101.30	102.28	101.15
Formula units at calculation on 29 atoms							
Cu^{1+}	4.84	4.32	4.76	4.88	4.95	4.81	3.26
Ag	5.16	5.68	5.24	5.06	5.05	5.19	6.74
Total	10.00	10.00	10.00	9.94	10.00	10.00	10.00
Zn	1.64	1.52	1.61	1.65	1.70	1.69	1.66
Fe	0.39	0.37	0.39	0.39	0.38	0.37	0.36
Cu^{2+}	0.04	0.16	0.02	–	0.05	0.16	0.17
Hg	–	–	–	–	–	–	–
Cd	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Total	2.09	2.07	2.04	2.06	2.15	2.24	2.21
As	2.17	2.14	2.11	2.06	1.83	1.82	1.72
Sb	1.87	1.89	1.94	1.99	2.16	2.15	2.28
Total	4.04	4.03	4.05	4.05	3.99	3.97	4.00
S	12.86	12.90	12.91	12.95	12.86	12.79	12.79
Se	–	–	–	–	–	–	–
Total	12.86	12.90	12.91	12.95	12.86	12.79	12.79
Sb#	46	47	48	49	54	54	57
Cu#	2	8	1	0	2	7	8

Note: *Au, Pb, Ni, Co, In, Ge were not detected*

sample an. 69) in tennantite.

The micro-indentation hardness of fahlores decreases in a series from tennantite to tetrahedrite, from 365 (sample an. 9) to 330, 318, and 308 kgs/mm^2 (samples an. 7, 18, and 31). It is maximal in the high-silver fahlores: 307 and 302 kgs/mm^2 (argentotennantite, samples an. 69 and 70).

Conclusions

The Kvartsitovye Gorki deposit is the less deep one from plutonogene gold deposits; it is original by composition and evolution of chemical composition of fahlores. The studied fahlores are stoichiometric by chemical composition, their crystals are often zoned by chemical composition, a smooth change of chemical composition from zone to zone is characteristic. Fahlores are poor by Bi, Te, Se, Tl, Cd, Sn; contents of Au, Pb, Ni, Co, Ge, and In are below detection limits.

Fahlores of productive assemblage are the most diverse. Earlier fahlores are enriched by mercury, especially in the less deep ore body IV (to 7 wt %). In fahlores of late generations of productive assemblage, the contents of mercury are lower in tens times. Evolution of fahlores of productive assemblage of the industrial ore bodies I and IV is different: in the ore body IV, from early to late generations, the contents of silver and relative content of antimony increase; in the deep-penetrating ore body I, from early to late generations the relative content of antimony decreases and the contents of silver increase. Just among the late generation of fahlores in the ore body I, argentotennantite occur.

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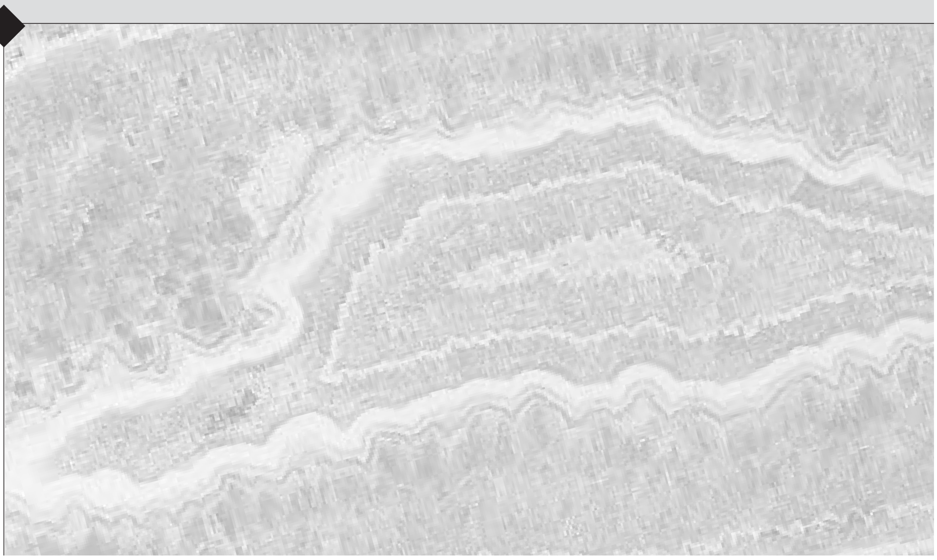
Crystal Chemistry, Minerals as Prototypes of New Materials, Physical and Chemical Properties of Minerals



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METACOLLOIDAL GOLD

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The processes of aggregation and crystallization of natural colloidal gold, formed by mechanic way during grinding of gold particles in contemporary placers and in process of the hydrothermal sol-gel synthesis, are studied. It is shown that, in the first case, the friable heterodispersed globular sediment transformed in the dendrite-like intergrowths and films with pores of hexagonal outlines was an initial form of coagulate. In the second case, that was the compact clots and films transformed during the process of syneresis and coalescence in the flat gold particles with a mosaic-block structure. The new aggregative type of core-shell structures of gold with blocks enriched by gold and inter-block space enriched by silver was found. The epitaxial correlations between gold and quartz by a law $(10\bar{1}1)_{SiO_2} \parallel (001)_{Au}$ и $[12\bar{1}0]_{SiO_2} \parallel [100]_{Au}$ was ascertained for the gold nanoparticles.
1 table, 7 figures, 18 references

The colloidal gold, by generally accepted determination, is the metal gold, consisting of hydrophobic, positive charged particles of nanometric size, which are located in the form of suspension in the liquid; the diphase system with a liquid dispersion medium and ultrasmall gold particles is the gold sol, and the falling flaky sediment is the gold gel. The process of the gold sol coagulation, beginning in the liquid phase under the influence of electrolytes, is accompanied by the rapid crystallization of the sediment, its ageing and syneresis with the isolation of the dispersed phases in a rest dispersion liquid, being still heterogeneous, with the following coalescence of the solid nanoparticles. The metacolloidal gold is the gold formed at the expense of crystallization of the gel sediment.

The process of formation of colloidal gold in nature conforms to the above-mentioned well-known scheme, which is realized mainly in two different geological environments. One of them is connected with formation of the thin colloidal layer with finest gold suspension over the surface of gold particles, which is grinded under influence of thin clastic material in a water stream in alluvium at normal temperature and pressure. The time of mechanical influence on gold, by the geological scale, is small (months, years), although, it significantly excels the duration (hours, days) of such type experiments. Another, the most distributed in nature, method is the hydrothermal sol-gel synthesis of colloidal gold, realized in the periods of the pressures decrease in hydrothermal system as a result of strong supersaturation of solutions in local parts of the forming gold-quartz ore bodies, mainly in the epithermal deposits. The fall of coagulates is caused by the reduction reactions of the high-concentrated dissolved gold salts with a formation of the unstable gold sol. The process takes place at high temperatures (~200 °C) and pressures up to 0.5 GPa, in multicomponent solutions with low salinity of alkaline type (pH 8.5 – 9.0) with dissolved salts (predominating $HSiO_3^- > HCO_3^-$) and gases $N_2 > CO_2 > H_2S$ (Laz'ko *et al.*, 1981). The rapidly proceeding initial stages of the natural sol-gel synthesis are changed by a long period of aggregation and transformation, which is estimated by tens of million years. The features of the initial gel nature of matter are entirely razed; their traces can be found by study of textural-structural correlations of mineral aggregates that was a theme of the special studies in the middle of the last century (Textures..., 1958).

The clarification of peculiarities of the colloidal gold aggregation in the natural processes was a purpose of present study. The samples of native gold from quartz veins of the epithermal deposits of Zabaikalie (Balei-Taseevskoe) and Kolyma (Agatovoe) and also the placer gold from the contemporary alluvial sediments of the Lena River basin (East Siberia) were the objects of study. The works were carried out with the electron microprobe analysis and method of analytical electron microscopy (scanning and transmission), with application of the aimed replicas from the fresh or etched fracture of samples.

Metacolloidal gold in river alluvium

The borders and outgrowths of redeposited gold on the gold particles from placers are known for a long time under a name of the new gold. It was studied long time, beginning from the early works of F. Freize (Freize, 1931), and later was described in the works of P. Ramdor (Ramdor, 1962), N.V. Petrovskaya (Petrovskaya, 1973), and many other researchers. It is known that processes of corrosion and refinement of the gold particles surface with formation of the high-fineness shells precede to formation of the new gold, containing, in contrast to the high-fineness shells, the significant amounts of the silver admixture. In contemporary placers, at the relatively short-time stay of gold particles in river alluvium, the high-fineness shell is often absent, and new gold precipitates on the corrosive surface of particles of initial gold.

On corrosive surface of studied flat gold particle from the Ugakhan River placer (Lenskii region, East Siberia), the thickness of the new gold film is 20-30 microns. The broken film, incompletely covering surface of gold particle, is composed by a friable aggregate of heterodispersed globular particles, single or aggregated. The single globules with ideal spherical form are from 20 to 120 nm in diameter; they also form the doubled intergrowths with the point surface of contact (Fig. 1). The subsequent development of process of confluence (coalescence) of globules results in formation of the curved wire-like intergrowths with the side branches at angels close to 90° and 60°. At the ends of these dendrite-like intergrowths, the globular form rests. Formation of a porous film with uneven surface is the final result of aggregation of initially globular forms of gold. The largest pores up to 700 nm in size have typical hexagonal outlines inherited from the dendrite-like intergrowths with the side branches oriented at angels of 60° and 90° to the basis stem part.

In contrast to nanometric single globules, the larger (hundreds of nanometers in diameter) spherical ends of the side branches of dendritoids in a number of cases are covered by the small (10-20 nm in size) triangle vicinal forms or thin lamellar outgrowths curved at angles of 120°. A part of such spherical formations is badly polygonized. In spite of absence of clear crystallographic shape, both small and larger aggregated globules give the well-visible ring patterns of microdiffraction, which are characteristic for face-centred cubic structure of polycrystalline gold.

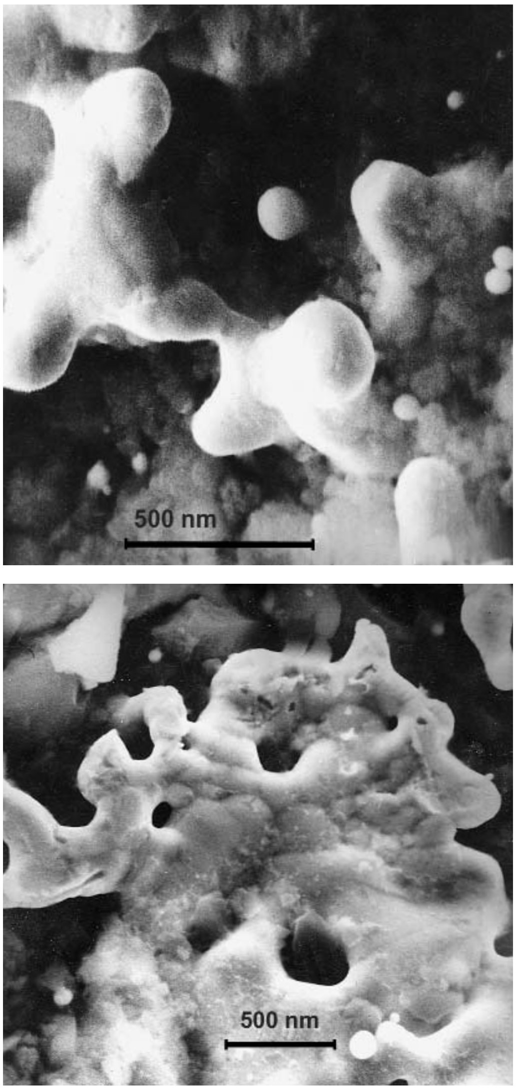


Fig. 1. *Globular outgrowths on the surface of placer gold: a — dendrite-like intergrowths of globules with different size; b — film of intergrowing globules. REM. Length of scale lines is 100 and 500 nm*

Metacolloidal gold in epithermal deposits

The metacolloidal gold is widespread in the gold-quartz and gold-sulphide-quartz ores of the epithermal gold-silver deposits within the quartz veins with banded and festoon-banded texture. The aggregations of gold are located according to thin-festoon curved layers of chalcedony-like quartz, or their thin inclusions saturate quartz aggregates, tincturing them in brownish and yellowish colours. Also the roundish ovoid aggregations of gold were noted (Petrovskaya, 1973), and in thin cavities of exfoliation are the friable aggregates of the thread-like and ribbon-like gold. In deposits of such type, known around the world, gold contains variable amount of the Ag admixture right up to high concentrations (usually 30-40% of Ag), it is remarkable by morphological diversi-

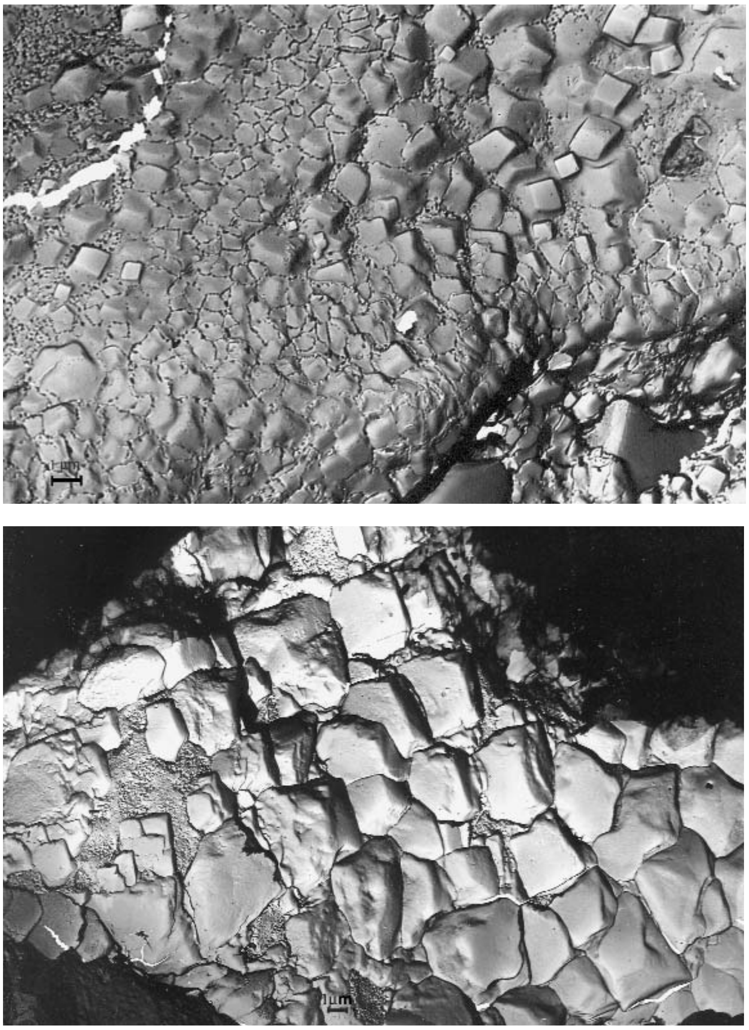


***Fig. 2**. Porous cracks of syneresis and the cubic blocks in gold on quartz from the Agatovskoe deposit (Kolyma). PEM, etch., replica. Length of scale line is 1 micron*

ty, occurring in the form of crystals and their intergrowths, dendrites, skeletal formations, and xenomorphic lamellae. All particles of gold are characterized by the mosaic-block structure, which is absent in gold grains from deposits of other genetic types.

Mosaic structure of the high-silver gold was discovered in the second half of the last century, and thin details of inner structure of gold particles were minutely considered earlier (Petrovskaya, Frolova, 1969; Petrovskaya, 1973; Petrovskaya *et al.*, 1977). The genesis of mosaic-block structures was interpreted from general positions; polygene nature of them with accumulation of admixtures in front part of layer-growing faces and (or) with the post-crystallization transformations of the solid gold-silver solution, forming gold particles, was admitted (Petrovskaya, 1973).

New view on origin of the mosaic-block structures of gold, or a broad view, on origin of characteristic structures of aggregates of metacolloidal gold, that is stated in present work, is based on analysis of peculiarities of growth phenomena during process of natural sol-gel synthesis that took place at formation of the epithermal gold-silver deposits.

The multistage processes of ageing of coagulate, falling from solution on the mineral matrix in the form of the flat islet-like films or in the form of roundish or elongated clots play the leading role in formation of complex structures of metacolloidal gold.

Formation of syneresis cracks, that break the gel sediment on blocks bordered by the thin-porous rest matter is the initial stage of ageing (Ostwald ripening mechanism) of the flat spread films. The degree of porosity in borders reaches 50%; the form of pores is roundish; size of pore is 30-100 nm. The thickness of borders is from 100 nm to 2-3 microns. The blocks nearly 1 micron in size with the knob outlining in the centre are transformed in the crystalline polyhedra oriented by the threefold axis perpendicular to a plane (110) on the surface of matrix. The form of crystals is predominantly cubic; sometimes, it is complicated by the octahedron and dodecahedron faces (Fig. 2). The process of collective crystallization (coalescence) does not always reach the formation of the well-shaped crystal polyhedra, remaining separating blocks in the form of concretions of roundish and irregular shape, which are badly polygonized. The octahedral form of blocks was noted together with cubic form.

During precipitation and subsequent crystallization of the gold films on the surface of the quartz rhombohedron faces, the regular distribution of the gold cubic blocks by a law $(001)_{Au} \| (10\bar{1}1)_{SiO_2}$ was observed. The graphical comparison of two different adjoining planes (Fig. 3) shows the parallel orientation of the gold atoms in the rows $[\bar{1}00]$ and [010] and the silica-oxide tetrahedra in the rows on $[\bar{1}2\bar{1}0]$ and $[10\bar{1}2]$. The sections in the same planes of the gold and quarts structures are congruent by area with a precision up to ±1.5% at superposition of 25 unit cells of gold on 12 unit cells of quartz. Taking into account the pseudocubic structure of the quartz crystals with rhombohedral habit, $rr(10\bar{1}1):(\bar{1}101) = 85°46'$, one can say about the epitaxis of gold and quartz, which is almost exactly maintained at sizes of the gold particles not less than 2 nm, overgrowing on the surface of the quartz rhombohedra. At increase of particle sizes, the parallelism of planes of two minerals is broken, the arising tensions results in the origin of the linear dislocations, which result in the twisting of planes (001) of gold that was mentioned earlier (Novgorodova, 2004).

The collective crystallization, accompanying the syneresis processes, also took place during transformation of the interblock rest matter. The thin-porous cellular structure of borders is changed by the dendrite-like or «knitted» forms of the curve enlarged (to 100-150 nm) gold particles (Fig. 4).

The complex nanostructures of metacolloidal gold mentioned in the previous work (Novgorodova, 2004) are also owed by their origin to phenomena of the gel ageing, which falls in the form of clots on the surface of the quartz grains. The typical structures of the kneed-shaped gold aggregations with one of more openings and radial dispersing cracks in the centre are formed, as it was ascertained ear-

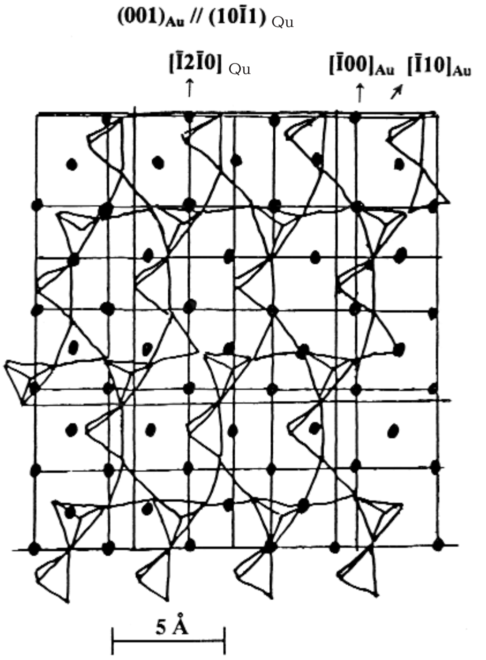


***Fig. 3**. Graphic superposition of planes (001) of gold and (10I1) of quartz*

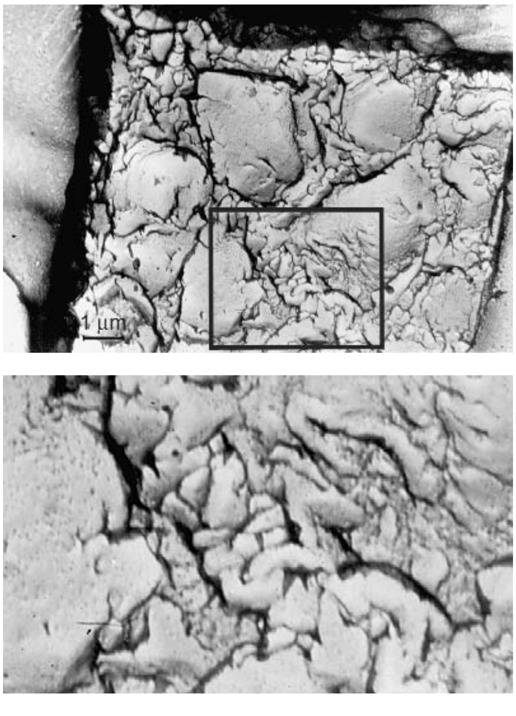


***Fig. 4**. Distorted «knitted» forms of nanoparticles of gold in the interblock space. PEM, etch., replica. Length of scale line is 1 micron (a) and 100 nm (b). Balei-Taseevskoe deposit (Zabaikalie)*

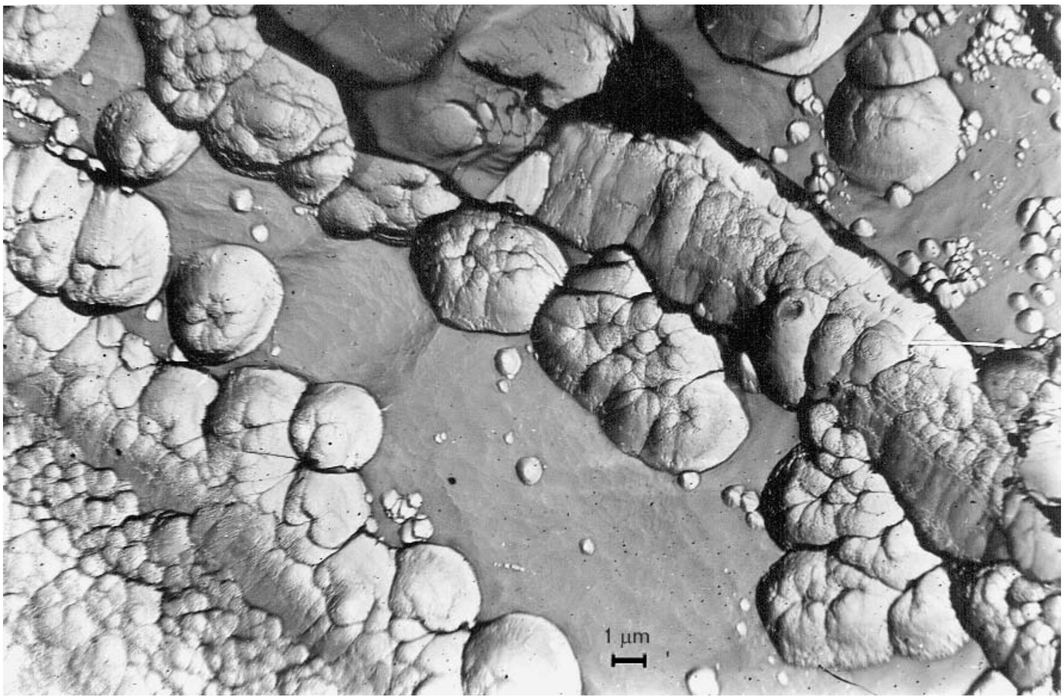
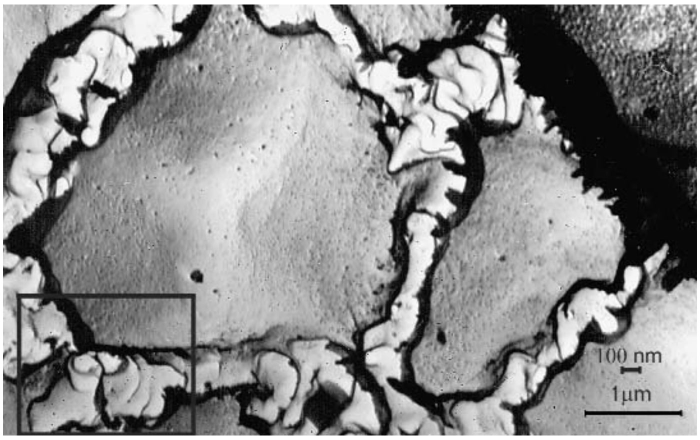


***Fig. 5**. Roundish and columnar aggregates of gold nanoparticles on quartz. PEM, etch., replica. Length of scale line is 1 micron. Agatovskoe deposit (Kolyma)*



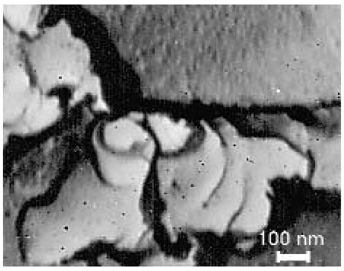


***Fig. 6**. Core-shell structure of native gold (a) and nanocone of gold in shell (b). PEM, etch., replica. Length of scale line is 1 micron and 100 nm. Agatovskoe deposit*

lier (Chukhrov, 1955), as a result of separation of dispersion phase. Transformation of the high-viscous rest brings to formation of the zoned aggregates with the radial disposed blocks in the centre and the columnar aggregates at the periphery. Diversity of arising structures depends in many respects from a ratio of the dispersion medium and dispersed phase in the gold coagulate, i.e. from degree of its supersaturation. In a high-viscous central part of clot, the blocks separated at the borders of the syneresis radial cracks do not have crystallographic outlines; features of rotary rotation of these blocks are considered earlier (Novgorodova, 2004); that is an evidence that in process of coalescence, the coherence of borders of neighbouring blocks was not yet reached. In the less viscous rest matter of borders and interblock space, the thin dendrites and intergrowths of the larger distorted crystals border the blocks or form the columnar aggregates on the quartz matrix (Fig. 5). It is known that formation of nanocolumns can be a result of the growth on inclined plane of base (Karabacak

Table1. **Variations of chemical composition (wt %) of gold with mosaic-block structure.**

No. of, sample-deposit	Phase	Au	Ag	Total	Stoichiometry	
					Empirical	Theoretical
KS 1390 Balei-Taseevskoe	6-1	83.94	13.60	97.53	$Au_{3.08}Ag_{0.92}$	Au_3Ag
	6-2 block	99.69	1.10	100.79	$Au_{3.92}Ag_{0.08}$	Au
	6-3	85.17	13.28	98.45	$Au_{3.11}Ag_{0.89}$	Au_3Ag
	6-4	73.38	25.33	98.66	$Au_{4.90}Ag_{3.10}$	Au_5Ag_3
	6-5	81.34	17.02	98.36	$Au_{3.17}Ag_{0.83}$	Au_3Ag
KS 845 Balei-Taseevskoe	8 block	89.14	9.00	98.14	$Au_{3.37}Ag_{0.62}$	Au
	10	87.83	10.99	98.82	$Au_{3.25}Ag_{0.75}$	Au_3Ag
	11	74.84	24.37	99.21	$Au_{5.00}Ag_{3.00}$	Au_5Ag_3
	12 block	92.15	5.33	97.48	$Au_{3.62}Ag_{0.38}$	Au
	13	80.86	17.95	98.81	$Au_{2.85}Ag_{1.15}$	Au_3Ag
	14	71.15	27.57	98.72	$Au_{4.68}Ag_{3.32}$	Au_5Ag_3
A-1234 Agatovskoe	A-1 block	63.14	36.42	99.56	$Au_{1.95}Ag_{2.05}$	AuAg
	A-1'	54.70	44.25	98.95	$Au_{3.22}Ag_{4.78}$	Au_3Ag_5
	A-2 block	64.12	35.21	99.33	$Au_{1.99}Ag_{2.00}$	AuAg
	A-3 block	64.10	35.71	99.81	$Au_{1.98}Ag_{2.02}$	AuAg
	A-3'	53.15	46.80	99.95	$Au_{3.06}Ag_{4.93}$	Au_3Ag_5
	A-4 block	63.23	36.18	99.41	$Au_{1.96}Ag_{2.04}$	AuAg

et al., 2003).

