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New Data on Minerals. 2011. Volume 46. 168 pages, 138 photos, drawings and schemes.
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This issue includes the articles about new mineral species found from rocks of the Dara-i-Pioz alkaline massif, Tajikistan: byzantievite, Ba, Ca, REE, Ti, and Nb silico-phospho-borate with complex structure and orlovite, titanium analogue of polythionite, which is a new member of mica group. Rare minerals, rooseveltite and preisingerite from the Oranzhevoye ore field, Verkhne-Kalagininsky massif, Magadan region, Russia, mannardite from carbonaceous-siliceous schists, South Kirgizstan and Kazakhstan, and palladoarsenide and mayakite from sulfide of ores of Norilsk field are described. The new data of fahlores and secondary minerals at the Labedinoe deposit, Central Aldan, Li mineralization from the Glubostrovskoye granitic pegmatite, South Urals, and mineralogy of wood tin at the Dzhailinda deposit, Khingan-Oloi tin district are given. The published and novel data of uranium oxides and hydroxides are reviewed. The experimental study of crystallization products of chalcopyrite solid solution was carried out.

In section "*Mineralogical museums and collections*", stone-cutting articles of the Peterhof lapidary factory in the collection of the Fersman Mineralogical Museum, Russian Academy of Sciences are described. The other two articles are devoted to the history of first catalogues of the museum collections and the attribution of marble specimens of Florentine marble mosaic and ruin marble involved in the first Mineral catalogue by M.V. Lomonosov. The exhibition "Amazing stone" held in 2011 in the Fersman Mineralogical Museum and the new acquisitions to the museum 2009–2010 are also reported in this section.

An article about Yu.L. Orlov, talented mineralogist, the head of the Fersman Mineralogical Museum from 1976 to 1980, is placed in section "*Persons*".

A section "*Mineralogical notes*" briefly informs about the new data of the process of formation of skeletal crystals of calcite from carst cavities, reports bilbinskite from the cementation zone of gold-telluride deposits (Aginskoe, Kamchatka and Pionerskoe, Syan Mountains), and the minerals from metakimberlites of the Udachnaya-Vostochnaya Pipe, Northern Yakutia. This journal is interest for mineralogists, geochemists, geologists, workers of natural history museums, collectors, and amateurs of stone.

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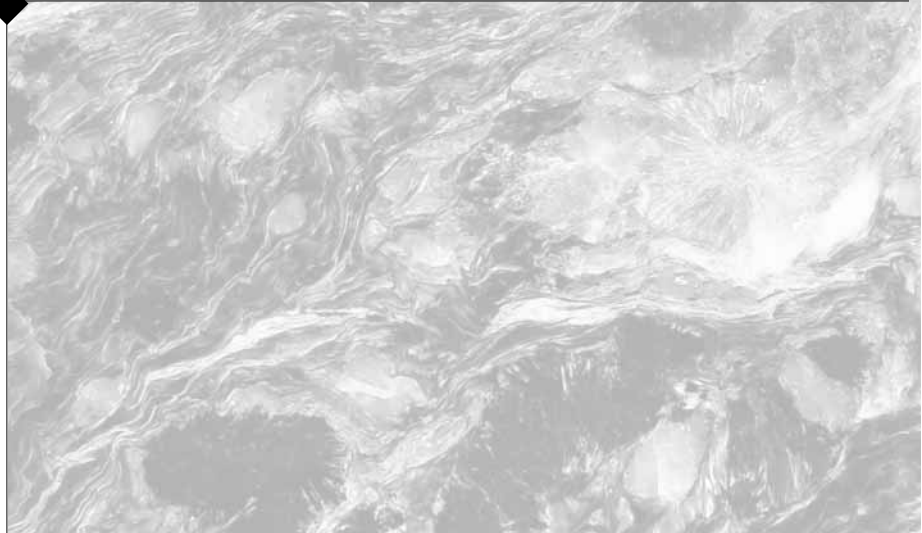
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**New Minerals
and Their Varieties,
New Finds
of Rare Minerals,
Mineral Paragenesis**



BYZANTIEVITE, Ba₅(Ca,REE,Y)₂₂(Ti,Nb)₁₈(SiO₄)₄[(PO₄)₄(SiO₄)₄(BO₃)₉O₂₁[(OH),F]₄₃(H₂O)_{1.5}, A NEW MINERAL¹

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A new silico-phosphate of Ba, Ca, REE, Ti, and Nb found in the Darai-Pioz alkaline massif, Tajikistan, has been named byzantievite because of its complex chemical composition and structure, reminiscent of the complex, but well-organized structure of the Byzantine Empire. The new mineral was discovered on a rock composed of microcline, quartz, aegirine and ferrileakeite; accessory minerals are: calcybeborosilite-(Y), pyrophanite, stillwellite-(Ce), danburite, thorite and pyrochlore. The new mineral occurs as tabular grains up to 0.5 x 1.8 mm in size and aggregates of these grains up to 2.5 mm in size. Byzantievite is brown with a pale-yellow streak. Luster is vitreous, slightly greasy on fracture surfaces. Cleavage is not observable; fracture is conchoidal. The Mohs' hardness is 4.5–5. The mean (10 measurements) microhardness VHN is 486 kg/mm². The measured density is 4.10(3) g/cm³, calculated density is 4.15 g/cm³. Byzantievite is optically negative, uniaxial, $\omega = 1.940$, $\varepsilon = 1.860 \pm 0.005$. The new mineral is pleochroic from light brown along ε to very pale brown along ω ; absorption is $\varepsilon \gg \omega$. The symmetry is hexagonal, space group R3, $a = 9.128(5)$; $c = 102.1(1)$ Å; $V = 7363(15)$ Å³, $Z = 3$. The crystal structure was solved to $R_1 = 13.14\%$. The strong reflections in the X-ray powder – diffraction pattern are (d , Å; l ; hkl): 4.02(2)(-1 2 12); 3.95(2)(-222); 3.112(10)(1 1 24; -1 2 24); 2.982(4)(-321; -231); 2.908(2)(1 1 27; -138; 128); 2.885(2)(-3 2 10; -2 3 10); 2.632(2)(030); 2.127(2)(0 0 48). The chemical composition is as follows (electron microprobe, average value and range of content of 60 point analyses; B₂O₃ was determined by SIMS; H₂O on the basis of structural data; wt.%): SiO₂ 4.73(3.15–5.84), Nb₂O₅ 10.97 (10.35–12.82), P₂O₅ 3.83(2.64–4.88), TiO₂ 15.21(13.84–16.56), ThO₂ 1.48(1.48–1.88), UO₂ 0.55(0.29–0.35), La₂O₃ 4.01(3.27–4.41), Ce₂O₃ 9.19(6.76–9.73), Nd₂O₃ 3.35(3.42–4.42), Pr₂O₃ 1.02(0.17–1.77), Sm₂O₃ 0.71 (0.58–1.23), Dy₂O₃ 1.25(1.05–1.30), Gd₂O₃ 0.95(0.68–1.49), Y₂O₃ 7.39(5.21–9.00), B₂O₃ 5.09(4.38–6.12), FeO 0.49(0.48–0.73), BaO 13.30(12.76–14.91), CaO 8.01(5.41–10.31), SrO 1.95(1.08–2.17), Na₂O 0.16 (0.00–0.22), H₂O 6.00, F 1.80(1.30–2.08), O = F (-0.76), total is 100.68. The empirical formula, calculated on the basis of 124.5 anions for the grain used for the structure analysis is: Ba_{5.05}[(Ca_{8.99}Sr_{0.96}Fe_{0.42}²⁺Na_{0.10}) $\Sigma_{10.47}$ (Ce_{3.46}La_{1.54}Nd_{1.20}Pr_{0.30}Sm_{0.26}Dy_{0.41}Gd_{0.32}Th_{0.36}U_{0.17}) $\Sigma_{8.03}$ Y_{3.53}(Ti_{12.31}Nb_{5.30}) $\Sigma_{17.61}$ (SiO₄)_{4.65}(PO₄)_{3.12}(BO₃)_{8.89}O_{22.16}(OH)_{38.21}F_{4.89}(H₂O)_{1.5}. The simplified formula is Ba₅(Ca,REE,Y)₂₂(Ti,Nb)₁₈(SiO₄)₄[(PO₄)₄(SiO₄)₄(BO₃)₉O₂₁[(OH),F]₄₃(H₂O)_{1.5}. The compatibility index 0.003 (from calculated density) and -0.009 (from measured density). The type material was deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia.

4 figures, 3 tables, 18 references.

Keywords: byzantievite, silico-phospho-borate of Ba, Ca, REE, Ti, Nb, new mineral, Darai-Pioz, Tajikistan, alkaline rocks.

A new silico-phospho-borate mineral with an extremely complex composition and simplified formula Ba₅(Ca,REE,Y)₂₂(Ti,Nb)₁₈(SiO₄)₄[(PO₄)₄(SiO₄)₄(BO₃)₉O₂₁[(OH),F]₄₃(H₂O)_{1.5} was discovered in the Darai-Pioz massif, Tajikistan. To reflect the complexity and chemical diversity of the structure of this mineral, we have named it byzantievite. From nearly twelve centuries (374–1453), the Byzantine Empire was home to many nations and religions. The

structure of the Byzantine Empire was very complex, but nevertheless, this state was well-organized, effective and had a major influence on European and World culture.

Occurrence

Byzantievite was discovered from one specimen collected from the moraine of the Darai-Pioz glacier, Tajikistan (N 39°27', E 70°43'). The

¹ – The mineral was considered and recommended for publication by the Commission on New minerals and mineral names of the Russian mineralogical society and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA on 2th of April 2009.

valley of the glacier cuts the multiphase igneous complex of the same name, whose marginal zone of tourmalinized granite of Late Carboniferous age changes toward the center to biotite granite of Late Carboniferous to Early Permian age; the central part comprises quartz and quartz-free aegirine syenite of Permian age. A stock of Upper Permian to Middle Triassic cancrinite foyaitite occurs in the southeastern massif. All listed igneous rocks are cut by Early to Middle Triassic fine-grained granite (Dusmatov, 1971). Pegmatites, hydrothermal rocks and carbonatites variable in composition and age and containing extensive REE, B, Li, Cs, Zr, Ti, Nb, and Ba mineralization are abundant in the massif (Dusmatov and Mogarovsky, 1971; Maiorov and Gavrilin, 1971).

Unfortunately, most of the massif is covered by the glacier or is hard-to-reach rock outcrops, strongly hampering investigation. Therefore, most mineralogical and petrographic data for the massif have been obtained on glacier debris.

The first data on the Darai-Pioz massif are related to the 1932–1936 Tajik-Pamir Expedition (Moskvin, 1937). Since then, many researchers have studied this massif. Vyacheslav Dzhuraevich Dusmatov contributed substantially to the mineralogical study of Darai-Pioz and his doctoral thesis is a thorough review of the geology and petrography of this massif (Dusmatov, 1971). The mineralogy, geochemistry and petrography of the massif are discussed in many papers (Dusmatov, 1968₁, 1968₂; Semenov and Dusmatov, 1975; Efimov, 1983; Vladykin and Dusmatov, 1996; Mogarovsky, 1987; Pekov *et al.*, 2000; Belakovskiy, 1991; Grew *et al.*, 1993; Reguir *et al.*, 1999).

The Darai-Pioz massif is characterized by a high boron content. According to Dusmatov *et al.* (1972), the average boron content in the rocks of the massif is (ppm): 900 in tourmalinized granite, 74 in fine-grained biotite granite, 130 in porphyry granite, 53 in quartz syenite, 75 in aegirine syenite, 415 in alkaline pegmatite, and 60 in albitite. Currently, twenty four boron minerals with dominant boron at one structural site have been found in the massif. Nine new minerals have been discovered at this massif: byzantievite, calcybeborosilite-(Y), kapitsaitite-(Y), kirchhofite, maleevite, pekovite, tadzhikite-(Ce), tadhikite-(Y), and tienshanite. It is of interest that eight boron minerals found at Darai-Pioz contain REE (including Y) as species forming elements and eight minerals contain Ba. Moreover, the mutual occurrence of boron with REE, Y, and Ba (as in byzantievite) is extremely characteristic feature of the minerals from this massif. The importance of boron in the Darai-Pioz massif is

exhibited not only as elevated boron content and mineral diversity, but also as unique rocks, in which reedmergerite, NaBSi_3O_8 , a boron analogue of albite, is the major rock-forming mineral (Dusmatov *et al.*, 1967). Leucosphenite, stillwellite-(Ce), and danburite are typical accessory minerals of certain pegmatites in this massif; calcybeborosilite-(Y) is typical of fenitized rocks. The diversity of phosphorous minerals in the massif is more modest; currently, only three minerals containing phosphorous as an essential element are known here: fluorapatite (abundant in variable rock types) monazite-(Ce) (sporadical findings), and byzantievite.

Byzantievite was found in a coarse-grained rock composed mainly of approximately equal amounts of microcline, quartz, aegirine and ferrileakeite. Microcline occurs as white (with a weak yellowish-green tint) coarse anhedral grains (up to 3 cm across) with well-developed perthite ingrowths of albite. Quartz occurs as semitransparent slightly smoky grains ranging from 0.5 to 2 cm in size. Aegirine is present as euhedral crystals (up to $4 \times 6 \times 15$ mm) and dark grass-green aggregates of these grains are randomly distributed in quartz-microcline. Ferrileakeite occurs as long dark grains and aggregates up to 2 cm in length, frequently intergrown with pyroxene. Titanite, nalivkinite and zircon are minor phases. Accessory minerals are calcybeborosilite-(Y), pyrophanite, stillwellite-(Y), danburite, thorite, pyrochlore and byzantievite. The composition of selected minerals from this described assemblage is given in Table 1.

Byzantievite occurs as intergrowths (up to 2.5 mm in size) of tabular grains (Fig. 1) in quartz and microcline, frequently intergrown with aegirine, zircon, thorite, calcybeborosilite-(Y) and pyrophanite.

Physical properties

Byzantievite occurs as lamellar and tabular grains flattened parallel on {001} with poorly-formed faces reaching 0.5×1.8 mm in size, and as aggregates of grains. Nearly all grains are deformed to some extent; fractures are healed by quartz and calcybeborosilite-(Y) that hampers separation of pure material for examination. The mineral is brown with a pale-yellow streak. Luster is vitreous and slightly greasy on fracture surfaces. Byzantievite is semitransparent and transparent in small flakes. Cleavage is not observed; the fracture is conchoidal. The Mohs' hardness is 4.5–5. Microhardness (VHN) measured with PMT-3 (calibrated with NaCl) with loading 50 g is 486 (average of 10 measurements ranging from 463 to 522) kg/mm². The



Fig. 1. Segregations of byzantievite and associated minerals: (a) lamellar brown byzantievite in an aegirine-quartz-microcline matrix; (b) aggregate of byzantievite, calcybeborosilite-(Y), zircon, and aegirine in microcline. Oblique light. Width of image is 6 mm.

density of byzantievite determined by flotation in Clerici solution is 4.10(3) g/cm³; the calculated density is 4.15 g/cm³.

The mineral is optically negative. The refractive indices, measured by the immersion method on spindle stage are (589 nm): $\omega = 1.940$, $\epsilon = 1.860 \pm 0.005$. Byzantievite is strongly pleochroic from light brown along ϵ to very pale brownish along ω ; absorption is $\epsilon \gg \omega$.

Byzantievite is luminescent neither short nor longwave UV range (240–400 nm).

IR spectra were measured with Avatar (Thermo Nicolet) and Specord-75IR spectrophotometers in KBr disks. However, due to ingrowths of different phases in byzantievite, sufficient material to measure a good IR spectra could not be obtained. In the recorded IR spectra of the mineral, the strongest absorption is in the region 500–700 cm⁻¹, a broad band with three major peaks at 550, 590, 650 cm⁻¹ due to superimposed bands of Si-O and P-O bending vibrations and M-O stretching vibrations, where M is Ca, Y, REE. The narrow band at 740 cm⁻¹ most likely corresponds to Ti-O stretching vibrations; the broad

Table 1. Chemical composition (wt.%) of minerals associated with byzantievite

Component	1	2	3	4	5	6	7
SiO ₂	52.39	51.88	29.63	27.16		35.29	22.45
TiO ₂	0.89	0.42	37.54	0.15	53.32	11.28	14.97
SnO ₂	n.a.		0.18			0.17	
ZrO ₂						0.13	0.37
Nb ₂ O ₅			1.94		0.57	0.43	0.20
Al ₂ O ₃	0.57	0.39	0.12			1.06	0.17
Fe ₂ O ₃	*16.96	32.76					
FeO	*10.38		0.97	5.82	15.52	22.35	14.85
MnO	1.68	0.57		0.28	31.37	12.28	12.12
MgO	2.57	0.19				0.65	0.10
ZnO	0.38	0.05				0.43	0.38
CaO	0.37	2.22	24.30	12.09		2.30	
BaO	n.a.	n.a.		0.15			29.60
Na ₂ O	7.80	11.73	1.54			1.33	
K ₂ O	2.09					2.49	
Li ₂ O	1.18	0.17	n.a.	n.a.	n.a.	1.23	n.a.
CS ₂ O						2.46	
H ₂ O	1.12	n.a.	n.a.	n.a.	n.a.	2.88	2.08
F	1.98	n.a.	1.23	n.a.	n.a.	1.49	3.50
-O=F	0.83	-	0.52	-		0.63	1.47
Total	99.53	100.34	98.16	79.28	100.77	97.62	99.32

Notes: n.a. denotes that the component was not analyzed; an empty cell denotes that the content of the component is below detection limit. Li was determined from a microsample by emission flame spectrophotometry, FMD 4 spectrometer; the content of H₂O is calculated.

(1) Ferrileakeite (dark green nearly black) (average of 5 point analyses), Camebax microbeam, 15 kV, 20 nA, ZAF; fluorine content was corrected with the PAP procedure:

(Na_{0.33}K_{0.40})_{0.73}(Na_{1.91}Ca_{0.06})_{2.00}(Fe_{1.31}²⁺Mg_{0.58}Mn_{0.22}Zn_{0.04})_{2.15}(Fe⁺³_{1.93}Ti_{0.10})_{2.03}Li_{0.72}(Si_{1.92}Al_{0.10})O₂₂(OH)_{1.05}F_{0.95}2.00 (the formula is calculated with the WinAmphcl program on the basis of 23 O atoms (taking into account (F+OH) = 2); *Fe⁺² and Fe⁺³ are calculated from average normalization between (Si+Al+Mg+Ti+Mn+Fe+Zn+Li) = 13 atoms and (Si+Al+Mg+Ti+Mn+Fe+Zn+Li+Ca+Na) = 15 atoms (Yavuz, 2007);

(2) Aegirine (green), Camebax microbeam, 15 kV, 20 nA, ZAF: (Na_{0.88}Ca_{0.09}Li_{0.03})_{1.00}(Fe_{0.94}³⁺Mn_{0.02}Mg_{0.01}Ti_{0.01})_{0.96}(Si_{1.98}Al_{0.02})_{2.00}O₆ (calculated on the basis of 6 O atoms);

(3) Titanite (average of 11 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine was measured with 10 kV, 55 nA, TAP crystal, corrected with the PAP procedure. Total also includes (wt. %): 0.78 Ce₂O₃, 0.45 Nd₂O₃.

(Ca_{0.88}Na_{0.10})_{0.98}(Ti_{0.95}Nb_{0.03}Fe_{0.03}Ce_{0.01}Nd_{0.01})_{1.05}Si_{1.00}O_{4.89}F_{0.13} (calculated on the basis of 3 cations);

(4) Calcybeborosilite-(Y), JEOL Superprobe 733, INCA, 20 kV, 2 nA. Total also includes (wt. %): Y₂O₃ 14.60; La₂O₃ 1.20, Ce₂O₃ 4.48, Pr₂O₃ 0.45, Nd₂O₃ 2.61, Sm₂O₃ 0.62, Gd₂O₃ 1.18, Dy₂O₃ 2.59, Ho₂O₃ 0.12, Er₂O₃ 1.38, Yb₂O₃ 0.56; UO₂ 1.17 ThO₂ 1.97; SrO 0.70; B and Be were not measured;

(5) Pyrophanite (average of 2 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, (Mn_{0.6}Fe_{0.33})_{1.00}(Ti_{1.00}Nb_{0.01})_{1.01}O₃ (calculated on the basis of 3 O atoms);

(6) Nalivkinite (average of 10 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine content was measured at 10 kV, 55 nA, TAP crystal, calculation with PAP procedure (Li_{1.09}K_{0.70}Cs_{0.23})_{1.02}(Na_{0.57}Ca_{0.54})_{1.11}(Fe_{4.12}Mn_{2.29}Mg_{0.21}Zn_{0.07})_{6.69}(Ti_{1.88}Nb_{0.04}Zr_{0.01}Sn_{0.01})_{1.94}(Si_{1.78}Al_{0.28})_{0.06}O₂₄(OH)_{4.12}F_{1.04}O_{1.84}7.00 (calculated on the basis of \sum (Si, Al, Ti, Nb, Sn, Zr) = 10 atoms; O and OH are calculated from charge balance);

(7) Bafertsite (average of 3 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine content was measured at 10 kV, 55 nA, TAP crystal, calculation with PAP procedure Ba_{1.01}(Fe_{1.05}Mn_{0.89}Zn_{0.02}Mg_{0.01})_{2.00}(Ti_{0.98}Zr_{0.02}Nb_{0.01})_{1.01}(Si_{1.96}Al_{0.02})_{1.98}O₈(OH_{0.98}F_{0.96})_{1.97} (calculated on the basis of 6 cations; OH calculated from charge balance). Analyst L.A. Pautov.

band with peaks at 950 and 1000 cm^{-1} is assigned to Si-O stretching vibrations. The narrow strong bands with maxima at 1190 and 1270 cm^{-1} correspond to P-O and B-O stretching vibrations, respectively.

According to the Gladstone-Dale relation, the compatibility index is superior: $1-K_p/K_C = 0.003$ using $D_{\text{calc}} = 4.15 \text{ g/cm}^3$ and $1-K_p/K_C = -0.009$ using $D_{\text{meas}} = 4.10 \text{ g/cm}^3$.

Chemical composition

Химический состав византиевитаду Si The chemical composition of byzantievite was measured with an electron microprobe. It was not possible to separate sufficient material to determine the H_2O concentration directly, and the H_2O content was calculated on the basis of the crystal structure. As the composition of the new mineral

is extremely complex, it was determined in three laboratories (A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow; Department of Geological Sciences, University of Manitoba, Winnipeg, Canada; Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements, Moscow) with energy- and wavelength-dispersion methods. Seventy point analyses were obtained for nine grains (Table 2). The BSE image shows darker areas (with lower mean atomic number) related to fractures in some grains of byzantievite (Fig. 2). Examination of these areas show that they contain the same elements in similar ratios as normal byzantievite and most likely are caused by greater metamictization and probable hydration of the new mineral. We tried to avoid such altered areas during analysis, but it is possible, that these altered material was sometimes present in the zone of X-

Table 2. Chemical composition (wt.%) of byzantievite

Component	1		2		3		4
	Average	Range of content	Average	Range of content	Average	Range of content	Semiquantitative data of ICP OES
SiO_2	4.52	4.19–5.80	4.73	3.15–5.84	3.82	3.74–3.99	n.a.
Nb_2O_5	11.38	10.43–12.17	10.97	10.35–12.82	13.32	11.90–13.83	>4
P_2O_5	3.58	2.99–3.87	3.83	2.64–4.88	3.97	3.69–4.29	>2
Ti	15.90	15.36–16.47	15.21	13.84–16.56	15.37	14.38–15.92	>9
ThO_2	1.65	1.39–1.84	1.48	1.48–1.88	1.30	1.11–1.50	1.4
UO_2	0.74	0.36–0.76	0.55	0.29–0.35	n.a.		0.3
La_2O_3	4.06	3.78–4.45	4.01	3.27–4.41	3.88	3.72–4.04	3.3
Ce_2O_3	9.17	8.53–10.22	9.19	6.76–9.73	8.11	7.63–8.61	8.1
Nd_2O_3	3.26	2.96–3.48	3.35	3.42–4.42	3.09	2.87–3.28	2.6
Pr_2O_3	0.79	0.37–1.21	1.02	0.17–1.77	n.a.		0.8
Sm_2O_3	0.73	0.58–0.84	0.71	0.58–1.23	0.54	0.30–0.73	0.8
Dy_2O_3	1.22	0.93–1.61	1.25	1.05–1.30	0.79	0.64–1.00	1.2
Gd_2O_3	0.93	0.68–1.23	0.95	0.68–1.49	0.77	0.69–0.93	0.9
Y_2O_3	6.44	6.14–6.85	7.39	5.21–9.00	6.33	5.84–8.00	6.1
B_2O_3	5.00		5.09	4.38–6.12	4.52	4.26–4.77	>1
FeO	0.49	0.29–0.59	0.49	0.48–0.73	n.a.		1.2
BaO	12.51	12.25–12.93	13.30	12.76–14.91	12.25	11.90–12.75	13.0
CaO	8.15	7.72–8.57	8.01	5.41–10.31	8.81	8.71–8.89	8.2
SrO	1.61	1.45–1.77	1.95	1.08–2.17	1.74	1.57–1.91	1.7
Na_2O	0.10	0.06–0.16	0.16	0.00–0.22	n.a.		0.5
H_2O^*	6.00		6.00		n.a.		
F	1.50		1.80	1.30–2.08	n.a.		
-O=F	0.63		0.76				
Total	99.10		100.68				

Notes: n.a. denotes that the component is not analyzed; empty cell denotes that the content of the component is below detection limit.

(1) Average and range of content of 10 point analyses of the grain that was used to determine the crystal structure of the mineral. Cameca SX-100 operated at 15 kV, 10 nA, beam diameter 10 microns. Standards are: fluorophlogopite (F), albite (Na), barite (Ba), $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (Nb), diopside (Si, Ca), fayalite (Fe), titanite (Ti), apatite (P); ThO_2 (Th), UO_2 (U), LaPO_4 (La), CePO_4 (Ce), NdPO_4 (Nd), PrPO_4 (Pr), SmPO_4 (Sm); Dy_2O_3 (Dy), GdPO_4 (Gd), and YAG (Y). Data were corrected with the PAP procedure. Analyst Panseok Yang. B_2O_3 was measured with SIMS, Cameca IMS 4F, analyst S.G. Simakin; H_2O^* calculated from the structural data.

(2) Average and range of content of 60 point analyses of six grains; 11 compositions were measured with a JXA-50A scanning electron microscope equipped with a Link spectrometer operated at 20 kV, 2 nA, beam diameter 1 micron; 6 compositions were measured by WDS with a Camebax-microbeam electron microprobe operated at 15 kV, 20 nA, beam diameter 5 microns, fluorine was measured at 10 kV, 20 nA; 43 compositions were measured with a JXA-733 scanning electron microscope equipped with an INCA EDS operated at 20 kV, 2 nA, beam diameter 1 micron, B_2O_3 was measured with JXA-733, STE crystal, acceleration voltage 10 kV, current 100 nA, beam diameter 20 microns; standard is stillwellite-(Ce). Content was calculated with PAP procedure. Analyst L.A. Pautov;

(3) Average and range of content of 7 point analyses of one grain. Camebax-microbeam electron microprobe operated at 15 kV, 15 nA, beam diameter 5 microns. Standards are: [Стандарты] LiNbO_3 (Nb), Ba glass (Ba), Y_2SiO_5 (Si, Y), ilmenite (Fe, Ti), apatite (P), thorite (Th), light blue diopside (Ca), Sr glass (Sr), $\text{KLa}(\text{MoO}_4)_2$ (La); $\text{LiCe}(\text{WO}_4)_2$ (Ce), $\text{LiNd}(\text{MoO}_4)_2$ (Nd), $\text{LiSm}(\text{MoO}_4)_2$ (Sm), $\text{LiDy}(\text{WO}_4)_2$ (Dy), and $\text{LiGd}(\text{MoO}_4)_2$ Gd. B_2O_3 was measured at 10 kV, 20 nA, beam diameter 5 microns. Standard is boron nitride. Content was calculated with PAP procedure. Analyst I.M. Kulikova.

(4) Composition of one grain after acid decomposition determined with ICP OES (Vista PRO, VARIAN), in addition, it was determined (wt. %): $\text{Al}_2\text{O}_3 - 0.06$; $\text{BeO} - 0.09$; $\text{Cr}_2\text{O}_3 - 0.05$; $\text{Er}_2\text{O}_3 - 0.5$; $\text{Eu}_2\text{O}_3 - 0.09$; $\text{Ho}_2\text{O}_3 - 0.2$; $\text{Lu}_2\text{O}_3 - 0.01$; $\text{Tb}_2\text{O}_3 - 0.2$; $\text{Yb}_2\text{O}_3 - 0.2$; $\text{Sc}_2\text{O}_3 - 0.003$; $\text{MnO} - 0.08$; $\text{ZnO} - 0.008$; $\text{Li}_2\text{O} - 0.05$; $\text{ZrO}_2 - 0.005$. Analyst L.A. Pautov.

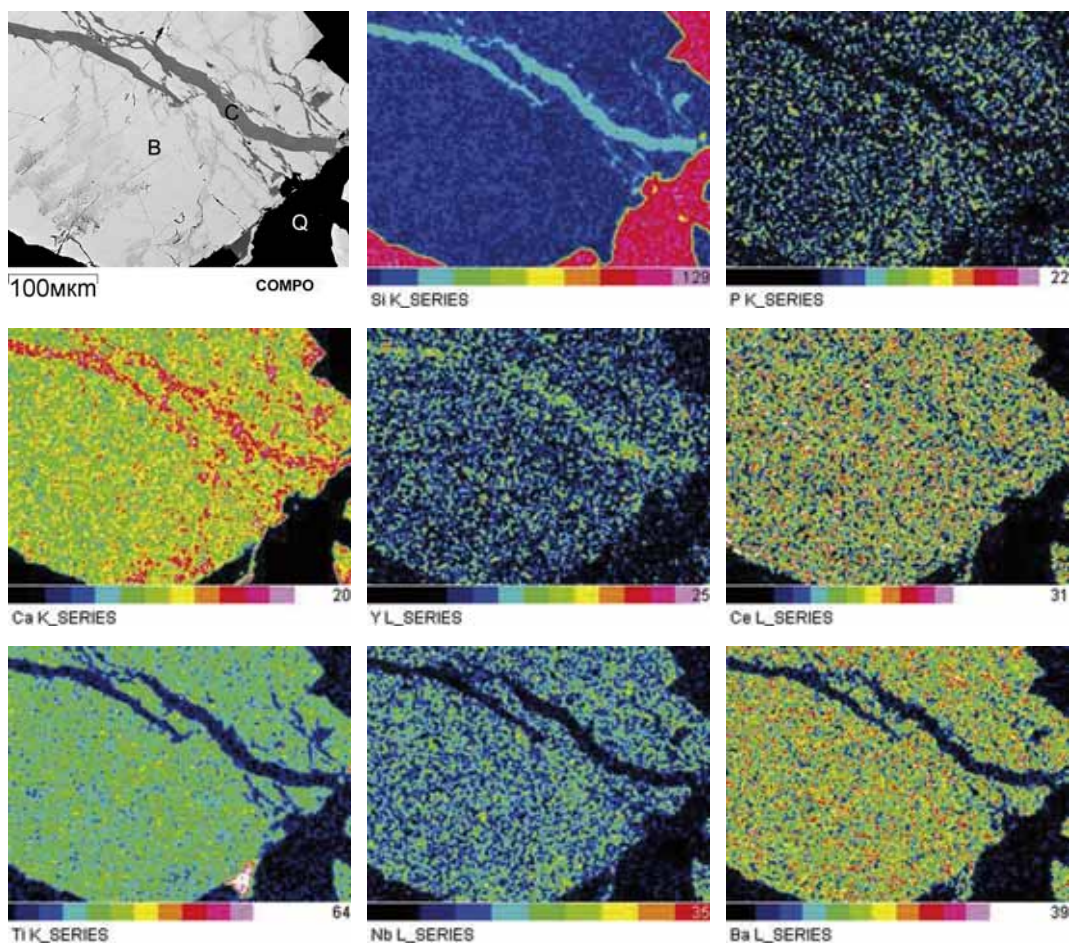


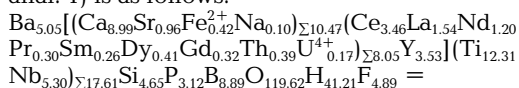
Fig. 2. Grain of byzantievite (B) with veinlet of calcybeborosilite-(Y) (C) in quartz (Q). COMPO image and X-ray distribution maps of elements.

ray generation. Significant variation in the measured chemical composition of byzantievite is probably caused not only by chemical substitution in the mineral, but also by such alteration. In variation diagrams (Fig. 3), this is a clear negative correlation between Ca and REE + Y, and between Si and P. There is not a well-developed correlation between Nb and Ta. This may be due to: inevitable analytical errors, altered areas in the mineral grains, and probable occupancy of a few sites by one element, and the presence of extensive vacancies. In our opinion, the latter is predominant factor here (Sokolova *et al.*, 2010).

The lithium and beryllium contents of byzantievite were measured with SIMS and ICP-OES. A fragment of the grain used for solution of the crystal structure (Table 2, anal. 1) was studied with a Cameca IMS-4F ion microprobe (analyst S.G. Simakin, Institute of Microelectronics and Informatics, Russian Academy of Sciences) oper-

ated at O_2^- primary beam with an energy of 14.5 keV focused to the spot of 10–20 microns. The absolute concentration of each element, calculated from the element/ $^{30}Si^+$ ratio of intensity of ion current using calibrated constants, are (wt.%): 0.07 Li_2O ; 0.002 BeO . To analyze by ICP-OES, a grain of the new mineral (after checking the chemical composition with EDS) was dissolved and the intensities of the lines of determined elements were measured; the concentration of the elements was calculated by the ratio method (with reference to the element Ca).

The empirical formula calculated on the basis of 124.5 anions (O + F), for the grain used for the solution of the crystal structure (Table 2, anal. 1) is as follows:



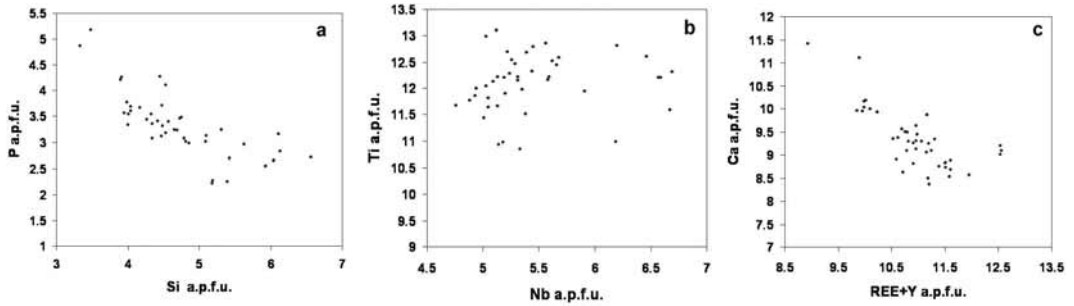
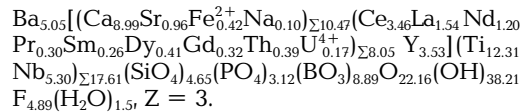


Fig. 3. P versus Si (a), Ti versus Nb (b), and Ca versus REE+Y (c) variation diagrams in atoms per formula unit of byzantievite.

Table 3. X-ray powder-diffraction data of byzantievite

<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>hkl</i>
1	4.56	4.560	-1 2 0
1	4.23	4.231	1 1 9
2	4.02	4.020	-1 2 12
2	3.95	3.937	-2 2 2
1	3.56	3.555	-1 2 18
			1 1 18
1	3.40	3.405	0 0 30
1	3.25	3.300	-2 2 17
		3.217	0 1 29
10	3.112	3.111	1 1 24
			-1 2 24
4	2.982	2.984	-3 2 1
			-2 3 1
1	2.931	2.925	-2 3 7
2	2.908	2.912	1 1 27
		2.907	-1 3 8
			1 2 8
2	2.885	2.865	-3 2 10
			-2 3 10
1	2.762	2.763	-1 3 14
			1 2 14
2	2.632	2.633	0 3 0
1	2.412	2.409	-1 2 36
			1 1 36
1	2.264	2.271	-1 2 39
			1 1 39
		2.260	-2 4 6
			2 2 6
1	2.201	2.202	-2 4 12
			2 2 12
2	2.127	2.128	0 0 48
1	1.928	1.928	-1 2 48
			1 1 48
>1	1.894	1.895	-2 4 30
			2 2 30
1	1.835	1.836	2 2 33
			-2 4 33
1	1.725	1.722	0 4 29
1	1.508	1.507	-3 6 9
			3 3 9
1	1.493	1.493	-2 6 1

Notes: Analyst L.A. Pautov.



E.V. Sokolova *et al.* (2010) suggested the simplified formula of byzantievite on the basis of cation groups determined by cation sites in the structure; in this case, vacancies were omitted to avoid an overly complicated formula: $\text{Ba}_5(\text{Ca}, \text{REE}, \text{Y})_{22}(\text{Ti}, \text{Nb})_{18}(\text{SiO}_4)_4[(\text{PO}_4)_1(\text{SiO}_4)]_4(\text{BO}_3)_9\text{O}_{21}[(\text{OH}), \text{F}]_{43}(\text{H}_2\text{O})_{1.5}, Z = 3$. Note that in the empirical and simplified formulae, the number of "additional" oxygen atoms (i.e., not incorporated into silicate, phosphate, borate, and hydroxyl anions) is different: 22, 16 and 21, respectively, to the oxyanions introduced as integers in the idealized formula. The empirical and simplified formulae are written with different numbers of oxygen atoms in order to retain the number of anions per formula unit as 124.6; this is very important as the empirical formula of byzantievite was calculated on the basis of this fixed number of anions.

X-ray crystallography

The X-ray powder-diffraction pattern of byzantievite was recorded with an RKD-57.3 camera, FeK α -radiation, and quartz as an internal standard. The X-ray powder-diffraction data are given in Table 3. The unit-cell dimensions calculated by the least-squares method on the basis of 16 reflections for hexagonal symmetry are: $a = 9.128(5)$; $c = 102.1(1)$ Å; $V = 7363(15)$ Å³. The X-ray powder-diffraction pattern of byzantievite is unique and has no analogues among natural and synthetic compounds.

The crystal structure of byzantievite, hexagonal *R*-cell, space group *R*3 and unit-cell dimensions: $a = 9.1202(2)$, $c = 102.145(5)$ Å, $V = 7358.0(5)$ Å³, $Z = 3$, was solved with a single crystal by direct methods and refined to $R_1 = 13.14\%$ on the basis of 3794 reflections with $[F_o > 4\sigma|F|]$ from an experimental set of reflections measured

with MoK α -radiation on a Bruker *P4* diffractometer equipped with a CCD detector (Sokolova *et al.*, 2010). The crystal structure of byzantievite is a framework of polyhedra dominated by Ti, Ba, Ca, Y, and REE cations and SiO₄ and PO₄ tetrahedra, and BO₃ triangles. The independent part of the structure is shown in Fig. 4; the whole structure is constructed by repetition of the independent part by the R translation. Sixteen polyhedron layers parallel to (001) are distinguished in the independent part of the structure. Layers B, H, J, and P consist of (Ti,Nb) medium-sized polyhedra, and layers A and B-G are composed of large Ba and (Ca,REE) polyhedra. In the crystal structure, there are 50 cation sites which may be divided into three groups with occupancies of 100%, ~67%, and ~17%, respectively. The presence of three groups of cation sites allow us to distinguish three components in the structure of byzantievite: one fully ordered with 100% occupancy of cation sites, and two disordered with ~67% and ~17% occupancy of cation sites. We suggest that the latter two parts are linked by hydrogen bonds (Sokolova *et al.*, 2010).

The holotype sample of byzantievite has been deposited in the A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, registration number 3791/1.

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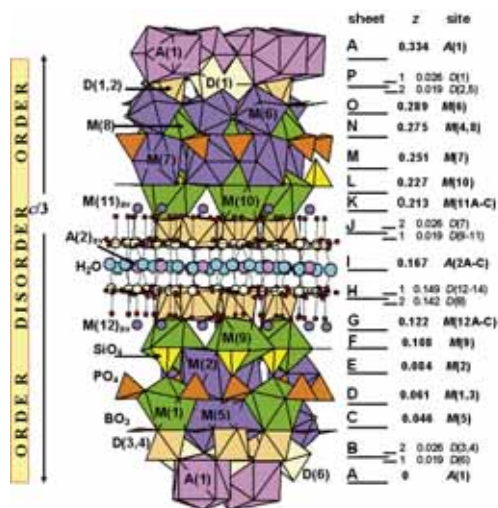


Fig. 4. General view of one third of the crystal structure of byzantievite parallel to [001]. (BO₃) triangles, (SiO₄) and (PO₄) tetrahedra are red, yellow and orange, respectively. Cation polyhedra are shown for cation sites occupied more than 50%: [12]-fold Ba polyhedra are pink; [10]- and [8]-fold M polyhedra are green and violet; Ti octahedra are dark yellow [D(2-5,7,8)] and light yellow [D(1,6)]. Atoms at the sites occupied less than 50% are depicted as spheres: A(2A-C) pink, D(9-14) pale yellow, M(11A-C) and M(12A-C) violet; triple sites A(2A-C), M(11A-C), and M(12A-C) are shown as one sphere; A(2)av, M(11)av, and M(12)av, where av = average. Fluorine atoms and OH groups are depicted as small yellow and red spheres; H₂O groups as large light blue spheres. Bonds D(9-14) – anions are shown as thin black lines. Sixteen polyhedron sheets parallel to (001) are depicted as horizontal black lines in the right part of this Figure (these sheets correspond to the 1/3 of the c parameter). Each sheet is characterized by the Z coordinate and cation sites, which compose this sheet. The sheets composed of Ti octahedra (B, H, J, and P) are divided into two subsheets, e.g. B₁ and B₂, where 1 and 2 correspond to light yellow and dark yellow octahedra.

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ORLOVITE, $\text{KLi}_2\text{TiSi}_4\text{O}_{10}(\text{OF})$, A NEW MINERAL OF THE MICA GROUP¹

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Orlovite is a new mineral of the mica group, the titanium analogue of polyolithionite. It was discovered in highly quartz rocks in association with pectolite, baratovite, faizievite, aegirine, polyolithionite, leucosphenite, fluorite and other minerals in a moraine of the Darai-Pioz glacier (Tajikistan). The mineral is colourless with a glassy to pearly luster. It occurs in flaky aggregates up to 2 cm in size. Cleavage is perfect along (001). Mohs hardness is 2–3. Density (measured) $D_m = 2.91(2)$ g/cm³, density (calculated) $D_c = 2.914$ g/cm³. The mineral is optically negative, biaxial, $n_p = 1.600$, $n_m = 1.620$, $n_g = 1.625$, all ± 0.002 , $2V_m = -52(2)^\circ$, $2V_c = -52.6^\circ$. Orlovite is monoclinic, $C2$, $a = 5.199(3)\text{\AA}$; $b = 9.068(7)\text{\AA}$; $c = 10.070(4)\text{\AA}$; $\alpha = 90^\circ$, $\beta = 99.35(2)^\circ$, $\gamma = 90^\circ$, $V = 468.4(4)\text{\AA}^3$, $Z = 2$. The strongest X-ray lines [d , (\AA), (I , %), (hkl)]: 9.96 (40) (001), 4.48 (67) (002), 3.87 (40) (111), 3.33 (100) (-121), 2.860 (35) (-113), 2.600 (28) (130), 2.570 (30) (-131), 2.400 (31) (014), 1.507 (20) (-206). IR – spectra (the strongest absorption bands) are as follows: 3600, 1130, 1087, 985, 961, 878, 776, 721, 669, 613, 567, 530, 512, 458, 405 cm⁻¹. Chemical composition (microprobe, Li_2O , Rb_2O – ICP OES, H_2O – SIMS, wt.%): SiO_2 – 58.31, TiO_2 – 18.05, Nb_2O_5 – 0.50, Al_2O_3 – 0.22, FeO – 0.40, MnO – 0.03, K_2O – 11.13, Cs_2O – 0.24, Li_2O – 7.25, Rb_2O – 0.69, H_2O – 0.21, F – 4.35, $-\text{O}=\text{F}_2$ – -1.83, total – 99.55.

The empirical formula of orlovite is $(\text{K}_{0.97}\text{Rb}_{0.03}\text{Cs}_{0.01})_{1.01}\text{Li}_{2.00}(\text{Ti}_{0.93}\text{Nb}_{0.02}\text{Fe}_{0.02}\text{Al}_{0.02})_{0.99}\text{Si}_4\text{O}_{11.04}(\text{F}_{0.94}\text{OH}_{0.10})_{1.04}$. Simplified formula $\text{KLi}_2\text{TiSi}_4\text{O}_{10}(\text{OF})$. The mineral is named to honor the well-known Russian mineralogist, doctor of mineralogy Yury Leonidovich Orlov (1926–1980), Director (1976–1980) of the A.E. Fersman Mineralogical museum, RAS, specialist in the mineralogy of diamonds and gem stones, and author of more than 50 works including the classical monographs “Mineralogy of Diamond” and “Morphology of Diamond”.

4 tables, 3 figures, 25 references.

Keywords: orlovite, titanian mica, new mineral, Darai-Pioz, Tajikistan, alkaline rocks.

Site of occurrence and association

Orlovite was discovered in samples of the Upper Darai-Pioz alkaline massif, collected on a moraine of the Darai-Pioz glacier (Garmsky region, Central Tadjikistan). The first data on the geological structure of the region, and the petrography and mineralogy of the massif were obtained by Moskvina (1937). The most comprehensive works on the Darai-Pioz massif, including a geological map on the scale 1:25000, and details of the mineralogy, geochemistry and geochronology is that of Vyacheslav D. Dusmatov (1968; 1969; 1970; 1971). The Darai-Pioz alkaline massif is remote, and its central part is cut by a glacier, that moves from north to south. Due to this fact, bedrock outcrops are inaccessible. Moreover, the massif itself is exposed as steep cliffs of the glacial valley. For this reason, the major work on the mineralogy and petrogra-

phy of the massif has been done on blocks of rocks in the moraine of the Darai-Pioz glacier.

One of the characteristic features of the Darai-Pioz alkaline massif is the wide variety of minerals of micas present: muscovite, annite, taeniolite, polyolithionite (Ganzeev *et al.*, 1976; Vladykin *et al.*, 1995; Vladykin, Dusmatov, 1996), sokolovaite (Pautov *et al.*, 2006) and orlovite. In addition, in the Darai-Pioz alkaline pegmatites, the authors have discovered three more tetrasilica lithium-caesium micas – potentially new minerals that are now under study. These minerals are as follows: caesium analogue of orlovite: $\text{CsLi}_2\text{TiSi}_4\text{O}_{10}(\text{OF})$, caesium analogue of taeniolite: $\text{CsLiMg}_2\text{Si}_4\text{O}_{10}\text{F}_2$ and the Fe^{+2} analogue of sokolovaite: $\text{CsLiFe}_2\text{Si}_4\text{O}_{10}\text{F}_2$. Orlovite is a titanium analogue of polyolithionite, and it is the first completely titanian mica from the mica group. High-titanium micas (3–14 wt.% TiO_2) belonging to the phlogopite-annite series from alkaline

¹ – The mineral was considered and recommended for publication by the Commission on New minerals and mineral names of the Russian mineralogical society and approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA on 2nd of April 2009.

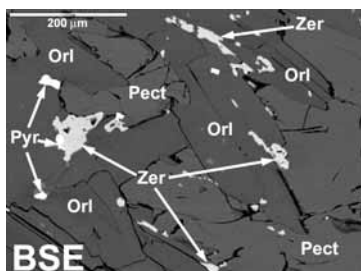
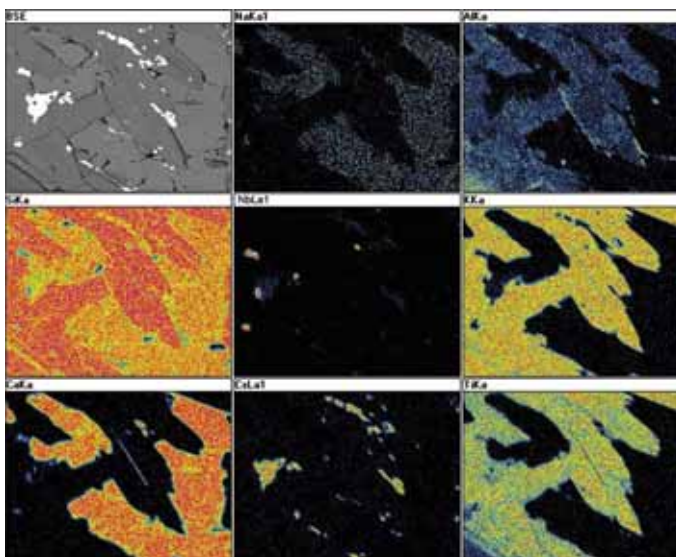


Fig. 1. Intergrowth of orlovite (Orl) with zeravshanite (Zer), pyrochlore (Pyr) and pectolite (Pect.) Image in the BSE mode and in the characteristic X-rays of the elements indicated. Scale bar is 200 μm .



basalts and some types of metamorphic rocks have been described by numerous researchers (Rosenbusch, 1910; Freudenberg, 1920; Prider, 1939; Ushakova, 1971; Mansker *et al.*, 1979; Dymek, 1983; Ryabchikov *et al.*, 1981; Koval' *et al.*, 1988; Cruciani and Zanazzi, 1994; Shaw, Penczak, 1996; Greenwood, 1998; Ibhi *et al.*, 2005; Chukanov *et al.*, 2008; 2010). Unlike orlovite, all of them are titanium-bearing micas, but not completely titanian.

Orlovite occurs in a rock consisting mainly of quartz (up to 80%) with several rare accessory minerals. We have discovered more than 30 boulders, fragments of this rock, from 0.2 up to 2 m in diameter, with different degrees of roundness. All examples of this rock have been found in the moraine sediments of the glacier; it is not found in the bedrock. Unfortunately, this rock had no contacts with any other rock-type in the boulders. This rock is composed of middle to coarse-grained aggregates of quartz of icy appearance. Appearance of these Si-rich rocks is very characteristic because of the presence of idiomorphic black crystals of aegirine with brilliant facets, large violet-pink plates sodgianite, red-brown translucent lenticular crystals of stillwellite-(Ce), poorly-bounded crystals of pale yellow-pink reedmergnerite, green elongated prismatic crystals of turkestanite and large crystals of polyolithionite. In addition, galenite, calcite, neptunite, sugilite, pyrochlore, minerals of the eudialyte group, tadjikite, baratovite, native bismuth, sphalerite, fluorite, fluorapatite, fluoapophyllite, sokolovaite, kapitsaite-(Y), pekovite, zeravshanite, and faizievite occurs in this rock. A characteristic feature of this essentially quartz rock is the presence of brown polyminer-

al aggregates (up to 25 cm in size) consists of pectolite, quartz, fluorite, aegirine, polyolithionite and other minerals. Segregations of orlovite occur mainly in intergrowth with pectolite, quartz, baratovite, neptunite, leucosphenite, zeravshanite, faizievite and pyrochlore (Fig. 1). Orlovite forms lamellar, colorless grains up to 2 mm in size.

Physical properties

Orlovite is colorless, in aggregates it appears white. In hand specimens it can not be distinguished from polyolithionite. In the short-wave ultra-violet light, it luminesces with a bright yellow light, in long-wave ultra-violet light it does not luminesce. Streak is white. It is characterized by glassy up to pearly luster. Cleavage is perfect on (001). In thin sheets the mineral is flexible. Mohs hardness is estimated to be 2–3. Hardness of microindentation equals to 94 kg/mm² (an average value out of 15 measurements ranged from 87 up to 106 kg/mm²). Microhardness is measured using a PMT-3 device loaded with a 10 g weight, graduated on NaCl. The density was determined using the flotation method in Clerici solution. The measured density of the mineral is 2.91 (2) g/cm³. Calculated density is 2.014 g/cm³. Orlovite is optically negative, biaxial, $2V_{\text{meas}} = -52.5(2)^\circ$, $2V_{\text{calc}} = -52.6^\circ$. The indices of refraction measured at 589 nm by the immersion method are: $n_p = 1.600(2)$, $n_m = 1.620(2)$, $n_g = 1.625(2)$, all ± 0.002 . Dispersion is weak, $r < v$. The IR-spectrum of orlovite was obtained with an Avatar IR-FT spectrometer (Thermo Nicolet); the major absorption bands are: 3600,

1130, 1087, 985, 961, 878, 776, 721, 669, 613, 567, 530, 512, 458, 405 cm^{-1} . The IR-spectrum is close to that of polyolithionite (Fig. 2).

Chemical composition

Orlovite was analysed with an JEOL JCXA-50A electronic microprobe analyzer and with using of ICP-OES and SIMS methods (Tab. 1). JCXA-50A was operated at 20 kV and 2 nA for energy-dispersive work (EDS) and at 15 kV and 25 nA for wave length spectrometers (WDS). Si, Ti, Nb, Al, Fe, Mn, Cs, and K were analyzed by EDS and F was measured by WDS. Standards were as follows: microcline USNM143966 (Si, Al, K), ilmenite USNM 96189 (Ti, Fe), synthetic LiNbO_3 (Nb), metal manganese (Mn), synthetic $\text{CsTbP}_4\text{O}_{12}$ (Cs), MgF_2 (F). Grains of the new mineral are homogenous and free of ingrowths of other minerals. The data were processed using a ZAF-correction program. Concentrations of Li and Rb in the mineral were obtained by ICP-OES. The mineral was digested in concentrated

$\text{HF} + \text{HNO}_3$ and evaporated to damp salts. Further HNO_3 was added and the solution was evaporated to the dry residue for complete removal of all fluorides. The resulting residue was diluted in 2% HNO_3 and the solution was analyzed using an ICP-OES Vista Pro instrument (Varian). The H_2O content of orlovite was determined using SIMS (secondary-ionic mass-spectrometry). The analysis was done on a Cameca IMS-4F in the Institute of Microelectronics and Computer Science of the Russian Academy of Sciences; the method is that of Smirnov *et al* (1995). The beam of primary ions O^{2-} was used and absolute concentrations of each element were calculated from the ions intensities relative to Si ($\text{E}/^{30}\text{Si}^+$ ratio), using calibrating constants. The mineral was normalized to $\text{Si} = 4$, giving the empirical formula $(\text{K}_{0.97}\text{Rb}_{0.03}\text{Cs}_{0.01})_{1.01}\text{Li}_{2.00}(\text{Ti}_{0.93}\text{Nb}_{0.02}\text{Fe}_{0.02}\text{Al}_{0.02})_{0.99}\text{Si}_4\text{O}_{11.04}(\text{F}_{0.94}\text{OH}_{0.10})_{1.04}$. The simplified formula of orlovite is $\text{KLi}_2\text{TiSi}_4\text{O}_{11}\text{F}$. The compatibility index $(1 - \text{K}_p/\text{K}_c) = 0.121$, corresponding to the poor category. It is probable that the refraction indices are strongly influenced

Table 1. Chemical composition of orlovite (wt.%)

Compo- nents	1	2	3	4	5	6	7	8	9	10	Average
Al_2O_3	0.09	0.28	0.18	0.44	0.08	0.30	0.15	0.46	0.07	0.13	0.22
SiO_2	57.98	58.40	59.34	57.56	57.66	58.88	58.32	57.95	58.56	58.42	58.31
K_2O	10.87	11.24	10.99	11.45	11.35	11.01	10.97	10.99	11.13	11.26	11.13
TiO_2	18.03	17.70	18.01	17.56	18.54	18.15	18.11	17.78	18.27	18.09	18.05
Nb_2O_5	0.30	0.38	0.58	0.69	0.41	0.61	0.55	0.35	0.53	0.63	0.50
FeO	0.28	0.34	0.48	0.25	0.55	0.46	0.39	0.50	0.26	0.44	0.40
MnO	0.04	0.00	0.06	0.03	0.01	0.04	0.07	0.01	0.05	0.03	0.03
Cs_2O	0.22	0.34	0.39	0.11	0.19	0.09	0.29	0.40	0.31	0.02	0.24
Rb_2O^*	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69
Li_2O^*	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25	7.25
F	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35	4.35
H_2O	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Total	100.58	101.18	102.53	100.59	101.29	102.04	101.35	100.94	101.68	101.52	101.38
-O=F	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83	-1.83
Total	98.75	99.35	100.70	98.76	99.46	100.21	99.52	99.11	99.85	99.69	99.55
Calculation at $\text{Si} = 4 \text{ apfu}$											
Al	0.01	0.02	0.01	0.04	0.01	0.02	0.01	0.04	0.01	0.01	0.02
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
K	0.96	0.98	0.95	1.02	1.00	0.95	0.96	0.97	0.97	0.98	0.97
Ti	0.95	0.91	0.91	0.92	0.97	0.93	0.93	0.92	0.94	0.93	0.93
Nb	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02
Fe^{+2}	0.02	0.02	0.03	0.01	0.03	0.03	0.02	0.03	0.01	0.03	0.02
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01
Rb	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Li	2.01	2.00	1.97	2.03	2.02	1.98	2.00	2.01	1.99	2.00	2.00
F	0.95	0.94	0.93	0.96	0.95	0.93	0.94	0.95	0.94	0.94	0.94
H	0.10	0.10	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10

Note. * – the data are received by the ICP-OES method. Analysts A.A. Agakhanov and L.A. Pautov. .

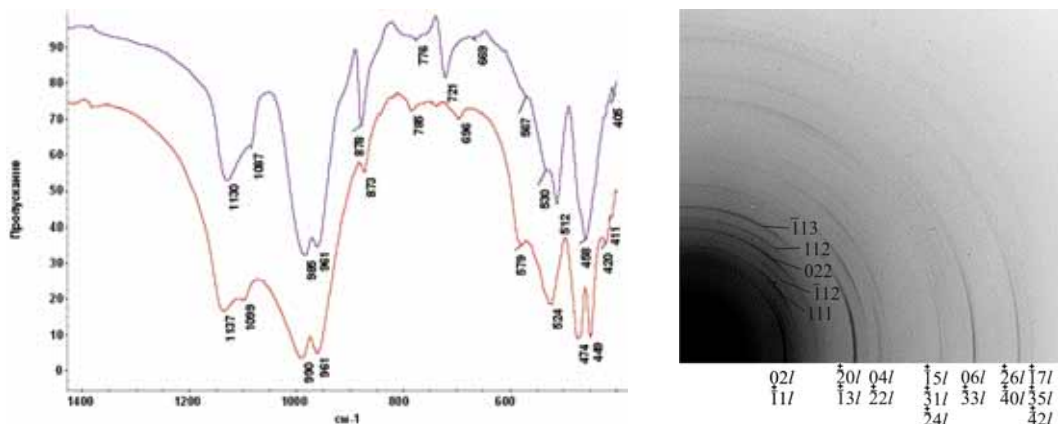


Fig. 2. IR-spectra of orlovite (upper) and polyolithionite (bottom) from Darai-Pioz. Preparation – tablets of mineral with KBr. FT-IR spectrometer Avatar (Thermo Nicolet). Analyst A.A. Agakhanov.

Fig. 3. Oblique texture electron diffraction pattern of orlovite (substrate tilted 60° from normal).

by the degree of distortion of Ti-O polyhedra in different minerals. For example, such problems are also encountered in calculating the compatibility index for layered titanosilicates from the lamprophyllite group for which $(1-K_p/K_c)$ also classifies as poor.

X-ray and electron diffraction data

It was not possible to study the new mineral by single-crystal X-ray diffraction as all crystals are strongly deformed. The X-ray powder diffraction pattern of orlovite (Tab. 2) were measured using DRON-2 diffractometer with $\text{CuK}\alpha$ -radiation. To eliminate the effect of possible preferred orientation, a Debye powder pattern was obtained on a RKU-114M camera using $\text{FeK}\alpha$ -radiation. We used quartz as an internal standard. The cell dimensions were refined from the powder diffraction pattern with a monoclinic cell (space group $C2$), $a = 5.199(3)$; $b = 9.068(7)$; $c = 10.070(4)\text{\AA}$, $\beta = 99.35(4)^\circ$, $V = 468.4(4)$, $Z = 2$. The unit cell parameters of orlovite and polyolithionite are close.

Electron diffraction studies of orlovite were performed with EMR-100M electronograph

operated at 100 kV. Oblique texture electron diffraction patterns (substrate tilted 60–63° from normal) (Fig. 3) revealed high degree of crystal structure crystallinity, monoclinic symmetry, polytype modification 1M(3T), space group $C2$ and unit cell parameters: $a = 5.21(1)$; $b = 9.026(3)$; $c = 10.05(1)\text{\AA}$; $\beta = 99.6(1)^\circ$; $V = 466(2)\text{\AA}^3$. Comparison of orlovite with similar minerals is shown in Table 4.

The holotype specimen of orlovite is stored in the Fersman Mineralogical Museum, RAS, Moscow (registration number 3824/1).

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Table 2. X-ray powder-diffraction data of orlovite

Powder pattern		Diffraction pattern		Calculated	
<i>I</i>	d_{meas} Å	<i>I</i>	d_{meas} Å	d_{calc}	<i>hkl</i>
2	9.92	40	9.96	9.936	001
2	4.95	12	4.98	4.968	002
7	4.48	67	4.48	4.465	110
		8	4.32	4.307	-111
4	3.87	40	3.87	3.873	111
10	3.33	100	3.33	3.326	-121
2	3.12	12	3.12	3.114	112
				3.111	013
4	2.86	35	2.860	2.861	-113
1	2.67	2	2.669	2.674	023
3	2.60	28	2.600	2.604	130
3	2.57	30	2.570	2.572	-131
			2.565	2.565	200
2	2.50	16	2.489	2.484	004
			2.497	2.497	113
3	2.40	31	2.400	2.396	014
			2.391	2.391	201
			2.389	2.389	-132
2	2.136	16	2.137	2.135	-133
			2.142	2.142	202
1	2.070	4	2.083	2.084	212
			2.062	2.062	042
2	1.993	16	1.990	1.987	005
		3	1.732	1.733	-301
			1.728	1.728	134
			1.727	1.727	115
2	1.654	17	1.654	1.655	204
			1.656	1.656	006
			1.647	1.647	-135
1	1.557	8	1.557	1.557	242
			1.556	1.556	026
			1.555	1.555	224
2	1.507	20	1.507	1.507	-206
			1.503	1.503	-331
1	1.348	9	1.348	1.349	-236
			1.551	1.551	-136
			1.551	1.551	-325
2	1.300	15	1.300	1.301	117
			1.298	1.298	206

Note: Debye-Scherrer method – RKD-114, Fe-anode, Mn-filter, URS-501M. Diffractometer DRON-2, Fe-anode, graphite monochromator, 1°/min. Internal standard – quartz. Analyst A.A.Agakhanov.