Core-shell structures of metacolloidal gold

The core-shell structures are the zoned structures of nanoparticles with core and shell, which are distinguished by chemical composition. Such structures are known for many pairs of metals and compounds synthesized for different purposes of nanotechnologies. The core-shell structures of gold with a silver shell were synthesized in the form of nanoparticles with a size nearly 20 nm and more; it is noted that at decrease of the nanoparticles size the core-shell structures cannot be formed. The reasons of immixability of gold and silver at formation of the core-shell structures in a range of the nanoparticles sizes of ~20 nm remain uncertain (Shibata *et al.*, 2002).

Arising at crystallization of natural gels, the polycrystalline constructions have the zoned structure with the poly- and monoblock core and a border composed by aggregate of the smaller, crystallographically distorted particles. The distortion of forms is especially visible in the case, when blocks are brought together and borders are narrow (150-200 nm). In conditions of the constrained space, such unusual forms as nanotubes and nanocones are formed, which were not earlier known both for natural and synthesized gold. The diameter of the gold nanocone at the basis is ~100 nm, in upper part it is -200 nm (Fig. 6). By analogy with the synthesized nanoparticles, one can suppose that a process of the planes twisting is determined by the dislocation mechanism, for nanotubes it is determined by dislocations with angle and screw components, and for nanocones it is determined by disclines (Pokropivny, Pokropivny, 2003).

Differing by sizes, which are larger at two-three orders than the synthesized nanoparticles with core-shell structure, the natural polycrystalline constructions show the morphological similarity to them. One failed to obtain, with necessary precision, the difference in chemical composition of core and shell of the zoned polycrystalline constructions, by electron microprobe analysis method because of low locality of the method. Estimation of chemical composition in the first approximation was made by the method of microprobe scanning along the profile with a step in 1 micron. Relatively large blocks and their aggregations and also the interblock space with size in several microns were studied. The obtained data (Table, Fig. 7) reflect with convincingness the tendency to enrichment of the interblock space and borders by silver around cores with increased content of gold. The calculated chemical compositions approach to stoichiometric ones. In relatively high-fineness (average fineness is 750-850) lamellar gold from the Tasseevskii region of the Baleiskoe deposit, the aggregations of blocks of

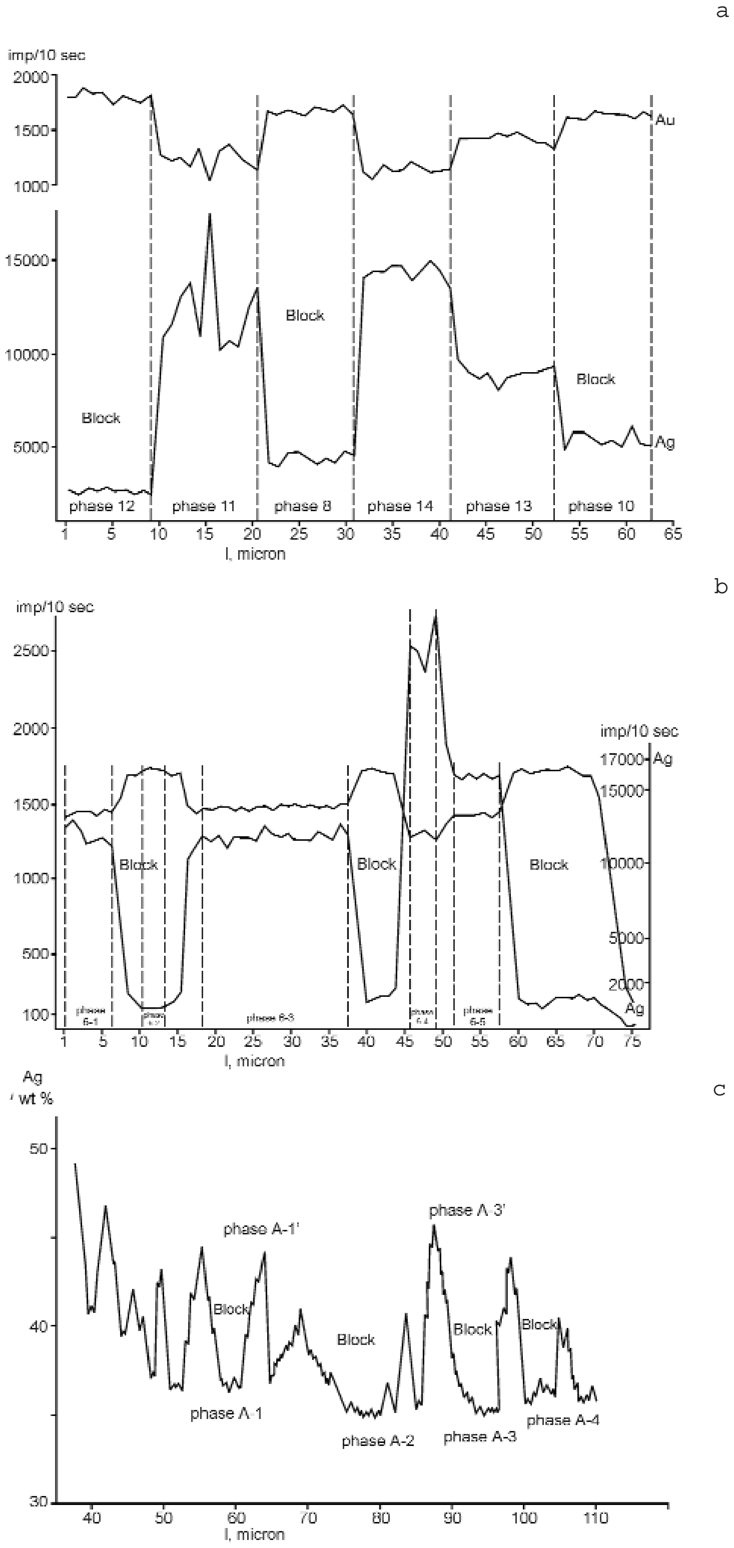


Fig. 7. *Variations of chemical composition along profile through gold particle with mosaic-block structure: a, b — Balei-Taseevskoe deposit; c — Agatovskoe deposit. Numbers of phases correspond to numbers in Table*

almost pure gold are bordered by the porous or dendrite-like interblock matter with chemical compositions close to Au_3Ag and Au_5Ag_3. In low-fineness gold from the Agatovskoe deposit, the blocks have chemical composition AuAg, and borders around them are Au_3Ag_5. Since microprobe analyses, which results are given in Table, were calculated with averaging by several, not less than 10, measurements, the more precision studies of chemical composition with locality J100 nm are necessary, and the above-mentioned data should be considered as preliminary.

Discussion

The evident differences in morphology of metacolloidal gold precipitated of the surface of placer gold in river alluvium and occurring in the gold-quartz veins of epithermal deposits are caused by the differences in kinetics of sedimentation and subsequent aggregation of colloidal nanoparticles, which is connected, in its turn, with obvious differences in physical-chemical parameters of the mineral-forming medium. The slow precipitation of colloidal particles of new gold, formed by mechanic way during grinding of gold particles in water stream, results in formation of the friable branched forms (Brechignac *et al.*, 2001), and their heterodispersed state reduces coalescence (Hoogenboom *et al.*, 2002) and prevents to formation of the large coherent domains. The polycrystalline patterns of microdiffraction of electrons obtained from such gold confirm this conclusion. The wire-like forms, as it is shown in the work (Hui *et al.*, 2003), usually consist of the incoherent domains of polyhedral form (distorted icosahedral polyhedra of Frank-Kasper and hollow polyhedra of Bernal), however, it is impossible to check it on natural samples.

The compact clots and films of gold, falling from the supersaturated hydrothermal solutions, have the long history of ageing, aggregation and recrystallization, which final result is formation of the mosaic-block structures of gold with heterogeneous distribution of silver admixture. Following experimentally ascertained facts require discussion.

1. In the process of syneresis and coalescence at early stages of ageing of coagulate penetrated on quartz matrix, the gold blocks of cubic form are quite often formed, whereas, at texturation of sediment, it was necessary to expect the primary orientation of particles on most compact packing plane of octahedron (111). The reason of that, as it was shown above, is in epitaxial correlations between atomic structure of face (001) of gold and pseudocubic structure of face of rhombohedron of quartz, at that $(10\bar{1}\bar{1})$ of quartz $\parallel$ (001) of gold and $[\bar{1}2\bar{1}0]$ of quartz $\parallel$ [100] of gold. The orienting influence of square base on growth of cubes of face-centred metals is also ascertained experimentally; it is shown that first 50 atomic layers in cubes have the ideal perfect structure (Zhang *et al.*, 2002). We should also note that contact between Au (metal) and SiO_2 (insulator) provides with the tunnel effect at current passing through solder with chemical composition Au-SiO_2-Si, unfortunately, the state of the boundary layer remains unknown (Pal *et al.*, 2004). Nevertheless, probability of the tunnel effect rise in the gold-quartz intergrowths is interesting for elaboration of electroimpulse methods of ore concentration.

2. The process of coalescence with separation of blocks and interblock space are accompanied by the clearly pronounced heterogeneity in distribution of gold and silver. Blocks in all analysed samples have increased content of Au. Since diffusion of particles in viscous matter of gels is troubled and even practically impossible (Chukhrov, 1955), it is necessary to admit that regrouping of initially heterogeneous by chemical composition nanoparticles with forward and rotary movement along thin cracks of membrane type, arising during syneresis, causes such effect. In that case, the membrane permeability for nanoparticles with high contents of Au must be higher than for the high-silver nanoparticles. Formed by this way, the aggregative core-shell structures are distinguished from synthesized ones not only by sizes but also by way of formation. In synthesis of core-shell nanostructures, the method of consecutive penetration of the Ag salts on already formed gold nanoparticles is applied; whereas in natural matter, the processes of self-organization of colloidal coagulate prevail.

3. It is accepted to consider that coalescence of nanoparticles in colloidal coagulate is realized under influence of the weak long-ranged forces of Van-der-Vaals type. However, recently for explanation of complicated movements of nanoparticles, joining in crystalline constructions, the formalism of thermal and statistic models of Casimir is engaged, which is used in quantum electrodynamics (Gopinathan *et al.*, 2002).

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DELHAYELITE CRYSTALS FROM RISTSCHORRITES OF THE RASVUMCHORR PLATEAU (KHIBINY MASSIF)

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The small (to 0.2x0.3x2 mm) well-shaped delhayelite crystals, sometimes double-terminated, were found in the Khibiny massif in the macrocrystalline fenaksite aggregations in ristschorrites of the Rasvumchorr plateau. The crystals are prismatic, elongated on c axis, in different degree flattened on b axis; 10 simple forms are determined (measured for the first time). Parameters of the rhombic unit cell are as follows: a = 6.52(1); b = 24.83(6); c = 7.07(1) Å; V = 1144.95 Å^3. The studied delhayelite is characterized by the highest content of the alkaline elements known for delhayelites; the content of H_2O is low (by the IR spectroscopy data and chemical analyses), especially in the grey, darkest crystals, representing unaltered delhayelite. The X-ray powder pattern (the most intensive lines are as follows (d, A (I)): 3.10 (10), 3.03 (9), 2.87 (9), 1.910 (10), 1.630(10)) and the IR spectrum are given.
3 tables, 2 figures, 14 references.

The well-shaped small (to 0.2x0.3x2 mm in size) delhayelite crystals, sometimes double-terminated, were found in the crystalline aggregations of ultraagpaitic minerals coarse ristschorrites of the Rasvumchorr plateau (the Central mine). Delhayelite, Cl- and F-bearing alumosilicate of Ca and alkaline elements, was found for the first time by M.D. Dorfman in 1952, in pegmatites among the massive urtites of the Material'naya adit (Mt. Yukspor), and described under the name «mineral No. 3» (Dorfman, 1958). In 1959, a new mineral, delhayelite, was described (Sahama, Hytцnen, 1959) from kalsilite-bearing melilite-nepheline lavas of the Shaheru volcano (DR Congo). Since that time, for the Khibinian «mineral No. 3», similar, but not identical to delhayelite from Congo, the name «delhayelite» was accepted (Dorfman, 1962). The mineral is quite widely spread in massive urtites and ristschorrites containing the beds of apatite-nepheline ores (Kostyleva-Labuntsova *et al.*, 1978). The lamellar mica-like delhayelite grains reach 10 cm in length and sometimes form large (up to 30 cm in size) monomineral aggregations.

The delhayelite crystals found by us are confined to the branching veinlet-like (up to 4 cm in size) and nest-shaped (up to 7 cm in diameter) macrocrystalline aggregations with irregular and unclear borders. They are composed by fenaksite, in which lomonosovite, villiaumite, djerfisherite, and rasvumite are noted. The grey, light grey and colourless delhayelite crystals form inclusions in fenaksite (Sokolova *et al.*, 1993). Moreover, in cavities among crystalline aggregates of fenaksite, the smaller (up to 0.1x0.2x1 mm) delhayelite crystals occur; their lagest face overgrows on the fenaksite prismatic crystals (4x5x8 mm in size).

Five colourless and grey translucent crystals were measured with the Goldschmidt two-circle goniometer (Tabl. 1). The symbols of faces were detected by a method of double ratios of cosines (the Wul method) and verified by the trigonometric formulae. In the accepted orientation, the axes ratio is as follows: *a:b:c* = 0.8101:1:0.866. They are more close to the structural orientation by Chiragov and Mamedov (1974) (*a:b:c* = 0.266:1:0.288), distinguishing by the segments on axis *a* and *c*, which are three times larger.

According to the measurements, the prismatic crystals of delhayelite are elongated on

Table 1**. Faces coordinates of delhayelite crystals**

Symbols of faces	Data of measurements (average values)		Calculated coordinates	
	φ	ρ	φ	ρ
010	0°00′	90°00′	0°00′	90°00′
160	11 36	90 00	11 50	90 00
340	42 42	90 00	42 10	90 00
110	50 59	90 00	51 00	90 00
025*	0 00	20 30	0 00	19 06
011*	0 00	40 30	0 00	40 54
223*	50 54	41 10	51 00	42 30
111	50 59	53 59	51 00	54 00
443*	50 54	62 00	51 00	61 24
322*	60 40	58 56	61 42	61 18

* *Found only on one crystal*

c axis and flattened on b axis in different degree (Fig. 1). In prismatic zone, the face (010) is the best developed, the cleavage is distinctly pronounced by this face; other faces are very narrow.

Parameters of the rhombic unit cell of the studied delhayelite are close to the parameters determined earlier for other samples: a=6.52(1); b=24.83(6); c=7.07(1)Å; V=1144.95Å^3. The X-ray powder pattern contains more than 50 lines (Tabl. 2).

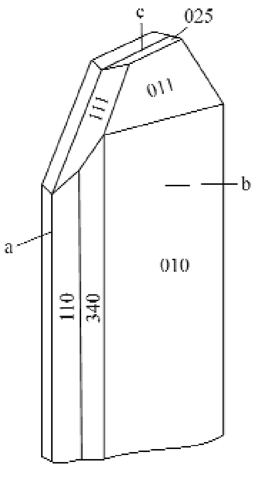
Chemical analyses of four delhayelite crystals (Cameca MS-46 electron microprobe instrument) are given in Table 3, where also analyses of the Khibinian lamellar delhayelite, the mineral from Congo and hydrodelhayelite are presented.

It is well-known, that delhayelite is easily hydrated. In all known analyses is H_2O (to 2 wt %), which is an evidence of the late hydrothermal or hypergene alteration of mineral that results in formation of hydrodelhayelite (Chiragov, 1978; Dorfman, Chiragov, 1979). The carrying-out of Na, F, Cl, and partly K takes place (Chiragov, Mamedov, 1974; Ragimov *et al.*, 1980; Canillo *et al.*, 1970).

Water was not determined in the delhayelite crystals because of lack of material. Therefore the IR-spectra of the studied crystals with those of lamellar delhayelite specimens with the known H_2O content (an. 6 in Table 3) and with IR-spectra of the hydrodelhayelite with the highest content of H_2O (an. 8 in Table 3), were compared.

The IR spectra (Fig. 2) were obtained with a Specord 75 IR spectrophotometer in the range 400-4000 cm^{-1}. The standards were gaseous ammonia and polystyrene. Samples were prepared by a standard method, as pellets with KBr. The spectrum of KBr was subtracted automatically. In the range 500-800 cm^{-1} (the most sensible to fine structural peculiarities of silicates), all samples of delhayelite give the same set of narrow bands with the absorption maximums at 590, 607-608, 635-636, 662-665, and 701-703 cm^{-1}. In the range of water molecules vibrations, the IR spectra of coarse-lamellar delhayelite and of the studied crystals are identical (Fig. 2, spectrum 1): they contain a weak broad band of stretching vibrations in a range of 3300-3700 cm^{-1} and two weak bands of H-O-H bending vibrations in the frequency ranges 1560-1585 and 1625-1640 cm^{-1}. Presence of two types of the stretching H-O-H angles is an evidence of polytypic state of water molecules in delhayelite. The comparing samples insignificantly differ only by position of the maximum in a range of 1070-1090 cm^{-1} (1077 and 1086 cm^{-1} respectively). In this interval, the stretching vibrations of the Si-O-Si bridge, as well as stretching vibrations of the SO_4-groups are shown. Possibly, these samples differ by content of the sulphate anions (in these samples sulphur was not determined).

The IR spectrum of hydrodelhayelite is strongly distinguished from the spectrum of delhayelite in all range 400-4000 cm^{-1}, that is an evidence of significant changes of del-



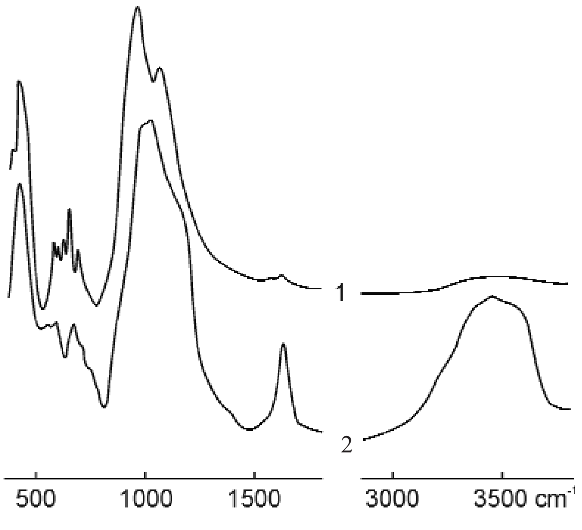


***Fig. 1**. Delhayelite crystal from inclusions in fenaksite*

***Fig. 2.** The IR spectra of delhayelite (1) and hydrodelhayelite (2)*

hayelite in the process of the hydrodelhayelite formation, which affects not only on large cations and water molecules but also on all covalent-bonded system (double layer). In particular, together with the series of the low-distinct strong bands of stretching vibrations of water molecules (3325-3520 cm^{-1}) and a band of bending vibrations of water molecules (1640 cm^{-1}) in the spectrum of hydrodelhayelite is the well-pronounced shoulder at 3210 cm^{-1} and also very bad-pronounced shoulders at 3040 and 1715 cm^{-1}, which can be the evidence of existence of the acidic-basic equilibrium of the following type: $(Si\text{-}O\text{-}H)^{+\delta} + H_2O$ $Si\text{-}O +$ H_3O^+. Together with delhayelite and hydrodelhayelite, in pegmatites of Khibiny there is a number of related minerals with the intermediate degree of hydration, which give the individual sets of narrow bands in a range 500-800 cm^{-1}.

As analyses showed, the studied delhayelite is characterized by the highest content of potassium ever analysed delhayelites (Dorfman, 1958; Kostyleva-Labuntsova *et al.*, 1978; Ageeva, 2002; Ageeva, Borutsky, 2004; Sharygin, 2002; Pekov, Podlesnyi, 2004). The potassium content in crystalsof delhayelite, forming inclusions in fenaksite, is higher that than in the accessory delhayelite from ristschorrites. In the latter, analysed by O.A. Ageeva (2002) for the first time, the content 17.32 – 18.87 wt % of K_2O or 3.35-3.65 K per formula was detected (electron microprobe analyses, 16 samples). The content of K_2O is inconstant and always exceeds the theoretical value by calculation on the following formulae: $K_7(Na_3Ca)Ca_4[AlS_{i7}O_{19}]_2F_4Cl_2$ (Canillo *et al.*, 1970) and $K_3Na_2Ca_2[(Al,Si)_8O_{19}](F,Cl)_2$ (Chiragov, Mamedov, 1974). This discrepancy was noted earlier (Ageeva, 2002; Ageeva, Borutsky, 2004; Sharygin, 2002), and for the studied delhayelite crystals it is more remarkable (to 3.94 K per formula). Apparently, the K site in the crystal structure requires refinement.

Table 2. **X-ray powder data of delhayelite from ristschorrites of the Rasvumchorr plateau (Fe-radiation, D=114.6 mm)**

hkl	*I*	*d* (Å)	*hkl*	*I*	*d* (Å)	*hkl*	*I*	*d* (Å)
200	5	12.94	322	4	2.303	233	2	1.585
110	1	6.71	802	4	2.258	314	3	1.565
400	1	6.24	003	6	2.176	433	4	1.547
–	2	6.04	303	7	2.103	342	5	1.527
301	1	5.07	431	0.5	2.089	533	5	1.522
401	2	4.43	11.1.1	4	2.045	442	7	1.503
311	2	4.10	912	5	2.003	633	0.5	1.492
411	1	3.79	722	2	1.975	124	2	1.479
601	1	3.49	032	10	1.910	804	6	1.444
511	7	3.44	731	2	1.880	14.2.2	1	1.429
220	6	3.36	023	7	1.851	814	5	1.414
102	6	3.24	223	3	1.833	624	2	1.395
710	3	3.19	930	6	1.792	724	5	1.369
800	10	3.10	14.0.0	2	1.778	11.4.1	2	1.362
121	9	3.03	040	7	1.757	942	7	1.354
112	7	2.94	632	7	1.732	824	2	1.339
402	9	2.87	903	3	1.710	651	3	1.309
801	7	2.815	440	3	1.701	052	3	1.297
421	7	2.753	623	2	1.687	252	2	1.291
502	3	2.712	10.3.1	1	1.655	332	2	1.282
412	5	2.660	104	10	1.630	452	3	1.271
621	7	2.458	033	2	1.598			

Table 3. **Chemical composition of delhayelite and hydrodelhayelite (wt %)**

No. of sample. Constituent	1	2	3	4	5	6	7	8
Na_2O	7.29	7.04	7.20	7.45	6.88	6.52	3.20	0.22
K_2O	20.20	20.14	20.75	19.91	17.94	18.37	9.27	6.13
CaO	13.02	12.74	12.77	12.59	14.55	14.52	7.99	12.72
SrO	0.41	0.21	0.47	0.09	0.12	–	–	0.22
MgO	0.00	0.04	0.00	0.08	0.14	0.17	1.03	0.21
MnO	0.13	0.14	0.09	0.12	0.08	0.10	0.07	0.18
Fe_2O_3	0.69	0.55	0.53	0.57	0.67	0.54	2.72	0.65
Al_2O_3	5.76	5.52	5.99	6.26	6.48	6.59	9.22	8.46
TiO_2	0.00	0.00	0.00	0.00	0.07	Cл.	0.09	0.01
SiO_2	47.42	47.02	46.67	48.11	46.36	46.34	52.60	55.53
H_2O^+	n. d.	n. d.	n. d.	n. d.	1.23	1.49	5.93	5.58
H_2O^-	n. d.	n. d.	n. d.	n. d.	1.06	0.42	3.35	9.62
F	2.31	2.41	2.49	2.59	2.81	2.80	0.33	–
Cl	3.69	3.89	3.99	3.83	3.47	3.42	3.91	0.15
-O=F_2, Cl_2,S	1.83	1.88	1.95	1.89	1.99	1.94	1.01	0.03
Total	99.09	97.85	99.20	99.71	100.21*	99.34	100.01**	99.65
Formula coefficients (calculation on Si+Al=8)								
Na	2.09	2.04	2.08	2.08	1.98	1.87	0.78	0.05
K	3.80	3.84	3.94	3.66	3.39	3.46	1.49	0.96
Ca	2.06	2.04	2.04	1.94	2.31	2.30	1.08	1.66
Sr	0.04	0.02	0.04	0.01	0.01	0.00	–	0.02
Mg	0.00	0.01	0.00	0.02	0.03	0.04	0.19	0.04
Mn	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.02
Fe	0.08	0.06	0.06	0.06	0.06	0.07	0.26	0.06
Al	1.00	0.97	1.05	1.06	1.15	1.13	1.37	1.22
Ti	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Si	7.00	7.03	6.95	6.94	6.87	6.85	6.63	6.78
F	1.08	1.14	1.17	1.18	1.32	1.31	0.13	–
Cl	0.92	0.99	1.01	0.94	0.87	0.86	0.84	0.03

Note: ** – analysis total also contains (wt %): BeO – 0.17; REE_2O_3 – 0.11; S – 0.06. ** – analysis total contains SO_3 – 1.31 wt %. An. 1-4 – crystals of delhayelite from ristschorrites, the Rasvumchorr plateau; analyst T.I. Golovanova; 5, 6 – macrolamellar delhayelite: 5 – from pegmatite in massive urtite, Mt. Yukspor, analyst L.D. Nikitina (Dorfman, 1958); 6 – from pegmatite in ristschorrite, the Apatite circus of the Mt. Rasvumchorr, analyst G.M. Varshal (Kostyleva-Labuntsova et al., 1978); 7 – lamellar delhayelite from calcite-bearing melteigite-nepheline lavas of the Shaheru volcano, DR Congo (Sahama, Hytonen, 1959); 8 – hydrodelhayelite from pegmatite in ristschorrite, the Apatite circus of the Mt. Rasvumchorr, analyst G.M. Varshal (Kostyleva-Labuntsov a et al., 1978)*

For our delhayelite specimen, the surplus of Ca and deficiency of Na, which were noted for lamellar delhayelite (Sharygin, 2002), are not characteristic.

The original delhayelite from Congo (an. 7, Tabl. 3) is probably partly altered; it differs by lower content of the alkaline elements and high content of H_2O and occupy the intermediate position between proper delhayelite and hydrodelhayelite by chemical composition.

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Mineralogical Museums and Collections

UDC: 549.2

PLATINUM OF THE UGOLNYI STREAM (NORILSK) FROM THE FERSMAN MINERALOGICAL MUSEUM COLLECTION

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Three specimens from the Mineralogical Museum, catalogued as «platinum» from placer of the Ugolnyi stream (Norilsk), appeared to be complicated mixture of zoned minerals. By chemical composition the following mineral phases were found: tetraferroplatinum, ferronickelplatinum, isoferroplatinum, minerals of the atokite-zvyagintsevite series, stannopalladinite.
It is supposed that formation of particular pseudomorphs of fine-grained aggregates, in which minerals of Pd-Sn-Pb-Cu system and isoferroplatinum prevail, after monocrystals of tetraferroplatinum is connected with local combination of different stages of formation of precious metal mineralization.
1 table, 5 figures, 7 references.

In funds of the Mineralogical Museum are three specimens registered as platinum from the Ugolnyi stream (Norilskii region). These are the first Museum specimens from the Norilsk deposits. Two of them (41647 and 46887) were received from professor Orest Evgenievich Zvyagintsev, researcher of chemistry of precious metals, one of organizers of industrial mining of platinoids in the USSR.

The samples were registered in collection of the Museum in 1938 and 1949. Judging by author's label appended to the specimen 41647 (Fig. 1), it was mined during panning out of placer of platinoids of the Ugolnyi stream in September, 1938. Pencil caption made in the Museum on this label runs: «From O.E. Zvyagintsev who has analogous Pt». That allows supposing that other samples keeping in the Museum were possibly mined at the same time. It is not excluded that also this find resulted in issue of joint decree of the Communist Party Central Committee and Soviet Government of April 7, 1939, «On forcing of building of Norilsk industrial complex».

In 1948, academician Vladimir Afanasievich Obruchev, the most well-known geologist, geographer, author of books «Plutoniya» and «Sannikov's Land» presented a platinum specimen from the Ugolnyi stream (45863) to the Fersman Museum.

It is difficult to expect accurate data about genealogy of specimens from the Norilsk deposits found in 30-40s of 20th century. Since 1935 till 1956 the Norilsk deposits were mined by Norillag (one of soviet concentration camps). First mines of the Ugolnyi Sream and Gora Rudnaya deposits, nickel, cobalt, and copper factories were built by prisoners, whose number had been continuously increased from 1200 in 1935 to nearly 60 000 in 1949 (Norilsk Calvary, 2002).

Evidences about that time can be picked up in diaries of former prisoner of Norillag, Efrosiniya Kersnovskaya, who was there in 1944 (Kersnovskaya, 2000-2004).

«*What an unsightly Norilsk appeared through rain shroud! Coal mines and places, where peoples, deprived all human rights, live, work and die, made this place even more ugly. We could quite enough «admire» Zero picket, i.e. geodesic point where counting of route Norilsk-Dudinka began.*

Black gorge, along which a black stream flows, and some black buildings cling along it, whistling wind, also black, black slush, on which they ordered us, frozen, hungry, and tired, to squat, — all that made our reflections by no means lighter than surrounding landscape...

The most part of mines and pits are in two mountains, between which the Ugolnyi stream flows. The Mt. Saint Helene is at its southeast bank. Ore bodies of huge thickness and intricate form are contained in it. It is mined very intensively: both open quarry, in the manner of Easter cake, and simultaneously cutting deep into the mountain. At another bank of the Ugolnyi stream to northwest is the Shmidt mountain, or plainly «Shmitikha», as a cake «Napoleon»: thick layers of coal are alternated with intercalations of barren rock...

Nickel was the main ore mined in Norilsk. Copper, cobalt, and molybdenum were mined too. Platinoids, i.e. platinum, gold, and silver, went in waste of concentrating factory, so-called «tails». By pipes they were transferred in tundra, and lakes were filled up by them: amount of platinoids in «tails» is insignificant and their mining was considered unprofitable...»

Now this Ugolnyi stream is at the south outlying districts of Norilsk. Its placers are not entirely worked till now (Geomarkinform, 2004).

Table 1. **Microprobe analyses of phases in grain of specimen 41467, wt.%**

	Pt	Pd	Fe	Ni	Cu	Sn	Pb	Rh	Ag	Au	S	Σ
1	75.29	0	18.14	3.99	2.34	0	0	0	0	0	n.d.	99.75
2	74.85	0	18.06	3.91	2.28	0	0	0	0	0	n.d.	99.09
3	74.96	0	18.02	3.79	2.31	0	0	0	0	0	n.d.	99.07
4	60.94	2.61	18.75	12.61	3.70	0	0	0	0	0	n.d.	98.60
5	66.76	2.17	17.68	8.20	3.66	0	0	0	0	0	n.d.	98.48
6	30.59	30.02	9.40	4.06	6.17	13.24	0	0	0	0	n.d.	93.48
7	84.24	0	9.74	0.51	0.62	0	0	1.83	0	0	n.d.	96.94
8	15.13	51.42	0.81	0	4.94	23.50	1.70	0	0	0	n.d.	97.5
9	0.24	59.29	0.11	0.00	0.47	0	39.84	0	0	0	n.d.	99.95
10	0	59.23	0.41	0	7.06	17.56	16.08	0	0	0	n.d.	100.34
11	0	57.90	0.46	0	8.76	16.22	17.72	0	0	0	n.d.	101.06
12	0.58	64.35	0.49	0.09	1.12	7.74	27.35	0	0	0	н.о	101.72
13	0	56.65	0.54	0	9.39	11.79	18.67	0	0	0	n.d.	99.16
14	0	57.09	0.51	0.10	9.66	12.59	20.62	0	0	2.33	n.d.	102.9
15	n.d.	0	37.18	17.61	0	n.d.	n.d.	n.d.	13.61	0	31.35	99.75

* *n.d. — not determinated*

They have alluvial origin and are genetically related to rocks of west branch of the Norilsk I intrusion.

Museum specimens mined during panning out of placer of the Ugolnyi stream are represented at Figure 2. Size of grains is 1-10 mm. Grains are cube-shaped, parallelepiped-like, flattened. Features of skeletal growth are visible on many of them. Surface of grains is dull, brownish-grey; edges are slightly rounded.

Initial diagnostics of them as «platinum», obviously, was checked with quantitative analysis of surfaces of faces in 1970-1980s. As a result of that on museum labels the mark (Pt_3Sn) and note «rustenburgite» in the box with sample 41647 have appeared. A perspective to have in the museum collection the large crystals of rustenburgite (Pt Sn) forced to study these samples in more details. Preliminary electron microprobe analysis of surfaces of crystals has confirmed the presence of tin in them (at predominance of Pt and presence of significant admixture of Pd). However, strong ferromagnetism of considerable part of grains is evidence of presence of iron-platinum intermetalids in them.

New data on mineralogical compositions of these grains was obtained by study of section of one of them, with size 2 mm and cube-like form. Only after polishing the zoning of the grain, the well-polishing central zone with the most high relief and dull periphery with smaller hardness than central zone according to its relief, have been found. Analyses of some phases of this grain are given in Table 1.

Analyses 1-3 by chemical composition match to copper-nickel variety of tetraferroplatinum, $Pt_{0.95}Fe_{0.80}Ni_{0.16}Cu_{0.09}$. They correspond to central part of the grain (zone A at Fig. 3), in which among associating phases the rounded inclusions 20-100 μm in size, determined as magnetite, are found.

Around central part of the grain is a zone 20-100 μm in size, with small inclusions, which obviously resulted from exsolution (zone B at Fig. 3). They form lamellae, reticulate ingrowths in matrix, round-drop-shaped grains. Size of grains is up to 10μm, thickness of lamellae is up to 5 μm. Analyses 4 and 5 in Table 1 reflect the chemical composition of this zone. Averaged formula in calculation on 4 atoms is as follows: $Pt_{1.44}Pd_{0.10}Cu_{0.26}Fe_{1.42}Ni_{0.78}$. Among mineral phases known so far only ferronickelplatinum closely matches these analyses. Enrichment of this zone by Ni and Pd is notable as compared to central zone. Analysis 6 shows the composition of one of the phases resulted from exsolution. Probably, some material of matrix is presented in this analysis, an exsolution results in formation of phases enriched by Pd, Sn, and Cu. Close to periphery, aggregate with lamella-shaped exsolutionary phases is changed by a zone of Pd-Cu-Sn-Pb phases, more dark in back-scattered electrons (Fig. 4).

Peripheral zone (zone C at Fig. 3), 100-500 μm in size, represents fine-grained aggregate, in which phases of the Pd-Cu-Sn-Pb system, 2-50 μm in size, and the Pt-Fe system, less than 5 μm in size, prevail (Fig. 5). Grains in this zone are often surrounded by grey in

Fig. 1. *Specimen 41647 from the Museum collection with labels:*
On the label the following is written with pen:
Coll. N. 2959,
large platinum
from placer
at the Ugolnyi stream,
Norilsk. September, 1938.
The following is written with pencil:
from O.E. Zvyagintsev
who has analogues Pt.

Fig. 2. *Specimens registered as platinum from the Ugolnyi stream from the Museum collection. a — 41647, b — 45863, c, d — 46887 (d — more detailed image of three grains). Diameter of a coin is 17 mm.*

reflected light phases, in which composition only Fe is detected. Probably, these are iron hydroxides, resulting in brown colour of «platinum» grains surfaces. The Pt-Fe phases of this zone are distinguished from matrix of central zone by increased content of Pt and insignificant amounts of Ni, Cu and also notable presence of Rh, which was not registered in other phases. Analysis 7 made for such grain allows to consider it as isoferroplatinum, ($Pt_{2.69}$ $Rh_{0.11}$ $Cu_{0.06}$ $Fe_{1.09}$ $Ni_{0.05}$).

Phases of the Pd-Cu-Sn-Pb system the most significant differ on ratios of Sn and Pb. Maximal content of tin is noted for phase 8, ($Pd_{2.25}Pt_{0.36}Cu_{0.36}$ $Fe_{0.07}Sn_{0.92}Pb_{0.04}$), which can be identified as stannopalladinite. Enriched by lead phase 9, ($Pd_{2.93}Pt_{0.01}Cu_{0.04}Fe_{0.01}Pb_{1.01}$), among known mineral phases, can be identified as zvyagintsevite. Phase at the periphery of grain, which has averaged chemical composition, $Pd_{2.43}Cu_{0.54}$ $Fe_{0.04}Sn_{0.63}$ $Pb_{0.36}$, (analyses 10, 11) can be presumably determined as lead stannopalladinite.

At the outside surface of studied grain are phases 12, $Pd_{2.91}Pt_{0.01}Cu_{0.08}Fe_{0.04}Sn_{0.31}Pb_{0.64}$, (tin-enriched atokite), 13 and 14 with almost similar atomic content of Sn and Pb, $Pd_{2.42}$ $Cu_{0.67}Fe_{0.04}Sn_{0.45}Pb_{0.41}$ and $Pd_{2.34}Cu_{0.66}$ $Au_{0.05}Fe_{0.04}Ni_{0.01}Sn_{0.46}Pb_{0.43}$ respectively. In phase 14, admixture of gold is noted, which was not detected in other analysed phases. Sulphide phase (analysis 15) identified as argentopentlandite, $Ag_{1.04}Fe_{5.47}Ni_{2.46}S_{8.03}$, intergrows with it. Silver and gold are present also in chemical composition of electrum, forming inclusions to 10 μm in size in the outside zone of the «platinum» grain.

Smoothed, winding borders between zones in this grain do not correlate with its facing and, obviously, are not connected with grain growth, but resulted from secondary processes. Heterogeneity of peripheral zones is another evidence of that.

One can suppose that here we deal with local superposition of two stages of precious metal mineral formation. Earlier formed crystals of copper-nickel tetraferroplatinum were exposed to influence of fluids, forming assemblage of minerals of the Pd-Cu-Sn-Pb chemical composition typical for the Norilsk deposits (Questions..., 1973; Minerals..., 1986; Sulphide Copper-Nickel Ores..., 1981). Some components of these mediums (in particular, Pd and Sn, transported in fluid phase (Spiridonov, 2003)), obviously, diffuse in crystals of tetraferroplatinum, forming the zone of Pt-Pd-Sn solid solutions, which are disintegrated when temperature decreases. Further influence of these

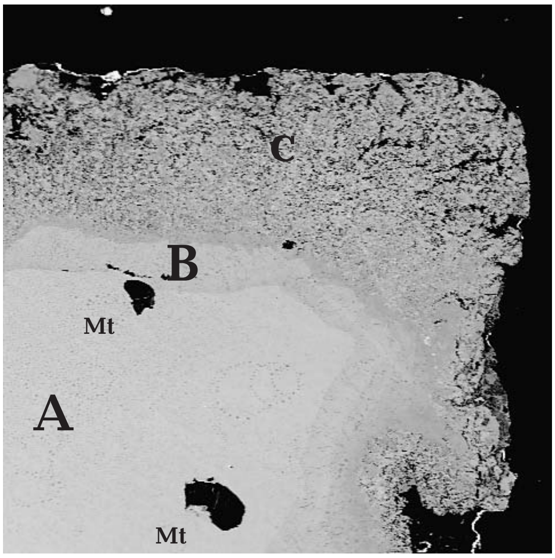

Fig. 3. *Image of a grain from the specimen 41647 in back-scattered electrons. Image size is 1500 μm Mt — magnetite.*

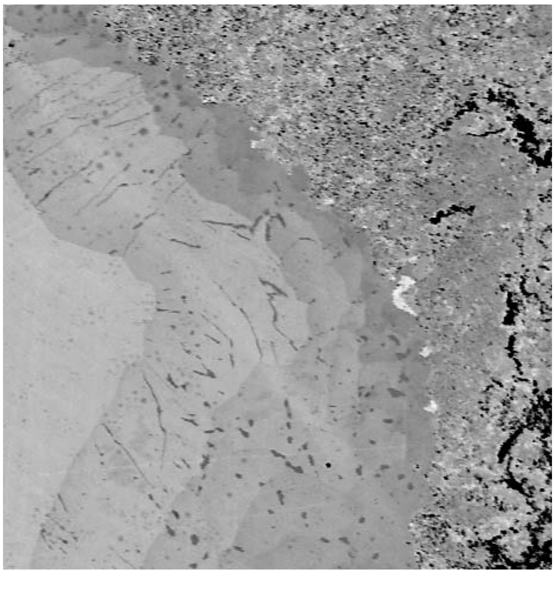

Fig. 4. *Image of a part of B zone in back-scattered electrons. Image size is 500 μm.*

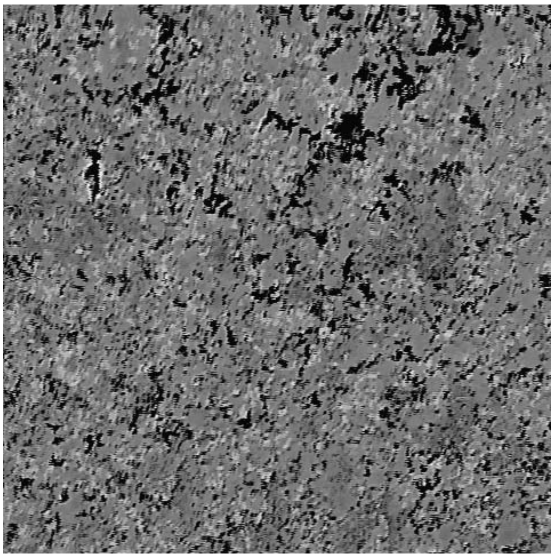

Fig. 5. *Image of a part of C zone in back-scattered electrons. Image size is 250 μm .*

liquids results in pseudomorphic substitution of outside zone of crystals. In this case, platinum of disintegrated primary phases forms the outside zone of grains of isoferroplatinum, and excess iron is transformed to hydroxides.

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UDC 549:069.

MINERALS NAMED IN HONOUR OF THE COLLABORATORS OF THE A.E. FERSMAN MINERALOGICAL MUSEUM

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Almost three hundred years history of existence and development of the Fersman Mineralogical Museum is closely connected with names of widely-known scientists who made an important contribution to development of mineralogy. Names of 28 outstanding mineralogists, collaborators of the Museum, became a part of the history of mineralogy forever. 23 mineral species, 9 mineral varieties, and stony-iron meteorites, pallasites, were named in their honour. In the article the scientific interests and attainments of collaborators of the Museum, whose names were conferred to minerals, are briefly described; also brief characteristic of these mineral species and varieties is given. 28 photos, 100 references.

A history of foundation and development of the Fersman Mineralogical Museum is closely connected with outstanding Russian statesmen and scientists. Creation of museum collection began in 1716, when a large at that time collection, consisting of 1195 specimens, was bought in Danzig from the doctor of medicine Gotwald by order of Emperor Peter I. This small on contemporary representations collection has become a basis of one of the biggest world collections of minerals. The collection was deposited at the first Russian museum, the Cabinet of Curiosities. The Mineral Cabinet attached to the Cabinet of Curiosities was opened; later it was reformed in the Mineralogical Museum. At present collection of the Fersman Mineralogical Museum RAS contains more than 139 thousand specimens. For nearly three hundred years history many widely-known scientists worked in the Museum; mineral collection were increased, classified, and studied by their efforts. Numerous expeditions in different regions of Russia, and then the Soviet Union, were organized. Thematic expositions were created according to the most progressive contemporary knowledge on mineralogy. Vast work on popularisation of attainments of mineralogy was carried out. Names of 28 outstanding mineralogists, collaborators of the Museum, became history of mineralogy. 24 mineral species and 9 mineral varieties were named in their honour.

Lomonosovite and beta-lomonosovite were named in honour of **Mikhail Vasilievich Lomonosov** (1711-1765), outstanding Russian naturalist of 18th century, academician, one of the first collaborators of the Mineralogical Cabinet. Nearly 5 years Mikhail Vasilievich investigated the collection and composed a catalogue which was published in 1745; in this work the chapters, containing descriptions of crystals, precious and decorative stones, fossils (in all nearly 3000 samples), were written by M.V. Lomonosov. M.V. Lomonosov's input in development of Earth sciences in Russia is great. He created conceptions about connection of minerals with volcanism, earthquakes, and mountain formation, which were stated in the work «A word about metals origin by Earth shaking» (Lomonosov, 1757). In the work «On Earth layers» M.V. Lomonosov has paid attention to duration of geological processes and alteration of Earth face under their influence (Lomonosov, 1763, 1949). Mikhail Vasilievich was the first who began to speak about ore veins with different age; he believed that formation of minerals, including metals, was a non-stop process. In the thesis «On origin and nature of nitre», M.V. Lomonosov, basing on results of measurements of nitre crystals, correlated for the first time the main law of crystallography, the law of constancy of interfacial angles, with inner structure of crystals; he supposed that crystals consisted of separate globular corpuscles, which were packed in closest way, that determinated crystal form; thus he was the author of the doctrine about atomic structure of crystals (Lomonosov, 1949).

Lomonosovite, $Na_4Ti_2(TiO_2[Si_2O_7]^{u2}_2 \cdot 2Na_3[PO_4]^{\star}$, and **beta-lomonosovite,** $Na_4Ti_2|Ti(O,OH,F)_2 [Si_2(O,OH,F)_7]^{u2}_2 \cdot 2Na_3H_3 [PO_4]_2$, was found by V.I. Gerasimovskii in pegmatites among sodalite syenites in the Lovozero alkaline massif. **Lomonosovite** occurs in the form of lamellar-tabular segregations up to 7x5x0.6 cm in size. The mineral is dark brown to black, some segregations are pink-violet; lustre is vitreous to brilliant on cleavage plans and from vitreous to greasy on fracture. Hardness is 3-4; cleavage is perfect on {100}. Lomonosovite is associated with gakmanite, lamprophyllite, eudialyte, arfvedsonite, microcline, ramzaite (Gerasimovskii, 1950).

Mikhail V. Lomonosov

Vasilii M. Severgin

Beta-lomonosovite forms lamellar-tabular segregations up to 5x4x0.3 cm in size. It is light, yellowish-brown, sometimes with pink tint. Beta-lomonosovite is associated with microcline, aegirine, gakmanite, ussingite, nepheline, ramzaite, lamprophyllite, eudialyte, murmanite (Gerasimovskii, 1962).

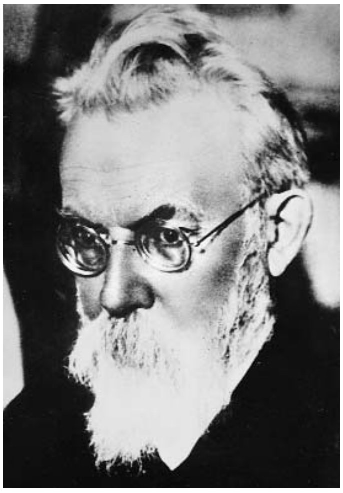
Severginite was named in memory of **Vasilii Mikhailovich Severgin** (1765-1826), academician, scientific leader of the Mineral Cabinet since 1804, director of the Mineral Cabinet since 1807 till 1826. Russian scientist-mineralogist, known by the fist fundamental works on mineralogy in Russian, consecutive naturalist-materialist, continuator of traditions of Lomonosov's school in natural history, Vasilii Mikhailovich, basing on careful study of already accumulated to that time materials of the Mineral Cabinet, has created a mineral classification by chemical and physical features; he has arranged exposition of the Mineral Cabinet, according to it classification. In the end of 18th – beginning of 19th century, the Mineral Cabinet has been changed by diligence of V.M. Severgin in the main base of mineralogical investigations of the Russian Academy of Sciences. V.M. Severgin has elaborated M.V. Lomonosov's ideas about joint occurrence of minerals, which was named contiguity of minerals by Vasilii Mikhailovich. Later this ideas has been developed in doctrine about parageneses and paragenetic mineral assemblages. V.M. Severgin is the author of such works as «The first fundamentals of mineralogy or natural history of fossil bodies» (Severgin, 1798), «Experience of mineralogical Earth description of the Russian State» (Severgin, 1809) and «New system of minerals based on external distinguishing features» (Severgin, 1816).

Severginite, synonym is manganaxinite, $\{Ca_2(Mn,Fe)Al_2(OH)[Si_2O_7]_2BO\}^{u2}$, is an end-member of isomouphous series axinite – severginite. The mineral contains up to 14.79 wt % MnO or 95-100 mol. % of severginite. It was found by G.P. Barsanov in the specimens from the Tungatarovskoe deposit of metamorphosed sedimentary silicate manganese ores at the South Urals. The mineral forms wedge-shaped crystals (to several millimetres in size), massive grainy shelly segregations with bright-yellow colour on fresh fracture. Hardness is 6.5-7, cleavage is perfect on {100} and imperfect on {001}, {110}, and {011}. Severginite is associated with quartz and manganese oxides (Barsanov, 1951).

Koksharovite was named in honour of Nikolai Ivanovich Koksharov (1818-1892), academician, director of the Mineralogical Museum since 1866 till 1873, and prominent Russian mineralogist of 19th century. N.I. Koksharov saw his own main objective in implementation the colossal work on measurement of crystals: «It seems to me that by means of large number of observations and precise measurements it is possible to ascertain many things, which is not yet found out, and also obtain a key to understanding of some laws that determine correlations of crystal form, chemical composition, and specific weight». N.I. Koksharov created the fundamental work «Materials for mineralogy of Russia» in six volumes (Koksharov, 1852-1855, 1856, 1858, 1862, 1872). In 1863 his lectures on mineralogy was published (Koksharov, 1863).

Koksharovite, synonym is edenite, $NaCa_2(Mg,Fe^{2+})_4(OH)_2[Al_{0.5}Si_{3.5}O_{11}]_{u2}$, is a mineral of the amphibole group, colourless to light bluish-green, with vitreous lustre. Hardness is 5-6.

Nikolai I. Koksharov



Vladimir I. Vernadsky

It forms grainy and columnar aggregates. Koksharovite occurs in contact-metasomatic formations, crystalline dolomites, grainy limestones, and altered magnesium-bearing basic igneous rocks.

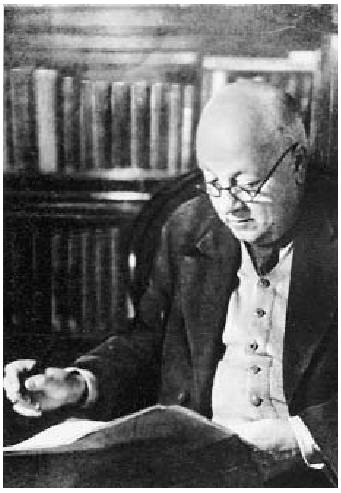
New mineral species, **vernadite**, and **vernadskite**, antlerite pseudomorph after dolerophanite, were named after the name of **Vladimir Ivanovich Vernadsky** (1863-1945), academician, director of the Mineralogical Museum since 1912 till 1919. Vladimir Ivanovich Vernadsky is a founder of genetic mineralogy, biogeochemistry, and idea about noosphere. He considered mineralogy as chemistry of the earth crust; that allowed him including natural waters and gases in a number of objects of mineralogy and that result in formation of new sciences, hydrochemistry and geochemistry. He developed genetic, dynamic ideas about mineral and has practically reformed mineralogy. V.I. Vernadsky wrote: «I have put in a basis the wide study of mineralogical processes of the earth crust, paid main attention not only on study of process product (mineral) but also on the process, not only on statistic study of process products but also on the dynamic study of the process». He elaborated the most interesting part of mineralogy, isomorphism. His outstanding organization abilities have proved useful to foundation in the Museum the chemical-mineralogical laboratory and the laboratory of spectral analysis, to attraction to museum work a number of prominent chemists and mineralogists, to organization of many expeditions that have provided very important scientific results and supplemented museum collection. Mineralogical material was systemized, the following collections were separated: systematic, deposits, crystals, pseudomorphs, and a collection of forms of mineral aggregates. V.I. Vernadsky has published nearly 400 scientific works, 30% of them are on mineralogy. Main works on mineralogy are following: «Experience of descriptive mineralogy» (Vernadsky, 1908-1922); «Earth silicates, alumosilicates and their analogues» (Vernadsky, 1937); «History of minerals of the Earth crust» (Vernadsky, 1923-1936).

Vernadite, $MnO_2 \cdot nH_2O$ f $Mn(OH)_4$, has been found by A.G. Betekhtin in metamorphosed sedimentary manganese ores at the South Urals as a product of oxidation of calcium-bearing rhodonites. This powdery ocherous mass is dark brown or pitch-black in massive varieties. The mineral is opaque or translucent with red-brown colour; it has high lustre and it is brittle. Hardness is 2-3; fracture is conchoidal. Vernadite is associated with braunite, hematite, chalcedony, quartz, rhodonite, spessartine, piemontite, psilomelane, pyrolusite (Betekhtin, 1937).

Vernadskite is a pseudomorph of antlerite, $Cu_3^{2+}(OH)_4[SO_4]$, after dolerophanite, $Cu_2^{2+}O[SO_4]$. It occurs as a product of interaction of acid fumaroles with dolerophanite at Vesuvius. Vernadskite was described by F. Zambonini as an aggregate of pale-green crystals associated with dolerophanite, anglesite, conichalcite (Zambonini, 1935).