Table 3. Electron diffraction data of orlovite

No	<i>I</i>	d_{meas} Å	<i>hkl</i>	d_{meas} Å
1 ellipse				
1	8	4.461*	110	4.465
2	2	4.302*	$\bar{1}11$	4.311
3	7	3.863*	111	3.866
4	4	3.593*	$\bar{1}12$	3.585
5	8	3.343*	022	3.336
6	5	3.096*	112	3.101
7	8	2.860*	$\bar{1}13$	2.861
8	2	2.663*	023	2.665
9	3	2.492*	113	2.489
10	1	2.304	$\bar{1}14$	2.313
2 ellipse				
11	10	2.592	130	2.596
			$\bar{2}01$	2.594
12	9	2.569	200	2.569
			$\bar{1}31$	2.565
13	8	2.382	201	2.391
			$\bar{1}32$	2.384
14	6	2.140	202	2.139
			$\bar{1}33$	2.130
15	2	1.966	133	1.962
			$\bar{2}04$	1.953
16	1	1.732	134	1.721
			$\bar{2}05$	1.713
17	6	1.647	204	1.651
			$\bar{1}35$	1.644
18	4	1.513	135	1.515
			$\bar{2}06$	1.508
19	6	1.343	136	1.343
			$\bar{2}07$	1.338
20	3	1.295	206	1.294
			137	1.289
3 ellipse				
21	6	2.256	040	2.257
22	5	2.237	220	2.232
23	5	2.140	$\bar{2}22$	2.156
24	1	2.049	042	2.054
4 ellipse				
26	5	1.705	$\bar{3}11$	1.705
			150	1.703
			$\bar{2}41$	1.702
5 ellipse				
26	8	1.504*	060	1.504
6 ellipse				
27	7	1.286	400	1.284
			$\bar{2}62$	1.282
7 ellipse				
28	1	1.251	170	1.251
			$\bar{4}21$	1.251
			$\bar{3}51$	1.252

Note: EMR-100M electronograph, oblique texture electron diffraction pattern of orlovite (substrate tilted 68° from normal), standard – TICl. Analyst G.K. Bekenova

* – Reflections for calculation of unit cell parameters. Intensity of reflections is estimated visually. * – Reflections according to which parameters of unit cell are calculated. Intensity of reflections are estimated visually.

Table 4. Comparison data for orlovite, polyolithionite and tainiolite

Features of mineral	Orlovite	Polyolithionite	Tainiolite
Source	This work	JCPDS 21-952; Anthony <i>et al.</i> , 1995	JCPDS 31-1045; Anthony <i>et al.</i> , 1995
Formula	CsLi ₂ TiSi ₄ O ₁₀ (OF)	KLi ₂ AlSi ₄ O ₁₀ F ₂	CsLiMg ₂ Si ₄ O ₁₀ F ₂
Space group	C2	C2/m	C2/m
a, Å	5.199	5.186	5.227
b, Å	9.068	8.968	9.057
c, Å	10.070	10.029	10.133
β, °	99.35	100.4	99.86
Z	2	2	2
Strong lines of X-ray	9.96 (40)	9.87 (20)	9.95 (85)
d _{meas} , Å (I)	4.48 (67)	4.93 (90)	4.98 (35)
	3.87 (40)	4.47 (50)	4.51 (25)
	3.33 (100)	3.59 (100)	3.611 (20)
	2.860 (35)	3.31 (100)	3.325 (100)
	2.600 (28)	3.29 (90)	3.106 (30)
	2.570 (30)	3.07 (100)	2.883 (25)
	2.400 (31)	2.867 (70)	2.602 (20)
	1.990 (16)	2.580 (70)	2.575 (25)
	1.507 (20)	1.974 (90)	2.396 (35)
		1.641 (40)	1.995 (30)
Density, g/cm ³ (meas/calc)	2.91/2.914	2.58–2.82/2.84	2.83–2.90/2.80
Optical properties (optical sign)	Biaxial (-)	Biaxial (-)	Biaxial (-)
n _p	1.600	1.53	1.522–1.540
n _m	1.620	1.551–1.556	1.553–1.570
n _g	1.625	1.555–1.559	1.553–1.570

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ON THE DISCOVERY OF ROOSEVELTITE, PREISINGERITE, TRÖEGERITE, AND ZEUNERITE IN Bi-As-Cu-U-MINERALIZATION FROM THE ORANZHEVOYE ORE FIELD, VERKHNE-KALGANINSKY MASSIF, MAGADAN REGION, RUSSIA

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New data on bismuth, arsenic, uranium and copper minerals (rooseveltite, preisingerite, zeunerite, and tröegerite) obtained with the help of an optical microscope and scanning electron microscope equipped with a Link detector are represented in the article. The minerals were established within Bi-As-Cu-U-mineralization at the Oranzhevoye ore field of the Verkhne-Kalganinsky massif in sulfide-quartz, arsenopyrite-quartz and sulfide-quartz-chlorite veinlets that intersect andesites. The following secondary minerals: scorodite, rooseveltite and preisingerite replace arsenopyrite, bismuthinite, tetradymite, and native bismuth. Uranium minerals – zeunerite and tröegerite – also associate with these minerals. Roosevelite and preisingerite are established in Russia for the first time. Character of occurrence of rooseveltite and preisingerite indicates that they formed during low-temperature metasomatic (hydrothermal) processes. The established association – arsenopyrite, pyrrhotite, chalkopyrite, and minerals of bismuth (bismuthinite and native bismuth, rooseveltite and preisingerite), tellurium (tetradymite), tin (stannite), gold and silver (tellurides, akanthite, native silver) – allowed to attribute this mineralization to the gold-polyarsulfide-quartz formation.

6 figures, 2 tables, 16 references.

Keywords: rooseveltite, preisingerite, zeunerite, tröegerite, Verkhne-Kalganinsky massif, Oranzhevoye ore field, Bi-As-Cu-U-mineralization.

Introduction

Oranzhevoye ore field of the Verkhne-Kalganinsky massif has received its name due to the bright colour anomaly connected with vast and intensive contact-metamorphic and metasomatic alterations of rocks composing it. According to the analytical researches, the area of the Oranzhevoye ore field is characterized by the sporadic increased contents of gold and silver. The increased contents of useful components are observed in formations of the following two types: 1) in arsenopyrite-sericite-scorodite-quartz nests in fault zones (size of nests vary from 0.1 up to 1 m) and in the veins of the "crust" shape with uplifted contents (according to the data by L.I. Rtishcheva – up to 58 ppm of gold and 2 kg/ton of silver; according to our data – up to 25 ppm of gold and 100 ppm of silver); 2) in separate arsenopyrite-muscovite-quartz veinlets (1–5 ppm of gold and silver). In addition, development of Bi-As-Cu-U-mineralization at this ore field occurs. Within this mineralization, several minerals have been established that earlier in Russia have not been recorded.

As the studying of polished sections with the help of an optical microscope and electron microscope equipped with a Link detector has

shown, arsenopyrite, chalkopyrite and pyrrhotite were the most widespread ore minerals. In addition, minerals of bismuth (bismuthinite and native bismuth, rooseveltite, preisingerite), tellurium (tetradymite), tin (stannite), gold (established only according to the gross chemical analysis of rocks) and silver (akanthite and tellurides) are also established here. The association of minerals established allows to attribute the revealed mineralization to the gold-polyarsulfide-quartz (connected with intrusions) formation. Arsenopyrite, bismuthinite, tetradymite, and native bismuth are replaced by secondary minerals: scorodite, rooseveltite BiAsO_4 and preisingerite $\text{Bi}_3\text{O}(\text{OH})(\text{AsO}_4)_2$. Tröegerite $(\text{UO}_2)_3(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O} (?)$ and zeunerite $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$ also occur in the same association (Soboleva, Pudovkina, 1957), $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10 - 16\text{H}_2\text{O}$ (Frondel, 1951). As for this ore field, these minerals are discovered for the first time. Roosevelite and preisingerite are established for the first time in Russia.

Rooseveltite is an isostructural mineral to monazite. Extremely fine size of this mineral does not allow to obtain X-ray diffraction pattern of the phase established by us. But we conditionally name it as rooseveltite, because of the fact that tetra-rooseveltite is much more rare phase in nature and from the greater degree of

probability of detection rooseveltite exactly, and also because of low-temperature genesis of this mineral. After 1946, rooseveltite was established in several deposits of the world with a complex Fe-Bi-Cu-Zn-Pb-Au-As-S-mineralization. As a rule, it was established in their hydrated zone. For the first time it was discovered in Bolivia at the Potosi deposit (Palache *et al.*, 1951), and then in Germany (Walenta, 1992; Roberts *et al.*, 2001). Rooseveltite was later described from the following several deposits: in Uzbekistan (Chatkal sky ridge, Nizhneaktashsky deposit) (Minerals of Uzbekistan, 1976), in Argentina (Bedlivy *et al.*, 1972; Minlka, 2002), Spain (Schnorrer, 2000), Greece (Sejkora, 1994; Sejkora *et al.*, 2006; Šrein *et al.*, 2008), Australia (Rankin *et al.*, 2002), Portugal and Great Britain. In the majority of the listed cases, as well as in the Oranzhevoye ore field, rooseveltite associates with preisingerite.

Troegerite and zeunerite were firstly described as secondary minerals of oxidation zones of the uranium and uranium-arsenate deposits in Germany in 1871 and 1872, respectively (Weisbach, 1871; Weisbach, 1872). Since then they have been discovered in numerous deposits of Europe (in Austria, Italy, France, Great Britain, Portugal, Spain, and Sweden), and also in Canada, USA, Argentina, Chile, Mexico, Japan, China, Iran, and Africa. Zeunerite and troegerite are also described in Russia (deposits Severnoye, Chukotka; Lastochka, Khabarovsk territory; Korolevskoye-Chasovoye, Transbaikalia) (Chernikov *et al.*, 1997). Zeunerite is a widespread mineral, and troegerite occurs rarely.

Occurrences of rooseveltite, preisingerite, zeunerite and troegerite in the Oranzhevoye ore field

The most significant occurrences of rooseveltite and preisingerite are established in the sulphide-quartz and sulphide-quartz-chlorite veinlets intersecting andesites in the right board of the Oranzhevaya river, arsenopyrite-

quartz veinlets in the left board of the Obydennaya river, and in arsenopyrite-muscovite-quartz veinlet (3 cm in thickness) intersecting metamorphosed hornfels rock in the right board of the Chalym stream. The main sulphide mineral in these veinlets is partly fragmented and cataclased arsenopyrite. In the presented article we shall stop more in detail on the most characteristic occurrences of rooseveltite and preisingerite.

In the first case (Oranzhevaya river) rooseveltite is established in the arsenopyrite-quartz – chlorite veinlet with a breccia texture and a layered fabric. Detrital part is presented by large aggregates of arsenopyrite. Rooseveltite forms aggregates of thin-lamellar individuals or earthy accumulations of prismatic or isometric forms, dirty-grey coloured among the chlorite-quartz main part of the veinlet. Size of the aggregates reaches 0.1 – 0.2 mm. Radiating and thin branching veinlets of rooseveltite are characteristic for aggregates of rooseveltite in this sample (Fig. 1). The character rooseveltite aggregates – their spatial association to the cracks, radiating from its large accumulation thin veinlets, also located closer to thinner cracks – specifies its formation, probably, during late low-temperature (hydrothermal) metasomatic processes.

Rooseveltite is also established in the fragment of substantially arsenopyritic (with quartz) cataclased vein with a massive structure (Oranzhevaya river). Pyrrhotite and intergrowths of chalkopyrite and stannite are observed in the intergranular space of the cataclased and corroded aggregates of arsenopyrite and pyrite. Scorodite develops along the cracks in arsenopyrite grains. Feathering cracks are observed in the veinlet's exocontact. Along these cracks, chains of micron size drop-like sulphosalt are observed (precisely not identified). Rooseveltite develops mostly along bismuthinite (Fig. 2), sometimes along arsenopyrite and, as a rule, is in close intergrowth with preisingerite. In addition, branching microveinlets of these minerals (thickness – 0.0n mm) occur in quartz. Pyr-

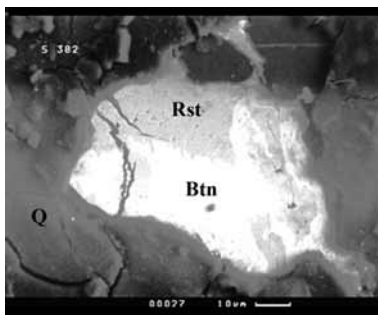
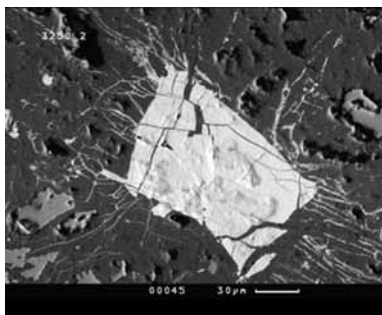


Fig. 1. Platy crystal of rooseveltite (white) among chlorite (dark grey) in association with scorodite (light grey). Oranzhevaya river (BSE).

Fig. 2. Rooseveltite (Rst) developing along bismuthinite (Btn) among quartz grains, Oranzhevaya river (BSE).

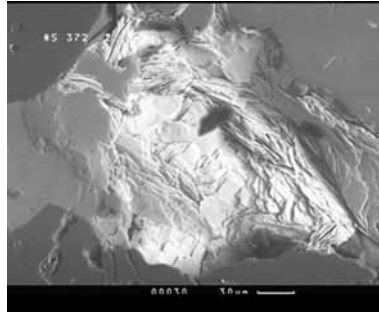
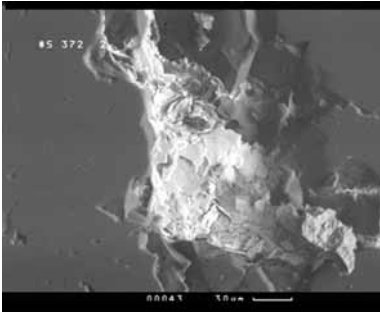


Fig. 3. Aggregate of platy crystals of zeunerite (white) in a cataclastic crack in quartz, Oranzhevaya river (BSE).

Fig. 4. Zeunerite (white) intergrowing with arsenopyrite (light grey) in a crack of a quartz grain (BSE).

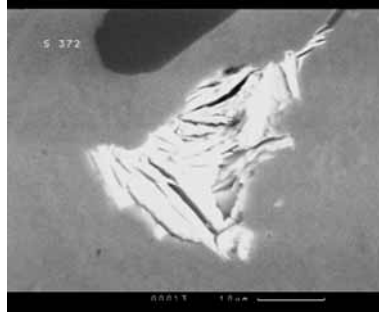
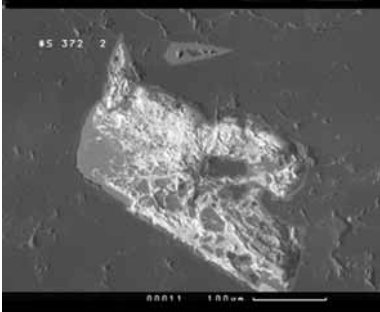


Fig. 5. Zeunerite (white) developing along arsenopyrite (light grey) on a joint of quartz grains (BSE).

Fig. 6. Aggregate of tröegerite platy crystals (white) in a crack of the quartz grain, Oranzhevaya river (BSE).

rhotite is replaced by marcasite-pyrite aggregate. The size of rooseveltite aggregates varies from the 0.0n up to 0.1–0.2 mm. According to the character of its aggregates and relationship with earlier minerals of arsenic and bismuth, rooseveltite and preisingerite are later minerals and, probably, the products of low-temperature metasomatic transformation of the specified minerals.

Tröegerite and zeunerite are established in the same sample. Zeunerite forms aggregates of fine thin-lamellar individs of yellowish colour in cracks of quartz grains or on their joint (Fig. 3–5). Length of individs does not exceed 30 microns (thickness of plates – from 0.0n up to 1–2 microns), size of aggregates – about 300–400 microns. As a rule, it is tightly associated with arsenopyrite or replaces it (Fig. 5). Tröegerite forms aggregates of lamellar individs similar in the morphology with zeunerite. Its aggregates are more finely and do not exceed 60–80 microns and are observed in the quartz grain cracks (Fig. 6). As well as rooseveltite and preisingerite, zeunerite and tröegerite are, probably, later-hydrothermal phases.

Rooseveltite develops on minerals of bismuth in quartz veinlets intersecting andesites that expose in the boards of the Chalyms river. Aggregates of bismuth minerals are associated to the cracks of cataclase in quartz. Intergrowths of tetradymite and native bismuth (about 0.3 mm in size) are established in this occurrence.

Rooseveltite is also established in the occurrence on the left board of the Obyden-naya river in area of a watershed with one of its small tributaries, in deluvium. The samples are represented by sericite-calcite-quartz nests (up to 5 cm in diameter) in fragments of quartz – arsenopyrite vein with a twisting-banded structure from the crumpling zone. The rock has a green shade of colour because of the replacement of arsenopyrite by scorodite. Rare relic impregnation of chalcopyrite, arsenopyrite, galenite, and ilmenite is observed. Rooseveltite and scorodite develop in cavities remaining from the earlier, completely leached, minerals. Fine aggregates of native silver occur in small cavities in galenite.

Chemical composition

As a whole, the composition of rooseveltite and preisingerite is very close to the theoretical composition of these minerals (Table 1). It is interesting to note for rooseveltite established in the chlorite-arsenopyrite veinlet observed in the right board of the Oranzhevaya river, that it is characterized by an unusual to this mineral significant content of lead – from 3 up to 6% (Table 1, analyses 1–8). Substantial differences from the theoretical composition are not established for its other samples (Table 1).

Chemical compositions of tröegerite and zeunerite also practically do not differ from the theoretical formulas. Significant impurity of

Table 1. Chemical composition of rooseveltite and preisingerite from the Oranzhevoye ore field, wt. %

Mineral № an.	Rooseveltite Pb-containing								Properly rooseveltite					Preisingerite				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
FeO	1.49	0.84	0.57	0.69	3.31	0.70	0.86	1.42	0.67	1.57	0.61	1.06	0.93	0.00	0.44	0.63	0.65	0.00
CuO	0.05	0.12	0.06	0.00	0.22	0.00	0.00	0.00	0.07	0.10	0.06	0.10	0.00	0.00	0.14	0.18	0.19	0.00
NiO	0.13	0.08	0.02	0.08	0.06	0.06	0.00	0.14	0.08	0.00	0.00	0.00	0.06	0.00	0.06	0.05	0.05	0.00
CoO	0.16	0.06	0.00	0.07	0.00	0.00	0.00	0.00	0.04	0.04	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00
ZnO	0.22	0.30	0.10	0.09	0.08	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.28	0.00
SO ₃	1.81	1.09	0.57	0.75	1.01	0.72	0.57	0.67	0.54	0.61	0.88	0.61	0.82	0.00	0.00	0.26	0.00	0.00
As ₂ O ₃	29.00	29.55	30.01	30.14	31.61	29.85	29.87	30.91	30.70	30.79	30.20	31.87	31.18	33.03	23.35	23.96	24.51	24.51
SeO ₃	0.45	0.39	0.51	0.00	0.84	0.30	0.64	0.47	0.00	0.04	0.00	0.00	0.17	0.00	0.37	0.26	0.46	0.00
TeO ₃	0.40	1.08	0.76	0.84	1.06	0.57	1.09	0.60	0.12	0.00	0.00	0.29	0.00	0.00	0.00	0.01	0.00	0.00
Sb ₂ O ₃	0.21	0.56	0.53	0.20	0.48	0.02	0.43	0.19	0.31	0.26	0.17	0.40	0.15	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	59.78	59.88	57.17	60.09	56.74	60.08	58.59	57.23	64.66	63.42	66.30	62.67	64.19	66.97	74.66	73.16	72.83	74.53
PbO	4.02	3.32	6.43	3.78	3.84	4.53	5.68	5.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	97.72	97.26	96.72	96.72	99.25	96.84	97.80	96.96	97.19	96.84	98.23	97.00	97.57	100.00	99.03	98.80	98.98	99.04
Quantity of atoms in formula calculation onto the cation sum: 2 – for rooseveltite and 5 – for preisingerite)																		
Fe	0.07	0.04	0.03	0.03	0.15	0.03	0.04	0.07	0.03	0.08	0.03	0.05	0.04	0.00	0.06	0.08	0.08	0.00
Cu	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.00
Ni	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
Co	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.00
S	0.08	0.05	0.02	0.03	0.04	0.03	0.03	0.03	0.02	0.03	0.04	0.03	0.04	0.00	0.00	0.03	0.00	0.00
As	0.86	0.89	0.92	0.93	0.89	0.92	0.91	0.93	0.94	0.93	0.92	0.96	0.94	1.00	1.91	1.92	1.96	2.00
Se	0.01	0.01	0.01	0.00	0.02	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.03	0.00
Te	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Sb	0.01	0.02	0.02	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Bi	0.88	0.89	0.87	0.91	0.79	0.92	0.88	0.85	0.98	0.95	1.00	0.94	0.96	1.00	2.98	2.89	2.87	3.00
Pb	0.06	0.05	0.10	0.06	0.06	0.07	0.09	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note. Rather low total value of rooseveltite analyses due to the quality of its polishing and its association, in some cases, with cavities in arsenopyrite. The most characteristic chemical compositions of the minerals are chosen from the complete data base (properly rooseveltite – more than 20 analyses, Pb-containing rooseveltite – 15 analyses). Analysis 14 – theoretical composition of rooseveltite, analysis 18 – theoretical composition of preisingerite.

iron in zeunerite, probably, inherited from arsenopyrite (it occurs in cracks and intergrowth with this mineral) is its characteristic feature (Table 2).

Conclusion

As a result of the researches carried out, the character of the complex Bi-As-U-mineralization belonging to the gold-polysulphide-quartz formation of the Oranzhevoye ore field is investigated. This mineralization is established in the indicator ore formations exposing on the earths surface and presumably bedding above the latent ore bodies as rather thin (0.2–2 m) metasomatic nests and veinlets intersecting intrusive rocks and hornfels. These formations are mainly composed of arsenopyrite-quartz-sericite mineralization. Chalcopyrite, pyrite and galenite, minerals of tellurium (tetradymite), bismuth (bismuthinite, native bismuth, rooseveltite, preisingerite), tin (stannite), silver (native silver, akanthite and tellurides of silver), uranium and uranium-copper arsenates

(tröegerite, zeunerite) are established as accessory minerals. Gold as independent mineral phase is not observed by us (it is traced only according to the chemical analysis). It is possible to characterize the mineralization of the investigated object as polystadial imposed mineralization of the mixed type – As-Ag-Au and Ag-Fe-Bi-As-Cu-U-sulphide.

Mineralogical studying of the Oranzhevoye ore field of the Verkhne-Kalganinsky massif has allowed – for the first time in Russia – to establish two low-temperature mineral of bismuth: rooseveltite and preisingerite. Both minerals are characterized by chemical composition close to the described in other deposits of the world (Bedlivy *et al.*, 1971, etc.). In addition, the variety of rooseveltite enriched in lead (Pb-containing rooseveltite from occurrences in the board of the Oranzhevaya river) was found. It is possible to consider polymorphic this feature of the Oranzhevoye ore field – a substantial impurity of lead (3–6.5 wt.%). Its nature, however, still demands additional investigation.

Table 2. Chemical composition of zeunerite and tröegerite from the Oranzhevoye ore field, wt.%

Mineral № an.	Tröegerite				Zeunerite		
	1	2	3	4	5	6	7
FeO	0.15	0.00	1.01	0.64	0.78	1.25	0.00
CuO	0.00	0.00	6.25	7.42	6.34	6.21	7.49
NiO	0.00	0.00	0.05	0.00	0.01	0.00	0.00
CoO	0.19	0.00	0.18	0.14	0.11	0.00	0.00
ZnO	0.04	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.32	0.00	0.09	0.05	0.00	0.04	0.00
As ₂ O ₅	19.42	17.63	17.67	18.21	17.48	20.38	21.65
SeO ₃	0.42	0.00	0.58	1.18	0.00	0.00	0.00
TeO ₃	0.00	0.00	0.24	0.00	0.00	0.00	0.00
Sb ₂ O ₃	0.07	0.00	0.49	0.44	0.82	0.30	0.00
Bi ₂ O ₃	0.09	0.00	0.00	0.00	0.00	0.00	0.00
UO ₂	58.61	65.81	53.07	51.79	54.39	50.76	50.87
Total	79.30	83.44	79.64	79.87	79.93	78.95	80.01
Quantity of atoms in formula (calculation onto the sum of cations equal to 5)							
Fe	0.03	0.00	0.15	0.10	0.12	0.19	0.00
Cu	0.00	0.00	0.86	1.00	0.88	0.84	1.00
Ni	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Co	0.03	0.00	0.03	0.02	0.02	0.00	0.00
Zn	0.01	0.00	0.00	0.00	0.00	0.00	0.00
S	0.05	0.00	0.01	0.01	0.00	0.01	0.00
As	2.12	1.93	1.68	1.69	1.68	1.91	2.00
Se	0.04	0.00	0.05	0.10	0.00	0.00	0.00
Te	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Sb	0.01	0.00	0.04	0.04	0.07	0.03	0.00
Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00
U	2.72	3.07	2.15	2.05	2.23	2.03	2.00

Note. Analysis 2 – theoretical composition of tröegerite without H₂O, analysis 7 – theoretical composition of zeunerite without H₂O.

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MANNARDITE FROM VANADIUM-BEARING SCHISTS OF KAZAKHSTAN AND CENTRAL ASIA

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Mannardite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{V}_2)\text{O}_{16}$ is found in carbonaceous-siliceous schists of the Karatau Ridge (areas Balacauskandyk and Kurumsak), Kazakhstan, and in the Kara-Chagyr and Kara-Tangi, Southern Kyrgyzstan. At Kara-Tangi, it is present as rare grains 10 micron or less in size in assemblages with quartz, pyrite, chalcocopyrite, sphalerite, fluorapatite, nickelalumite, and kyrgyzstanite. At Kara-Chagyr, mannardite occurs as small grains under 10 micron in size in quartz veinlets with pyrite, Ce-phosphate, Ba-V-bearing muscovite, nickelalumite, and ankinovichite. In the Balacauskandyk and Kurumsak areas, it forms grains up to 50 micron and aggregates up to 100 micron and larger in size being present in quartz veinlets with Ba-V-bearing muscovite, chernykhite (Kurumsak), V-bearing rutile, Nd, La, and Y phosphates, barite, and hematite. Mannardite from Balacauskandyk is studied in most detail. The mineral has black colour, deep brown in thin scales, and metallic luster. Micro-hardness measurements (from 5 repeated tests) are averaged at 628 kg/mm². Density is determined at 4.34(3) g/cm³, by measurement and 4.40 g/cm³ by calculation. Mannardite is anisotropic in reflected light, showing dark-gray color. Unit cell parameters are: $a = 14.37(1)$, $c = 5.922(6)\text{\AA}$, $V = 1223(2)\text{\AA}^3$. Intensive X-ray powder diffraction peaks are as follows: (d , \AA ; l ; hkl): 3.590(4)(400); 3.211(10)(420); 2.844(3)(112); 2.476(7)(312); 2.276(4)(620); 2.227(5)(332); 1.892(5)(352); 1.690(4)(660); 1.592(5)(732). Chemical composition (average by 19 microprobe analyses, wt.%): BaO 20.58; TiO₂ 58.10; V₂O₅ 18.07; Cr₂O₃ 0.40; H₂O(calc.) 1.98; Total 99.13. Empirical formula: $\text{Ba}_{1.10}(\text{Ti}_{5.94}\text{V}_{1.97}\text{Cr}_{0.04})\text{O}_{16} \cdot 0.90\text{H}_2\text{O}$. Mannardite from Kara-Tangi contains up to 2.4 wt.% of Cr₂O₃. Along with micas and sulvanite, mannardite is one of early concentrators of vanadium in these rocks. The majority of mannardite is associated with netted quartz veins, which belong to the type of alpine veins. This article discusses the mechanism of formation of these veins during the regional metamorphism of sediments.

2 tables, 6 figures, 33 references.

Key words: mannardite, cryptomelane group, vanadium-bearing schist, Kara-Tau, Kara-Chagyr.

Introduction

Mannardite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{V}_2)\text{O}_{16}$ a rare complex titanate, was first described in quartz-carbonate veins crosscutting shales and sandstones in Rough Claims (British Columbia) and in the Brunswick polymetallic deposit (Scott and Peatfield, 1986). A mineral of similar composition, but containing no H₂O, was found at the same time in the Kantsi silver deposit in China (Scott and Peatfield, 1986). Later on, mannardite was found in the Upper Silurian and Lower Devoian schists of the Turkestan Ridge, Kyrgyzstan (Pautov, 1994). We found mannardite while studying carbonaceous-siliceous schists in a number of locations: the Kara-Tangi uranium-vanadium deposit, Kara-Chagyr vanadium locality (South Kyrgyzstan), and the Balacauskandyk and Kurumsak vanadium deposits, North-Western Karatau, Kazakhstan.

Along with several minerals close in composition and structure – redledgite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{Cr}_2)\text{O}_{16}$, ankangite $\text{Ba}(\text{Ti}_6\text{V}_2)\text{O}_{16}$, priderite $\text{K}_2(\text{Ti}_6\text{Fe}_2^+)\text{O}_{16}$, and henrymeyerite $\text{Ba}(\text{Ti}_7\text{Fe}^{+2})\text{O}_{16}$ – mannardite belongs to the hollandite structure type ($AB_8\text{O}_{16}$). All these minerals crys-

tallize with tetragonal symmetry. They often contain superstructures associated with different types of ordering of the tunnel A-cations (Ba, K, Na), which results in an increase of the c -dimension and causes a slight deviation from the original hollandite structure (Dmitrieva *et al.*, 1992; Mitchell *et al.*, 2000).

Titanates with the hollandite structure occur in very diverse geological settings – hydrothermal veins of ore deposits (Scott and Peatfield, 1986; Xiong *et al.*, 1989; Ivanov *et al.*, 1996; Biagioni *et al.*, 2009), carbonaceous-siliceous schists (Pautov, 1994; Karpenko, 2010), metamorphic rocks of carbonate-silicate composition (Reznitskii *et al.*, 2007), carbonatites (Zhuravleva *et al.*, 1978; Mitchell *et al.*, 2000), kimberlites and lamproites (Mitchell and Meyer, 1989), and mantle hartzburgite and lherzolite xenoliths (Kogarko *et al.*, 2007). Interest in this group of minerals has grown over the past few decades, in part due to the experimental studies showing transformation of feldspar structures into hollandite-type structures under high pressure (Zhang *et al.*, 1993). In a practical sense, compounds of this type act as adsorbents in water treatment, especially for streams contaminated with

heavy metals and radionuclides (Zhang *et al.*, 1993; Foley *et al.*, 1997; Mitchell *et al.*, 2000).

Occurrence

Vanadium-bearing carbonaceous-siliceous-argilliferous rocks with roscoelite were first noticed at the Karatau Ridge (Kazakhstan) by N.A. Kozlov and V.A. Sokolov in the early 1940s. That set the ground for the discovery and development of the Karatau uranium-vanadium deposits (Kozlov and Sokolov, 1944). The geology and mineralogy of the Karatau vanadium-bearing schists were further described in numerous works by S.G. Ankinovich and E.A. Ankinovich (Ankinovich and Ankinovich, 1954; Ankinovich, 1964; Ankinovich *et al.*, 1979; etc.). The geochemistry of the schists was studied by V.M. Kholodov (1968), G.K. Bekenova (2007), and V.Yu. Karpenko (2010) who obtained new mineralogical data and reviewed the available information on the Karatau schists. These rocks belong to the Lower Cambrian vanadium-bearing carbonaceous-siliceous schist formation, which is represented in Southern Kazakhstan by the Kurumsak Suite. It includes a vanadium-rich horizon 7 to 12 m in thickness (so-called "ore horizon"), which has vanadium contents (by metal) up to 2.5 wt.% (Ankinovich *et al.*, 1979). This ore zone consists mainly of phthanites rhythmically alternating with carbonaceous-quartz-argillaceous schists which form the bulk of the horizon. This ore horizon also shows increased contents of Mo, Re, Cu, Zn, Ni, Pb, U and carbonaceous matter (up to 10–15 wt.% in phthanites), and is exceptionally uniform in lithological and chemical composition over vast areas of the Lower Paleozoic section (Geology..., 1986). The mineralogy of these schists is notably rich, featuring more than 160 mineral species, including 12 new minerals (Bekenova, 2007; Karpenko, 2010). The best-studied deposits (areas) are Bala-sauskandyk, Kurumsak and Ran. The early vanadium and vanadium-bearing minerals in the Karatau carbonaceous-siliceous schists are represented by mica group: barium-vanadium-bearing muscovite (phengite) (Ankinovich *et al.*, 1992) and vanadium micas – roscoelite and chernykhite (Ankinovich *et al.*, 1997; 2001).

Carbonaceous-siliceous schists of Southern Kirgystan were described by D.I. Mushketov and V.N. Weber as early as 1909–1913 while compiling geological maps of this region (Belov *et al.*, 1989). The Radium Expedition

(Shcherbakov, 1924) and the Tadjik-Pamir Expedition also made significant contributions to geological and mineralogical studies of these schists. " ... Over 200 km by latitude along the Altai and Turkestan Ridges, there is a remarkable zone of siliceous and carbon-rich schists, which contains, among the products of intense thermal alteration, special formations rich in V_2O_5 , NiO, CuO and some other elements" – this brief description was given by A.E. Fersman to this region, which has quite a complicated geological and tectonic structure (Fersman, 1928). The carbonaceous-siliceous schists form olistoliths in the Lower and Middle Carboniferous Malyaran mǎlange complex. The size of the blocks ranges from several meters to tens and even hundreds of meters.

Slickenside surfaces are common in these strata. The stratigraphic affiliation of the olistolith blocks is not always clear; most likely, they are residual blocks of Cambrian-Silurian formations (Belov *et al.*, 1989). These schists are characterized by elevated contents of V, Ni, Zn, Cu, Mo and U. The carbonaceous-siliceous schists of the Kara-Chagyr and Kara-Tangi are most notable in this respect. Their outcrops show fairly confined but rich vanadium mineralization, represented by the nickelalumite-group minerals (ankinovichite, alvanite, nickelalumite, kyrgyzstanite), kurumsakite and related minerals, Zn-bearing folborite, vanadium-bearing minerals of the alunite group, carnotite, tuyamunite, a variety of Zn-Ni-V phases (united under the common name "kolovratites") (Karpenko, 2010).

Micas are less widespread in Southern Kirgystan than at Karatau. Our studies showed that mannardite is another efficient concentrator of vanadium in the carbonaceous-siliceous schists of the Karatau Ridge.

Mineral assemblages

At Kara-Tangi, mannardite was found in carbonaceous-siliceous schists from the dumps of the uranium mine, which was developed in the early 1970s (personal communication, V.M. Rogovoi). The "black" schists are composed of quartz and argillaceous-carbonaceous matter which forms lenticular nodules up to 1 mm. Quartz is present as micro-granular aggregates (grain size 0.05–0.50 mm, mean size 0.08–0.10 mm). The rock is penetrated by numerous quartz veinlets which can contain cavities encrusted with quartz crystals and lamellar crystals of later minerals – nickelalumite $(Ni,Zn)Al_4(SO_4)(OH)_{12} \cdot 3H_2O$, kyrgyzs-

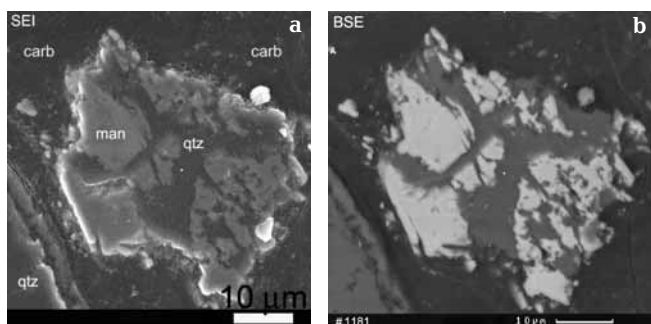


Fig. 1. Micrograins of mannardite (*man*) in quartz (*qtz*) among the carbonaceous matter (*carb*), Kara-Tangi. Scale marker 10 micron; secondary electron (SEI), back-scattered electrons (BSE) images; characteristic X-ray maps of the specified elements.

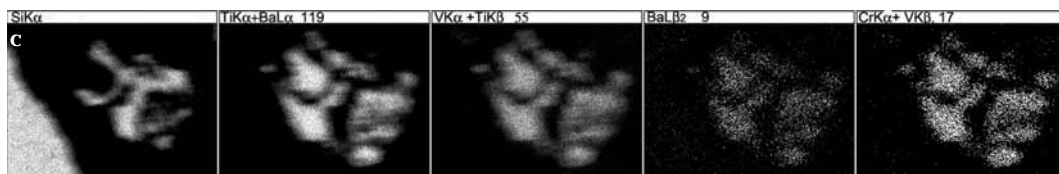


Fig. 2. A typical "quartz net" specimen with mannardite; Karatau Ridge, Kazakhstan.

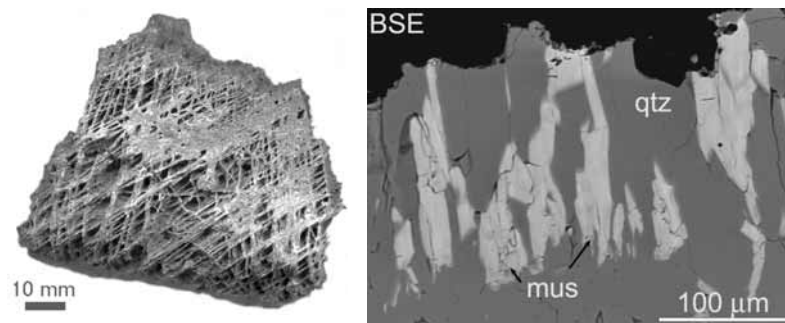


Fig. 3. A fragment of a selvad veinlet (*qtz*) with in-growing (or possibly co-growing) lamellar grains of Ba-V-bearing muscovite (*mus*), Balasauskandyk, Karatau. BSE image.

tanite $(\text{Zn,Ni})\text{Al}_4(\text{SO}_4)(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$ and Al-hydroxide forming after the former two minerals. Rare grains (10–20 micron in size) of pyrite, chalcopyrite, cadmium-bearing sphaerite (1.44 wt.% Cd), fluorapatite and mannardite are occasionally present. Mannardite occurs as rare and quite uniformly distributed spots 10 micron and less in size (Fig. 1). The mannardite from Kara-Tangi contains up to 2.4 wt.% Cr_2O_3 (Table 1).

At Kara-Chagyr, mannardite was found in quartz veinlets in a carbonaceous-siliceous matrix, where it is associated with pyrite, a non-identified cerium phosphate, and rare grains of barium-vanadium-bearing muscovite (8.6 wt.% V_2O_5). Aggregates of lamellar crystals of ankinovchite, $(\text{Ni,Zn})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ and silicon-bearing nickelalumite (up to 6.8% SiO_2) are often present in cavities in the largest veinlets. The size of the mannardite grains here is no more than 10 microns. The composition of Kara-Chagyr mannardite is given in Table 1; it is almost completely free of chromium, unlike Kara-Tangi mannardite.

At Balasauskandyk, mannardite was found during analysis of a specimen of so-called "quartz-roscoelite net" (Fig. 2), which appears as a net aggregate formed by intersecting veinlets. These veinlets are composed of parallel rods of quartz and barium-vanadium-bearing muscovite (7.9–8.2 wt.% V_2O_5 , 6.9–8.3 wt.% BaO) (Fig. 3). Unlike localities of S. Fergana, mannardite is more abundant here, with its grain size ranging from 15 to 50 micron, while aggregates can reach more than 100 micron in size.

In polished section it can be often seen as square cross sections of single crystals. In some cases, chains of mannardite grains are observed, which trace along the axial lines or casing of veinlets of rod-shaped quartz. In some cases mannardite grains are visible to the naked eye, as they give a grayish tint to quartz. In addition to vanadium-bearing muscovite, which is closely intergrown with quartz, mannardite is associated with a number of phosphates of Ce, La, Nd, and Y* (Fig. 4), vanadium-bearing rutile (1.25 wt.% V)

* – in phosphates the ratio $(\text{REE}+\text{Y})/\text{P}$ (*apfu*) = 1; X-ray pattern obtained for the Nd-dominant phosphate is quite close to churche-Nd (Podporina *et al.*, 1983).

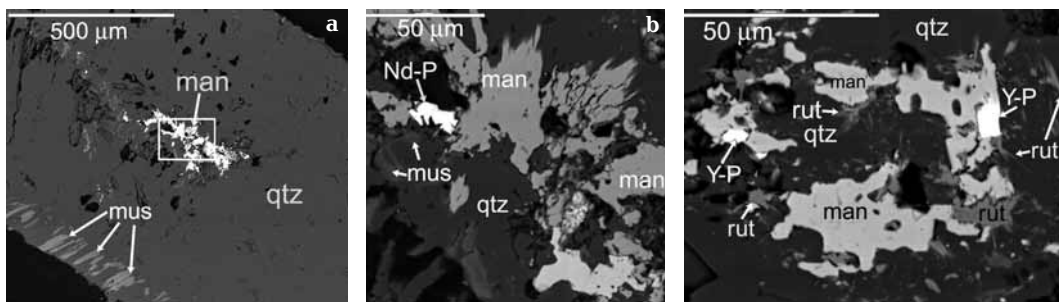


Fig. 4. Mannardite in a veinlet of parallel-rod quartz: (a) mannardite (man) with Nd-phosphates (Nd-P) in quartz (qtz) with V-bearing muscovite (mus); (b) fragments marked on Fig. 4a; rut – V-bearing rutile; Balasauskandyk, Kazakhstan. BSE image.

Fig. 5. Mannardite grain (man) in aggregate with V-bearing rutile (rut), Y-phosphate (Y-P) in a quartz (qtz) veinlet. Balasauskandyk. BSE image.

(Fig. 4 and 5), strontium-bearing barite (1.17–1.30 wt.% SrO), and hematite. Only traces of chromium were found in the mannardite from Balasauskandyk (Table 1).

We also found mannardite in the specimens of netted quartz aggregates from a mine dumps at Kurumsak, together with chernykhite, barium-vanadium-bearing muscovite and barite. In general, mannardite was observed in almost all specimens of quartz net, collected from various area of Kurumsak and Balasauskandyk.

Physical properties

A fraction (-250 micron) significantly enriched in mannardite was extracted by bromoform treatment from a grounded specimen of a quartz net aggregate from Balasauskandyk. Several tens of mannardite grains (30–100 microns in size) from this fraction were placed on electrically conductive carbon tape, and their composition was measured under the scanning electron microscope equipped with an energy-dispersion spectrometer (SEM-EDS). Several grains, free of inclusions of other minerals were removed from the tape and used for studying the physical, optical, and X-ray properties of this mineral.

Mannardite is black with metallic luster; it is opaque, brittle, and its micro-hardness, measured by PMT-3 (calibrated by NaCl) under 100 g load, is $VHN = 628 \text{ kg/mm}^2$ (mean value of 5 measurements ranging from 463 to 732 kg/mm^2). The density of mannardite was determined by suspending three grains in Clerichi liquid solution; the value obtained was $4.34(3) \text{ g/cm}^3$, and the calculated density is 4.40 g/cm^3 (using the average composition, Table 1, an. 4). In transmitted light, only the thinnest edges of the mineral

are translucent, exhibiting deep brown color. In reflected light, mannardite is anisotropic, dark gray, with reflectivity lower than that of redledgeite, which is similar to mannardite in properties and structure (some grains of redledgeite were included in the thin section for comparison). This observation is consistent with the measurements of other authors (Ivanov *et al.*, 1996; Scott and Peatfield, 1986).

Chemical composition

Mannardite was analyzed using a Cam-Scan-4D scanning electron microscope with a Link ISIS energy-dispersion spectrometer (20 kV, specimen current 4 nA on metallic cobalt). Standards used are as follows: barite (Ba), ilmenite USNM 96189 (Ti, Fe), V_2O_5 (V), Cr_2O_3 (Cr), and benitoite (USNM 86539) as control sample. The composition of mannardite is given in Table 1 (an. 1–4), together with analyses of redledgeite from Saranovskoe deposit (Urals) for comparison. A characteristic feature of Kara-Tangi mannardite is the presence of chromium (up to 2.4 wt.%). Fig. 6 shows the correlation between V and sum of trivalent cations (Cr+Fe) for vanadium and vanadium-bearing titanates with the hollandite structure (mannardite, redledgeite, ankanite, and several non-identified phases). In general, the data corresponding to mannardite are confined to the line connecting the idealized compositions $Ba(Ti_6(Cr^{+3}, Fe^{+3})_2)O_{16}$ and $Ba(Ti_6V_2^{+3})O_{16}$, but do not always coincide with it, as neither do the data points of other phases. The reason for this deviation is that the mineral compositions correspond to the formula $Ba_x(Ti_{8-2x}Me_{2x}^{+3})O_{16}$ ($x \sim 1.0-1.3$), as a consequence of the structural vacancies in hollandite type phases (Gatthouse *et al.*, 1986; Xiong *et al.*, 1989, Dmitrieva *et al.*, 1992; Foley *et al.*, 1997). In this

Table 1. Chemical compositions of mannardite (1–9) and redledgeite (10) (wt.%)

Components	1	2	3	4	5	6	7	8	9	10
BaO	18.32	18.37	16.84	20.58 (19.12-21.58)	18.96 (17.72-19.49)	18.22	19.27	19.4	19.8	20.29
TiO ₂	58.54	58.95	59.18	58.10 (56.46-59.00)	57.49 (56.35-58.60)	59.37	58.69	60.1	60.2	60.00
V ₂ O ₃	16.25	16.27	19.53	18.07 (17.51-18.39)	18.59 (17.98-19.11)	18.98	18.43	16.3	12.2	1.12
Cr ₂ O ₃	2.29	2.46	–	0.40 (0.00-1.03)	–	0.83	1.78	1.9	1.9	12.45
Fe ₂ O ₃	0.20	–	–	–	–	0.00	0.00	–	3.7	2.80
H ₂ O (calc.)	2.20	2.24	2.42	1.99	2.10	2.31	2.18	2.15	2.10	2.03
Total	97.80	98.28	97.97	99.14	97.52*	99.73**	100.35	99.85	99.90	99.33***
Amounts in unit formula (per O = 16 atoms)										
Ba ⁺²	0.98	0.97	0.89	1.10	1.02	0.95	1.01	1.02	1.04	1.07
Ti ⁺⁴	5.98	5.99	5.98	5.94	5.95	5.94	5.88	6.03	6.07	6.09
V ⁺³	1.77	1.76	2.10	1.97	2.05	2.02	1.97	1.75	1.32	0.12
Cr ⁺³	0.25	0.26	0.00	0.04	0.00	0.09	0.19	0.20	0.20	1.33
Fe ⁺³	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.28
Al ⁺³	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
H ₂ O	1.02	1.03	1.11	0.90	0.98	1.05	0.99	0.98	0.96	0.93

Note: calculation for H₂O was done taking into account the theoretical concentration of the water molecules in channels H₂O = (2-Ba, apfu). The analysis sums include: * – 0.38 wt. % SiO₂; ** – 0.02 wt. % K₂O; *** – 0.65 wt. % Al₂O₃. An. 1–9 – mannardite: 1, 2 – carbonaceous-siliceous quartz from mine dumps, Kara-Tangi, Kyrgyzstan; 3 – carbonaceous-siliceous schist from the cleaning tails, Kara-Chagyr, Kyrgyzstan; 4, 5 – quartz-roscoelite “net”, Balasauskandyk, Kazakhstan (4 – average of 19 analyses, scatter of values is shown in parenthesis; 5 – specimen of G.K. Bekenova, average of 7 analyses, scatter of values is shown in parenthesis); 6, 7 – South Kyrgyzstan (materials of the Daudinskaya crew, South Kyrgyz Geological Survey Expedition, Osh, Kyrgyzstan; analyst I.M. Kulikova (Pautov, 1994)); 8 – Rough Claims, British Columbia, Canada; grain used for decoding the mineral structure (Scott, Peatfield, 1986); 9 – Brunswick No.12 (ore body), Bathurst, New Brunswick, Canada (Scott, Peatfield, 1986); 10 – redledgeite, Saranovskoe Deposit, Central Urals (M.M. Moiseev sample).

Analytical parameters: 1–4, 9, 10 – CamScan-4D, EDS Link ISIS, 20 kV, 4 nA. Analyst V.Yu. Karpenko; 5 – Jeol Superprobe 733, EDS Inca. Analysts P.E. Kotelnikov and V.L. Levin. Dash denotes values under the detection limit.

graph, there are strong deviations of the compositions of niobium-bearing K-Ba titanates from the Star Mine kimberlites (South Africa) from the correlation line. This is probably due to the presence of Nb⁵⁺ at an octahedral site and the presence of K⁺ as a channel cation (Mitchell and Meyer, 1989). The presence of H₂O in Balasauskandyk mannardite was confirmed by infrared spectroscopy: absorption bands at 1597, 3460 and 3518 cm⁻¹ (the spectra were obtained using a Hyperion 2000 FT-IR microscope with ATR-objective of Bruker; analyst A. Cherevan, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences). An indirect indicator of the presence of H₂O in mannardite is the low totals in the microprobe analyses.

X-ray Data

The X-ray powder-diffraction pattern was obtained for Balasauskandyk mannardite by photographic techniques (URS-50, FeK α -radiation, Mn-filter, camera RKD-57.3, cylinder dia. 0.15 mm, internal standard: quartz, Table 2). The pattern is similar to those of other titanates of the hollandite structure

type (for example, redledgeite). The main difference between these X-ray data and that of other mannardites known to date (Scott and Peatfield, 1986; Pautov, 1994) is the presence of a weak peak at $d = 5.04\text{\AA}$ (220) and indexed in the $I4_1/a$, space group of mannardite (Szymanski, 1986). The units cell parameter of Balasauskandyk mannardite are: $a = 14.37(1)$, $c = 5.922(6)\text{\AA}$, $V = 1223(2)\text{\AA}^3$.

Many researchers (Mitchell and Meyer, 1989; Biagioni *et al.*, 2009) have noted the need for a better nomenclature for this group. We also encountered difficulties in the nomenclature of the hollandite group, which is not in accord with IMA nomenclature criteria.

The hollandite structure type is based on a rutile-like framework, with tunnels occupied by large atoms (Ba, K, Pb, Sr) and H₂O groups. This framework is formed by M -octahedra, which are occupied in titanates by Ti⁺⁴, V⁺³, Cr⁺³, Fe⁺³, Fe⁺², Al⁺³, Nb⁺⁵. The dominating constituent is Ti, its content ranging from 5.8 to 7.0 apfu, while the sum of cations in this site is 8.0. Hence, formally following the conventional nomenclature rules, redledgeite Ba(Ti₆Cr₂)O₁₆, henrymeyerite Ba(Ti₇Fe⁺²)O₁₆ and ankangite Ba(Ti₆V₂)O₁₆

Table 2. X-Ray powder diffraction data for mannardite and redledgeite

1		2		3		
I	d/n, Å	I	d/n, Å	I	d/n, Å	hkl
		—	—	20	7.10	200
2	5.04	—	—	5	5.05	220
4	3.590	20	3.587	50	3.570	400
10	3.211	100	3.201	100	3.195	420
3	2.844	10	2.836	30	2.831	112
		—	—	10	2.536	440
7	2.476	70	2.473	60	2.470	312
4	2.276	30	2.264	30	2.257	620
5	2.227	50	2.224	40	2.217	332
		10	2.031	30	2.033	152
2	1.992	20	1.985	30	1.985	460
5	1.892	70	1.887	50	1.885	352
2	1.800	5	1.792	20	1.788	800
1	1.745	5	1.737	20	1.735	820
4	1.690	50	1.690	40	1.685	660
5	1.592	80	1.586	60	1.583	732
3	1.480	20	1.475	30	1.474	004
2	1.456	5	1.452	20	1.448	572
5	1.400	40	1.394	50	1.393	192
3	1.348	20br	1.341	20	1.339	424,392
1	1.337	20br	1.332	20	1.325	10.4.0, 772
1	1.240	—	—	10	1.234	624
<1	1.202	10	1.192	10	1.193	12.0.0
1	1.162	10	1.156	10	1.154	11.3.2, 972
		10	1.139	—	—	804
2	1.117	10	1.119	20	1.117	10.8.0
		20	1.111	20	1.109	664
		10br	1.070	—	—	12.6.0
2br	1.0332	10	1.030	20	1.027	13.1.2, 7.11.2
2br	1.0129	10	1.010	10	1.007	3.13.2
2br	0.9917	—	—	—	—	10. 4 4

Note: reflections used for calculation of the cell parameters are shown in bold.

1 — mannardite, Balasaukandyk, FeK α -radiation, Mn-filter. URS-50; analyst V.Yu. Karpenko; 2 — mannardite (holotype), Rough Claims, British Columbia, Canada, (Scott and Peatfield, 1986); 3 — redledgeite (holotype), Red Ledge, California, USA (USNM 95846) (Scott, Peatfield, 1986).

from Monte Arsiccio (Italy) (Biagioni *et al.*, 2009), which belong to the $I4/m$, space group, should have been considered as one mineral species, as neither Cr, nor Fe nor V in these minerals are dominant. However, dominance of one or another cation at the (2+) or (3+) valent octahedral position (which compensates the excess charge of the tunnel cations) in the minerals of the hollandite structure type was taken as sufficient reason to recognize it as a distinct species.

Another typical feature of this group is the variation in symmetry, even in specimens from the same locality. For example, redledgeite from its original locality Red Ledge (California, USA) proposed, has been assigned the following space groups: $I4_1/a$ (Szymanski, 1986); $I2/m$ (Gatehouse *et al.*, 1986); $I4/m$ (Foley *et al.*, 1997).

Genesis and discussion of results

As mentioned above, mannardite is associated with the quartz-roscoelite netted formations (Fig. 2), which were described in detail by Ankinovich and Ankinovich (1954). These rocks are typical of the Karatau schists and South Fergana occurrences. The "delicate quartz web" in carbonaceous-siliceous schists of Kara-Chagyr drew the attention of Fersman (1928). Such netted aggregates appear as framework of cells, formed by a system of quartz veinlets (fractions of millimeter to 20 mm in thickness) oriented in three intersecting directions: fractures of tear, fractures of shear, and break fractures. The quartz veinlets are composed of parallel-rod aggregates (Fig. 3). In the weathered zones, frameworks with almost hollow cells are found. These structures are so typical of the carbonaceous-siliceous schists that the geologists working at the Karatau Ridge deposits came up with the terms "quartz-roscoelite net" and "netted ores", because these formations contain the majority of vanadium-concentrating minerals — micas, sulvanite and now mannardite. The quartz netted structures occur uniformly over a "vast territory of the bituminous schists, from Talassky Ridge to Ulutau" (Ankinovich and Ankinovich, 1954), without any signs of strengthening or weakening of quartz formation, and localized strictly within the ore horizon. This fact suggests that such quartz net are not formed by action of hydrothermal solutions associated with some deep intrusion. Ankinovich and Ankinovich (1954) explain the origin of these frameworks by "pseudohydrothermal effects" as a result of

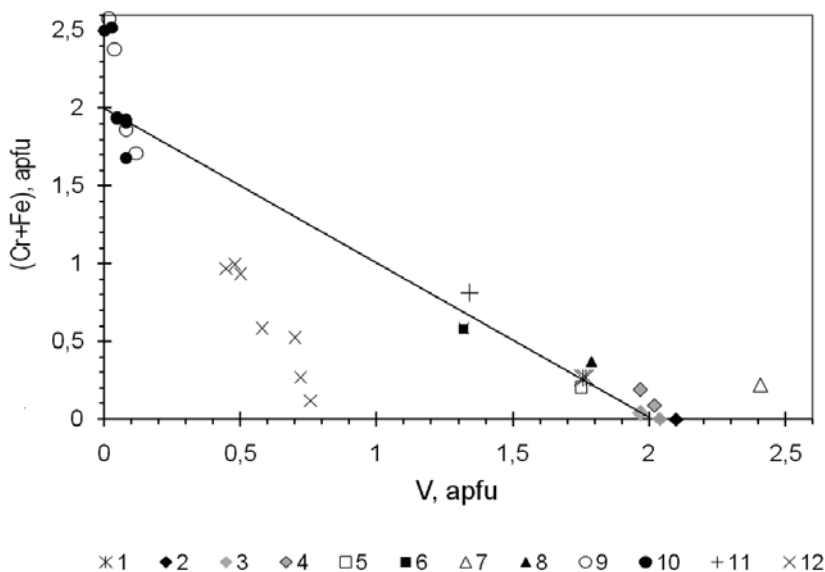


Fig. 6. Variation in V versus (Cr+Fe) for vanadium and vanadium-bearing natural phases of the hollandite structure type.

1–6 – mannardite (1 – Kara-Tangi, Kyrgyzstan; 2 – Kara-Chagyr, Kyrgyzstan; 3 – Balasauskandyk, Kazakhstan; 4 – northern slope of the Turkestan Ridge, Kyrgyzstan; 5 – Rough Claim, Canada; 6 – Brunswick, Canada); 7, 8 – ankangite (7 – Shiti, China; 8 – Monte Arsiccio, Italy); 9, 10 – redlegite (9 – Saranovskoye Deposit, Central Urals, Russia; 10 – Red Ledge, California, USA); 11 – “Ba-Ti-V-hollandite”, Tuvish pipe, Southern Tien-Shan; 12 – niobium-bearing K-Ba-V-titanates, Star Mine, South Africa. 1–3 – this study; 4 – Pautov, 1994; 5, 6 – Scott and Peatfield, 1986; 7 – Xiong *et al.*, 1989; 8 – Biagioni *et al.*, 2009; 9 – Ivanov *et al.*, 1996; 10 – Scott, Peatfield, 1986; Gatehouse *et al.*, 1986; Foley *et al.*, 1997; 11 – Dmitrieva *et al.*, 1992; 12 – Mitchell and Meyer, 1989.

regional metamorphic alteration of the sediment discharged along one or several impermeable barriers. The mechanism of the formation of these nets, according to later studies (Fyfe *et al.*, 1981; Spiridonov *et al.*, 2000), involve in filling of the hydraulic-fracture systems with silica from sediment and release of pore solutions with low-grade metamorphism. The vertical distribution of the netted structures within the ore horizon is related to the various degree of plasticity of the parent rocks (Ankinovich and Ankinovich, 1954). The vanadium-bearing horizon at Karatau consists of alternating layers of bituminous and siliceous schists. Of these two types of rocks, bituminous schists are more brittle and become more susceptible to disintegration and fracture. Some quartz nets strongly resemble the theoretically simulated fracture systems developing in a block of rock under a constant static stress (Fyfe *et al.*, 1981).

Metamorphic pore solutions caused leaching of many elements from the schists and their re-deposition in the quartz-net zones. These quartz veins and veinlets are similar to Alpine-type veins. In the Karatau veins of that type Ankinovich and Ankinovich (1954) found calcite, fluorapatite, rutile, pyrite,

sphalerite, roscoelite, dolomite, orthite, clinzoisite, epidote, tremolite, sericite (barium-vanadium-bearing muscovite), barite, tetrahedrite, chalcopyrite, clinocllore, zircon, albite, titanite, sulvanite, galenite, molybdenite, patronite, breithauptite and native gold. Later, Ankinovich and co-authors (1972; 1997) found chernykhite, and we have discovered mannardite and rare-earth phosphates.

The presence of mannardite in the schists of the South Fergana and in similar rocks of Karatau suggests that common processes occurred during the formation of the vanadium-bearing strata in those regions.

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THE VARIETY OF FAHLORES AND THE EPIGENETIC MINERALS FROM THE LEBEDINOE DEPOSIT

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The new results of the mineralogical study of the Lebedinoe deposit are discussed. In addition to Zn-bearing tetrahedrite (sandbergerite), tetrahedrite-tennantite, and tennantite (Nenasheva *et al.*, 2010), Te-bearing fahlores (goldfieldite-tennantite-tetrahedrite, goldfieldite-tennantite, and Te-bearing tennantite-tetrahedrite), tetrahedrite with significant Ag, and anisotropic tetrahedrite-tennantite were identified. These minerals were found in varied assemblages, whose mineral composition indicate the conditions of ore formation: the composition of mineral-forming fluid, temperature, and pH value. The chalcocite polysomatic series minerals, digenite, anilite, spionkopite, and yarrowite, used as geothermometer were discovered in the ores.

7 figures, 9 tables, 17 references.

Keywords: fahlores, bournonite, hessite, petzite, anilite, spionkopite, yarrowite, bayldonite, clinotyrolite, strashimirite, leogangite, Lebedinoe deposit.

Introduction

Nenasheva *et al.* (2010) characterized in detail the Lebedinoe deposit. The deposit is reported according to Fastalovich and Petrovskaya (1940) and Petrovskaya (1973). Below is very brief description of the deposit. Weakly metamorphosed Cambrian dolomite overlapping eroded granite is intruded by Upper Jurassic to Lower Cretaceous numerous small intrusions. These are predominantly intermediate stocks, laccoliths, and dikes with elevated alkalinity. The metasomatic sulfide-carbonate bodies, occasionally as vein apophyses are hosted in dolomite along horizontal faults (Petrovskaya, 1973). Pyrite is dominant ore mineral; chalcopyrite is also occurs; in some veins, there is hematite. Galena, sphalerite, pyrrhotite, galenobismutite, tetrahedrite, native gold, bornite, cobaltite, and sylvanite are less frequent. Supergene minerals are iron hydroxides, jarosite, cuprite, chalcocite, covellite, malachite, azurite, cerussite, gypsum, and melanterite (Fastalovich, Petrovskaya, 1940; Nenasheva *et al.*, 2010).

Experimental and results

The thin polished sections were examined with an OPTON optical microscope. The chemical composition was determined with a

CamScan-4D scanning electron microscope equipped with a Link ISIS energy dispersion system (EDS) operating at 20 kV and current absorbed at metallic cobalt of 4 nA. The X-ray powder diffraction patterns were recorded at an URS-50 diffractometer with an RKD 57.3 mm camera, FeK α -radiation, Mn filter. The sample was selected from thin polished section and mount in resin ball.

The optically heterogeneous objects studied are composed of ore minerals (pyrite, galena, and bornite are the major) submerged into quartz-carbonate-arsenate matrix. In addition, pyrrhotite, covellite, digenite, anilite, spionkopite, and yarrowite were identified with electron microprobe.