V.I. Vernadsky has named pink variety of beryl the **vorobievite** in memory of **Viktor Ivanovich Vorob'yov** (1875-1906), scientific curator of the Mineralogical department of the Peter the Great Geological Museum of the Emperor Academy of Sciences (A.E. Fersman Mineralogical Museum was named so since 1900 till 1906). Talented young scientist made efforts to arrange mineral collection, to study and to enlarge it. V.I. Vorob'yov was a

Viktor I. Vorob'yov



Alexander E. Fersman

researcher of geological formation and mineralogy of the Caucasus, the Urals, and Siberia. He studied tourmalines from different deposits of the Urals (Shaitanka, Lipovka, Sarapulka), the Ceylon Island, the USA, Saxony (Vorob'yov, 1901); garnets (grossular from Yakutia, demantoid and uvarovite from Ural alluvial placers) (Vorob'yov, 1897); prehnite from Mongolia; beryl, euclase, quartz, and feldspars from the Urals (Vorob'yov, 1905).

Vorobievite is a variety of beryl, containing Cs (to 3.1% Cs_2O) and Li (to 1.39% Li_2O). It was found at the Urals. Vorobievite forms tabular and short-columnar crystals from nearly colourless to pale-pink and bright-pink colour (Vernadsky, 1908).

Fersmanite and **fersmite** was named by the name of **Aleksandr Evgenievich Fersman** (1883-1945), prominent mineralogist, academician, and director of the Mineralogical Museum since 1919 till 1930. The great merit in further development of the Museum in the Academy of Sciences as scientific museum establishment belongs to A.E. Fersman. Main tasks, which were put by A.E. Fersman to the Museum staff, can be combine in three main groups: 1) accumulation of comparative scientific material, its systematisation, and creation of exhibitions for science popularisation; 2) organization of large expeditions for exploration of mineralogy in different region of the country; 3) development of laboratory research base of the Museum. To carry out these tasks the new laboratories and a special library were created, the new young staff was engaged. Sphere of interests of A.E. Fersman was extremely wide: mineralogy, crystallography, geochemistry, mineral recourses, and technology of mineral raw materials. He was a researcher and an organizer of industrial exploration of a number of deposits of the Kola Peninsula, the Urals, Middle Asia, an author of a theory of pegmatite genesis. Results of his scientific studies were published a lot. Main works by A.E. Fersman on mineralogy are following: «Gems of Russia» (Fersman, 1921); «Pegmatites. Volume 1. Granite pegmatites» (Fersman, 1940); «Geochemistry», 4 volumes (Fersman, 1955, 1958, 1959); «Mineral resources of the Kola Peninsula» (Fersman, 1941).

Fersmanite, $Ca_5Na_3Ti_3Nb[Si_2O_7]_2O_8F_2$, was found by A.N. Labuntsov in rich in aegirine nepheline pegmatites in the Khibiny alkaline massif. The mineral is dark brown to goldish-yellow; streak is white with pale-brown tint; lustre is vitreous. Hardness is 5-5.5. Fersmanite forms pseudotetragonal, thick-tabular crystals, intergrowths. Fersmanite is associated with feldspathoids, pectolite, aegirine, lamprophyllite, rinkite, sulphides (Labuntsov, 1929).

Fersmite, $(Ca,Ce,Na)|(Nb,Ti,Fe,Al)_2(O,OH,F,)^3_6$, is rare accessory mineral of the nepheline syenites and carbonatites. It was found and described by E.M. Bonshtedt-Kupletskaya and T.A. Burova. The mineral occurs in miarolitic cavities in dikes of albitized pegmatites. Colour is black, dark brown, lemon-yellow, yellow-brown; lustre is pitch. Hardness is 4-4.5; the mineral is brittle; fracture is conchoidal. Fersmite is associated with columbite, pyrochlore, plagioclase, microcline, biotite, apatite, titanite, quartz, zircon, xenotime (Bonshtedt-Kupletskaya, Burova, 1946).

In 1955 E.I. Semenov and T.A. Burova have named a new mineral, **labuntsovite**, in honour of **Aleksandr Nikolaevich Labuntsov** (1884-1963), collaborator of the Mineralogical Museum since 1922. A.N. Labuntsov studied mineralogy of the Khibiny and Lovozero, actively supplemented collection of the Museum. In

1926 he discovered apatite deposit in the Khibiny. He studied in details pegmatites of North Karelia, was a curator of works on determination of absolute age. He worked in Middle Asia, Sayany, at the Slyudyanka and the Urals. A new mineral, fersmanite, has been found in the Khibiny Tundras by A.N. Labuntsov; in 1926 titanoelpidite was described, which was not a variety of elpidite in fact, but a new mineral species later named labuntsovite. At present over 30 mineral species belonging to the labuntsovite family are discovered. First discoverer of the uranium ore in the USSR. He has published over 70 scientific works devoted predominantly to minerals of the Khibiny, including the monograph «Pegmatites of North Karelia and their minerals» (Labuntsov, 1939).

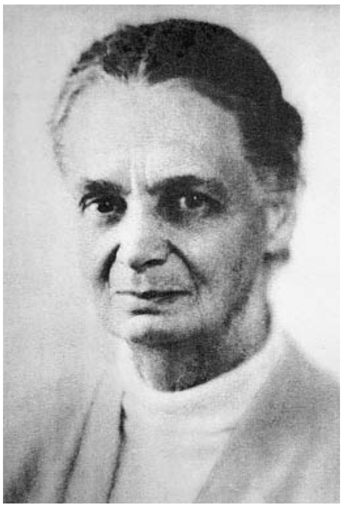
Labuntsovite, $|(Ti,Nb)_9(O,OH)_{10}[Si_4O_{12}]_4^{u3}$ $(K,Ba,Na,Ca)_8(H_2O)n$, was found in pegmatites of the Khibiny and then Lovozero massifs in the cavities among druses of albite or natrolite in the form of pink prismatic crystals up to 12x3x2 mm in size or radial-fibrous intergrowths. Hardness is 6; cleavage is perfect on {102}. The mineral is quite widespread in the Lovozero and especially in the Khibiny massifs. Labuntsovite is associated with albite, natrolite, aegirine, nepheline, ramzaite, eudialyte, murmanite, and microcline (Semenov, 1955).

Irina Dmitrievna Borneman-Starynkevich (1890-1988), mineralogist and chemist, worked in the Mineralogical Museum since 1922 till 1932. She has solved a problem of separation of Ti, Nb, and Ta by chemical method, elaborated a method of determination of rare-earth elements in calcium phosphates. She studied rare minerals of the Khibiny and Lovozero (eudialyte, lamprophyllite, enigmatite, murmanite). She investigated isomorphism in titanosilicates and phosphates. About this work of Irina Dmitrievna V.I. Vernadsky said that this was the best and most important work on chemical mineralogy. I.D. Borneman-Starynkevich was engaged in detection of an admixture of rare-earth elements in uranium ore. Mineralogists use her work «Guide on calculation of mineral formulas» (Borneman-Starynkevich, 1964) till now. A number of such large works on mineralogy as «Isomorphous substitutions in minerals» (Borneman-Starynkevich, 1951) belongs to pen of I.D. Borneman-Starynkevich. Bornemanite and thorium-bearing loparite, irinite, were named in honour of Irina Dmitrievna Borneman-Starynkevich.

Yu.P. Men'shikov with co-authors found **bornemanite**, $BaNa_3\{(Na,Ti)_4[(Ti,Nb)_2O_2(Si_4O_{14})](F,OH)_2\}[PO_4]$, in natrolite zone of pegmatoid vein called Yubileinaya in the Lovozero alkaline massif and described it in 1975. Bornemanite forms yellow lamellar segregations, 10x8x0.2 mm in size, occurring along cleavage and on the surface of large tabular crystals of lomonosovite, rarely it forms segregations of curved lamellae in natrolite. Lustre is pearly; hardness is 3-4; cleavage is perfect on {001} (Men'shikov *et al.*, 1975).

Irinite, thorium-bearing loparite, was found by L.S. Borodin and M.E. Kazakova in agpaitic pegmatites confined to complex of foyaites composing the central part of the massif of nepheline syenites. Segregations of irinite are confined to the zone of albitization of arfvedsonite-microcline pegmatite. The mineral forms crystals, 0.5-1 cm in size, colour is red-brown, brown-yellow. Lustre is greasy. Irinite is associated with aegirine, microcline, arfvedsonite, catapleiite (Borodin, Kazakova, 1954).

Alexander N. Labuntsov



Irina D. Borneman-Starynkevi

The mineral **belyankinite** and a variety of creedite, **belyankite**, were named in honour of **Dmitrii Stepanovich Belyankin** (1876-1953), academician-secretary of Department of geological-geographic sciences of AS of the USSR since 1949 till 1953, director of the Mineralogical Museum since 1947 till 1952. D.S. Belyankin was a researcher of geology, petrography and mineralogy of the Il'meny and Vishnevye Mountains (the Urals), the Caucasus and Zakavkazie. He studied mineralogy of refractories, including clays and feldspars. He researched cristobalite and other minerals SiO2. He was interested in role of water in composition of minerals. Annual issue of «Proceedings of the Mineralogical Museum» («New data on minerals») and mineralogical meetings known as Mineralogicheskiy krujok were recommenced under the guidance of D.E. Belyankin. He has discovered and studied many rocks, discovered a new mineral, vishnevite. His main works are following: «Introduction in crystallography and mineralogy», Part 1; «Crystallography», Part 2; «Mineralogy» (Belyankin, 1934); «Petrographic tables. Textbook for practical studies» (Belyankin, 1915); «Crystallooptics» (Belyankin, 1951).

Belyankinite, $Ca(Ti,Zr,Nb)_6O_{13}\cdot 14H_2O$, was described by V.I. Gerasimovskii and M.E. Kazakova in pegmatites of alkaline massif. The mineral occurs in the form of lamellar and lamellar-tabular segregations 20x12x0.5 cm in size. Colour is light yellowish-brown, altered varieties are pale-yellow. Lustre is pearly; hardness is 2-3. Belyankinite is associated with microcline, aegirine and nepheline (Gerasimovskii, Kazakova, 1950).

Belyankite is a variety of creedite, $Ca_3[SO_4][Al_2F_8(OH)_2]\cdot 2H_2O$. It was found by M.D. Dorfman in mine workings of Central Kazakhstan. The mineral is connected with kaolinized granites jointing to quartz-topaz greisens. Belyankite forms flattened or rarely kidney-shaped concretions 2x1.5x1-9x10x1-2 cm in size. In cavities it occurs in the form of small, colourless, elongated-prismatic crystals up to 0.5x0.7 mm in size. Colour is white, porcelaneous; lustre is vitreous. Belyankite is associated with kaolinite, fluorite, and pyrite (Dorfman, 1950).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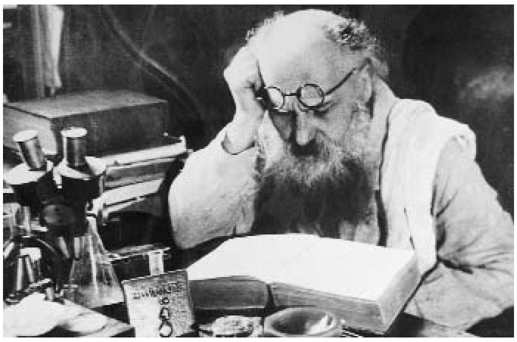
Dmitrii S.

A new mineral, **nenadkevichite**, and variety of coffinite, nenadkevite, were named by name of **Konstantin Avtonomovich Nenadkevich** (1880-1963). K.A. Nenadkevich, member-correspondent of the Academy of Sciences of the USSR. He worked in the Mineralogical Museum. Being chemist and mineralogist, he studied new forms of mineral resources, invented methods of extraction of rare metals from ores. He has suggested technology of production of metallic bismuth from domestically produced raw materials and smelted the first experimental batch of it. Main his scientific works are following: «To question of soda industry in the USSR (Doroninskoe soda lake)» (Nenadkevich, 1924); «Electrolytic method of separation of nickel and cobalt» (Nenadkevich, 1945).

Nenadkevichite, $|(Nb,Ti)_2(O,OH)_2[Si_4O_{12}]|^{u}_{3}\cdot (Na,K)_{2-x}(H_2O)_4$, was found by M.V. Kuz'menko and M.E. Kazakova in 1947 in natrolite-albite pegmatite occurring in lujavrites. Nenadkevichite forms lamellar segregations from several millimetres to 4x2.5x0.4 cm in size between microcline crystals. Colour is dark brown, brown, brownish-pink to pink. Hardness is 5; cleavage is perfect on {001} (Kuz'menko, Kazakova, 1955).

Nenadkevite is a variety of coffinite, $U[(SiO_4)_{1-x}(OH)_{4x}]$. It was found by V.A. Polikarpova in the zones of sodium metasomatosis of iron-uranium deposit in the USSR. The mineral forms intergrowths of the finest long-prismatic crystals (0.001-0.05 mm in size) and compact masses with black, green-black, brown, red-brown, orange and yellow colour depending on chemical composition. Nenadkevite is associated with brannerite, uraninite, U-bearing malacon, and apatite (Polikarpova, 1956).

Kryzhanovskite was named by N.I. Ginzburg after honour of **Vladimir Il'ich Kryzhanovskii** (1881-1947), scientific curator (since 1907 till 1932) and director (since 1932 till 1947) of the Museum. The Mineralogical Museum was the main occupation of creative life of V.I. Kryzhanovskii during 40 years. Under his guidance museum collection was replenished. All museum collections were moved from St.



Belyankin

Petersburg to Moscow. New expositions were created. The Museum became a scientific institution with the task of researching of minerals composition and properties besides of keeping and conservating of specimens. V.I. Kryzhanovskii was the best mineralogist-diagnostician of that time. His main mineralogical interests were connected with mineralogy of the Urals: pegmatites of Il'meny and Vishnevye Mountains; with minerals of Lipovka, Mokrusha, Murzinka, Shaitanka, Adui. V.I. Vernadsky wrote about V.I. Kryzhanovskii: «It is difficult to compute and rightly estimate the work of that kind, which is not expressed in a book, but in museum creation, deliberate and continuous selection, classification, and use of material, collected in museum, by everyone who are looking for data». 42 works are published, including «Chevkinite from the Il'meny Mountains» (Kryzhanovskii, 1924); «Observations in the Il'meny mineralogical reserve in summer 1926» (Kryzhanovskii, 1927a); «Pegmatite veins in environs of Urga in Mongolia» (Kryzhanovskii, 1927b).

Kryzhanovskite, $MnFe^{3+}_2(OH)_2[PO_4]_2 \cdot H_2O$, was found in pegmatites of Kalba. It occurs in the form of prismatic crystals up to 2-3 cm in size, has brown, greenish-brown, bronze colour and vitreous lustre. Hardness is 4; cleavage is perfect on {001}. Kryzhanovskite is associated with triphylite, sicklerite (Ginzburg, 1950).

E.I. Semenov named a new mineral, **kupletskite**, in honour of **Boris Mikhailovich Kupletskii** (1894-1965), collaborator of the Mineralogical Museum. B.M. Kupletskii was a researcher of mineral resources of the Kola Peninsula, Karelia and other regions of North of the USSR, Siberia, the Urals (Il'meny Mountains), Middle Asia (Turkestan Range), and West Mongolia. He studied basic and ultrabasic rocks of Monche-Tundra (Kupletskii, 1937), alkali-basic massif Afrikanda, deposit of graphite at Aliber (East Siberia), tungsten at the Urals.

Kupletskite, $(K,Na)_3\{(Mn,Fe^{2+})_7\ (OH,F)_4\ (Nb,Ti)_2\ (OH,F)_3[Si_4O_{12}]^{u2}_2\}_{u2}$, was found in pegmatites of the Lovozero massif of nepheline syenites. It forms lamellar segregations up to 5x3x1 cm in size, consisting of single flakes with perfect cleavage on {100}, sometimes it occurs in the form of needle-shaped or small-flaky segregations. Colour is dark brown, black; lustre is high, vitreous. Hardness is 3. Kupletskite is associated with schizolite, neptunite, ramzaite, eudialyte (Semenov, 1956).

A.P. Khomyakov with co-authors has named a new mineral discovered by them, **bonshtedtite**, in memory of **El'za Maksimovna Bonshtedt-Kupletskaya** (1897-1974), collaborator of the Museum since 1920. She was a researcher of mineralogy of the Kola Peninsula. Since 1920 till 1923 and since 1929 till 1930 she took part in expeditions of the Academy of

Konstantin A. Nenadkevich

Boris M. Kupletskii

Vladimir I.
Kryzhanovskii
El'za M.

Bonshtedt-Kuplet
skaya
Ekaterina E.

Sciences in Khibiny, studied minerals of alkaline massifs of the Khibiny Tundras. She researched mineralogy of agpaitic pegmatites using museum specimens in Norway, Denmark, and Germany. In 1940^{th} E.M. Bonshtedt-Kupletskaya studied mineralogy of rare-metal deposits of the Urals and pegmatites of the Vishnevye Mountains (Bonshtedt-Kupletskaya, 1951b). She was an author and deputy chief editor of the first six volumes of encyclopaedic reference-book «Minerals» («Nauka» AN SSSR), which has been published since 1960 till now. She is an author of works: «Determination of specific gravity of minerals» (Bonshtedt-Kupletskaya, 1951a); «New minerals, 1954-1972» (Bonshtedt-Kupletskaya, 1974).

Bonshtedtite, $Na_3Fe^{2+}[CO_3][PO_4]$, was found in the Khibiny and Kovdor alkaline massifs at the Kola Peninsula. In the Khibiny the mineral has been found in core of bore-holes at depth 540-1875 m. It forms small tabular crystals up to 0.5x2x5 mm in size, transparent, colourless or it has pinkish, yellowish, greenish tint, vitreous or pearly lustre. Hardness is 4; cleavage is perfect on {100} and {010}. Bonshtedtite is associated with thermonatrite, cancrinite, shortite, burbankite, trona, ferrotychite, aegirine, albite, potassic feldspar, calcite, etc. In the Kovdor massif bonshtedtite forms small-grained aggregate in shortite mass (Khomyakov *et al.*, 1982).

A.P. Khomyakov with co-authors name a new mineral, **kostylevite**, after **Ekaterina Evtikhievna Kostyleva-Labuntsova** (1894-1975). E.E. Kostyleva-Labuntsova has been working in the Mineralogical Museum since 1932 till 1943. She was engaged in study of zeolites of Nizhnyaya Tunguska, topazes of the Urals and Mongolia, non-metalliferous mineral resources, mineralogy of the Khibiny. Classification of agpaitic pegmatites, revelation of peculiarities of mineralogy of the contact zone of the massif, typomorphic peculiarities of rock-forming minerals, titano- and zirconium silicates, apatite have occupied the central place during study of mineralogy of the Khibiny. New mineral species, ramzaite (1923) and yuksporite (1932) was found and studied by Ekaterina Evtikhievna. More than 100 works were published. She was an author of large monographs and information editions, including: «Minerals of the Khibiny and Lovozero Tundras» (Kostyleva-Labuntsova, 1937); «Some methods of study of ore-bearing quartz» (Kostyleva-Labuntsova, 1964); «Mineralogy of the Union» (Kostyleva-Labuntsova, 1936); she was a co-author of a monograph «Mineralogy of the Khibiny massif» (Kostyleva-Labuntsova *et al.*, 1978), which was awarded to A.E. Fersman premium in 1983.

Kostylevite, $|Zr[Si_3O_9]|^{u3}K_2(H_2O)$, was found in core of bore-hole of the Khibiny alkaline massif in the form of colourless, water-transparent columnar crystals with vitreous lustre. Hardness is 5. The mineral is associated with aegirine, natrolite, pectolite, lomonosovite, potassic feldspar, scherbakovite, rasvumite, arctite, villiaumite, halite, thenardite, umbite, eudialyte (Khomyakov *et al.*, 1983b).

In 1954 E.M. Es'kova and M.E. Kazakova named a new mineral, **scherbakovite**, in honour of **Dmitrii Ivanovich Shcherbakov** (1893-1966), well-known geologist and geochemist. D.I. Shcherbakov was a researcher of Middle Asia, Zabaikalie, Kazakhstan, the Urals, the Crimea, Karelia, and the Kola Peninsula. He was an organizer of the Tajik-Pamirs expeditions. He studied mineral resources and metallogeny of this region. He paid a lot of attention to description of material composition of ores of separate

Kostyleva-Labuntsova

Dmitrii I. Shcherbakov

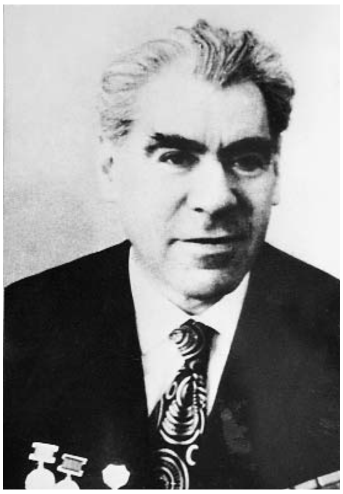
deposits of Hg, Sb, Sn, fluorite, considering minerals as a result of physical-chemical processes. In geochemical studies he found regularities confirming in many cases uniformity in co-occurrence of different elements. He was an author of more than 450 scientific works, including: «Peculiarities of metallogeny of Middle Asia» (Shcherbakov, 1935); «About maps of prognosis for magmatogene ore deposits» (Shcherbakov, 1952).

Scherbakovite, $K_2NaTi^{4+}_2O(OH)[Si_4O_{12}]$, was found in pectolite-natrolite pegmatite vein genetically connected with alkaline rocks. The mineral forms long-prismatic, elongated on c axis crystals up to 1.5-2 cm long, 0.3-0.8 cm wide, and 0.05-0.2 cm thick. Colour is dark brown; lustre is vitreous on faces and greasy on fracture. Hardness is 6.5. Scherbakovite is associated with natrolite, pectolite, potassic feldspar, astrophyllite, apatite, albite, galena, sphalerite, molybdenite, etc. (Es'kova, Kazakova, 1954).

In 1966 V.I. Vasil'ev has named a variety of metacinnabar, **saukovite**, in memory of **Aleksandr Aleksandrovich Saukov** (1902-1964). A.A. Saukov, geochemist, member-correspondent of the Academy of Sciences of the USSR. His main researches were devoted to geochemistry of rare elements, especially mercury. He has invented the method of detection of small amounts of mercury, studied its distribution in rocks. He dealt with questions of genesis of mercury deposits and has suggested a method of their prospecting on the basis of study of «dissemination nimbuses» (Saukov, 1936). He studied a problem of migration of chemical elements, invented geochemical methods of prospecting for deposits of mineral resources (Saukov, 1975).

Saukovite is a variety of metacinnabar, containing zinc and cadmium. It is an intermediate member of isomorphous series metacinnabar HgS — hawleyite CdS. Saukovite was found in mercury ores of quartz-barite-carbonate veins of the Ulandu and Kuraiskaya ore zone of the Gornyi Altai. It forms grains up to 1-1.5 mm in size with black, grey-black colour and high metallic to brilliant lustre. Saukovite is associated with cinnabar, hematite, chalcopyrite, pyrite (Vasil'ev, 1966).

In 1986 a new mineral was named **ginzburgite** in honour of **Natan Il'ich Ginzburg** (1907-1993) by A.V. Voloshin with co-authors. N.I. Ginzburg worked in the Mineralogical Museum since 1942 till 1956, researched mineralogy and geochemistry of rare-metal pegmatites, studied the zone of hypergenesis of pegmatites, regularities of formation and metasomatic substitution of tantalo-niobates and other rare-metal minerals during



Natan I. Ginzburg

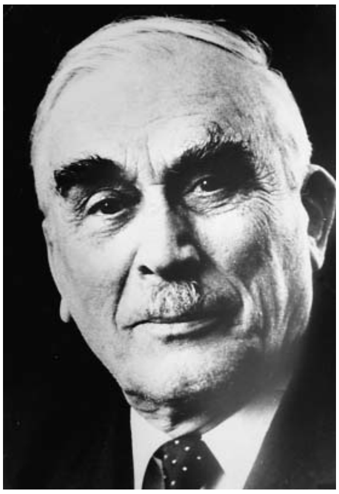
development of pegmatite process, isomorphism of micas, tourmalines, tantalo-niobates and other minerals with complex composition. He has discovered three new mineral species and found more than twenty for the first time at the territory of the USSR. He suggested to use typomorphic features and minerals-indicators of mineralization in prospecting purposes (Ginzburg, 1989). He is an author of 280 publications, co-author of wide-known three-volume monograph «Ore deposits of the USSR». Since 1958 till 1968, 35 numbers of the series «Geology of deposits of rare elements» has been published under the editorship of N.I. Ginzburg and with his assistance.

Ginzburgite, or roggianite, $Ca_2[Be(OH)_2 Al_2Si_4O_{13}]\cdot 2.5H_2O$, was found in zones of hydrothermal alteration of desiliconized pegmatites of the Urals. It forms spherulites with radial structure and up to 2 cm in diameter. The mineral is colourless, white; lustre is vitreous; cleavage is perfect on {110}. Ginzburgite is associated with bavenite, behoite, bityite, analcime, phillipsite, albite (Voloshin *et al.*, 1986).

In 1963 M.D. Dorfman with co-authors named a new mineral, **barsanovite**, in honour of **Georgii Pavlovich Barsanov** (1907-1993). In 1969 barsanovite was discredited, but in 1999 it was proved as an individual mineral species, but it was accepted under the name **georgbarsanovite**. G.P. Barsanov was a collaborator of the Mineralogical Museum since 1930, and since 1953 till 1976 he was the director of the Museum, since 1961 on a voluntary basis. Researcher of rare-metal mineralization of the Il'meny Mountains (the Urals). Creator of the theory of metamict process. In 50th years of 20th century he created the scientific fundamentals of almost all expositions of the Museum in accordance with standard of mineralogy of that time, including expositions: «Structural-chemical classification of minerals»; «New minerals and mineral varieties discovered at the territory of Russia and the USSR»; «Reasons of mineral colour». Author of 144 scientific works, including: «Mineralogy of jaspers of the USSR (Urals, Altai)» (Barsanov, Yakovleva, 1978); «Mineralogy of industrial and semi-precious varieties of fine-grained silica» (Barsanov, Yakovleva, 1984); «To mineralogy of South Osetia» (Barsanov, 1937). G.P. Barsanov was the permanent editor of publication of this magazine in 1948-84 (named «Proceedings of the Mineralogical Museum of Academy of Sciences of the USSR» since 1949 till 1963; «Minerals of the USSR» in 1963-64; «New Data of Minerals of the USSR» since 1965 till 1981; «New Data on Minerals» since 1981).

Georgbarsanovite, $Na_{12}(Mn,Sr,REE)_3 Ca_6Fe^{2+}_3 Zr_3NbSi_{25}O_{76}Cl_2\cdot H_2O$, was found in aegirine-augite-nepheline-feldspar pegmatite in the upper course of the Petrelius River in the Khibiny Tundras. Georgbarsanovite replaces eudialyte, from which it is difficultly distinguished. It forms compact segregations with irregular outlines up to 8-10 cm in diameter. Colour is reddish-brown, rarely yellowish-green; lustre is vitreous. Hardness is 5.5; cleavage is imperfect on {0001} (Dorfman *et al.*, 1963).

A.P. Khomyakov with co-authors have named a new mineral species, **sobolevite**, in memory of **Vladimir Stepanovich Sobolev** (1908-1982), academician, director of the Mineralogical Museum since 1980 till 1982. V.S. Sobolev is well-known mineralogist, researcher of mineralogy and petrology of the Siberian platform. He studied regularities of alkaline-basic and alkaline-ultrabasic magmatism of the



Aleksandr A. Saukov

Georgii P. Barsanov

Siberian platform. Comparing these data with the African platform, he came to the conclusion about presence of diamonds in the north part of the Siberian platform (Sobolev, 1936). He has formulated the most important relations between inner structure of silicates, their properties, and genesis peculiarities (Sobolev, 1949). He actively developed researches on metamorphism and metamorphic facies (Zavaritskii, Sobolev, 1961). He is on author of about 200 scientific works.

Sobolevite, $Na_{11}(Na,Ca)_4 (Mg,Mn^{2+}) Ti_4O_3F_3 [Si_2O_7]_2[PO_4]_4$, was found in a pegmatite of the Lovozero alkaline massif. The pegmatit mineral composition is close to those of this massif pegmatites of ultraagpaitic type. Parallel intergrowths with lamprophyllite and lomonosovite are typical for sobolevite. Sobolevite forms flattened crystals up to 5 mm wide, nearly 0.1-0.3 mm thick, with brown colour and high submetallic or pearly lustre on plane of lamellae and pitch lustre on transversal fracture. Hardness is 4.5-5 (Khomyakov *et al.*, 1983a).

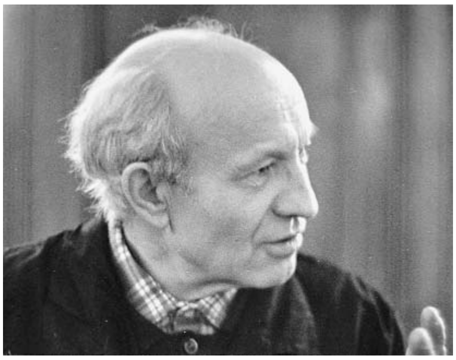
E.P. Shcherbakova with co-authors named a new mineral, **godovikovite**, in honour of **Aleksandr Aleksandrovich Godovikov** (1927-1995), well-known mineralogist, director of the Mineralogical Museum since 1983 till 1995. A.A. Godovikov was a open-minded mineralogist, specialist in field of theoretical and experimental mineralogy, crystal growth. Basing on contemporary knowledge on structure of atoms, he developed ideas about types of chemical bonds in minerals. He introduced a notion about force characteristics, which became a basis of revelation of the relations between structure of atoms and possibility of formation of some or other chemical compounds, including minerals. As a result Aleksandr Aleksandrovich has suggested the new classification of minerals. He is an author of the new Museum exhibition «Structural-chemical classification of minerals». A number of the new exhibitions were created under scientific guidance of A.A. Godovikov: «Caves», «Agates in igneous and sedimentary rocks». Together with V.I. Stepanov and M.A. Smirnova he created a unique exposition «Natural mineral forms». Earlier existed expositions were modernized and widened. A.A. Godovikov gathered the collection of minerals (nearly 4500 specimens), which he has donated to the Museum. He was an editor of magazine «Proceedings of the Mineralogical Museum of the Academy of Sciences of the USSR. New data on minerals» since 1985 till 1991. He is an author of 272 scientific works, including 15 monographs, 17 author's certificates. The main works are following: «Mineralogy» (Godovikov, 1975, 1983); «Chemical fundamentals of mineral systematisation» (Godovikov, 1979); «Structural-chemical systematisation of minerals» (Godovikov, 1997).

Godovikovite, $NH_4(Al,Fe^{3+})[SO_4]_2$, was found by B.V. Chesnokov in waste banks of coal mines of city Kopeisk (the South Urals) in 1982. It is one of the main minerals of sulphate crusts, originating during sulphate decomposition of fragmental products of waste banks. Aggregates of godovikovite are usually compact or porous, chalk-like 0.5-2 mm in size, sometimes thin-dispersed, forming stalactite-shaped segregations. Colour is white; lustre is dull (Shcherbakov *et al.*, 1988).

Dorfmanite was named by name of **Moisei Davidovich Dorfman**, collaborator of the Mineralogical Museum since 1957. M.D. Dorfman was born in 1908. He is a researcher of min-

Vladimir S. Sobolev

Moisei D. Dorfman



Aleksandr A. Godovikov

eralogy of wolframite deposits of Zabaikalie, Kazakhstan, pegmatites of the Khibiny. He is an author of classification of nepheline-bearing rocks. He has revealed that in the Khibiny there are the products of an intense pre-glacial process of chemical weathering, which were earlier rejected; he has found contemporary area zirconium crust of weathering. He discovered several new minerals. He is an author of 120 publications, including three monographs: «Mineralogy of pegmatites and zones of weathering in ijolite-urtites of the Mt. Yukspor of the Khibiny massif» (Dorfman, 1962); «Mineralogy of the Khibiny massif» (Kostyleva-Labuntsova *et al.*, 1978); «Mineralogical and geochemical peculiarities of the Khan-Bogdinskii massif of alkaline granites» (Dorfman *et al.*, 1981).

Dorfmanite, $Na_2[HPO_4]\cdot 2H_2O$, soluble hydrous phosphate of sodium, was described for the first time in the Khibiny by M.D. Dorfman and K.K. Abrashev in 1963, later its study was finished by Yu.L. Kapustin with co-authors. The mineral occurs in the form of thin powdery coatings on the fresh surface and in cavities of pegmatites of the Mts. Kukisvumchorr, Yukspor, Karnasurt, Alluaiv, Koashva. Walls of cavities are formed by druses of crystal of needle-shaped aegirine, anorthoclase, lomonosovite and covered by compact mass of dorfmanite (Kapustin *et al.*, 1980).

Collective of authors headed by L.A. Pautov has named a new mineral discovered by them, **vistepite**, in memory of **Viktor Ivanovich Stepanov** (1924-1988), collaborator of the Mineralogical Museum since 1986 till 1988, mineralogist-encyclopaedist. V.I. Stepanov, outstanding master of visual diagnostics of minerals, attached great importance to ability seeing evolution of studied object. He was a researcher of caves of the Crimea, Middle Asia, and the Caucasus. He has divided facies of cave minerogenesis and corresponding them types of mineral aggregates in those growing in air medium by film feeding, under surface of water, or at the border air — water. Viktor Ivanovich studied ore deposits of Central Kazakhstan, Middle Asia, Zakavkazie, North Caucasus, mines of the Il'meny reserve, mineralogy of Podmoskovie, Equatorial Guinea. Together with A.A. Godovikov he created the exposition «Caves», together with A.A. Godovikov and M.A. Smirnova he made the exposition «Natural mineral forms». He collected the unique collection of minerals (nearly 20 000 samples) and donated it to the Mineralogical Museum.

Vistepite, $Mn_5Sn^{4+}B_2Si_5O_{20}$, was found in rhodonite body at the north slope of the Inyl'chek range (Kirgizia). It forms orange-yellow sheaf-like aggregates up to 15 mm in size. Lustre is vitreous. Vistepite is associated with rhodonite, quartz, tephroite, galena, huebnerite, chalcopyrite, sphalerite, stannite, rhodochrosite (Pautov *et al.*, 1992).

In 2001 N.V. Chukanov and co-authors have named a new founded mineral as **novgorodovaite**, in honour of **Margarita Ivanovna Novgorodova**, well-known mineralogist, director of the Mineralogical Museum since 1996. Under the guidance of M.I. Novgorodova collections of the Museum are actively being supplemented by new minerals and genetically interesting specimens, various temporal exhibitions in Russia and abroad have been organized. Publications: 5 monographs, proceedings on mineralogy of V.I. Vernadsky, new guide-book on the Museum, booklet on exposition «Natural mineral forms» have been issue; publication of the magazine «New data on minerals» is recommenced. The magazine is issued in Russian and in English for the first time. Scientific interests of M.I. Novgorodova are in the field of genetic mineralogy: study of problems of mineralogical indica-

Victor I. Stepanov
Margarita I.

tors of ore genesis, which diverse aspects are connected with research of phase and structural heterogeneity of minerals depending on conditions of origin, growth, and post-crystallization transformations; study of native metals, intermetallides, carbides, and other minerals (Novgorodova, 1983, 2004); research of phase mineral transformations, which take place under extreme conditions of microexplosive phenomena in minerogenesis (Novgorodova *et al.*, 2003).

Novgorodovaite, $Ca_2(C_2O_4)Cl_2 \cdot 2H_2O$ was found in the Fersman Mineralogical Museum collection specimens were collected from core of borehole cutting evaporite sediments of Chelkar salt dome (Ural region, Kazakhstan). The mineral forms grainy aggregates with grains up to 7 mm in size. Separate grains are translucent, colourless. Novgorodovaite is associated with anhydrite, gypsum, halite, bishofite, hilgardite (Chukanov *et al.*, 2001).

Semenovite was named in honour of **Evgenii Ivanovich Semenov**, collaborator of the Museum since 1996. E.I. Semenov (born in 1927) is a researcher of minerals of rare-earth elements. He showed that each of sixteen rare-earth elements has proper minerals and genetic types of concentrations. He discovered nearly 30 new minerals, suggested new systematisation of minerals, basing on multivalent ions with low coordinate number. He created new classification of deposits basing on paragenetic mineral assemblages. Main scientific works are following: «Typochemism of mineral of alkaline massifs» (Semenov, 1977); «Systematisation of minerals» (Semenov, 1991); «Metallization and mineralization of rare-earth elements, thorium, uranium (lanthanides and actinides)» (Semenov, 2001).

Semenovite, $(Ca,Na)_8Na_{0\text{-}2}Ce_2H_x(Fe^{2+},Mn,Zn,Ti)[(Si, Be)_{10}(O,F)_{24}]^{u2}_{2}$, was found in alkaline massif Ilimaussaq (South Greenland) in cavities and cracks of albite, containing epididymite and eudidymite. The mineral forms crystals 0.1-1.0 mm in size, rarely up to 10 mm in size with dipyramidal habit and reddish-brown, pale-brownish-grey colour; lustre is vitreous. Semenovite over grows on eudidymite. Natrolite grows on semenovite crystals (Petersen *et al.*, 1972).

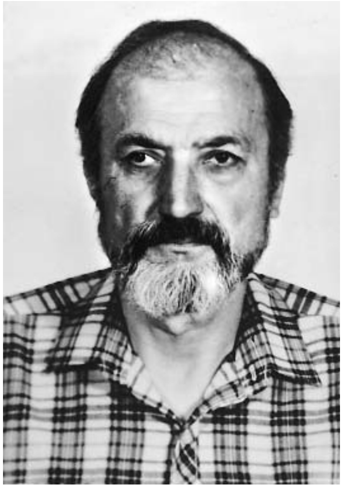
In 1988 a new mineral, **chernikovite**, was named in honour of **Andrei Andreevich Chernikov** (born in 1927), collaborator of the Museum since 1997, researcher of mineralogy and geochemistry of hypergenesis zone of uranium deposits as well as noble metal deposits in black-shale series. Main scientific works of A.A. Chernikov are following: «Exogenous epigenetic deposits of uranium» (Chernikov, 1965); «Behaviour of uranium in the zone of hypergenesis» (Chernikov, 1981); «Deep hypergenesis, mineral and ore formation» (Chernikov, 2001).

Chernikovite, $[(UO_2)(PO_4)]^{u2} \cdot [(H_3O) \cdot (H_2O)_3$, was found for the first time by A.A. Chernikov in the USSR in 1958; it was named «hydrogen-autunite», then it was found in Brasilia. Chernikovite forms mica-like elongated lamellae. Colour is light yellow and lemon-yellow; lustre is vitreous (Atencio, 1988).

A new mineral, *dusmatovite*, found by L.A. Pautov with co-authors in 1996 was named in honour of **Vyacheslav Dzhuraevich Dusmatov** (1936-2004). V.D. Dusmatov worked in the Mineralogical Museum in 2001-04. He was a researcher of mineralogy, geochemistry, and petrology of alkaline rocks and their pegmatites as well as granite pegmatites of Tajikistan. He has discovered several new minerals, including

Novgorodova Eugene I.

Andrei A. Chernikov



Semenov Vyacheslav D.

Dusmatov Peter S.

tadzhikite-(Ce), baratovite, darapiosite, tienshanite, cesium kupletskite, sogdianite. He found for the first time at the territory of the USSR such minerals as reedmergnerite, stillwellite-(Ce), green variety of leucosphenite. He is an author of nearly 200 publications, including three monographs, among which there are «Marble onyx of Middle Asia» (Dusmatov, 1997); «Chemical composition of micas of the Darai-Piyoz massif» (Dusmatov, 1996).

Dusmatovite, $K(K,Na)(Zn,Li)_3(Mn,Y,Zr)_2[Si_{12}O_{30}]$, was found in pegmatites of the alkaline massif Darai-Piyoz (Tien Shan, Tajikistan). It forms aggregates of irregular form (40x50 mm in size) with dark blue to violet colour. Streak is light blue; lustre is vitreous. Dusmatovite is associated with quartz, microcline, aegirine, tadzhikite-(Y), cesium kupletskite, hyalotekite, betafite, and polylithionite (Pautov *et al.*, 1996).

Not only minerals was named in honour of collaborators of the Museum but also general name for all stony-iron meteorites, consisting of olivine grains cemented by iron. They were named pallasites in honour of academician **Peter Simon Pallas** (1741-1811), chief of nature-chamber in the Cabinet of Curiosities since 1767. P.S. Pallas organized expeditions in many regions of Russia in 1768-1774 and in 1719-1801. They explored a vast territory from Petersburg to the Caspian Sea, from the Urals to Zabaikalie. In 1772 P.S. Pallas brought from the Yenisei taiga the famous meteorite, weighing 687 kg, which later were named «Pallasovo Zhelezo» (Pallas's iron). Academician E.F. Khladni ascertained for the first time significant difference its structure and structure of earth substance. Thus, he has scientifically proved a possibility of appearance of extraterrestrial substance on the Earth. That was the beginning of a new science, meteoritics. Basing on study of sea shells at the territory between Uralsk and Astrakhan' (these shells cab be found at the bottom of contemporary Caspian and Black seas), P.S. Pallas concluded that the Caspian Sea were connected with the Black Sea earlier and the sea level of the former was higher. Reports of these expeditions were published in the work «Travels on different provinces of the Russian Empire» (Pallas, 1776).

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WHAT ARE EXHIBITS SILENT ABOUT

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New information about some items of the Collection of decorative and precious stones of the Fersman Mineralogical Museum RAS is presented in the article.
3 colour photos, 6 references.

Remarkable collections kept in the world museums reflect many aspects of human culture. Collections in whole and especially exhibitions give to visitors the idea about evolution of science, about views, tastes, and predilections of different generations and whole nations, about uniqueness and resemblance of disappeared civilizations, and about many other evidences of the past and present. All that is presented to audience in the form of series of material exhibits, illustrating some aspects of science or art.

Since material is usually selected under certain point of view and reflects the main idea of exhibition (or collection in whole) surplus data which do not concerned to it are inevitably lost. They can not be obtained directly from exhibits, but meanwhile a lot of their features represent considerable independent interest. Among such features are: information about previous owner, ways and methods of acquisition and treatment of an exhibit or whole collection, about historical events or events of private character, which accompanied acquisition or loss of an exhibit by owner, and also information about relations of different exhibit owners, their contacts with mining workers, masters — stone-cutters, artists, and ets. This is the invisible, intangible part of museum treasures, in absence of which the exhibit (even very valuable) becomes an object, which does not have its own place in cultural-historical or natural-historical heritage.

Unfortunately, it is often that well-known natural-historical or art collections both museum or private are not documented properly. This is concerned to many, still more it is characteristic for collections of natural-historical profile.

To find out the real history of museums items is on the main goals of museum research work.

What do we know about the Mineralogical Museum items, that is impossible to reflect in exhibitions and even in inventory books? In this article there are some new data on items kept in the Museum Collection of decorative and precious stones. Present day computer technique allows to add this information to standard exhibits characteristic in our database.

Unexpected connections

In the Mineralogical Museum there are two things made in Roman mosaic technique: one is entirely and the other is partly. These are: a magnificent clock and a modest plaquette, which were received by the Museum in 1926 from different sources. They have nothing to do with each other, differing both in value of used materials and in skills of authors. Nevertheless, it turned out, that there is some historical connection between the items which reveals itself in certain episodes of biographies of their authors.

The clock was given to the Mineralogical Museum by the State Hermitage. This is a real cutstone masterpiece, representing an antique triumphal arch with the clockwork in its wonderful upper part (Photo 1).

The arch is made from marble of different colour (white, red, motley); white details being decorated with insets of deep blue Badakhshan lazurite, gilt bronze, and two marvellous miniature mosaics of war trophies. The red arch vault is caissoned and decorated with bronze rosettes. Its entablature leans on four malachite columns with bronze bases and capitals. There are malachite pilasters on the arch walls behind them. Frieze is decorated with bronze ornament in the form of bukranion (bulls' skulls) connected by garlands. All this construction is based on the socle made of red and white marble. There is a plate of green porphyry in its basement. Labradorite insert in bronze frame is set into white marble.

Top of the clock is crowned by bronze trophies and a figurine of Glory. Before knight's armours there is a shield from reddish-brown agate in a tracery bronze frame and with bronze Gorgon's head in the centre. The remaining hole testifies that there were another shield there some other decoration, which did not survive. Traces of vanished features one can see in a spot simmetrical to Glorea's figurine and under the arch wall in the center of square inset made of fragments of thin banded fluorite (only a bronze dovel survived).

On the back wall of the arch there is following inscription: «Raffaelli Fece Milano 1814».

We have no information about clock location during 1814-1926.

History of appearance of this clock in Russia is forgotten. There is a verbal legend in the Museum that it was a gift of Josephine Beauharnais to Alexander I. Formerly there was a figurine of Napoleon under the arch, and the clock was made by Jacomo Raffaelli in honour of Napoleon. It is a mistake obviously, since analogous clock was made in Vatican workshop by the same master in 1804 and in the same year it was presented to Napoleon by Papa Pius (Gonzalez-Palacion Rottgen, 1982; Masinelli, 2000). It is known as «Napoleon's» clock and, apparently, this name was used as basis of mistaken version that under the arch of our clock there was bronze Napoleon.

«Napoleon's» clock, which are in the collection of Gilbert in Los-Angeles now, was more lucky than our's. It still has got symmetrically to figurine of Glory there is a figurine of trumpeting Victory, and under the arch there is a bronze figurine of Mars with a spear and a shield with Gorgon's head as has. Possibly, earlier our shield was not also fixed above, but there was undoubtedly some detail, fastened by two dowels and hid the bolts screw the armours. «Napoleon's» clock, unlike ours, has two figurines at the sides of Glory and Victory, a cock and a griffin; also a dog and a wolf are mentioned in literature (Gonzalez-Palacion Rottgen, 1982). Arch of Napoleon's clock is made from marble, agate, jasper, lazurite, amethyst, and labradorite; the latter is mentioned as very rare stone in that time. This gift of Papa to Napoleon, according to abundance of allegoric attributes, bronze and mosaic pictures of trophies, figurines of Mars, Glory, and Victory, was regarded as refined flattery to Napoleon, whom Pius VII was forced to crown. The clock was in Malmaison, where till 1814 Josephine lived, later it has appeared in the collection of Alexander Kleinwort. Further its fate is clearly traced, but where it was after Malmaison and till Kleinwort's collection, it is not clear. For this period of time there is only some versions (Rottgen, 1982; Masinelli, 2000).

An appearance of one more such clock in Russia (the arch, to be exact, since the clock was not preserved) made by Raffaelli in 1801 is enigmatical. In was recieved the State Hermitage in 1936 from a private collection. It is not known more about its fate. Red and white marble, labradorite, lazurite, malachite are used here; columns and pilasters are made from jasper-agate (Mavrodina, 1999).

As we can see, the similar plot was used in all three clocks of Raffaelli, and practically, the same set of decorative stones. The main distinction is in material of columns and pilasters: jasper-agate (1801), amethyst (1804), and malachite (1814).

What can we say about version, according to which the clock of the Mineralogical Museum was presented to Alexander I by the Empress Josephine? For this version it was necessary that this clock were in her possession. Whether it could be? To dissolve this question let's remind some facts of the history of Napoleon, his confidants, and J. Raffaelli.

Jacomo Raffaelli (1753-1836) was born in the family, which dealt with production of smalts in Vatican workshop for a long time. His artistic talent became apparent early, he studied painting, was a mosaic-artist, and he became an innovator in this business after he had invented a method of making of smalts with different form (by stretching at the fire); very small pieces (tessera) could be made by this method. He was recognized the head of the school of miniature mosaic (mosaico in piccolo); the similar insets between pilasters were made by this method in all three mentioned clocks.

Became the master, Raffaelli worked not only for papal court but also for foreign ones. He was well-known also in Russia and even was invited to Petersburg for organization the production of smalts and creation of mosaic workshop there. However, he did not come to Petersburg, since Alexander I considered the Raffaelly's terms on excessive (Mavrodina, 1999). These events took place were in 1802-1803. Almost in the same time (in 1804) the son of Josephine, Eugene Beauharnais, who was in Italy conquered by Napoleon and was appointed by Bonaparte in a year as a vice-king of this country, ordered to create in Milan a mosaic workshop analogous to papal one. J. Raffaelli headed it. Experienced master carried on a business successively, and together with other works, in 1814 made one more clock kept now in the Mineralogical Museum, the copy of «Napoleon's» clock in which he only changed some decorative stones by the others.

After Napoleon's dethrone (1815), Raffaelli returned to Rome. The interest of Russian court to the great mosaic-master did not cease, and he became an adviser of Alexander I. In 1812 Eugene Beauharnais was recalled by Napoleon from Italy and took command of 4th corps of a Large Army fought in Russia. He took part in many battles, including battle at Borodino, and acted as skilful commander and very brave person. In 1813 he came back to Italy and in 1814 left it forever and settled in Bavaria, got married to the daughter of the King, Amalia-Augusta. In 1815, on Vienna congress, where questions of post-war arrangement of Europe were discussed, Eugene became close friends with Alexander I, who was favourable disposed toward entire Beauharnais family. By encouragement of Russian Emperor, he obtained lands in Bavaria and a title of the duke of Leuchtenberg and Eischtadt.

This brief excursus in biography of Eugene Beauharnais is necessary in connection with a version that the Museum clock came to Russia from Josephine Beauharnais. Possibly, her son when he left Italy took away together with many other treasures the clock like Emperor's one. And, possibly, it also was given to Josephine who presented it to Alexander I together with other things (as for example cameo Gonzago).

From the other hand, if the clock was took away from Milan by E. Beauharnais, he could present it to Russian Emperor, since their relationships were friendly and Alexander petitioned about him to Bavarian King. And Josephine might be mentioned in the legend about clock in connection with family name Beauharnais.

The following fact contradictory to these version: the clock was not included in the inventory of the Hermitage, it was on the list of unregistered things till delivery to the Mineralogical Museum. Although it might be in the private apartments of some members from tsar's family and it appeared in the Hermitage after nationalization of property of numerous emperor's relatives.

One more idea concerning the history of this clock in Russia arises in connection with marriage of son of Eugene Beauharnais, Maximilian (1817-1952), the duke of Leuchtenberg, with daughter of Nikolai I, grand princess Maria Nikolaevna. When he got married, he remained in Russia forever. Possibly, he brought the clock together with many other things .

The second mosaic thing, mentioned above is a small plaquette (21x14 cm in size) with the image of a cross (Photo 2). It is indirectly connected with name of J. Raffaelli too.

After refusal of J. Raffaelli to come to Petersburg, the idea to create own mosaic workshop did not leave the Russian court. It was done already in the reign of Nikolai I.

They needed the workshops for smalt production badly since the grand Isaak Cathedral was being built and they decided to make the mosaic icons for the Cathedral. In 1848, for organization of smalt production, several Vatican masters came to Petersburg by permission of Papa; there were J. Raffaelli Vincenzo and his nephew Pietro among them. They arrived in the Russian capital «for building of a hearth and a stove and for stove supervision» (Mavrodina, 1999, p. 233). The experienced mosaic-masters were necessary for a new workshop. There was nobody in Russia who could teach them. Therefore, in 1845, it was decided to teach Russian artist at Vatican mosaic workshop in Rome. In 1847 «model workshop of St. Nikolai» was founded «by pleasure of the Tsar Nikolai Pavlovich and by petition of the prince Grigory Petrovich Volkonsky».

Nikolai I chose gifted artists who were dispatched to study mosaic work in Rome. They were only four, and Vasily Egorovich Raev (1807-1870), famous landscape and historical painter was among them. I.S. Shapovalov, S.F. Fedorov, and E.G. Solntsev went in Rome together with him. V.E. Raev, being serf, was graduated to Arzamas Art School and, after freedom in 1839, was an external student of the Academy of Arts. In 1847-1848 Raev studied mosaic work in the workshop of St. Nikolai in Rome. His first students' work was the plaquette kept in the Mineralogical Museum now (Photo 2). There is white cross on the black background in the frame of simple ornamental pattern on it. The work made of multicoloured marble in style of Roman mosaic. Artistic value of this thing is quite doubtful (both on subject and performance). But from the historical point of view, it is undoubtedly interesting, since there is an inscription made by V. Raev with the information mentioned above (Photo 2b) on its back side.

This is the first mosaic work made by Russian artist in Rome in 1847. In the inscription V.E. Raev mentioned only himself and I.S. Shapovalov, but it is known that in the same year, 1847, all four artists in Rome began to create a twice-diminished copy of mosaic floor found in 1870 during excavation of thermae of the Old Roman town Otriculum near Rome. The artists supplemented the antique original by mythic personages and flora. The mosaic was brought in Petersburg and set into the floor of the Pavilion hall in the Hermitage. The round table desk made by the same masters and representing multiple-diminished copy of the same mosaic is demonstrated in the same place. They were busy with this work in 1847-1851. Master M. Barbery, their Roman teacher, leaded the works.