The names of fahlores are given according to Mozgova and Tsepina (1983). Sb-bearing fahlores are predominant. Tetrahedrite with significant Zn (sandbergerite) is associated with galena, famatinite, arsenosylvanite, anglesite, and copper arsenates: bayldonite, leogangite, and euchroite (Nenasheva *et al.*, 2010). Content of Zn ranges from 5.14 to 8.07 wt.% corresponding to 1.32–2.04 *apfu*. Ag is present in all compositions varying from 0.65 to 4.37 wt.% that corresponds to 0.10–0.68 *apfu*. Concentration of Sb ranges from 23.53 to 28.16 wt.% exceeding 3 *apfu* and corresponding to 3.25–3.85 *apfu* (Nenasheva *et al.*, 2010). There is no clear correlation between Zn and As. However, there is positive

Table 1. Electron microprobe data (wt.%) of fahlores

№ an.	Sample	Cu	Ag	Fe	Zn	Pb	Sb	As	Te	S	Se	Total
1	53/278(area 7)	41.58		0.01	6.68	0.56	14.68	7.40	2.59	25.44		98.94
2		46.27			2.69		5.75	8.73	10.77	25.98		100.19
3		45.37			1.61		7.16	5.89	12.83	25.44		98.30
4		47.27			1.62		5.18	6.90	11.83	25.68		98.48
5		47.21			3.36		4.78	9.23	9.48	26.03	0.36	100.45
6	53/278(area 6)	41.99			7.56		14.86	8.34	1.70	25.95		100.40
7*		44.73		0.14	3.36		7.66	7.23	9.25	26.00		98.37
8*		44.87			3.66		10.92	5.28	9.71	25.57		100.01
9*	53/278(area 4)	46.05			2.13		9.56	4.49	11.11	25.68		99.02
10*		47.26			2.29		8.96	5.91	10.34	26.60		101.36
11*		46.99			0.79		10.99	3.24	13.52	25.81		101.34
12*		46.13			3.12		9.58	4.72	10.26	25.04	0.69	99.54
13*		45.30			3.13		11.32	5.54	9.55	25.97		100.81
14*		45.49			2.86		8.25	7.62	10.26	27.15		101.63
15*		46.04			2.10		6.79	7.63	11.56	26.47		100.59
16*		46.33			2.38		7.99	6.75	11.04	25.30	0.36	100.15
17*		43.96			4.63		9.48	8.06	6.63	25.23	0.46	98.45
18**		42.62			8.74		9.21	12.88	0.77	26.43		100.65
19**		42.35			8.25		10.34	12.71	0.52	27.89		102.06
20**		42.10			7.58		8.61	13.75	0.75	27.44		100.23
21**		43.18			7.74		9.78	13.59	0.17	26.88		101.34
22**		43.46			7.16		8.67	12.18	2.28	26.43		100.18
23**		44.25			5.35		5.98	11.05	5.80	26.58		99.01
24**		44.32			4.67		5.78	11.93	5.52	26.33	0.64	99.19
25**		41.69			9.12		6.84	15.46	0.59	26.59		100.29
26**	53/278(area 6)	43.56			5.55		7.52	10.66	5.35	26.66		99.30
27**		44.04			5.45		10.80	7.84	5.30	26.47		99.90
28	2 (area 2)	34.89	4.93	4.52	2.92	0.87	27.31			24.33		99.77
29		35.63	4.26	4.02	3.37		27.47			24.62		99.37
30		35.45	4.79	4.84	2.61		27.60			24.49		99.78
31		36.66	3.44	4.58	3.18		23.67	2.31		24.91		98.75
32		35.83	4.87	4.90	2.64		24.94	1.28		24.89		99.35
33		36.15	3.62	4.52	3.50		23.84	2.50		24.87		99.00
34		35.62	3.69	4.72	3.06		24.28	2.07		24.37		97.81
35	2 (area 3)	35.46	2.88	4.12	2.99	2.14	25.10	1.30		23.50		97.49
36	242/1-2	41.13		0.62	7.79		18.01	7.20		25.88		100.63
37		41.68		0.43	8.31		18.50	7.07		26.59		102.58
38		41.05		0.38	8.22		18.84	7.26		25.88		101.63
39		41.65		0.32	8.63		18.81	6.87		25.93		102.21
40		41.79		0.47	8.56		13.17	10.37		26.74		101.10
41		41.68		0.40	7.83		15.03	9.44		26.81		101.19
42		41.54		0.33	8.09		16.36	8.59		26.22		101.13
43		39.49		1.42	7.11		18.73	6.00		25.26		98.01

Notes: * – light zone, ** – dark zone. Analyses 1–35 were performed by V.Yu. Karpenko, anal. 36–43, by L.A. Pautov.

correlation between Sb and Zn + Ag. Previously, Mozgova and Tsepina (1983) reported such correlation.

Tennantite-tetrahedrite and tennantite associated with sylvanite, arsenosylvanite, and Ca and Cu arsenate (tyrolite $\text{Ca}_2\text{Cu}^{2+}_5(\text{OH},\text{O})_4(\text{AsO}_4)_2(\text{CO}_3)\cdot 6\text{H}_2\text{O}$ or clinotyrolite $\text{Ca}_2\text{Cu}^{2+}_5(\text{OH},\text{O})_{10}[(\text{AsO}_4)_2(\text{SO}_4)]_4\cdot 10\text{H}_2\text{O}$) are characterized by negative correlation between As and Sb (Nenasheva *et al.*, 2010).

Te-bearing fahlores, goldfieldite-tennantite-tetrahedrite (Tables 1, 2; anal. 8, 9, 11–13), goldfieldite-tennantite-tetrahedrite (Tables 1, 2;

anal. 2, 5, 7, 10, 14–17, 23, 24, 26, 27), and Te-bearing tennantite-tetrahedrite (Tables 1, 2; anal. 1, 6), and Te-bearing tetrahedrite-tennantite (Tables 1, 2; anal. 18–22) are associated with galena, quartz, native gold, secondary copper sulfides of the chalcocite, $m\text{Cu}_2\text{S}\cdot n\text{CuS}$, polysomatic series, and copper arsenates. Fahlores occur as anhedral grains filling occasionally interstices between grains of quartz, galena, and pyrite and sometimes overgrowing quartz crystals (Fig. 1). Content of Te ranges from 0.17 to 13.52 wt.% corresponding to 0.02–1.71 *apfu*. Te-bearing

Table 2. Formulae of fahlores calculated on the basis of 29 atoms in the unit cell

Nº an.	Sample	Formula	Δ , % – valence balance
1	53/278 (area 7)	$\text{Cu}_{10.00}(\text{Cu}_{0.58}\text{Zn}_{1.65}\text{Pb}_{0.04})_{2.27}(\text{Sb}_{1.95}\text{As}_{1.60}\text{Te}_{0.17})_{3.72}(\text{S}_{12.84}\text{Te}_{0.16})_{13.00}$	3.0
2		$\text{Cu}_{10.21}(\text{Cu}_{1.34}\text{Zn}_{0.66})_{2.00}(\text{Sb}_{0.75}\text{As}_{1.85}\text{Te}_{1.20})_{3.80}(\text{S}_{12.86}\text{Te}_{0.14})_{13.00}$	3.0
3		$\text{Cu}_{11.10}(\text{Cu}_{0.60}\text{Zn}_{0.40})_{1.00}(\text{Sb}_{0.96}\text{As}_{1.29}\text{Te}_{1.65})_{3.90}\text{S}_{13.00}$	1.7
4		$\text{Cu}_{10.41}(\text{Cu}_{1.60}\text{Zn}_{0.40})_{2.00}(\text{Sb}_{0.69}\text{As}_{1.46}\text{Te}_{1.42})_{3.60}(\text{S}_{12.92}\text{Te}_{0.08})_{13.00}$	2.4
5		$\text{Cu}_{10.47}(\text{Cu}_{1.19}\text{Zn}_{0.81})_{2.00}(\text{Sb}_{0.62}\text{As}_{1.93}\text{Te}_{0.98})_{3.53}(\text{S}_{12.74}\text{Se}_{0.07}\text{Te}_{0.19})_{13.00}$	0.2
6	53/278 (area 6)	$\text{Cu}_{10.29}(\text{Cu}_{0.17}\text{Zn}_{1.83})_{2.00}(\text{Sb}_{1.93}\text{As}_{1.76}\text{Te}_{0.21})_{3.90}\text{S}_{12.81}$	2.2
7*		$\text{Cu}_{10.21}(\text{Cu}_{1.13}\text{Zn}_{0.83}\text{Fe}_{0.04})_{2.00}(\text{Sb}_{1.01}\text{As}_{1.55}\text{Te}_{1.17})_{3.73}\text{S}_{13.06}$	1.7
8*		$\text{Cu}_{10.30}(\text{Cu}_{1.10}\text{Zn}_{0.90})_{2.00}(\text{Sb}_{1.45}\text{As}_{1.14}\text{Te}_{1.11})_{3.82}(\text{S}_{12.88}\text{Te}_{0.12})_{13.00}$	1.9
9*	53/278 (area 4)	$\text{Cu}_{10.31}(\text{Cu}_{1.47}\text{Zn}_{0.53})_{2.00}(\text{Sb}_{1.26}\text{As}_{0.97}\text{Te}_{1.42})_{3.67}\text{S}_{13.02}$	2.6
		$\text{Cu}_{11.31}(\text{Cu}_{0.47}\text{Zn}_{0.53})_{1.00}(\text{Sb}_{1.26}\text{As}_{0.97}\text{Te}_{1.42})_{3.67}\text{S}_{13.02}$	1.2
10*		$\text{Cu}_{10.26}(\text{Cu}_{1.45}\text{Zn}_{0.55})_{2.00}(\text{Sb}_{1.16}\text{As}_{1.24}\text{Te}_{1.28})_{3.68}\text{S}_{13.06}$	1.7
		$\text{Cu}_{11.26}(\text{Cu}_{0.45}\text{Zn}_{0.55})_{1.00}(\text{Sb}_{1.16}\text{As}_{1.24}\text{Te}_{1.28})_{3.68}\text{S}_{13.06}$	2.0
11*		$\text{Cu}_{10.13}(\text{Cu}_{1.81}\text{Zn}_{0.19})_{2.00}(\text{Sb}_{1.46}\text{As}_{0.70}\text{Te}_{1.71})_{3.87}\text{S}_{13.00}$	5.3
		$\text{Cu}_{11.13}(\text{Cu}_{0.81}\text{Zn}_{0.19})_{1.00}(\text{Sb}_{1.46}\text{As}_{0.70}\text{Te}_{1.71})_{3.87}\text{S}_{13.00}$	1.7
12*		$\text{Cu}_{10.57}(\text{Cu}_{1.22}\text{Zn}_{0.78})_{2.00}(\text{Sb}_{1.26}\text{As}_{1.02}\text{Te}_{1.30})_{3.60}(\text{S}_{12.68}\text{Se}_{0.14})_{12.82}$	3.9
		$\text{Cu}_{11.57}(\text{Cu}_{0.22}\text{Zn}_{0.78})_{1.00}(\text{Sb}_{1.26}\text{As}_{1.02}\text{Te}_{1.30})_{3.60}(\text{S}_{12.68}\text{Se}_{0.14})_{12.82}$	0.1
13*		$\text{Cu}_{10.17}(\text{Cu}_{1.24}\text{Zn}_{0.76})_{2.00}(\text{Sb}_{1.49}\text{As}_{1.18}\text{Te}_{1.20})_{3.87}\text{S}_{12.96}$	3.9
		$\text{Cu}_{11.57}(\text{Cu}_{0.24}\text{Zn}_{0.76})_{1.00}(\text{Sb}_{1.49}\text{As}_{1.18}\text{Te}_{1.20})_{3.87}\text{S}_{12.96}$	0.2
14*		$\text{Cu}_{10.00}(\text{Cu}_{1.18}\text{Zn}_{0.68})_{1.86}(\text{Sb}_{1.06}\text{As}_{1.59}\text{Te}_{1.26})_{3.91}\text{S}_{13.23}$	0.9
		$\text{Cu}_{11.00}(\text{Cu}_{0.18}\text{Zn}_{0.68})_{0.86}(\text{Sb}_{1.06}\text{As}_{1.59}\text{Te}_{1.26})_{3.91}\text{S}_{13.23}$	2.8
15*		$\text{Cu}_{10.00}(\text{Cu}_{1.48}\text{Zn}_{0.51})_{1.99}(\text{Sb}_{0.88}\text{As}_{1.61}\text{Te}_{1.43})_{3.92}\text{S}_{13.08}$	3.7
		$\text{Cu}_{11.00}(\text{Cu}_{0.48}\text{Zn}_{0.51})_{0.99}(\text{Sb}_{0.88}\text{As}_{1.61}\text{Te}_{1.43})_{3.92}\text{S}_{13.08}$	0.3
16*		$\text{Cu}_{10.32}(\text{Cu}_{1.42}\text{Zn}_{0.58})_{2.00}(\text{Sb}_{1.06}\text{As}_{1.45}\text{Te}_{1.39})_{3.90}(\text{S}_{12.70}\text{Se}_{0.07})_{12.77}$	6.8
		$\text{Cu}_{11.32}(\text{Cu}_{0.42}\text{Zn}_{0.58})_{1.00}(\text{Sb}_{1.06}\text{As}_{1.45}\text{Te}_{1.39})_{3.90}(\text{S}_{12.70}\text{Se}_{0.07})_{12.77}$	3.3
17*		$\text{Cu}_{11.19}\text{Zn}_{1.14}(\text{Sb}_{1.26}\text{As}_{1.74}\text{Te}_{0.84})_{3.84}(\text{S}_{12.73}\text{Se}_{0.10})_{12.83}$	0.6
18**		$\text{Cu}_{10.34}\text{Zn}_{2.06}(\text{Sb}_{1.16}\text{As}_{2.65}\text{Te}_{0.09})_{3.90}\text{S}_{12.70}$	3.2
		$\text{Cu}_{10.34}\text{Zn}_{2.06}(\text{Sb}_{1.16}\text{As}_{2.63})_{3.81}(\text{S}_{12.70}\text{Te}_{0.09})_{12.79}$	1.2
19**		$\text{Cu}_{10.00}(\text{Cu}_{0.06}\text{Zn}_{1.90})_{1.96}(\text{Sb}_{1.26}\text{As}_{2.56}\text{Te}_{0.06})_{3.90}\text{S}_{13.13}$	2.2
20**		$\text{Cu}_{10.00}(\text{Cu}_{0.14}\text{Zn}_{1.77})_{1.91}(\text{Sb}_{1.08}\text{As}_{2.81}\text{Te}_{0.09})_{3.98}\text{S}_{13.10}$	1.3
21**		$\text{Cu}_{10.19}(\text{Cu}_{0.19}\text{Zn}_{1.81})_{2.00}(\text{Sb}_{1.23}\text{As}_{2.77})_{4.00}(\text{S}_{12.86}\text{Te}_{0.02})_{12.82}$	2.1
		$\text{Cu}_{10.19}(\text{Cu}_{0.19}\text{Zn}_{1.81})_{2.00}(\text{Sb}_{1.23}\text{As}_{2.77}\text{Te}_{0.02})_{4.02}\text{S}_{12.80}$	2.6
22**		$\text{Cu}_{10.31}(\text{Cu}_{0.30}\text{Zn}_{1.70})_{2.00}(\text{Sb}_{1.10}\text{As}_{2.52}\text{Te}_{0.28})_{3.90}\text{S}_{12.79}$	2.7
		$\text{Cu}_{10.31}(\text{Cu}_{0.30}\text{Zn}_{1.70})_{2.00}(\text{Sb}_{1.10}\text{As}_{2.57}\text{Te}_{0.07})_{3.60}(\text{S}_{12.79}\text{Te}_{0.21})_{13.00}$	2.4
23**		$\text{Cu}_{10.20}(\text{Cu}_{0.72}\text{Zn}_{1.28})_{2.00}(\text{Sb}_{0.77}\text{As}_{2.31}\text{Te}_{0.71})_{3.79}\text{S}_{13.00}$	1.1
24**		$\text{Cu}_{10.06}(\text{Cu}_{0.88}\text{Zn}_{1.12})_{2.00}(\text{Sb}_{0.74}\text{As}_{2.50}\text{Te}_{0.68})_{3.92}(\text{S}_{12.88}\text{Se}_{0.13})_{13.01}$	1.8
25**		$\text{Cu}_{10.06}\text{Zn}_{2.14}(\text{Sb}_{0.86}\text{As}_{3.16})_{4.00}(\text{S}_{12.71}\text{Te}_{0.07})_{12.78}$	2.9
26**	53/278 (area 6)	$\text{Cu}_{10.09}(\text{Cu}_{0.67}\text{Zn}_{1.33})_{2.00}(\text{Sb}_{0.97}\text{As}_{2.23}\text{Te}_{0.66})_{3.86}\text{S}_{13.05}$	1.2
27**		$\text{Cu}_{10.26}(\text{Cu}_{0.68}\text{Zn}_{1.32})_{2.00}(\text{Sb}_{1.40}\text{As}_{1.65}\text{Te}_{0.66})_{3.71}\text{S}_{13.04}$	0.1
28	2 (area 2)	$(\text{Cu}_{9.32}\text{Ag}_{0.78})_{10.10}(\text{Fe}_{1.37}\text{Zn}_{0.76}\text{Pb}_{0.07})_{2.20}\text{Sb}_{3.81}\text{S}_{12.88}$	0.6
29		$(\text{Cu}_{9.47}\text{Ag}_{0.67})_{10.14}(\text{Fe}_{1.22}\text{Zn}_{0.87})_{2.09}\text{Sb}_{3.81}\text{S}_{12.96}$	0.6
30		$(\text{Cu}_{9.41}\text{Ag}_{0.75})_{10.16}(\text{Fe}_{1.46}\text{Zn}_{0.67})_{2.13}\text{Sb}_{3.82}\text{S}_{12.88}$	0.5
31		$(\text{Cu}_{9.61}\text{Ag}_{0.53})_{10.14}(\text{Fe}_{1.36}\text{Zn}_{0.81})_{2.17}(\text{Sb}_{3.24}\text{As}_{0.51})_{3.75}\text{S}_{12.93}$	0.5
32		$(\text{Cu}_{9.42}\text{Ag}_{0.75})_{10.17}(\text{Fe}_{1.46}\text{Zn}_{0.68})_{2.14}(\text{Sb}_{3.42}\text{As}_{0.29})_{3.71}\text{S}_{12.97}$	1.4
33		$(\text{Cu}_{9.47}\text{Ag}_{0.56})_{10.03}(\text{Fe}_{1.35}\text{Zn}_{0.89})_{2.24}(\text{Sb}_{3.25}\text{As}_{0.56})_{3.81}\text{S}_{12.91}$	0.5
34		$(\text{Cu}_{9.49}\text{Ag}_{0.58})_{10.07}(\text{Fe}_{1.43}\text{Zn}_{0.79})_{2.22}(\text{Sb}_{3.38}\text{As}_{0.47})_{3.85}\text{S}_{12.86}$	1.3
35	2 (area 3)	$(\text{Cu}_{9.69}\text{Ag}_{0.46})_{10.15}(\text{Fe}_{1.28}\text{Zn}_{0.79}\text{Pb}_{0.18})_{2.25}(\text{Sb}_{3.58}\text{As}_{0.30})_{3.88}\text{S}_{12.72}$	3.0
36	242/1-2	$\text{Cu}_{10.27}(\text{Zn}_{1.89}\text{Fe}_{0.18})_{2.07}(\text{Sb}_{2.35}\text{As}_{1.52})_{3.87}\text{S}_{12.80}$	1.6
37		$\text{Cu}_{10.19}(\text{Zn}_{1.97}\text{Fe}_{0.12})_{2.09}(\text{Sb}_{2.36}\text{As}_{1.46})_{3.82}\text{S}_{12.89}$	0.2
38		$\text{Cu}_{10.20}(\text{Zn}_{1.99}\text{Fe}_{0.11})_{2.10}(\text{Sb}_{2.44}\text{As}_{1.53})_{3.97}\text{S}_{12.74}$	3.1
39		$\text{Cu}_{10.29}(\text{Zn}_{2.07}\text{Fe}_{0.09})_{2.16}(\text{Sb}_{2.42}\text{As}_{1.44})_{3.86}\text{S}_{12.69}$	3.0
40		$\text{Cu}_{10.15}(\text{Zn}_{2.02}\text{Fe}_{0.13})_{2.15}(\text{Sb}_{1.67}\text{As}_{2.14})_{3.81}\text{S}_{12.88}$	0.5
41		$\text{Cu}_{10.18}(\text{Zn}_{1.86}\text{Fe}_{0.11})_{1.97}(\text{Sb}_{1.92}\text{As}_{1.95})_{3.87}\text{S}_{12.97}$	0.8
42		$\text{Cu}_{10.24}(\text{Zn}_{1.94}\text{Fe}_{0.09})_{2.03}(\text{Sb}_{2.10}\text{As}_{1.80})_{3.90}\text{S}_{12.82}$	1.4
43		$\text{Cu}_{10.14}(\text{Zn}_{1.77}\text{Fe}_{0.41})_{2.18}(\text{Sb}_{2.51}\text{As}_{1.31})_{3.82}\text{S}_{12.85}$	1.0

Notes: * – light zone, ** – dark zone. Compositions 1 and 6 correspond to Te-bearing tennantite-tetrahedrite, 18–22, to Te-bearing tetrahedrite-tennantite, 2–5, 7, 10, 14–17, 23, 24, 26, and 27, to goldfieldite-tetrahedrite-tennantite, 8, 9, 11, 13, to goldfieldite-tennantite-tetrahedrite, 25, to tennantite, 28–35, to tetrahedrite, 36–39, 41–43, to anisotropic tennantite-tetrahedrite, and 40, to tetrahedrite-tennantite.

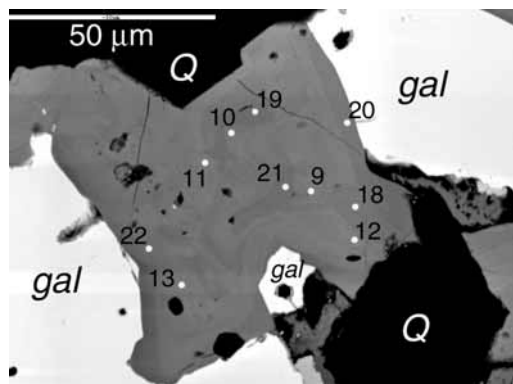
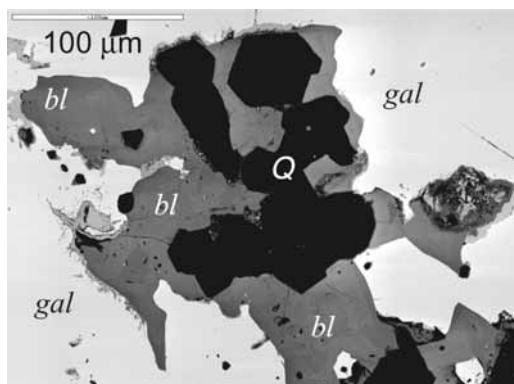


Fig. 1. Te-bearing fahlore overgrowing crystals of quartz. Quartz is black; fahlore is grey; and galena is light grey (BSE-image). Sample 53/278, area 4.

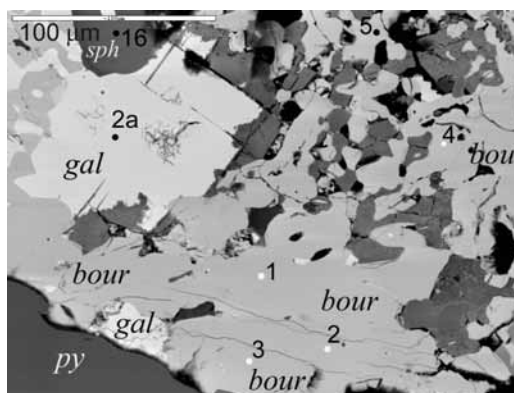


Fig. 2. Zonation of Te-bearing fahlore. Te-bearing fahlore is grey, light zones is composed of goldfieldite-tennantite-tetrahydroite (Tables 1, 2; anal. 2–17), dark zones are composed of goldfieldite-tennantite and Te-bearing tennantite-tetrahydroite (Tables 1, 2; anal. 1, 18–27). Galena (gal) is white, quartz (Q) is black (BSE-image). Sample 53/278, area 4.

Fig. 3. Grains of chalcopyrite, bournonite, and tetrahedrite filling interstices between large (up to 100 microns) segregations of galena, sphalerite, and pyrite. (gal) Galena, (py) pyrite, (sph) sphalerite, (bour) bournonite, and (bl) fahlore. Digits correspond to numbers of analyses in Tables 6 and 7 for sulfides and bournonite, respectively (BSE-image). Sample 2, area 3.

fahlores occur as zoned crystals (Fig. 2). Zones are well distinguished by reflection and Te concentration. The light zones are goldfieldite-tennantite-tetrahydroite and goldfieldite-tetrahydroite-tennantite with Te content ranging from 6.63 to 13.52 wt.%; dark zones are goldfieldite-tetrahydroite-tennantite and Te-bearing tennantite-tetrahydroite with lower Te (up to 6 wt.%). In reflected light, Te-bearing fahlores are of pink tint; they are brighter than the other fahlores, weakly birefracted and hardly noticeable anisotropic. The intensity of pink tint is caused probably by the increasing Te in the composition. Rahmdor (1962) reported birefractance and anisotropy of goldfieldite. The valence balance in fahlores containing more than 10 wt.% Te was calculated taking into account that the content of Cu^+ in such minerals is more than 11 atoms, because surplus charge originating from substitution of Te^{4+} for $(\text{As}, \text{Sb})^{3+}$ is compensated by depolarization due to reducing Cu^{3+} occupying vacancies in the framework to Cu^+ . Mozgova and Tsepina (1983) made this point and it was confirmed by the study of the

composition of Te-bearing fahlores from 11 volcanogenic and hydrothermal quartz-sulfide vein deposits of the gold-sulfide assemblage (Nenasheva, 2009). Belov (1952) noted the probable existence of Cu^{3+} in fahlore.

Tetrahydroite containing more than 4 wt.% Fe (up to 4.90) and significant Ag (2.88–4.87 wt.%), Zn (2.61–3.37 wt.%) is associated with pyrite, chalcopyrite, sphalerite, bournonite, hematite, copper sulfides (covellite, spionkopite, yarrowite, anilite, and geerite), tellurides (hessite, petzite, and altaite), and arsenates (leogangite and bayldonite) (Tables 1, 2; anal. 28–35). In some areas, such tetrahydroite fills interstices between grains of sphalerite, quartz, chalcopyrite, and galena. In the other areas, it together with bournonite fills interstices between quite coarse (up to 100 microns) grains of galena, sphalerite, and chalcopyrite (Fig. 3); in this case, grains of chalcopyrite are heterogeneous. Thin rims, small lamellas (1–2 microns in width), and point segregations of copper sulfides of the chalcocite polysomatic series (Fig. 4) are clearly observable in them.

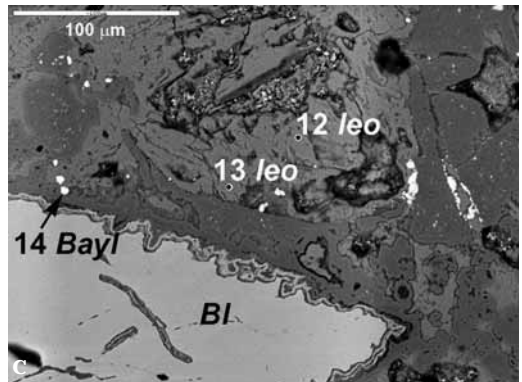
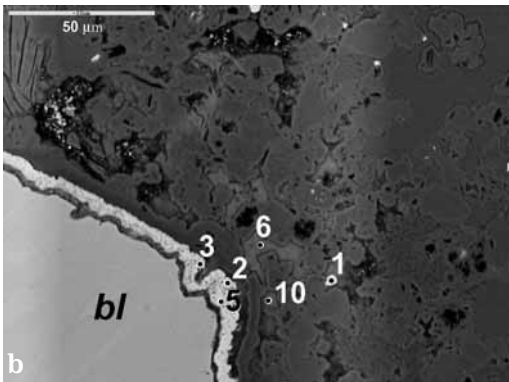
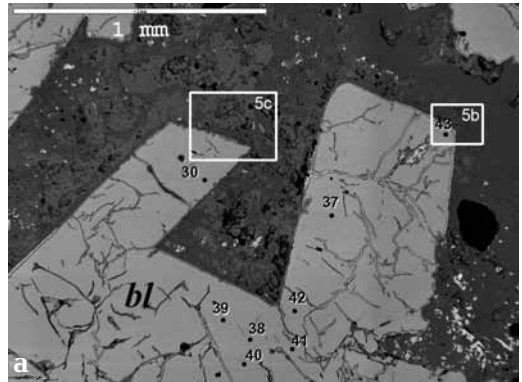
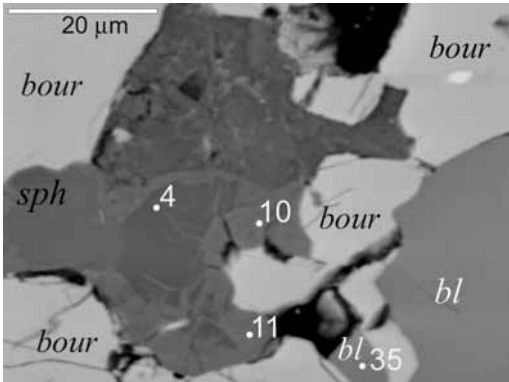


Fig. 4. Heterogeneous grains of chalcopyrite and copper sulfides of the chalcocite polysomatic series replacing chalcopyrite. (cp) Chalcopyrite, (an) anilite, (ge) geerite, (sp) spionkopite, (yar) yarrowite, (cov) covellite. Digits corresponds to numbers of analyses in Tables 6 and 1 for sulfides and fahlore, respectively (BSE-image). Sample 2, area 3.

Fig. 5. Large segregation of crinkly fractured anisotropic tennantite-tetrahedrite (light grey); the fractures are healed by secondary minerals: copper arsenates (darker tints of grey); (b, c) magnified fragments of selected areas. (bayl) Bayldonite, (leo) leogangite. Digits correspond to numbers of analyses in Tables 1, 4 (BSE-image). Sample 242/1-2.

Zn-rich tennantite-tetrahedrite (sandbergerite) differs from the aforementioned tetrahedrite, Te-bearing tetrahedrite-tennantite, and tennantite in brighter reflection like that of galena, visible bireflectance, and clear anisotropy (Tables 1, 2; anal. 36–43). In cross polars, it is well seen that sufficiently coarse grains are broken to the randomly oriented anhedral fine grains with different reflection allowing observation the bireflectance. Insignificant red inner reflections are observed in cross polars. Coarse segregations of this fahlore are broken crinkly fractures, which are healed by secondary minerals (Fig. 5), which are presumably arsenates; the latter was confirmed by reflections of euchroite and leogangite in the X-ray diffraction pattern of the fahlore (Table 3). The chemical composition of anisotropic fahlore corresponds to Zn-rich tetrahedrite-tennantite (sandbergerite). Anisotropic sandbergerite (Tables 1, 2; anal.

36–43) differs from isotropic once (Nenasheva *et al.*, 2010; Table 1; anal. 25–26) in the absence of admixture of Ag, Cd, and Pb. Tellurium that causes weak anisotropy of Te-bearing fahlores, is absent in anisotropic sandbergerite. The X-ray powder diffraction pattern of anisotropic tennantite-tetrahedrite (sandbergerite) (Table 3) is well consistent with that of tennantite given in the Peacock's atlas (Berry, Thompson, 1962). The unit cell dimension calculated on the basis of 12 reflections (Table 3; reflections nos. 5, 7, 8–13, 15–17, 19, and 20) is 10.1886 Å. In the X-ray powder diffraction pattern, there are reflections indexed in the unit cell of tennantite, but are absent in the X-ray powder diffraction pattern given in the Peacock's atlas (Table 3; reflections nos. 14, 29, 39, 41, 44, 47, and 57). It should be noted that many reflections of anisotropic tennantite-tetrahedrite are stronger in comparison with intensity of reflections

Table 3. X-ray powder diffraction data of anisotropic Zn-rich tennantite-tetrahedrite

Sample 242/ 1-2 $a = 10.1886 \text{ \AA}$, $V = 1057.5 \text{ \AA}^3$				Tennantite $T_d^3 - I43m$, $a = 10.21 \text{ \AA}$			Bournonite $a = 8.15$, $b = 8.70$, $c = 7.80 \text{ \AA}$			Euchroite $a = 10.05$, $b = 11.50$, $c = 6.11 \text{ \AA}$		Leogangite $a = 21.77$, $b = 12.327$, $c = 10.72 \text{ \AA}$, $\beta = 92.85^\circ$	
Berry, Thompson, 1962													
Mikheev, 1957													
Lengauer et al., 2004													
No	<i>I</i>	$d_o(\text{obs.})$	$d_o(\text{calc.})$	<i>hkl</i>	<i>hkl</i>	<i>I</i>	$d_o(\text{obs.})$	$d_o(\text{pac.})$	$d_o(\text{obs.})$ (<i>I</i>)	$d_o(\text{obs.})$ (<i>I</i>)	$d_o(\text{obs.})$ (<i>I</i>)	$d_o(\text{obs.})$ (<i>I</i>)	
1	1	7.21	7.204	011						7.2 (10)			
2	0.5	5.46								5.8 (4)		5.44 (0.5)	
3	0.5	5.16	5.094?	002?						5.2 (10)			
4	3	4.43							4.37 (4)	5.00 (8)			
5	1	4.15	4.159	112	112	1	4.15	4.17	4.08 (3)	4.14 (4)			
6	3	3.90							3.90 (8)				
7	2	3.62	3.602	022	022	0.5	3.60	3.61	3.68(2)	3.73 (8)		3.728 (0.3)	
8	7	3.24	3.22	013	013	0.5	3.23	3.23	3.27(2)	3.29 (2)		3.625 (0.5)	
9	10	2.94	2.941	222	222	10	2.94	2.95	2.99(4)	2.94 (7)		3.09 (0.4)	
10	1	2.82	2.826	023					2.82 (2)	2.81 (8)			
11	2	2.71	2.723	123	123	1	2.71	2.73	2.74 (10)	2.63 (7)		2.672 (0.4)	
12	7	2.54	2.547	004	004	3	2.55	2.55	2.69 (4)	2.69 (4)		2.63 (0.6)	
13	4	2.40	2.401	033	114,033	2	2.40	2.41	2.59 (5)	2.55 (7)			
14	1	2.29	2.278	024					2.37 (1)	2.34 (6)			
15	1	2.17	2.172	233	233	0.5	2.17	2.18	2.30 (1)	2.26 (6)			
16	2	2.08	2.080	224	224	0.5	2.07	2.08	2.16 (0.5)	2.21 (5)			
17	4	1.994	1.998	015,134	015,134	2	1.994	2.00	2.02 (0.5)	2.07 (6)			
18	2	1.907							1.985 (3)	1.95 (7)			
19	4	1.861	1.860	125	125	2	1.855	1.865		1.90 (6)			
20	8	1.803	1.801	044	044	8	1.801	1.807	1.848 (4)	1.84 (6)			
21	1	1.745	1.747	035,334	035,334	0.5	1.746	1.751		1.78 (4)			
22	2	1.696	1.698	006,244	006,244	0.5	1.695	1.702	1.765 (6)	1.74 (4)			
23	3	1.655	1.653	235,116	116,235	2	1.653	1.656		1.71 (6)			
24	1	1.612	1.611	026	026	0.5	1.608	1.615	1.664 (2)	1.65 (7)			
25	0.5	1.590	1.591	045,344					1.631 (2)	1.61 (4)		1.618 (0.3)	
26	1	1.569	1.572	154,145	145	0.5	1.568	1.576		1.562(5)			
27	7	1.535	1.536	226	226	7	1.535	1.540		1.524 (4)			
28	0.5	1.516	1.519	036,245						1.513 (8)			
29	1	1.494	1.502	136									
30	2	1.473	1.471	444	444	1	1.467	1.475	1.480 (1)				
31	2	1.444	1.441	055,345,017	017,055,345	1	1.439	1.445		1.451 (7)			
32	0.5	1.425	1.427						1.427 (2)				
33	0.5	1.409	1.413	046						1.409 (4)			
34	1	1.386	1.386	127,255	336,255,127	0.5	1.386	1.390		1.385 (2)			
35	1	1.365	1.362	246	246	0.5	1.358	1.365	1.389 (1)				
36	1	1.297	1.294	156	237,156	0.5	1.296	1.297	1.365 (1)				
37	2	1.275	1.274	008	008	2	1.274	1.276					
38	1	1.258	1.254	018,147, 455	118,147, 455	0.5	1.254	1.257					
39	0.5	1.236	1.139	446,028									
40	2	1.220	1.218	356	356	1	1.217	1.220					
41	1	1.202	1.201	066									
42	3	1.185	1.184	057,347	138,057, 347	2	1.185	1.186					
43	4	1.169	1.169	266	266	3	1.169	1.171					
44	1	1.157	1.154	257									
45	1	1.142	1.139	048	048	1	1.139	1.141					
46	1	1.126	1.125	338,019	019,338, 129	0.5	1.126	1.128					
48	3	1.099	1.099	129,556,167	129,167, 556	1	1.100	1.101					
49	0.5	1.088	1.086	466	466	0.5	1.086	1.089					
50	1	1.077	1.074	158, 457	039,158,457	0.5	1.074	1.076					
51	0.5	1.068	1.068	139									
52	2	1.054	1.051	239, 367	239,367	0.5	1.052	1.054					
53	6	1.043	1.040	448	448	3	1.041	1.043					
54	2	1.032	1.034	566, 049									
55	1	1.024	1.024	177									
56	1	1.013	1.014	186,467,168									
57	1	1.003	0.999	268									
58	4	0.985	0.985	377, 666		2	0.980						
59	2	0.983											
60	4	0.976				1	0.970						
61	1	0.975											

Notes: The condition of reflection is $h+k+l = 2n$.

in the X-ray powder diffraction pattern given in the Peacock's atlas. It is explained by the superimposed strong reflections of euchroite $\text{Cu}_2(\text{OH})[\text{AsO}_4] \cdot 3\text{H}_2\text{O}$ (Table 3; reflection nos. 3, 5, 7, 9, 11–13, 15–17, 19, 21–24, 31). According to the presence of reflections of euchroite in the X-ray powder diffraction pattern of anisotropic tennantite-tetrahedrite, euchroite got into preparation from crinkly fractures cutting the fahlore. The reflections (Table 3; nos. 2, 7, 11, and 24) in the X-ray powder diffraction pattern are probably caused by the admixture of leogangite $\text{Cu}_{10}^{2+}(\text{OH})_6[\text{AsO}_4]_4[\text{SO}_4] \cdot 8\text{H}_2\text{O}$. In addition, indexing of twelve reflections (Table 3; reflection nos. 4, 6, 10, 18, 25, 28, 32, 51, 55, 56, 59, and 61) in dimensions of tennantite was failed. Reflections 10, 18, 25, and 28 belong to euchroite and reflections 4, 6, and 32 are attributed to bournonite, CuPbSbS_3 . The assignment of high angle reflections (reflection nos. №№ 51, 55, 56, 59, 61) is not clear. The electron microprobe measurement of phases filling these fractures was failed because the fractures are very narrow (about 1–2 microns, Fig. 6) and filling matter is heterogeneous. Optical properties of at least two phases are similar to arsenates, which immediately contact with anisotropic tennantite-tetrahedrite. These two phases occur as larger grains. In reflected light, one phase is light grey with weak light bluish tint and greenish yellow or yellowish orange translucence in chips; another phase is dark grey with greenish tint. In cross polars, the first phase is yellow-orange to brown, and the second phase is emerald-green. According to electron microprobe data, light grey phase with light bluish tint is bayldonite $\text{PbCu}_3(\text{OH})_2[\text{AsO}_4]_2$ (Table 4; anal. 1–5, Fig. 6a), while dark grey phase with greenish tint is leogangite $\text{Cu}_{10}^{2+}(\text{OH})_6[\text{AsO}_4]_4[\text{SO}_4] \cdot 8\text{H}_2\text{O}$ (Table 4; anal. 12–13, Fig. 6b). Thus, in the narrow fractures cutting grains of anisotropic tennantite-tetrahedrite, bournonite and three arsenates, bayldonite, leogangite, and euchroite $\text{Cu}_2(\text{OH})[\text{AsO}_4] \cdot 3\text{H}_2\text{O}$, were identified. In addition, in the same sample, the other copper arsenates (duftite, clinotyrolite, strashimirite, clinoclase, and cornwallite), copper carbonate (azurite and malachite), and hematite were found with electron microprobe (Table 4).

Anisotropy of tennantite-tetrahedrite accounts for by pressure that results in crinkly

fractures filled by copper arsenates, but the other explanations are probable.

Minerals associated with fahlores

As aforementioned, the fahlores studied are associated with varied minerals (Table 5). Nenasheva *et al.* (2010) reported chemical data and characteristic some of them: bornite, famatinite, sulvanite, arsenosulvanite, angle-site, tyrolite, clinotyrolite, and certain minerals of the chalcocite polysomatic series. The other phases are briefly characterized below.

The electron microprobe data of galena, pyrite, chalcopyrite, sphalerite, cubanite, and copper sulfides of the chalcocite polysomatic series (anilite, geerite, spionkopite, and yarowite) are given in Table 6. In the second line of each analysis of galena, pyrite, chalcopyrite, and cubanite, the composition normalized to 100% for convenient comparison with theoretical composition are given. As seen from the table, compositions of galena and pyrite are close to theoretical. Chalcopyrite and cubanite were measured with well-shaped crystal (Fig. 6) occurred between grains of leogangite $\text{Cu}_{10}^{2+}(\text{OH})_6[\text{AsO}_4]_4[\text{SO}_4] \cdot 8\text{H}_2\text{O}$. The crystal is heterogeneous. The areas of chalcopyrite and cubanite are distinguished. Within the crystal, chalcopyrite is chemically variable and contains lower sulfur (Table 6; anal. 5, 6, 7) in comparison with theoretical composition. The composition of cubanite is close to theoretical (Table 6; anal. 8, 9). The close intergrown chalcopyrite and cubanite indicate that the initial composition of the crystal corresponded to that of high-temperature solid solution of chalcopyrite (iss) identified experimentally at 350–300°C (Sugaki *et al.*, 1975). The exsolution at 250–300°C (Ramdohr, 1950) resulted in the formation of chalcopyrite variable in composition and cubanite.

Chalcopyrite and copper sulfides of the chalcocite polysomatic series associated with covellite and hematite fill interstices between grains of bournonite, galena, sphalerite, fahlore with thin rims, fine lamellas (1–2 microns in width), and point segregations of copper sulfides of the chalcocite polysomatic series being clearly observable in some grains of chalcopyrite (Fig. 3, 4). Electron microprobe measurements (Table 6; anal. 10–14)

Table 4. Electron microprobe data (wt.%) of arsenates

№ an.	Sample	Cu	Ag	Fe	Zn	Pb	As	Sb	V	S	Total
1	242/1-2	25.00	0.00	4.35	0.40	24.49	20.68	1.05		0.21	76.18
2		24.96	0.81	1.92	0.75	26.87	19.13	1.92		0.44	76.80
3		26.12	0.34	1.85	0.62	26.67	19.83	1.13		0.35	71.02
4		26.34	0.77	2.00	0.79	25.78	18.49	1.86		0.42	76.45
5		27.17	0.10	3.51	0.26	26.44	19.32	0.60		0.15	77.55
6		40.59		2.46	0.74		20.78	2.42		0.74	67.73
7	242/5 (area 1)	37.25					19.05		0.26	0.91	62.12
8		33.34		7.80			16.86		0.68	0.33	59.88
9		36.36		5.17			15.36		0.79	0.09	58.94
10	242/1-2	34.16	0.08	11.00	1.22	0.73	19.59	3.13		0.49	70.49
11		14.33		3.60	0.85	27.09	12.35				58.22
12		39.66	0.12	0.47	0.69	0.29	19.45	1.20		1.00	62.94
13		39.56	0.04	1.23	0.65	0.20	20.90	1.39		1.09	65.10
14	242/6 (area 1)	35.24		7.72			21.47	0.81	0.27	3.28	69.73
№ an.	Sample	Mineral and mixed minerals						Δ, % – valence balance			
1	242/1-2	Bayldonite + hematite + arthurite						3.4			
2		Bayldonite + hematite +						0.8			
3		Bayldonite + hematite +						1.6			
4		Bayldonite + hematite +						0.1			
5		Bayldonite + hematite +						1.7			
6		Strashimirite + hematite						0.3			
7	242/5 (уч.1)	Clinotyrolite						1.6			
8		Clinotyrolite + strashimirite + hematite						0.9			
9		Clinotyrolite + cornwallite + hematite						1.1			
10	242/1-2	Olivenite + hematite						0.8			
11		Duftite + clinoclase						1.7			
12		Leogangite						0.6			
13		Leogangite						0.7			
14	242/6 (area 1)	Leogangite + hematite						0.4			

Notes: Including Ca (wt. %): anal. 7 – 0.94, anal. 10 – 4.65, anal. 11 – 0.87, anal. 12 – 1.17; and Mn (wt. %): anal. 8 – 0.06, anal. 9 – 0.04, anal. 13 – 0.09. Analyst L.A. Pautov; the compositions were recalculated by V.Yu. Karpenko.

Table 5. Characteristic of fahlores and their assemblages

№	Fahlore	Assemblage
1	Isotropic tetrahedrite with significant amount Zn-sandbergerite	Galena, chalcocopyrite, pyrite, famatinite, sulvanite, anglesite, copper arsenates: bayldonite, leogangite, and euchroite.
2	Tetrahedrite-tennantite and tennantite	Galena, chalcocopyrite, pyrite, sulvanite, arsenosulvanite, and Ca and Cu arsenates: tyrolite $\text{Ca}_2\text{Cu}_5^{2+}(\text{OH},\text{O})_4(\text{AsO}_4)_2(\text{CO}_3) \cdot 6\text{H}_2\text{O}$ or clinotyrolite $\text{Ca}_2\text{Cu}_5^{2+}(\text{OH},\text{O})_{10}[(\text{AsO}_4)_1(\text{SO}_4)_4] \cdot 10\text{H}_2\text{O}$.
3	Anisotropic tennantite-tetrahedrite with significant amount Zn-sandbergerite	Chalcocopyrite, cubanite, grains of pyrite and galena partially replaced by secondary products including hematite and copper arsenates: bayldonite, leogangite, euchroite, duftite, clinotyrolite, strashimirite, clinoclase, and cornwallite. Veinlets of azurite and malachite are observable in specimens.
4	Tetrahedrite containing more than 4 wt.% Fe (up to 4.90 wt.%) and significant amount Ag (up to 4.87 wt.%) and Zn (up to 3.37 wt.%)	Pyrite, galena, chalcocopyrite, sphalerite, bourmonite, hematite, copper sulfides of the chalcocite polysomatic series $m\text{Cu}_2\text{S} \cdot n\text{CuS}$, tellurides (hessite, petzite, and altaite), arsenates (leogangite and bayldonite).
5	Goldfieldite-tennantite-tetrahedrite	Galena, pyrite, quartz, native gold, anglesite, secondary copper
6	Goldfieldite-tennantite	sulfides of the chalcocite polysomatic series $m\text{Cu}_2\text{S} \cdot n\text{CuS}$ (djurleite,
7	Te-bearing tennantite-tetrahedrite	digenite, roxbyite, anilite, geerite, spionkopite, and covellite).

Table 6. Electron microprobe data (wt. %) of sulfides and sulfates

№ an. Sample	Mineral	Pb	Fe	Cu	Zn	S	Total	Formula	Δ , %
1	53/278 (area 7) gal	85.40				13.19	98.59	Pb _{0.99} S _{1.01}	0.1
2	2 (area 3) gal	86.36				13.28	99.64	Pb _{1.00} S _{1.00}	0.0
3	53/278 (area 7) py	46.81				53.91	100.72	FeS _{2.00}	0.0
Theoretical chalcopyrite			30.43	34.63		34.94	100.00	CuFeS ₂	
4	2 (area 3) cp		27.91	33.51	2.03	33.65	97.10	Cu _{1.00} Fe _{0.95} Zn _{0.06} S _{1.99}	0.2
			28.74	34.51	2.09	34.65	100.00		
5	127/1 cp		28.90	32.37		33.85	95.12	Cu _{0.98} Fe _{0.99} S _{2.03}	2.7
			30.38	34.03		35.59	100.00		
6			30.04	32.54		34.083	96.66	Cu _{0.97} Fe _{1.02} S _{2.01}	0.2
			31.07	33.66		35.25	100.00		
7			29.50	33.10		34.33	96.93	Cu _{0.98} Fe _{1.00} S _{2.02}	1.5
			30.43	34.14		35.41	100.00		
Theoretical cubanite			41.20	23.40		35.40	100.00	CuFe ²⁺ Fe ³⁺ S _{3.00}	
8	127/1.		39.03	21.81		34.53	95.37	Cu _{0.97} Fe _{0.99} ²⁺ Fe _{0.99} ³⁺ S _{3.05}	2.9
			40.92	22.87		36.21	100.00		
9			41.32	23.98		34.70	100.00	Cu _{1.03} Fe _{1.01} ²⁺ Fe _{1.01} ³⁺ S _{2.95}	3.0
10	2 (area 3) yar + sp	0.79		64.45		27.73	95.10	(Cu _{16.53} Ag _{0.32} Pb _{0.06}) _{16.91} S _{14.09} or (Cu _{7.22} Ag _{0.32}) _{7.54} Pb _{0.06} Cu _{9.31} ²⁺ S _{14.09}	
11	2 (area 3) an + ge		2.00	72.58		23.40	97.97	(Cu _{4.79} Fe _{0.15}) _{4.94} S _{3.06} or Cu _{3.94} ⁺ (Cu _{0.85} ²⁺ Fe _{0.15}) _{1.00} S _{3.06}	2.9
12	2 (area 2) yar		2.89	63.43		30.94	97.75	Cu _{6.40} Ag _{0.04} Fe _{0.44} S _{8.12} → (Cu _{1.96} Ag _{0.04}) _{2.00} (Cu _{6.44} ²⁺ Fe _{0.44}) _{6.88} S _{8.12}	2.9
13	2 (area 2) kov			65.23		32.98	98.22	Cu _{0.995} S _{1.001}	0.2
14				64.11		32.20	96.31	Cu _{1.002} S _{0.998}	0.4
15	2 (area 3) sph		4.12		61.93	32.98	99.03	(Zn _{0.92} Fe _{0.07} ²⁺) _{0.99} S _{1.00}	1.0
16	2 (area of fahlore) sph		3.74	0.63	61.60	33.45	99.42	(Zn _{0.91} Fe _{0.06} ²⁺ Cu _{0.01}) _{0.98} S _{1.01}	3.0
17	53/278 (area 6) angl	68.08				10.39	99.28	Pb _{2.02} S _{1.99} O _{8.00} or PbSO ₄	0.5

Notes: Δ , % – valence balance. * – including Ag (wt. %): 2.13 (anal. 10), 0.49 (anal. 12). Composition 17 anal. contains 20.81 wt. % O. Composition 2 anal. is average of two compositions. Composition 10 is attributed to the sample presenting mixture of yarrowite (72%) and spionkopite (28%). Legend: galena (gal), pyrite (py), chalcopyrite (cp), cubanite (cb), spionkopite (sp), yarrowite (yar), anilite (an), geerite (ge), covellite (cov), sphalerite (sph), and anglesite (angl). Analyst V.Yu. Karpenko.

revealed heterogeneity of these areas. The compositions 10 and 11 are calculated to electroneutral formula only assuming the examined grains are mixtures of yarrowite with spionkopite (anal. 10) and of anilite with geerite (anal. 11). The compositions 12–14 correspond to that of yarrowite (anal. 12) and covellite (anal. 13, 14). Electron microprobe data of hematite (49.97 wt.% Fe, 22.66 wt.% O, 1.05 wt.% S, total 73.42) are calculated to formula Fe_{1.92}S_{0.05}O_{3.03}. The presence of S accounts for the impurity of any sulfate phase Fe³⁺[SO₄]₃·nH₂O. According to calculation, in this case, the formation of 0.05 molecules of Fe³⁺[SO₄]₃·nH₂O requires 0.1 atom of Fe³⁺ and 0.3 atom of oxygen. After residue of these

amounts of Fe³⁺ and S, formula of hematite becomes neutral – Fe_{1.82}O_{2.73} (valence balance – Δ , % = 0).

In this sample at adjacent area, more complex assemblage of galena, sphalerite, bournonite, hessite, petzite, altaite, and quartz is observed (Fig. 7a). The X-ray images of this area in the thin polished section are shown in Fig. 7b with well distinguishable grains of hessite (AgL_{α1}) and bournonite (SbL_{α1}). The electron microprobe data of sulfosalts and tellurides are given in Tables 7 and 8. In reflected light, bournonite is very similar to fahlore. It is light grey with greenish tint. Birefractance and anisotropy are absent or extremely weak, so their documentation is impossible. The chemi-

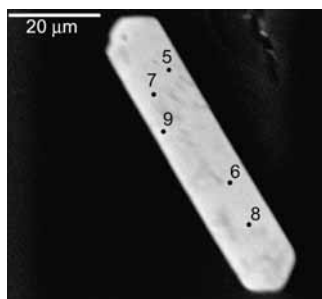


Fig. 6. Exsolved chalcopyrite crystal to form cubanite. Digits correspond to numbers of analyses in Table 6 (BSE-image). Sample 127/1.

cal composition of bournonite PbCuSbS_3 in the ore of the Lebedinoe deposits is as follows, wt. %: 41.09 – 42.44 Pb, 13.19 – 14.47 Cu, 22.68 – 24.78 Sb, 18.59 – 19.65 S (Tables 7, 8; anal. 1 – 10) that is weakly different from theoretical (42.54 Pb, 13.04 Cu, 24.65 Sb, 19.77 S).

The following telluride minerals were identified: altaite, PbTe , hessite, Ag_2Te , and petzite, Ag_3AuTe_2 . In reflected light, altaite is white, isotropic. According to electron micro-

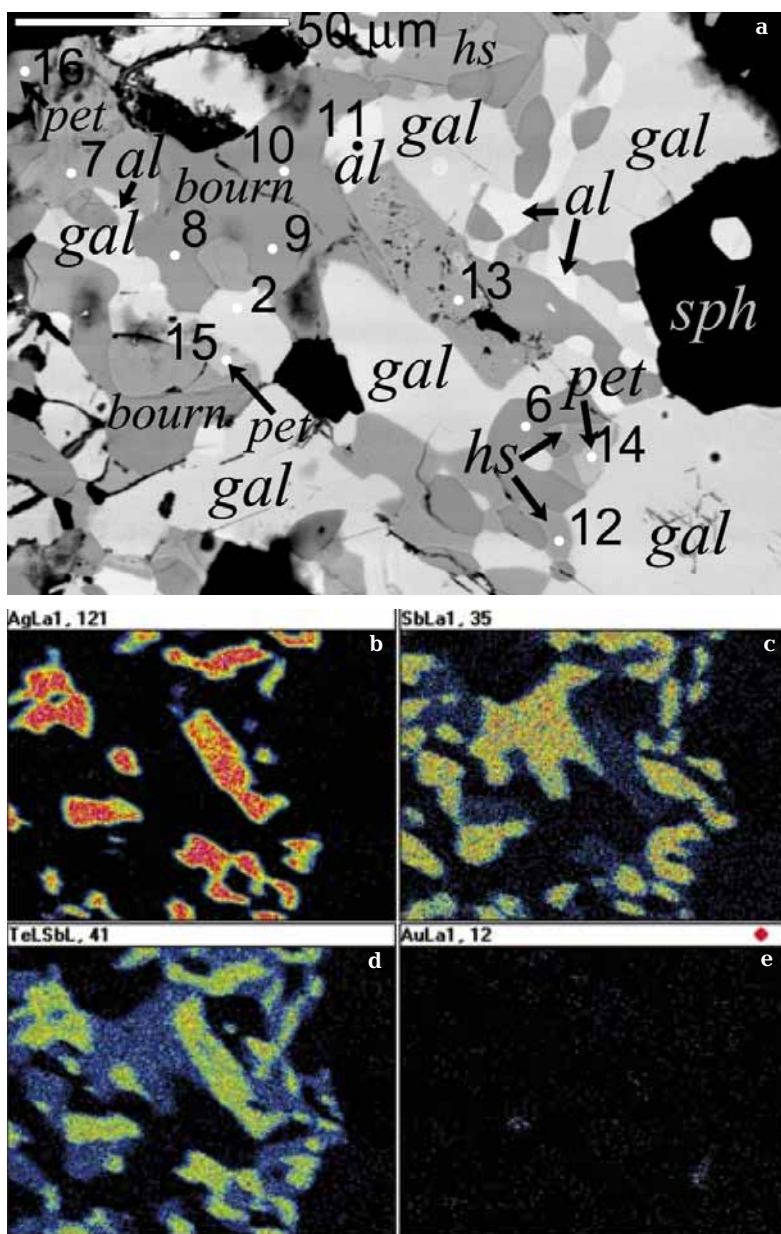


Fig. 7. Assemblage of galena (gal), sphalerite (sph), bournonite (bour), hessite (ges), petzite (pet), altaite (alt), and quartz (Q): (a) BSE-image, (b) X-ray elemental distribution map. Grains of hessite (AgLa_1), bournonite (SbLa_1) and hessite with bournonite ($\text{TeLa}_1 + \text{SbLa}_1$) are well distinguished. Digits correspond to numbers of analyses in Tables 6 and 7 for sulfides and bournonite, respectively. Sample 2, area 3.

Table 7. Electron microprobe data (wt. %) of sulfosalts and tellurides

№ an.	Mineral	Sample	Cu	Ag	Au	Zn	Sb	Pb	Te	S	Total
1	Bourmonite	2 (area 3)	14.47				23.76	41.74		19.00	98.96
2			13.62			0.19	23.20	41.09		18.59	96.69
3			14.36			0.92	22.68	41.27		19.16	98.39
4			13.82				23.36	43.70		18.81	99.69
5			14.47			0.75	23.41	42.44		19.65	100.96
6			13.19				23.26	42.00		18.74	97.19
7			13.42				23.49	41.65		18.92	97.48
8			14.02				24.35	42.71		19.23	100.31
9			13.60				24.78	42.27		19.32	100.33
10			14.30				24.20	41.97		19.62	100.09
11	Altaite	2 (area 3)		3.32				59.84	36.74		99.90
								61.96*	38.04*		100.00*
12	Hessite	2 (area 3)		60.31			1.21		35.94		97.65
13				60.07			1.30		36.37		97.74
14	Petzite	2 (area 3)		42.53	21.87			1.10	32.66		98.00
15				41.13	22.53			1.08	32.48		97.22
16			0.66	40.44	22.78				31.39		95.27
			Theoretical petzite		41.71	25.42				32.87	

Notes: * – After excluding Ag and normalization to 100%. Including Se (wt. %): 0.36 (anal. 9), 0.20 (anal. 12) Composition 5 contains 0.24 wt. % As. Analyst V.Yu. Karpenko.

Table 8. Formulae of sulfosalts and tellurides

№ an.	Mineral	Sample	Formula	Δ , % – valence balance
1	Bourmonite	2 (area 3)	$\text{Cu}_{1.13}\text{Pb}_{0.99}\text{Sb}_{0.96}\text{S}_{2.92}$	2.5
2			$\text{Cu}_{1.08}\text{Pb}_{1.00}\text{Sb}_{0.96}\text{S}_{2.93}$	2.3
3			$\text{Cu}_{1.11}\text{Zn}_{0.07}\text{Pb}_{0.97}\text{Sb}_{0.91}\text{S}_{2.93}$	1.0
4			$\text{Cu}_{1.08}\text{Pb}_{1.05}\text{Sb}_{0.95}\text{S}_{2.92}$	3.0
5			$\text{Cu}_{1.09}(\text{Pb}_{0.98}\text{Zn}_{0.06})_{1.04}(\text{Sb}_{0.92}\text{As}_{0.02})_{0.94}\text{S}_{2.94}$	1.8
6			$\text{Cu}_{1.05}\text{Pb}_{1.03}\text{Sb}_{0.96}\text{S}_{2.96}$	1.3
7			$\text{Cu}_{1.06}\text{Pb}_{1.01}\text{Sb}_{0.96}\text{S}_{2.96}$	0.7
8			$\text{Cu}_{1.08}\text{Pb}_{1.01}\text{Sb}_{0.98}\text{S}_{2.93}$	2.8
9			$\text{Cu}_{1.04}\text{Pb}_{1.00}\text{Sb}_{0.99}(\text{S}_{2.94}\text{Se}_{0.02})_{2.96}$	1.5
10			$\text{Cu}_{1.09}\text{Pb}_{0.98}\text{Sb}_{0.96}\text{S}_{2.96}$	0.2
11	Altaite	2 (area 3)	$\text{Pb}_{0.95}\text{Ag}_{0.10}\text{Te}_{0.95}$	5.0
			or $\text{Pb}_{1.002}\text{Te}_{0.998}$ *	0.4*
12	Hessite	2 (area 3)	$(\text{Ag}_{1.96}\text{Sb}_{0.03})_{0.99}(\text{Te}_{0.99}\text{Se}_{0.02})_{1.01}$	1.5
13			$\text{Ag}_{1.96}\text{Sb}_{0.03}\text{Te}_{1.00}$	2.4
14	Petzite	2 (area 3)	$\text{Ag}_{3.09}\text{Au}_{0.87}\text{Pb}_{0.04}\text{Te}_{2.00}$	1.0
15			$\text{Ag}_{3.03}\text{Au}_{0.91}\text{Pb}_{0.04}\text{Te}_{2.02}$	0.5
16			$\text{Ag}_{3.01}\text{Au}_{0.93}\text{Cu}_{0.08}\text{Te}_{1.98}$	1.5

Notes: * – After excluding Ag and normalization to 100%.

Table 9. Minerals of the Cu-S system

Mineral	Symmetry	Godovikov, Nenasheva, 2007		Gablina, 2008		Products of thermal stability, phase transitions °C
		Composition	Cu/S	Composition	Limit of	
Chalcocite high synthetic	↓ Hexagonal	Cu ₂ S	2.000	Cu ₂ S	435	Digenite high
Chalcocite low	↓ Monoclinic	Cu ₂ S	1.993–2.001	Cu _{1.993-2.001} S	80–103	Chalcocite high
Tetrachalcocite	↓ Tetragonal	Cu ₄₉ S ₂₅ → Cu ₄₆ ⁺ Cu ₂ ²⁺ S ₂₅	1.960	Cu _{1.96-2.0} S	?	Digenite high
Djurleite	↓ Monoclinic	Cu ₃₁ S ₁₆ → Cu ₃₀ ⁺ Cu ₁ ²⁺ S ₁₆	1.938	Cu _{1.93-1.96} S	93 ± 2	Chalcocite low + digenite low
Roxbyite	↓ Monoclinic	Cu ₉ S ₅ → Cu ₈ ⁺ Cu ₁ ²⁺ S ₅	1.800	Cu _{1.72-1.82} S	50–90	
Digenite high	↓ Cubic	Cu ₂ S	2.000	Cu ₂ S	>1000	Melt
Digenite low	↓ Trigonal, pseudo-cubic	Cu ₉ S ₅ → Cu ₈ ⁺ Cu ₁ ²⁺ S ₅	1.800	Cu _{1.75-1.78} S	75–83	Digenite high
Anilite	↓ Rhombic	Cu ₇ S ₄ → Cu ₆ ⁺ Cu ₁ ²⁺ S ₄	1.750	Cu _{1.75} S	30–75	Digenite low
Geerite	↓ Trigonal	Cu ₃ S ₂ → Cu ₂ ⁺ Cu ₁ ²⁺ S ₂	1.500	Cu _{1.5-1.6} S	?	?
Spionkopite	↓ Hexagonal	Cu ₃₉ S ₂₈ → Cu ₂₂ ⁺ Cu ₁₇ ²⁺ S ₂₈	1.393	Cu _{1.4} S	157	Covellite
Yarrowite	↓ Hexagonal	Cu ₉ S ₈ → Cu ₂ ⁺ Cu ₇ ²⁺ S ₈	1.125	Cu _{1.1} S	157	Covellite
Covellite	↓ Hexagonal	3CuS → Cu ₂ ⁺ S • Cu ²⁺ [S ₂]	1.000	CuS	507	Digenite
X-bornite				Cu _{5-x} FeS ₄	75–140	Chalcopyrite + bornite

Notes: Arrows indicates pH decreasing, copper realizing, and increasing importance of bivalent copper.

probe measurements, the mineral contains 3.32 wt.% Ag (Tables. 7, 8; anal. 11). According to handbook edited by Bonshtedt-Kupletskya, few Ag in altaite occurs as admixture. Ag in altaite from the Stepnyak gold deposit (Kazakhstan) belong to native silver (Minerals, 1960). Carrier of Ag in altaite from the Kalgoorlie deposit is aguilarite (Ramdohr, 1962). Altaite from the Lebedinoe deposit occurs as grains of 5–10 microns in size, which being magnified 825 times in microscope look homogeneous; the association is similar to that in the Stepnyak deposit; neither Se nor S were detected, therefore it can be concluded that Ag in altaite occurs as tiny inclusions of native silver. This admixture probably explains the non-uncharged formula of altaite with good sum of elements 99.90 wt.%. If Ag is excluded than formula becomes uncharged (balance valence is 0.4%).

Hessite is present as tiny elongate grains (Figs. 7a, 7b). The reflection is high similar to galena. Bireflectance is very weak; anisotropy ranges from light grey with cream tint to light

grey with light bluish tint. The composition (Tables 7, 8; anal. 12, 13) is close to theoretical (Ag 62.86, Te 37.14 wt.%), but admixture of Sb slightly greater than 1 wt.% and Se 0.2 wt.% was detected.

The composition of petzite Ag₃AuTe₂ is also close to theoretical (Tables 7, 8; anal. 14–16). With well relation of components (electroneutrality of formulae < 1.5), the compositions have lowered total (lowered gold content) that accounts for by small size of grains ~ 3–5 microns. In reflected light, petzite is hardly brighter hessite; it is isotropic, greyish white.

Discussion

Thus, fahlores of the Lebedinoe deposit are extremely varied in: (1) character of univalent metals (in addition to Cu, Cu-Ag were identified); (2) elemental set of bivalent metals (Zn, Zn-Fe, Fe-Zn, Cu-Fe, and Cu-Zn); and (3) character of semimetals (significantly Sb, Sb-As, As-Sb, Sb-As-Te). They were estab-

lished in various assemblages (Table 5). Galena, chalcopyrite, pyrite, and copper arsenates were found in all assemblages.

In addition, in assemblage no. 1 (Table 5), isotropic sandbergerite is associated with famatinite, sulvanite, anglesite, and copper arsenates: bayldonite, euchroite, and leogangite. According to Betekhtin (1950), anglesite is formed in the cementation zone of the deposits containing copper sulfides in addition to lead and zinc sulfides and in the oxidizing zone of Pb-Zn sulfide deposits. The temperature of formation of this assemblage can be higher 250–300°C.

The assemblage of tetrahedrite-tennantite and tennantite with sulvanite, arsenosulvanite, and Ca and Cu arsenates (tyrolite and clinotyrolite) is the next (Table 5; no. 2). Sulvanite indicates introduction of arsenic in mineralizing fluid.

Anisotropic tennantite-tetrahedrite (Table 5; no. 3) is associated with chalcopyrite, cubanite, pyrite, and galena partly replaced by arsenates: bayldonite, leogangite, euchroite, duftite, clinotyrolite, clinoclase, strashimirite, and cornwallite. Close intergrown chalcopyrite and cubanite testify to high-temperature exsolution of chalcopyrite at 250–300°C (Ramdohr, 1950) indicating lowering temperature of formation of the described ores.

The assemblage of tetrahedrite (Table 5; no. 4) containing > 4 wt.% Fe (up to 4.90) and significant Ag (up to 4.87 wt.%) and Zn (up to 3.37 wt.%), bournonite, tellurides (hessite, petzite, and altaite), hematite, copper sulfides of the chalcocite polysomatic series $m\text{Cu}_2\text{S} \cdot n\text{CuS}$, and arsenates (leogangite and bayldonite) resulted from next change of mineral-forming conditions, introduction of Ag, Fe, and Te in mineralizing fluid, and temperature decreasing below 155°C, that is indicated by anisotropic hessite AgTe , which transforms to cubic modification at 155°C (Minerals, 1960). It is notable that tetrahedrite in this assemblage is Te-free. Probably, Te is used up the formation of hessite, petzite, and altaite.

Later generation of fahlore contains significant Te. At the Lebedinoe deposit, Te-bearing fahlores are identified in association with copper sulfides of the chalcocite polysomatic series with tellurides (hessite, petzite, and altaite) being absent. Tellurium species

are transforming that was previously reported in assemblages of the Kochbulak deposit (Kavalenker *et al.*, 1980).

The immediate contact of yarrowite (Table 6; anal. 15) and covellite (Table 6; anal. 13, 14), which are the Cu-poorest copper sulfides, testifies to the acidic mineral-forming environment, because these minerals are formed in acidic medium (Gablina, 1997). This is supported by the high activity of Cu and As, and copper arsenates in the ores which are stable in acidic, neutral, and weakly alkaline medium (pH 2.5–8.7). With the background activity of Cu and As, copper arsenates are not formed (Charykova *et al.*, 2010). Yarrowite and spinokopite are stable up to 157°C (Table 9). Finding of mixed anilite and geerite (Table 6; ansl. 11) is testimony to the formation temperature below 75°C, because at this temperature anilite transforms to low-temperature digenite (Table 9). Unfortunately, the data of the stability field of geerite are absent.

The finding of hematite associated with copper sulfides and anisotropic tetrahedrite-tennantite contradicts the statement by Fastalovich and Petrovskaya (1940) that "hematite is never found with minerals of polymetallic assemblage".

Thus, two mineral species (tennantite and tetrahedrite) according to nomenclature of fahlores suggested by Mozgova nad Tsepin (1984), were identified in the ores of the Lebedinoe deposit, among them five varieties (tennantite-tetrahedrite, goldfieldite-tennantite-tetrahedrite, goldfieldite-tetrahedrite-tennantite, Te-bearing tennantite-tetrahedrite, and Te-bearing tetrahedrite-tennantite) were distinguished. Such diversity is caused by change of mineral formation conditions: change of the composition of ore-forming hydrothermal fluids, decreasing temperature of formation, changing of redox potential and pH of mineral-forming medium.

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PALLADOARSENIDE Pd₂As – A PRODUCT OF MAYAKITE PdNiAs DESTRUCTION IN NORILSK SULFIDE ORES

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The paper describes mineral assemblages and genesis of mayakite and palladoarsenide in magmatic magnetite-pentlandite-chalcopyrite ores of the lower horizons of the Mayak Mine (Talnakh Deposit, Norilsk Ore Field). The mayakite studied here contained up to 1.5 wt.% Pt, whereas palladoarsenide contained up to 3 wt.% Cu and up to 2 wt.% Ni that substitute Pd. Microprobe analyses – 9 for mayakite and 4 for palladoarsenide – are presented in the paper. Palladoarsenide forms linear and branching metasomatic veinlets in mayakite and incomplete pseudomorphs after fine mayakite grains. Palladoarsenide is present at the locations where the ores are tectonized and have veinlets and metasomes of chlorite, carbonates, serpentine, anhydrite, makinawite, and magnetite. In these ore formations, ferroaugite is almost completely replaced by chlorite, carbonates, serpentine, and smectites. Possibly, palladoarsenide originated from the epigenetic processes of low-grade metamorphism (zeolite and prehnite-pumpellyite facies), which are widely abundant in the northwest of the East Siberian Platform, where the Norilsk Ore Field is located.

8 figures, 2 tables, 27 references.

Key words: palladoarsenide, mayakite, norilsk sulfide ore, low-grade metamorphism.

Norilsk Ore Field

The Norilsk Co-Ni-Cu sulfide ore field contains 75% of the world resources of palladium and features a numerous amounts of palladium minerals. Those include stannides, plumbides, bismuthides, arsenides, antimonides, bismuthides-tellurides, cuprides-stannides, and other intermetallides (Genkin, 1968; Kulagov, 1968; Begizov *et al.*, 1974; Zolotukhin *et al.*, 1975; Genkin *et al.*, 1976; Begizov, 1977; Genesis..., 1981; Evstigneeva and Genkin, 1986; Mitenkov *et al.*, 1997; Naldrett, 2004; Spiridonov, 2010).

The Norilsk Ore Field is located in the northwestern corner of the ancient East Siberian Platform, in the zone of edge dislocations. The Norilsk deposit in the southwestern part of the ore field and the Talnakh deposit in the northeastern part of it belong to the plate cover of the platform. In this region, the Riphean-Vendian-Paleozoic sedimentary formations of the plate cover have the maximum thickness up to 14 km. The plate cover in the Norilsk region is dislocated, split by numerous faults, its sedimentary rocks and overlying volcanic formations folded to form systems of flat brachysynclines and somewhat steeper anticlines. The cores of the bra-

chysynclines are built by the multi kilometer strata of plateau basalts, traps formation, P₂-T₁ (Godlevskii, 1959). Some of the latest elements of the traps are gently dipping band-shaped ore-bearing gabbroid intrusions. The deposits are associated to the Norilsk, Upper Talnakh, and Taimyr intrusions of olivine gabbro-dolerites, gabbro-norite-dolerite, gabbro-anorthosites, gabbro-peridotites, troctolites, and gabbro-diorites. These rocks intruded along the zone of the steeply dipping Norilsk-Kharalakh Fault with northeastern strike, and cross-cut the plate cover down to the bottom of the basalt strata. Magmatic sulfides are present as dissemination in ore-bearing intrusives, bodies, veins, and impregnations at the lower endocontact of these intrusives with underlying hornfelses; less abundant – in the main bulk of the intrusive and in the supra-intrusive zone. The isotope age of all constituents of the traps formation – volcanites, intrusive rocks, and magmatic Ag-Au-Pt-Pd-Co-Ni-Cu sulfide ores is 251 Ma (Naldrett, 2004; Spiridonov and Gritsenko, 2009). The isotope composition of lead in the ore-bearing intrusive rocks, magmatic sulfide ores, galena and Pd-Pt intermetallides of the Norilsk and Talnakh deposits is

quite different. The isotope composition of lead of intrusive rocks, magmatic sulfide ores, and Pd-Pt intermetallides at Talnakh deposit is noticeably more radiogenic (Spiridonov *et al.*, 2010). This is evidence to the genetic relation of the ores to particular intrusions.

According to metaphoric expression of Mikhail Nikolaevich Godlevskii, the Norilsk sulfide ore is the "kingdom of sulfide solid solutions". Crystallization differentiation is the governing process in solidification of the Co-Ni-Cu-Fe sulfide melts. The early crystallization products are represented by the monosulfide solid solution (Mss) with hexagonal structure and composition close to pyrrhotite. Later crystallization products, enriched in copper to a various degree, Pd, Pt, Ag and Au, are represented by the intermediate solid solution (Iss) with cubic structure and composition varying from cubanite to chalcopyrite with variable nickel content. The lower and marginal zones of the magmatic sulfide deposits are composed of pyrrhotite group minerals – the products of solid phase transformations of Mss. These are gradually replaced by pyrrhotite, troilite, chalcopyrite, and cubanite in various combinations, and other minerals of the chalcopyrite group (talnakhite, mooihoeckite) – the product of solid phase transformations of Iss. Both these varieties contain a significant amount of pentlandite as decomposition products of the Mss and Iss.

Minerals of platinum group elements in norilsk sulfide ores

Although the minerals of noble metals were extensively studied by M.N. Godlevskii, E.A. Kulagov, A.D. Genkin, A.A. Filimonova, T.L. Evstigneeva, V.D. Begizov, C.F. Sluzhenikin, G.A. Mitenkov, N.S. Rudashevskii, V.A. Kovalenker, E.V. Sereda, E.N. Sukhanova, I.N. Tushentsova, A.P. Glotov, and other researchers, we are only starting to understand the actual complexity of the noble metal mineral formation in the Norilsk sulfide ore deposits. The major part of Pd, Pt, Au, and Ag in these ores is represented by their own minerals, and minor quantities of these metals are contained in sulfides (e.g. palladium and silver in pentlandite, etc.). The minerals of platinum group elements (PGM) are similar in all the ore types, from pyrrhotite ores to chalcopyrite ores, talnakhite ores, and mooihoeckite ores, only the quantitative ratios of PGM vary (Mitenkov *et al.*, 1997; Spiridonov, 2010).

Most geologists believe that PGM are products of magmatic crystallization. In 1960s, A.D. Genkin proposed that PGM could form at

late-magmatic or post-magmatic conditions under the action of fluids (Genkin, 1968). Later on, it was proved (Kulagov, 1968; Genkin *et al.*, 1976; Evstigneeva and Genkin, 1986; Spiridonov *et al.*, 2003) that some of the PGM are metacrystals. The most recent observations show that the all of PGM in the norilsk ores originated from the replacing of the sulfide aggregates, silicates, and oxides in intrusive rocks and hornfelses (Spiridonov, 2005; 207; 2010). The exocontact zones of the sulfide aggregates, as well as the silicate matrix of the hornfelses spacially separated from the sulfides, contain metacrystals of atokite, tetraferroplatinum, rustenburgite, michnerite, sperrylite (formations up to 8 mm in size present in hornblende aggregates), electrum, mayakite, polarite, paolovite, and kotulskite. The size of the PGM metasomes is determined by the size of sulfide bodies: e.g. a few microns near the sulfide drops. Hence, the PGM genesis is likely pneumatolytic. When they form, Pd, Pt, Au, Ag, Sn, Te, As, Sb, and Bi are brought by the fluids that originated at the stage of sulfide formation; in this process, Cu, Pb, Fe, and Ni are extracted from the replaced sulfide minerals. Through this mechanism, mayakite replaced pentlandite (pentlandite relics are common in mayakite metacrystals) (Spiridonov *et al.*, 2004). Some of the zones of the sulfide ores are dominated by stannides of Pd and Pt, whereas another zone may contain antimonides of Pd and Pt, and the next one – bismuthides and bismuthides-tellurides of Pd and Pt, and others – arsenides and arsenides-stannides of Pd and Pt. The PGM in Norilsk sulfide ores formed at extremely low sulfur fugacity ($f S_2$) under highly reducing conditions.

Early stage pneumatolytic PGM. These are the solid solutions with extensive replacement of Pd-Pt-Au and Sn-Sb-Bi-Pb-Te-As with characteristic decomposition patterns. Intergrowths of gold-containing tetraferroplatinum Pt₂Fe (Fe, Ni, Cu) with lamellae of gold-platinum-lead-bearing atokite Pd₃Sn as well as intergrowths of gold-platinum-lead-bearing atokite Pd₃Sn with lamellae of tetraferroplatinum are quite common. Also abundant are PGM metacrystals with the bulk composition (Pd,Pt)(Sn,Sb,Bi,Te,As) – equiatomic platinoid solid solutions. These minerals are composed of the products of decomposition of equiatomic platinoid solid solutions, which are usually represented by antimony-bearing paolovite (matrix) associated with a mass of geversite (PtSb₂) – insizvaite (PtBi₂) lamellae and niggliite (PtSn) microgrowths. The products of joint recrystallization of the above minerals are widely present.

Middle stage pneumatolytic PGM are mainly the products of transformation of the early

PGM, which typically occurs with addition of tellurium. Altaite PbTe and moncheite $\text{Pt}(\text{Bi}, \text{Te})_2$ are products of this process. Moncheite plates are often overgrown by aggregates of zonal crystals of maslovite (PtBiTe), tellurium- and bismuth-bearing geversite, and tellurium- and antimony-bearing insizvaite. Alteration of early gold-bearing tetraferroplatinum and atokite with breakdown lamellae resulted in the formation of the aggregates of tetraferroplatinum (without breakdown patterns), zoned crystals of rustenburgite (Pt_3Sn), and atokite (Pd_3Sn) (also without breakdown patterns). These minerals are associated with zvyagintsevite (Pd_3Pb), stannopalladinite (Pd_5CuSn_2), and Au-Cu minerals. Low-tellurium parageneses are present: (1) thin-lamellar and graphic intergrowths of polarite (Pd_2PbBi), stannopalladinite, plumbopalladinite (Pd_3Pb_2), associated with mayakite and tetraferroplatinum; (2) plate aggregates of paolovite, paolovite with antimony-bearing paolovite, paolovite with stibiopalladinite (Pd_5Sb_2), all cemented by bismuth-bearing geversite and antimony-bearing insizvaite. Later minerals in this stage include taimyrite (Pd, Pt), Cu_3Sn_4 and tatyanaite (Pt, Pd), Cu_3Sn_4 , which form replacement borders around large crystals of rustenburgite-atokite and pseudomorphs after their smaller crystals.

Late stage pneumatolytic PGM. The late pneumatolytic PGM are dominated by palladium minerals associated with minerals of Au-Ag, altaite, and hessite. The aggregates of these minerals grow over the earlier PGM and Au-Cu minerals, corroding them and forming separated nests. Commonly present are tellurium-bearing sobolevskite (PdBi), frudite (PdBi_2), non-zonal and zonal electrum and kustelite, bismuth-free geversite, antimony-free insizvaite, and cabriite (Pd_2CuSn).

Latest pneumatolytic PGM. The latest-formed mineral is sperrylite (PtAs_2), its crystal size varying from several microns to 11 cm. The sperrylite crystal boundaries cross-cut tetraferroplatinum, paolovite, insizvaite, geversite, rustenburgite, atokite, taimyrite, sobolevskite, frudite, cabriite, electrum and kustelite.

Mayakite PdNiAs in the Talnakh ore deposit, Mayak mine

Mayakite – monoclinic PdNiAs – was discovered and studied by T.L. Evstigneeva (Genkin *et al.*, 1976; Evstigneeva *et al.*, 2000) in the ore specimens from the eastern wing of the Komsomolskii mine, Talnakh ore deposit. Further on, mayakite from Talnakh deposit was described in several published studies (Begizov, 1977; Barkov *et al.*, 2000; Spiridonov, 2010).

The Mayak mine locates in the southeastern part of the Talnakh Deposit. The lower part of the Upper Talnakh ore intrusion and underlying hornfelses contain lenses and veins of massive sulfide ores of pentlandite-chalcocopyrite composition, sometimes with noticeable contents of magnetite (at the upper contact of the gently dipping veins) and ferroaugite. PGM form small metasomes in sulfide ores, which are distributed quite unevenly and are typically associated with either the upper selvage of gentle veins and bodies or lower contacts of xenoliths gabbro-dolerite and hornfelses in sulfide veins. PGM are more rare in silicate matrix at the exocontact zones of the sulfide ores. The size of the nests composed by noble metals ranges up to 7 mm, but typically less than 1 mm. The PGM are predominantly related to the middle stage and in some places contain significant amount of sperrylite.

Mayakite is present in magnetite-pentlandite-chalcocopyrite matrix as separated meta-crystals, oval-shaped metasomes, more often polymineral aggregates with tetraferroplatinum, polarite, palarstanide $\text{Pd}_3(\text{As}, \text{Sn})$, plumbopalladinite, stannopalladinite (Fig. 1–4). In these aggregates, mayakite and other PGM are often overgrown by platinum, palladium-bearing tetraauricupride AuCu (Fig. 5), and zvyagintsevite (Fig. 6). Also, mayakite is present in intergrowths with stillwaterite Pd_8As_3 (Fig. 6), and the contacts of mayakite with polarite are often traced by frudite borders (Fig. 7).

The locations where the mayakite and palladoarsenide specimens were taken for microprobe analysis are marked by numbers in the figures; the numeration of analyses in the figures and tables is identical. The chemical composition of mayakite is quite constant with respect to main components (Table 1). The contents of impurity elements vary quite widely (wt.%): Pt 0–1.4, Fe 0.1–0.5, Au 0–0.2, Pb 0.01–0.4. The average composition of mayakite is given by (based on 9 analyses, wt.%): Pd 43.31; Pt 0.36, Au 0.09; Ni 24.39; Fe 0.14; Cu 0.09; As 31.38; Pb 0.10; Sn 0.05; Bi 0.05; Te 0.02; Total 99.98%; Calculation for 3 atoms corresponds the formula $\text{Pd}_{0.98}\text{Ni}_{1.00}\text{Fe}_{0.01}\text{As}_{1.01}$.

Palladoarsenide Pd_2As as a product of mayakite PdNiAs alteration in the sulfide ores of the Talnakh deposit, Mayak mine

Palladoarsenide – monoclinic Pd_2As – was discovered and studied by V.D. Begizov in the ores of the Talnakh deposit, which are developed by the Oktyabrskii mine (Begizov *et al.*, 1973; Begizov, 1977). The first find of palladoarsenide is represented by small veinlets and irregular-

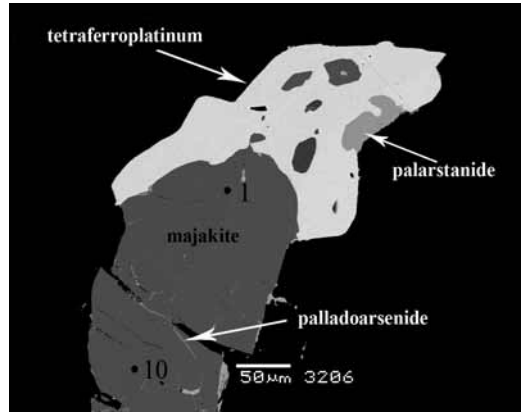
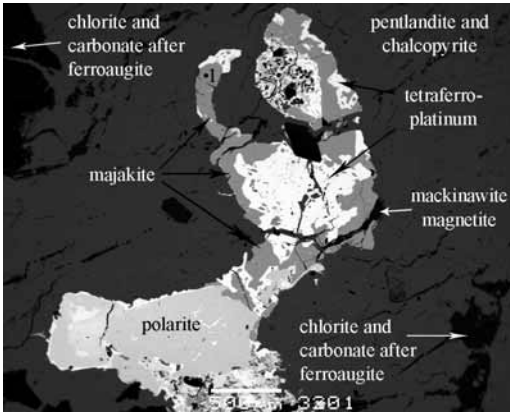


Fig. 1. Intergrowth of mayakite with tetraferroplatinum and polarite in the matrix of chalcopyrite and pentlandite. The ores contain veinlets of mackinawite, magnetite, chlorite, and carbonates. Ferroaugite is replaced by chlorite and carbonates. (BSE= image). From here on: specimen location: deep horizons of the Mayak Mine, Talnakh deposit. Numbers indicate the place and analysis for a particular mineral studied by electron microprobe.

Fig. 2. Intergrowth of mayakite, tetraferroplatinum, and palarstanide; thin streaks of palladoarsenide in mayakite (detail from Fig. 1) (BSE= image).

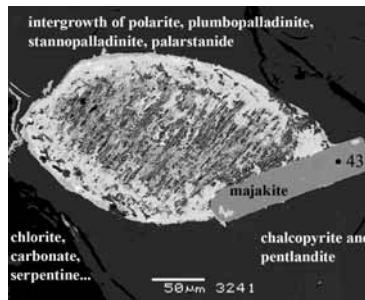
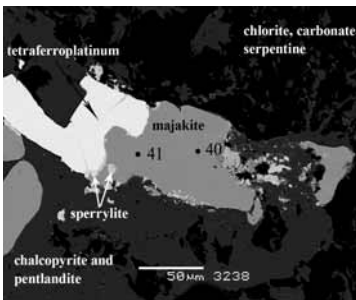


Fig. 3. Intergrowth of mayakite with tetraferroplatinum. Ferroaugite in sulfide matrix is replaced by aggregates of chlorite, carbonates, and serpentine (BSE= image).

Fig. 4. Intergrowth of a regular-shaped mayakite metacrystal with an oval aggregate of polarite plates, plumbopalladinite, stannopalladinite, and palarstanide in the matrix of chalcopyrite and pentlandite. Ferroaugite in the sulfide matrix is replaced by chlorite, carbonates, and serpentine (BSE= image).

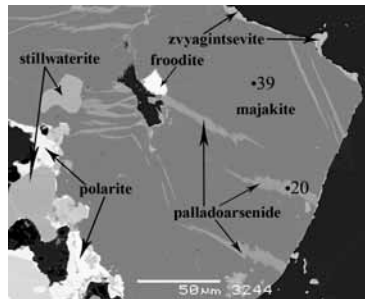
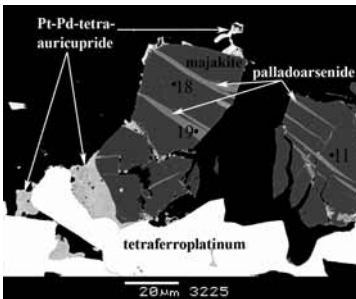


Fig. 5. Intergrowth of mayakite and tetraferroplatinum with a border of platinum and palladium-bearing tetra-auricupride. Mayakite contains a net of metasomatic palladoarsenide veinlets. (BSE= image).

Fig. 6. Intergrowth of mayakite, stillwaterite, polarite, zvyagintsevite, and frudite. Mayakite contains a net of metasomatic palladoarsenide veinlets. (BSE= image).

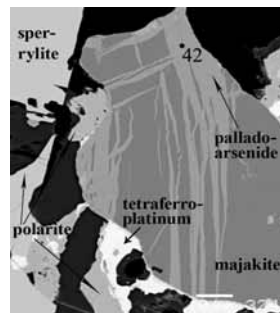
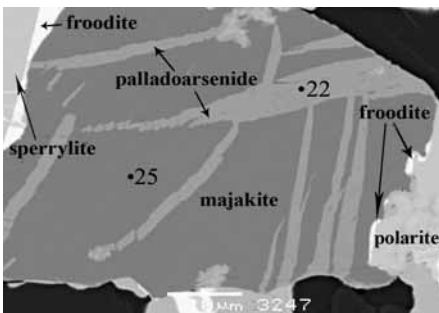


Fig. 7. Intergrowth of mayakite, polarite, and frudite. Mayakite contains a net of metasomatic palladoarsenide veinlets. (BSE= image). The scale bar — 10 microns.

Fig. 8. Intergrowth of mayakite, tetraferroplatinum, and polarite. Mayakite contains a net of metasomatic palladoarsenide veinlets. (BSE= image). The scale bar — 10 microns.

Table 1. Chemical composition of mayakite (wt.%) from magnetite-pentlandite-chalcopyrite ores, Mayak mine, lower horizons

Components	Analysis №								
	1	10	11	18	25	39	40	41	43
Pd	42.73	42.90	42.80	42.41	43.29	43.82	44.00	43.53	44.34
Pt	1.06	nd	0.80	nd	nd	1.40	nd	nd	nd
Au	nd	0.15	0.03	0.14	0.21	nd	0.03	0.22	nd
Ni	24.60	25.01	24.24	24.69	24.73	23.03	24.63	24.40	24.14
Fe	0.48	0.09	0.10	0.17	0.07	0.08	0.07	0.08	0.12
Cu	0.08	0.12	0.07	0.07	0.04	0.18	0.02	0.13	0.13
As	31.10	31.14	31.65	32.45	31.25	31.40	31.50	30.82	31.10
Bi	0.08	0.06	nd	0.07	0.09	0.07	nd	nd	0.11
Sn	0.05	0.08	0.13	nd	0.01	0.03	0.10	0.05	nd
Pb	nd	0.38	nd	0.01	nd	0.19	nd	0.30	0.06
Te	nd	0.02	0.07	nd	nd	nd	nd	0.09	0.01
Total	100.08	99.95	99.89	100.01	99.69	100.17	100.35	99.62	100.01
Atomic coefficient in formula calculated for 3 total atoms									
Pd	0.987	0.992	0.993	0.975	1.002	1.025	1.012	1.012	1.027
Pt	0.013		0.010			0.017			
Au		0.002		0.002	0.003			0.003	
Total	1.000	0.994	1.003	0.977	1.005	1.042	1.012	1.015	1.027
Ni	0.992	1.007	0.982	0.991	1.000	0.940	0.990	0.991	0.976
Fe	0.020	0.004	0.004	0.007	0.003	0.003	0.003	0.003	0.005
Cu	0.003	0.004	0.003	0.003	0.001	0.007	0.001	0.005	0.005
Total	1.015	1.015	0.989	1.001	1.004	0.950	0.994	0.999	0.986
As	0.983	0.984	1.004	1.021	0.990	1.004	0.992	0.980	0.985
Bi	0.001	0.001		0.001	0.001	0.001			0.001
Sn	0.001	0.002	0.003			0.001	0.002	0.001	
Pb		0.004				0.002		0.003	0.001
Te			0.001					0.002	
Total	0.985	0.991	1.008	1.022	0.991	1.008	0.994	0.986	0.987

Note: Electron microprobe Camebax, analyst I.M. Kulikova. Sb – not detected; nd – below detection limit.

shaped grains in chalcopyrite. It is not mentioned in later descriptions of the Norilsk Ore Field. As an accessory mineral, palladoarsenide was found in many deposits containing noble metals: chromites in the Stillwater layered basite-hyperbasite massif, USA (Volborth *et al.*, 1986), Bushveld, South Africa (Oberthür *et al.*, 2004), alpine type massifs of Oman (Auge, 1986; Ahmed, Arai, 2003), sulfide ores associated with Canadian komatiites (Chen *et al.*, 1993), Bulgarian porphyry-copper deposits (Auge *et al.*, 2005), and telethermal gold-palladium deposits (Cabral *et al.*, 2002).

We identified palladoarsenide in PGM aggregates with mayakite in the ores of deep horizons of the Mayak mine. Palladoarsenide forms straight and branching metasomatic veinlets in mayakite, incomplete pseudomorphs after small grains of mayakite (Fig. 5–8). The veinlets range up to 70 micron in length and 8–12 micron in thickness. In reflected light, palladoarsenide is almost undistinguishable from the surrounding mayakite. Therefore, its reliable identification is

only possible by electron microscopy. This type of analysis provides new quality estimates of the chemical composition of the rare palladium arsenide (Table 2).

In the palladoarsenide, significant path of palladium (up to 10% of atoms) is substituted by copper, nickel, and iron, and, to a less extent, by platinum and gold. Copper impurities can comprise up to 2.8 wt.%, and nickel 2.2 wt.%. Note that there is almost no copper is present in the parent mineral, mayakite. In the studied palladoarsenide, only a negligible fraction of arsenic atoms is substituted for lead, bismuth, tin, and tellurium. The average composition of the palladoarsenide from the metasomatic veinlets in mayakite of the Talnakh deposit is as follows (based on 4 analyses, wt.%): Pd 68.67; Pt 1.03, Au 0.13; Cu 1.49; Ni 1.35; Fe 0.34; As 26.10; Pb 0.17; Sn 0.03; Te 0.03; Bi 0.02. This composition recalculated for 3 formula atoms corresponds the formula $(\text{Pd}_{1.84}\text{Pt}_{0.02}\text{Cu}_{0.07}\text{Ni}_{0.06}\text{Fe}_{0.02})_{2.01}\text{As}_{0.99}$. Probably, the mechanism of palladoarsenide formation is: $2\text{PdNiAs} \rightarrow \text{Pd}_2\text{As} + 2\text{Ni} \ell + \text{As} \ell$.

Table 2. Chemical composition of palladoarsenide (wt.%) in metasomatic veinlets in mayakite from magnetite-pentlandite-chalcopyrite ores, Mayak mine, lower horizons

Components	Analysis №			
	42	19	20	22
Pd	68.08	69.15	67.84	69.59
Pt	3.75	nd	0.35	nd
Au	0.17	nd	0.36	nd
Cu	0.44	2.21	2.77	0.54
Ni	0.81	1.17	1.23	2.19
Fe	0.66	0.21	0.18	0.30
As	25.85	26.36	25.86	26.32
Bi	nd	0.06	nd	nd
Pb	nd	nd	0.44	0.23
Sn	0.07	nd	nd	0.04
Te	0.09	nd	0.04	nd
Total	99.92	99.16	99.07	99.21
Atomic coefficient in formula calculated for 3 total atoms				
Pd	1.850	1.840	1.810	1.845
Pt	0.056		0.005	
Au	0.002		0.005	
Cu	0.020	0.100	0.125	0.025
Ni	0.040	0.055	0.060	0.105
Fe	0.034	0.010	0.010	0.015
Total	2.002	2.005	2.015	1.990
As	0.998	0.995	0.980	1.005
Pb			0.005	0.005

Note: Electron microprobe Camebax, analyst I.M. Kulikova. Sb — not detected; nd — below detection limit.

Palladoarsenide occurs in the zones where ores are sectioned by tectonic fractures and contain veinlets and metasomes of chlorite, carbonates, serpentine, anhydrite, mackinawite, and magnetite. In these ores, ferroaugite is almost entirely replaced by chlorite, carbonates, serpentine, and smectites (Fig. 1, 3, and 4). The formation of palladoarsenide is likely to be related to epigenetic processes of low-grade metamorphism in condition of zeolite and prehnite-pumpellyite facies, which are well represented in the north-west of the East Siberian Platform (Spiridonov *et al.*, 2000; Spiridonov and Gritsenko, 2009). Mobility and addition of copper, which occurs on replacement of mayakite by palladoarsenide, is a characteristic process of low-grade metamorphism. Nickel and arsenic released due to destruction of mayakite might be involved in the formation of arsenide-carbonate veins, which are very common in the Talnakh region (Spiridonov and Gritsenko, 2009).

In the chromite ores of Stillwater (Volborth *et al.*, 1986) and Oman (Auge, 1986; Ahmed, Arai, 2003), as well as in the sulfide ores of the Thompson komatiite belt (Chen *et al.*, 1993),

palladoarsenide is present in the serpentine zones, which correlates with our observations in Talnakh.

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MINERALOGY OF WOOD TIN FROM THE DZHALINDA DEPOSIT

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Mineralogy of wood tin from the Dzhaldinda deposit located in the Khingan-Olonoy tin district has been studied. The wood tin is reniform aggregates up to 5 cm in size of concentric zoned cassiterite. Significant later quartz filling tiny fractures in cassiterite layers is close intergrown with cassiterite. Microinclusions of dzhaldindite were identified in wood tin; acanthite, preisingerite (?), native bismuth and thorium-bearing monazite-group minerals were found at the deposit for the first time.

11 figures, 2 tables, 8 references.

Keywords: wood tin, Dzhaldinda tin deposit, Khabarovsk krai, cassiterite, dzhaldindite, acanthite, preisingerite, native bismuth, monazite.

The Dzhaldinda deposit located in the central part of the Malyy Khingan ridge belongs to the Khingan-Olonoy tin-district; it is a typical member of the rhyolitic assemblage (Geology..., 1986). The deposit is related to the paleovolcanic neck filled with the Upper Cretaceous effusive quartz porphyry. These porphyries are silicified, sericitized, and kaolinitized along northeast striking fault zone. Ore mineralization is reniform aggregates of wood tin filling cavities and fractures in silicified rocks (Betekhtin, 1964).

Previously, we studied gemmological features of wood tin from the Dzhaldinda deposit for possible usage as gem material (Petrochenkov, 2011). This article discussed the mineralogical features of mineral of wood tin.

Mineralogy and structure of wood tin

According to the X-ray examination performed on a X^o PetroPRO device, analyst I.S. Naumova, wood tin from the Dzhaldinda deposit consists of cassiterite, quartz, and X-ray amorphous phase (average 76, 17, and 7%, respectively). The X-ray amorphous phase can be related to both cassiterite and opal; the latter frequently occurs at the deposits of rhyolitic assemblage.

The typical structural feature of the ores is the reniform cryptocrystalline aggregates of cassiterite up to 5 cm in size (Komarova, 1959). These aggregates are concentric zoned that is caused by the alternated variously colored zones. Large kidneys frequently composed of intergrown fine kidneys (from 3 to 15 mm) which are overgrown by new layers of cassiterite and include predominantly quartz zones (Figs. 1, 2).

Cassiterite occurs as dark grey and black concentric layers ranging from 0.05 to 0.5 mm in width (Figs. 3a, 3b). Part of these layers consist of fine (< 0.01 mm) crystals or are cryptocrystalline (Figs. 3c, 3d). Another part is massive aggregates of long prismatic and spear-shaped crystals reaching 0.3 mm along long axis (Fig. 3b). Parallel twins with size increased to 0.5 mm are common. Sector extinction in crossed polars is observed. Red and orange thin layers of cassiterite (~0.015 mm) are also characteristic (Fig. 3a).

Tiny spherulites of cassiterite of 0.01 to 0.04 mm in diameter occur in the quartz dominant zones (Fig. 3b). Black core of these spherulites is composed of cryptocrystalline or amorphous cassiterite. Rims of the spherulites consist of light brown tiny (0.005–0.008 mm) prismatic crystals. Aggregates of intergrown spherulites reach 0.3 mm in size. The spherulites are later than cassiterite forming kidneys and are simultaneous with quartz.

Quartz fills small veinlets up to 0.1 mm wide occurring as rather dense grid on separate places of wood tin (Fig. 3c). Concentric quartz veinlets and predominantly quartz areas up to 2 mm in size with tiny inclusions of cassiterite, and areas composed of quartz and cassiterite are typical (Figs. 2, 3d). Predominantly isometric complexly outlined centered crystals of quartz ranging from 0.005 to 0.07 mm in size of complex are randomly oriented, their forms are mainly isometrical with a complex contour, their size vary from (Figs. 3c, d). According Betekhtin (1964) and Genkin and Murav'eva (1963), quartz in wood tin is later than cassiterite and replaces the latter.



Fig. 1. Polished plate of wood tin from the Dzhallindadeposit. Vernadsky State Geological Museum, Russian Academy of Sciences, No 46722.

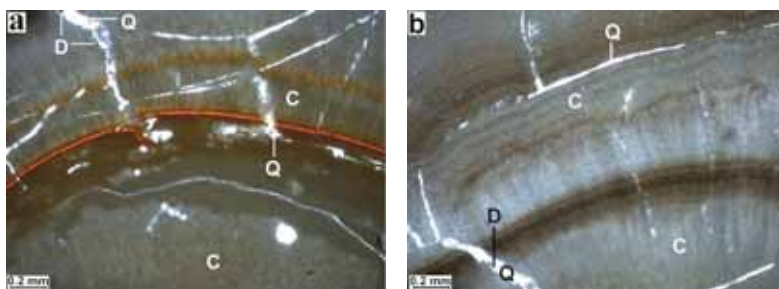


Fig. 2. Polished section of wood tin from the Dzhallinda deposit. (C) Cassiterite, (Q) quartz.

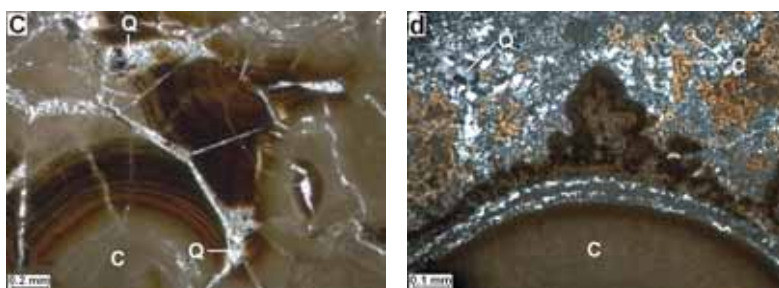


Fig. 3. Photomicrograph of fragments of wood tin: (a, b) nickols //, (c, d) nickols +. (C) Cassiterite, (Q) quartz, (D) dzhallindite.

Electron microprobe study

The chemical composition of wood tin was measured with a "Superprobe-8100" electron microprobe equipped with an "Inca" energy dispersion system at All-Russia Institute of Mineral Resources, analyst N.I. Chistyakova.

Electron microprobe measurements indicate that grey and black cassiterite, the contains (wt.%): up to 0.33 Fe, up to 1.0 Si up to 3 As up to 0.7 In, and up to 0.5 Ta. These are resulted from microinclusions of quartz and other minerals. We studied red veinlet in wood tin between the zone of filled by of grey cassiterite and the fine-grained cassiterite-quartz aggregate composed of (Fig. 3a). This veinlet is about 30 microns in thickness. In its central part a small crack (3 microns thick) is

observed. Red cassiterite contains Fe (0.67 – 1.69 wt.%), which is significantly higher than in grey cassiterite. Content of other measured elements is comparable. Probably, red color of cassiterite in wood tin is caused by inclusions of iron oxides formed as a result of recrystallization of cassiterite. Extremely fine size prevents accurate determination of these microinclusions with electron microprobe.

As a result, numerous inclusions of dzhallindite and for the first time inclusions of acanthite, preisingerite (?), native bismuth, and monazite were found in wood tin at the Dzhallinda deposit

Dzhallindite $\text{In}(\text{OH})_3$ was discovered by Genkin and Murav'eva (1963) at the Dzhallinda deposit. They reported dzhallindite as a

secondary supergene mineral replacing indite (FeIn_2S_4) that was also described for the first time at this deposit (Genkin, Murav'eva, 1963). Later, dzhalindite was identified in gold-base metal ore at the Bugdaya deposit (Eastern Transbaikalia). According to Kiseleva *et al.* (2008), dzhalindite was resulted from neutralization of thermal solutions corroding In-bearing sphalerite.

We have found dzhalindite in quartz veinlets and cassiterite-quartz zones of, where it occurs as numerous isometric inclusions ranging from 1–2 to 100 microns in size (Figs. 4–8). In binocular loupe, in polished section, inclusions of dzhalindite are white. The composition of dzhalindite studied here is consistent with previous data (Genkin, Murav'eva, 1963; Kiselev, 2008). The content of In in dzhalindite varies from 61 to 63 wt.%. Permanent Si (up to 0.61 wt.%) in dzhalindite indicates microinclusions of quartz in the mineral. The following elements are occasionally detected in dzhalindite, wt.%: up to 4.1 Fe, up to 0.56 P up to 0.99Al and up to 0.52 As.

In large segregations of dzhalindite, there are darker in back-scattered electron image square or trapezoidal zones of predominant size 7–12 microns (Fig. 6). Concentration of Fe in the dark zones is 1.5–4.1 wt.%, whereas in the bulk dzhalindite it does not exceed 0.13 wt.%. In the dark Fe-bearing zones of dzhalindite, concentration of In decreases that was previously observed in dzhalindite

from the Bugdaya deposit (Kiseleva, 2008). Proper iron minerals in the ark zones were not identified. Bivalent iron is probably replaces indium in the lattice of dzhalindite by close ionic radii of these elements.

The composition of dzhalindite calculated from theoretical formula $\text{In}(\text{OH})_3$ is as follows, wt.%: 69.2 In, 30.8 (OH) group. At the same time, according to previous articles (Genkin, Murav'eva, 1963; Kiselev, 2008) and this study, concentration of In in the mineral does not exceed 63 wt.% and content of the (OH) group is 28 wt.%, i.e., the deficiency of total is 9 wt.%, that is probably caused molecular water.

Rare elongated irregular-shaped inclusions of Ag sulfide of 0.5–3 microns in size are observed in dzhalindite (Fig. 7). According to the electron microprobe data, these inclusions contain, wt%: 85–88 Ag and 12.5–13 S that corresponds to the chemical composition of **acanthite** – Ag_2S .

Rare Bi arsenate (Table 1) closely intergrown with dzhalindite is observed in quartz. Isometric or elongated segregation of this mineral up to 20 microns in size is complexly countered (Fig. 8). In reflected light, "large" segregations of bismuth arsenate is black. Lamellar structure of the mineral (Fig. 9) is exhibited at high magnification. Width and length of lamella reaches 2 and 10 microns, respectively. Fan-shaped aggregates up to 15 microns in size are formed as a result of intergrowing.

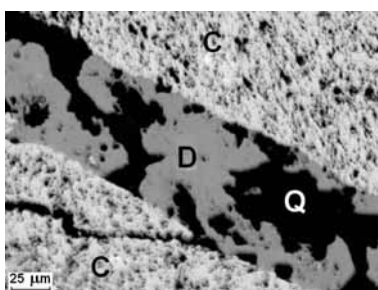
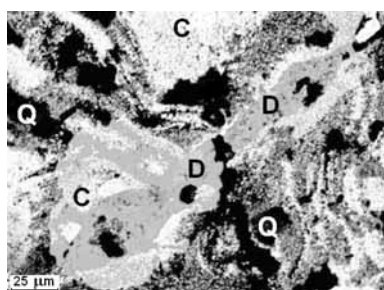


Fig. 4. Back-scattered electron image of inclusions of dzhalindite (D) in cassiterite (C) and quartz (Q).

Fig. 5. Back-scattered electron image of quartz veinlet (Q) with inclusions of dzhalindite (D) in cassiterite.

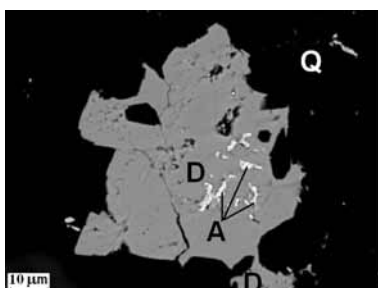
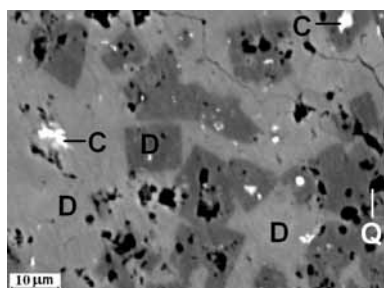


Fig. 6. Back-scattered electron image of Non-uniform structure of dzhalindite exhalations (D) with cassiterite (C) and quartz (Q) inclusions.

Fig. 7. Back-scattered electron image of inclusions of acanthite Ag_2S (A) in dzhalindite (D); (Q) quartz.

Table 1. Chemical composition of preisingerite (?) inclusions in wood tin

№ spectrum	Component, wt.%				Total
	As	Pb	Bi	O*	
1	16.23	4.44	60.23	15.96	96.86
2	15.39	3.62	58.58	15.23	92.82
3	15.00	3.66	59.42	15.14	93.22
4	15.05	1.91	58.76	15.20	90.92
5	14.76	1.80	58.75	15.24	90.55
6	14.48	0.80	60.54	15.80	91.62
7	14.28	0.76	59.33	15.19	89.56
8	15.90	4.76	58.74	15.60	95.00
9	16.29	4.21	58.47	15.74	94.71
10	15.86	6.03	56.81	15.46	94.16
11	16.43	5.22	58.17	15.85	95.67
12	15.64	4.18	58.48	15.39	93.69

Notes: A JXA-8100 electron microprobe (Jeol, Japan) operating at accelerating voltage 20 kV, current 20 nA, and beam diameter 2 microns. Analytical lines are AsL α , PbM α , BiM α . Standards were used: natural FeAsS, synthetic PbS, and Bi $_2$ S $_3$. Analyst N.I. Chistyakova. * – oxygen calculated by stoichiometry.

Preisingerite Bi $_3$ O(OH)(AsO $_4$) $_2$ and rooseveltite BiAsO $_4$ (Semenov, 2002) are similar in chemical composition to the revealed bismuth arsenate. Theoretical composition of preisingerite is as follows (wt.%): 66.9 Bi, 16 As, 0.1 H, and 17 O. The composition of rooseveltite is as follows (wt.%): 60 Bi, 21.5 As, and 18.5 O. According to electron microprobe data (Table 1), the average chemical composition of bismuth arsenate is as follows, wt.%: 58.86 Bi, 15.44 As, and 3.45 Pb, that is closer to the formula of preisingerite Bi $_{2.79}$ Pb $_{0.17}$ O(OH)(As $_{1.02}$ O $_4$) $_2$ than to that of rooseveltite (Bi $_{1.11}$ Pb $_{0.07}$) $_{1.18}$ As $_{0.82}$ O $_4$ (calculated on the basis of total cations). Taking in to account oxygen calculated by stoichiometry, average total is 93.4 wt.%. The deficient total is caused by the fine size segregations of bismuth arsenate and hydroxyl groups in the mineral. Presumably, Bi $^{+3}$ is replaced by Pb $^{+2}$, due to their close ionic radii and charge deficiency of cation group is balanced by hydroxyl group presenting in preisingerite. Additional study is required to accurately determine this phase.

Previously, rooseveltite and preisingerite were reported from the Oranzheviy ore field related in the Upper Kalganinsky pluton, Magadan region (Krinov, 2011). Rooseveltite occurring as tiny aggregates replacing bismuthinite and occasionally arsenopyrite is closely intergrown with preisingerite. Micro-

veinlets of these minerals also cut quartz. Interestingly, rooseveltite contains high Pb (3–6 wt.%, average 4.4 wt.%). These data are consistent with our results indicating possible existence of both minerals in wood tin at the Dzhalinda deposit. Krinov *et al.* (2011) referred the formation of rooseveltite and preisingerite to low-temperature decomposition of the earlier arsenic and bismuth minerals that also could occur at the Dzhalinda deposit.

Inclusions of **native bismuth** are found in the cassiterite-quartz zone (Fig. 10). These irregular-shaped inclusions reach 15 microns in size. According to the electron microprobe data, the inclusions contain Bi up to 99.8 wt.% (one analysis shows 0.4 wt.% Cu).

Numerous inclusions of Ce- and Th-bearing mineral – presumably **monazite-(Ce)** – (Ce,La,Y,Th)[PO $_4$] – were observed in dzhalindite enclosed in quartz (Fig. 11, Table 2). The larger idiomorphic prismatic crystals of this mineral reach 16 microns in length along long axis and 7 microns in width (Fig. 11).

The examination of single crystal testifies to the highly variable content of constituents (Table 2). Ca, Pr, Nd, Cm, Pb which can incorporate into the monazite structure were also measured. The presence of In appears to be caused by the inclusions of dzhalindite in which monazite is enclosed. The total content varies from 86.4 to 92.9 wt.% resulting from the size of monazite crystals (first microns) and complex chemical composition of these crystals. The absence of enhanced radiation in the specimens of wood tin indicates insignificant microinclusions of monazite.

The hourglass structure (Fig. 11) is clearly displayed in the crystal of this mineral enriched in Ce and Th. Three symmetrical zones are distinguished in the crystal: black rim and grey and white zones in the central part. Black rim (Table 2, spectra 5–6) has higher Y, La, Ce, Pr, Nd, Cm and lower Th and Ca in comparison with white zone in which Y was not detected (Table 2, spectra 3–4). Average composition of black rims corresponds to the formula calculated on the basis of total cations (Ca $_{0.08}$ Y $_{0.08}$ La $_{0.20}$ Ce $_{0.42}$ Pr $_{0.03}$ Nd $_{0.15}$ Sm $_{0.02}$ Pb $_{0.02}$ Th $_{0.01}$) $_{1.01}$ [P $_{0.99}$ O $_4$], that of white zones corresponds to the formula – (Ca $_{0.23}$ La $_{0.12}$ Ce $_{0.21}$ Pr $_{0.02}$ Nd $_{0.07}$ Sm $_{0.01}$ Pb $_{0.02}$ Th $_{0.31}$) $_{0.99}$ [P $_{1.01}$ O $_4$]. The intermediate content of these elements in grey zones (Table 2, spectra 1–2) corresponds to the following formula (Ca $_{0.12}$ Y $_{0.02}$ La $_{0.16}$ Ce $_{0.28}$ Pr $_{0.02}$ Nd $_{0.09}$ Sm $_{0.02}$ Pb $_{0.03}$ Th $_{0.20}$) $_{0.94}$ [P $_{1.03}$ O $_4$]. Thus, the formula of

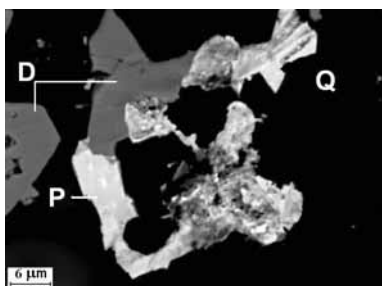


Fig. 8. Back-scattered electron image of inclusions of dzhalindite (D) and preisingerite (?) (P) in quartz (Q).

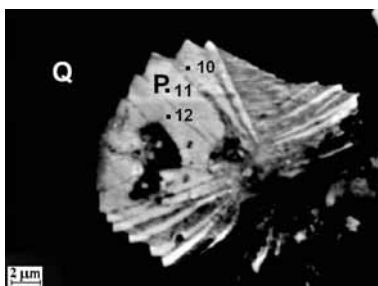


Fig. 9. Back-scattered electron image of inclusions of preisingerite (?) (P) in quartz (Q). 10–12 correspond to the spectrum numbers in Table 1.

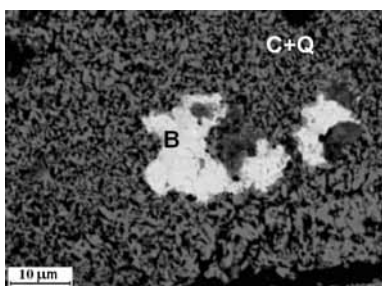


Fig. 10. Back-scattered electron image of inclusions of native bismuth (B) in cassiterite – quartz layer (C+Q).

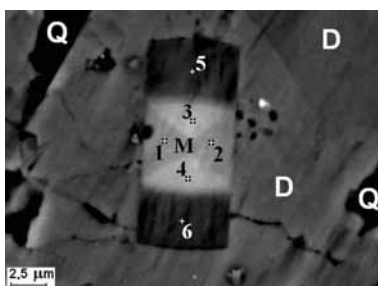


Fig. 11. Back-scattered electron image of hourglass crystal of the monazite group mineral (M) in dzhalindite (D). 1–6 correspond to the spectrum numbers in Table 2.

Table 2. Chemical composition of inclusions of monazite group minerals in wood tin

№ spectrum	Component, wt. %												
	P	Ca	Y	In	La	Ce	Pr	Nd	Sm	Pb	Th	O*	Total
1	11.84	2.84	0.81	1.92	8.32	15.50	1.68	4.67	0.86	1.61	17.61	25.25	92.92
2	11.42	2.80	0.63	1.59	8.00	13.84	0.52	4.43	0.96	2.75	16.99	24.02	87.95
3	11.12	3.21	0.00	0.56	5.97	11.82	0.82	3.42	0.44	2.04	25.64	23.51	88.55
4	11.45	3.20	0.00	0.53	5.32	10.28	0.79	3.57	0.71	1.22	25.89	23.69	88.65
5	12.47	1.16	2.24	1.41	9.94	20.67	1.43	7.50	1.59	2.28	0.64	25.08	86.41
6	12.51	1.10	2.72	1.60	9.90	20.80	1.64	8.10	1.24	1.37	0.50	25.27	86.75

Notes. A JXA-8100 electron microprobe (Jeol, Japan) operating at accelerating voltage 20 kV, current 2 nA, and beam diameter 2 microns. Analytical lines are PK α , CaK α , YL α , InL α , LaL α , CeL α , PrL α , NdL α , SmL α , PbM α , ThM α . Standards were used: synthetic AlPO $_4$, Ca $_2$ Fe $_2$ O $_7$, Y $_2$ O $_3$, InAs, LaPO $_4$, CeP $_5$ O $_{14}$, PrPO $_4$, NdP $_5$ O $_{14}$, SmP $_5$ O $_{14}$, PbS, ThO $_2$. Analyst N.I. Chistyakova.
* – oxygen calculated by stoichiometry.

black rims corresponds to monazite-(Ce), whereas central zones are Th-rich analogue of this mineral.

In this case, grey zones are considered as monazite-(Ce) because Ce is higher in formula than Th, while white zones correspond to Th-dominant analogue of monazite. More accurate determination of this mineral was failed due to fine aggregates of this phase. Note that microinclusions of the monazite group minerals of the similar chemical composition we found in spacimans of wood tin from the Dominion Creek placer, Canada.

Conclusions

Abundant wood tin consisting of fine to cryptocrystalline and amorphous cassiterite

as reniform aggregates is the feature of ore mineralogy at the Dzhalinda. Quartz filling thin fractures and small cavities in cassiterite and in places intimately intergrowing with the latter is in large quantities in wood tin.

In our opinion, the extensive replacement of cassiterite by quartz as reported by Betekhtin (1964) and Genkin and Murav'eva (1963) at comparable low pressure and temperature of fluids characteristic of the deposition of wood tin at the deposits of the rhyolitic assemblage is unlikely. Microinclusions of dzhalindite and bismuth minerals (preisingerite (?) and native bismuth) are undoubtedly later than cassiterite and are simultaneous with quartz. Usually magmatic monazite group minerals were probably in-

roduced into hydrothermal solution as a result of dissolution of quartz porphyries hosting orebodies.

The conclusion of the conditions of wood tin deposition at the Dzhalingda deposit is debatable and the decision of this problem requires the additional facts.

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MINERALOGY OF THE GLUBOSTROVSKOYE OCCURRENCE OF MASUTOMILITE ON THE SOUTHERN URALS

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Glubostrovskoye occurrence is a granite pegmatite with large plates of masutomilite and Li-containing muscovite. Topaz, beryl, manganocolumbite, cassiterite, monazite-(Ce), microlite and other accessory minerals also occur there. The structure of the pegmatite is characterized and the data on the morphology and chemical composition of minerals are resulted. The following concentrations of elements are determined in violet and pinkish-violet ferroan masutomilite (crystals are up to 5–20 cm in size) (wt.%): MnO 5.85; Li₂O 3.98; Rb₂O 1.67. Late pinkish beryl is enriched with rare alkalis, monazite-(Ce) – with samarium, zircon – with hafnium. In microlite we have found partial pseudomorphoses of parabiomicrolite on it. These pseudomorphoses contain the following elements (wt.%): BaO 10.10; UO₂ 4.98; Ta₂O₅ 73.60; Nb₂O₅ 5.49; SnO₂ 2.74. It is the first finding in the Urals and in Russia. 7 tables, 10 figures, 11 references.

Keywords: masutomilite, topaz, beryl, microlite, parabiomicrolite, Glubostrovskoye occurrence, Southern Urals.

History of discovery and geological structure of the Glubostrovskoye occurrence

Glubostrovskoye occurrence of lithium (lepidolite) was accidentally discovered in 5 km to the north-west from the Tayginka settlement, on the ridge of the Zayachiy mountains, in the boggy intermountain lowland in 200 m to the north from the coast of the Glubostrovo lake (Fig. 1). In 1956, pegmatite vein was discovered during laying of electric transmission facility in a hole dug for a support. During hunting in the late autumn when the bog has frozen slightly, geologist D.P. Groznetsky has found out large plates of lepidolite in the pegmatite blocks. Next year Slyudianogorsky party of the "Uralgeolnerud" trust drilled 40 drill holes of hand boring ("Empire" drill) to the depth up to 1–5 m in the peat layer, up to blocks and crumbs of rocks, on the Glubostrovskoye occurrence. During winter of 1958, Ilmenogorsky party of the Expedition No. 8 dug 40 bore pits to the depth up to 1.5 m (with soil freezing). During summer of 1958, survey-and-research works of the scale 1:10000 on the area of about 2 square km (Talantsev, 1959) was carried out. Results of the works appeared to be unfavourable: concentration of lithium in lepidolite reached up to 5.6 wt.% Li₂O, but in samples of the pegmatite its content was very low (0–0.5 wt.% Li₂O); small sizes of the vein and marshiness of the site were adverse to exploitation of the occurrence. The vein has been left, and we do not know the published works concerning its mineralogy. The mentioning about the Glubostrovskoye occurrence of lithium is in 12-th volume of "Geology of the USSR" (1973), in the table of deposits and occurrences

of precious and semiprecious stones of the Urals. Still then 14-years old S.V. Kolisnichenko has bought this book in Leningrad. But only in 1980 with a group of young geologists he could try to find the vein not knowing that it was in a bog. They have not found the vein. Only in autumn of 2008, shovelman Vasily Lezhnev from the Tayginka settlement – the amateur of minerals and the hunter – has accidentally discovered blocks of pegmatite with violet leaflets of mica. In 2009 he showed us this place. But it was impossible to conduct works in this place because of the presence of water. In dry summer of 2010 we had this opportunity; the water level fell almost one meter down. The history of this finding is briefly published (Kolisnichenko, Zakharov, 2010). Some times in that summer we carried out stripping work (with assistants – I.V. Karlov, A.V. Bobrov, T.M. Rakhmatullin, K.A. Zaharov, R.M. Rakhmatullin, D.A. Shumilin, A.G. Korablyov, and E.P. Makagonov) on the vein. On the place of two old bore pits one small mine has been engaged, a number of old bore bits has been cleared away and two new ones has been worked, dumps of the old bore pits have been partly reviewed and a number slimes has been received. The marshland has not allowed revealing completely the sizes, the form and the structure of the vein. But the data received appeared to be extremely interesting and are given below (we also use materials on the geology of the site).

According to the data of A.S. Talantsev (1959), the northern part of the ridge of the Zayachiy mountains represents submeridional anticlinal fold, overthrown to the west (see Fig. 1). The axial part of the structure consists of the Lower Proterozoic metamorphic biotite-

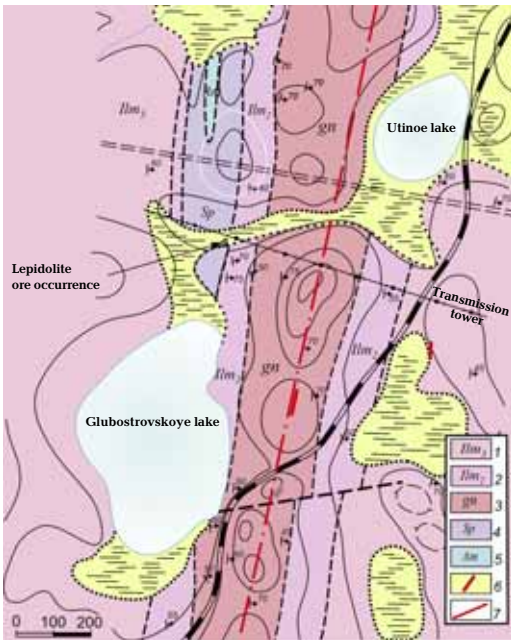


Fig. 1. Geological map of the northern part the Zayachiy ridge (according to Talantsev, 1959; simplified).

1 – amphibolites with biotite quartzite-gneisses layers; 2 – biotite gneisses with layers of amphibolites; 3 – microcline gneisses with orthite (allanite); 4 – serpentinites; 5 – amphibolites; 6 – granite pegmatites; 7 – tectonic fault. Glubostrovskoye occurrence of lithium micas is specified by an arrow.

microcline gneisses of the Vishnevogorsky series with orthite and magnetite, and its wings from the west and from the east consist of alternating amphibolites, biotitic gneisses and quartzites of the Ilmenogorsky series. The ultrabasic rocks have been attributed by him to peridotites (according to our data, these rocks are olivine – enstatite orthopyroxenites with 15–20% of olivine), serpentinitized, talked and amphibolized in a different degree and containing fine-grained dissemination of magnetite and chromite. Serpentinitized ultrabasic rocks are surrounded by amphibolic rocks and include rare vein bodies of plagioclases with a rim of radiate-lamellar tremolite (for example, in 100 m to the north-west from the Glubostrovskaya vein). All rocks are intersected by more young sublatitudinal faults of a wrench fault type (according to the form of lowlands we assume also presence of submeridional faults and faults of north-western directions). Several veins of granite pegmatites containing topaz and beryl (one them containing amazonite) are known in the axial part of the Zayachiy ridge (they are not examined in this article).

Glubostrovskaya vein of granite pegmatite was proven according to the data of hand boring. Its form appeared to be a drop-shaped body with prospective northeast strike. It was specified, that such form can be deformed, and the size of the vein can be overestimated owing to the vein's disruption (Talantsev, 1959), and northeast and southwest "tails" of the vein have not been confirmed. The following zones were allocated in its structure: marginal – fine-grained zone of aplitic pegmatite with chlorite and garnet (according to our data, the zone is not clearly graphical with gradual transition to graphical); intermediate zones – graphical and block, without sharp borders; and central zone with development of cleavelandite and lepidolite, considered as result of the replacement of a microcline belonging to the block zone (Fig. 2a).