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*) Being quite gifted person, Maximilian Leuchtenbergsky occupied many important positions in the state, including ones connected with mining. His son, Nikolai Maksimilianovich Romanovsky (this family name and Prince title were conferred by Nikolai I) was well-educated person, but especially he was interested in mineralogy. He described several minerals from the Urals, including leuchtenbergite named in honour of his father. Nikolo-Maksimilianovskaya mine in the Nazyam Mountains of the South Urals was named after him. Since 1865 he headed the Mineralogical Society of Russia

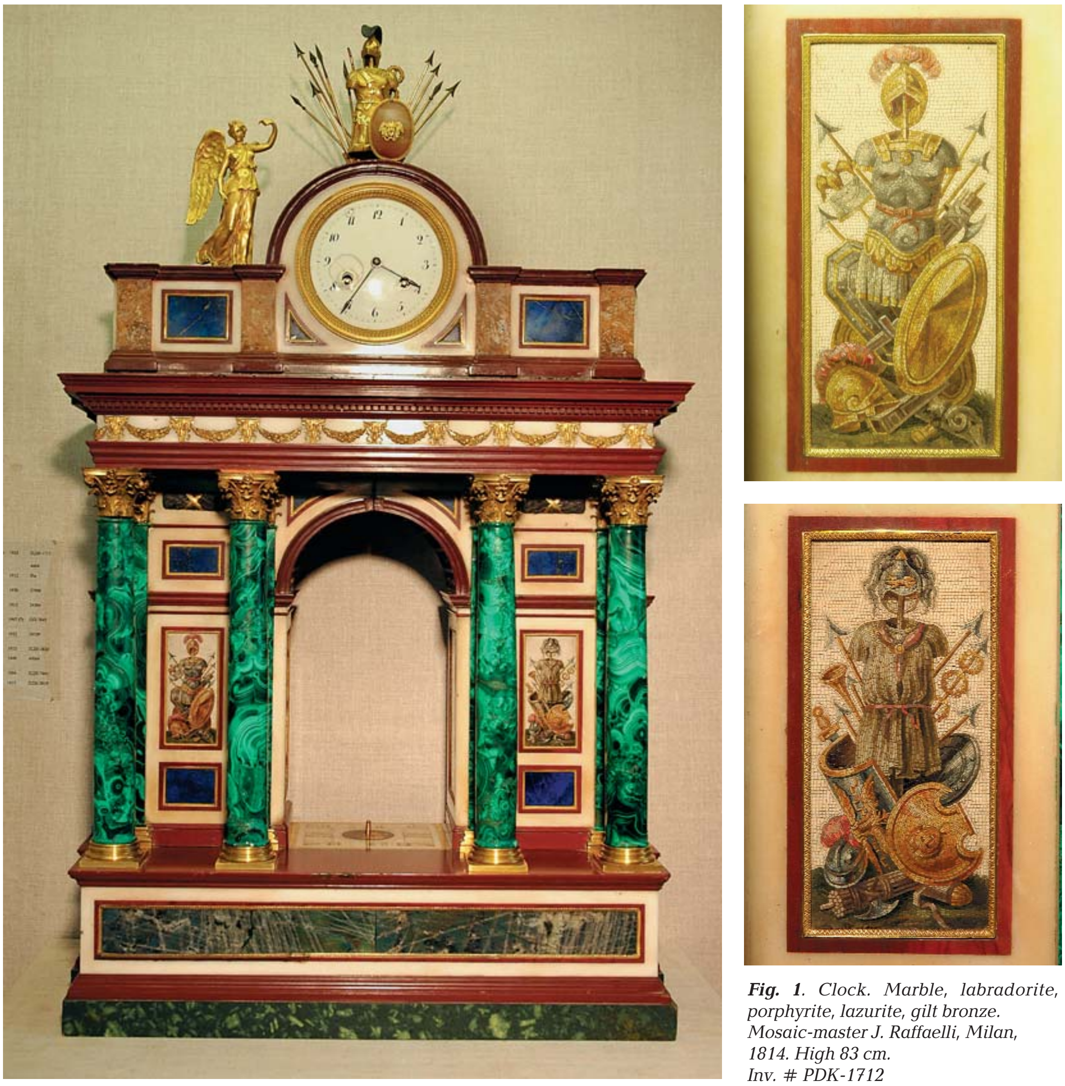

Fig. 1. *Clock. Marble, labradorite, porphyrite, lazurite, gilt bronze. Mosaic-master J. Raffaelli, Milan, 1814. High 83 cm. Inv. # PDK-1712*

Соизволенiемъ Государя
Императора Николая
Павловича и ходатайствомъ
Князя Григорiя Петровича
Волконскаго, основана въ
Римѣ Русская Мозаичная
школа, въ которую первыми
учениками вступили: Василiй
Раевъ и Иванъ Шаповаловъ.
Первымъ опытомъ былъ этотъ
Крестъ начатый Раевымъ въ iюнѣ
1847 года.

1585

Fig. 2. *Plaquette with the image of the cross. Marble. V.E. Raev, Rome, 1847. Size is 21x14 cm. Inv. # PDK-1585.*
a) front side; b) back side of the plaquette. Inscription was made by V.E. Raev

Fig. 3. *Cups from treasure-house of the princes Radzivills in the Nesvij Castle:*
a) Size is 14.8x10.7 cm, high is 4.2 cm. Inv. # PDK-1639;
b) Size is 18x14 cm, high is 7 cm. Inv. # PDK-1634;
c) Size is 18.3x12 cm, high is 5.2 cm. Inv. # PDK-1643;
d) Size is 13x11 cm, high is 3.8 cm. Inv. # PDK-1644;
e) Size is 17x15 cm, high is 5.5 cm. Inv. # PDK-1645

After return to Petersburg, becoming the mosaic-master, V. Raev in 1851 and 1852 worked in Saint Petersburg mosaic workshop. It is known that he and three other mosaic-masters mentioned above took part in creation of grandiose mosaic icons in the Isaac Cathedral. In 1851 V.E. Raev became an academician. His pictorial works pictures are in the Russian Museum, State Tretiakov Gallery, Tropinin Museum.

In 1926 the Mineralogical Museum received V. Raev plaquette from State Museum Fund among items being earlier in the store-rooms of the Gatchina and Stroganov's Palaces (archives of the State Hermitage. Fund IV, volume 2, op. 4, affair 192).

Radzivills' cups

In 1926 the State Hermitage gave a number of stone-cut items to the Mineralogical Museum. There were five cups of quartzite with different colour among them: red, light and dark grey (archives of the State Hermitage. Fond IV, op. I, affair 49). These things were never exhibited in the Museum, since both material and form of these items are unspectacular and do not stand up the comparison with other exhibits of the collection. However, from historical positions, they, obviously, are among the most interesting ones in our collection.

In tsar's treasure-house these cups came in 1813 from the famous Nesvij Castle (Byelorussia), which was for several centuries a property of one of three branches of the old Lithuanian princely family of Radzivills.

Radzivills were first mentioned in historical data about 1400th. In 1518 they obtained a title of princes of the Roman Imperia and for several centuries took up very high position in Rzeczpospolita. In fact, they were the apanage princes who not only had enormous treasures but also own considerable military forces. Many representatives of this family became famous in battles, and, thanks to congener connections with king family, authority of some of them was almost absolute. Polish-Lithuanian history was closely connected with Russia. And Radzivills were active figures of that time. So, Lithuanian marshal, Stanislav Radzivill (1559-1599), was one of the commanders of the forces of king Stephan Batory fought against Ivan the Terrible in Livonian War of 1579-1582. Historians, poets, writers, and outstanding church figures were among princes too.

Probably, Karl Stanislav Radzivill (1734-1790) was one of the most famous representatives of the family, who was widely known as «pane kokhanku» (in this way he usually addressed companions). He was a favourite of gentry, the richest reveller, cheery fellow, and jester who did not yield to anybody. Contemporary of the Catherine II, he in no way wanted to submit authority of her protege, Polish king Stanislav August Ponyatkovsky, and to adopt reforms, by which the Orthodox believers (dissidents) became equal in rights with Catholics.

Since 1767 opponents of Ponyatkovsky periodically created numerous opposite parties (confederations) struggled for independence of Poland. Most of them were the small groups (178 of them were counted), which struggle with each other more often then with Russia, their general enemy. There were also large organizations. The centre of one of them was the town of Bar (Podolia). Karl Stanislav Radzivill headed it.

Separate and uncoordinated acting confederates could not resist the Russians. In 1768 the forces under the command of A.V. Suvorov were sent against Lordly Confederation by prince N.V. Repnin, plenipotentiary minister of Poland. Confederates were defeated, and their leaders either became reconciled with inevitability and were forgiven by Catherine, or escaped.

Karl Radzivill has also escaped. And during wanderings on different countries he met an extraordinary person. She was young, intelligent, beautiful, had incredible success. But the main: she pretended to the Russian throne. She named herself the princess Volodimirskaya, a daughter of Tsarina Elizabeth and Aleksei Razumovsky (in Russia she was known as princess Tarakanova). Radzivill could not miss such magnificent case. Would he reckon on success or only wanted to annoy to Catherine II, but he in every way supported this prominent adventuress, and together they wanted to obtain the help of Turkey, carrying war with Russia since 1769. However, their dreams did not come true. Russia and Turkey made peace (Kuchuk-Kainarji, 1774), the count Aleksei Orlov, commander of navy that defeated the Turks in the Chesmen bay, considerably promoted that. Interest of Radzivill to the princess faded, and the count Orlov captured her and brought to Petersburg. She soon died of consumption in the Petropavlovskaya fortress.

Karl Radzivill later was forgiven by Catherine and lived in Nesvij that was returned to him. He died in 1790, childless. Single successor of Nesvij line of Radzivill family was his nephew Dominick born in the same year, 1790, not long before Karl death.

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[*] In the inventory the cups were attributed as feldspar ones

Young Dominick, as his uncle, leaded dissolute life, was keen of gambling games, horses, became famous for scandalous divorce suit. He dreamed about military carrier. In 1805 he took the loyal oath to Alexander I.

At that time Napoleon shook Europe. Soon after wars of 1805-1807 he declared Polish lands conquered from Prussia the Warsaw duchy. Polish and Lithuanian gentry apprehended this step as restoration of independent Rzeczpospolita. Inspired Dominick Radzivill with his family left Nesvij and came to Warsaw under authority of Yuseph Ponyatkovsky, to fight for freedom of Poland. He invested enormous money (216 thousand zlotys) in Polish army and, although he did not have military education, became the uhlan colonel and battled in Napoleon's troops with Russia. During retreat of Napoleon's army, the regiment of Radzivill left Poland. A hope on independence of Rzeczpospolita disappeared.

Alexander I declared forgiveness to the Poles who battled on the Bonaparte's side, if they would lay down arms and would return to peace life. Dominick Radzivill rejected the suggestion and continued to carry war against Russia. On October 30, in battle at Hanau (Hessen, Germany) he was mortally wounded and died in several days. The line of Nesvij Radzivills faded with him. His possessions and treasures passed to Russian troops.

The treasures were fantastic. Material cultural values accumulated during several centuries: collections of arms, diverse artistic works, jewellery, precious services, medals, coins, spacious library, invaluable archives, etc. were collected here. All this attracted conquerors and robbers. Nesvij was repeatedly conquered both by the Swedes and the Russians. And in 1812 for participation of Dominick Radzivill in Napoleon's war against Russia, the Nesvij Castle was again taken by Russian troops, and its treasures were confiscated. It was the colonel Knoring who imprisoned the steward of castle Albreht Burgelsky and got the information where the hidings were. He took from the castle carpets, clocks, antique articles, musical instruments, and clothes. Then, with a corps of Moldavian army of admiral P.V. Chichagov, the major-general S. Tuchkov appeared in the castle and took out «different brilliants, silver and gold articles, and also other things». In 1812 P.V. Chichagov who pursued the receding Frenchmen seized eleven boxes with treasures. In report to Alexander I he wrote: « I found treasures here: pearls, brilliants, etc. I took out all that I could, and You can decide, what to do with it. I did not see, but it is said that there were things deserving museums. All is avaluated for more than a million roubles». Lists of these things are kept («Vyartanne 6», Minsk, 1999, p. 208-217): pictures, arms, bronze statuettes, clocks, different gold articles, etc. Then S. Tuchkov again returned to the castle and interrogated A. Burgelsky under torture, and again he took out huge amount of valuables. In whole losses of the castle were estimated minimum in 10 million Polish zlotys. However, there is an opinion that more them two tonns of treasures are in the castle hidings up to now (Col. of Byelorussian Culture Fund «Vyartanne 2», 1994; «Vyartan-`ne 3», 1996; «Vyartanne 6», 1999).

Later some treasures were removed from the Nesvij too. But for us those treasures are important that were confiscated in 1812 and got to the Hermitage in 1813. There are many items from the castle there now. There were five modest cups of a plain inexpensive stone among very expensive highly artistic things. Later these cups were given to the Mineralogical Museum of the Academy of Sciences.

Here is there defailed decription:

The first cup is oval, smooth, made of fine-grained light gray quartzite. Now on the even light background of stone a lot of black dots and strokes are observed. Through magnifier it is visible that this is just a surface grime in cracks and caverns. In fact the stone is monochromatic, without natural inclusions (Photo 3a).

The second cup of quartzite with alternating streaks of light and dark grey colour. Dark colour is caused by inclusions of small mica flakes. Cup is roughly oval. Its long sides are not rounded gradually but are parallel to each other. Places of joining of these parallel and rounded parts are marked on the outer side of the cup by four convex edges going from the cup top to its basis (Photo 3b).

The third cup is oblong octagonal. The edges well pronounced on roundish sides of cup go from corners on its top to the octagonal basis. The cup is cut of monochromatic yellow-grey quartzite, between translucent grains of which the rare small segregations of clayey matter with dark colour and flakes of light mica are observed (Photo 3c).

The fourth cup is analogues to previous one by form; it is made of red ferruginized quartzite; small grains of colourless quartz in it are rounded by segregations of dust-like red hematite (Photo 3d).

The fifth cup has complicated form, in which there are both angular and roundish details. On the outside surface of the cap the places of jointing of different parts are also marked by edges. There are also grooves at transition from straight lines to roundish ones. It is made of ferruginized brownish-red turning to yellowish-brown quartzite. On the plain background the small lighter roundish and, rarely, bright dark brown spots are distinctly seen; they are caused by segregations of iron compounds (Photo 3e).

Quartzite is a widespread material; therefore, it is difficult to suppose which region this rock derived from. Since the middle of 18th century, remarkable red («crimson») quartzite was mined in Shoksha (Karelia); and it's locality is said to be unique. It is used for facing of buildings, for pedestals, *etc*., and it is so good that Napoleon's tomb was made of it. Among our cups one is cut from material that is very similar to Shokshian one (PDK-1644). Stone of the cup PDK-1645 is quite similar to it. There is no idea about the occurrence of stone for three other cups. Compact high-grade quartzites occur at the Ukraine and in many other regions of Europe. It is set much as facing and building material, but not for stone-cut articles, especially for small plastic figures.

Judging by time of appearance of the cups in the Hermitage, they are dated not late than 18th century. Hard stone that is widespread in European articles of that time is quartz and its varieties, especially chalcedony (in all its diversity). By beauty, behaviour during processins, it excels quartzite in many times. Therefore, the usage of the later for even such not too complex articles as our cups seems quite strange. We would rather think that these cups are either from the places where beautiful decorative material was not accessible or these cups are quite old. Otherwise, how is it possible to explain their appearance among treasures of the most influential Polish-Lithuanian magnates? One only can suppose that they were appreciated by the owners not for beauty, but for something else. Possibly, these were trophies obtained in fight or they were connected with some other events, dear to owners, since they were kept together with great values. And it is possible... It is possible to conjecture infinitely... We hope that ultimately the researchers of history of the Nesvij Castle, and its collections, which are kept now in different museums, will be able to restore the history of these things with lost biography.

And in the meanwhile the exhibits keep silent.

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The author expresses the great gratitude to the director of NIKMZ «Nesvij», Galina Mikhailovna Kondrat'eva for providing with materials on the history of the Nesvij Castle and its owners.

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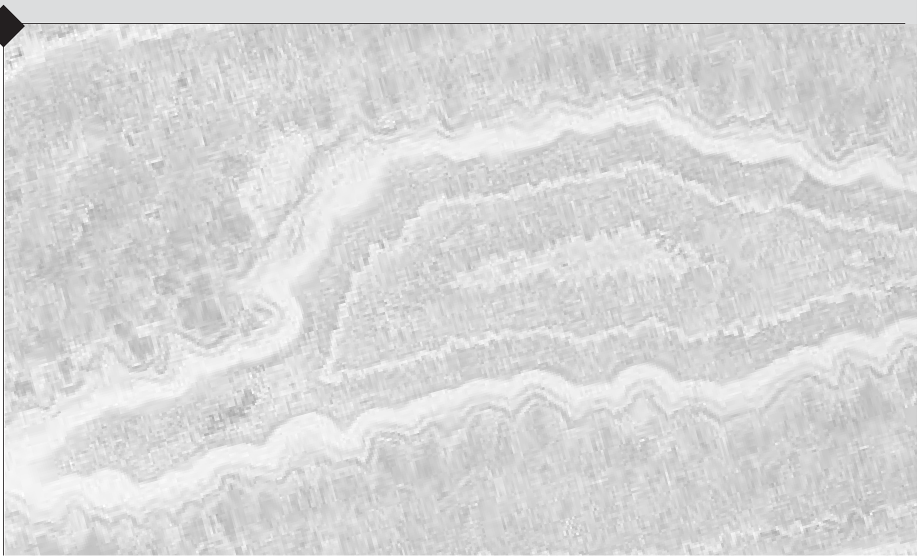
Mineralogical Notes



UDK 549.9

MINERAL TYPES OF ORES OF EUROPE

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Books on minerals and deposits of various geological provinces (the Urals) and countries (Germany, RSA, USA) are numerous, but such books on whole continents are rare. Series of monographs «Mineral deposits of Europe» (Mir, 1982, etc.) do not include Eastern part of Europe, especially Russia.

This article represents brief tables with the main mineral types of ores of the territory from Portugal to the Urals. East Europe, and first of all Russia, has besides oil and gas the great number of other types of valuable ores, unknown in West Europe. Types of ores are determined according to the mineral concentrate: pyrochlore, columbite, loparite, which have different genesis (carbonatite, granite, nepheline-syenite), but not according to the countries, metals (for example, niobium, as it is accepted in the series «Mineral deposits of Europe»).

There are a lot of deposits of cinnabar (mercury), apatite (phosphorus), magnetite (iron), eudialyte and baddeleyite (zirconium) in Europe.

Large, world-range deposits of uraninite (as in Canada and Australia), tantalite, diamonds, non-ferrous metals, gold are absent here.

Tetragonal dipyramidal crystal of tin dioxide, cassiterite, can be suggested as a mineral symbol of Europe. It was the mineral that used for tin extraction to make bronze in England (Cornwall) («Bronze Age» of Humanity).

As is concerned to chemical element europium, in minerals (allanite, monazite) from one of the most widespread European rocks, leucocratic granites, it usually strongly yields in abundance to such rare-earth elements as samarium and gadolinium. Only in oolitic monazite from schists and their placers in Normandy (France) and at the Timan europium prevails.

Minerals, determining types of ores	**Formulas**	**Deposits**
Oxides		
Magnetite	$\mathbf{Fe}_3O_4$	Kursk, Russia, quartzites
		Kiruna, Sweden, syenites
		Magnitogorsk, Urals, skarns
Titanomagnetite	$(\mathbf{Fe},\mathbf{V},\mathbf{Ti})_3O_4$	Kachkanar, Urals, pyroxenites
Chromite	$Fe\mathbf{Cr}_2O_4$	Saranka, Urals, ultrabasites
Ilmenite	$Fe\mathbf{Ti}O_3$	Irsha, Ukraine, placers
Rutile	$\mathbf{Ti}O_2$	Irsha, Ukraine, placers
Perovskite	$Ca\mathbf{Ti}O_3$	Afrikanda, Kola Peninsula, pyroxenites
Baddeleyite (technical)	ZrO_2	Kovdor, Kola Peninsula, ultrabasites
Cassiterite	$\mathbf{Sn}O_2$	Cornwall, Great Britain, greisens
Pyrolusite	$\mathbf{Mn}O_2$	Nikopol, Ukraine, sedimentary rocks
Uraninite	$\mathbf{U}O_2$	Prshibram, Czech Republic, hydrothermalites
		Krivoi Rog, Ukraine, albitites
Loparite	$Na\mathbf{Ce}(Ti,\mathbf{Nb},\mathbf{Ta})_2O_6$	Lovozero, Kola Peninsula, foidites
Pyrochlore	$NaCa\mathbf{Nb}_2O_6F$	Vishnevogorsk, Urals, carbonatites
		Sebl'yavr, Kola Peninsula, carbonatites
Pandaite	$Ba\mathbf{Nb}_2O_6 \cdot H_2O$	Sokli, Finland, crusts of carbonatites
Microlite	$NaCa\mathbf{Ta}_2O_6F$	Echassier, France, granites
Tantalite	$Mn\mathbf{Ta}_2O_6$	Voron'ya Tundra, Kola Peninsula, pegmatites*
Columbite	$Fe\mathbf{Nb}_2O_6$	Vigo, Spain, granites
Fergusonite	$Y(\mathbf{Nb},\mathbf{Ta})O_4$	Vigo, Spain, granites
Scheelite	$Ca\mathbf{W}O_4$	Felbertal, Austria, skarns
Wolframite	$Mn\mathbf{W}O_4$	Panasqueira, Portugal, hydrothermalites
Chrysoberyl (precious)	$BeAl_2O_4$	Malyshevo, Urals, pegmatites

*Pegmatites and hydrothermalites mainly derived from granites.

Semibold — elements of economical value.Isostructural minerals are included in brackets.

Hydroxides		
Gibbsite	$\mathbf{Al}(OH)_3$	Visokopole, Ukraine, sedimentary rocks
Bohmite	$\mathbf{Al}O\ OH$	Krasnaya Shapochka, Urals, sedimentary rocks
Diaspore	$H\mathbf{Al}O_2$	Krasnaya Shapochka, Urals, sedimentary rocks
Goethite	$H\mathbf{Fe}O_2$	Kerch, Crimea, sedimentary rocks
Montroseite	$H\mathbf{V}O_2$	Padma, Karelia, hydrothermalites
Silicates		
Quartz (technical)	SiO_2	Puiva, Urals, hydrothermalites
Spodumene	$\mathbf{Li}AlSi_2O_6$	Voron'ya Tundra, Kola Peninsula, pegmatites
Pollucite	$\mathbf{Cs}AlSi_2O_6$	Voron'ya Tundra, Kola Peninsula, pegmatites
Petalite (technical)	$LiAlSi_4O_{10}$	Polokhovo, Ukraine, pegmatites
Nepheline	$(Na,\mathbf{K},\mathbf{Rb})(\mathbf{Al},\mathbf{Ga})SiO_4$	Khibiny, Kola Peninsula, foidites
Microcline (technical)	$KAlSi_3O_8$	Belomor'e, Karelia, pegmatites
Muscovite (technical)	$KAl_3Si_3O_{10}F_2$	Belomor'e, Karelia, pegmatites
Phlogopite	$KMg_3AlSi_3O_{10}F_2$	Kovdor, Kola Peninsula, ultrabasites
Topaz (precious)	$Al_2SiO_4F_2$	Volyn', Ukraine, pegmatites
Beryl (precious)	$\mathbf{Be}_3Al_2Si_6O_{18}$	Malyshevo, Urals, pegmatites
Genthelvite	$Zn_4(\mathbf{Be}SiO_4)_3S$	Perga, Ukraine, microclinites
Leucophane	$NaCa\mathbf{Be}Si_2O_6F$	Zhitkovichi, Byelorussia, hydrothermalites
Aegirine	$Na(Fe,\mathbf{Sc},\mathbf{V})Si_2O_6$	Krivoi Rog, Ukraine, albitites
Kyanite	$\mathbf{Al}_2SiO_5$	Keivy, Kola Peninsula, schists
Titanite	$Ca(\mathbf{Ti},\mathbf{Nb})SiO_5$	Khibiny, Kola Peninsula, foidites
Eudialyte	$Na_{16}Ca_6Fe_3\mathbf{Zr}_3Si_{26}O_{74}Cl_2$	Lovozero, Kola Peninsula, foidites
Zircon (technical)	$ZrSiO_4$	Mariupol, Ukraine, syenites Verkhnedneprovsk, Ukraine, placers
Hydrosilicates		
Chrysotile (technical)	$Mg_6Si_4O_{10}(OH)_8$	Bazhenovo, Urals, ultrabasites
Kaolinite (technical)	$Al_4Si_4O_{10}(OH)_8$	Cornwall, Great Britain, crusts of granites
Chamosite	$\mathbf{Fe}_3Al_2Si_3O_{10}(OH)_8$	Elzas, France, sedimentary rocks
Talc (technical)	$Mg_3Si_4O_{10}(OH)_2$	Trimouns, France, sedimentary rocks
Sepiolite (technical)	$Mg_4Si_6O_{15}(OH)_2\cdot 6H_2O$	Madrid, Spain, sedimentary rocks
Clinoptilolite (technical)	$KNaAl_2Si_7O_{18}\cdot 6H_2O$	Sokirnitsa, Ukraine, sedimentary rocks
Carbonates *etc.*		
Siderite	$\mathbf{Fe}CO_3$	Kremikovtsy, Bulgaria, hydrothermalites
Rhodochrosite	$\mathbf{Mn}CO_3$	Kremikovtsy, Bulgaria, hydrothermalites
Magnesite (technical)	$MgCO_3$	Satka, Urals, sedimentary rocks
Calcite (technical)	$CaCO_3$	Urals, sedimentary rocks
Bastnasite	$\mathbf{Ce}CO_3F$	Zhitkovichi, Byelorussia, hydrothermalites
Strontianite	$\mathbf{Sr}CO_3$	Westfal, Germany, hydrothermalites
Ulexite	$NaCa\mathbf{B}_5O_9\cdot 4H_2O$	Studenitsa, Serbia, sedimentary rocks
Phosphates		
Amblygonite	$\mathbf{Li}AlPO_4F$	Caceres, Spain, greisens
Monazite	$(Ce,\mathbf{Eu})PO_4$	Normandy, France, placers
Apatite	$(Ca,\mathbf{Sr},\mathbf{Ce})_5(PO_4)_3F$	Khibiny, Kola Peninsula, foidites
Francolite	$Ca_{10}(\mathbf{P},C)_6O_{24}F_2$	Vyatka, Priuralie, sedimentary rocks

Sulphates		
Gypsum (technical)	$CaSO_4 \cdot 2H_2O$	Donbass, Ukraine, sedimentary rocks
Thenardite	Na_2SO_4	Madrid, Spain, sedimentary rocks
Kainit	$\mathbf{KMg}SO_4Cl\cdot 3H_2O$	Stassfurt, Germany, sedimentary rocks
Barite (technical)	$BaSO_4$	Meggen, Germany, sedimentary rocks
Celestine	$\mathbf{Sr}SO_4$	L'vov, Ukraine, sedimentary rocks
Alunite	$K\mathbf{Al}_3(SO_4)_2(OH)_6$	Beregovo, Ukraine, hydrothermalites
Haloids		
Cryolite (technical)	Na_3AlF_6	Ivigtut, Greenland, greisens
Fluorite	$Ca\mathbf{F}_2$	Pokrovo-Kireevo, Ukraine, hydrothermalites
Halite	$NaCl$	Donbass, Ukraine, sedimentary rocks
Sylvite	$\mathbf{K}Cl$	Solikamsk, Urals, sedimentary rocks
Carnallite	$\mathbf{KMg}Cl_3\cdot 6H_2O$	Solikamsk, Urals, sedimentary rocks
Carbides *etc*		
Diamond (precious)	C	Arkhangelsk, Russia, kimberlites Koiva, Urals, granulites
Graphite (technical)	C	Zavalie, Ukraine, granulites
Amber (precious)	$C_{10}OH_{16}$	Palmniken, Russia, sedimentary rocks
Coal (energetic)	(C,H)	Pechora, Russia, sedimentary rocks
Lignite (energetic)	(C,H,O)	Tula, Russia, sedimentary rocks
Sulphides *etc*		
Sulphur	S	Rozdol, Ukraine, sedimentary rocks
Chalcopyrite	$\mathbf{Cu}FeS_2$	Riotinto, Spain, hydrothermalites
Pyrite	FeS_2	Riotinto, Spain, hydrothermalites
Chalcosine	$\mathbf{Cu}_2S$	Lyublin, Poland, schists
Acanthite	$\mathbf{Ag}_2S$	Saxony, Germany, hydrothermalites
Sphalerite	$\mathbf{Zn}S$	Blyava, Urals, hydrothermalites
Galena	$\mathbf{Pb}S$	Rodopy, Bulgaria, hydrothermalites
Cinnabar	$\mathbf{Hg}S$	Almaden, Spain, hydrothermalites
Molybdenite	$\mathbf{Mo}S_2$	Yaurioki, Kola Peninsula, greisens
Pentlandite	$\mathbf{Ni}_4Fe_5S_8$	Outokumpu, Finland, hydrothermalites
Sperrylite	$\mathbf{Pt}As_2$	Pechenga, Kola Peninsula, basites
Cobaltite	$\mathbf{Co}AsS$	Saxony, Germany, hydrothermalites
Sylvanite	$\mathbf{AgAu}Te_4$	Sekertimb, Romania, hydrothermalites
Metalls		
Gold	$\mathbf{Au}$	Berezovsk, Urals, hydrothermalites
Silver	$\mathbf{Ag}$	Kutna Gora, Czech Republic, hydrothermalites
Palladium	$\mathbf{Pd}$	Monchegorsk, Kola Peninsula, basites
Platinum	$\mathbf{Pt}$	Nizhnii Tagil, Urals, placers
Antimony	$\mathbf{Sb}$	Senyaioki, Finland, hydrothermalites

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WONDERFUL DRAWINGS OF MINERALS BY VICTOR SLYOTOV AND VLADIMIR MAKARENKO

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In eightieth years of the last century I had friendly contacts with a small group of active and talented young men, amateurs of minerals, friends of Victor Arnol'dovich Slyotov. I has «grandiloquently» addressed to one of them:

Be a person in great and small,
While the fire in soul burns.
And my advice: grow as crystal!
Don't split in spherulite!