As a result of our works on clearing of some accessible bore pits, driving of new open pits and survey of the occurrence's area by hand probe on about a meter depth it appeared, that pegmatite vein had another sizes, form, structure, and bedding (Fig. 2b). Its probable extent was more than 25 meters at the maximal seen thickness of about 10 m and southwest dip. The northern part of the vein is appeared to be intersected by a fault or eroded by ancient water streams of the former small river channel on a place of the present bog. Because of a thick layer of peat in the vein's environment (up to 4–5 m) its host rocks were not established authentically and were shown on the vein's structure map as serpentinites. However we have taken a fine crumb of grains and aggregates of Na-Ca amphiboles (more characteristic for amphibolites or gneisses) from bottoms of some bore pits situated outside the vein.

Zones of the pegmatite on their structure basically were similar to those allocated earlier with that only a difference that block zone was much smaller, and aggregates of lepidolite with albite, topaz, beryl, and accessory minerals were mainly located in it. The part of its quartz nucleus was also opened in its northeast wall.

Works of the Ilmenogorsky party on this site practically were not accompanied by analytical researches (except for definition of contents of lithium and beryllium). In their report the following minerals composing the vein (according to their external attributes) have been briefly mentioned: microcline-perthite, albite, quartz, muscovite, topaz, lepidolite, zinnwaldite, fluorite, chlorite, and garnet.

But the first stripping works of 2010 have surprised with a finding of large violet plates of lepidolite (up to 10–20 cm in diameter), "co-

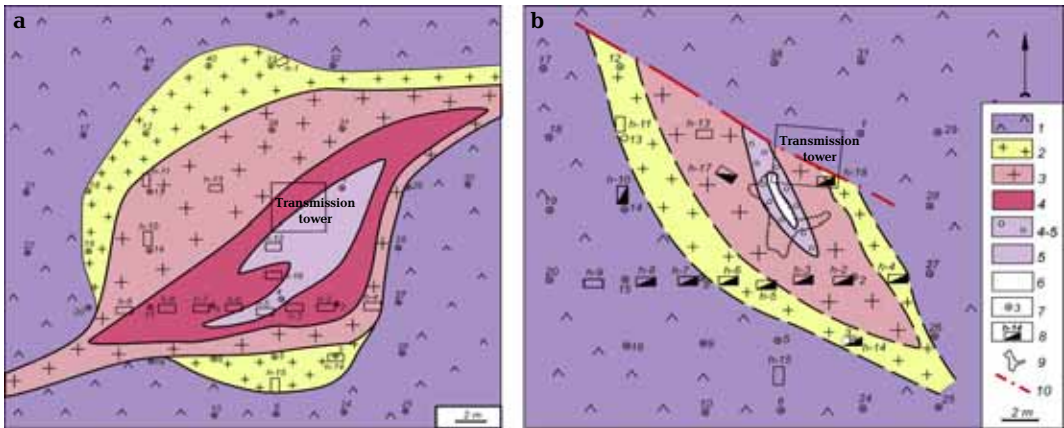


Fig. 2. The scheme of zonation of the pegmatite (a – according to Talantsev, 1959; b – our data).

1 – host rocks – "serpentinites" (gneisses, more probable); 2 – medium-grained not clearly graphic quartz-oligoclase-microcline pegmatite with siderophyllite, passing into small-block large-graphic pegmatite; 3 – graphic quartz-microcline pegmatite with muscovite; 4 – «central pegmatoid block» (a; according to Talantsev, 1959); 4–5 – block zone with masutomilite; 6 – uranium nucleus; 7 – bore holes of hand drilling; 8 – bore pits (cleaned are underlined); 9 – mine contour; 10 – prospective fault.

lumns" of translucent bluish and grayish-white topaz (up to 5–20 cm), spessartine, columbite, and also green-yellowish and pinkish beryls (Kolisinichenko, Zakharov, 2010). According to further researches, lepidolite has been determined as masutomilite, and according to studying of pegmatite samples and slices (from the vein's crumb), oligoclase, manganocolumbite, monazite-(Ce), cassiterite, microlite, parabariomicrolite, zircon, Ca- and Mn-containing almandines, allanite-(Ce), siderophyllite (chlorite and fluorite were not found) have been revealed. In slices from a crumb of host rocks from bottoms of bore pits situated outside the vein in addition to earlier specified minerals ferroactinolite, hastingsite, magnesiohornblende, Fe-containing diopside, epidote, magnetite, ilmenite, and chalcopyrite (diagnosed on physical properties, X-ray diffraction patterns and partial microprobe analyses) were determined.

Microcline and quartz prevail in peripheral medium-grained not clearly graphical zone of the pegmatite with a thickness of no more than 1 m (with gradual transition to a large-graphical small-block zone). Oligoclase of No. 12–15 is less revealed, Ca-containing almandine, siderophyllite, limonitized magnetite occur more seldom, pyrite grains in the form of cubes up to 1–1.5 mm in size and also black-brown allanite-(Ce) almost totally replaced by microgranular aggregate of presumably nontronite and hisingerite occur as rare grains. Rare bar-like grains of siderophyllite up to 2–3 cm in size and allanite-(Ce) up to 1.5 cm in size (also Mn-containing almandine and translucent yel-

low-brownish zircon of a "hyacinth" facet in the form of sheaf-like joints up to 2–3 mm) occur in the large-graphical pegmatite zone.

Graphical quartz-microcline pegmatite composes the main volume of an opened part of the vein. The width of this zone is about 1–2 m. Large blocks of white and yellowish-white feldspar more than 10–20 cm in size represent a typical "Jewish" stone with various patterns of quartz ingrowths in sectors of growth of different microcline facets containing about 5–8% of albite ingrowths. Small allocations of aggregates of twinned albite grains up to 1–2 cm in size, plates of grey muscovite (sometimes having surfaces of joint growth with quartz, microcline, albite and Mn-containing almandine), and also fine grains of the following accessory minerals – manganocolumbite, magnetite, zircon, monazite-(Ce) – occur in the vein's zone. The quantity of albite and size of quartz grains, pinkish-grey muscovite and spessartine gradually increases in this zone in the direction to the center of the vein.

Transition to the block zone is indistinct and also is insufficiently opened because of the mining-and-technical conditions. The zone begins with a rather narrow "strip" (10–15 cm) with an abundance of thick-platy pinkish-green-gray muscovite, quartz and split cleavelandite, with original branches-veins in the graphical zone reflecting a dynamic regime existing during the formation of the vein. In one of big samples with grayish (sometimes translucent microcline), albite, spessartine, manganocolumbite, and monazite-(Ce) occur grains of green-yellowish beryl (up to 3–6 cm

in size), and also a bluish translucent topaz 1–2 cm in size (of polygonal-conic form) as a result of co-crystallization with feldspars and quartz. Aggregate of muscovite with albite, quartz, and microcline passes in large – and not clearly graphical small-block zone forming an original subzone (with a width of about 20–30 cm) with prevalence of albite and quartz and rather well development of large thick plates of pinkish-violet (lilac) masutomilite up to 5–20 cm in diameter and polygonal-conic grains of grayish- or bluish-white topaz (up to 10–20 cm in length) partly replaced by the fine-grained aggregate of dark-violet Mn-containing muscovite. Some small grains of topaz are replaced totally with preservation of their primary form.

The subsequent subzone 10–15 cm in width is formed by the medium-grained albite aggregate, light-colored pinkish-violet muscovite (grains of 0.5–1.5 cm in size), adularia-like microcline and almost colorless quartz. We also meet here isometric-platy grains of manganocolumbite and cavities of dissolution on a place of some mineral with compound-twisting borders. In these transitive subzones the most interesting accessory mineralization is also concentrated.

Typical large-block quartz-microcline pegmatite with a thickness not less than 1 m with rare albite and mica is stripped only partly, as well as its quartz nucleus. Huge in size crystals of microcline (up to 30–40 cm) have induction surfaces of joint growth with rare small blocks of light grey quartz. In the extracted pieces of quartz there are many healed cracks. We also meet here sites of small drusy cavities where on crystals of transparent grayish quartz from below there is a thin white peripheral zone, and on the top facets there is a powder of rosette-like fine-grained aggregates of pale lilac and pinkish-yellowish mica-"foamy". This mica overgrows also on fragments of microcline grains in the form of dense crustified aggregates with formation of residual microcavities in which fine prismatic crystals of colorless transparent quartz with rhombohedron facets on "head" crystallized later. The same quartz sometimes also occurs on walls of cavities in places of dissolution of subsometric grains of unstated mineral (possibly fluorite, but we have not found relicts).

Methods and results of investigation of pegmatite minerals and host rocks minerals

A number of minerals are crystallomorphologically characterized (we use Fedorov table

SF-4 as a goniometer; idealized crystal forms are drawn with the help of the program SHAPE-7.1 and CoreDRAW-11). Some minerals are investigated optically (in immersion with a set of standard liquids ИЖ-1) and in reflected light on the microscope Olympus BX51. X-ray diffraction patterns of minerals are obtained on X-ray diffractometer DRON-2.0, CuK α -radiation, speed of record 0.02°/min, powder pattern are obtained on URS-2.0 with RKD-57.3 mm, Fe-radiation and are identified on the ASTM base with the control of prevalence of heavy elements in their structure by X-ray fluorescence analysis on the device INNOV. The fluorescence spectrum of a powder of different beryls is obtained on the pulse cathodoluminescence analyzer KLAIVI-R. For the following minerals: siderophyllite, oligoclase and allanite-(Ce) the spectra of prevailing elements in their structure (REMMA-202M) are received. The chemical composition of minerals is determined in the Institute of mineralogy of the Russian Academy of Sciences, Urals Branch (Miass) by silicate analysis; rare alkalis are determined by atomic absorption analysis (Perkin-Elmer 3110). X-ray microprobe analysis is executed by V.A. Muftakhov in the Fersman Mineralogical Museum of the Russian Academy of Sciences (Moscow) on the X-ray microanalyzer JEOL-733 Superprobe with energy dispersive spectrometer LINK, operated at 20 kV, absorbed current at 5 nA and beam diameter of 2 microns. Standards are as follows: quartz, albite, orthoclase, diopside, barite, ilmenite, scheelite, fluorapatite, chlorapatite; metals: Mn, Ta, Nb; oxides of Zr, Sn, U, Th, Sb, Y, Dy; phosphate glasses: LaP₅O₁₄, CeP₅O₁₄, PrP₅O₁₄, NdP₅O₁₄, SmP₅O₁₄.

Potassium feldspar from the graphic pegmatite, according to its ordering may be attributed to an intermediate microcline with a 0.8 degree of X-ray triclinity and contains about 5–6 mol.% Na-phase. In the block zone of pegmatite, microcline is close to the maximal that is typical to the majority of granite pegmatite veins.

Among the micas from the Glubostrovskaya vein, muscovite and masutomilite are most widespread, and siderophyllite and illite are rare.

Siderophyllite is a black mica of the marginal zone of the vein. It is diagnosed only on presence of K, Si, Al, and Fe (practically without Mg) in energy dispersive spectrum and according to the refraction index $n_m \approx 1.63$; it contains in its structure about 2–3 wt.% F (according to microprobe analysis with WDS). In some samples it is partly hydrated.

Table 1. Chemical composition of micas of the Glubostrovskaya vein (wt.%)

No an.	SiO ₂	Al ₂ O ₃	FeO	MnO	K ₂ O	Na ₂ O	Rb ₂ O	Li ₂ O	F	H ₂ O	Total
1	44.70	30.52	5.17	1.28	9.40	0.46	1.02	0.97	2.40	3.90	99.82
2	45.50	21.80	4.27	5.85	9.60	0.25	1.67	3.98	7.70	—	100.64*
3	46.15	34.72	0.52	1.20	10.00	0.13	0.58	0.02	n.d.	5.65	98.97
4	n.d.	n.d.	0.27	0.17	10.70	0.46	0.40	<0.02	n.d.	n.d.	
Empirical formulas (muscovite is calculated on 7 cations, masutomilite — on 8 cations)											
1	(K _{0.89} Na _{0.07} Rb _{0.05}) _{1.01} (Al _{1.30} Li _{0.29} Fe _{0.32} Mn _{0.08}) _{1.99} (Si _{2.62} Al _{1.38}) ₄ O ₁₀ (OH) _{1.02} F _{0.56} ;										
2	(K _{0.98} Rb _{0.09} Na _{0.04}) _{1.11} (Li _{1.26} Al _{0.93} Mn _{0.40} Fe _{0.29}) _{2.90} (Si _{2.87} Al _{1.13}) ₄ O ₁₀ F _{1.97} ;										
3	(K _{0.96} Rb _{0.03} Na _{0.02}) _{1.01} (Al _{1.83} Mn _{0.06} Fe _{0.03} Mg _{0.02} Ca _{0.01} Li _{0.01}) _{2.00} (Si _{2.76} Al _{1.24}) ₄ O ₁₀ (OH) _{1.51} .										

Note. 1 — lithium-ferriferous muscovite, 2 — ferroan masutomilite, 3 — manganous muscovite dark-violet (pseudomorphoses on topaz), 4 — pinkish muscovite ("foamy"). FeO content is calculated from Fe₂O₃; water is determined as a loss during calcination (minus fluorine). * — in analysis 2 it is also revealed 0.02 wt. % Cs₂O. n.d. — not determined, dash — element is not revealed. Analyst M.N. Maljaryonok — chemical analyses (analyses 1–3) and atomic absorption (rare alkalis and analysis 4).

Table 2. Results of calculation of X-ray patterns of lithium-ferriferous muscovite (1), ferroan masutomilite (2), pseudomorphoses of muscovite (3) on topaz and late muscovite-"foamy" (4)

1		2		3		4	
<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>
9.96	51	9.96	33	10.04	53	10.01	29
4.98	16	4.97	7	5.02	40	5.01	31
3.486	2	3.86	6	4.48	2	4.45	1
3.321	100	3.637	10	3.501	2	3.488	1
3.199	4	3.349	14	3.344	100	3.335	100
2.990	4	3.310	100	3.203	3	3.195	1
2.861	2	3.085	14	2.993	3	2.987	1
2.786	2	2.899	11	2.795	3	2.790	1
2.569	1	2.672	6	2.558	3	2.556	1
2.491	9	2.585	7	2.507	11	2.503	12
1.993	34	2.482	11	2.006	51	2.127	1
1.648	1	1.987	37	1.664	1	2.003	62
1.423	2	1.657	4	1.651	1	1.669	1
		1.516	2	1.524	1		

Note. X-ray diffractometer DRON-2.0, CuK α -radiation, 0.02°/min. Tests 1 and 2 — with vaseline. Analyst T.M. Rjabuhina.

According to the composition, pinkish-greenish-grey large-plate **muscovite** from the block zone of the vein is lithium-ferriferous and containing F, with a considerable impurity of manganese that cause a pinkish shade of mica (Table 1, analysis 1); its X-ray diffraction pattern is closer to the polytype 1M (Table 2). Intergrowths of muscovite with quartz, albite, topaz and microcline are most often, but we also meet its intergrowths with masutomilite (without replacement features) and accessory minerals.

Masutomilite in this vein amazes us with size of plates (up to 15–20 cm) and depth of

pinkish-violet shade of colour (Fig. 3). Unfortunately, long contact with water in summer and freezing in winter has led to quite often fractionizing of samples during their extraction. Masutomilite is ferroan, containing the following elements (wt.%): MnO 5.85, Li₂O 3.98 and Rb₂O 1.67 (Table 1, analysis 2), polytype 1M. According to the A.S. Talantsev's report (1959), this mineral ("lepidolite") contained 5.6 wt.% Li₂O (without indication of the method used and without the complete analysis).

Fine-grained dark-violet muscovite, forming partial or full pseudomorphoses on topaz (Fig. 4), is distinguished by small impurity of iron, lithium and rubidium (Table 1, analysis 3) with presence of 1.2 wt.% MnO (as in lithium-ferriferous large-lamellar muscovite). Its X-ray pattern is closer to the polytype 2M₁.

Aggregates of late pinkish and pinkish-yellowish mica-"foamy" from the central part of the vein are composed by muscovite (according to the X-ray diffraction pattern — illite 2M₁), poor in Fe and Mn (Table 1, analysis 4). Its thin intersecting small veins sometimes occur in dark-violet muscovite pseudomorphoses on topaz.

Topaz forms two differing morphological types. Earlier bluish translucent and transparent grains of topaz are small (up to 2 cm), with rhomboid section of the habitus prism *m* {110}. They form aggregates with lithium-ferriferous muscovite and greenish-yellowish beryl in the subzone of transition to the block pegmatite. In the block zone, in aggregates with masutomilite topaz occurs in crystals up to 10–20 cm in size, cloudy, greyish-or bluish-white in colour, with "square" section of habitus prism *l* {120}, advanced basal plane *c* {001} and small facets of a prism *y* {021}, visually determined on some heads of crystals replaced by muscovite (see Fig. 4b). Several clear iso-

metrical pseudomorphoses on topaz are found in grey quartz of the quartz nucleus. The chemical composition of topazes was not determined, but according to the dimension $d_{040} = 2.198 - 2.200 \text{ \AA}$ on their X-ray patterns, the content of fluorine in topazes is about 18.5–19 wt.% (Popova, Dolgopyat, 1989).

Different in colour **beryl** (Fig. 5), differs also in the composition of impurities. Pinkish beryl from the block zone contains more alkalis (Li and Rb – in 4 times, Cs almost in 10 times, Na and K – almost twice) in comparison with greenish-yellowish beryl from the association with lithium-ferriferous muscovite (Table 3). A wide strip in the region of about 720 nm is precisely shown in the cathodoluminescence spectrum of pinkish alkaline beryl. X-ray pat-

terns of differently coloured samples of beryl are practically identical.

Garnets in pegmatite have different composition, colour and size and vary as follows: from rare and fine grains of pale-pink **Ca-containing almandine** in the endocontact zone of the vein and orange-red **manganous almandine** in the graphic zone up to rather large pinkish-orange and pale-orange spessartine (up to 1–1.5 cm in diameter) in the block zone of the pegmatite (Table 4.).

Manganocolumbite in the graphic zone of the pegmatite is fine-grained (up to 1–2 mm in size), short-columnar or tabular and lengthened along the axis [001] (Fig. 6a, b), and in the block zone it is tabular, flattened along the axis [100] and reaches up to 1–2 cm in size (Fig. 6c, d).

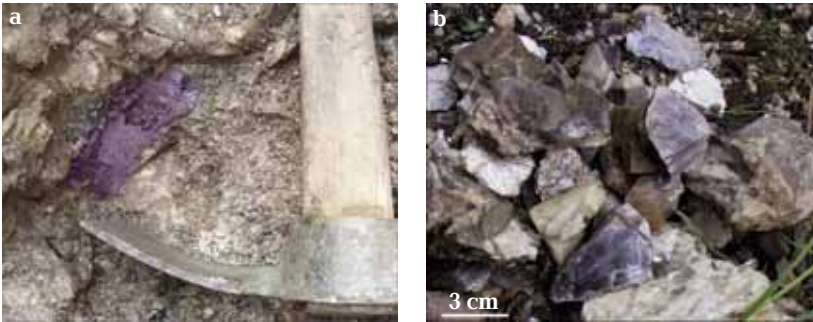


Fig. 3. *Masutomilite* (20 cm) in the mine wall (a) and its fragments in the dump (b).

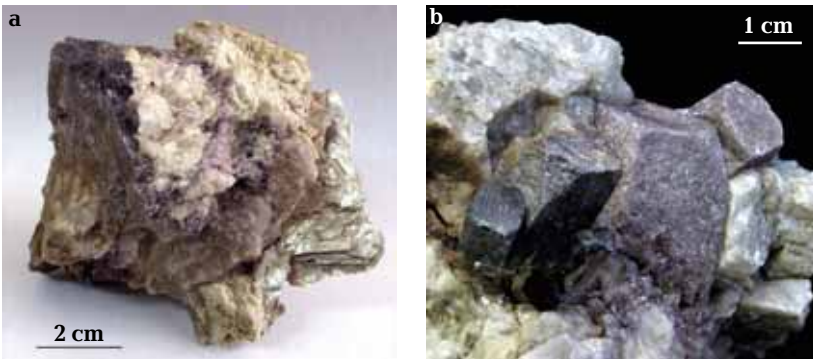


Fig. 4. Topaz (in the center), replaced from edges by dark-violet fine-grained muscovite (a), and complete pseudomorphoses of such muscovite on topaz with preservation of crystals form (b).

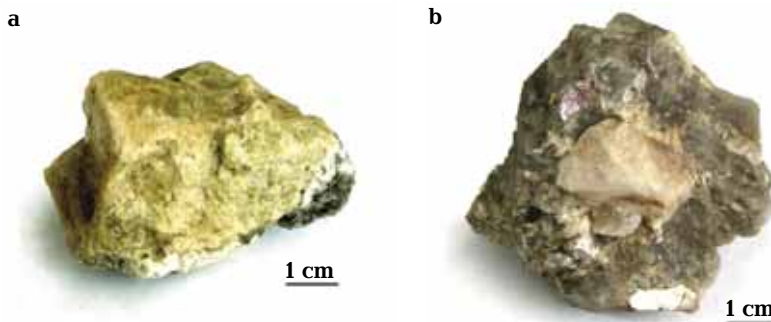


Fig. 5. Two types of beryl: early greenish-yellow (a) and later pinkish alkaline (b).

Table 3. Contents of impurities in beryl different in colour

Colour of beryl	ppm			wt. %	
	Li	Rb	Cs	Na	K
Yellowish	101.7	16.7	28.3	0.08	0.04
Pinkish	400.0	77.0	277.5	0.14	0.07

Note. Atomic-absorption method, analyst M.N. Maljaryonok.

Table 4. Chemical composition of garnets from the pegmatite (microprobe, wt.%)

	1	2	3	4
SiO ₂	37.55	36.60	36.43	36.47
TiO ₂	0.07	0.02	—	—
Al ₂ O ₃	21.05	20.53	20.58	20.65
FeO	24.90	24.03	8.14	4.14
MnO	6.59	17.53	34.75	38.72
MgO	0.38	0.06	—	—
CaO	9.14	1.02	0.22	0.30
Total	99.68	99.79	100.12	100.28

Formulas (calculated on 8 cations)

1	(Fe _{1.68} Ca _{0.79} Mn _{0.45} Mg _{0.05}) _{2.97} Al _{2.00} (SiO ₄) ₃ ; Ca-containing almandine
2	(Fe _{1.66} Mn _{1.23} Ca _{0.09} Mg _{0.01}) _{2.99} Al _{2.00} (SiO ₄) ₃ ; Mn-containing almandine
3	(Mn _{2.42} Fe _{0.56} Ca _{0.02}) _{3.00} Al _{2.00} (SiO ₄) ₃ ; Fe-containing spessartine
4	(Mn _{2.69} Fe _{0.26} Ca _{0.03}) _{3.00} Al _{2.00} (SiO ₄) ₃ ; spessartine

The composition of the early manganocolumbite from the graphic zone and the same mineral in internal parts of tabular grains from the block zone is characterized by increased contents of Nb₂O₅ (50–60 wt.%) and FeO (1.7–2.1 wt.%) and lower concentration of Ta₂O₅ (19–27 wt.%); later zones of manganocolumbite tabular crystals contain 37–48 wt.% Ta₂O₅ (Table 5; Fig. 7). A slight surplus of cations (Mn + Fe) is observed in the empirical formulas calculated according to the results of microprobe analyses that can be caused by presence of thin films composed by hydroxides of these elements on the thinnest cracks in manganocolumbite.

Fine grains of brown **cassiterite** (1–2 mm in diameter), inside which it is possible to distinguish darkly and light-coloured thin zones, are presented by subisometrical twins on {101} with habitus facets of the dipyrramids {111} (Fig. 8). Its most light, brownish-yellowish zones (containing 99.4 wt.% SnO₂) include insignificant impurities of MnO and Ta₂O₅ (0.07–0.12 wt.%). The composition of black-brown grain is as follows (wt.%): SnO₂ 86.64; Ta₂O₅ 10.64; Nb₂O₅ 0.91; MnO 1.73; FeO 0.07; total 99.99 (average from two analyses). It corresponds to the empirical formula

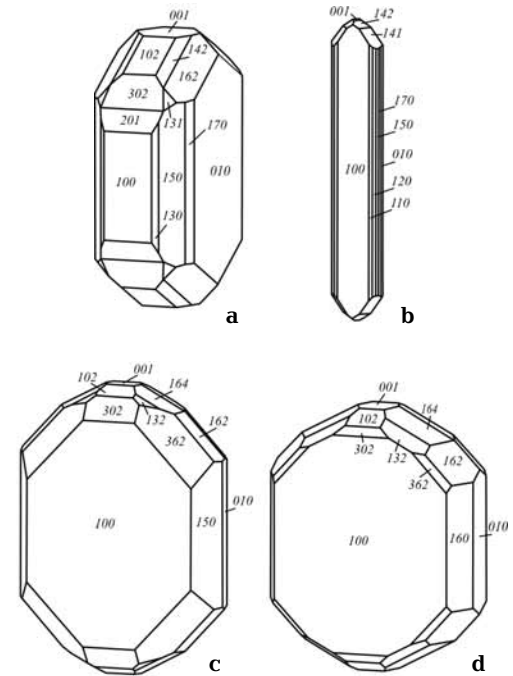


Fig. 6. Form of crystals of manganocolumbite from the graphic pegmatite (a, b) and block zone of the vein (c, d).

(Sn_{0.88}Ta_{0.07}Mn_{0.04}Nb_{0.01})O₂. In other similar grains the ratio Mn:Ta = 1:2, that gives the basis to assume the presence of about 4 mol.% of "manganotantalite" end member MnTa₂O₆ (or microinclusions of manganotantalite, yet not found) in cassiterite.

Crystals of **monazite-(Ce)** in the pegmatite are brownish-yellow, transparent up to translucent, up to 1–3 mm in size. They vary in shape, but they are rather simple in form (Fig. 9). Among the rare-metal elements, in the earlier crystals prevail Ce and Nd, and in the later monazite (from the block zone) prevail Ce and Sm; the latest monazite also contains more thorium at the relative uniformity of the composition (Table 6).

Fine-grained crystals of **microlite** (up to 1–1.5 mm in diameter) are very unusual in this vein: they are translucent grayish-yellow, greenish and brownish-greenish octahedrons with narrow and rare "strips" of rhombic-dodecahedron facets and even more rare tiny facets of the cube (according to their appearance, grains can be accepted for xenotime). Sometimes crystals are spotty in colour or obviously zonal, cloudy brownish, with a greenish translucent or transparent peripheral zone. Impurities of Sn, U and insignificant of Ba are

Table 5. Chemical composition of manganocolumbite crystal zones (microprobe, wt.%)

	Fig. 7a			Fig. 7b			
	1	2	3	4	5	6	7
MnO	17.60	17.23	17.32	18.93	17.70	18.16	17.34
FeO	1.68	0.35	0.32	0.18	—	—	2.07
Nb ₂ O ₅	54.45	33.40	33.14	52.23	39.82	44.50	60.89
Ta ₂ O ₅	25.50	48.34	48.56	27.44	41.35	37.48	18.80
TiO ₂	0.70	0.65	0.64	0.55	0.65	0.11	0.54
SnO ₂	—	—	—	0.28	0.11	0.03	—
Total	99.93	99.97	99.98	99.61	99.63	100.28	99.64
Formulas (O=6)							
1	(Mn _{0.93} Fe _{0.09}) _{1.02} (Nb _{1.53} Ta _{0.43} Ti _{0.03}) _{1.99} O ₆						
2	(Mn _{1.01} Fe _{0.02}) _{1.03} (Nb _{1.05} Ta _{0.91} Ti _{0.03}) _{1.99} O ₆						
3	(Mn _{1.02} Fe _{0.02}) _{1.04} (Nb _{1.04} Ta _{0.92} Ti _{0.03}) _{1.99} O ₆						
4	(Mn _{1.01} Fe _{0.01}) _{1.02} (Nb _{1.49} Ta _{0.47} Ti _{0.03} Sn _{0.01}) _{2.00} O ₆						
5	Mn _{1.01} (Nb _{1.21} Ta _{0.76} Ti _{0.03}) _{2.00} O ₆						
6	Mn _{1.01} (Nb _{1.32} Ta _{0.67} Ti _{0.01}) _{2.00} O ₆						
7	(Mn _{0.89} Fe _{0.11}) _{1.00} (Nb _{1.67} Ta _{0.31} Ti _{0.02}) _{2.00} O ₆						

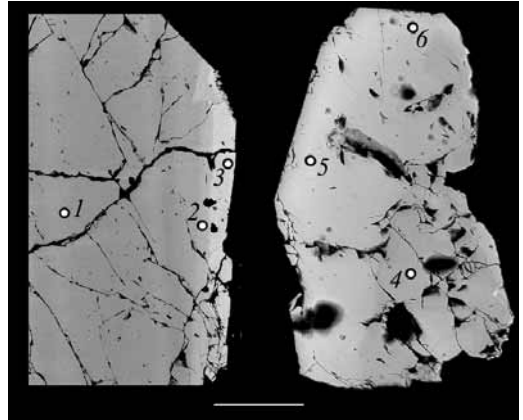


Fig. 7. Parts of zonal crystals of manganocolumbite. BSE (figures near points – numbers of analyses in Table 5).

Note. Analyses 1–3 and 4–6 – consecutive zones of two crystals from the center to the edge (from the block zone of the vein); analysis 7 – earlier manganocolumbite from the graphic zone of the pegmatite.

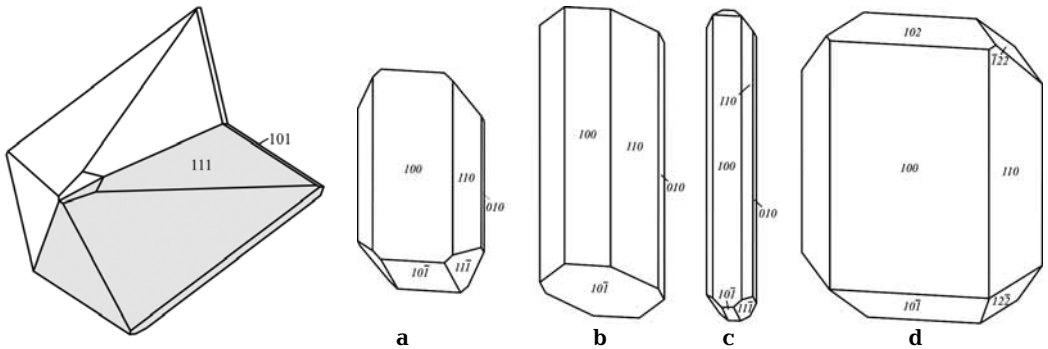


Fig. 8. Twin of cassiterite along {101}.

Fig. 9. Form of monazite-(Ce) crystals in consecutive zones the pegmatite (from early to late).

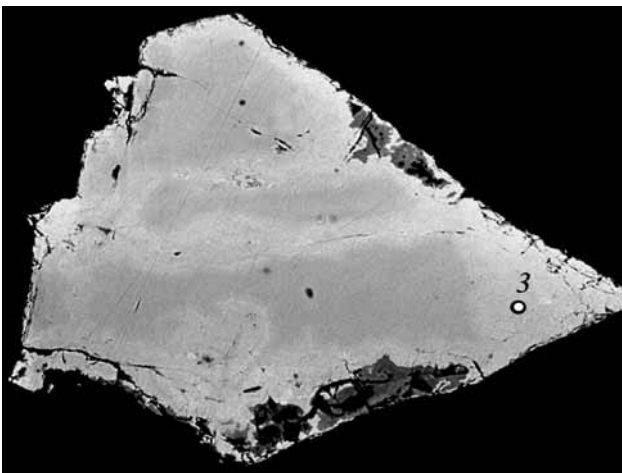


Fig. 10. Grain of microlite (light grey) with more light sites of its replacement by paraboriomicrolite. BSE (point 3 – see Table 7).

Table 6. Chemical composition of monazite-(Ce) (microprobe, wt.%)

	1	2	3	4
CaO	1.35	2.36	2.37	2.71
La ₂ O ₃	5.41	4.80	4.68	4.18
Ce ₂ O ₃	21.72	17.75	15.98	15.89
Pr ₂ O ₃	5.29	2.44	2.46	2.98
Nd ₂ O ₃	15.52	9.71	9.94	9.84
Sm ₂ O ₃	5.13	14.13	13.58	13.79
Gd ₂ O ₃	8.38	9.78	9.72	9.41
Tb ₂ O ₃	—	0.19	0.18	0.61
ThO ₂	5.57	7.85	8.20	8.38
UO ₂	1.09	0.47	0.66	1.23
P ₂ O ₅	27.87	29.05	29.08	29.15
SiO ₂	1.27	1.00	1.10	0.82
Total	98.60	99.53	99.55	98.99

Formulas (O = 4)

- $(\text{Ce}_{0.32}\text{Nd}_{0.22}\text{Gd}_{0.11}\text{La}_{0.08}\text{Pr}_{0.09}\text{Sm}_{0.07}\text{Ca}_{0.06}\text{Th}_{0.05}\text{U}_{0.01})_{1.0}(\text{P}_{0.95}\text{Si}_{0.05})_{1.00}\text{O}_4$
- $(\text{Ce}_{0.26}\text{Sm}_{0.19}\text{Nd}_{0.14}\text{Gd}_{0.13}\text{La}_{0.07}\text{Pr}_{0.04}\text{Ca}_{0.10}\text{Th}_{0.07})_{1.00}(\text{P}_{0.97}\text{Si}_{0.04})_{1.01}\text{O}_4$
- $(\text{Ce}_{0.25}\text{Sm}_{0.19}\text{Nd}_{0.14}\text{Gd}_{0.13}\text{La}_{0.07}\text{Pr}_{0.04}\text{Ca}_{0.10}\text{Th}_{0.07}\text{U}_{0.01})_{1.00}(\text{P}_{0.97}\text{Si}_{0.04})_{1.01}\text{O}_4$
- $(\text{Ce}_{0.23}\text{Sm}_{0.19}\text{Nd}_{0.14}\text{Gd}_{0.12}\text{La}_{0.06}\text{Pr}_{0.04}\text{Ca}_{0.10}\text{Th}_{0.08}\text{U}_{0.01})_{0.97}(\text{P}_{0.89}\text{Si}_{0.03})_{1.01}\text{O}_4$

Note. Analyses 2–4 – in one crystal from the center to the edge.

determined in different grains (Table 7, analyses 1–2). In some grains (from the periphery and near cracks), the microlite is replaced by uraniumiferous **parabariomicrolite** (Fig. 10). This mineral was not observed earlier in the Urals. The process of replacement obviously occurred with removal of Na, Ca, and F and influx of Ba (Table 7, analysis 3). Rare brownish-white crystals and split joints of **zircon** (cyrtolite) 1–3 mm in size are characterized by a high concentration of HfO₂ (10–13 wt.%) and a small impurity of thorium and uranium (0.1–0.4 wt.%).

Discussion of results and conclusions

Glubostrovskaya vein of granite pegmatites is closest to the known in Urals veins of the Svetlinskoye pegmatite field (Talantsev, 1988) and Murzinka (Popova *et al.*, 2002) with beryl, topaz, microlite, casserite, monazite, ferrocolumbite, manganocolumbite, manganotantalite and lithium-bearing micas – muscovite and lepidolite. But the Glubostrovskaya vein is distinguished by the presence of large plates of ferroan masutomilite reaching up to 5–20 cm in size. In pegmatites of the Urals, less-ferroan pinkish-violet masutomilite reaching up to 2 cm in size and containing 6.6–7.7 wt.% MnO overgrown on muscovite was found in the Ilmeny mountains (Belogub, 1992). In the

Table 7. Chemical composition of microlite (1–2) and parabariomicrolite (3) from the Glubostrovskaya vein (microprobe, wt.%)

	1	2	3
Na ₂ O	4.50	5.30	—
CaO	9.95	10.15	0.69
MnO	—	—	0.16
BaO	0.34	0.20	10.10
SnO ₂	1.74	2.12	2.74
UO ₂	4.95	0.42	4.98
Nb ₂ O ₅	4.50	5.52	5.49
Ta ₂ O ₅	70.60	72.70	73.60
F	3.35	3.50	—
Total	99.93	99.91	97.76

Formulas (analyses 1–2 are calculated on 4 cations, analysis 3 – on 5 cations)

- $(\text{Na}_{0.82}\text{Ca}_{1.00}\text{U}_{0.10}\text{Sn}_{0.07}\text{Ba}_{0.01})_{2.00}(\text{Ta}_{1.80}\text{Nb}_{0.19})_{1.99}\text{O}_6\text{F}_{1.00}$
- $(\text{Na}_{0.93}\text{Ca}_{0.98}\text{Sn}_{0.08}\text{U}_{0.01}\text{Ba}_{0.01})_{2.01}(\text{Ta}_{1.78}\text{Nb}_{0.22})_2\text{O}_6\text{F}_{0.99}$
- $(\text{Ba}_{0.67}\text{U}_{0.19}\text{Ca}_{0.13}\text{Mn}_{0.02})_{1.01}(\text{Ta}_{3.39}\text{Nb}_{0.42}\text{Sn}_{0.18})_{3.99}\text{O}_{10}(\text{OH})_2$

Note. Dash – element is not revealed. Conditions of microprobe analysis (as well as in the previous tables) are specified in the text; fluorine is determined with the help of WDS on JXA-733 in the Institute of Mineralogy, UB RAS, (Miass), analyst V.A. Muftakhov.

Mokrusha vein of the Alabashka field, free of Fe brownish-violet masutomilite with 5 wt.% MnO is observed in crystals of lithium micas as internal zones (up to 1 cm in thickness) alternating with trillithionite (zinnwaldite) and replaced by polyolithionite to the periphery (Popova *et al.*, 2002). Masutomilite with 8 wt.% MnO that forms an internal zone in a 10-cm plate of mica with an external zinnwaldite (trillithionite) zone was firstly time discovered in Japan (in a small cavity in granite pegmatite of the Tanakamiyama deposit) in 1975. Ferroan masutomilite with 4.27 wt.% MnO was also found in the same place, in the Tavara deposit (Minerals, 1992). Masutomilite is known from pegmatites of Algeria, Czech Republic, USA (<http://www.mindat.org/min-2588.html>). Ferroan masutomilite from the Glubostrovskoye occurrence of lithium in the Southern Urals differs from the Japanese one not only by its size, but also by higher concentrations of iron and manganese and lower concentration of lithium. Late pinkish beryl is enriched with rare alkalis, monazite-(Ce) is enriched in samarium, and zircon is enriched in hafnium.

Parabariomicrolite of the Glubostrovskaya vein as well as Brazilian parabariomicrolite from the granite pegmatite Alto du Giz in Brazil (Ercit *et al.*, 1986; cited according to: Kudryashov, Rozhdestvenskaya, 1988) metasomatically overgrows on microlite, but differs from the

Brazilian one by its yellowish-greenish colour and contains essential impurities of U, Ca, Nb, Sn (see Table 7, analysis 3). As far as it is known, the parabiomicrolite discovery is the first in the Urals and in Russia (and the second in the world).

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SIMPLE URANIUM OXIDES, HYDROXIDES $U^{4+} + U^{6+}$, SIMPLE AND COMPLEX URANYL HYDROXIDES IN ORES

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The review of published and new own data of simple uranium oxides revealed that the formation of five simple oxides is probable: nasturan, sooty pitchblende, uraninite, uranothorianite, and cerianite. Among simple oxides, nasturan, sooty pitchblende, and uraninite are the most abundant in ores varied in genesis and mineralogy. Uranothorianite or thorium uraninite (aldanite) is occasional in the ores, while cerianite is believed in U-P deposits of Northern Kazakhstan.

Hydrated nasturan is the most abundant among three uranium (IV + VI) hydroxides in uranium ores. Insignificant ianthinite was found in few deposits, whereas cleusonite was identified only in one deposit. Simple uranyl hydroxides, schoepite, metaschoepite, and paraschoepite, are widespread in the oxidized ores of the near-surface part of the Schinkolobwe deposit. They are less frequent at the deeper levels and other deposits. Studtite and metastudtite are of insignificant industrial importance, but are of great interest to establish genesis of mineral assemblages in which they are observed, because they are typical of strongly oxidized conditions of formation of mineral assemblages and ores.

The X-ray amorphous urhite associated with hydrated nasturan and the X-ray amorphous hydrated matter containing ferric iron and U^{6+} described for the first time at the Lastochka deposit, Khabarovsk krai, Russia are sufficiently abundant uranyl hydroxides in the oxidized uranium ores.

Significant complex uranyl hydroxides with interlayer K, Na, Ca, Ba, Cu, Pb, and Bi were found basically at a few deposits: Schinkolobwe, Margnac, Wölsendorf, Sernyi, and Tulukuevo, and are less frequent at the other deposits, where quite large monomineralic segregations of nasturan and crystals of uraninite were identified. In the other cases, uranium is leached from the oxidizing zone down to background, or richer oxidized ores are formed (Sernyi, Rössing, Shakoptar, and Pap deposits). These features of oxidized uranium ores are theoretically and economically important.

2 figures, 5 table, 50 references.

Keywords: uranium oxides (IV + VI), uranium hydroxides, simple and complex uranyl hydroxides, economic ores, X-ray amorphous matter, deposits.

Uranium (IV + VI) oxides are part of nearly all economic fresh uranium ores. Simple and complex uranium oxides are known. Complex oxides, brannerite, davidite, samarskite, and others are not discussed here and data of them are not given requiring the extensive additional material that causes increasing size of this article. Simple oxides identified in most economic ores and in the oxidizing zone are replaced by significant hydroxides; however, different versions of ore replacement are more frequent.

The aim of this study is review of published and new data to find out the importance of simple uranium (IV + VI) oxides in the formation of economic ores and alteration of these ores under oxidizing conditions as well as to establish the conditions of formation of varied uranium (IV + VI) hydroxides, simple and complex uranyl hydroxides, and

uranium leaching with oxidizing simple oxides and their natural assemblages at certain deposits. In addition to the formation of uranium hydroxides, the precipitation of uranyl arsenates or vanadates and X-ray amorphous of hexavalent uranium is important to discuss in the case of change of parameters of oxidizing zone in comparison with parameters of fresh ores; other theoretically and economically important features of oxidizing uranium ores are also discussed.

Simple uranium oxides

The features of five simple uranium oxides are given in Table 1. No vorlanite ($CaU^{6+}O_4$) (Galuskin *et al.*, 2011) is given here. Possibly, its formula is incorrect, because the X-ray data ($a = 5.3813\text{Å}$) correspond to uraninite, in which this dimension ranges from 5.38 to

Table 1. Simple uranium (IV+VI) oxides

Mineral, formula	Morphology of crystals, a_0 (Å)	Color and other characteristic features
Uraninite $UO_{2.0-2.9} \cdot nPbO, ThO_2, TR_2O_3$ и and less frequent CaO, where n ranges from 0 to few units	Octahedron and cube, a_0 5.38-5.65	Black, with semimetallic to resinous luster. Hardness 5.06-7.6; density 7.6-10.8
Nasturan $UO_{2.02-2.9} \cdot nPbO$ mCaO, where n and m range from 0 to few units	Sinter or kidney-shaped coloform dense seggregations, a_0 5.34-5.45	Black, with resinous luster. Hardness 4.7-5.9; density 4.9-7.7
Sooty pitchblende $UO_{2.08-2.96}$ and X-ray amorphous hydrated oxides and other uranium (IV + VI) minerals and phases	Loose films a_0 5.35-5.42 и and X-ray and poor-crystallized phases	Dark grey to light grey, dull. Hardness 1-3; density 3.8-4.8
Uranothorianite (Th,U) O_2 + UO_3 + PbO	Cubic crystals frequently with small octahedron faces, a_0 5.05-5.96	Dark grey. Translucent in thin chips. Hardness 6.5-7, density 8.7-9.9; n_{cr} 2.2. Isotropic
Cerianite-(Ce) (Ce,Th,U) O_2 + UO_3 + PbO	Small cubes and octahedra, powder seggregations, a_0 5.411-5.482	Dark greenish, amber yellow to brownish yellow with resinous luster, translucent, isotropic, $n > 2$

5.65Å (Table 1). The probable formula of the mineral studied by Galuskin *et al.* (2011) is $n(CaU^{4+}O_2) \cdot m(UO_3)$, where n is much less than m . Such formula corresponds to highly altered Ca-bearing uraninite.

Among other simple oxides, the first three (uraninite, nasturan, and sooty pitchblende) are the most abundant in uranium ores. Up to now, mineralogists consider them as morphological varieties of uraninite although as seen from the table, they have individual morphology and are slightly different in composition. In addition, these minerals are different in origin. Uraninite is the highest-temperature uranium oxide (400–260°C), coloform nasturan is characteristic of medium to low-temperature assemblages (250°C and less), and friable sooty pitchblende is typical of supergene product. Four varieties of uraninite different in composition are distinguished: (1) uraninite containing global clarke of concentration Th and REE; (2) aldanite (uranothorianite) (up to 46–69 wt.% ThO_2 and 0.7–13 wt.% REE_2O_3); (3) broggerite (up to 15 wt.% ThO_2 and 1–6 wt.% REE_2O_3); and (4) cleveite (nivenite) enriched in REE up to 15 wt.%. Aldanite, broggerite, and cleveite, compositional varieties of uraninite, are accessory minerals of granitic and syenitic pegmatites and some igneous rocks. The Th- and REE-free uraninite economic ores are

formed in varied geological environments. Economic deposits of uraninite are reported from granitic pegmatites (Namibia, Norway, Canada, Madagascar, Alaska), skarn (Bancroft, Ontario, Canada; Mary Cathline, Australia), Proterozoic basal conglomerates (Witwatersrand, South Africa; Eliot Lake, Canada; Jacobino, Brazil), and occasional hydrothermal deposits (Schinkolobwe, Democratic Republic of Congo). Heinrich (1962), Formation... (1974), Laverov *et al.* (1983), Typomorphic features... (1989), Frondel (1958), and Chernikov (2006–2007) described in detail these uranium deposits.

To obtain new concepts of the formation of uraninite ores, the mineralogy of the Rössing large deposit, Namibia, Southwestern Africa related to granitic pegmatites, where uraninite is the major mineral of the fresh ores (Berning *et al.*, 1976) should be discussed. The oxidizing zone of this deposit is similar to that of the Sernyi uranium deposit, Turkmenistan in both mineralogy and uranium grade. The major minerals of fresh ores at these deposits are different. At the Rössing deposit, this is crystalline uraninite, whereas at Sernyi, coloform nasturan. In the oxidizing zone of both deposits, insignificant uranyl and uranium hydroxides were found; at the Sernyi deposit, these are becquerelite, schoepite, and hydrated nasturan; at Rössing, this

is gummite, mixture of uranyl hydroxides and silicates (Fig. 1). Later uranyl silicates, beta-uranophane and uranophane are abundant in the oxidizing zone of these deposits. Carnotite is widespread at both deposits. In addition, at the Sernyi deposit, strelkinite and tyuyamunite were found. Other uranyl minerals are less frequent in the oxidizing zone of the both deposits. It is possible that the character of vertical distribution of uranium content at these deposits is similar too. At the Sernyi deposit, the oxidized ores are three times richer and mixed ores containing relict nasturan and sooty pitchblende are 2.8 times richer in uranium down to 1 m deep than fresh ores, i.e., like the Tomas Range uranium-fluorite deposit, Utah, USA, at Sernyi, supergene processes were important to form orebodies. Probably, at the Rössing deposit, these processes have an effect on the concentration of uranium in ores.

Nasturan characteristic mineral of economic hydrothermal and supergene deposits was found at certain Sn-W deposits, for example Butygychag, Northeastern Russia, occurrences and deposits in Khabarovsk krai, Northern Transbaikalian Region, and Cornwall, Great Britain. According to new unpublished data of Russia deposits and literature of Cornwall, at all objects, nasturan is associated with arsenopyrite, nickeline, galena, and chalcopyrite to form veinlets cutting earlier Sn-W ore veins.

The largest bodies of nasturan with uraninite and coffinite are formed in the discordance-type deposits with rich uranium, gold-uranium, copper-uranium, and base metal-uranium ores. The deposits located in the Aligator River district (North Territory, Australia) and Athabasca, western Canadian Shield (Northwest Territory, Canada) are the most typical and are reported in (Uranium..., 1980; Laverov *et al.*, 1983; Kulish, Mikhailov, 2004). No large this type deposits are found in Russia.

Hydrothermal uranium deposits with nasturan are known in Russia and abroad. According to the new data of ore samples, certain deposits described during exploitation as proper uranium are complex, gold-uranium. For example, in the oxidizing and cementation zones enriched in U at the Sernyi deposit (Chernikov, 2001, 2006–2007,



Fig. 1. Gummite (orange) and beta-uranophane (yellow) fill cavities in pegmatite at the Rössing deposit, Namibia.

2010), a high grade of Au (up to 15 g/t) was determined in carbonate veinlets superimposed on nasturan. Among other proper hydrothermal uranium deposits with nasturan, the following subtypes are distinguished: nasturan-carbonate, nasturan-fluorite, nasturan-quartz, nasturan-bituminous, and nasturan-hydromica. Complex ores are distinguished: U-Zr, U-As-Pb-Zn, U-Cu, and U-Mo, in which nasturan-bearing veins cut earlier mineral assemblages (Typomorphic features... 1989). In addition, at many deposits, especially at deep levels, for example Tulu-kuevo, Southeastern Transbaikalian Region, there are nanoscaled and X-ray amorphous segregations corresponding to hydrated nasturan in composition.

The great concentration of nasturan is known from hydrothermal deposits of so called five-element association, where the mineral is associated with Co, Ni, and Fe arsenides, and native silver and bismuth, and occasionally native As (Canada; Ore Mountains, Germany and Czech Republic). The Aktepe deposit (Uzbekistan) attributed to this type is small and probably, is rather poor explored.

At the Witwatersrand largest Au-U deposit, nasturan and uraninite associated with native gold and pyrite were deposited in the cement of conglomerate composed of quartz pebble. At U-P, U-V, U-coal, and infiltration

uranium deposits, nasturan and sooty pitchblende precipitate in siltstone, sandstone, limestone, and coal beds. They are associated with Mo, Cu, and Zn sulfides, V minerals, and native arsenic, selenium, and rhenium.

Sooty pitchblende (residual and regenerated) occurred below the oxidizing zone (in the cementation zone) of endogenic deposits or zone of strata oxidation of supergene ores are frequently polymineralic; in addition to nasturan, uranium silicates, phosphates, and titanates and the X-ray amorphous and nano-scaled U-bearing phases economically important and nearly not mentioned in literature are established in these ores. At many strata oxidation deposits and cementation zones of endogenic deposits (Chernikov, 1981), X-ray amorphous and nanoscaled phases are uranium (IV + VI) oxides or silicates or phosphates, which are easily leached by the any mode of recovery. At the other deposits, for example, Dariuot group, Mongolia, these phases consist of U-bearing oxides of Ti, U-bearing alteration products of anatase and probably ilmenite (Chernikov, Kostikov, 2006), from which uranium is difficultly recovered by in situ well leaching of uranium. According to new data, the same phases are characteristic of certain potential areas in the Vitim, South Vitim, and Eravnoe districts discussed by Khomentovsky *et al.* (2000).

Cerianite [cerianite-(Ce)] was described for the first time in lenses hosted in altered carbonate rock from wall rock of nepheline syenite of the Sudbury uranium district (Ontario, Canada) (Graham, 1955). These lenses up to 0.3 m in length contain cerianite-(Ce), carbonate, nepheline, feldspar, tremolite, magnetite, ilmenite, and apatite. The mineral contains admixture of other *REE* and Th. Complete relative substitution of CeO_2 , UO_2 , ThO_2 , La_2O_3 and partial substitution of Y_2O_3 , In_2O_3 and ZrO_2 was identified (Duwez, Odell, 1950; Rüdorff, Valet, 1952; Padurow, Schusterius, 1953). Uranium was not measured in cerianite by chemical methods. According to the X-ray data of strongly radioactive metamictic cerianite-Ce ignited at 1000°C from microcline pegmatite Nesöya, East Antarctica (Matsumoto, Sakomoto, 1982) and Aktass, Kazakhstan (Kudaibergenova, Zubov, 2007), U content in this mineral is possibly higher than Th. Most d-spacings of

ignited cerianite-(Ce) from Nesöya and Aktass (Table 2) are closer to those of synthetic uraninite, rather than thorianite. The unit-cell dimension of ignited cerianite-(Ce) (5.451Å) is remarkably different from that of standard cerianite-(Ce) (5.411Å) and synthetic thorianite (5.6Å). According to these data, it is closer to synthetic uraninite (5.46Å). Hence, high radioactivity of cerianite-(Ce) from East Antarctica and Kazakhstan is caused by uranium, rather than thorium.

Like Ce, cerianite in most types of uranium ore is insignificant, it may be very important to form complex uraniferous carbonatite and U-P deposits. At least, predominant Ce among *REE* was established in certain U-bearing apatites of U-P deposits in Northern Kazakhstan. Korolev *et al.* (1983) noted 35.5% Ce with 27.6% La, 15.6% Nd, and less content of the other *REE* in apatite from gneiss. The author of this article revealed the similar *REE* content in apatite from the Tastykol deposit, Northern Kazakhstan. The presence of Ce as cerianite is well allowable.

Thorianite and uranothorite (U^{4+}Th) O_2 or Th-bearing uraninite (aldanite) are basically found in placers worldwide. Pegmatites are considered to be a source of these minerals (Sri Lanka; India; Siberia, Russia). In the placers, thorianite is associated with zircon, ilmenite, and thorite, while in pegmatites, with zircon, monazite, and beryl.

Th-bearing uraninite along with uranothorite is the major ore mineral in peralkaline granitic complexes of the Bokan Mountain located south of town Alaska, USA. Coffinite and brannerite were also identified in these ores. At the Ross Adams mine in this district, in 1957–1977, 1000 t of U_3O_8 was recovered with the grade of this oxide in the ore about 1% (Boze *et al.*, 1974; Yang, 1985). In the other cases, thorium uraninite is insignificant in non-economic ores and is accessory minerals in granite and granitic pegmatites.

Uranium (IV+VI) hydroxides

This group consists of hydrated nasturan, ianthinite, and cleusonite (Table 3). First of them, described as hydronasturan (Getseva, 1956) is frequent in ores. It is resulted from both hydration of nasturan in supergene zone and precipitation from uraniferous under-

Table 2. Interplanar-spaces and unit-cell dimension of cerianite, thorianite, and uraninite

Cerianite-(Ce), Nesöya, 1000°C, 7 hours			Cerenianite-(Ce) (ASTM)		Thoriantite synthetic (ASTM)		Uraninite synthetic (ASTM)		Cerianite-(Ce), Aktass, Kazakhstan	
<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁
	3.193	49	—	—	—	—	—	—	—	—
	3.182	45	—	—	—	—	—	—	—	—
111	3.51	100	3.124	100	3.234	100	3.14	100	3.14	100
200	2.723	40	2.706	29	2.800	35	2.73	50	2.71	10
220	1.929	48	1.913	51	1.980	58	1.926	80	1.90	20
			1.926	46	—	—	1.926	80	—	—
311	1.643	45	1.632	44	1.689	64	1.645	90	1.63	5
222	—	—	1.562	5	1.611	20	1.574	40	1.57	5
400	—	—	1.353	5	1.396	20	1.365	30	1.35	5
<i>a</i> ₀ = 5.451			<i>a</i> ₀ = 5.411		<i>a</i> ₀ = 5.600		<i>a</i> ₀ = 5.46		—	

Table 3. Uranium (IV+VI) hydroxides

Mineral, formula	Symmetry, unit- cell dimensions (Å)	Morphology of crystals. Color, luster, density (D), hardness (H)	Optical parameters	Strong reflections in X-ray diffraction pattern (intensity)	Other characteristic features
Hydrated nasturan (hydronasturan) UO _{2.3-2.9} •3-9H ₂ O	X-ray amorphous or poor-crystallized cubic phases	Dense aggregates. Dark grey;; vitreous; D 4.3-4.7; H 2-4.5	<i>n</i> 1.715-1.781 decreases as O ₂ and H ₂ O increase	X-ray amorphous, occasional weak diffuse reflections	Reflectance 6.4-11.4%.
Ianthinite U ₂ ⁴⁺ (UO ₂) ₄ O ₆ (OH) ₄ •9H ₂ O	Orthorhombic, <i>a</i> ₀ 11.52; <i>b</i> ₀ 7.15; <i>c</i> ₀ 30.3.	Tabular. Violet; vitreous; D 5.16 (calc. 5.03); H 2-3	<i>γ</i> 1.92; <i>β</i> 1.9; <i>α</i> 1.674, perfect cleavage parallel to (001), clear cleavage parallel to (100)	7.61 (10); 3.81 (6); 3.59 (6); 3.35 (6); 3.22 (9); 1.68 (5)	Pleochroic: violet — <i>γ</i> , colorless — <i>α</i>
Cleusonite (Pb,Sr)(U ⁴⁺ ,U ⁶⁺) (Fe ²⁺ ,Zn) ₂ (Ti,Fe ²⁺ , Fe ³⁺) ₁₈ (O,OH) ₃₈	Trigonal, <i>a</i> ₀ 10.576; <i>c</i> ₀ 21.325.	Tabular.	—	—	—

ground waters penetrated in the ore zone at depth. In the oxidizing zone, nasturan is gradually replaced through hydrated nasturan to urhite, which in turn is replaced by the X-ray amorphous hydroxides described for the first time, containing ferric iron, and enriched in Nb₂O₅ and SiO₂. Chemical analyses are below. In turn, uranium hydroxides with ferric iron are replaced by uranyl silicates.

Cleusonite found in two localities in the western Swiss Alps near Cleuson (Switzerland) in greenschist facies gneiss is Pb-Sr

hydrous oxides of tetra- and hexavalent uranium, ferrous and ferric iron, and zinc and titanium. It is associated with uraninite, tennantite, and hematite. Its economic importance is unclear.

Ianthinite, the only uranyl hydroxide mineral containing tetravalent uranium is found in small amount at the Schinkolobwe deposit (Thoreau, R. du Trieu de Terdonck, 1933; Gerasimovsky, 1956), in fluorite veins with nasturan in Wölensdorf, Bavaria, Germany, and at the Bigai, La Crusel, and Boi Noir

deposits, France (Branche *et al.*, 1951; Guillemin, Protas, 1959). At the Tulukuevo deposit, L.N. Belova identified ianthinite in hydroxide subzone at the depth of 90–120 m (Ishchukova *et al.*, 2005). It is economically insignificant.

Simple uranyl hydroxides

Holfertite, $U_{1.75}^{6+}Ti^{4+}Ca_{0.25}O_{7.17}(OH)_{0.67}(H_2O)_3$, found in fractures and cavities in rhyolite of the Searale Canyon, Thomas Range, Utah, USA (Sokolova *et al.*, 2005) is not discussed in this article. This mineral was not established in uranium ores. In addition, it is described as uranyl mineral with U^{6+} in its formula, whereas uranyl compounds contain linear group UO_2^{2+} , triatomic doubly charged cation presents independent structural unit in the mineral and affects its properties. The formula suggested by the authors of the cited paper does not correspond to uranyl minerals and given data do not allowing it reliable establishment.

Schoepite, metaschoepite, and paraschoepite (Crist, Clark, 1960) are simple hydrous uranyl hydroxides with variable content of free water. In this case, the formula of paraschoepite is not exactly determined. Well-shaped tabular crystals of schoepite and paraschoepite were observed in samples from the Schinkolobwe deposit (Democratic Republic of Congo). There, these minerals are abundant near surface as alteration product of uraninite or ianthinite. Under near-surface conditions, the minerals are intimately associated with curite and soddyite; they are less frequent at the deeper level of the oxidizing zone of the Schinkolobwe deposit. At this level, these minerals associated with becquerelite precipitate on the crusts of ianthinite (Vaes, Guillemin, 1959). At the deposits Wölensdorf, Bavaria, Germany and Great Bear Lake, Canada, these minerals precipitate on nasturan or occur as pseudomorphs after ianthinite adjacent to nasturan.

The formation of schoepite and paraschoepite in near-surface environment by replacing autunite and phosphuranylite is reported (Gritsaenko *et al.*, 1959; Chernikov, 1963; Belova, 1975). The author of this paper has studied in detail the similar phases considered as paraschoepite and schoepite from

the certain occurrences in the Kyzylsai deposit, Kirgizia and Taboshary deposit, Tajikistan. In the both cases, they are mixture of boltwoodite or uranophane, clay minerals, and varieties of mineral described as phosphurancalcite (Chernikov, Sidorenko, 1978). In the other cases, the opinion that schoepite and paraschoepite are resulted from replacing autunite and phosphuranylite under near-surface conditions, is appeared to be wrong.

Studtite, $UO_4 \cdot 4H_2O$, and metastudtite, $UO_4 \cdot 2H_2O$ (structural formulae are given in Table 4) are extremely unusual minerals, in which uranyl peroxide indicates high oxidized conditions during the formation of these minerals. They are described from Schinkolobwe and Menzenschwand, South Black Forest, Germany (Walenta, 1974; Deliens, Piret, 1983; Smith, 1988). Despite their insignificant economic importance, these minerals are of great interest to establish origin of mineral assemblages.

Complex uranyl hydroxides

Numerous uranyl hydroxides containing interlayer free H_2O and cations K, Na, Ca, Ba, Cu, Pb, and Bi are identified. Previously, some of them were suggested to be uranates, but crystallochemical study shows that these minerals belong to uranyl hydroxides (Crist, Clark, 1960; Protas, 1959, 1964). Among these minerals, very rare compreignacite from the Margnac deposit, Haute-Vienne, France (Protas, 1964) was found in the oxidation products of nasturan to be associated with bilietite and becquerelite. Rameauite (Cesbron *et al.*, 1972) is Ca-bearing variety and agrinierite is Ca-Sr variety of compreignacite. These minerals were described from the same deposits in the same alteration products of nasturan.

The Margnac deposit comprises a series of silicified NW and NE-trending fractures in granite. Occasionally, these fractures contain barite and fluorite with disseminated nasturan. Rare minerals accompanying nasturan are micrograins of iron sulfides, galena, sphalerite, chalcopyrite, and extremely rare bismuthinite. In some places, these fractures are cut by albitized and chloritized granite containing red calcite and hematite. In granite, cavities with leached quartz are found. Ura-

niium mineralization that is nasturan and coffinite completely replacing albite, in these places is maximal. In the oxidation zone, zoning of fractures is exhibited (outward):

- a – dark nodules of "gummite" with ianthinite, schoepite, and relict nasturan;
- b – red and orange "gummite" with becquerelite, billietite, schoepite, compreignacite, agrinierite, and rameauite; rameauite is the most abundant minerals among them;
- c – yellow to pale yellow massive to powder-like uranophane; calcite crystals in fractures in "gummite" are occasional;
- d – highly altered limonitized granite (Cesbron *et al.*, 1972).

Becquerelite, calcium uranyl hydroxide, previously assigned to simple uranyl hydroxide (Getseva, Savel'eva, 1956; Soboleva, Pudovkina, 1957; Frondel, 1958) is sufficiently widespread in the oxidized zone of the Schinkolobwe deposit. It occurs adjacent to uraninite, but after ianthinite; the latter is frequently replaced by schoepite (Thoreau, du Trieu de Terdonck, 1933; Vaes, Guillemin, 1959). Ianthinite exhibiting the initial stage of uraninite alteration is replaced by schoepite under oxidized conditions. The oxidized rim around crystals of uraninite reaching 15–20 cm across is largely composed of becquerelite and curite. Both other uranyl hydroxides and uranyl silicates are less frequent in this zone. An orange zone next to the zone of becquerelite-curite consists of curite and uranyl silicates. Becquerelite in the orange zone is nearly absent. In addition to curite and becquerelite, numerous uranyl hydroxides were found in the oxidized zone: billietite, fourmarierite, vandendriesscheite, wölsendorfit, masuyite, studtite, richetite, and protasite. However, all listed minerals are minor.

Becquerelite as alteration product of nasturan is reliably determined also in the ores of the Wölsendorf deposit in fluorite veins. At the Margnac deposit, becquerelite associated with compreignacite (see above) occurs in the zone of orange "gummite". Frondel (1958) reported insignificant becquerelite as alteration product of nasturan at the sandstone-type deposits of the Colorado Plateau, USA. The formation of the mineral associated with schoepite and fourmarierite predates the precipitation of uranyl vanadates (carnotite and

tyuyamunite) in the oxidizing zone of these deposits. Frondel (1958) noted the mineral in the oxidizing zone of the other uranium deposits in the USA and Canada. In the former Soviet Union, becquerelite was found in the oxidizing zone of the Sernyi, Turkmenistan and Botta Burum, Kirgizia.

The X-ray amorphous urhite first described by Getseva (1956) is quite abundant among simple hydrated oxides of hexavalent uranium. It was studied in detail at the Lastochka deposit, Khabarovsk krai. Figure 2 shows hydrated nasturan replaced by the secondary uranium minerals. The chemical composition of hydrated nasturan, urhite, and alteration products is given in Table 5. Initial alteration products of urhite and hydrated nasturan are replaced by Fe-rich U-bearing X-ray amorphous matter. As a result, isometric clusters are formed around nasturan or uranyl hydroxides (Fig. 2). The mechanism of formation of this matter is unclear. The chemical composition is characterized by high Si, H_2O , and Fe^{3+} and U^{6+} oxides (Table 5). The comparison of given compositions clearly indicates strong release of uranium during oxidation of nasturan and supergene alteration of residual products of its transformation. Simultaneously with release of uranium, Si, Al, H_2O , and Fe are introduced in the residual products replacing nasturan.

Residual oxidized products of nasturan of all stages of supergene alteration are enriched in Zr, Nb, Ti, and occasional Mo in comparison with primary mineral exceptional crusts of uranophane opened by trenches, in which only 0.0n % were measured. Uranium leached from oxidized nasturan and residual products of its alteration precipitates partially in fractures in the wall rocks at the same level and partially below, in the cementation zone.

Kopchenova *et al.* (1975), who reported the stage alteration of fine nasturan in albitite, revealed the gradual replacement of nasturan by the X-ray amorphous uranium hydroxides, hydronasturan and urhite, which replaced uranium, calcium, and lead silicates. Ishchukova *et al.* (2005) gave the following structure of the oxidizing zone of the Tulukuevo deposit (after Belova). Below 120 m from the surface, primary ores with nasturan in U ore and nasturan, coffinite, and molybdenite in U-Mo ore were

Table 4. Hydroxides of hexavalent uranium

Mineral, formula	Symmetry, unit-cell dimensions (Å)	Morphology of crystals. Color, luster, density (D); hardness (H)	Optical parameters	Strong reflections in X-ray diffraction pattern (intensity)	Other characteristic features
Urhite $\text{UO}_3 \cdot 1.7\text{-}3.1\text{H}_2\text{O}$	X-ray amorphous	Brown, amber yellow; vitreous; D 3.8-4.17; H 2-3	n 1.647-1.680	X-ray amorphous	—
Studtite $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$	Monoclinic; a_0 11.85; b_0 6.80; c_0 4.25; β 93°51' ($C2/m$)	Fibers. Yellow.	γ 1.68; β 1.555; α 1.545 (1.537)	5.93 (10) 3.40 (8) 2.96 (6) 2.23 (6)	—
Metastudtite $(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2$	Orthorhombic; a_0 6.51; b_0 8.78; c_0 4.21 ($Immm$)	-/-	—	5.24 (10) 4.41 (7) 3.80 (7) 3.54 (8)	—
Schoepite $[(\text{UO}_2)_6\text{O}_2(\text{OH})_{12}] \cdot 12\text{H}_2\text{O}$ and Metaschoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 10\text{H}_2\text{O}$	Orthorhombic; a_0 14.74 and 14.73; b_0 16.66 and 16.72; c_0 14.36 and 13.99 ($Pbca$) and ($Pbna$)	Prismatic. Yellow; vitreous; D 2-2.7; H 2-3	γ 1.735; α 1.685-1.705	7.34 (vs) 3.57 (ms) 3.22 (s) 2.01 (ms)	Pleochroic: yellow — γ , β ; colorless — α
Paraschoepite $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 2\text{H}_2\text{O} (?)$	Orthorhombic; a_0 15.22; b_0 16.83; c_0 14.12 ($Pbca$)	Columnar. Yellow; vitreous	γ 1.74; α 1.785	7.88 (7) 3.38 (9) 3.09 (10) 2.89 (10) 2.08 (9) 1.82 (8) 1.59 (8)	-/-
Compreignacite $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2 \cdot 7\text{H}_2\text{O}$	Orthorhombic; a_0 14.85; b_0 7.175; c_0 12.187; ($Pnmm$)	Prismatic. Yellow; D 5.03; H 3	γ 1.802; α 1.798	7.40 (vs) 3.70 (s) 3.58 (s) 3.53 (ms) 3.34 (s) 3.19 (ms)	Pleochroic: yellow — γ ; colorless — α
Rameauite $\text{K}_2\text{Ca}(\text{UO}_2)_6\text{O}_6(\text{OH})_4 \cdot 9\text{H}_2\text{O}$	Monoclinic; a_0 14.22; b_0 14.26; c_0 13.97 ($C2/c$)	Prismatic. Orange; D 5.6	2V 32°	7.12 (vs) 3.57 (s) 3.495 (vs) 3.14 (vs) 3.12 (vs)	Perfect cleavage parallel to {010}
Agrinierite $(\text{K}_2\text{Ca,Sr})(\text{UO}_2)_3\text{O}_4 \cdot 4\text{H}_2\text{O}$	Orthorhombic; a_0 14.04; b_0 24.07; c_0 14.13 ($Cmmm$)	Tabular. Orange; D 5.7	2V 55°	7.08 (vs) 6.05 (s) 3.52 (s) 3.49 (s) 3.13 (vs)	Perfect cleavage parallel to {001}
Vandenbrandeite $\text{Cu}^{2+}(\text{UO}_2)(\text{OH})_4$	Triclinic; a_0 7.86; b_0 5.44; c_0 6.10 ($P1$)	Tabular. Dark green; D 5.03; H 4	γ 1.80; β 1.78; α 1.76; 2V great	5.25 (6) 3.87 (7) 3.47 (6) 3.16 (10) 1.83 (8)	Perfect cleavage parallel to {110}
Becquerelite $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	Orthorhombic; a_0 13.84; b_0 12.38 c_0 14.92 ($Pnma$)	Prismatic. Yellow; adamantine; D 5.9; H 2-3	γ 1.820-1.835; β 1.805-1.25; α 1.725-1.750; 2V 32°	7.50 (10) 3.75 (8) 3.56 (8) 3.22 (9) 2.58 (7)	Pleochroic: yellow — β , α ; colorless — γ
Protasite $\text{Ba}(\text{UO}_2)_3\text{O}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	Monoclinic; a_0 12.29; b_0 7.22; c_0 6.96 (Pn)	Tabular. Orange; metallic	γ 1.83; α 1.79; 2V 60-65°	7.06 (50) 3.14 (100) 3.11 (35) 2.496 (35)	Good cleavage parallel to {010}

Table 4.

Billietite Ba(UO ₂) ₆ O ₄ (OH) ₆ •8H ₂ O	Orthorhombic; a ₀ 7.15; b ₀ 12.07; c ₀ 15.08 (<i>Pnma</i>)	Tabular. Yellow; adamantine; D 5.18-5.36; H 2-3	γ 1.839-1.79; β 1.832-1.78 α 1.733-1.725; 2V 35-47°	7.53 (10) 3.77 (9) 3.17 (8) 2.03 (6) 1.654 (4)	Pleochroic: yellow – γ; colorless – α
Vandendriesscheite Pb ₃ (UO ₂) ₂₀ O ₁₂ (OH) ₂₂ •22H ₂ O	Orthorhombic; a ₀ 13.96-14.12; b ₀ 14.36-16.80; c ₀ 14.30-14.72. (<i>Pmma</i>)	Prismatic. Orange; adamantine; D 4.5-5.5; H 3	γ 1.820-1.89; β 1.81-1.882; α 1.76-1.79; 2V up to -50°	7.41 (8) 3.61 (9) 3.22 (10) 2.55 (4) 2.01 (4)	Pleochroic: yellow – γ; colorless – α
Fourmarierite Pb(UO ₂) ₄ O ₃ (OH) ₄ •4H ₂ O	Orthorhombic; a ₀ 14.00-14.1; b ₀ 16.47-16.75; c ₀ 14.39-14.55 (<i>Pbmn</i>)	Tabular. Red; adamantine; D 5.74; H 3-4	γ 1.04-1.94; β 1.9-1.92; α 1.85-1.865; 2V up to 55°	3.45 (9) 3.09 (10) 2.44 (6) 1.996 (6) 1.07 (8)	Pleochroic: yellow – γ; colorless – β, α
Masuyite Pb(UO ₂) ₃ O ₃ (OH) ₂ •3H ₂ O	Orthorhombic; a ₀ 14.09-13.9; b ₀ 12.08-12.31; c ₀ 14.27-14.98 (<i>Pbmn</i>)	Tabular. Orange-red; D 5.08	γ 1.917; β 1.906; α 1.785; 2V -50°	7.10 (10) 3.54 (8) 3.15 (9) 2.51 (5) 1.984 (6)	Pleochroic: yellow – γ, β; colorless – α
Curite Pb ₂ (UO ₂) ₃ O ₇ •4H ₂ O	Orthorhombic; a ₀ 12.50-12.55; b ₀ 13.01; c ₀ 8.37-8.40 (<i>Pna2</i>)	Prismatic. Orange; adamantine; D 7.19-7.4; H 4-5.	γ 2.12-2.15; β 2.07-2.11; α 2.05-2.06; 2V great	6.28 (10) 3.97 (9) 3.14 (8) 2.55 (6) 1.74 (5)	Pleochroic: dark red – γ; orange – β; yellow – α
Wölsendorfite Pb ₇ (UO ₂) ₁₄ O ₁₉ (OH) ₄ •12H ₂ O	Orthorhombic; a ₀ 11.92-11.95; b ₀ 13.96-13.99; c ₀ 6.90-7.02	Prismatic. Orange; D 6.8	γ 2.09 α 2.05	3.45 (9) 3.09 (10) 2.44 (6) 1.97 (8)	Good cleavage along {001}
Spriggite Pb ₃ [(UO ₂) ₆ O ₈ (OH) ₂]•3H ₂ O	Monoclinic. a ₀ 28.36; b ₀ 11.99; c ₀ 13.998 (<i>C2/c</i>)	Prismatic. Orange; vitreous; D 7.0; H - 4	γ 1.891 α 1.807	6.92 (60) 3.46 (80) 3.10 (100) 1.918 (60)	Strongly pleochroic from light yellow to dark orange
Richetite Pb ₉ (UO ₂) ₃₆ (OH) ₂₄ O ₃₆ -	Triclinic.	Dark green. Adamantine	γ 1.99 β 1.98	–	Pleochroic: green – γ; pale yellow – β
Bauranoite Ba(UO ₂) ₂ O ₃ •5H ₂ O and metabauranoite Ba(UO ₂) ₂ O ₃ •2H ₂ O	Orthorhombic.	Dense aggregates. Brown; adamantine; D 5.39-5.42	γ 1.932-1.960; β 1.94; α 1.911-1.925	–	–
Kalkuranit Ca(UO ₂) ₂ O ₃ •5H ₂ O and metakalkuranit Ca(UO ₂) ₂ O ₃ •2H ₂ O	Unknown.	Orange; waxy; D 4.62-4.9	–	–	–
Uranosphenite Bi(UO ₂) ₂ O ₂ (OH)	Monoclinic.	Long. Orange; D 6.12-6.89; H 2-3.	γ 2.05-2.06; β 1.981-1.985; α 1.955-1.959; 2V great	5.25 (6) 3.87 (7) 3.47 (6) 3.16 (10) 1.83 (8)	Non pleochroic
Clarkeite (Na,K, Ca,Pb)(UO ₂)O(OH) •0-1H ₂ O	Trigonal.	Reddish brown; waxy; D 6.39; H 4-5.	γ 2.11; β 2.098; α 1.997; 2V 30-50°	5.77 (8) 3.34 (9) 3.17 (10) 1.968 (7)	–

Notes. Reflections in X-ray diffraction pattern (s) strong, (ms) medium strong, and (vs) very strong.

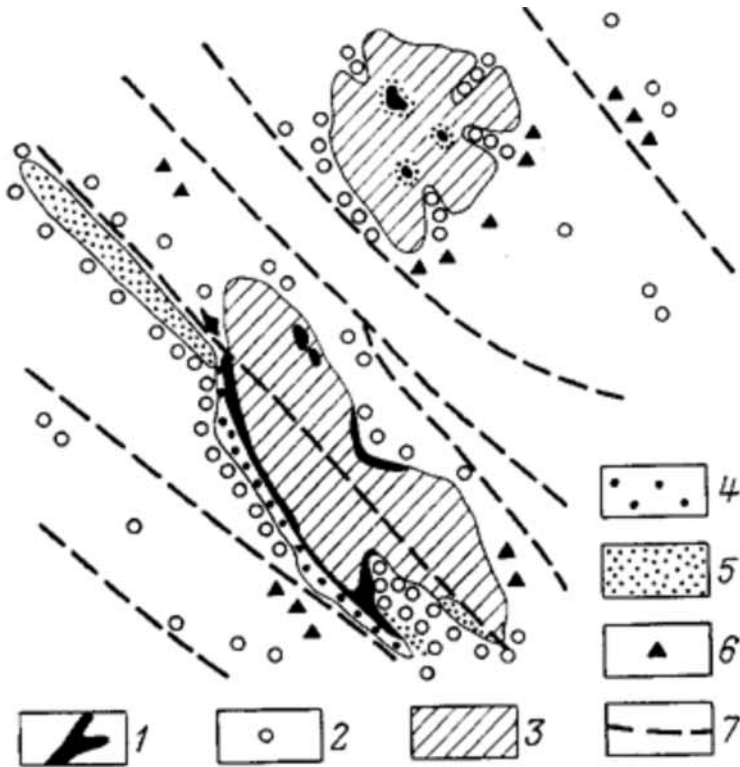


Fig. 2. Replacement of nasturan by oxidized minerals, Lastochka deposit, Khabarovsk krai.

(1) Relicts of nasturan; (2) beta-uranophane; (3) brown Fe- and U-bearing mineral; (4) curite-furmarierite-type hydroxides; (5) urhite; (6) limonite; (7) fractures.

identified at the deposit. At the depth of 120–90 m, there is the hydroxide subzone with ianthinite, schoepite, and paraschoepite after U ore and umohoite, mourite, and molybdenite after U-Mo ore, silicate-hydroxide subzone with protasite, wölsendorfite, bauranoite, uranospinite, novö ekite, chernikovite, and other uranium micas developed after U ore, and calcurmolite, iriginite, moluranite, and umohoite replacing Mo-U ore are traced upward from the level 60–90 m. Uranophane and beta-uranophane are found in the both ore types. According to our data, minor kalkuranit with metamorphic variety reported from the occurrences at the Murun massif (Rogova *et al.*, 1973) was observable in the silicate-hydroxide subzone. Down to 60 m from the surface, silicate subzone with uranophane and beta-uranophane in U ore and iriginite and calcurmolite in Mo-U ore follows. Down to 30 m, subzone of uranium leaching with Fe-Mn hydroxides, occasional uranophane and powellite after U-Mo ore is observed.

At the other Russia's and abroad deposits, the stage replacement of nasturan by uranyl minerals is less clear; subsequence of minerals is frequently disturbed. Commonly, the stage formation of minerals with oxidation of dense U ore is caused by sulfides, arsenides, and coffinite in the nasturan and uraninite veins. For example, the oxidation of coffinite associated with nasturan at the beginning of the process results in the precipitation of uranyl silicates rather than hydroxides, while arsenides cause the formation of uranyl arsenates. In the gallery at the Lastochka, a block of nasturan ore with small inclusions of As-bearing pyrite was found. The supergene alteration of this block resulted in the precipitation of trögerite and uranospinite after fresh nasturan.

The high permeability of orebodies causes the dissolution of nasturan rather than its hydration. For example, at the Uchkuduk-type deposits, Tajikistan, the oxidation of uranium ores hosted in sand was not accom-

Table 5. Chemical composition (wt.%) of hydrated nasturan and alteration products, Lastochka (Tumannyi) deposit, Khabarovsk krai, Russia

Oxides	Hydrated	Urhite	Urhite	U-Fe phases		Brownish		Uranophane	Uranophane
	nasturan					yellow veinlet			
UO ₂	31.76	—	—	—	—	—	—	—	—
UO ₃	51.65	66.02	61.30	26.14	18.72	49.0	46.33	52.75	46.47
SiO ₂	2.25	5.24	5.84	12.12	21.25	9.48	11.51	21.57	23.56
Al ₂ O ₃	2.15	0.17	1.35	4.82	5.67	2.41	3.06	5.92	10.50
Fe ₂ O ₃	—	2.06	7.06	36.95	36.87	2.58	3.70	0.64	0.28
CaO	2.54	2.03	2.50	1.12	1.58	2.40	2.30	5.28	4.63
MgO	—	0.71	0.27	0.58	0.48	0.41	0.36	0.35	0.30
PbO	1.80	1.90	2.43	—	1.00	0.91	1.00	—	—
ZrO ₂	0.55	0.62	1.28	1.22	0.30	2.10	3.35	—	—
Nb ₂ O ₅	4.86	3.70	3.15	2.11	1.40	9.00	8.00	—	—
As ₂ O ₅	0.15	3.33	0.12	—	0.73	—	0.02	—	—
K ₂ O(Na ₂ O)	—	—	—	—	0.23	1.23	1.22	0.32	0.46
MoO ₃	0.06	0.04	0.03	0.05	0.01	4.86	4.65	0.04	—
TiO ₂	—	0.30	0.70	0.67	0.19	1.93	2.55	show	show
H ₂ O	2.44	13.33	14.03	11.89	11.9	11.9	11.69	12.85	13.63
Cl	—	—	—	—	—	1.72	—	—	—
Total	100.21	99.45	100.06	97.67	100.33	99.93	99.74	99.72	99.83

panied by the formation of uranyl minerals and orebodies are separated from the oxidized brown sand colored by Fe³⁺ hydroxides by light band from which U and Fe are completely leached. The similar phenomenon is observable at the roll deposits of the South Kazakhstan, Siberia, Transbaikal Region, and sedimentary basins in Bulgaria. When the permeability of orebodies is irregular, nasturan is replaced by uranophane and shrökingerite rather than by uranyl hydroxides. For example, at the Rizak deposit, Kurama Ridge, Uzbekistan, located in mountainous district, modern oxidized zone begins its formation and veinlets of gummite with curite, becquerelite and billietite were observed at the surface. At few cm below surface, pockets of nasturan and hydrated nasturan retain in the gummite veinlets. Aside the gummite veinlets, uranophane occurring as thin crusts and earthy films fills fractures in wall rocks. In addition to uranium minerals, only Mn oxides, calcite, and kaolinite were observable in

this place. Downward, content of nasturan and hydrated nasturan increases in the veinlets and at a few meters below surface, these minerals are predominant. In this place, the ore-bearing fracture joins with a post-ore fracture zone. Content of nasturan in the orebody below junction of ore-bearing fracture and post-ore fracture zone sharply decreases, whereas concentration of uranophane significantly increases. No uranyl hydroxides were found in these places, although the oxidized zone is traced deeper. Sooty pitchblende is occasional in the oxidized ores.

Conclusions

Thus, according to new and literature data, simple oxides in uranium ores are nasturan, sooty pitchblende, and less frequent Th- and REE-free uraninite. Uranium-bearing cerianite is probable at complex carbonatite and U-P deposits and Th-bearing uraninite is the major ore mineral of peralkaline granite

of the Bokan Mountains, Alaska. Uraninite and nasturan are established to be transformed in different way in relation to permeability. Dense monomineralic segregations of uraninite and nasturan are oxidized to form hydroxide minerals. Currently, numerous simple and complex uranyl oxides, three uranium (IV + VI) oxides, and a few X-ray amorphous phases of hexavalent uranium are reported. Overwhelming majority of uranyl hydroxides occur in a few deposits: Schinkolobwe, Wölsendorf, Margnac, Tulukuevo, and Lastochka, where quite large monomineralic segregations of nasturan or uraninite crystals. Uranyl hydroxides are also formed as a result of oxidation of uraninite in pegmatite.

In the water-permeable areas, simple oxides are replaced by uranyl silicates omitting hydroxide stage or uranium is leached from the oxidized ore without formation any uranyl minerals. The oxidation of ore with sooty pitchblende in sand results in nearly complete removal of uranium. Gritsaenko *et al.* (1959) reported the leached oxidation zones. Highly leached oxidized zone is characteristic of most deposits in the Streltsovka structure, Southeastern Transbaikal Region and other deposit in Russia and abroad. Here-with, in the most cases, significant part is carried out of the orebody. In the other deposits, basically located in arid areas, a richer oxidized ore is formed: Sernyi, Turkmenistan; Rössing, Southwestern Africa, U-V deposits Shakoptar and Maili Sai, Kirgizia, and Pap, Uzbekistan (Chernikov *et al.*, 2010).

In addition, oxidation of nasturan associated with arsenides, As-bearing pyrite or native arsenic results in the formation of trögerite and other uranyl arsenates at the initial stage of nasturan transformation (Aktepe, Uzbekistan; Lastochka, Khabarovsk krai), rather than uranyl hydroxides. Hence, the stages of the formation of the oxidizing zone at the uranium deposits suggested by Belova (1975) are a rare particular instance with minor uranium hydroxides in uranium ores. During formation, the oxidizing zone both increases and decreases in size in comparison with size of primary orebody. In the humid areas, uranium is leached down to a significant depth in the oxidizing zone; in the other cases, content of uranium does not change substantially with oxidation of nasturan and uraninite ore

or significantly increases in comparison with fresh ore.

These features of uranium ore oxidizing are important for both theory and economics. In particular, they should be into account to elaborate exploration criteria for uranium deposits prospected by outcrops of orebodies as it was noted previously (Chernikov, 2010). Poor-crystallized nanoscaled X-ray amorphous matter is important because it reflects on technological properties of the ores especially when uranium is leached in situ by well.

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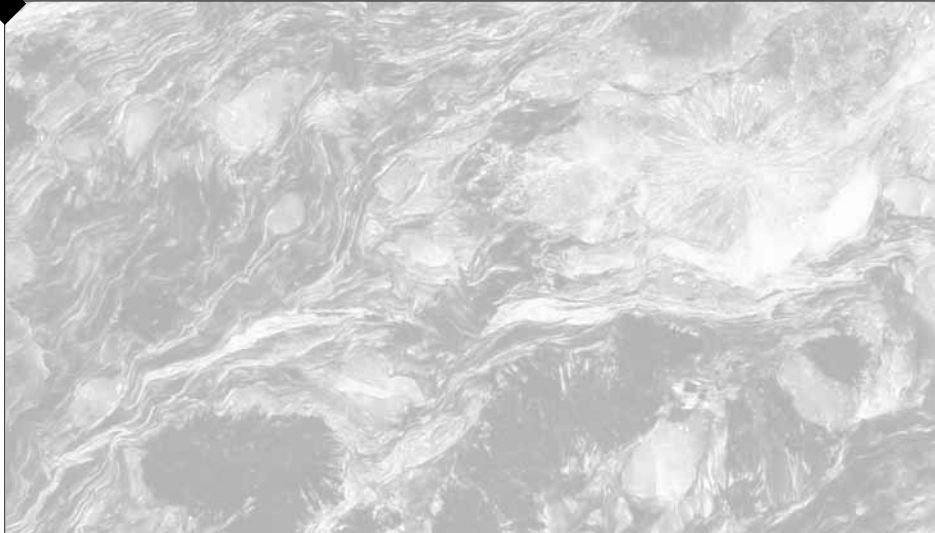
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**Crystal Chemistry,
Minerals
as Prototypes
of New Materials,
Physical and Chemical
Properties of Minerals**



EXPERIMENTAL STUDY OF CRYSTALLIZATION PRODUCTS OF CHALCOPYRITE SOLID SOLUTION

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In order to understand the conditions of formation of cubanite CuFe_2S_3 , talnakhite $\text{Cu}_9\text{Fe}_8\text{S}_{16}$, mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ and haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$ in magmatic Cu-Fe ores of the Norilsk type the method of melt cooling from 1150–1100°C up to room temperature and subsequent annealing at 600 and 800°C phase associations of the central part of Cu-Fe-S system have been synthesized: 50 at.% of S, Cu/Fe = 1.22–0.25, 47 at.% S, Cu/Fe = 1.12–0.63 and 45 at.% S, Cu/Fe = 1.44–0.69. According to the received results, cubic cubanite enriched in copper (Cu/Fe \geq 0.5) crystallizes in associations with tetragonal chalcopyrite $\text{Cu}_{1-x}\text{Fe}_{1+x}\text{S}_2$ and cubic talnakhite. The new data concerning steady phase equilibriums of mooihoekite with bornite Cu_5FeS_4 and cubic pc phase of the haycockite composition with cubic cubanite enriched in iron (Cu/Fe \leq 0.5) bornite and pyrrhotite Fe_{1-x}S are received.

1 figure, 1 table, 20 references.

Key words: Cu-Fe-S system, chalcopyrite solid solution, crystallization of melt.

Introduction

Cubic talnakhite $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ (Bud'ko, Kulagov, 1963; Cabri, 1967), tetragonal mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (Cabri, Hall, 1972; Muraviova *et al.*, 1972), rhombic haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$ (Cabri, Hall, 1972) and cubic cubanite CuFe_2S_3 (Cabri, 1973) are attributed to the products of crystallization of chalcopyrite (Yund, Kullerud, 1966) intermediate (Merwin, Lombard, 1937) solid solution established experimentally in the central part of the Cu-Fe-S system at 800–300°C. Together with chalcopyrite CuFeS_2 these minerals are the basic components of the magmatic Cu-Fe ores of the Norilsk type. Close of compositions and complex intergrowths with each other and other sulfides complicate diagnostics of natural minerals and do not allow to determine unambiguously their age relations and to connect features of their composition and structure with definite conditions of crystallization. The basic experimental researches of the Cu-Fe-S system (Yund, Kullerud, 1966; Kullerud *et al.*, 1969; Cabri, 1973; Barton, 1973; Likhachiov, 1973; Sugaki *et al.*, 1975; Vaughan, Craig, 1981; Vaughan, Craig, 1997; Tsujmura, Kitakaze, 2004) are connected with the sphere of existence of chalcopyrite solution at 800–300°C. Conceptions about phase equilibriums at low temperatures are not clear and inconsistent, because they are based on the results of investigation of natural phase associations and results of extrapolation of isolated experimental data in the sphere of low temperatures (Vaughan, Craig, 1981; Vaughan, Craig, 1997).

The purpose of the presented work is synthesis of steady at room temperature phase associations of the central part of the Cu-Fe-S

system for determination of phase compositions and phase equilibriums in the sphere of chalcopyrite solid solution.

Methodics

Up to now the most complete experimental research of phases from the sphere of chalcopyrite solid solution is the work by L.J. Cabri (Cabri, 1973). The scheme of phase relations of the central part of the Cu-Fe-S system at 600°C constructed by Cabri agrees with the corresponding scheme of R.A. Jund and G. Kullerud at 700°C (Yund, Kullerud, 1966) and is an evident illustration of high-temperature and possible low-temperature phase associations in relation to the formation of tetragonal chalcopyrite (557°C, Yund, Kullerud, 1966). Hence, the scheme of Cabri (black hatch lines on the Fig.) has been used as a basis for a choice of initial compositions of samples synthesized in the presented work. As evident from the Figure, initial compositions of the synthesized samples correspond to compositions of possible phase associations with the listed above products of crystallization of the chalcopyrite solid solution (iss on the Figure).

Synthesis of samples is performed from the following elements: carbonyl iron A-2, copper B3 and ultrapure sulfur additionally dehydrated by melting in vacuum. All samples have been synthesized in evacuated quartz ampoules by a method of melt cooling from 1150–1100°C up to room temperature. The temperature of melt (\approx 1070°C) is determined according to the results of the thermal analysis of the most infusible initial samples. The mode of cooling has been chosen experimentally in view of the data on temperatures of the iss crystallization. Cooling was

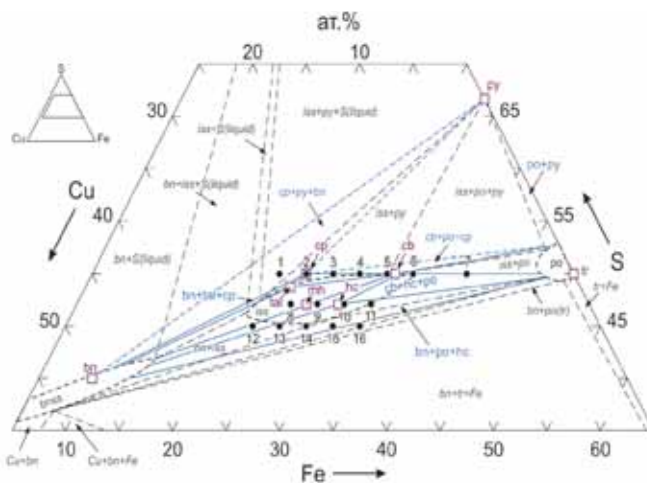


Fig. 1. The scheme of relationships of the phases synthesized in the presented work (continuous blue lines) on the scheme of phase relations of the central part of system Cu-Fe-S from Cabri (Cabri, 1973) at 600°C (hatch black lines, Cabri, 1973). 1–16 – initial compositions of the synthesized samples. *iss*, *bnss* and *po* – areas chalcopyrite, bornite and pyrrhotite solid solutions. □ – stoichiometric compositions of minerals: tetragonal chalcopyrite CuFeS_2 (*cp*), bornite Cu_5FeS_4 (*bn*), pyrite FeS_2 (*py*), troilite FeS and products of crystallization of chalcopyrite solid solution (*iss*): talnakhite $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ (*tal*), cubanite CuFe_2S_3 (*cb*), mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (*mh*) and haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$ (*hc*). On the Figure by hatch blue lines equilibria with participation of phases present in insignificant quantities (designated by asterisk in the Table) are designated. These phases are formed after *iss* crystallization (Cabri, 1973).

carried out in two stages. The first stage – fast cooling (with a rate of 50° per hour) up to 1000, 900, 850 or 800°C and keeping at these temperatures from several hours up to 10 days. The second stage – slow cooling (with a rate of 60° per a day) up to 300°C, keeping at 300°C from several hours up to 3 months, further cooling up to room temperature with the switched off furnace. Fast cooling was performed for determination of the *iss* composition at temperatures of melt crystallization (1000–850°C, Yund, Kullerud, 1966) in view of the data on the melt existence at 800°C (Tsumjura, Kitakaze, 2004). It is a mode I. Further representative parts of the synthesized samples annealed at 600°C within 1.5 months, and at 800°C – within 20 days with the subsequent cooling in cold water. It is a mode II.

Synthesized samples have been investigated by methods of optical microscopy and X-ray analysis. Polished sections are prepared from half of each sample (section along the center from top- down). The chemical composition of phases is determined by microprobe analysis with the help of microanalyzer "Camebax-Micro". Chalcopyrite CuFeS_2 is used as a standard. Accelerating voltage – 20 kV, current of absorbed electrons – 40 nA, angle of sampling – 40°, time of account – 10 seconds on each analytical line, diameter of probe – 2–3 microns. Precision of determination of all components is within the limits of 2 relative %. Detection limit of elements C_{\min} is calculated

according to 2 δ -criterion at a significance level of 99%. C_{\min} is as follows (in weight %): Cu – 0.04; Fe – 0.03; S – 0.01. X-ray phase analysis was performed with the help of diffractometer DRON-3.

Results

For the phases synthesized in the presented work the following standard names of their natural analogues of stoichiometric composition and corresponding structure are used: cubic talnakhite $\text{Cu}_9\text{Fe}_8\text{S}_{16}$, tetragonal bornite Cu_5FeS_4 , chalcopyrite CuFeS_2 and mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$, rhombic cubanite CuFe_2S_3 and haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$. Thus in the presented work, as well as in the work by Cabri (Cabri, 1973), for the synthesized phases with cubanite and haycockite compositions the cubic structure (fcc and pc, respectively) is established.

Results of synthesis of phase associations of the central part of the Cu-Fe-S system (samples with the following compositions: 50 at.% of S, Cu/Fe = 1.22–0.25; 47 at.% of S, Cu/Fe = 1.12–0.63 and 45 at.% of S, Cu/Fe = 1.44–0.69) containing the listed above products of *iss* crystallization are shown in the Table and on the Figure. For the samples synthesized by cooling of the melt from 1150°C up to room temperature (modes I), composition of all synthesized phases is presented. For the samples synthesized according to the mode I with subsequent annealing at

Table 1. Results of synthesis of the samples belonging to the central part of system Cu-Fe-S

N of sample Initial composition: S, Cu, Fe, at.% Cu/Fe	Synthesis according to modes I				Synthesis according to modes II						
	Phases	Composition of phases, at.%, weight %			Total, weight %	Composition of phases, at.%, weight %			Total, weight %		
		Cu	Fe	S		Cu	Fe	S			
1 50, 27.5, 22.5 1.22	cp	25.28	24.86	49.86	99.79	25.29	24.98	49.73	99.71		
		34.90	30.17	34.72		34.86	30.26	34.59			
	bn	47.90	10.79	41.31	99.28	30.41	23.38	46.21	99.46		
		60.78	12.04	26.46		40.72	27.52	31.22			
	py*						bn, bn				
1a 50, 27.5, 22.5 1.22	tal	27.64	23.34	49.02	99.79	26.92	24.63	48.45	99.36		
		38.00	28.19	33.99		36.64	29.45	33.27			
	iss	32.70	20.51	46.79	99.48	32.31	21.33	46.36	99.27		
		43.76	24.13	31.59		43.08	25.00	31.19			
					29.62	23.34	47.04	39.80	27.58	31.92	99.30
							bn, bn				
5 50, 17.5, 32.5 0.54	tal + cb	25.54	25.81	48.65	99.65	27.72	24.53	47.75	99.72		
		34.97	31.07	33.61		37.68	29.30	32.74			
8 47, 28, 25 1.12	tal	27.04	24.12	48.84	98.85	26.29	24.63	49.08	98.80		
		36.68	28.75	33.42		35.80	29.48	33.52			
	cp	25.43	24.71	49.86	99.10			bn			
		34.86	29.76	34.48							
bn	48.32	11.59	40.09	98.90							
	60.69	12.80	25.41								
2 50, 25, 25 1	cp	24.36	25.83	49.81	99.06	24.81	25.69	49.50	99.00		
		33.43	31.15	34.48		33.94	30.90	34.16			
	bn*, py*					24.98	26.06	48.96	98.76		
						33.99	31.16	33.61			
3 50, 22.5, 27.5 0.82	cp + cb	23.34	27.87	48.79	99.80	23.19	27.46	49.35	98.83		
		32.16	33.74	33.90		31.74	33.02	34.07			
	py*					23.16	28.59	48.25	99.69		
						31.79	34.49	33.41			
4 50, 20, 30 0.67	cp	22.72	27.67	49.61	99.92	19.82	30.14	50.04	99.49		
		31.50	33.72	34.70		27.56	36.84	35.09			
	cb	17.64	33.08	49.28	99.57	20.08	30.30	49.62	99.05		
		24.54	40.44	34.59		27.71	36.78	34.56			
5a 50, 17.5, 32.5 0.54	cp	22.08	28.28	49.64	99.13	20.93	29.29	49.78	98.99		
		30.47	34.23	34.49		28.86	35.50	34.63			
	cb	18.15	32.48	49.37	99.40	17.34	33.13	49.53	98.55		
		25.20	39.62	34.58		23.92	40.17	34.46			
	py*, po*				19.54	31.90	48.56				
	bn*				26.92	38.62	33.75	99.29			
6 50, 15, 35 0.43	cb	16.33	34.07	49.60	99.46	16.56	34.06	49.38	99.56		
		22.86	41.90	35.03		23.10	41.73	34.73			
	hc	22.41	30.65	46.94	99.51	23.66	30.46	45.88	98.80		
		30.38	36.52	32.10		31.78	35.95	31.07			
po	2.01	47.90	50.09	99.51	19.86	32.00	48.14	99.49			
	2.88	60.39	36.24		27.34	38.72	33.43				
							po, po				

Table 1.

7 50, 10, 40 0.25	cb	14.74	35.07	50.19		15.31	35.62	49.07	
		20.72	45.34	35.61	99.67	21.31	43.58	34.46	99.35
	po	1.08	48.50	50.42		<i>17.37</i>	<i>33.75</i>	<i>48.88</i>	
		1.55	61.30	36.58	99.43	<i>24.00</i>	<i>41.00</i>	<i>34.08</i>	<i>99.08</i>
						<i>21.28</i>	<i>31.53</i>	<i>47.19</i>	
						<i>38.94</i>	<i>37.68</i>	<i>32.37</i>	<i>98.99</i>
							<i>po, po</i>		
9 47, 25.5, 27.5 0.93	mh	25.64	27.21	47.15		25.81	27.52	46.67	
		34.74	32.34	32.25	99.33	35.03	32.83	31.97	99.83
	bn	45.37	13.68	40.95					
		58.10	15.40	26.46	99.96				
12 45, 32.5, 22.5 1.44	mh	25.82	27.17	47.01		25.95	27.19	46.86	
		34.91	32.29	32.07	99.27	35.11	32.33	31.98	99.42
	bn	46.19	12.92	40.89		31.75	23.46	44.79	
		59.04	14.51	26.37	99.92	42.06	27.31	29.93	99.30
								bn	
10 47, 23, 30 0.77	hc	23.29	29.19	47.52		22.79	29.37	47.84	
		31.73	34.96	32.68	99.36	30.94	35.05	32.77	98.76
	bn	49.40	11.05	39.55					
		62.37	12.26	25.19	99.82		bn		
13 45, 30, 25 1.20	hc	23.71	29.40	46.89		24.53	28.22	47.25	
		32.09	34.97	32.02	99.08	33.16	33.54	31.80	98.93
	bn	47.52	12.86	39.62		<i>24.65</i>	<i>29.17</i>	<i>46.18</i>	
		60.24	14.34	25.35	99.93	<i>33.34</i>	<i>34.69</i>	<i>31.52</i>	<i>99.55</i>
								bn, bn	
11 47, 20.5, 32.5 0.63	hc	22.56	30.12	47.32		22.66	29.68	47.66	
		30.75	36.09	32.55	99.81	31.00	35.69	32.91	99.60
	bn	49.20	10.85	39.95					
		62.87	12.18	25.75	100.80		bn, po		
	po	1.65	47.85	50.50					
2.37		60.46	36.62	99.46					
14 27.5, 27.5, 45 1	hc	23.09	30.05	46.86		22.83	30.39	46.78	
		31.63	36.18	32.38	100.19	31.09	36.36	32.13	99.58
	bn	46.33	13.67	40.00					
		58.76	15.24	25.60	99.60		bn, po		
	po	1.27	48.46	50.27					
1.81		60.85	36.24	98.90					
15 25, 30, 45 0.83	hc	22.56	30.45	46.99		23.54	29.84	46.62	
		30.60	36.30	32.16	99.06	31.94	35.58	31.90	99.42
	bn	44.52	14.90	40.58		<i>23.65</i>	<i>29.94</i>	<i>46.41</i>	
		56.50	16.62	25.99	99.11	<i>32.22</i>	<i>35.85</i>	<i>31.90</i>	<i>99.97</i>
	po	1.17	48.76	50.07					
1.68		61.88	36.47	100.03		bn, po			
						<i>bn, po</i>			
16 45, 22.5, 32.5 0.69	bn	54.50	6.90	38.60					
		67.73	7.54	24.20	99.47		<i>bn, po</i>		
	po	1.86	48.08	50.06					
		2.67	60.68	36.36	99.97				

Note: modes: I – cooling of samples from 1150°C with different speed in the interval 1000–850°C and further cooling up to room temperature, II – annealing of the samples synthesized according to the mode I at 600°C (usual font) and 800°C (italics) with cooling up to room temperature in cold water. For annealed samples (mode II) compositions of crystallization products of solid solution *iss* are shown. Composition of other phases (specified by badges) was not determined. Phases: cp – chalcopyrite, bn – bornite solid solution, py – pyrite, cb – cubanite, po – pyrrothite, tal – talnakhite, mh – mooihokite, hc – haycockite. * – Phases present in insignificant quantities on the surface or in cavities within the synthesized samples.

600 and 800°C (modes II) — only composition of corresponding products of iss crystallization is presented. Influence of the cooling mode on phase composition of the investigated products of the melt crystallization has been established for samples of compositions No 1 and 5 and is discussed below. The scheme of relations of the synthesized phases is constructed according to the results of the modes I synthesis (blue lines on the Figure). Equilibriums with participation of the phases present in insignificant amount (they are designated by an asterisk in the Table) are shown by blue hatch lines on the Fig. 1.

Talnakhite $\text{Cu}_9\text{Fe}_3\text{S}_{16}$ it is synthesized in the samples No 1 and 1a, having the following composition: 50 at.% of S, Cu/Fe = 1.22, and in the sample No 8 with sulfur content — 47 at.% and Cu/Fe = 1.12. Talnakhite in it is in association with chalcopyrite and bornite. In the sample No 5 (50 at.% of S, Cu/Fe = 0.54) it is in the association with cubanite. In the sample No 1 cooled quickly up to 1000 or 900°C, talnakhite and chalcopyrite form very thin disinyegration structure. Only composition of chalcopyrite from this structure is determined. In the sample No 1a with the same composition as the sample No 1, but cooled quickly up to 800°C, talnakhite and iss are established. The composition of iss is located on the line talnakhite — bornite and corresponds to the extreme iss, enriched in copper, established at 600°C. The composition of the sample No 5 cooled quickly up to 1000°C corresponds to the composition of the mix of cubanite with talnakhite, and after the annealing at 600°C it is close to the talnakhite composition and to the initial composition of the sample No 8. In the sample No 8 which has been quickly cooled up to 850°C and kept at this temperature for 4 days, segregations of chalcopyrite and talnakhite, forming a disintegration structure larger than in the sample No 1. Both phases in this structure are easily determined. Except for the characteristic for talnakhite reflex 7.50, the X-ray diffraction pattern of the mix of talnakhite with chalcopyrite differs from the X-ray diffraction pattern of chalcopyrite by the bifurcation of the reflex 3.04, inverse ratio of intensities tetragonal doublets 1.870—1.856; 1.592—1.575 and displacement of reflexes 1.870 —1.856 towards big angles according to the reduction of interplanar spacing which is connected with an increase of the Cu/Fe ratio. Bifurcation of the reflex 3.04 on the X-ray diffraction pattern confirms the presence of two phases, and inverse ratio of intensities of tetragonal doublets 1.870—1.856; 1.592—1.575 corresponds to the greater content of cubic talnakhite in comparison with tetragonal chalcopyrite. Thus, talnakhite is synthesized during the

cooling of the melt of the composition: 47—50 at.% of S, Cu/Fe = 1.12—1.22 in association with chalcopyrite and bornite, and also from the melt of the composition 50 at.% of S, Cu/Fe = 0.54 in association with cubanite.

Cubanite CuFe_2S_3 is synthesized in the samples NN 3—7 which initial compositions are located on the line chalcopyrite — cubanite — pyrrhotite (Fig.). In the samples NN 3—5a (50 at.% of S, Cu/Fe = 0.82— 0.54) cubanite is in the association with tetragonal chalcopyrite, in the sample No 6 (50 at.% of S, Cu/Fe = 0.43) — with pyrrhotite and haycockite, and in the sample No 7 (50 at.% of S, Cu/Fe = 0.25) — with pyrrhotite. During the change of the samples composition from chalcopyrite to cubanite, the quantity of cubanite increases in it. Phases form the disintegration structure that is often not seen during the microprobe analysis that complicates determination of their composition and quantitative ratios. It was appeared possible separate determination of composition of chalcopyrite and cubanite only in the samples No 4 and 5a that have been quickly cooled up to 900— 850°C and are maintained at 850°C during 4—10 day. In the sample No 5a, cooled quickly up to 800°C, only cubanite was synthesized which composition is close to the initial composition of the sample and corresponds to the composition of cubanite, synthesized in the sample No 5a annealed at 600°C (Cu 17.34, Fe 33.13, S 49.53). X-ray diffraction patterns of the mix of chalcopyrite and cubanite correspond to the X-ray diffraction pattern of the tetragonal chalcopyrite with shift of reflexes 1.870 and 1.856 towards smaller angles according to the increase in interplanar spacings during the reduction of the Cu/Fe relation. Besides, X-ray diffraction pattern of the mix of cubanite and chalcopyrite of the sample No 5a with the prevailing content of cubanite, as well as X-ray diffraction pattern of the mix of talnakhite and chalcopyrite of the sample No 8, differs from the X-ray diffraction pattern of chalcopyrite by bifurcation of the reflex 3.04 and an inverse ratio of intensities of tetragonal doublets: 1.870—1.856; 1.592—1.575. In the sample No 6 cubanite is synthesized in the association with haycockite and pyrrhotite. In the sample No 7 synthesized according to the mode I the composition of cubanite corresponds to the initial composition of the sample No 6 and to the composition of the extreme member, enriched in iron iss at 600°C. In the same sample, annealed at 800°C, cubanite of the stoichiometric composition is synthesized in the association with pyrrhotite and iss which composition lies on the line haycockite — pyrrhotite and corresponds

to the initial composition of the sample No 11. As it could be seen from the Table and Figure, the composition of cubanite of the sample No 5a is close to the composition of the stoichiometric cubanite from the chalcopyrite side, and sample No 6 – from the side of pyrrhotite. Thus, enriched in copper ($\text{Cu/Fe} \geq 0.5$) cubanite CuFe_2S_3 crystallizes in association with chalcopyrite or talnakhite (sample No 5) depending on the mode of cooling, and enriched in iron ($\text{Cu/Fe} \leq 0.5$) – with haycockite and pyrrhotite.

Mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ is synthesized in the samples No 9 (47 at.% of S, $\text{Cu/Fe} = 0.93$) and No 12 (45 at.% of S, $\text{Cu/Fe} = 1.44$) in association with bornite regardless of the mode of synthesis. As it could be seen from the Fig. 1 and Table, the initial composition of the sample No 9 is close to the composition of mooihoekite, and the sample No 12 – lies on the line bornite – mooihoekite, and corresponds to the iss composition after the annealing at 800°C. Unlike cubanite and talnakhite that crystallize in the form of a disintegration structure with chalcopyrite, mooihoekite is a homogeneous phase and can easily be determined.

Haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$ (a phase of the haycockite composition with cubic pc structure) is synthesized in the sample No 10 (47 at.% of S, $\text{Cu/Fe} = 0.77$) and No 13 (45 at.% of S, $\text{Cu/Fe} = 1.20$) in association with bornite, in samples NN 11 (47 at.% of S $\text{Cu/Fe} = 0.63$) and 14–15 (45 at.% of S, $\text{Cu/Fe} = 1–0.83$) in association with bornite and pyrrhotite, and also in the described above sample No 6 in association with the enriched in iron cubanite and pyrrhotite. Haycockite, as well as mooihoekite, is easily determined.

Thus, phase associations of the central part of the Cu-Fe-S system are synthesized by the method of melt cooling, and compositions of phases and phase equilibria are determined in the field of crystallization of the chalcopyrite solid solution.

As it could be seen from the Figure, the constructed scheme of mutual relations of synthesized phases agrees with experimental researches of the Cu-Fe-S system at 600°C (Cabri, 1973). Investigation results of phase composition of the samples annealed at 800°C do not conform to T. Tsudzhimura and A. Kitakaze's data (Tsumura, Kitakaze, 2004) on the instability of the equilibria bn-iss, bn-po and existence of melt at 800°C. According to the results of the thermal analysis of initial samples, crystallization of melt in the investigated area of the system is finished at the temperature $\approx 854^\circ\text{C}$. It conforms to the data of Yund and Kullerud (Yund, Kullerud, 1966). Compositions and phase mutual relations

of the products of iss crystallization synthesized in the present ed work correspond to the literature data on their natural analogues (Bud'ko, Kulagov, 1963; Cabri, 1967; Cabri, Hall, 1972; Muraviova *et al.*, 1972; Fiulimonova *et al.*, 1974; Genkin *et al.*, 1981; Distler *et al.*, 1996).

Discussion

Synthesized phase associations can be subdivided onto two groups according to the composition and character of crystallization. The first group – association of talnakhite with chalcopyrite and bornite (samples NN 1, 1a, 5, and 8) and enriched in copper cubanite with talnakhite and chalcopyrite (samples NN 3–5a) – is characterized by complex structures of disintegration and sensitivity to the mode of cooling. The second group is characterized by equilibria of haycockite with enriched in iron cubanite, pyrrhotite (sample No 6), haycockite with bornite (sample No 10), haycockite with bornite and pyrrhotite (samples NN 11, 13–15). As it could be seen from the Figure, the mentioned groups of phase associations are divided by the line of the equilibrium bornite-mooihoekite-cubanite. Above this line lies the area of crystallization of phase associations of the first group, and lower – of the second. According to agreed data of Yund, Kullerud and Cabri (Yund, Kullerud, 1966; Cabri, 1973), phase associations of the first group are in agreement with enriched in sulfur area iss and iss + bn, and phase associations of the second group are in agreement with the area iss with pyrrhotite and bornite (dashed lines without a line py-iss on the Fig. 1). Thus, after the crystallization of iss, cooling of phase associations of the first group occurs in the presence of free sulfur and it causes dependence of their phase composition on the mode of cooling. Crystallization and cooling of iss in the second group of phase associations occurs in conditions of invariant equilibrium and it is, probably, a principal cause of haycockite crystallization in cubic (pc) form instead of rhombic (Hall, 1975). Different conditions of cooling after iss crystallization of different composition are proved by various behaviour of gold, silver, platinum and palladium during crystallization of melts of the mentioned groups of phase associations (Kravchenko, 2009; Kravchenko, Nigmatulina, 2009). In the presented work we are not discussing phase associations bornite + pyrite + chalcopyrite and chalcopyrite + cubanite + pyrrhotite (blue hatch lines on the Figure) which are present at insignificant quantities and, according to the data of Yund and Kullerud, are formed after the melt crystallization (Yund, Kullerud, 1966).

Conclusions

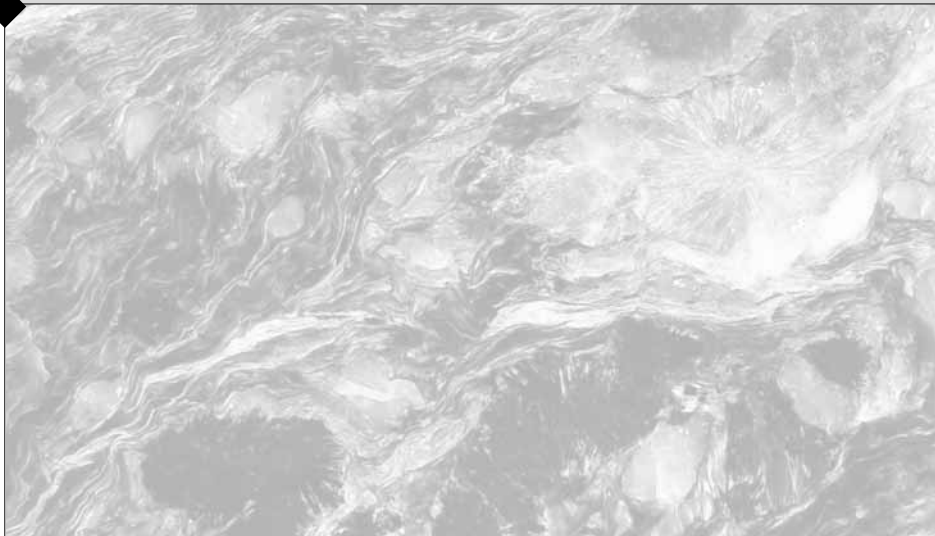
1. Phase associations: talnakhite + chalcopyrite, chalcopyrite + cubanite, cubanite + talnakhite, cubanite + pyrrhotite, cubanite + pyrrhotite + haycockite, mooihokite + bornite, haycockite + bornite, haycockite + bornite + pyrrhotite, bornite + pyrrhotite are steady at room temperature products of crystallization of melts of the central part of the Cu-Fe-S system (50 at.% of S, Cu/Fe = 1.22—0.25; 47 at.% of S, Cu/Fe = 1.12—0.63 and 45 at.% of S, Cu/Fe = 1.44—0.69). At the same time in associations with chalcopyrite or talnakhite cubic fcc cubanite CuFe_2S_3 enriched in copper (Cu/Fe \geq 0.5), crystallize, and in associations with haycockite and pyrrhotite — cubanite enriched in iron (Cu/Fe \leq 0.5) crystallize.

2. Established in work phase equilibriums: bornite — talnakhite — chalcopyrite, talnakhite — chalcopyrite — cubanite and mooihokite — cubanite have been previously predicted by L.J. Cabri and S. Hall according to the results of investigations of natural associations and Cu-Fe-S system (Cabri, 1967, 1973; Cabri, Hall, 1972). The same authors have assumed the existence of the following equilibriums: mooihokite — talnakhite, mooihokite — haycockite — troilite and mooihokite — haycockite — copper. However, the equilibrium established in the presented work (cubanite — haycockite) contradicts with the equilibrium mooihokite — haycockite — troilite, and the equilibrium bornite — haycockite — pyrrhotite contradicts with the equilibrium mooihokite — haycockite — copper. For understanding of the reasons of the existing contradictions further more detailed investigation of the synthesized samples and corresponding natural mineral associations is necessary.

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Mineralogical Museums and Collections



MASTERPIECES OF THE PETERHOF CUTTING FACTORY IN THE FERSMAN MINERALOGICAL MUSEUM OF THE RUSSIAN ACADEMY OF SCIENCES

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A brief history of the Peterhof Cutting Factory is documented, the art pieces mastered at the factory and kept in the Fersman Mineralogical Museum are described. 30 figures, 8 references.

Key words: Fersman Mineralogical Museum, stone cutting masterpieces, the Peterhof Cutting Factory.

Establishment of a new Russian capital city at the beginning of the 18th century stimulated a great interest in mining and cutting of construction stones and, later, of gems necessary for decoration of Imperial palaces.

Old standards and skills used in stone architecture of tower-chambers and castles made of soft stone became a thing of the past. New cities of European standard demanded huge quantity of various materials, including hard stone and cutting facilities at the local factories. The country had neither this nor that.

In 1719, Tsar Peter the Great set up a special department, Berg-Kollegium, for exploration and mining of deposits in the country. Due to its work, the country started development of its metal, building stone and, later, decorative stone deposits.

Cutting of stone was difficult. At the beginning, the local craftsmen could only roughly cut the stone, whereas the detailed work was entrusted to invited foreign craftsmen. The scale of work was miserable comparing to tremendous demand, and the Emperor started reforming this industry.

In 1721, following the Emperor's decree, a "windmill and barn" were built. Soft stones, mainly marble and alabaster, were sawed and polished there. Soon, a windmill was replaced by a watermill that was also used for glass polishing, which was in demand at that time.

In 1731, the factory was almost burnt down in a fire, and, three years later, the Empress Anna Ioanovna published a decree for construction of a new one. Construction was headed by Isaac Bruckner from Basel, a former craftsman of mathematical instruments in the Imperial Academy of Sciences. At the factory, he started cutting hard stones for building, and, since the late 1740s, he set up an artistic stone workshop. Josef Bottom

supervised these works. He was also entrusted to cut precious gems and diamonds and was quite successful in this, even inventing "quite a pleasing machine" for cutting of diamonds (Mavrodina, 2007, p.28). Long time after that, Bottom improved the factory equipment, including necessary machinery and instruments for fine haberdashery works.

In the middle 1750s, during the reign of Elizaveta Petrovna, 87 people were employed at the factory, including craftsmen of agate, diamond, gold and haberdashery. They successfully cut and framed gemstones for decoration of quite diverse items ranging from jewelry masterpieces to parade gears for the horses. Small items like snuffboxes, small glasses, plates, bowls and other masterpieces started to appear (Mavrodina, 2007). During Elizaveta Petrovna's reign, the factory began to manufacture initially quite imperfect pictures, made using the technique of Florentine mosaics (Ibid, p.28).

In 1751, to supply these and other stone-cut works with necessary material, a group of stone cutters and polishers headed by Unterschichtmeister Selezhev was sent to Siberia (to the Urals). Raw materials mined by this expedition were used for manufacturing of large items like table tops, chimneys, and architectural details. Rough cutting of them was fulfilled in Yekaterinburg, and in winter the semi-finished articles were delivered to Peterhof by sledges where they were finished and decorated.

In 1763, in the beginning of the reign of Catherine the Great, Betskiy, the President of the Academy of Sciences, became a manager of the factory. Under his management, assortment of the masterpieces was sufficiently widened. In addition to small things, tables, chimneys, and vases, church utensils and iconostases were manufactured. The largest

and perfectly cut masterpieces were manufactured under personal supervision of Bottom. In his time, a carved relief was introduced. Catherine the Great was a great lover and judge of stone-cutting craft, and she wrote with pride to her foreign correspondents that Russian craftsmen were working better than Italian ones (Mavrodnia, 2007, p. 30).

As the factory still needed plenty of various stone materials, Catherine the Great published in 1765 a Decree about setting up a special department in Yekaterinburg called an "Expedition for Exploration of Different Sorts of Gems".

By the middle of the 18th century, many gems had already been found and mined in Russia. The Urals were the main place for their exploration and mining. Since the times of Alexei Mikhailovich (in 1668), first gemstones, such as rock crystal, amethyst, topaz, tourmaline and beryl, were discovered in the River Neiva area in the Urals. But these were still isolated finds. Exploration efforts and mining of raw materials in the first half of the 18th century were also insufficient to satisfy the demands, although since the times of Elizaveta Petrovna, rock crystals and "tumpases" were found in the Urals. Since 1723, in the remote area to the east of Baikal, in the Sherl Mountain and in Adun-Chilon, topaz, aquamarine and heliodor were discovered. In the first half of the 18th century, the Urals' first marble and jasper deposits were also found (jasper was first mentioned in 1742). But all these discoveries were still insufficient. To improve the situation, according to enactment of Katherine the Great, craftsmen and apprentices of Peterhof Factory accompanied by a group of soldiers had been dispatched to the Urals from "the Expedition". The expedition was headed by Major General Danneberg. The two mosaic specialists from Florence, the brothers Jean-Baptist and Valery Tortora, participated in it.

Two years later, Danneberg presented to the Petersburg Court specimens from more than 300 gem deposits of the Urals and a map with their location. Due to this expedition, marble, jasper and such a famous gem "for haberdashery works" like amethyst appeared in Peterhof. Amethyst was from the Tal'yan Deposit (the name originated from "ital'yanets" — an Italian man, a link to the Tortora brothers, who participated in the exploration and mining of local amethyst)

and from mines along the River Ambarka and districts of Yuzhakovo, Alabashka, and Sizikovo. Rock crystals and "tumpases" also supplemented a list of gems which came to Peterhof.

In the second half of the 18th century, in addition to the Urals' deposits, beryl and topaz were mined to the east of Lake Baikal (since the 1770s). In the Baikal area, lazurite was found on the Rivers Slyudyanka (in 1775) and Malaya Bystraya (in 1785). And finally, in the very end of the century (1798), a magnificent rhodonite deposit was discovered near the Maloye Sedel'nikovo Village in the Urals. From then on, intensive exploration and mining works for gems in Russia continued non-stop until the 20th century.

Since the factory could not satisfy enormous appetites of the Imperial Court, a new stone building was promptly built by Felton in 1780. By the end of the reign of Katherine the Great, the factory was able to manufacture plenty of large-scale, voluminous works and individual mosaic masterpieces from hard stone, such as table tops and the like. Besides, craftsmen of the factory participated in the laying out of stone and smalto mosaic floors, as well as decorative panels in the Chinese Palace of Oranienbaum. Having been started during the Empress Elizaveta time, cutting of gems, of which most popular were topaz and aquamarine, was widened sufficiently.

Since 1800 until 1811, Earl Stroganov was in charge of the factory. Prior to this, he was a head of the Yekaterinburg Factory. In his time, mechanical devices were renewed, a sluice was repaired, and many other problems were solved. Josef Bottom approved a staff of 86 employees and divided them according to qualification into craftsmen and apprentices, who fulfilled tasks of variable difficulty. Clear forms of accountability have been introduced.

In addition to the manufacturing of masterpieces for individual purposes and for decoration of the interiors, the factory cut building stone and blocks of hard rock for the Kazan Palace and Bourse (Stock Exchange) in St.-Petersburg.

During this time, the factory manufactured plenty of large objects. To diversify the masterpieces, Bottom requested from Stroganov to obtain the drafts of new items from the Academy of Arts. Since that time, first names of artists-architects, who designed the

masterpieces, were first mentioned, including famous Giacomo Quarenghi (1744–1817) and Andrei Voronikhin (1759–1814). Voronikhin introduced a new, for the factory, technique of combining the gems and voluminous metal plastic in one composition (Mavrodina, 2007, p. 32–33).

Since the beginning of the 19th century, Russian gems and masterpieces gained first recognition in the West. The Factory was now receiving purchase orders from abroad. In spite of that, the enterprise was in a very lamentable state. During that time, after the death of Stroganov, it passed under the curatorship of Earl Guriev, manager of the Cabinet of Her Imperial Majesty. Part of its workshops was transformed to production of surgery instruments and writing paper.

In 1816, Guriev suggested reconstruction of the stone-cutting factory and organised a paper mill, with partial relocation of craftsmen from cutting factory to paper production and to the glass factory. Since that time, a factory was renamed into the Imperial Cutting Factory.

To reinforce the factory with qualified staff, craftsmen were obliged to teach the younger workers. Honoured pupils from the Peterhof Popular College were sent to the Academy of Arts, an internship sponsored by the Cabinet of Her Imperial Majesty. Its graduates were expected to work in all the Russian state cutting factories in Peterhof, Yekaterinburg and Kolyvan.

Nevertheless, all these measures failed to improve the general situation, and, by the end of the 1820s, the factory was in standstill. Very few of the large artistic crafts were manufactured.

Only in 1829, changes started to occur after a factory was transferred to the Ministry of Udels (Regions) under the charge of Earl Perovski. Kazin was appointed a new head manager. A factory was again renovated. Reconstructed workshops were equipped with new machines for sawing of stone blocks, crushing of emery and cut works. Production was classified into "fine and art" crafts for the Imperial House and "ordinary or petty" things ordered by private clients. From 1830 to 1847, a bronze workshop was functioning at the factory. It supplied decoration for the stone crafts.

From 1830, the factory started to work with malachite. Consequently, it earned a title "Russian Mosaic". Malachite cut into thin lamina was glued onto a prepared mould,

with preservation or even completion of stone natural pattern. Malachite was used for large vases, pediments, table tops, consoles, standard lamps and the like. Many of them were decorated by gold-plated bronze. After closure of the bronze workshop at the factory, the "English Shop of Nicholls & Plinke" became a supplier of bronze to the enterprise.