Life tectonic faults, «vpuki and vypuki» (Russian substitutions of terms «synclines» and «anticlines»; it is attributed to Vera A. Varsanof'eva) of long-awaited democracy dispersed this interesting group. One of them, philosopher by nature, has got this degree in the area of Mineralogy and flew away to London, where he had a job at a petrol station. Another guy deals with the physics of minerals. The third guy gifted geologist and mathematician is unfortunately far from mineralogy now.

Life of Victor Slyotov developed otherwise. After graduating from the Geological department of the Lomonosov MSU, as early as «perestroika» began, he was crippled by bandits for refusal to sign a self-slander. Bandits were just punished, but Victor obtained physical inability for all remained life. But love to stones and habit to work were stronger than circumstances, and he began to fulfil his old idea: to draw minerals.

In 2004 V.A. Slyotov was awarded to honorary title of laureate of the international premium «Philanthropist» for prominent achievements of invalids in culture and art (special premium «For novelty and originality in creation»). Project «Mineral Drawings» obtained its first recognition! Originality of ideas and quality of their artistic performance in albums «Mineral Drawings» have amazed the jury. In 2001-2004 three such albums were published, two later with subheading «Ontogeny of minerals in drawings». Drawings are interesting not only for artists but also for mineralogists, however, we shall note that all three albums of drawings by V. Slyotov and V. Makarenko are not a regular scientific work: they are unsystematic both in selection of mineralogical objects and in order of arrangement of drawings. This is certainly art approach: the object is interested for creator — both as artist with aesthetic point of view and mineralogist with scientific point of view. However one recollects H. Heine: «Nightingales sing without rules, only when desire». But scientific part in drawings is more than essential.

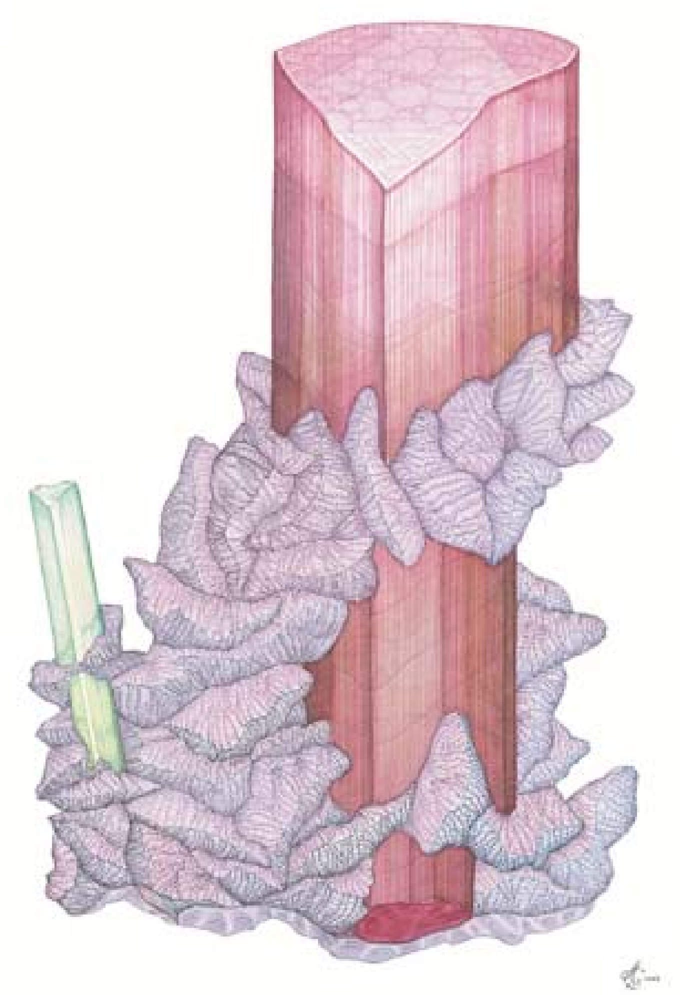
Science and art have different cognitive potentials, and their unity in obtaining universal general information about environment and world of stones is especially valuable. Artistic image of mineralogical object, which is created by specialist understanding a point of fact, has an extra significance for interpretation of mineral genesis and fist of all for revelation of the way of growth, dissolution, and recrystallization of minerals in druses and concretions, i.e. the questions insignificantly known and in essence raised by V. Slyotov.

Detailed images of morphology, especially the surface of crystals and spherulites, which are drawn during study of minerals under binocular (stereomicroscope), give the «rich food» for genetic mineralogy and first of all minerals ontogeny, that studies development of mineral individ and aggregates, their «life». Mechanism of formations and development of germs of crystals and spherulites, their further growth and subsequent mineralogical events: dissolution, recrystallization, regeneration, etc. And all that by features recorded on the minerals. Victor Slyotov entirely follows to the ideas of founder of mineral ontogeny, professor D.P. Grigor'ev who encouraged mineralogists to study and understand stones as true source of main and different mineralogical information and aesthetic beauty.

Subtitle «Ontogeny of minerals in drawings» on the second issue clearly determines mineralogical tendency, in which mineralogist and artist Victor Slyotov and his student and co-author, artist Vladimir Makarenko work.

Many graphic (white-black) drawings are made by authors with such accuracy and detailed elaboration (minuteness) that they do not demand explanations of specialists who can estimate novelty and scientific value of good and in many respects unique factual material.

Examples of plastic deformations of antimonite crystals by growing in them thin-grained aggregate of partly crystallized quartz grains are wonderful (Fig. 12, 13, N. 1). Many colour drawings (water-colour) made by V. Slyotov together with V. Makarenko are very informative and a



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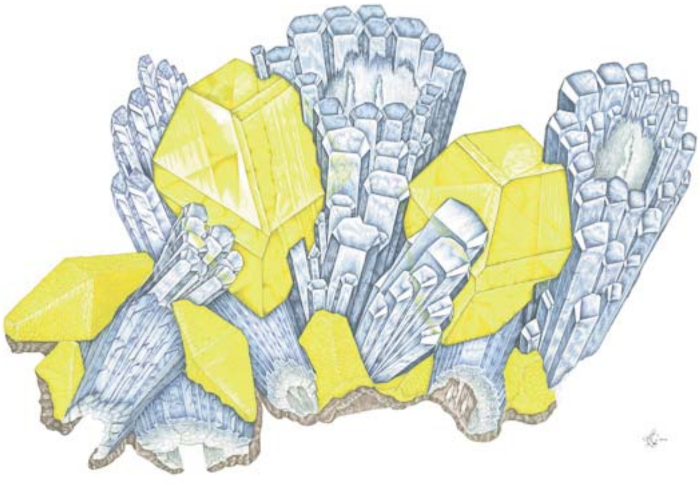
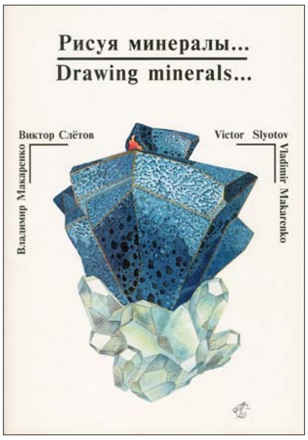
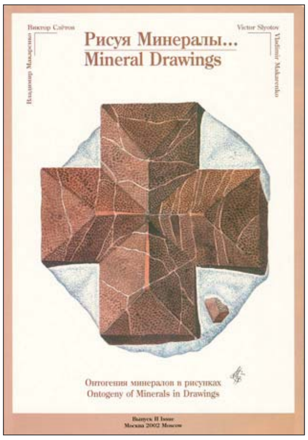




Рисуя минералы...
Drawing minerals...
Виктор Слётов
Victor Slyotov
Владимир Макаренко
Vladimir Makarenko



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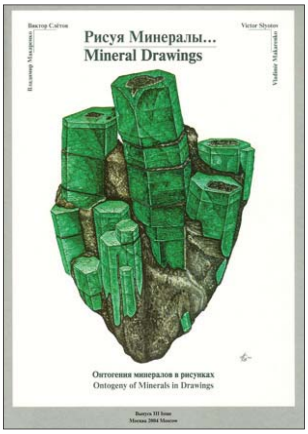

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Fig. a. *Tourmaline with asymmetrical spherocrystals of lepidolite, 3 cm. The Borshchovochnyi range, Eastern Zabaikalie, Russia*

Fig. b. *Crystals of sulphur of two generations and intergrowths of celestine with features of recrystallization. 1.5 cm. Shor-Su, Uzbekistan* c

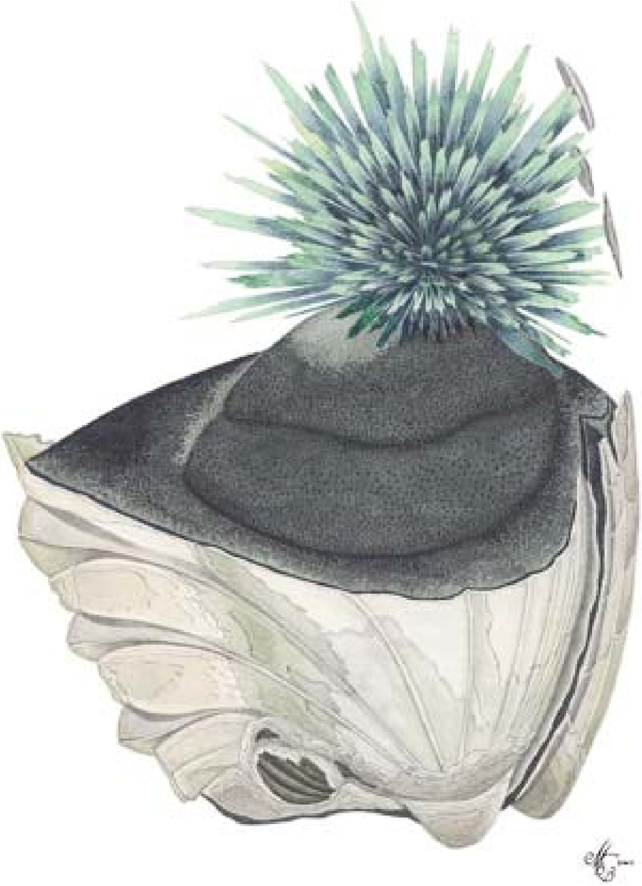


Fig. c. *Vivianite in shell. 3.5 cm. Kerch, Crimea, Ukraine*

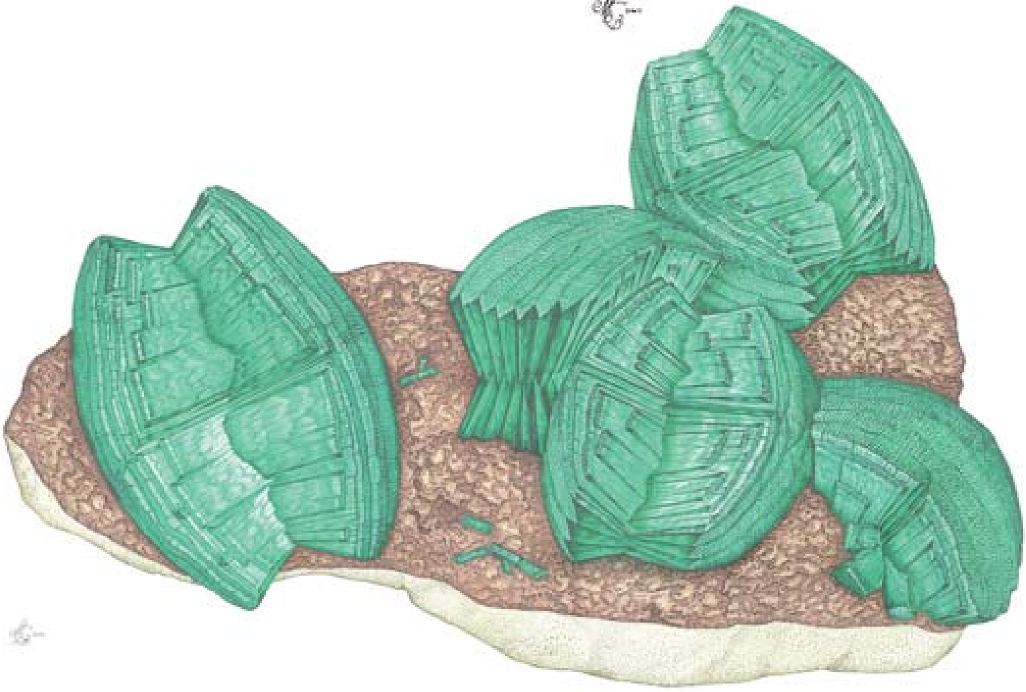
Fig. d. *Malachite, splitting of «sheaves» of tabular crystals twinned on the [100], on quartzite. 4 cm. Kazakhstan*

Fig. e. *Cave calcite, «anomalous crystallictites». 7 cm. Kyrgyzia*

Fig. f. *Crystallictite dendrite of cave calcite with trillings. 7.5 cm. Kyrgyzia*

Fig. g. *Gypsum antholites. 12 cm. Tajikistan*

d



e

f

g

marvellous too. Here it is enough to mention the picture of simultaneous recrystallization of two different mineral individs, celestine and natural sulphur with features of simultaneous dissolution and growth (Fig. 24, N. 3). All colour drawings are an excellent supplement to graphic materials. Many of them undoubtedly are amazing for collectors, amateurs, and connoisseurs of minerals. V. Slyotov's graphical images of silica concretions and V. Makarenko's colour Indian ink drawings of smoky quartz and amethyst in the first issue are gorgeous. Gypsum antholites growing by its basis on porous basement (Fig. 1, N. 2), vivianite in a shell (Fig. 30, N. 2), covellite sheet on chalcopyrite crystal (Fig. 24, N. 2), alexandrite twin (back cover, N. 2) and many other things are excellently drawn.

In «colour» image of brightly coloured minerals the complexities in combination of colours appeared. That in small specimen is excellently combined, during magnification on paper can look rather coarse (Fig. 20, N. 3). In that case it would be possible to «deviate from nature» and to use to less saturated colours for quartzite.

Authors choice of mineral object and technique of image are rather emotional and are not deprived elegancy and refinement. But for the crystallographic purposes, the perspective, shadows, creating and underlining effect of specimen dimension, are not shown and taken into account everywhere. In all that is shown, the drawing is minute, and hardly perceptible thickening of lines or strokes becomes enough for sensation of tridimensionality perception of crystals and druses. The only remark is concerned — Fig. 8, N. 1, where one octahedron looks convex.

Precise scientific drawings what motive the artist would not be guided by are extremely labour-consuming. Nevertheless, we hope the authors will continue their creative job and the new special art albums on mineral ontogeny will be issued.

V. Slyotov's attempt of to use mineral forms for creation of abstract artistic images (Fig. 11, N. 2), dendritic art landscapes (Fig. 6, N. 1; Fig. 8 and 9, N. 2), pictures of turned specimen of limonite (Fig. 10, N. 2) is interesting.

The albums are an excellent present for collectors and amateurs of stones; which extends their ideas about mineral world. For specialists interesting in mineral genesis, it is in many respects the collection of scientific articles in pictures, containing a little known and new information. For teachers of mineralogy, natural sciences or natural history the albums give a possibility to arrange from separate figures different thematic posters for students, for example, «Minerals of silica» (crystals and aggregates of quartz, geods and concretions of chalcedony, agates), using more than 20 lists; «Skeleton crystals and dendrites» (18 drawings); «Spherulits and fibrous aggregates» (20 drawings); «Mineral aggregates of caves» (9 drawings); «Twin intergrowths» (10 drawings), etc.

An unfortunate imperfection of the albums is their price that is relatively high for ordinary scientific employers and students. Unfortunately, the albums were published only with authors' support, and the price was established in hope though in any measure to compensate their expenses.

It is real pleasure to say great thank you to the director of the Fersman Mineralogical Museum RAS, Doctor of Geological-Mineralogical Sciences, Professor Margarita I. Novgorodova and collaborators of this Museum Tatiana M. Pavlova, Alexander A. Evseev, Dmitriy I. Belakovsky who in their best way promoted the publications. Realization of project «Mineral Drawings» hardly would possible without their unselfish help and support.

It would be desirable to trust that further fruitful collaboration of the authors and the Mineralogical Museum, where was the presentation of the first album «Drawing Minerals» took place and the exhibition of works of V.A. Slyotov and V.S. Makarenko was organized, will be even more successful, and they will please experts and amateurs of minerals with new interesting works. It is also appropriate to mention that there are 192 specimens of different minerals in Museum collection presented by Victor.A. Slyotov.

One can see in the Internet the drawings of V. Slyotov and V. Makarenko in the gallery of visual art «Hieroglyph» in section «Art-criticism» on personal pages of the authors *(http://www.hiero.ru/Vivianit), (http: //www.hiero.ru/Anapait)* and in the gallery «Way to stones» (*http://hiero.expo.ru/gallery/mineral/index.html)* at the same site.

http://www.hiero.ru/Vivianit
http://www.hiero.ru/Anapait
http://hiero.expo.ru/gallery/mineral/index.html

Discussion

UDC 549.0

ESSAYS ON FUNDAMENTAL AND GENETIC MINERALOGY: 1. WHAT ARE THE «MINERAL» AND «MINERAL SPECIES»?

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At present, the existing nomenclature and systematisation of minerals is based on *chemical principles*, according to the statement that mineral is a chemical compound, though natural, but only one from million ones known to science. However, mineralogy is a *geological*, *natural-historic science*, and mineral is not only chemical compound but also a *natural geological body*, the main form of inanimate matter in nature, a stable phase of mineral-forming processes, which has its own geological history, the object of *geology*. Consequently, the nomenclature of minerals, their systematisation and classification must be *natural*, i.e. be based not only on formal descriptive laws of chemistry but also should reflect the real correlation of chemical composition and crystal structure of minerals with concrete geological conditions of their formation, as well as their evolution in geological processes. By analogy with other *natural* science, biology, it is shown that minerals as well as living organisms, can be studied at different levels of organization of matter, which are characterized by proper elementary discrete systems and phenomena. Special level is one of them, and system concept of *mineral species* is a genetic concept.

There is a conclusion that recommended formal merely *chemical* (or crystallochemical) criteria of the IMA CNMMN do not correspond to natural principles of classification of *mineral species*, and describe objects of mineral science from the one side, only at the level of inner structure of compounds, without taking into account the essence of mineral as a stable phase of geological processes, with natural variations of its chemical composition, structure and properties within the field of its stability.

17 references

Mineralogy, as a part of geological science, is a *natural-historical* science. It means that mineralogy studies *natural objects*, as they exist in nature (independently from interference, wishes or ideas of a human, in all their *complexity*, *diversity*, *and historical development*. In contrast from geochemistry, which deals with Earth crust substance at the level of chemical elements, mineralogy studies *compounds of chemical elements (minerals)*. Minerals are diverse. They differ not only by set of combining chemical elements but also by complexity of these compounds. As the main form of existence of inanimate matter in the nature, minerals *are originated*, *exist*, *and are destroyed*, i.e. «live» in the geological processes; reacting on changes of physical-chemical parameters of mineral-forming (or «mineral-keeping») medium, they, of course, can change morphology, chemical composition and structural peculiarities from their «birth» to «death».

A mineral is assumed to have crystal structure (it means that the structure can be detected by X-ray methods). Therefore metacolloids and other thin-dispersed formations, arising as a result of deceleration of germs growth, are excluded from a number of minerals as defective ones. This is the first of misunderstanding in mineralogy, the crystal structure of thin-dispersed aggregates exists and can be detected by more precise methods of electron.

All mentioned above fundamentally can help us to distinguish the objects of mineralogy from the objects of chemistry. However, *chemical* nomenclature and systematic of minerals are generally based, as it was suggested by J. Berzelius in 1814 on chemical principles (Course of mineralogy, 1936; Frank-Kamenetskiy *et al.*, 1977; From Commission..., 1977; Bulakh, 1977, 1978, 2000, 2004; Lazarenko, 1978; Bokiy, 1978, 1997; Nickel, Grice, 1998; Nickel, 1992; Nickel, Grice, 1999, etc.). Chemists consider it *natural*, since, by their opinion, it «is simultaneously a law of nature» (Bokiy, 1985, 1997).

Mineralogists: who are they, geologists or chemists?

«Widely chemistry extends its hands
in humane affairs...»
D.I. Mendeleev

If we consider «minerals» only as a part of 15 million of «chemical compounds» synthesized by chemists, there is no problem. Their nomenclature and systematisation (classification), as well as the other chemistry objects, must be, of course, formalized by chemical laws, and new mineral names must correspond to the principals suggested by the International Union on Chemistry. For mineralogists-»chemists», considering minerals only as chemical compounds, this is quite normal. G.B. Bokiy (1997) wrote in his last work «Systematisation of natural silicates» following: «It is possible to consider that a single attainment in classification of minerals for the last 100 years is that it was accepted to characterize minerals by chemical composition» (Page 3). «Mineralogy, although it is considered *as special* science, nevertheless represents a doctrine about inorganic compounds, forming our Earth, and *it is only a part of chemistry, on which ideas it is based entirely*» (Page 18, italics is our).

Academician A.E. Fersman did not agree with these ideas. A half a century ago he wrote: «Since study of mineral in all its properties, crystal, physical, mechanical and chemical properties, at the background of study the mineral not as a self-sufficient body, but as a part of a whole Earth's crusts, the mineralogy in our country has now come to raising of a number of the most important and profound problems of science. One should remember that mineral is not simply chemical compound from textbook on chemistry, but a natural body with all complexity of its laws and its history» (Fersman, 1945. Selected Works. V. 5. 1959. P. 552).

Distinctions between «chemical» and «geological» approaches in mineralogy are the most clearly revealed by determination of the main concept of mineralogy, «mineral species».

«Mineral species» is quite often considered *as the least* unit of organization of mineral matter (Lazarenko, 1961), «the most lower» taxon in systematisation, after G.B. Bokiy (1978, 1997). It seems to me to be wrong. «*Species*» should not be the least unit, but first of all *the comparable one* for all classes and groups of mineral with both simple and complicated composition and structure, in the whole mineral kingdom. It is not so, this is not a *species*, but *variety of species*, describing more «fine» distinctions, which can not be comparable directly for different minerals. So as *species-forming* features of mineral, the following ones should be chosen: first, *the most essential* ones, secondly, their *natural (genetic)* characteristics and properties.

What do mineralogists-»chemists» suggest us? Practically, to descent on elementary level and consider correlations of separate chemical elements in minerals. According to recommendations of the IMA CNMMN, the «*rule of 50 %*» is the main one determining boundaries between mineral species among continuous solid solutions, i.e. predominance («domination») of one of the chemical element over other ones (Frank-Kamenetskiy *et al.*, 1977; From Commission..., 1977). Recently the «rule of 50%» is extended even on ratios of elements in each of non-equivalent sites in the crystal structure of mineral (Nickel, Grice, 1998; Nickel, Grice, 1999). It is obvious this approach completely discredits mineralogy as *geological science*, since in minerals with complex composition and crystal structure, in which there are more than ten cation structural sites, each of which can be isomorphically occupied up to a third by chemical elements of Mendeleev's table (for example, in eudialyte), it is possible to reveal an innumerable multitude of variants, and all them, according to recommendations of the CNMMN, can be registered as independent mineral species. However, from the point of view of geology, all of them are *eudialytes*, formed in quite definite field of stability under conditions of extremely high alkalinity of mineral-forming medium.

Nevertheless, this «subversive activity» of the CNMMN was delightfully accepted by some mineralogists. Provoking by these recommendations stream of «new minerals», for which names there is not enough mountains, rivers, and names of great scientists already, has flooded the literature, and threatening prognosis by A.P. Khomyakov (1990) to bring a number of mineral species to n 104 n 105 (basing on arithmetical calculation of possible combinations of chemical elements in crystal structures) becomes quite realizable. It is calculated that over 4000 minerals are described (Bokiy, 1997), and enthusiastic «selectionists» do not intend to stop on that. But it is time! A.E. Fersman (1938), and after him our and foreign prominent mineralogists-geologists as A.A. Saukov (1946), A.S. Povarennykh (1966), I. Kostov (1971), N.P. Yushkin (1977), V.S. Urusov (1983) *et al.*, explaining, what is the distinction of «*inanimate*» nature from «*animate*» one, repeatedly noted that a number of mineral species in nature is limited. A.E. Fersman, in particular, wrote: «A question about number of known in the Earth's crust mineral species obtains in whole more definite answer only at specification of the mineral species concept. M.N. Godlevskiy (1937) and A.G. Betekhtin (1937) absolutely properly introduced in the determination the physical-chemical principle, however, they could not avoid complications analysing dispersed-colloid systems and isomorphous mixtures. Merely formal approaches to classification of such multiphase systems are not applied; especially as mineral is a natural-historical body, for which absolutely specific and complex systems are appropriate and determined; especially as it is not possible to approach merely formal to subdivision of isomorphous series on independent species and varieties» (Fersman, 1938. Selected Works. V. 1. 1952. P. 846).

Mineralogists-geologists always objected to «chemical» formalism in delimitation of mineral species, they demanded its geological comprehension. A.K. Boldyrev (Course of mineralogy,

1936) admitted the «rule of 50%» for two-component compounds in case of continuity of a series, but in case of formation of intermediate compound he suggested to distinguish three phases (where «intermediate» phase could be isomorphous mixture, solid solution or chemical compound with variable composition) or consequently three mineral species in the following intervals of composition: 0-0.25, 0.25-0.75, and 0.75-100%. But he emphasized: «...if there is no more forcible bases for other subdivision» (!). However, if isomorphous mixture can not be satisfactorily described as two-component system, it is necessary to use triangle diagram for three-component system and to transform the «rule of 50%» into the «rule of 33%» (3 minerals); then in case of formation of «intermediate» compounds (7 minerals) the content of admixtures of other components in phases can not already exceed 17%. E.H. Nickel (Nickel, 1992) also points out that delimiting «point of 50%» transforms into «point of 33.3%» in three-component system (and in «25%» in four-component system), it is necessary to take into account at apportionment of single mineral species fields. So the delimitation of mineral species depends on choice of system for their description. That means that mineral species can not be correctly delimited in natural process without comprehension of this process.