Malachite remained popular for several decades. The factory manufactured plenty of malachite works for the Winter Palace which was severely damaged during the 1837 fire. Besides separate objects like vases, bowls, table tops, and others, all part of the project of architect Bryullov, a unique Malachite Hall was created. Its columns, pilasters, and table tops were cut during thirteen months. Among small objects of this time were caskets, blotters, handles, buttons and others.

The factory was also a producer of souvenirs. Replicas of the Alexander Column, built by Montferrand in front of the Winter Palace in 1834, were very popular.

In the 1830–40s, the factory was producing lazurite items. Lazurite was discovered in the southern Baikal area in the 18th century, but its quality was not favoured by the Court. As a result, expensive lazurite was imported from Badakhshan. Lazurite forms relatively small accumulations, and for this reason it was used for mosaics in a similar fashion to malachite.

At the same time, the traditional mosaics became popular, both cut and combined. It was used in production of the mosaic floors. These works were valued high and were very popular. However, there were no skilled mosaic craftsmen in Russia.

In 1847, a temporary workshop was built at the Pope's mosaic workshop in Rome to specifically teach the Russian artists. Professor Barberi taught four students (Raev, Shapovalov, Fedorov, and Solntsev) from the Imperial Academy of Arts. Craftsman Sokolov studied the art of cut mosaics in the workshop of Professor Gitano Bianchini (Chistyakova, 2005, 2009).

Upon return of Sokolov, mosaics started to prosper in Russia. The Peterhof Factory was manufacturing the Florence mosaics for the Royal Court. Simultaneously, large mosaic and stone-cutting works were initiated for the St. Isaac Cathedral, Peterhof Palace, and the New Hermitage.

In 1847, paper manufacturing has been closed at the factory, while stone cutting has

expanded, and demand for raw materials has increased. The factory received a permission to explore and mine decorative stones in the Perm and Orenburg Governorships, and also in Transbaikalia. It also continued to operate in the Altai, where jasper, multi-coloured porphyry, breccias and marbles were discovered in the 1700s. In 1806, an outstanding white-pink quartzite was discovered at Beloretsk on River Belaya. Since 1851, nephrite production began at the River Onot in Eastern Sayan, where it was discovered back in 1824.

Permikin (1813 – 1879) was one of the suppliers of decorative stones to Peterhof. He was a successful explorer and miner for many years, supplying lazurite from River Malaya Bystraya in Transbaikalia, nephrite from the Sayan, as well as marble and many other stones.

In the middle 19th century, stone-cutting factories prospered in Russia. The Peterhof Factory worked with diverse decorative stones, such as malachite, lazurite, orlets (rhodonoite), porphyry, aventurine, jasper, quartz, nephrite and others. Many large items are now in the Winter Palace, Old and New Hermitage. These are huge malachite vases, malachite and lazurite tables, and chandeliers.

Significant changes took place at the factory with abolishment of the Serfdom in 1861. The workers became free men; they received a right for pension and tax holidays for 12 years, as well as immunity to military service.

There were only 47 craftsmen left. The factory maintained its school where craftsmen's children could study. The study was free of charge, but in the end of education everybody had to work at the factory for at least 10 years.

The Royal Court required many high art stone items. In contrast to the others, the Peterhof Cutting Factory continued to prosper even after abolishment of the Serfdom. The selection of items for manufacturing was very strict. The lazurite items were especially valuable. They were manufactured only for the Royal family, whereas all other material could be used for private orders. This helped the factory to float financially.

In the 1860s, lazurite became more popular than malachite. The large items, such as vases, tables, and standard lamps, made same way as glued malachite items, were used for decoration of the parade interiors of the Royal palaces, as well as for plating many

small items. The lazurite items were precious gifts to the rulers of Western Europe. Sometimes they were sold to the European courts.

Mosaics were popular until the end of the 19th century. It was used to decorate tables, cup-boards and fire places. Many items were of similar quality to the Italian products. They were highly prized at the international exhibitions. In addition, the factory continued to process the precious stones.

In 1875, a factory was again rebuilt and received new equipment for its workshops. A museum and a reception hall have been built. These works were conducted by the architects Gun (1841 – 1925) and Rezanov (1817 – 1887).

In 1866, Gun became a director of the factory. He was a professor of the St.-Petersburg Academy of Arts and an Academician of Architecture. During almost 40 years of his activity, he created outstanding drafts for the stone products of the factory. At the turn of the centuries, many famous artists participated in such design works. Many famous jewelers contributed to the design of metallic frames for precious stones.

In the end of the 19th century, the factory was producing items of diverse style. The fashion for items, made in national style, became strong. Byzantine and Russian motifs were used as templates. Later, they were successfully used with the arrival of the style Modern.

In addition to the numerous works on decorating the interiors, the factory became involved since 1890 into huge and prestigious works to create Royal coffins in the Petropavlovsk Cathedral. Almost all sarcophagi were made from white marble. Only Alexander II grave was made from grey-green picturesque jasper from Revnya in Altai. The grave of the Empress Maria Alexandrovna was made from a unique quality and size block of pink orlets from the Urals.

In 1909, a factory was transferred under the jurisdiction of His Imperial Majesty Office. Mostovenko became a director. He was previously a manager of the Yekaterinburg Factory. During these years, electric machines were installed at the factory. Several other innovations were planned, but WWI interrupted all these works.

The orders for large items have completely stopped, and high art items became rare. Since 1914, the main products of the factory were stone details for various tools. These

were agate and jasper pediments for normal and surveying compasses, rock crystal standards for optical devices, marble and slate boards for electric equipment, agate and marble cups for the chemical laboratories.

After the 1917 October Revolution, the factory became part of the People's Commissariat for Education. It became a specialized enterprise for manufacturing precise stones for military purposes. As by-products, it kept producing small retail items from cheap stones. Other special works were now performed at the Russian Gemstone Trust (Fersman, 1961, Vol. 2, p. 132).

In 1930, a factory was renamed to the First State Factory for Precise Stones. During the WWII, it was destroyed. In 1949, the rebuilt factory became specialized in watches. In 1954, it was renamed into the Petrodvorets Watch Factory and was not producing art items anymore.

The precious and decorative stone collection of the Fersman Mineralogical Museum began to form after the Revolution. The museum already had some specimens of coloured stones. These were mostly polished samples, but they were not art items. Therefore, in 1914, Professor Vernadsky, who was a head of the Mineralogical Museum at that time, has reorganized all collected material into thematic collections, and collection of the decorative and precious stones was absent.

After the 1917 October Revolution, the stone items came to the museum from nationalised private collections. This stimulated establishment of the separate collection for demonstration of the application of natural stones in art. The collection also received some natural stones and art items made from it.

At that time, some outstanding scientists of the country, such as Fersman, Vlodayets, and Kryzhanovski, used to work for the museum. Due to their efforts, the museum received items from the Royal palaces, nobility villas and dissolved educational institutions during the 1920s, including many items of art and/or historical importance, such as stone-cut articles produced at the Peterhof Imperial Cutting Factory.

As it was mentioned above, the Peterhof Factory was producing stone items since the middle 18th century until the early 20th century. The Mineralogical Museum has received items produced (with few exceptions) bet-

ween 1880 and 1919. During these years, the spectrum of coloured stones was not very wide, and there were no many large art objects produced. The museum received mostly small items, predominantly from the Gatchina Palace, which belonged to the Royal family. Several items were received from the Hermitage, whose collection was also originally Royal.

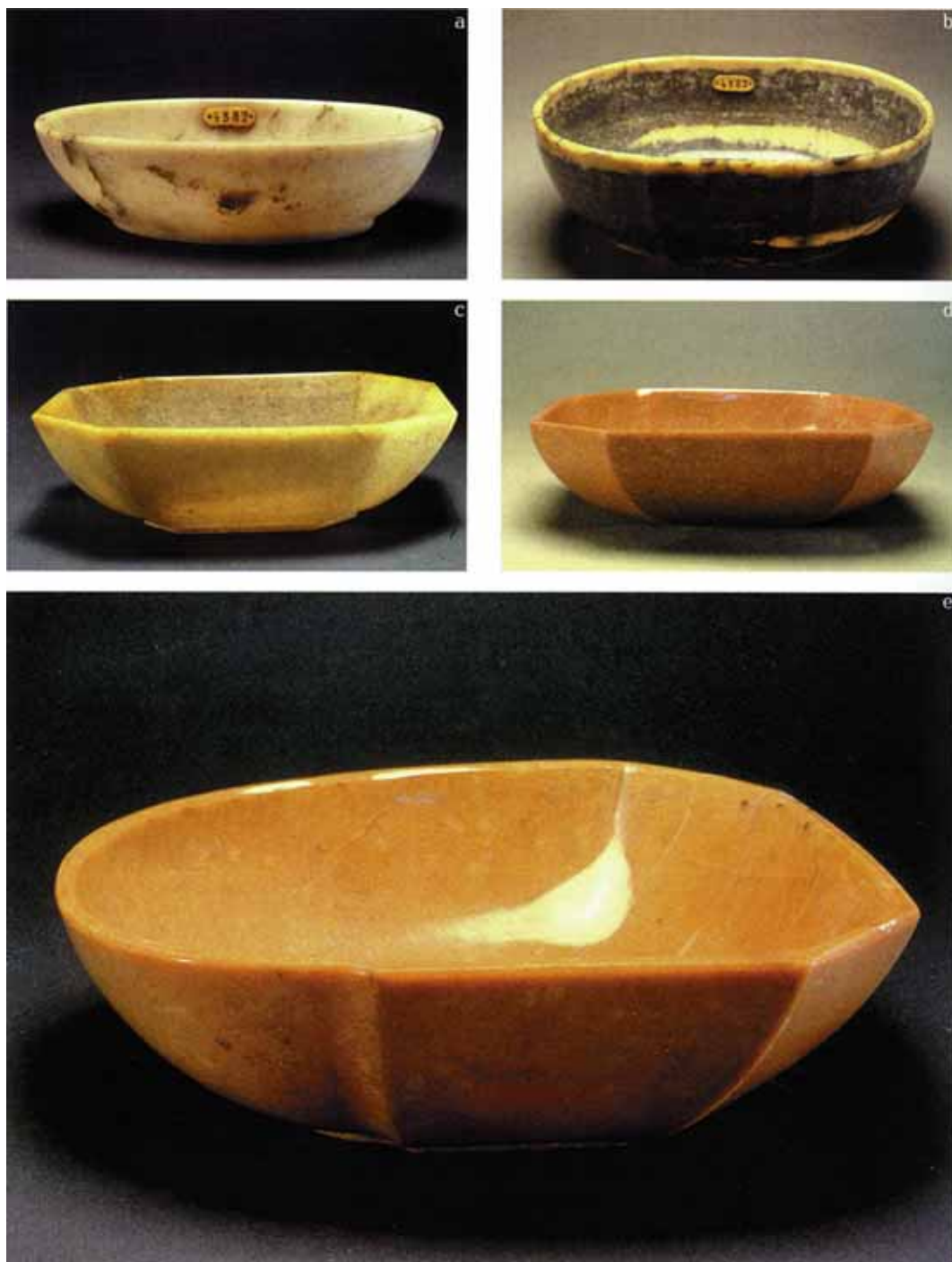
The spectrum of stones, used for the masterpieces of the Peterhof Factory, is not wide: quartzite, agate, orlets, nephrite, and limestone. Some diversity comes only from stones, such as diamond, tiger eye, labradorite, opal, turquoise, and others, which were used to decorate the other materials or were part of mosaic panels.

Below is the description of the stone items kept in the museum, which can be classified with various degree of certainty as products of the Peterhof Cutting Factory.

As it was said above, several items were produced before the turn of the 19–20th centuries. These are five cups cut from varicoloured quartzite. They are all elongated, oval, octahedral or more complex in shape (Fig. 1).

The museum received these cups from the Hermitage in 1926. The Hermitage has received them in 1813. They were part of the collection from the Nieswicz Castle in Belarus, which belonged to Dominic Radziwillowicz who was fighting Russia as an ally of the Bonaparte army. They were put into inventory of the Hermitage at the same time as the cups, which were classified by Mavrodina (2007, p. 51–58) as the items of the Peterhof Cutting Factory of 1760–1810. By analogy, the cups from the Mineralogical Museum can be also attributed to this period. Perhaps, before the 1812 War, they could be presented to Dominic, the owner of Nieswicz, or even earlier to his uncle Karl Radziwillowicz, with whom the Russian monarchs had very complex and changing relationships (Chistyakova, 2005).

It is important to say that the Russian Supreme Court always paid special attention to the design of parade and private apartments. At the turn of the 19–20th centuries, the Royal family was vividly interested in stone-cutting art. It is well known that members of the Royal family were collectors of the stone items produced by Faberge. They were frequent visitors to the Peterhof Cutting Factory, where they could often select attrac-



*Fig. 1. Cups from the Nieswiez Castle collection of the Princes Radziwillowie. Quartzite. Peterhof Cutting Factory 1760–1810. Received from the State Hermitage in 1926.
a) 14.8 x 10.7 cm. FMM № PDK-1639; b) 18 x 14 cm. FMM № PDK-1634; c) 18 x 12 cm. FMM № PDK-1643; d) 13 x 11 cm. FMM № PDK-1644; e) 17 x 15 cm. FMM № PDK-1645.*

tive items and even observe the manufacturing of the most valuable and time-consuming works (see a cabinet description below). In addition, Royal children were taught the basics of mineralogy using specially prepared collections (Generalov, 2007), which were often of art quality (Chistyakova, 2007₁). It is possible that the members of the Royal family were collecting minerals during their trips. For instance, the Great Prince K.N. Romanov brought a piece of basalt from the famous Fingal's Cave on the Staff Island near the western coast of Scotland after his trip to Europe (Chistyakova, 2007₂).

The documents of the Peterhof Imperial Cutting Factory reveal that His Majesty Alexander III brought some pebbles from Crimea in 1886, which he ordered to use for the manufacturing of cupboards (Mavrodina, 2007, p. 475). Perhaps, the Royals were interested in collecting such items for quite a while. During the following years, these pebbles were used to produce the mosaic tables and about 20 ash trays mentioned among the works of the Peterhof Factory before 1893.

The Mineralogical Museum received four ash trays, previously kept in the Gatchina Palace. Two of them are simple in shape. They are made from limestone, which has remains of ancient corals and shells. The other two are more complex in shape. They are made from patchy pale-brown limestone and grey-black limestone conglomerate (Fig. 2).

These objects are rather of historical importance, but many other items of the

Peterhof Factory undoubtedly belong to the high art items.

Quartz constitutes significant part of the museum collection from Peterhof. During the fashion for Old Russian motifs, the factory produced dippers, cups and wine bowls, reminiscent in shape of the old wooden and metallic examples. Since 1866, more than 20 large dippers, as well as approximately 20 small dippers, have been produced. Nephrite was most frequently used for these items. Quartz, belorechite (quartz from River Belaya in the Altai) and rhodonite were rarer.

A dipper, a typical item of such kind, was made from pure rock crystal (Fig. 3). Ideally polished and placed on the three profiled legs, it was decorated on the matt side by the cut ornament, becoming more and more complex at the edge of the item. At its handle, under it and on the opposite side are the circular salient parts, imitating the inserts of precious and coloured stones in the analogous ancient metal vessels. This is a rather rare case when creation of the stone item in the Old Russian style was achieved without metallic frame, but instead by imitating the form of the vessel in stone itself and carvings.

The 1886–1910 Inventory List of the Peterhof Factory contains several such dippers, cut from rock crystal and topaz. It is worth mentioning that a mistaken confusion of topaz with rauchtopyaz still persists, and previously colourless rock crystal was also considered as topaz. Fersman (Fersman, Vlodayets, 1922, p. 23) described this dipper as "dipper made from pure rock crystal

Fig. 2. Ash trays from limestone pebbles. Outskirts of Livadia, southern coast of Crimea. Length 9–11 cm. Peterhof Cutting Factory, end of the 1880s to the early 1890s. Received from the Gatchina Palace in 1926. FMM № PDK-1802, PDK-1787.

Fig. 3. A dipper in Old Russian style. Rock crystal. 18 cm. Peterhof Cutting Factory, 1893. Received from the Gatchina Palace in 1926. FMM № PDK-1798.





Fig. 4. A small vase with a handle, cut from the whole piece of rock crystal. Diameter 10 cm, height 11.5 cm. Peterhof Cutting Factory, 1898–1899. Received from the Gatchina Palace in 1926. FMM № PDK-1756.

Fig. 5. A shell. Quartz. Altai. 16 x 11 cm. Received from the Gatchina Palace in 1926. FMM № PDK-1780.

("topaz"), similar to the wooden dipper in the collection of the Karabanov Museum. The 1890 work is kept in the Gatchina Palace Museum".

In the 1741–1916 Inventory List of the Peterhof Cutting Factory (Mavrodina, 2007, p. 397), this masterpiece could not be found among the 1890 works, but it was twice mentioned as N546 among the works of 1889 (first, as a rock crystal dipper; second, as a topaz dipper). In the Inventory List, it is also mentioned that this dipper-like item was placed into the Karabanov Russian Museum (Dept. II, N22). It was valued at 655 Roubles and was presented to the Supreme Court on the 22nd of July, 1889 (Mavrodina, 2007, p. 479). In 1926, this dipper was transferred to the Mineralogical Museum of the Academy of Sciences.

The round vase with a handle (the basket) is a unique article cut from a single piece of rock crystal (Fig. 4). Quartz is a hard mineral. However, the vase's handle can be easily rotated. Such fine work is rare among the cut stones, more so considering that it is made from hard and fragile quartz. We do not know other examples of such craft in Russia. The fine cut items (like a sphere inside a sphere) are typical for Chinese art, but, as far as we know, they used quite a viscous material in China, such as nephrite or bone. The vase is very fine. It is decorated by relief carving in Rococo style, with shells, leaves and flowers. Its handle is covered by a similarly complex carving.

The inventory book of the museum reveals that the vase was made at the Peterhof Cutting Factory in the early 20th century. In the factory's Inventory List for the items made at the turn of the 19–20th centuries (Mavrodina, 2007, p. 487–493), there are only two quartz vases (without description). The vase N561 from topaz is dated to 1898 (again, rock crystal or smoky quartz was sometimes called topaz), valued at 1880 Roubles (p. 490). Another rock crystal vase is dated to 1899 (started in 1898, finished in 1899), valued at 690 Roubles (p. 491). Both of them were presented to the Royal Court. It is possible that the vase from the museum is one of them as it came from the Gatchina Palace.

The other two quartz items are finely cut large shells, made from transparent quartz from River Belaya in the Altai (Fig. 5).

The shells, made from various stones, are characteristic items of the Peterhof Factory during the last two decades of its existence. They were cut from nephrite, chert, quartz, rhodonite, and lazurite between 1891 and 1913. Quartz shells are first mentioned in 1893. Only several of them were made from quartz, whereas many more items were produced from other stones. Perhaps, it was difficult to work with them, because the River Belaya quartz is very fractured and can be easily broken into pieces. Shells were valued between 100 and 176 Roubles in 1913. They were all presented to the Supreme Court. The Mineralogical Museum received two of them from Gatchina in 1926.



Fig. 6. A small plate. Quartz. Altai. Diameter 12 cm. Peterhof Cutting Factory(?). Received from KEPS in 1927. FMM № PDK-2279.



Fig. 7. A tray for small items. Rock crystal, diamonds, enamel. Carving, cast, burelage. Size 7.4 x 5.3 cm. Peterhof Cutting Factory. Received from KEPS in 1927. FMM № PDK-2128.

The museum has a small plate made from similar River Belaya quartz (Fig. 6). Such articles were common for the Peterhof Factory. Some of them were bought by the members of the Royal family. In 1895, a small plate from white quartz was acquired by Great Prince Alexei Alexandrovich (Mavrodina, 2007, p. 488, N672).

It is only possible to infer with great caution that a small plate of the Mineralogical Museum was made at the Peterhof Factory. It was received from the Commission for Studying the Productive Forces (KEPS) in 1927.

The smallest quartz item from the Peterhof Factory in the museum collection is a flat carved crystal tray, whose edges are framed by golden burelaged leaves of the water lilac. Leaves are covered by green enamel, whereas the semi-opened bud with golden stamens is covered by rosettes of diamonds (Fig. 7).

The inventory book reveals that it was produced at the Peterhof Factory in 1889. We do not know the origin of this information. Unfortunately, the Inventory List of the factory for this year does not mention this item (Mavrodina, 2007, p. 474–484). Perhaps, a tray was made for private individuals and is not mentioned in the list for the Royal Court. It was also received from KEPS in 1927.

Supposedly, Peterhof also produced four carved items from smoky quartz and citrine (quartz of golden colour). The museum has two of them in its inventory (Fig. 8) marked as "carved vase, early 20th century" and "ash

tray in raw piece". The third item is an "ash tray in raw piece with carved female figure" (Fig. 9), and, finally, the fourth item (Fig. 10) is a "flat vase, China".

Among the mentioned items is the finely cut female figure with wings and a fish tail made from a single piece of citrine. Perhaps, it is a Siren, which was a semi-woman/semi-bird in antique times, later transformed into a woman-fish-bird. The item is finely carved and exploits warm colours of citrine to show a female figure. The possibility of this intricately carved figurine being too a product of the Peterhof Factory cannot be excluded.

The Inventory List of the factory has many items classified as an "ash tray" or a "vase", which may correspond to these quartz figures. Three of them came from the Gatchina Palace.

The fourth item is probably also produced in Peterhof. This is an oval low vase of fractured smoky quartz with numerous thread-shaped gas-liquid inclusions, reminiscent of accumulations of a down. The edge of the vase is decorated with a relief carving in the shape of leaves around the flower rosette. Its décor is not at all similar to the Chinese art items, although it is so mentioned in the inventory book of the museum. It was received from the State Hermitage in 1926.

Such items, judging from the Inventory List, were made between the end of the 19th and the early 20th century.

The facet rock crystal glassware with "water" (Fig. 11) can be deemed to originate from the Peterhof Factory as well. Such glass-



Fig. 8. A carved vase. Smoky quartz. Height 15 cm. Peterhof Cutting Factory(?), turn of the 19–20th centuries. Received from the Gatchina Palace in 1926. FMM № PDK-1754.

Fig. 9. A siren (a woman-fish-bird). Citrine. Height 11 cm. Peterhof Cutting Factory, turn of the 19–20th centuries. Received from the Gatchina Palace in 1926. FMM № PDK-1753.

es from colourless and white quartz, nephrite, lazurite and other stones are quite common masterpieces of the factory in 1889–1910. It is possible that they were popular, were relatively cheap and could be bought right at the factory by the members of the Royal family. In 1889, the Great Prince Alexei Alexandrovich bought a similar glassware, whereas Vladimir Alexandrovich bought such a glass in 1890. The Inventory List mentioned a topaz glassware "made following a personal draft of the Great Prince Alexei Aleksandrovich" (see Inventory List, 1892, p. 484, N712).

It is worth mentioning that the rock crystal glasses and vases "filled with water" could

be made at the other factories, such as Faberge, where the finely carved flowers were inserted into the specially drilled holes. Our assumption that our glassware is made at Peterhof is based purely on its arrival from the Gatchina Palace, where such non-utilitarian items were abundant.

In addition to the high quality quartz crystals, the factory used quartzite and chalcedony.

A flat and sphere-shaped vase (Fig. 12) was made from pink River Belaya quartzite. On three sides, it is decorated with flowers (popper, forget-me-not, etc.) and insects (bees, grasshopper, and dragon-fly). This is a rare

Fig. 10. An oval vase. Smoky quartz. Length 11 cm. Peterhof Cutting Factory, turn of the 19–20th centuries. Received from the State Hermitage in 1926. FMM № PDK-1659.

Fig. 11. A facet glassware "with water". Rock crystal. Height 8 cm. Peterhof Cutting Factory. Received from the Gatchina Palace in 1926. FMM № PDK-1758.





Fig. 12. A vase. Belorechite, chalcedony, rhodonite, turquoise, labrodorite, tiger eye, nephrite, lazurite. Height 12.5 cm. Peterhof Cutting Factory, 1900. Received from the Gatchina Palace in 1926. FMM № PDK-1808.



Fig. 13. A vase in Japanese style. Agate. Height 12 cm. Peterhof Cutting Factory, 1889. Received from the Gatchina Palace in 1926. FMM № PDK-1809.

case, with the exception of paper weight (see below), when there are additional relief decorations made from various stones. The stones are vari-coloured chalcedony, rhodonite, turquoise, tiger eye, nephrite, and lazurite. This unusual masterpiece was made in 1900. It is mentioned in the Inventory List as a "vase from Siberian River Belaya quartz with carving (flowers)" valued at 1300 Roubles. The vase has preserved an octahedral wooden box with a factory label on the internal side of the cover and three rounded holes for the legs. As all other mentioned items, it was received by the museum in 1926 from Gatchina.

An outstanding item from agate is the Japanese style vase. It is mentioned in the

factory list of 1889 (Fig. 13). The cup of the vase is elongated, ideally following the pattern of stone. It is polished inside, but outside it is decorated with almost invisible edges. The base is a circular pediment with a slithering bi-tailed and bare teethed marine monster. The tails end with clawed dragon laps supporting the vase.

The Inventory List (Mavrodina, 2007, p. 478) classifies this item as a "vase with dolphins from the whole cherty agate preserving the shape of the original stone. The base of the vase reminds of a dragon from the old Japanese vase shown in "L'Art pour tous" magazine. The vase is worth 1360 Roubles. It was manufactured during 1 year and 7

months. The final item is first of its kind ever made by the factory". A unique vase was presented to the Supreme Court on the 26th of February 1889 on birthday occasion of the Emperor Alexander III.

The inventory book of the museum describes this vase as a product of the Yekaterinburg Cutting Factory, but Fersman (Fersman, 1961, Vol. 2, p, 129) attributed it to Peterhof.

Also in 1889, a "cup in Japanese style, cut from single piece of cherty agate, with preservation of the stone shape" (Mavrodina, 2007, p. 479) was made. This small piece of agate somehow managed to attract attention of the craftsman, and he decided to follow its irregular and inconvenient shape. As a result, he produced a pale-grey coffee-coloured cup with bended base surrounded by a white flourishing branch of cherry tree (Fig. 14). The inventory book of the museum says that the cup was made after a drawing by Kudryavtsev. This information is absent in the Inventory List. This tiny item was also presented to the Court together with the above-described rock crystal dipper. The museum received it in 1926 from Gatchina.

Nephrite, discovered in 1824 on the River Onot in the Sayans, was used by the factory since the 1850s based on the Inventory List items. It was more frequently used since the

end of the 1880s. The first works mentioned it solely as nephrite, whereas later it was often additionally identified as Siberian or Murgabian (also known as Chinese).

The museum has several nephrite items, which can be classified to originate from Peterhof with various degree of certainty.

The plate on three small elongated legs in the form of loops (Fig. 15) is an outstanding carved article from green Sayan nephrite. Both sides of this thin transparent plate are covered by carving in the form of bended leaves (stylised spoons), spreading from the central five-leave rosette. A pattern of leaves on the front side of the item is complicated at the expense of them having been "curved" in half. One can be sure that this item was made in Peterhof, because it has a leather box. The internal side of the cover has a factory label. The bottom of the box, covered by blue velvet, has circular form matching the distance between the plate legs.

During this period, the Inventory List of Peterhof items mentions several nephrite plates. Many of them were presented to the Supreme Court. The museum received its plate from Gatchina in 1926.

It is possible that paired nephrite vases on rhodonite pediments (Fig. 16) were also produced in Peterhof. We previously conditionally considered them as products of the

Fig. 14. A small cup in Japanese style. Agate. Height 5 cm. Peterhof Cutting Factory, 1889. Received from the Gatchina Palace in 1926. FMM № PDK-1751.

Fig. 15. A carved plate. Nephrite. Sayan. Diameter 20 cm. Peterhof Cutting Factory, end of the 19th century. Received from the Gatchina Palace in 1926. FMM № PDK-1798. Received from the Gatchina Palace in 1926. FMM № PDK-1745.





Fig. 16. A vase on pediment. Nephrite (Sayan), rhodonite (Urals). Height 39 cm. Peterhof Cutting Factory. Received from the State Hermitage in 1926. FMM № PDK-1649, № PDK-1650.

Yekaterinburg Factory (Chistyakova, 2007₁).

The 1867 list of the Peterhof Factory mentioned "nephrite vases on the rhodonite pediments with gold-plated bronze handles — 2 — 316 Roubles" (Mavrodina, 2007, p. 459). They were made for the Supreme Court. It is not possible to trace where exactly they stayed in the Royal apartments, but it is known that they were in the Livadia Royal Palace back in 1902. One of the pediments preserved a label with a two-headed eagle saying "Property of HEM Emperor, Livadia, N (unclear in pencil), 1902".

Such a contrasting combination of bright-coloured nephrite and rhodonite is recorded several times in the Peterhof items. They are also known among the Yekaterinburg items in the middle of the 19th century. It is known that Yekaterinburg did not have its own bronze workshop, and such items were usually produced in Petersburg for them. To some extent, the vases can be considered as products of Peterhof due to their bronze handles mentioned in the Inventory List. However, there is no certainty about the origin of these vases.

A small oval vase from bright-green nephrite with carved handles in the form of leaf bunches, surrounding central flower rosettes at the end of the article, was also possibly made by the Peterhof craftsmen (Fig. 17). The nephrite items of the Peterhof Factory include many vases. However, only in two cases the list mentioned handles: two vases with gold-plated bronze handles (see above) and once again in the 1896 list (Mavrodina, 2007, p. 488, N703), where there is a "vase with nephrite handles". Perhaps, it is this particular vase from the museum, an oval and low (baseless) vase. The Inventory List does not mention for whom it was produced. Once again, to the museum itself it came together with the Royal items from Gatchina.

The circular carved vase in the style of second Rococo, made from beautiful yellow-green Murgab nephrite, is another outstanding masterpiece in the museum collection (Fig. 18). The vase is made in the form of a deep cup on three legs. It is decorated with salient spiral-bended and upward broadening blade turning into twisting endings. The blades are complex



Fig. 17. A small oval vase with carved handles. Nephrite. Sayan. 18 x 8 cm. Peterhof Cutting Factory(?), 1896. Received from the Gatchina Palace in 1926. FMM № PDK-1743.

Fig. 18. A vase. Nephrite. Murgab (China). Height 12 cm. Peterhof Cutting Factory(?), end of the 19th century. Received from the Gatchina Palace in 1926. FMM № PDK-1807.

in shape. They are narrow at the base, becoming wider upwards and transforming into a wavy banded edge of the vase. The repetition of the speckling salient details gives an iridescent effect to the vase. The blades are not entirely identical. Some of them are more narrow than the others or bended differently. This deviation from the standard has produced fragmentation of the specks with additional vividness to the vase. Some blades turn into double curls downwards, which form the legs of the vase. The base of the vase is even and salient. The internal walls are with complex surface and deepenings, corresponding to the salient blades outside. Such a complex wavy shape gives an impression that a vase is made from plastic material.

It is possible that this item is made to imitate in stone what could have been made from other raw materials. For instance, stone dippers were made to imitate wooden or metallic ones.

As it was mentioned above, nephrite items were produced in great quantities at the Peterhof Factory in the last decades of the 19th century. Unfortunately, the Inventory List does not often contain a precise description of the items, which would have allowed their confident identification. The described vase is conditionally attributed to Peterhof, because it was received from Gatchina. This Royal residence had the majority of the best Peterhof items. We do not know other Russian stone-carved workshops where such masterpieces could be produced.

The museum has another vase made from a single piece green-grey Murgab nephrite. It has a circular cup on the downward widening

base (Fig. 19). Almost all its surface is perfectly polished. The styled carved leaves decorate it. They form a banded edge of the vase. It also has large curls at the base. It is conditionally attributed to Peterhof.

There is no certainty in the origin of the other two exhibits in the collection of the Mineralogical Museum.

It is a vase-chair (open box for papers?) made from green Sayan nephrite with small black spots (Fig. 20). Thin transparent walls of the item are partly covered by a carving in the form of rocailles and curls with through cuts. The uneven edge is a series of carved leaves. It was received from Gatchina.

The second item is a pot on three legs. It is made from pale-green, locally almost white, Sayan nephrite (Fig. 21). The thinnest transparent walls of the circular and slightly flattened article transform upwards into a narrow vertical neck. It was also received from Gatchina.

The list of Gatchina items (Central State Archive of Literature and Arts St.-Petersburg (ЦГАЛИ СПб), f. 309, op. 1, d. 46. l. 24), brought from the mezzanine of the Arsenal square, where Alexander III used to live with his family, has a "polished nephrite pot on three legs" made at the Peterhof Cutting Factory. It is possible that this is the pot currently kept in the Mineralogical Museum. However, it could not be found in the Inventory List.

The beautiful Uralian rhodonite (orlets) was among the favourite stones of the turn of the 19–20th centuries. This stone was not known in the other parts of the world. As it



Fig. 19. A vase. Nephrite. Murgab (China). Height 13.5 cm. Peterhof Cutting Factory(?), end of the 19th century. Received from the Gatchina Palace in 1926. FMM № PDK-1806.

Fig. 20. A vase-chair. Nephrite. Sayan. Height 10 cm. Peterhof Cutting Factory(?). Received from the Gatchina Palace in 1926. FMM № PDK-1746.

Fig. 21. A pot. Nephrite. Sayan. Height 5 cm. Peterhof Cutting Factory. Received from the Gatchina Palace in 1926. FMM № PDK-1747.



was already mentioned earlier, it was discovered in the Urals in 1798. Already in 1800, Peterhof produced its first vases. However, the true rhodonite fashion came later, when malachite articles became rare. As well as malachite, it was considered to be a national Russian stone. The Peterhof Factory produced numerous diverse rhodonite items, mainly small in size vases, ash trays, glasses, knives, and dippers. In the Mineralogical Museum are the several items from the

Gatchina Palace. Among them are the two carved baskets of different size. They can be certainly attributed to the Peterhof Factory where such items were cut from different stones since the end of the 1820s.

A smaller basket (Fig. 22) is made in the form of a berry basket with a handle of crossing branches. Perhaps, it is mentioned in the 1890 Inventory List of the factory as an "orlets basket made in amateur style". The basket is worth 142 Roubles (Mavrodina, 2007, p. 480).

It looks, as if the item was among the "stone objects" of the Royal Palace in Gatchina Central State Archive of Literature and Arts St.-Petersburg (ЦГАЛИ СПб), f. 309, op. 1, d. 46, list 11, No 40). This item is made in a-la-Russe style (similar to the above described dipper), which was popular in Russia in the second half of the 19th century. The other rhodonite baskets from the Inventory List do not have individual descriptions. Almost all of them were made in 1890 – 1892.

The second basket from the museum collection is of a complex and indefinite shape of the basket itself, with non-standard positioning of the handle, consisting of several finely carved stems (Fig. 23). The fluid shape of the masterpiece, in combination with the plant motifs, is typical for the Modern style, which was very popular at the time. Perhaps, this particular basket is mentioned among the masterpieces from the mezzanine of the Arsenal square in Gatchina, such as an "ash tray of irregular shape with a handle in the form of long leaves" Central State Archive of Literature and Arts St.-Petersburg (ЦГАЛИ СПб), *Ibid.*, No 41).

The small flat cup of irregular shape is an outstanding carved rhodonite masterpiece from Peterhof. It is placed on the complex crossing of branches with the leaves (Fig. 24). The inventory book of the Mineralogical Museum describes it as a "vase in Chinese style designed by Gun and produced by Peterhof Factory in the 1890s". This text is

also present in the work by Fersman and Vlodavets about the Peterhof Factory (Fersman, Vlodavets, 1922, p.89, 93). The 1890 works of the factory have only one similar item. It is a "basket made from orlets in Japanese style from publication by Gonze". It is dated to 1890 (Mavrodina, 2007, p. 481). It is very possible that this particular vase is now in the collection of the museum.

The museum received a small egg in a golden frame and a vase-chair along with the above-described rhodonite items from the Gatchina Palace.

This hollow egg was produced from high quality bright-pink rhodonite. Its edges are framed by gold (Fig. 25). Perhaps, it was meant to contain a surprise inside, but it came empty to the museum.

The Peterhof Factory produced numerous Easter eggs during many years. The eggs were both solid and hollow, with and without frame. It is known that eggs with gold were produced by both local craftsmen and "English Shop of Nicholls & Plinke". Gold was not labeled, and, for this reason, the origin of these items is not clear. The egg came from the Gatchina Palace. Perhaps, this "orlets egg (box) with golden frame" belonged to the Great Prince Mikhail Alexandrovich. It was transferred to the Mineralogical Museum of the Academy of Sciences on 16.12.1926, item N414" Central State Archive of Literature and Arts St.-Petersburg (ЦГАЛИ СПб), f. 309, op. 1, d. 39, No 421).

Fig. 22. A basket. Rhodonite. Urals. Length 8 cm. Peterhof Cutting Factory. Received from the Gatchina Palace in 1926. FMM № PDK-1765.

Fig. 23. A basket. Rhodonite. Urals. Length 14 cm. Peterhof Cutting Factory. Received from the Gatchina Palace in 1926. FMM № PDK-1766.





Fig. 24. A vase in Japanese style. Rhodonite. Urals. Size 13 x 10 cm. Peterhof Cutting Factory, 1890s. Received from the Gatchina Palace in 1926. FMM № PDK-1764.

Fig. 25. An egg. Rhodonite, gold. Length 3 cm. Peterhof Cutting Factory. Received from the Gatchina Palace in 1926. FMM № PDK-1767.

Fig. 26. A vase-chair. Rhodonite. Urals. Height 9 cm. Peterhof Cutting Factory(?). Received from the Gatchina Palace in 1926. FMM № PDK-1768.

The vase-chair made from orlets (Fig. 26) is a vase (or covered box) for small items or paper. Chinese motifs were used for its decoration. Legs and decorations on the sides in the form of curved branches and flowers remind cut details of the above-mentioned rhodonite vase made in Chinese style.

The description of this vase could not be found in the Inventory List of the factory. It is deemed to have been produced at Peterhof because it came to the museum from Gatchina together with the other Peterhof items.

Cover plates, or stone paper-weights, were very popular items of the 19th century. They were manufactured from diverse material in Peterhof and Yekaterinburg. In the Urals, they were produced by amateurs.

As it was mentioned in the article on mosaic works in the Mineralogical Museum (Chistyakova, 2009), the collection has a

press-weight from the Stroganovs, which is mentioned in the Inventory List as a product of the Peterhof Cutting Factory worth 140 Roubles in 1898. By that time, the factory has significantly reduced production of such items. The Inventory List of 1898 does not mention them at all. Perhaps, it was a private order. Earlier, we described this item, proposing that it could be a product of the Yekaterinburg Cutting Factory. The problem of its origin remains unresolved.

The jasper handles for the table tools (Fig. 28) are an example of inexpensive items, which were manufactured at the factory during many years since the middle 18th century. Many members of the Royal family ordered them. For instance, the Princess Eugenia Maximilianovna ordered knife handles in 1896 (see the "Inventory List", p. 488). The Mineralogical Museum received handles

from KEPS, which was a source of many items in the Museum.

The Peterhof Factory produced three eggs of vari-coloured jasper collected in the Orsk region in the Southern Urals (Fig. 28). It was mentioned earlier that the factory was a producer of Easter eggs during many years. The Empress Alexandra Fedorovna personally gave them as a present to many visitors, who were allowed for the Paschal greeting with the Emperor. The museum notes mentioned that eggs were produced in the early 20th century. The museum received them from Kadykina in 1919.

One of the late works of the factory, when it stopped production of large high art mas-

terpieces, was a low oval-shaped plate from patchy pink-green jasper from the River Filippovka in the Altai (Fig. 29). The plate came to the museum from the Stroganov collection in 1919, mentioned that this is a work of the Peterhof Factory of 1914. However, this item is not mentioned in the Inventory List of the items produced during that year.

The mosaic panels, kept in the Mineralogical Museum, undoubtedly represent a peak of the cutting art of the Peterhof Cutting Factory. They decorate doors and a draw box of the two-sided cabinet (Fig. 30). It is described in details in the article about mosaic works of the museum collection (Chistya-



Fig. 27. Knife handles. Jasper. Outskirts of Orsk, Urals. Length 8.5 cm. Peterhof Cutting Factory(?). Received from KEPS in 1925. FMM № PDK-2103.



Fig. 28. Easter eggs. Jasper. Outskirts of Orsk, Urals. Length 6 cm. Peterhof Cutting Factory, early 20th century. Received from Kadykina in 1919. FMM № PDK-576-578.



Fig. 29. A small oval plate. Jasper. Altai. Length 13 cm. Peterhof Cutting Factory, 1914. Received from the Stroganov collection in 1919. FMM № PDK-1133.

Fig. 30. A cupboard-cabinet from Amboina tree. Panel of the Florence mosaic. Marble, lazurite, jasper, labradorite, amazonite, agate, tiger eye (quartz with inclusions), opal, queensite (pink opal), and others. Height 160 cm. Peterhof Cutting Factory, 1885–1893. Received from the Laboratory of Stone, USSR Ministry for Construction Materials, in 1962. FMM № PDK-5381.



kova, 2009). For this reason, this paper contains only its brief description.

A cabinet is made from the precious tropical Amboina tree. In addition to the panel, it is decorated by beautiful gold-plated bronze. The work on this cabinet, as well as on the other two similar cabinets, continued from 1884 until 1893. All of them were meant to decorate the palace interiors. Members of the Royal family were constantly interested in the progress of this work. Today, two out of three items are in the Hermitage.

We know that all three cabinets were demonstrated at the 1893 World Columbus Exhibition in Chicago, where the Peterhof Cutting Factory has received a bronze medal and an honorary diploma.

A panel with 'tropical forest and parrots against the blue background', which decorates the cabinet doors kept in the Mineralogical Museum, was produced after a drawing received by the factory from Henri Dasson, one of the most important producers of furniture and art objects in Paris. In St.-Petersburg, the Academician Baron Klodt made water-coloured paintings of the mosaic and its split into individual fragments. The paintings were then given to several craftsmen, and they were again reassembled into a single panel afterwards.

The extremely fine work consists of lazurite, marble, prase, opal, pink opal, tiger eye, jasper, petrified wood, and amazonite. The small pattern required cutting the tiny plates from stones with absolutely different properties, which were then polished together, which is always difficult even for experienced craftsmen.

In the Inventory List, a cabinet is mentioned among the 1897 works. Its 1897 price was 9.361 Roubles. When a cabinet was sent to the Chicago Exhibition, it was estimated to value 28,100 Roubles (Mavrodina, 2007, p. 153, 490). A cabinet was transferred to the Mineralogical Museum in 1962 from the Stone Laboratory of the USSR Ministry for Construction Materials.

The Mineralogical Museum collection of the masterpieces produced at the Peterhof Cutting Factory is not large and does not represent the significance of Peterhof in development of the stone-cutting art in Russia. However, even such a small number of items manifests the highest art level of stone works at the factory and the colossal development of skills of its craftsmen, who started from

simple cups in 1760–1780 and mastered the manufacturing of fantastic mosaic masterpieces by the end of the 19th century.

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THREE CATALOGUES FROM THE FERSMAN MINERALOGICAL MUSEUM ARCHIVE

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The first master catalogues of the Mineral Cabinet of the Kunstkamera which became the fundamentals of the collection of the Mineralogical museum of Academy of Science are reviewed in this article. These are: the first printed Mineral Catalogue from 1745 (compiled by I.G. Gmelin, I. Amman and M.V. Lomonosov) and handwritten catalogues from the Mineralogical museum archive – by J.G. Lehmann (1766) and J.G. Georgi (1789). Also the Mineralogical museum archive preserved the Catalogue of the Gottwald's Museum whose collection was acquired by Peter the Great for the Kunstkamera in 1714.

33 references.

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This or any other procedure is merely a dam against the spring tide of memories which surges toward any collector as he contemplates his possessions. Every passion borders on the chaotic, but the collector's passion borders on the chaos of memories.

Walter Benjamin.

Unpacking my Library.

Over a period of XVIII century the master catalogues of the collection of the ("Fersman" – at present) Mineralogical museum of the Russian academy of Science ("Mineral Cabinet of the Kunstkamera" – in the past) were compiled several times in Latin. The first description of the mineralogical collections of the Kunstkamera, the "Mineral Catalogue" was published in 1745 within the master Catalogue of the Imperial museum – Kunstkamera (Musei Imperialis..., 1745). The authors, academicians I.G. Gmelin, I. Amman and M.V. Lomonosov, were facing a difficult task: to give mineralogical definitions and describe the specimens and to compile the uniform Collection of the Mineral Cabinet from chaotic and scattered rarities dispersed over collections acquired during several decades.

Next catalogue of the mineral collection of the Kunstkamera was compiled by Johann Gottlob Lehmann¹ (Lehmann, 1766). After collections were moved in 1766 to the renovated after the fire Kunstkamera building, the Mineral Cabinet displays were arranged according to the mineralogical classification by J.G. Lehmann (Backmeister, 1779). Not only the structure of exhibition changed: the mineral collection was replenished with multiple new specimens. At the times of the first catalogue of the mineral collection of the 1745 was under compilation, the Mineral Cabinet occupied three halls of the

Kunstkamera – PP, QQ, RR – and was accommodated by 16 display cases (Palaty, 1744; Lomonosov, 1954.). After twenty years, the united mineral collection of the Kunstkamera was divided into three parts: the Russian Mineral Cabinet, the Foreign Mineral Cabinet and the "Old" Mineral Cabinet or the "Grotto" – a picturesque room decorated with shells, fossils, minerals and other items regarding Mineral world or ore mining (Backmeister, 1779; Belyaev, 1793).

Conventionally we date the considered Lehmann catalogue to the 1766 – according to the data by A.F. Gebel, the keeper of the Mineralogical museum of the Academy of Science through 1860–80s (Gebel, 1886). Here we review the very same Lehmann's catalogue from the Archive of the Mineralogical museum, with remarks by A.F. Gebel on its cover: "Lehmann's Catalog. Neues Exemplar. Bd. I und II. Im I. 1862 aus der academischen Bibliothek erhalten Ad. Goebel fur mineral Museum" – Lehmann's catalogue. New issue. Vol. 1 and 2 in 1862 was taken from the academician library for the Mineralogical museum by Adolph Gebel (Lehmann, 1766).

1766 indicates the time of compiling the catalogue by J.G. Lehmann and not a precise date of manuscript creation as we are dealing with the inventory list ("new copy"). Scientific literature bears the evidence that J.G. Lehmann made first descriptions according to his own systematics in the 1750s when collections of the Kunstkamera rescues after the fire we stored in the Demodov's mansion. Later, the collections were moved back into renovated building, and on the basis of the Lehmann's Catalogue one made a list with the lost specimens crossed out and the new ones – added (Solskiy, 1961).

¹ – Johann Gottlob Lehmann (1719 – 1767).

When Princess Ekaterina Romanovna Dashkova became the president of the Academy of Science, the Mineral Cabinet was rearranged according to the new systematics by J. Wallerius (Belyaev, 1793). This was the time of creation of the last in the XVIII century Mineral catalogue of the *Kunstkamera*, which was compiled by J.G. Georgi in 1786 – 1789: "Index Lithophylacei Rossici Musei Academiae scientiarum Petropolitanae" and "Index Lithophylacei exotici Musei Academiae scientiarum Petropolitanae" – inventories of Russian and Foreign Mineral Cabinets of the *Kunstkamera*. At the same time, the fossil collection of the Mineral Cabinet of the *Kunstkamera* was described in another catalogue "Enumeratio fossilium Rossiae indigenorum et exoticorum..." (Severgin, 1814).

The above mentioned "Georgi Catalogue", kept in the archive of the Fersman Mineralogical museum RAS (Index..., 1789) – is a list "Index Lithophylacei Rossici Musei Academiae scientiarum Petropolitanae" (Catalogue of Russian minerals of the Imperial academy of Science Museum), marked as a copy of the original Catalogue (Georgi's Katalog der russischen Mineralien und Gesteine (1786 – 1789), Copie des Georgischen Originale – the Georgi Catalogue of Russian minerals and rocks (1786 – 1789). Copt of the Georgi's original). According to the title list, this manuscript can be dated as 1789, however one should consider notes made for the Lehmann's Catalogue, from the Mineralogical museum archive.

It is appropriate to consider the catalogue of the Gottwald's collection – the first large mineral collection, that was acquired by Peter the Great and became the fundament of the Mineral Cabinet (Gmelin, 1954). It is obvious that in order to understand specifics of description of the Mineral catalogue 1745, one should compare it both with the later descriptions by Lehmann and Georgie, and the earlier Catalogue of the Gottwald's Museum.

Here we consider the inventory of the Christoph Gottwald's collection, from the Mineralogical museum (Gottwaldianum museum) Archive. By the courtesy of Natalia Pavlovna Kopaneva, the senior scientist of Department of the *Kunstkamera* history and Russian science of the XVIII century (M.V. Lomonosov Muesum) RAS, who discovered the beginning of this inventory (2 sheets) in the Section of Manuscripts RASL (Musaei Gottwaldiani...), we now have an opportunity to combine two parts of the handwritten manuscript and get the full concept on the mineral collection of Christoph Gottwald. Also author is very grateful to Anna

Sergeevna Smirnova, the scientist of the Institute of linguistics RAS, Department of "M.V. Lomonosov's Dictionary" for decoding and translation of the Latin part of the Gottwald's Catalogue of the Mineralogical museum (Gottwaldianum museum) Archive.

We know nothing about the exact date of the Gottwald's Catalogue from the Fersman Mineralogical museum Archive and RASL, but undoubtedly, this collection was formed far earlier than the Mineral Cabinet of the *Kunstkamera*. Dr. Christoph Gottwald of Danzig (1636 – 1700) founded the collection which his son, Johann Christoph (1670 – 1713) kept and supplemented. The Gottwald's collection was acquired at the auction in Danzig in 1714 (Margócsy, 2010; Reve, 2006) and arrived to the *Kunstkamera* in 1716 (Palaty, 1744).

In the Russian literature the name of the acquired collection for the *Kunstkamera* is stably known as the "Mineral Cabinet of Dr. Gottwald"; however it is clear from the inventory, that the collection of the naturalist from Danzig contained not only minerals and fossils, but botanic, zoological collections and art pieces (Gottwaldianum museum). According to the Gottwald's Museum Catalogue, minerals occupied three display cases; conchological and zoological collections – the forth case; botanic, the smallest one – the fifth case; and art collection (Artificialia) was described separately and contained more than hundred items. Here we will consider only mineralogical part of the Gottwaldianum museum ignoring the other parts.

The question on how adequately this inventory reflects the structure and sense of the Gottwald's collection is still open. Was is an inventory compiled by the son of Christoph Gottwald; or auction inventory that came along with the collection for sale; or it was compiled in the *Kunstkamera* in St.-Petersburg – we do not know. The printed versions of the Catalogue of the Gottwaldianum museum were published several times, every copy referred to the certain part of the collection.

There are at least three different versions of the printed Catalogue of the Gottwaldianum museum, representing various parts of the collection. The latest one – is the Catalogue of the conchological and anatomy collections 1782 (Schröter, 1782) and also Catalogue of the conchological and anatomy collections 1714 (Gottwald, 1714₂); apparently the earliest is the one that was distributed prior to the auction where the Gottwald's collection was purchased for Peter the Great: "Museum Gottwaldianum, sive catalogus rerum variorum, tam naturalium,

quam artificialium ... collectarum a ... C. Gottwaldio, & J. C. Gottwaldio, quas publica auctione 1714 dividet G. Mattern" (Gottwald, 1714). This very catalogue was referred to by academician V.I. Vernadsky who mentioned that the Gottwald's collection contains mostly minerals collected on the German territory (Vernadsky, 1988). Despite the vagueness mentioned, the handwritten Catalogue of the Gottwald's collection from the Fersman Mineralogical museum RAS Archive remains the important source. Over centuries it is known to the historians of the Mineralogical museum, it was widely referred to (Severgin, 1814; Gebel, Information...; Solskiy, 1861) and used as the work material. The complete correlation of the mineral descriptions in the Gottwald's Catalogue and the Mineral Catalogue of the Kunstkamera and also attribution of existing museum items after the Gottwald's Catalogue was never made, despite several attempts. In particular, in the XIX century the Mineralogical museum keepers Konstantin Grewinkg and Adolph Gebel devoted themselves to the history of the early collections of the Mineralogical museum of the Academy of Science (Gebel, Information...).

In Russian literature, with reference to the handwritten Gottwald's Catalogue from the Mineralogical museum archive, it is often indicated that the number of specimens in the Mineral collection of Dr. Gottwald was "1195 pieces" (Severgin, 1814; Gebel, Information..., Solskiy, 1961). These data is to be considered cautiously. This number was first given by V.M. Severgin (Severgin, 1814); however he noted himself that this list does not comprise "ambers, fossils, droplets and the like". We note, that rough estimate of ambers in the Gottwald's Catalogue gives us the number exceeding three hundred specimens. Along with that, in this catalogue there listed the number of boxes and not specimens (or – also often – specimens in plural, without precise number). The last fact clearly indicates the difficulty of the total estimate of the mineral specimens from Gottwaldianum museum. The same can be said about the Mineral catalogue of the Kunstkamera 1745 (Lomonosov, 1954₁) where rather often we see the word "specimens" in plural, instead of exact number. That is why one has to consider the number of museum items described in the Mineral Catalogue 1745 (indicating to include approximately 3000 specimens), with care. We certainly can speak about inventory items, but we have to take into account the style of specimens arrangement that was different in every catalogue; this cir-

cumstance can disturb our understanding of the collection growth trends.

We can only affirm that, according to I. Gmelin, who judged about the composition of the Kunstkamera mineral collection not only by descriptions but who was holding the specimens; the Gottwald's collection was the "major" part of the newly established Mineral Cabinet of the Kunstkamera (Gmelin, 1954).

These three catalogues of the Mineral Cabinet of the Kunstkamera (Gmelin-Amman-Lomonosov, Lehmann and Georgi) clearly demonstrate the changes in the principles of description of the mineral collections in the XVIII century.

By the modern museum standards occurrence of the three different catalogues within half a century seems to be excessive (it is more convenient, obviously, to keep one inventory book and add new records to it). However, we should remember that in the XVIII century the catalogues of the Mineral Cabinet of the Kunstkamera were more like the exhibition guidebooks rather than inventories. "The Mineral Cabinet is a collection of all the mineral objects and their combinations, which arranged according to a certain order", indicated J.G. Lehmann (Lehmann, 1774). The specimens in the display cases were arranged according to one or another mineralogical classification, and changes in the system of description always resulted in changes of the collection catalogue (in the XVIII century there were several changes of system). Although every chapter of the catalogue contained blank pages for the further descriptions of the new acquisitions, the catalogue structure itself was getting out of date.

Thus, the catalogues of the Mineral Cabinet of the Kunstkamera shows us three different classification systems. The latest, by Georgi, was compiled according to the systematics by J. Wallerius². This is indicated by the notes within the catalogue, where the list of minerals is arranged by classes of the Wallerius system. The descriptions of the display cases of that time it is emphasized the "wise" new arrangement of minerals by the "Wallerius system" (Belyaev, 1793).

Lehmann arranged minerals according to his own system described in his "Mineralogy" (Lehmann, 1772), although very similar to the system by Wallerius (that was published in 1747, according to Adams, 1990). It is much more complicated to determine the system for the Mineral catalogue of 1745, because it is very tempting to accept an opinion by V.M. Severgin (who is widely believed to be the founder of mineralogy in Russia), that mineral description had no order: "No one knows, however, what System it was fol-

² – Johan Gottschalk Wallerius (1709 – 1785) – Swedish chemist and mineralogist.

lowed by, as the mentioned inventory has no Systematic order" (Severgin, 1914).

Some conception of a system, according to which the minerals were arranged in the Mineral catalogue, is given by I.G. Gmelin (apparently, it was him who was responsible to accept this system): "...to begin with, I separated ordinary looking stones from the specified ones. Then I unite them by certain types and, after that, began to write a catalogue of sandy, siliceous, rocky mica-ceous stones, selenites etc. without any order... Thinking of a method – as there is no method that deserves to be named such – I came over the following ideas. All stones with uncertain shape may be combined into three highest classes: formed 1) in the ground, 2) in live creatures, 3) in the water. The first class comprehends fertile and infertile. Some of fertile stones give sulfur, some – salts, others – metals... Infertile stones either melt into glass or transform into lime (Gmelin, 1954, p. 658).

Omitting some details of Gmelin's reasonings, we shall note, however, the researcher's approach in his cataloguing. By the first third of the XVIII century there existed multiple, even fantastic, classifications of minerals, but two major approaches – by Agricola³ and Gessner⁴ – were used more often.

Gessner developed complicated classification of minerals and fossils by their shapes. He defined 15 classes, where minerals were arranged from the simplest forms (class 1, geometric shapes; this class was represented, for instance, by pyrite which occurs as cubic crystals, etc.) to the extremely queer (class 7 – minerals resembling plants or grass, class 9 – looking like animals parts (hair) – as native silver wires etc.) (see Adams, 1990).

According to Agricola, systematics of minerals (or "fossils", by Agricola) should be based, first of all, on their physical properties: colour, weight, transparency, lustre, flavor, shape, structure. All the "fossils" were divided into two large groups: simple (composed of one material) and composite (of several different). The simple "fossils" were subdivided into four more classes: soils (terrae), thickened mineral sap (succus concretus), stones (lapides) and metals (metallum). The composite "fossils" were subdivided into two classes, "mixta" – mixed (those that can be divided only with fire) and "composita" – composite (that can be divided mechanically by hand or dissolved in water). Further, the "thickened mineral sap" were subdivided into more two types – greasy (sulfur, bitumen, orpiment) and

poor and dry (salts, alum); "stones" – into four types: proper stones (magnet, hematite, goethite, belemnites, ammonites), gemstones, marbles (marble, basalt, alabaster etc.) and building stones (limestone, sandstone). An example of the composed "fossils" – galena, siderite, arsenopyrite; of the mixed ones – any aggregates of several minerals, various conglomerates, for instance, the widely spread quartz with native gold.

We do not overview all the aspects of the mineral classification development, re-addressing those who interested to the specialized literature (Adams, 1990; Wilson, 1994; Jameson, 1995), however must note, that the system by Agricola determined the development of mineralogy for a long time, and was repeated in various versions. Kentmann⁵ was the first one, who applied Agricola's classification for describing mineralogical collection (Adams, 1990).

In particular, he described his own mineral collection ("Catalogus rerum fossilium Io. Kentmani"), that contained approximately 1600 specimens, in the small essay "Nomenclaturae rerum fossilium quae in Misnia praecipue et aliis quoque regionibus inveniuntur" (1565), that was published within one volume together with another papers on mineralogy (including work by Gessner on the mineral classification, mentioned above) (De omni..., 1565). Kentmann's catalogue was the first catalogue of a mineral collection, which was built on the scientific principles (in early works and theses – lapidies, all the minerals were arranged and considered without any scientific system, but alphabetically).

It is evident, from the Gmelin's work on the Mineral catalogue that he was trying to create his own classification, based, first of all, on a genesis. However, obviously, the fundament of his new classification in the Mineral catalogue was the system of Agricola – Kentmann, although slightly changed. At the same time, the importance of mineral shapes in mineral classification was resonant from Gessner's ideas and resulted in the "figure" stones class formation.

The inventory of the mineral collection from the Gottwald's Museum gives a slight idea about the system used for arranging minerals. Nevertheless, even the order the mineral classes were arranged by, is not completely understood now, the minerals were still separated by several groups: metals, salts, ambers, gemstones, fossils and others. It is typical that this order within the drawers of the cabinets is disturbed quite often by intrusion of specimens which did not fit "their

³ – Georgius Agricola (Latin) – real name (German) Georg Pawer (1494–1555) – German scientist, one of the founders of mineralogy.

⁴ – Conrad Gessner (1516–1565) – Swiss naturalist.

⁵ – Johannes Kentmann (1518–1574) – German medical doctor and naturalist.

own" place. For example, these are coloured stones (amethyst, marble, jasper, lapis, agates) fit between ambers and disturbed their order (Gottwaldianum museum). However, in the Mineral catalogue by Gmelin-Amman-Lomonosov also contains such cases. Thus, the "Marble paining" contains agates, jasper and onyx, with label "Stones under №80 and 84⁶ are located under this № because it was impossible to put them with the same-kind stones due to a tight space in the boxes" (Lomonosov, 1954₁). It is worthwhile to mention here that modern museums face the same free space problem.

The catalogue by Gottwald might be known to the authors of the Mineral catalogue of 1745, however at present we have no sufficient data to prove so. V.M. Severgin, examining the composition of Gottwald's collection, refers to its inventory as to the "original" one (Severgin, 1814). It is not completely obvious, whether he considers the handwritten Catalogue by Gottwald described in this paper, as there could be some other inventories. The same thing can be said about the nature of mineral description in the Mineral catalogue and Gottwald Catalogue. We already mentioned similarity of description of the Florentine (ruin) marble in these two catalogues (Novgorodova, 2010). However, apparently, here is not the same but the similar description – almost a template. If we consider the descriptions of the widely represented "exotic" stone – Florentine marble in the catalogues of rarities of XVII-XVIII centuries, we shall see that almost everywhere it was mentioned as a stone showing ruined towns and houses, trees, clouds etc. That is why, Lomonosov, who described marbles of the Mineral Cabinet of the Kunstkamera, probably had no need to synchronize with the Gottwald's collection inventory; he might know himself the "standard" description of the Florentine (ruin) marble, from other sources.

On the contrary, another description of a specimen from the Gottwald's Museum, given by Lomonosov in the Mineral Catalogue, is unexplainably detailed comparing to the Gottwald's Catalogue. Gottwald wrote: "...inter calculos humanos eminent Renalis et Bilarii ex corpore Serenissimi Regis Poloniae Joannis III exempti" – "... amongst human stones there are kidney and gall stones extracted from the body excellent king of Poland Ioann III" (Gottwaldianum museum). Lomonosov wrote: "131. Calculus e rene dextro serenissimi regis Poloniae Johannis III post mortem exemptus" – "131. The stone was found in the right kidney of king of Poland Ioann III, post mortally" (Lomonosov, 1954₁, p. 59). Where did Lomono-

sov find out about the right kidney? Was this stone such a fame that it did not require any information from the Gottwald's Catalogue? Or was there another source? Both catalogues have a lot in common that is not confined by the examples given; it is very interesting but we should better concentrate on the similarity and difference of the description structure in the catalogues reviewed.

In this sense, descriptions of amber in the Gottwald's Catalogue and by Lomonosov are most interesting for us. The first-rate extensive collection of ambers was the major specialty of the collection acquired from Danzig (About amber, 1739). Severgin notes that ambers from the Gottwald's collection were arranged according to the system by Dr. Hartman: "The ambers were probably arranged by colour, by insects and other objects included, by appearance, by kind of mining and by handicrafts made of them, as we can conclude upon D. Hartmann's work" (Severgin, 1814).

In the Gottwald's Catalogue along with this detailed differentiation the separate inventory lists of the amber collection (amber with insects inclusions, rough amber, figure amber) is also mentioned (Gottwaldianum museum, p. 8). The location of these separate inventory is unknown so far. Comparing description of amber in the Gottwald's Catalogue and the Mineral Catalogue, we see, that according to requirements of Hartmann's classification, the specimens which were described extremely fractionally by Gottwald, are aggregated by Lomonosov into two large groups: "Ambers with included insects" (which were of Gottwald's prime interest) and "Parti-coloured ambers" that comprised all the rest, including amber articles (Lomonosov, 1954₁). It is possible that such a impudent treatment of the "Dr. Hartmann's system" was evoked by a fairly low Lomonosov's opinion on it. Nevertheless, the authors of the Mineral catalogue were not brave enough to renounce these curious principles of classification and build on the new system – within the second large group there is some sort of an order, adopted from Gottwald.