D.P. Grigor'ev (1961) emphasized that concept of mineral species was formulated, basing on problem of classification of mineral individuals. This concept includes a multiplicity of individuals, which are chemically and structurally *identical*, but at the same time «minerogenesis does not seem now as passive deposit of mineral matter or body, but as a process of its development, in which correlated moments of origin, growth, and change of mineral, the signs of interaction of mineral and medium are traced... On the same basis the attention to questions of *development of mineral species, their changeability at minerogenesis under influence of changing factors: temperature, pressure, and chemism of medium* also becomes stronger» (italics is our).

Looking back to biologists

> *«...in every creation of nature we well see something that has long history...»*
> *Ch. Darwin*

G.B. Bokiy (1997) wrote that it is reasonable to compare the mineral classification with biological ones: «...objects of these classifications exists in nature independently from human activity». However, he noted, «biological classifications are complicated by that a phenomenon of evolution must be take into account in either degree for them. This moment is absent in classification of minerals» (P. 9-10). Unfortunately, only adoption of hierarchy of biological taxons by him was the result of this comparison, i.e. subdivision of minerals into *classes*, *subclasses*, *orders*, *suborders*, *families*, *genera*, and *species*. Essence of biological systematisation, its *naturalness* and *genetic sense* of distinguishing of *biological species*, apparently, was not comprehended and estimated at its true worth.

First of all we should mention that in biology there is no generally accepted determination of the main concept, *living matter*, since (as they consider) there are no criteria having a single meaning, that distinguish *living* matter from *inanimate* one. Biologists are not confused by that (after all, only *objectively existing* things can be studied, but not the things, that we have *decided* to include or not include in the objects of our study), but in contrast to us, biologists clearly realize that they *study living matter at different systemic levels of organization of life:* «molecular» — «cellular» — «tissue» — «organogenetic» — «ontogenetic» — «population» — «*specific*» — «biogeocoenotic» — «biospherical», for which it is possible to distinguish proper elementary discrete *structures* and *phenomena* (Yablokov, Yusufov, 1989; Levitina, Levitin, 2002). The most important of them are molecular-genetic, ontogenetic, population-specific, and biogeocoenotic levels of study. At all levels the study of form of matter organization, i.e. chemical composition and structure of molecules, from which organisms consist, structure of cells, tissues, separate organs, morphology of organisms from embryo to adult individuals, species and populations of organisms, and, finally, natural their communities (biocoenoses), is accompanied by study of their development, clarification of their genesis and mechanisms of transmission of genetic information during subsequent evolution. It is very important.

Before we will consider *population-specific* level, the most interesting to us, we shall note that some our worrying «mineralogists-chemists» recently attempt to inspire us that all biological *specific* distinctions can be reduce to fundamental chemical differences in structure of DNA molecules and in due time «reduce all variety of organic world to *biochemical* (i.e. *chemical*) characteristics. And in foretaste of such perspectives they find the support to propagation of chemical classification also in mineralogy. This is a primitive simplification! Without possibility to go into details (look through — Levitina, Levitin, 2002), we shall note that on *molecular-genetic level* in DNA molecules there are actually the special «parts», *genes*, controlling («encoding») their *reduplication*, i.e. break (with participation of special ferment of DNA-depended RNA-polymerase) of hydrogen bonds between purine and pyrimidine bases jointing double spiral of DNA, and following synthesis of complementary threads (i.e. following «doubling» of each of broken threads of DNA). By this way «kept» in genes heritable information is really transmitted to intracellular controlling systems during synthesis of macromolecules of cellular protein of organisms on matrix principle. However, this transmission occurs by the way of *covariance reduplication*, i.e. self-reproduction with *changes*, the single specific for life on the Earth property, providing with appearance of endless number of changes (*mutations*), that are inherited, but not always kept in hereditary populations. At that the least element of arising mutations is not a gene, but one of joining pairs of nucleotides of DNA. At present, DNA molecules of *primitive* discrete living particles (viruses, phages, bacteria, protozoa eukaryotes) and free reproducing sexual cells of multicellular organisms are studied in details; they are really have *relatively high degree of stability*, that provides possibility of their identical self-reproduction (*hereditability*). But also it goes obligatory with *insertion of changes*, that results from physical-chemical properties of the most bulky DNA molecules, since *degree of stability* of each complex molecular and supermolecular system is *confined* and from time to time suffers *structural changes* as a result of movement of atoms and molecules. If these changes will not at once result in lethal outcome, they will, according to the law of Tumofeev-Resovsky, will repeatedly gain strength by the way of covariance reduplication, that *gives possibility of inheritance also discrete deviations from initial state*. Consequently, formation of species at molecular-biochemical level is connected both with stability and changeableness of DNA.

But speciation takes place not only at molecular-biochemical level. *At ontogenetic level*, during life of *individuals*, from their birth to death, not only realization of heritable information but also control of viability of this genotype of organisms by the way of natural selection take place. This is as if repeated natural experiment on continuation and evolution of live on the Earth.

We are, first of all, of course, interested in *population-species level* of organization of living matter. Concept *species* in biology was introduced by Aristotle (384-322 BC), and that became fundamental after the works of J. Ray (1627-1705) and C. Linnaeus (1707-1778). However, conception about constancy, invariability of species at once resulted in creationism, i.e. ideas of their divine creation. In struggle against creationism the transformism of G.-L. Leclerc, comte de Buffon (1707-1788) and J.B. Lamarck (1744-1829) has been formed, and soon every changeability of organisms in nature was identified with speciation. (How it is known on that now happens in mineralogy.) In the beginning of 20th century, *typological conception about indivisibility of species has failed* finally, and not the species, but the concept of *geographical* race has become the main unit of classification in biology, i.e. binominal nomenclature was replaced by trinomial one, where besides *genus* and *species* even *subspecies* was included in. (For example, Vulpes vulpes vulpes — Fox Middle Russian, V. vulpes stepensis — Fox Steppe.) When it was found out that subspecies were also inconstant, one became to distinguish *seasonal*, *ecological*, *physiological* and *other races*. As a result, traditional «Linnaeus's» species was disintegrated into hundreds and thousands hereditably stable small forms. For example, species of wheat ordinary, Triticum vulgare Vill., was divided into several thousands smaller species. This situation resulted in that fundamental biological concept *species*, it seemed, was outdated (Yablokov, Yusufov, 1989).

Only in the beginning of 30th years of the 20th century, thank to the works of schools of N.I. Vavilov in the USSR and J. Clausen in the USA, the problem of species became approaching to its contemporary solution: *biological conception* of species has been created. Species has appeared to be a complex *genetic* system: individuals of one species have the same genofund and are defended from penetration of genes of other species by natural barriers of isolation. It has appeared, that *species* can include different by structure and the way of life forms (*subspecies, populations*), which representatives can from time to time interbreed and give fruitful posterity. That is transitions between species, subspecies, and populations are possible. These is the contemporary conception of *polytypical species*, that unites contradictory points of view on *species*, as the *main structural unit of organic world*, and *on species*, as complex developing *genetic system*. According to A.V. Yablokov and A.G. Yusufov (1989), species is a *multiplicity of individuals with general morphophysiological characteristics, which are able to cross with each other, giving fruitful posterity, and form a system of populations, forming general natural habitat. However, neither morphological nor geographical and physiological-biochemical* distinctions separately can not serve universal specific characteristics. That is the genetic unity of organisms turns out the main *criterion of species. Species turn out not genetically exclusive (closed), but genetically stable systems. We shall not consider phylogeny of species*, it is clear that for time of existence of life on the Earth not only biological species but also their single genera, classes, and even types of organisms have evolved.

Mineral at different levels of organization of mineral matter

> *«Mineral is not only physical-chemical system, it is a natural body, part of the most complicated geological environment, and must be studied only in connexion with these environment, in all complex analysis of that numerous factors, from which it is composed.»*
>
> *A.E. Fersman*

We suppose that in mineralogy, by analogy with biology, it is possible to distinguish different levels of study of mineral matter, that will allow better determining the place of the concept *mineral species* among other nomenclature units.

1. Atomic-crystallochemical level. This is, in fact, that is known to all mineralogists and that they are occupied. From analogies with biology it is evident that on this level in mineralogy its own *elementary discrete structures* — i.e. atoms and their groups, and *phenomena* — i.e. jointing them in crystals structures with «chemical» bounds of different type, can be distinguished. But it is not yet the *mineral species*. Just as both in biochemistry far from all can be reduced to structure of DNA molecules, but successively forming as a result of synthesis of protein *cells*, *tissues*, *organs* of organisms are specially studied, and in mineralogy atomic structures of matter and regularities of behaviour in them *separate atoms* as well as isolated discrete *groups of atoms* (for example, SiO_4-tetrahedra) are studied: polymerisation of tetrahedra in diortho-, different chain, banded, layer and framework radicals, their joining with heterosize and heterocharge cations. Translation of these elements (on matrix principle) in space to endless crystal structures allows distinguishing the periods of identity and *unit cells*. As in biology, during the process of mineral growth, at transition from structures of near order (unit cells) to structures of long-range order (macrovolumes of matter), variations appear and can be transmitted (compare with mutations): defects, dislocations, errors in packing of atoms (polytypism), substitution of SiO_4^-tetrahedra by AlO_4^-, FeO_4^-, BO_4^-, PO_4^-tetrahedra, and substitution of cations by microadmixture elements (isomorphism), inclusion of whole fragments of one structure in another one (domain structure, polysomatism), chemical and structural ordering of atoms (for example, Si/Al-ordering in the framework of feldspars and other alumosilicates), twinning, etc.

Just as living organisms, minerals are distinguished by degree of complexity of their organization: there are native elements (analogues of primitive unicellular organisms), intermetalides, mineral with simple and more complex variable composition, representing solid solutions, isomorphous series, structures with mixed radicals, mixed-layer silicates, «cellular» zeolite-like structures, silicates with broken frameworks, etc., these are the result of complicated adaptation of crystallizing mineral phase to changing by chemical composition and properties mineral-forming medium.

Matrix structure of crystal structure of minerals is described by space symmetry in of atoms pattern. Besides 14 known types of cells of A. Bravais, 32 species of symmetry, and 230 standard space groups of E.S. Fedorov, recently the non-standard space groups are distinguished; besides *general* symmetry of structure *the local* symmetry of its separate fragments is distinguished. The latter is especially important for description of coordination of microadmixtures in defects of crystals by spectroscopic methods of analysis and for explanation some physical properties of minerals. *The symmetry* of short-range and long-range order is distinguished, that reflects distinctions in structure of micro- (in unit cell) and macrovolume of mineral matter. It is clearly that symmetry reflects abstract order in arrangement of atoms in structure, and its change can be caused by different reasons, i.e. it is secondary and can not be the main factor for mineral species determination.

2. *Ontogenetic level*. Just as in biology, at this level the regularities of growth of single individuals, crystals (grains) and their aggregates, are studied. Detailed review of studies at that level is given in «Ontogeny» by D.P. Grigor'ev (1961): from origin of germs to different types of growth and recrystallization of individuals and aggregates. It is important for us that a crystal evolves during process of growth: its morphology, chemical composition, peculiarities of crystal structure, symmetry can be changed, the zones of growth or face sectors, which can be essentially different on chemical composition and properties can appear. Since, according to E.K. Lazarenko (1963), *mineral species is a multiplicity of mineral individuals of the same type structure and composition, changing in definite natural limits, then individuals characterized by continuous isomorphism should be considered as the sin-*

gle mineral species, and the other individual members of this series as the varieties of this *species*. It does not matter whether the content of isomorphous admixture exceeds 50 % or not (moreover, in separate structure site), since the real mineral matter and real variations of its composition during change of physical-chemical conditions of mineral-forming medium are studied. In biology *species* is a *totality of individuals*. Therefore reverse cases, when within the same mineral individual (crystal, grain) the several mineral species are detected in separate growth zones or crystal sectors (for example, hafnon in growth zones of zircon, in which Hf:Zr>50:50), by our opinion, are a nomenclature absurdity. Studies at ontogenetic level must include also solid phase transformations inside individuals (phase disintegration, polymorphous transitions, structural ordering, microtwinning), since they take place during change of conditions on certain stage of *existence* of mineral individual, although after its crystallization. That brings in its own complications in the problem of separation and delimitation of mineral species, but that is the real construction of studied mineral matter.

3. *Species level*, to which we has already turned and which is the main goal of this study, is summoned to determine criteria, by which unit *mineral species* should be distinguished as well as, and *species varieties of mineral species*. By analogues with biology it is possible to make a number of conclusions. First, *species* is a *genetic concept*, and its content is determined not only by chemical composition and crystal structure but mainly by behaviour in geological processes. We do not know *phylogeny* of mineral species: when, how, and in what forms did chemical elements combine chemical compounds on the Earth, what was physical-chemical conditions and how did they evolve. But we know that the same chemical elements at high pressures and temperatures form absolutely different compounds, than under moderate and hypergene conditions especially. We know that chemical elements of the Earth have been separated, or have been differentiated in some way. Much better (although far from all groups) we know *ontogeny* of minerals. If there are not enough natural observations, the physical-chemical experiments and synthesis of lost, relic, unstable compounds help us. They help us to recreate, reconstruct minerals on early stages of their existence. Just as a result of ontogenetic studies we detect the real totalities of evolving mineral individuals, which we can unite in really existing mineral species. By our opinion, *mineral species is a natural totality of mineral individuals, which, in the bounds of field of its stability, are able to change, in certain limits, both chemical composition and peculiarities of crystal structure in accordance with change of physical-chemical conditions of mineral-forming (mineral-keeping) medium, since beyond this field they are destroyed and replaced by other minerals.*

Second, *species* is a main, *commensurable* nomenclature unit, but it is *not the least*: in biology within the species the *subspecies* (our *varieties*), sorts, races, populations are distinguished, which in biological classification are not less significant, than species. The same is expediently to distinguish among minerals, for description of matter at different stages of process or in different geological environment. *Varieties* by chemical composition, structure, morphology, way of formation, etc. in mineralogical nomenclature should become more significant in study of analysis of mineral typomorphism for example.

Third, different groups of minerals are distinguished by complexity of their organization as well as living organisms, for which it is impossible to distinguish *all species-forming characteristics,* and the main criterion is *an ability to reproduce the self-similar*; apparently, in different groups of minerals it is also justified to distinguish mineral species on their own criteria, without adjustment their to universal templates.

Mineral *species is* an abstract concept, but it generalizes and «absorb» the properties and behaviour of concrete mineral individuals. Since this is a crystal phase in mineral-forming process, it is separated from co-existing phases by *division surface*. The presence of distinct division surface is the main criterion for determination of mineral species. Growth zones and face sectors do not have the division surface and belong to the single mineral individual including them, and, consequently, they are considered as the same mineral species. On the other hand, the products of phase disintegration (for example, perthites) have the division surface, so microcline and albite co-existing inside the single block-crystal of feldspar are different mineral species. However, on early high-temperature stage of phase disintegration co-existing K,Na- and Na,K-feldspars (with high content of isomorphous admixture of opposite component) during their X-ray study reveal distinctions in unit cell parameters a at equality of both parameters b and c, that shows the reservation of general Si,Al-framework in «disintegrated» feldspar. It is evident, in that case we do not have a right to distinguish microcline and albite phases, and have to do with one mineral species — K,Na-feldspar. The latter shows that content of a concept mineral species is concrete and can change at different physical-chemical parameters.

And the latter. From stated above it is obvious that «new minerals» registered by the IMA CNMMN, studied only by chemical and structural methods, are most often the varieties of already known minerals, since they are connected with gradual variations of chemical composition with local reconstruction of symmetry of sites during their occupation by isomorphous admixtures (Borutzky, 1997). Detailed study of their behaviour in geological processes so concretizes data about real minerals and their groups, that newest recommendations of the IMA CNMMN become simply absurd. These rules, as a matter of fact, are modest cover of our *lack of knowledg*e of minerals.

Conclusions

Thus, main misunderstandings concerning nomenclature in mineralogy are caused by the fact that many researches do not comprehend that mineralogy, as a part of geology, is a *natural-historical science*, and consequently, the concept of *mineral species* is *a genetic concept*. If this statement is accepted, then several conclusions follow from this:

1. Study of mineral matter is made at different organizational levels. The objects of this study — atoms, their complexes chemically bonded, structure, symmetry, defects, crystals, their aggregates, mineral species and individuals, varieties, and studied phenomena — isomorphism, polysomatism, polytypism, polymorphism, crystallization, growth of crystals, metasomatism, solid phase transformations, typomorphism, etc. are different at different levels. For each of them their own classifications are possible (systematisations of chemical compounds, structures, defects, etc.), reflecting the present day knowledge of crystallochemistry, physics of minerals, etc. Limitation of mineralogical science by study of minerals only at one level (for example, *chemical*), its transformation only in descriptive science, readdress of study of behaviour of minerals in geological processes to other sciences, petrology, lithology, geochemistry, by our opinion, result in transformation of mineralogy in chemistry and its extermination as geological science.

2. Study of minerals at *species* level reflects their behaviour as a phase of geological processes, the main form of existence of inanimate matter in nature. *Mineral species* is a multiplicity of mineral individuals, really existing in the certain *field of stability*, within the limits of which both *chemical composition and peculiarities of crystal structure* can *change* (according to the change of physical-chemical parameters of medium) but the species does not exist (*destroyed or replaced by other minerals*) *beyond the field of stability*. Isomorphous substitutions really observed in structure (independently from that whether they result in domination of some component or not), cases of zoned or sectored growth, chemical or structural ordering, polytypism, etc. do not result in formation of independent mineral species, if they occur within the field of stability.

3. *Mineral species* is not *the least*, but *comparable* nomenclature unit. With the purpose of detailed description of behaviour of minerals within the field of their stability the corresponding conventional varieties on morphology, chemical composition, structure, physical and spectroscopic properties, etc. can be distinguished. Determination of varieties is not less significant in mineralogy, than determination of mineral species.

4. Delimitation and distinguishing of new mineral species can be realized as a result of detailed physical-chemical study of minerals, obtaining and publication of evidences of independent existence of corresponding mineral phases in any concrete geological environment, but not as a result of volitional decision of some commissions, notwithstanding authoritative researches forming them are.

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BOOKS REVIEW

The Grandmasters of Mineral Photography, Mineralogical Almanac, special issue, M., 2004. — 136 p., 117 colour and 13 b/w photos, in soft cover. In English.

Do you pay attention, how do you admire the beautiful mineral? You look it first from the one side, then from the other, differently bring it to the light: you involuntarily form its general image in your mind.

All that is beyond the limits of photographic craft. All remained to a photomaster is only to choose one perspective and one light decision. But if he profoundly knows minerals and is able to intelligently deal with these poor graphic means, then he will be able to carry to spectator the image of a natural aesthetic masterpiece, although deprived of volume, but with expressiveness and informativeness. Moreover, a photomaster has also the magic ability to create the masterpieces from «useless» small crystals, which did not deserve their own places in the collection and even were thrown out in a dustbin, the good-for-nothing waste. Complex of the talent, art taste, command of photographer technique, and special knowledge allows to notice in the mineral that deserves the choice and to express this on a photo beautifully, expressively, and without formalistic exaggerations. And if one also succeeded in catching a «raisin», peculiar to every subject, then it is already an art.

Fourteen authors of the album, published to the 50th Anniversary of the international Tucson Shows, are the modern photographers of minerals from Russia, the USA, France, Italy, Germany, and Japan. All them, Roberto Appiani, Nelly Barriand, Louis-Domenique Bayle, Rainer Bode, Michail Bogomolov, Hidemichi Hori, Terry Huising, Mikhail Leybov, Olaf Medenbach, Harold and Erica Van Pelt, Jeffrey Scovill, Stefan Weiss, Wendell Wilson, are experienced and knowing mineralogists. Their names and photos are known to the readers by books and periodical issues: *World of Stones* and *Mineralogical Almanac*, *Lapis* and *Rock & Minerals*, *Mineralogical Record* and Mineralien Welt... Each author is represented by nine works and the brief biographical information.

Among 117 photoworks published in this gift album there are the best ones and quite disputable. It will be interesting to the reader to determine his preferences, to appreciate the creative styles of different masters, to thing under edifying examples of solution of uneasy graphic problems.

Boris Kantor

Chukanov, N.V., **Minerals of the Kerch Iron-Ore Basin in Eastern Crimea**. Editor I. Pekov. Mineralogical Almanac, vol. 8, M: 2005. — 112 p., 147 colour photos, 49 figures and b/w photos, 84 references. In English.

This volume acquaints with the history of study of Kerchian ores and minerals, the geology of the Crimea and iron-ore basin, the types of iron ores and fossilized fauna, the mud volcanism of the Azov-Black Sea basin etc. The main part is devoted to the detailed illustrated description of minerals of Kerchian iron ores, which since the end of the 1960th have attracted the soviet collectors and, with an appearance of the specimens abroad, have created them the agiotage popularity in the western collectors' world. The book contains the description of 160 mineral species of the Kerch Peninsula. The author devoted to their study, in the beginning as a collector and then as a scientist, the numerous field collections and observations, laboratory studies and bibliographical investigations.

Nikita V. Chukanov is a fancier and naturalist, connoisseur, expert and successful collector of minerals, and simultaneously persistent and thorough researcher, always carrying the work to significant conclusions. These qualities have supplied him with success in the scientific field; the discovery of several new minerals in short time is an evidence of that. At the Kerchian deposits he succeeded not only in obtaining a new data and in bringing in a system the mineralogy of Kerchian phosphates but also in standing a point in the old problem of «kerchinites»: to prove they are not, as was supposed, the proper minerals, but the peculiar mixtures of vivianite with a product of its oxidation, santabarbaraite.

The abundance of good photoillustrations (Mikhail Leibov) helps the reader to compose the notion about diversity of minerals of the Kerch Peninsula.

Along with the mineralogy of iron ores, the book includes the interesting information on mud volcanoes of the Kerch Peninsula.

The history of discoveries of the minerals reminds the reader about two cases of publications delays, which were the reason of a loss of the official priority by the native science. These are anapaite of A. Zaks (published in 1902) instead tamanite of S.P. Popov (the first findings in 1899, publication in 1903) and santabarbaraite of G. Pratesi (2003) instead oxykerchinite of S.P. Popov (1938).

As an example of morphologically original findings of the author, one can note the sheaf-like crystals of anapaite. The mention at the same place (p. 75) about anapaite crystals to 20 cm in size is unfortunately considered as a misprint.

The latest data obtained by N.V. Chukanov represents the doubtless interest for specialists-mineralogists. The book will be useful also for «advanced» amateurs and collectors interesting in minerals of the Kerch Peninsula.

Unfortunately, it is impossible to keep in translation the good Russian language distinguishing the texts of Nikita V. Chukanov. English translation is not without misprints and errors (in particular, incorrect use of terms «druse», «drusy»), nevertheless that does not trouble the comprehension by the English-language reader. At the same time, it would be necessary to note this book deserves the publication in Russian, since it is interesting for our specialists and fanciers.

Boris Kantor

Pekov I.V., Podlesnyi A.S. **Kukisvumchorr Deposit: Mineralogy of the Alkaline Petmatites and Hydrothermalites. Mineralogical Almanac**, vol. 7. M.: — 164 p., 121 colour photos, 225 b/w photos, schemes, drawings of crystals, 164 references.

«Kukisvumchorr Deposit» is the result of collaboration of the famous mineralogist with the well-known collector, whose collection is most representative for this deposit. The volume is devoted to 75-anniversary of the Kirovskii apatite mine in Khibiny, the first in Russia mine works beyond the Polar Circle.

The Kukisvumchorr deposit worked by the Kirovskii mine is a unique mineralogical object: on its territory 212 mineral species are noted, including 19 minerals discovered here (among them 6 by I.V. Pekov, and 11 ones were found for the first time in the collection of A.S. Podlesnyi), at that 39 mineral species are known in Knibiny only here. Pegmatite-hydrothermal complex of the deposit is strongly unusual even at the background of the unique alkaline Khibiny massif. It abounds in large cavities that gave the world best specimens of tens of minerals. Remarkable mineralogical finds of the Kukisvumchorr deposit are noted as a Appendix on pages 127-128.

Along with the questions of distribution, genetic conditions, assemblages and morphology of minerals of the deposit, including the data of original goniometric measurements and electron microprobe studies, the book contains the geological-petrological essay, history of study and developing, characteristic of pegmatites and hydrothermalites, geochemical and genetic peculiarities of the late mineralization. With particular interest and emotion, the reader will read 26 pages of «History of study and developing», which almost entirely consists of expressive quotations, documents, and archival photos.

Boris Kantor

Evseev A.A. **Atlas of the World for Mineralogist.** M.: Fersman Mineralogical Museum RAS; 2004. — 284 p., 275 maps-schemes. In Russian.

This edition, first in its class, has included the colossal volume of information accumulated by the author during the process of thirty-years topomineralogical investigations. In addition to author's card index, keeping the information about more than 100 thousands of occurrences of minerals, the numerous literature, information from Internet, data on mineralogical collections of museums, private communications were used.

The mineral kingdom is divided into 275 geographical regions, for each of them there is a map-scheme with indication of mineral occurrences, qualities of specimens, references, and also about mineralogical museums located in the region. The points of type localities are marked. The *Atlas* is a handbook, which is necessary to have at hand to each specialist and amateurs of minerals, desiring to widen his mineralogical range of interests. Although the Atlas is announced «for educational purposes», undoubtedly, it will become a handbook of scientists and museum collaborators.

The Atlas of A.A. Evseev will keep its absolute value as a source of information about historical findings and state of topomineralogical information at the moment of publication. At the same time, the essence of the work intends the constant renewal: collectors and museum collaborators do not sit without business and every day bring new, sometimes sensational findings. The present edition is an excellent initiative, corresponding to time, and it is necessary to wish the author to continue the work and have a possibility of reediting of the Atlas, when new information will be received. Possibly, it will be necessary to prepare simultaneously the more expensive edition, illustrated by photos of classic and new findings.

Boris Kantor

Pekov I.V., **The Lovozero Massif: History of Study, Pegmatites, Minerals.** M.: Association Ecost, 2001. — 464 p., 146 colour photos, 188 b/w photos, 109 figures, 501 references, hard cover.

«*The Lovozero massif is an astonishing phenomenon of nature*» (after Editor, academician Liya N. Kogarko); it more than a century attracts attention of Russian and world scientists. This is one of the largest plutons in the world, which is practically entirely composed by the extremely alkaline rocks. In them 340 mineral species are noted, a half of which are rare and rarest minerals. Here 73 new minerals have been discovered, including 23 mineral species, known only here.

The detailed mineralogical summaries include the minerals descriptions, accompanied by colour illustrations, drawings of crystals, history of discovery, data on chemical composition. The cadastre of mineral species gives a notion about reliability of present information. In the list of minerals, discovered in the Lovozero massif, the authors and data of discoveries, the places of the first findings, and the origin of names are indicated. There is a summary of crystals-giants etc. Also the issue «History of study and developing» is interesting, where the large volume of archival and published materials and photodocuments are collected and systematized, the estimation of a role of well-known researches is given.

The author succeeded in making his intention: «*...by character of exposition, he has created the scientific-popular book and, by correctness and validity of given data, strictness of the reference system, the scientific book, taking into account the experience of foreign editions of such type*». «The Lovozero Massif» is simultaneously both a handbook and a book for reading; it is interesting and informative both for the professional-mineralogist and for the amateur, collector, and also the reader who is not indifferent to history of science.

Boris Kantor