As it was mentioned earlier, it is difficult to reveal certain system in the Gottwald's collection description. However, every catalogue has a beginning – and this beginning is very demonstrative. The description of the Gottwald's collection starts with gold, silver and its ores, followed by lead, copper, tin, mercury, antimony ores etc. we know that Kentmann's scientific descriptions of collections started with "soils" (terrae). This is how the three

⁶ – Probably, misprint; should be "under №№ 80 – 84".

Mineral Catalogues: of 1945, Lehmann and Georgi start.

The fact that collector Gottwald paid respect to the amber "Dr. Hartmann's system" and disregarded scientific systematics tells us either about a character of the doctor from Danzig (who began his systematics description with gold), or about predominance of enthusiasm over the up-to-date scientific literature. Nevertheless, as it was mentioned above, we do know exactly who was the author of this inventory. In the XVII–XVIII centuries there were no generally accepted mineralogical classification. In the "First fundamentals of metallurgy" M.V. Lomonosov mentioned that mineral collectors in the systematic descriptions of their cabinets used to place first those minerals abundant in their region: "And where they occur and being produced, only their descriptions <mineral cabinets – comment by the author, DN> differ according to places and descriptors. When mineralogy is written by a Saxon, he mostly has silver and lead ores, Hungarian has gold ores, Englishman – tin, Swede – copper and iron. Moreover, each arrange the minerals collected by his own system and finally thinks that the underground nature chose its capital in his ore cabinet. Both before and nowadays the best mineralogical systems can be only the descriptions of the private mineral collections, arranged by people with vague knowledge in physics and mathematics (Lomonosov, 1954₂). We would remind that Lomonosov knew Christoph Gottwald's collection well, as was working on the catalogue for the Lunstkamera. On the basis of this quotation we can suppose that he also knew about the Gottwald's Catalogue. It is obvious, that he disregarded the system, presented in the Gottwald's Catalogue. Understanding all the complexity and importance of the task, Lomonosov deliberately started writing his "Mineralogy" only in his late years.

The curious systems of mineral classification at the first third of the XVIII century are going to the past, in scientists try to build a scientific, consistent and comprehensive system for description of the mineral world. The famous "Sistema Naturae" by Linnaeus, published in the 1735 and revolutionized biological sciences, turned out to be inapplicable for mineralogy.

I.G. Gmelin in his translation of the Sistema Naturae by Linnaeus counted more than twenty seven "Systems of Mineralogy" written by various authors in different European countries over 128 years, from 1647 till 1775, the year when the translation was published (Adams, 1990). V.M. Severgin, who contributed like no one else into development of mineralogy in

Russia and who was rather exacting about scientific terms definitions, published several versions of his "Mineralogy" over 33 years period with new mineral classification in almost every issue: by Kirwan (Severgin, 1791), Daubenton (Severgin, 1804), Leonhard and Karsten (Severgin, 1816), Werner (Severgin, 1824). Every time he explained the superiority of a certain systematics over the others.

In the last quarter of the XVIII century the idea about the primary importance of chemical composition in the mineral classification is being established. However, knowledge in chemistry were not developed enough to create chemical classification. J.G. Lehmann regretfully wrote: "It is needed to arrange matter according to the chemical bases, and therefore to study each of them thoroughly, to combine them within one class of the similar objects with the same significant parts and mixtures. It is easy to say so, but difficult to implement; many centuries will pass before the mineral kingdom will be ordered by this manner. And here I doubt that this would reach absolute genuineness as every day new objects are discovered and new mixtures are found" (Lehmann, 1772).

Thus, in the second half of the XVIII century there existed multiple "Systems of Mineralogy". Their majority did not differ much and were mostly based on the principles by Agricola and applied by Kentmann. Classification by Wallerius became popular for a while (published in 1747, Adams, 1990) and, even this was the fundament for one of the mineral catalogues for the Kunstkamera (Index..., 1789), there is no reason to consider it in detail. Wallerius did not contribute anything new to the mineralogical systematics and was using the principles of Agricola-Kentmann, but, rather, more consecutively and accurately. The same can be said about the classification by Lehmann – the author of the Mineral Catalogue of the Kunstkamera of 1766.

The turning point in development of the mineralogical descriptions occurred later, only with accepting ideas of systematics A.G. Werner and R.J. Haüy in the XIX century. However, this topic is another matter of investigation.

Thus, we have to consider the latest Mineral catalogues of the Kunstkamera as the most "complete" – the most scientific, strict, consistent and clear. However we should not forget how soon systems by Lehmann and Wallerius became obsolete. The "scientific" descriptions of minerals do not look appealing and obvious. In fact, everything we see in the catalogues by Lehmann and Georgi is a number of classes representing the "system of mineralogy" with timid

and uninformative filling. The system is obviously primary, and material itself is described rather schematically and indifferently; whereas the first Mineral catalogue of the *Kunstkamera* consists of live descriptions which included authors' doubts, comments and suppositions. The accuracy of a description of the marble Florentine mosaics made by Lomonosov, enabled the author to attribute several items kept in the Fersman Mineralogical museum RAS (see paper by D.D. Novgorodova, p.).

Another remarkable detail: in some cases along with colourful and detailed description of colour, pattern and shape of the marble sample, M.V. Lomonosov gives Italian names of this stone varieties: Rosso e giallo, pomarolo, Brentonico fiorito, rossetto di Franzia, sanguigno, Africano, Brocacello di Spagna, Pavonazo, Amaranto, Recovaro, Brentonico, Rosso Verona (Lomonosov, 19541). The later catalogues of the Mineral Cabinet, by Lehman and Georgi marble descriptions omit these names, all information that remained is colour and surface finish – what an unpleasant discovery for the modern researcher. This concerns not only marble, but also another parts: descriptions became more formal and compact, and absolutely saved from “extravagances” (including, in particular, description of shapes and size).

It is not quite obvious, whether excessive description is harmful for science, however, there is no doubt that for the museum researchers it is priceless. The museum keeper knows that the inventory labels tend to get lost or fade, the specimens in the collections – to mess up, and then – during revision and identification of the “lost” specimens – nothing can be compared with the colourful and detailed description of an item.

Summarizing the comparative investigation of the three catalogues of the Mineral Cabinet of the *Kunstkamera* regarding mineral systematics presented, we can affirm the trend of development of the mineralogical knowledge.

The Mineral catalogue by Gmelin-Amman-Lomonosov (1745) reveals nucleation of the scientific principles – although this work is mostly very close to the “curious” descriptions of minerals (chapters “Various stones grew into one”, “Stones with figures” – Lomonosov, 1954,), but already differs from Gottwald's Catalogue by the well-thought, even imperfect, mineralogical system.

Two consecutive catalogues – by Lehmann (1766) and Georgi (1786–1789) – strikingly differ from the Mineral catalogue (1745) by confidence, accuracy and strictness of ideas on the order in the mineral world. Thus, the catalogues

by Gottwald and Mineral catalogue by Gmelin-Amman-Lomonosov have obviously applied character – they combine detailed description and material for the scientific research simultaneously. Another situation with the catalogues by Lehmann and Georgi, where scientific ideas subordinate the factual material, and inexorable order of the “System of Mineralogy” sets the strict matrix to be filled with specimens in a certain sequence. Actually, it is unsuitably to consider these catalogues as a description of a collection, as the specimens from the Mineral Cabinet are represented there at most laconic and rather serve as a reason to demonstrate “Systems of Mineralogy”.

In general this shows the development of the *Kunstkamera* collection in the XVIII century – from the collection of “curiosities” appearing by the collector's fancy, to the strict scientific collection, arranged according to the up-to-date scientific discoveries. A little later, this process resulted in the final differentiation of sciences and the *Kunstkamera* sprang to various specialized scientific museums. The first Mineral catalogue of the *Kunstkamera*, even with all “flaws”, is the remarkable scientific work, which combines scientific research, courage of discoverers and fascinating description.

This paper on the mineral catalogues of the *Kunstkamera* is to be concluded the same way it began – with words by Walter Benjamin. We observed that the collection of curiosities of the Mineral Cabinet of the *Kunstkamera* transformed quickly into the scientific one. But the scientist in some sense is alike the collector, and museum curators, probably, comprehend weaknesses of both. “Even though public collections may be less objectionable socially and more useful academically than private collections, the objects get their due only in the latter. I do know that time is running out for the type that I am discussing here and have been representing before you a bit *ex officio*. But, as Hegel put it, only when it is dark does the owl of Minerva begin its flight. Only in extinction is the collector comprehended”. (*Walter Benjamin. Unpacking my Library*).

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SAMPLES OF MARBLE FLORENTINE MOSAIC AND RUIN MARBLES FROM COLLECTIONS OF THE FERSMAN MINERALOGICAL MUSEUM IN THE KUNSTKAMERA'S MINERAL CATALOGUE (1745)

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According to the descriptions by M.V. Lomonosov, in the Mineral catalogue of the Kunstkamera 1745, there were identified several specimens, kept in the Fersman Mineralogical museum RAS: five slabs of marble Florentine mosaics with pictures of Tuscany landscapes and, less corresponded, seven slabs of Florentine ruin marble, which are the earliest items in the collection of the Mineralogical museum and the first and the only samples attributed according to the Mineral catalogue of the Kunstkamera 1745. The date of acquisition of Dr. Gottwald's collection to the Mineral Cabinet of the Kunstkamera — the present Fersman Mineralogical museum RAS — is re-estimated and refined.

11 figures, 2 tables, 26 references.

Keywords: Florentine mosaics, marble, Kunstkamera, Lomonosov, Gottwald, pietra dure, ruin marble, Florentine marble, Mineral Catalogue, mineralogical collection.

The fundament of the Fersman Mineralogical museum RAS was the Mineral Cabinet of the Kunstkamera. Collection of minerals appeared in the Kunstkamera almost right after its establishment, when Peter the Great acquired the collection of Dr. Christoph Gottwald from Danzig (fig. 1) — Museum Gottwaldianum — which mostly consisted of minerals.

Russian sources (Halls..., 1744, introduction) indicate 1716 as a year of acquisition of the Mineral Cabinet of Dr. Gottwald. Albertus Seba's "collection of animals, birds, serpents, lizards and other curious creatures brought from Ost- and West-India" was acquired in the same year; a year later — the collection of anatomy items, herb and butterflies by "good old Dr. Frederik Ruysch". These three collections became a fundament of the Kunstkamera collection, which contained mostly personal items of Peter the Great, who added to it during his travels to Europe, and anatomical curiosities (Stanyukovich, 1953). In one of the remained catalogues from the Museum Gottwaldianum, of conchological and anatomical collections (Gottwald, 1714), among the handwritten notes by Jean Hermann, scientist from Strasbourg, we see another date of acquisition of the collection by Peter the Great, the earlier — 1714 (fig. 2): "The Gottwald's Museum after his death was sold out, according to the catalogue. The Museum Gottwaldianum was presented at the public auction in Gdansk in 1714... It was purchased by Russian Emperor Peter the Great for 20000 rubles" (Gottwald, 1714). The price that Russian Emperor paid for the "Museum Gott-

waldianum" mentioned twice (20000 rubles and 500 ducats). Possibly, Peter the Great acquired collection of Gottwald the senior (the founder of collection) — for 20 thousand rubles, and his son, Johann Christoph, who added his specimens to the collection — for 500 ducats.

The mentioned here copy of the Museum Gottwaldianum catalogue is kept in the Fund of Jean Hermann L'Universit  Louis Pasteur de Strasbourg. It belonged to remarkable naturalist and medical doctor from Strasbourg, Jean Hermann (1738 — 1800). In 1830 his extensive library (12000 volumes) was sold by his successors to Strasbourg. A part of his book collection, more than 2000 items, is kept in Strasbourg University. Handwritten notes by Hermann, occur on the title pages, margins and sheets of many books and represent a valuable material for science.

The difference in the dates of acquisition of the Gottwald's collection can be explained by an error in one of the sources — librarian Schumacher, who wrote the introduction to the guidebook of the Imperial Library and Kunstkamera (Halls..., 1744), or naturalist Hermann. Or simply by different understanding of the date of acquisition: the collection could be bought in 1714 in Danzig, and brought to St.-Petersburg only two years later.

The catalogue of the Museum Gottwaldianum was published in 1714, therefore the version about the purchase made same year. Such catalogues were printed in large number of copies and, prior to the auction, were sent to various potential buyers — collectors



Fig. 1. Christoph Gottwald (1636–1700), medical doctor and physicist from Danzig. Engraving by Gérard Edelinck (1640 – 1707). (Gottwald, 1714). Fund of Jean Hermann, L'Université Louis Pasteur de Strasbourg. Le Service de la Documentation de l'Université de Strasbourg (UdS).

Fig. 2. Catalogue of the anatomical collection and collection of shells of the Museum Gottwaldianum (Gottwald, 1714). Fund of Jean Hermann, L'Université Louis Pasteur de Strasbourg. Le Service de la Documentation de l'Université de Strasbourg (UdS): a – the title sheet; b – reverse side of the title sheet with the notes about acquisition of the Museum Gottwaldianum by Peter the Great in 1714 (the second paragraph from the top).

of rarities – in different countries (Margócsy, 2010). The Dr. Gottwald's collection was presented at the auction after death of Johann Christoph (1670 – 1713), son and successor of Christoph Gottwald.

Here is one interesting story: one collector from Danzig, Dr. Johann Philipp Breyn (Breyn, Breynius, Johann Philipp, 1680 – 1764) posted the collection catalogue to Hans Sloane to London. Hans Sloane (1660 – 1753) – English medic, naturalist, member of London Royal Society and its long-term president, was the known collector of curiosities and antiques. After his death his unique collection became the fundament of the British Museum. Sloane's interest to the Gottwald's collection reveals the value of the collection and authority and fame of Christoph Gottwald himself. However, despite this interest, the purchase never happened. The catalogue of the Gottwald's collection was delivered to London too late, and by the time when Sloane replied to Breyn asking to buy some items from the collection, the "Museum Gottwaldianum" was already acquired by the agents of Peter the Great, for the first Russian museum – the Kunstkamera Margócsy, 2010, p. 79 – 80). The letter from Sloane to Breyn where he mentioned about this vexing delay is dated 15 March 1714 (Sloane to Breyn, March 15, 1714, Forschungsbibliothek Gotha Chart. A 788, after Margócsy,

2010, p. 80). Therefore, the Gottwald's collection could not be purchased by Peter the Great (or, for Peter the Great) in 1716.

For the Fersman Mineralogical museum RAS, derived from the Mineral Cabinet of Dr. Gottwald, these details are very important and valuable. The history of the Mineralogical museum RAS traditionally estimated since moment of the purchase of the Christoph Gottwald's collection to the Kunstkamera (Sol'skiy, 1961; Barsanov & Kornetova, 1989, Godovikov, 1989), and, according to the data given above, should begin since 1714 and not since 1716.

The study of the Mineral collection of the Kunstkamera was initiated by Johann Gmelin in 1727 (Stanyukovich, 1953), the work on the Mineral catalogue, the first description of the collection – in 1731. This work was finalized by M.V. Lomonosov, and this was his first job at the Academy of Sciences. Gmelin indicated, that when he started working on description of the mineral part of the Kunstkamera, he found it reasonable to compile all the collections (Gmelin, 1954). This was the birth of the Mineral collection of the Kunstkamera. According to the Mineral catalogue, the collection listed approximately 3000 inventory numbers of minerals and ores, partially from Russian deposits.

Academician Gmelin wrote: "The collection of Dr. Gottwald of Danzig was the major,

but not the most remarkable part. There was another collection – one metallurgist from Saxony – the worst one. Then there were various drawers filled with minerals, partially brought from Sweden or Russia. In addition to that there was the mineral collection from brought from duchy Württemberg by Johann Georg Gmelin. Finally one should say about a few minerals brought by Herr Messerschmidt from Siberia (Gmelin, 1954).

Among the significant mineral collections arrived to the Kunstkamera and could be listed in the first catalogue we name the collection of Robert Areskin (1718) – imperial leibmedic, the first keeper of the imperial Kunstkamera and Library, the Cabinet of natural things of Peter the Great (after 1725) the collection of Y.V. Bruce (1735). Besides, mineral specimens could arrive to the Kunstkamera from the overseas, from I.D. Schumacher (according to the documents, he was a "librarian" and, in fact, a director of the Kunstkamera and adviser of the academic Office). By the order of Peter the Great in 1721 – 1722s he visited Germany, Holland, France, England, where he had to get acquainted with libraries and museums, to visit famous scientists, to find the gaps in the

St.-Petersburg collection and to purchase the missing material.

The first master catalogue of all the collection of the Kunstkamera was compiled in Latin and published in 1741 – 1745. It was titled "Musei Imperialis Petropolitani Vol. I – II. 1741 – 1745" (of Petersburg Imperial museum, Volumes 1 – 2. 1741 – 1745). The catalogue consisted of two volumes and included anatomical, botanic, mineral, numismatic collections, collection of arts and rarities and another collections of the Kunstkamera. The catalogue of the Mineral Cabinet of the Kunstkamera, *Catalogus minerarum*, was completed at the end of 1741 and published in 1745. It was included in the third part of the first volume of the catalogue of the Kunstkamera collections (*Musei...*, 1745).

The foreword of the description of minerals in the catalogue 1745 was "*Catalogus minerarum. Cam. PP. QQ. RR. SCRIN. 1 – 16*" (*Musei...*, 1745). Besides making changes in the completed articles (by Gmelin, who described ore minerals, salts and soils), Lomonosov created in full chapters "resins", "ambers", "objects, transformed into stones", "simple and large stones", "marbles", "rock

Table 1. Florentine mosaics. Marble. Comparison of descriptions of marble mosaics from the Mineral Catalogue by M.V. Lomonosov and items from the Fersman Mineralogical museum RAS

Latin text from the Mineral Catalogue 1745 (Lomonosov, 1954, p. 26)	Russian (<i>translated into English – ed.</i>) text from the Mineral Catalogue 1745 (Lomonosov, 1954, p. 194)	Marble specimens from the Fersman Mineralogical museum RAS. Inventory numbers. Size. * size of the specimens, indicated in the Mineral Catalogue 1745	Numbers on the reverse side
Tabula quadrilatera pedem unicum circiter longa, latitudinis minoris, in qua opere mosaico turris cum aplustri repraesentatur, cum plantatis in vicinia arboribus, in dentrite a natura pictis.	19. Quadrangular slab, nearly one foot long, smaller in its width, with images of a tower with flag and trees, of dendritic origin.	PDK-657 (fig. 3a) 23 x 16.5 cm * nearly one foot (30 cm)	21, 161, 657
23-30. Novem tabulae minores, prioris dimidium adaequantes, ubi aedificia varia, adstantibus ex dentrite arbusculis, opere mosaico depicta sunt.	22-30. Nine slabs, half size of the previous ones, with images of buildings and trees.	PDK-658 (fig. 3b) 9.5 x 15.5 cm PDK-659 (fig. 3c) 9.5 x 15.5 cm PDK-661 (fig. 3d) 10 x 16 cm PDK-663 (fig. 3e) 9.5 x 15.5 cm	658 659 27-167-661 663
31. Similis et aequalis tabula in semicirculum efformata.	31. The same slab, in a shape of half a circle.	Absent	



Fig. 3. Florentine mosaics from the collection of the Fersman Mineralogical museum RAS. Inventory numbers from the top to the bottom and from the right to the left: PDK-657, PDK-658, PDK-659, PDK-661, PDK-663. Author's photo.

crystals" and "precious stones". According to this catalogue, marbles were placed in the 7th locker (SCRIN. VII), and the Mineral Cabinet itself in 1741–1745 occupied three halls in the *Kunstkamera* – PP, QQ, RR. We can easily find these halls on the exposition plan of the *Kunstkamera* in 1741 (Halls..., 1741, Tab. 5) – on the first floor of the building.

The numbering of specimens was unique for every part of the catalogue. The chapter "Marbles" it begins with description of ruin (Florentine, by Lomonosov) marble, numbers

1–18. Plaquettes of Florentine mosaics are described in the same chapter "Marbles" under numbers 19–31 (Lomonosov, 1954).

Only five mosaics, described by Lomonosov, remained out of eleven (fig. 3): one large (16.5 x 23 cm) – the picture of a tower with red flag and four small with pictures of Tuscany landscapes (three – 9.5 x 15.5 cm, and one – 10 x 16 cm). Mosaic plaquettes from the Mineralogical museum still have the indexing of the Mineral catalogue of the *Kunstkamera*: numbers 21 (A tower with

red flag), 26 and 27 (Table 1). However, description of these samples in the Mineral catalogue gives us enough data for their identification: indication of a "tower with red flag" and "trees in dentrite" could not be missed by anyone with knowledge in the collection of the Fersman Mineralogical museum.

There is a question on the dating of the mosaic plaquettes arises, and it is pertinently to give some brief data on Florentine mosaics – one of the most masterly carving techniques.

Florentine mosaics (or, according to its historical name – *pietra dure*) was widely abundant in Italy in Renaissance epoch. This technique can be conditionally named as "stone inlay". Similarly to the wood inlay (marquetry), Florentine mosaics puts multi-coloured decorative stones platelets onto the surface close to each other, in order them to make a picture. In difference to inlay, there is no matrix in *pietra dure*, and pieces of stones are simply get glued to the stone surface.

In difference to the "Roman" mosaics, where small flat square stone platelets are almost equal in shape and size, and "draw" like an artist, in *pietra dure* there are platelets of different sizes and shapes are being packed close to each other. Quite often, contours of the platelets correspond to a shape of some object or part of a picture, along with that, mosaic masters, alike Chinese craftsmen, use the natural ornament of a stone.

Depending on the material being used there are two types of Florentine mosaics: *pietra dure* (when it consists of hard decorative stones) and *pietra tenere* (which consists of "soft" stones). Hardness of marble varies from 2 to 4 by the Mohs' scale, therefore, speaking of marble mosaics, one should use the term *pietra tenere*. Practically, the term *pietra dure* is often used for any Florentine mosaics.

The heyday of the mosaics *pietra dure* is normally related to Florence. When in 1588 the Grand Duke Medici Ferdinand I founded the mosaics workshop *Opificio delle pietre dure* in Florence, he, probably, did not realize that established a famous tradition that would last more than four hundred years. Stone mosaics became such popular, that starting with the XVII century the workshops *pietra dure* appeared in several European countries simultaneously (Koeppel, Giusti, 2008); however the Medici workshops, located in the Uffizi palace galleries, in Florence, were the leaders in the development of *pietra dure* craft. From time to time another workshops

enticed craftsmen from Florence to teach them the skill. The Medici workshops mastered both mosaics and furniture. The orders were coming from the Grand Duke residence and influential European courts.

Ornaments, patterns, pictures of birds, flowers, fruits and, finally, landscapes were the common plots of *pietra dure*, starting from the XVII century. Besides expensive large-scale things, the workshops created small, "card-size" mosaic plaquettes. Quite often they were used as insets in furniture or decorations for cabinets – lockers with many storage drawers.

Cabinets of the Renaissance epoch, decorated with finest silver, ivory, amber and gemstone insets, or engraved with porcelain platelets, were the most desirable objects for European noblemen. However, decoration was not only esthetic but informative.

Cabinet was the collector's treasure of that time. The famous samples, for instance, Augsburg cabinet of master Philipp Heinhöfer, 1625–1631 (MacGregor, 2008, p. 18), gives us impression about this sort of furniture. They were created not only as a storage space, but also as display cases – for demonstrating the collection of rarities. The "Cabinet of curiosities" itself is a locker with the owner's collection; this kind of furniture was popular exactly in the XVII–XVIII centuries – when the passion hobby of collecting rarities and curiosities was flourishing. Such cabinets could be gorgeous, as collection specimen itself – curiosity and rarity. In other cases they used a usual locker for storage, and then its doors were decorated with the curiosities from the collection.

Small plaquettes of Florentine mosaics, which were crafted in the multiple workshops in Florence, were used not only for the furniture and small boxes decoration, but also had their own value.

Marble in the very first collections of the Kunstkamera, according to the "Mineral catalogue" by M.V. Lomonosov (Lomonosov, 1954), is mostly represented by polished slabs (this shows us how the collectors preferred to keep samples of decorative stone). Naturally, Florentine mosaics platelets made of marble fitted such collections. The workshops *pietra dure* were selling both complete items decorated with stone mosaics, and separate mosaic platelets. Any tourist could bring home a set of Florentine plaquettes and either to leave them in his collection of rarities, or to decorate a cabinet with them. Later, in the XVIII–XIX centuries, such plaquettes were

Table 2. Ruin (Florentine) marble. Comparison of descriptions of marble mosaics from the Mineral Catalogue by M.V. Lomonosov and items from the Fersman Mineralogical museum RAS

Latin text from the Mineral Catalogue 1745 (Lomonosov, 1954, p. 25)	Russian (<i>translated into English – ed.</i>) text from the Mineral Catalogue 1745 (Lomonosov, 1954, p. 193–194)	Marble specimens from the Fersman Mineralogical museum RAS. Inventory numbers. Size. * size of the specimens, indicated in the Mineral Catalogue 1745.
1. Tabula quadrilatera oblonga, ex Marmore Florentino excisa, in quo rupes, rudera et nubes ad vivum depicta conspiciuntur, coloris fuscus et flaventis, ad extremitates ejus lamellae Marmoris candidioris agglutinatae sunt, cancellorum instar. Longitudo ejus dimidium pedem superat, latitudo vix adaequat.	Quadrangular slab, elongated, carved from Florentine marble. It shows naturally rocky mountains, ruined buildings and clouds; colour – dark-yellow. This slab is framed with the thin boards from white marble. The slab is longer than a half feet and almost equal wide.	PDK-2095 (fig. 4a) 13 x 18 cm *15 x 15 cm
2. Similis tabula minor per medium vena Quarzi tendente divisa.	2. The same slab, slightly smaller than the previous, divided by quartz vein in its middle.	PDK-2096 (fig. 4b) 10 x 21 cm
3. Tabula hujusmodi adhuc minor fuscioris coloris.	3. The same slab, even smaller than the previous and of darker colour.	PDK-662 (fig. 4d) 10.5 x 21 cm
4. Tabula ex Marmore Florentino, ut Nr. 3, confecta, quadrangula, 5 pollices circiter longa, 2 lata, sine marginibus, ex Marmore candidiore.	Slab from Florentine dark marble, similar to that under № 3, square, approximately 5 inches long, two - wide, with no edges and no white marble.	Absent (?) *5 x 12 cm
5. Simile Marmor iri tabulam ovalem excisum.	The same marble, carved like an oval slab.	Absent (?)
6-9. Quatuor orbiculi ex Marmore Florentino flavente fuscioris diametri bipollicaris.	Four round slabs from Florentine dark-yellow marble, to inches in diameter.	PDK-672 (fig. 4e) 6 cm *5 cm
10-11. Duo orbes majores ex Marmore Florentino flavente dilutioris.	10-11. Two round slabs, bigger than the previous, from Florentine pale-yellow marble.	PDK-4202 (fig. 4f) 5 x 5.7 cm
12-18. Septem tabulae, quatuor circiter pollices longae, 2 latae ex Marmore Florentino fuscioris, ut est Nr. 6, excisae.	12-18. Seven slabs approximately 7 inches long, two – wide, from Florentine dark marble, similar to that under № 6.	PDK-7835 (fig. 4c) 8 x 15 cm PDK-8099 (fig. 4g) 10.5 x 17 cm * 5 x 10 cm

torn out from the old shabby furniture sold at the auctions, and used again for decorating a new cabinet. Such cabinets are known to be from England, France and Germany – decorated with the platelets of Florentine mosaics brought from different places in Italy and Europe in various times. In this case, the researchers can distinguish the age difference of the mosaic decoration and the furniture (Koepppe, Giusti, 2008, p. 91).

Fortunately, we can date the marble mosaics of the Mineral catalogue with much confidence. These very images of Tuscany landscapes were mastered in the Medici workshops *Opificio delle pietre dure* at the end of the XVII century. Remained cabinet in one of the Medici villas (XVIII – XIX century) – the Villa del Poggio Imperiale – enables the scientists to date such mosaic plaquettes the 90s of the XVII century (Koepppe, Giusti, 2008). Also, similar plaquettes occurs in German furniture of the beginning of the XVIII century (Massinelli, 2000, p. 41 – 43, p. 47).

The samples of ruin marble (Table 2) are attributed less definite. The Mineral catalogue describes 18 samples of Florentine (ruin) marble. In the collection of the Fersman Mineralogical museum there are seven slabs with no date or source of acquisition known, and which description matches the description from the Mineral catalogue. However, they bear no old inventory numbers. The descriptions of the slabs (like any other polished sample of ruin marble) are standard and untypical; their sizes do not match those in the Mineral catalogue (except round medallions). The sizes of the mosaic plaquettes also do not match the description, but, nevertheless, this does not make us doubt our definition is correct. Besides, it is known, that misspells and mistakes in sizes in the Mineral catalogue – is not an unusual phenomenon (Lomonosov, 1954, comments, p. 656).

Five slabs of ruin marble, out of seven (FMM №№ PDK-662, PDK-2095, PDK-2096, PDK-7835, PDK-8099) designed in a same way (framed with white marble) and this design clearly matches with the Lomonosov's description in the Mineral catalogue (fig. 4). The rest two samples (small flat discs, №№ PDK-672, PDK-4202) correspond to descriptions and sizes shown in the Mineral catalogue (fig. 4).

For the sample № PDK-4202 we know the source of acquisition – from V.I. Kryzhanovskiy, in 1936. Besides, edges of this flat

disc were processed with another, more perfect tool, than that used for the disc № PDK-672. However we will note, that rectangular marble plaquettes are also processed carefully, and therefore the disc with jagged edges (№ PDK-672) is out of the series, rather than disc № PDK-4202

Despite the indicated nuance we will leave this sample among the others, before getting the new data, as formally it is almost match this list. The difference of the samples is normal for the cabinets of curiosities (also these discs could be acquired for the Kunstkamera from the different collection). Concerning the time and the source of this acquisition for the Mineralogical museum, which are recorded in the museum inventory, the museum history in Russia experienced even stranger cases (when the old specimens were catalogued in the museum books as purchased from the individual in the XX century) (“Drawn museum”..., 2004).

Another ruin marble samples are not easy to “decrypt” too. We cannot correspond every sample of seven with the only matching description from the Mineral catalogue. However we made an attempt, which results is represented in the Table 2. Besides matching descriptions (and sizes – in two cases), the design of the ruin platelets made us confident: black thin edging and white marble frame. In addition, thin platelets of marble are glued to the solid base – all these not a standard decoration of the ruin marble, but completely matches the design of the marble mosaics described above (doubtlessly matching with those described in the Mineral catalogue). In the museum collection there are other samples of the ruin marble, without frame or background: a platelet from Austria with natural chips on its unpolished edges and almost modern slab from Italy (1980s) – which is considerably thicker and of another design and size.

The important detail is that the decorative slabs of ruin marble reviewed, are made using the technique of Florentine mosaics. Besides composite frames, they have the same background as the marble Florentine slabs described above – solid flaky black slate. In Italy this stone is known as *paragone* (*pietra del paragone*, a touchstone), and was applied as a background for mosaics *pietra dure* in the XVII – XVIII centuries (Koepppe, Giusti, 2008, p. 370). Two samples of Florentine marble reviewed here (FMM, №№ PDK-7835 and PDK-8099) have another background, however it is obviously later museum restoration, as



Fig. 4. Ruin marble from the collection of the Fersman Mineralogical museum RAS. Inventory numbers from the top to the bottom and from the left to the right: a – PDK-2095, b – PDK-2096, c – PDK-7835, d – PDK-662, e – PDK-672, f – PDK-4202, g – PDK-8099.

Author's photo

light-gray layered marble was never used as a background for mosaics. Sometimes in Florence they used another stone as a background – black Belgian marble, as it was cheaper.

Thus we can assume with confidence, that the samples of Florentine (ruin) marble, described by M.V. Lomonosov in the Mineral catalogue – are those very items catalogued in the Fersman Mineralogical museum RAS collection.

Traditionally, these flat platelets of ruin marble are considered as Florentine mosaics, despite the pattern of ruins in a stone is natural and not made by the artist. Such platelets, "with natural landscape" were massively produced in the mosaics workshops, including Medici Workshops. The museum Opificio delle pietre dure keeps the pair of square panels of Florentine (ruin) marble, which are dated by the XVII century (Koepppe, Giusti, 2008, p. 159). Those are framed with wood and were apparently made as a wall decoration. One can tell, that despite the "ruins" observed on the section of the Florentine mosaics is exceptionally natural object, that occurs due to this rock structure, the decorative use of this feature is completely a merit of the carvers and artists, hence this justifies its application in the Florentine mosaics.

Similarly to the mentioned above marble mosaics sample, the plaquettes of ruin marble could be used as insets for furniture or as collectors rarities. We will find various examples of cabinets from the XVII – XVIII centuries, which were decorated with ruin marble plaquettes. The above mentioned Augsburg cabinet (1625 – 1631) was decorated with platelets of ruin marble, these are dissimilar to those described here, but this example shows popularity pietra paesina as a decorative stone in Europe in XVII – XVIII centuries (MacGregor, 2007, p. 18).

In Peter the Great's Kunstkamera the samples of ruin marble were considered as valuable items. Several decades later, after the Mineral catalogue was published, O.P. Belyaev, in his description of the most curious pieces from the different collections of the Kunstkamera, mentioned "several slabs of Florentine marble, where art contributed more into depicting villages and ruined towns than nature", within the collection of the Foreign minerals cabinet (Belyaev, 1800, p. 158).

In the context of the Mineral catalogue, there is a special interest to the materials of the marble plaquettes. Ruin marble (the mod-

ern name of this decorative material), as mentioned above, was described by Lomonosov in the catalogue under name "Florentine". In Italy this stone is known as "pietra paesina" – landscape stone. Strictly speaking, this is not marble, but fine-grained marl limestone with brecciated, displaces and once again harden layers. Different coloration of the various layers creates images resembling landscape forms or ruins.

Italian name of this stone – alberese, originates from the word *albere* – wood, as this rock often contains black manganese inclusions, dendrites, resembling branching plants (Price, 2007, p. 99). Lomonosov in the Mineral catalogue named this stone as "dentrinite", its modern name in Russia – lithography stone. In Italy this rock is considered to be a landscape stone which has three varieties: *alberese* itself – dendritic limestone, ruin marble (Florentine marble, *pietra paesina*) and layered stone from Arno river, *pietra d'Arno*, or *lineato d'Arno* (Koepppe, Giusti, 2008, p. 159). These rocks occur in Italy, in Northern Apennines, and were mined since ancient from the river Arno valley. We can find them in many Florentine mosaics of XVII – XVIII centuries (Koepppe, Giusti, 2008). It should be said, that the layered stone, *lineato d'Arno*, is the same Florentine ruin marble, the part representing "sky" with distinct layered structure, and not "ruins". The typical pattern of a *lineato d'Arno*, looking alike layered clouds can be seen in the top part of the specimen № PDK-2095 (fig. 4). Here, in one piece of rock there are two patterns – of *pietra paesina* and *lineato d'Arno*. Apparently, geologically strictly speaking, we cannot write about two varieties of a rock. More likely these are two patterns in one rock – Florentine marble.

It is difficult to tell when the first description of ruin marble was made. Some researchers (Serra *et al.*, 2010) consider it was made by the famous scientist-encyclopedist Athanasius Kircher, referring to his work "Underground world" (Amsterdam, 1664 – 65). Others state, that ruin marble was known since the II century BC, and in 1597 is was described by Agostino dell Riccio in his "Istoria delle pietre", with emphasis on its popularity in Florence (Koepppe, Giusti, 2008, p. 159).

In the XVII century the interest to a landscape stone increased and spread far away from Florence, and samples of "dentrinites" and "Florentine marble" became almost obligatory for any significant cabinet of

curiosities. One of the stars in the famous cabinet of Ole Worm (which, after his death, became the part of the Dutch Royal Kunstkamera, repeatedly visited by Peter the Great) was the three-dimensional art piece of ruin marble – a miniature globe (Worms, 1665, p. 550). Thus, despite ruin marble can be found not only in Tuscany (it occurs in Austria, Slovakia, Pakistan), it would remain in the world heritage items because of Florentine mosaics and collections of rarities.

Concerning *pietra paesina* (or “dentrite”), besides Italy, similar stone was mined in Germany for a long time; it is known to be “Solnhofen marble”. This is fine-grained limestone with dendritic inclusions.

Deposits of Solnhofen marbled limestone are located within the outskirts of Solnhofen town (Mittelfranken), in the region famous by deposits of marbled “Jurassic marble” limestone.

Probably, these names – “dentrite” (Kircher, 1664, T.1, p. 31), “albarese” (in Italy) and “Solnhofen marble” in Germany (Wirsing, 1775) – co-existed for a long time.

In his remarkable work devoted to mineralogy of Italy, Swedish mineralogist Johann Jacob Ferber describes “dentrite” as *albarese*. Ferber explained the names of Italian ornamental stones: “This marble (dentrite) is not homogeneous, but brought to life with finest and thinnest layers of solid limestone, usually gray, and is accompanied with multiple dendrites... Its name is *Alberese*, *Alberene* or *Albazzano*. Florentine marble, showing ruins, is also called *marmo Paesino*. Landscape marble and that with dendrites is called *Alberino*” (Ferber, 1776, c. 112).

Today, “Solnhofen marble” is a popular decorative material. Besides architecture, due to its fine-grained structure, it can be applied in lithography, therefore its common name in Russia – “lithography stone”.

Description of a landscape stone, or “dentrite”, was placed by Lomonosov into two chapters of the Mineral catalogue: “Marbles” and “Objects, transformed into stone”. We can conclude from Lomonosov’s descriptions, that he called “dentrite” both landscape stone and petrified wood. Now we know of course, that “woods” in a landscape marble are crystalline objects with branching structure, manganese oxides and not petrified plants.

Johann Gmelin explained the conditional name marble for a limestone, in his “A remark, necessary for understanding of the mineral catalogues” – the paper he wrote

after he started with the Mineral catalogue of the Kunstkamera. He specially indicated, that “marbles are only those stones which, besides their usual features have the ability to be processed by metal” – i.e. can be polished (Gmelin, 1954). This approach is being practiced by now – many kinds of limestone and other rocks, which can be polished, are named “marble” (even though it can be geologically wrong).

Mosaic slabs with Toscana landscapes are represented by traditional Florentine *pietra tenera*. All the five mosaics contain “landscape” stone (“dentrite” from the Mineral catalogue, Solnhofen marble) and ruin marble (“Florentine” by Lomonosov, majority of scientists from XVII–XVIII centuries and many modern sources). In general, ruin marble is used for mosaics quite often – both as a basis for painting and as a natural landscape, or as mixed yellowish-brownish stone.

It is interesting to mention, that the large mosaics “A tower with red flag” is framed with reddish marble breccia *Brocatello d’Espagna* (fig. 3). Researchers note, that this bright marble from Tortosa (Catalonia, Spain) was very popular in Spain and Italy since 16th century. It was used in architecture; the most famous examples – cathedrals in Tortosa and Naples. This stone was used for mosaics as well, especially in Florentine *Opificio delle pietre dure*, mosaics workshops of Medici – the place where the history of Florentine mosaics began (Price, 2007, p. 164).

The question about the source of these marble samples, described by M.V. Lomonosov in the Mineral catalogue of the Kunstkamera, is still open. Plaquettes of ruin marble and Florentine mosaics could have arrived from various collections – Gottwald, Bruce, Areskin, Peter the Great and others. On other hand, the material and the making of these slabs quite clearly indicate, that their origin is Florence.

Briefly, the results of this investigation are the following. The date of acquisition of the Dr. Gottwalds collection – the fundament of the Mineral Cabinet of the Kunstkamera and later, of the Fersman Mineralogical museum RAS – was specified. The history of the Mineralogical museum of the Academy of Science is traditionally estimated since acquisition of Christoph Gottwald’s collection to the Kunstkamera, and obviously, this date is 1714.

According to the descriptions of marbles from the Mineral catalogue, by M.V. Lomonosov, we identified several items kept in the

Fersman Mineralogical museum RAS collection: five marble slabs with Toscana landscapes in Florentine mosaics technique, and, less corresponded; seven slabs of Florentine ruin marble.

This attribution enables to list these marble mosaics and slabs of ruin marble from the Lomonosov's Mineral catalogue along with another mosaics from the Mineralogical museum. The stone mosaics is widely represented in the Fersman Mineralogical museum (Chistyakova, 2009). The small amount of specimens comprehend almost all known kinds of this arts&crafts: Roman, Florentine (pietra dure, solid rock mosaics), Russian and even three-dimensional. Marble mosaic and ruin marble slabs, discussed here, are the earliest samples of Florentine mosaics in the collection of the Fersman Mineralogical museum. Besides, these pieces belong to the earliest mineralogical collections in Russia, described by M.V. Lomonosov in the Mineral catalogue of the Kunstkamera and the only items from the Mineral catalogue which had been identified in the collection of the Mineralogical Museum RAS.

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EXHIBITION "WONDERS IN THE STONE" – 2011

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Exhibitions «Wonders in the stone» which are already carried out almost 50 years are one of the most appreciable initiatives of the Society of amateurs attached to the Moscow Society of Naturalists (MOIP). In 2011 the 45-th exhibition «Wonders in the stone» having a subtitle «Remarkable minerals of the Russia» has been organized in the Fersman Mineralogical museum belonging to the Russian Academy of Sciences.

6 figures, 3 references.

Key words: exhibition «Wonders in the stone», Society of mineral amateurs, Moscow Society of Naturalists (MOIP).

The history of annual exhibitions «Wonders in the stone» totals almost 50 years. These exhibitions are one of the most appreciable initiatives of the Society of amateurs attached to the Moscow Society of Naturalists (MOIP) founded in 1805 within the Moscow imperial university that become one of the first naturalist scientific public organization in the Russia.

We should consider 1964 as a date of foundation of the Society of amateurs (a hobby group in its beginning). In the same year under A.E. Fersman's recommendation this hobby group has been admitted in the petrographic section of the Moscow Society of Naturalists (MOIP). The first mineral exhibition of amateurs has taken place in 1965 in the Laboratory of mineralogy of USSR Academy of Sciences located on the Leninsky prospect in Moscow. The list of participants consisted of only 17 person – representatives of different professions connected by love and interest to the mineral world. The first exhibition has passed with great success, and amateurs have decided to organize it annual.

Since 1969 within almost 40 years the exhibition which has received the name «Wonders in the stone» was carried out in the Timiryazev Biology museum. The senior generation remembers about its improbable popularity in 1960-1980 years. The turn consisting of people wishing to get to the exhibition stretched along all Malaya Gruzinskaya street, and quite often the turn was accompanied by a horse militia (police). During 2–3 spring weeks of the exhibition it was visited by more than 30 thousand people. Such amount of visitors for some, even a large museum, it was a result of the whole year of work. Visiting of the exhibition «Wonders in the stone» for many people was the first acquaintance with the world of minerals; the example of collectors wakened interest to mineral collecting. Ranks of the Society members were replenished with new members. During the golden age of its activity at the end of 1980-th the number of its members came nearer to three hundred. Many amateurs travelling for mineral collecting all over the country gathered local minerals quite often containing specimens of a museum

quality. The geography of the exhibition also extended: amateurs from Kiev, L'vov, Alma-Ata, Sverdlovsk, Baku, Sevastopol and other cities brought their specimens to Moscow, and the number of the exhibition participants reached up to 100 persons. Exhibits were accepted by a severe jury, however, the exhibitions' subjects always are wide: specimens of minerals and paleontologic findings, ornaments and statuettes made from decorative stone, meteorites and hand-made goods made from cockle-shells or pebble could be placed in showcases. Three big halls were busy with show-cases of the exhibition. Number of samples in some years reached one and a half thousand. And the main thing: the exhibitions «Wonders in the stone» always was accompanied by the creative and lively atmosphere of people incorporated by common interest to wonderful natural formations – minerals.

Success of the activity of the Society during those years is connected in many respects with its members, unselfish enthusiasts, people belonging to different professions. The first head the amateurs group was Alexander Mihaylovich Orlov, head of the Laboratory of stone belonging to the Academy of Sciences of the USSR, the group's secretary was Olga Konstantinovna Mamurovskaya. For long years Anatoly Nikolaevich Korobkov was the permanent head of the Society. He was a professional aircraft designer and a pilot many years ago carried away in mineral collecting and processing of stone (Fig. 1). Successful work of the Society in 1970–1990 years was much promoted by the MOIP president academician A.L. Yanshin. This list of the amateurs Society promoters is possible and necessary to be continued; chronicles of the Society still wait for their author.

1990-th years were difficult for our country and have also affected the life of the amateurs Society. On the one hand, fans had an opportunity to communicate on a regular basis with the foreign colleagues, attend international exhibitions-and-fair. On the other hand, swift increase of commercial spirit affected the practice of amateurishness. But the exhibition «Wonders in the stone» still annually pleased their admirers. To



Fig. 1. The emblem of the exhibition. In the center a logotype of the Society of amateurs attached to the Moscow State University of Naturalists (MOIP) is placed. Author A.N. Korobkov.

Fig. 2. Remarkable findings of minerals of the former USSR, presented at the exhibition «Wonders in the stone» – 2011. Author A.A. Evseev.



the middle of the 2000-th the Society has undergone severe ordeal: Timiryazevskiy museum has refused to give exhibition areas to the amateurs because of the change of its management. Next, 43-d exhibition «Wonders in the stone» (2008) was placed on two small exhibition areas in the Zoological museum of the Moscow State University and Fersman Mineralogical museum of the Russian Academy of Sciences in rather reduced form. In winter 2009–2010 the exhibition was again sheltered by the Zoological museum. Fortunately, it did not become the end of a history of this remarkable initiative. In spring 2011 the 45-th exhibition «Wonders in the stone» was again opened for visitors, having placed in eight small show-cases within the entrance hall of the Fersman Mineralogical museum of the Russian Academy of Sciences.

And again, as once in 1960-th, a small group of enthusiasts – amateurs has brought on the exhibition specimens and wares from their domestic collections. It is wonderful, that among the participants of the exhibition there were veterans of the Society of amateurs: A.H. and V.V. Korobkov, Yu.I. Dubrovskiy, M.L. Feodor, G.P. Apekina, T.S. Shkrob, V.A. Klokov, N.M. Kunitsyna, N.G. Tabashkov, and M.E. Berezovskiy. Their own specimens have been exhibited also by M.Yu. Bahin, M.A. Kuzmin, Yu.V. Gladkov, V.E. Lashneva, E.Ya. Rofin, M.Yu. Povarennykh, L.A. Pastukhov. Fine photos of minerals were exposed by M.A. Bogomolov, several specimens were presented by the Geological museum of Mining university (Moscow).

Theme of the exhibition- 2011 has been suggested by the express inquiry «Ten remarkable minerals of the Russia» which has been started by one of the authors in the Mineralogical museum of the Rossiysky Governmental Geological

Research University RGGRU (10-th of October, 2010) and proceeded till May, 2011. Authoritative amateurs have also taken part in it (as A.N. Korobkov, B.Z. Kantor, Yu.I. Dubrovskiy, V.E. Lashnyova, N.M. Kunitsyna, M.Yu. Bahin). Serious mineralogists, such as A.P. Khomyakov, I.V. Pekov, and E.N. Zavyalov, members of museums with collections of minerals, and also students were participants of the initiative. More than 110 persons in all took part in it. It was offered to name in a short period of time 10 remarkable Russian minerals. Results of the inquiry are published in Internet (<http://geo.web.ru/druza/1-Ru-10min.htm> in Russian). It is easy to find it in Internet using, for example, Google search .

More than 200 minerals and color stones were named in total. The most popular on a poll (are specified in brackets) became quartz (50), malachite (43), charoite (38), emerald (35), topaz (35), astrophyllite (34), eudialyte (30), calcite (29), apatite (28), alexandrite (26), and amethyst (26). Except alexandrite all of them have been presented at the exhibition.

Despite of rather small scale of the exhibition and time of its preparation, it has turned out rather indicative and multifaceted reflecting the theme «Remarkable minerals of the Russia» (and the former USSR). First of all, at the exhibition were presented new minerals discovered in Russia, including crocoite and perovskite and rheniite (shown at the M.A. Bogomolov's remarkable photo) and charoite. Second, minerals of well-known Russian occurrences and deposits belonging to the so called classical ones: Dalnegorsk, Khibiny massif (Kola peninsula), Slyudyanka, Neroyka and others are exhibited. Third, at the exhibition there were placed novelties becoming recent mineralogical sensation: cuprite and azurite crystals from the

Rubtsovskoye deposit on the Altai. At last, traditionally favorite color stones were shown: agate, flint, jasper, amethyst, citrine, topaz, amazonite, malachite, lazurite, charoite and others.

Among various specimens of quartz that became most popular, according to the inquiry, mineral of Russia, its crystals with inclusions from the most significant Russian occurrences have been presented. It was the specimens of quartz with ingrowths of rutile from the Subpolar Urals (Korobkov's couple, Yu.I. Dubrovskiy), pyrite inclusions from the Astafyevskoye deposit, Southern Urals (Yu.I. Dubrovskiy), and actinolite inclusions from the Sinerechenskoye deposit, Russian Far East (N.G. Tabashkov).

Geography of exhibits – Remarkable Minerals from the Former USSR is shown on the map (Fig. 2).

The central show-case of the exhibition was occupied by the the Korobkov's couple (A.N. and V.V. Korobkov) samples: fine wares made by Anatoly Nikolaevich – landscape agate and jaspers in unique frameworks (Painting in the stone, 2009) and high quality wonderful speci-

mens of remarkable Russian minerals: quartz, agate, eudialyte (Fig. 3), astrophyllite, belomorite, almandine, amethyst, calcite, malachite, rhodonite, pyrite, apatite, lazurite, and also jasper.

A lot of participants, in their turn, have added the exposition by the stone processed with their own hands. Thus, M.E. Berezovskiy has presented a series of works in which the stone (mainly polished agate) was shown in combination with various kinds of wood.

Young participants of the exhibition – members of the geological hobby group under the direction of geography teacher M.A. Kuzmin (Central Okrug, school N 170) have presented specimens of high museum quality (grey and pink natrolite from the Khibiny and barite with a pyrite powder from the Belorechenskoye deposit were especially wonderful).

There was a highlight in each presented collection, in other words specimens which have involved attention of amateurs as well as of experts. It should be noticed, except for the mentioned, crystals of beryl from pegmatites from

Fig. 3. Eudialyte. 25 cm in size. Khibiny, Kola peninsula. Specimen: A.N. Korobkov.





Fig. 4. Agate. 8 cm. Northern Timan, Russia.
Specimen: Yu.I. Dubrovskiy.



Fig. 5. Blue topaz. 4 cm. Orlovskoye deposit, Eastern Transbaikalia. Specimen: of M.Yu. Povarennykh.



Fig. 6. Agate. 8 cm. Pstan, Central. Kazakhstan.
Specimen: E.Ya. Rofin. Photo: A.A. Evseev.

the gulf Biruli, Taymyr peninsula. This point as mineral occurrence has been not presented in collections of the leading mineralogical museums (Yu.I. Dubrovskiy). Fine agates from the river Shanda (Southern Urals) and Timan were given by the same author (Fig. 4). Druse of gypsum crystals from the cave in the Kugigitangtau ridge (Turkmenistan) and almandine crystal of the record size from the Shueretskoye deposit, Karelia have been presented by V.A. Klokov. Transparent blue crystal of topaz from the Orlovskoye deposit, Eastern Transbaikalia (Fig. 5) has been shown by M.Yu. Povarennykh. Druse of unusual isometric crystals of quartz from the Dalnegorsk has been presented by V.E. Lashnyova. The following wonderful specimens were also shown at the exhibition: collected and polished by the author crystals of grey corundum with asterism effect in albite from the Potaninsky mountains (Southern Urals) and landscape agate from the Pstan (Kazakhstan) (Fig. 6) (E.Ya. Rofin); pink apophyllite from the Akhaltsikhe region, Georgia (T.S. Shkrob); unusual black calcite crystal with antimonite inclusions from Khaydarkan, Kyrgyzstan (M.L. Fyodorov); fine specimen of the Uzbek turquoise (L.A. Pastukhov); amethyst geode with calcite from recent gathering in the Rusavkino occurrence, Moscow suburb (N.M. Kunitsyna); magnificent polished flints from the Middle Russia and jasper from the Sibaysky deposit (Southern Urals) (M.Yu. Bahin).

More detailed photoinformation on the exhibition one may receive from the following Internet address: <http://geo.web.ru/druza/m-UVK-2011.htm>.

The exhibition has worked for two months with big success. It was offered "to register it" in the Fersman Mineralogical museum forever.

Authors express sincere gratitude to all participants of the exhibition, and also special gratitude for works connected with the organization of the exhibition and presented materials on the history of exhibitions «Wonders in the Stone» and the Society of amateurs attached to the Moscow Society of Naturalists (MOIP) to its chairman Anatoly Nikolaevich Korobkov and his wife – Victoria Veniaminovna Korobkova.

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NEW ACQUISITIONS TO THE FERSMAN MINERALOGICAL MUSEUM RAS: THE REVIEW FOR 2009–2010

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In 2009–2010 to the main collection of the Fersman Mineralogical museum RAS were acquired 840 specimens of minerals, meteorites, tectites, stone artpieces etc. The systematic collection was replenished with 339 mineral species including 90 new mineral species for the Museum, 42 of which are represented by the type specimens (holotypes, co-types and their fragments). 5 of them were discovered with help of the Museum researchers. Two species were discovered in the specimens from the Museum collection. Geography of acquisitions includes 62 countries and also extraterrestrial objects. More than 77% of all the acquisitions were donated by 105 private persons and 2 organizations. Museum collecting resulted in slightly over 12% of acquisitions; 6,5% arrived from an exchange and 3% was purchased. Less than 2% is represented by another types of acquisitions. In this paper, the new acquisitions are described by mineral species, geography, acquisition type and donors. The list of the new acquisitions is given.

2 tables, 19 photographs, 6 references.

Keywords: new arrivals, Mineralogical museum, collection, minerals, meteorites, donors.

In 2009–2010 period 840 items were added to the main collections of the Fersman Mineralogical museum RAS. The majority of them (480 items) was cataloged to the systematic collection, 156 specimens – to the deposits collection, 108 – to the collection of formation and transformation of minerals, 34 – to the crystal collection and 19 – to the gem and lapidary arts collection. Along with that, 43 specimens were cataloged to the newly formed separate (within the main collection) collection of meteorites, tectites and impact rocks. The structure of the Museum main collection and criteria of new acquisitions were published described in the previous reviews (Belakovskiy, 2001, 2003).

More than three quarters of the cataloged items (670 specimens) arrived to the museum in 2008–2010s, the others were acquired earlier and were coming through various processing (preparation, diagnosis etc.). **This review comprehends only those specimens, which were cataloged in the inventory books of the main collection of the Museum during 2009–2010s. Here is no data on acquisitions of this period, which are undergoing preparation for the following cataloguing or were decided to get moved to the exchange or scientific collection.**

Distribution of acquisitions by mineral species

Systematic collection was replenished with 339 mineral species, 90 of which are new to the Museum (Table 1). Forty-two mineral species are represented by the type minerals – holotypes, co-types or their fragments,

acquired from the authors of description. Five of these mineral species were discovered in collaboration with the Museum staff. Two new mineral species, pertsevite-OH and cōmaraitite, were discovered on the specimens from the Museum collection.

The distribution of the mineral species by the number of specimens acquired is given in the Table 1.

We will change the tradition of reviewing the new acquisitions to the Museum (Belakovskiy, 2003, 2004, 2006) and describe first the most remarkable and significant part of acquisitions in these two years – the characterizing collection of the Rubtsovsk complex ore deposit in the Altai mountains, Russia. This collection (more than 70 specimens) is mostly the joint donation by Igor V. Pekov, Mikhail Yu. Anosov, Viktor V. Levitskiy and Alexander B. Nikiforov. Another, smaller part of the specimens was purchased by the Museum. Spectacular specimens of dendritic native copper were first discovered at this deposit several years ago, but the most gorgeous material was mined out in 2010. Besides of specimens of copper with cuprite (fig. 1), well-terminated cuprite crystals (fig. 2) and copper pseudomorphs after cuprite crystals (fig. 3), these collection include specimens, displaying various morphologic types of cuprite and native copper, and also various mineral associations of the Rubtsovsk deposit. This collection contains splendid specimens of iodides: iodargyrite (well-terminated crystals from several mm up to 1 cm) (fig. 4), and also marshite CuI (crystals up to 2 cm and pseudomorphs after azurite and cuprite) (fig. 5) and miersite – a

Table 1. Number of mineral species cataloged. New mineral species are in bold script, type minerals and fragments are marked with 't' after the name

1. Quartz	60	63. Ferberite	3	125. Alunite	1	187. Cancrisilite	1
2. Calcite	26	64. Fluorcanasite	3	126. Alunogen	1	188. Kanonaite	1
3. Magnetite	21	65. Zincolivenite	3	127. Algodonite	1	189. Kapundaite	1
4. Marshite	18	66. Schorl	3	128. Almandine	1	190. Carbonate-fluorapatite	1
5. Copper	18	67. Alumoåkermanite t	2	129. Alpersite	1	191. Carobbiite	1
6. Fluorite	17	68. Analcime	2	130. Andesine	1	192. Carrolite	1
7. Topaz	13	69. Åskagenite-(Nd) t	2	131. Andorite	1	193. Kaersutite	1
8. Epidote	12	70. Astrophyllite	2	132. Annabergite	1	194. Kyanoxalite t	1
9. Azurite	10	71. Aurichalcite	2	133. Arrojadite	1	195. Kinichilite	1
10. Elbaite	10	72. Baddeleyite	2	134. Arsenoflorensite-(La) t	1	196. Cinnabar	1
11. Aragonite	9	73. Bournonite	2	135. Auriacusite t	1	197. Clinoptilolite-Ca	1
12. Spodumene	8	74. Vanadinite	2	136. Afghanite	1	198. Covellite	1
13. Hematite	7	75. Vesuvianite	2	137. Balliranoite t	1	199. Coiraitite	1
14. Goethite	7	76. Gypsum	2	138. Bafertisite	1	200. Collinsite	1
15. Corundum	7	77. Graphite	2	139. Bentorite	1	201. Cordierite	1
16. Sphalerite	7	78. Decrespignyite-(Y)	2	140. Behoite	1	202. Coronadite	1
17. Beaverite	6	79. Dickthomssenite	2	141. Turquoise	1	203. Coesite	1
18. Galena	6	80. Dolomite	2	142. Bitikleite-SnAl t	1	204. Kröhnkite	1
19. Harmotome	6	81. Cámarait t	2	143. Bitikleite -ZrFe t	1	205. Cryptophyllite t	1
20. Hemimorphite	6	82. Kyanite	2	144. Britholite-(Ce)	1	206. Xenotime-(Y)	1
21. Iodargyrite 2H	6	83. Coquimbite	2	145. Burovaite-Ca t	1	207. Xocotatlite	1
22. Cassiterite	6	84. Conicalcite	2	146. Wadeite	1	208. Kuksite t	1
23. Smithsonite	6	85. Criedite	2	147. Valentinite	1	209. Kumtyubeite t	1
24. Spessartine	6	86. Cryptohalite	2	148. Vivianite	1	210. Kurilite t	1
25. Andradite	5	87. Cryptomelane	2	149. Whitlockite	1	211. Labradorite	1
26. Barite	5	88. Cuprite	2	150. Veatchite	1	212. Lazurite	1
27. Danburite	5	89. Cupronyite t	2	151. Vlasovite	1	213. Lafossaite	1
28. Oxyphlogopite t	5	90. Lamprophyllite	2	152. Vauquelinite	1	214. Lecoqite-(Y) t	1
29. Prehnite	5	91. Lepidocrocite	2	153. Vauxite	1	215. Löllingite	1
30. Silver	5	92. Lepidolite	2	154. Volkovskite	1	216. Libethenite	1
31. Fluorapatite	5	93. Linarite	2	155. Wollastonite	1	217. Lindbergite	1
32. Antlerite	4	94. Lindgrenite	2	156. Voloshinite t	1	218. Lithiophorite	1
33. Boulangerite	4	95. Lorenzenite	2	157. Vorlanite t	1	219. Litochlebite	1
34. Voronkovite t	4	96. Manganoeudialyte t	2	158. Wulfenite	1	220. Lovozerite	1
35. Hübnerite	4	97. Millerite	2	159. Vuoriyarvite-K	1	221. Laumontite	1
36. Jamesonite	4	98. Arsenic	2	160. Halite	1	222. Magnesiocopiapite	1
37. Diopside	4	99. Natrolite	2	161. Häuyne	1	223. Magnesioneptunite t	1
38. Dioptase	4	100. Nifontovite	2	162. Hedenbergite	1	224. Magnesite	1
39. Clinocllore	4	101. Nontronite	2	163. Heulandite-Na	1	225. Maikainite	1
40. Miersite	4	102. Pyrite	2	164. Heterogenite	1	226. Manganogrunerite	1
41. Manganoneptunite	4	103. Pearceite <i>Tac</i>	2	165. Hydrogrossular	1	227. Marialite	1
42. Molybdenite	4	104. Protoferro-anthophyllite t	2	166. Hydroxylwagnerite	1	228. Meionite	1
43. Oxammitite	4	105. Rockbrusgeite	2	167. Hydrocerussite	1	229. Melanterite	1
44. Rhodochrosite	4	106. Rutile	2	168. Hydrozinkite	1	230. Meniaylovite	1
45. Uvite	4	107. Sanidine	2	169. Hypersthene	1	231. Metaborite	1
46. Forsterite	4	108. Scorodite	2	170. Glauberite	1	232. Microcline	1
47. Stibnite	3	109. Stilbite	2	171. Hollandite	1	233. Minrecordite	1
48. Arsenopyrite	3	110. Stranskiite	2	172. Goyazite	1	234. Mozgovaite	1
49. Beryl	3	111. Antimony	2	173. Graftonite	1	235. Momoiite	1
50. Brewsterite	3	112. Tveitite-(Y)	2	174. Davidite	1	236. Murmanite	1
51. Wavellite	3	113. Tetraferriphlogopite	2	175. Depmeierite t	1	237. Murunskite	1
52. Bismuthinite	3	114. Tyrolite	2	176. Jaipurite	1	238. Muscovite	1
53. Hambergite	3	115. Titanite	2	177. Ginorite	1	239. Natrosilite	1
54. Goethite	3	116. Chalcantite	2	178. Johnsomervilleite	1	240. Nepheline	1
55. Malachite	3	117. Chovanite t	2	179. Dickite	1	241. Nickeltalmessite t	1
56. Oxyvanite t	3	118. Chegemite t	2	180. Dovyrenite	1	242. Nordite-(Ce)	1
57. Osarizawaite	3	119. Jarosite	2	181. Dravite	1	243. Numanoite	1
58. Paraershovite t	3	120. Averievite	1	182. Durangite	1	244. Obradovicite	1
59. Pyrophyllite	3	121. Agrellite	1	183. Zigrasite t	1	245. Okenite	1
60. Rostite	3	122. Adamite	1	184. Kainosite-(Y)	1	246. Opal	1
61. Siderite	3	123. Adranosite	1	185. Kaliophilite	1	247. Orthoclase	1
62. Stichtite	3	124. Actinolite	1	186. Cancrinite	1	248. Osumilite-Mg	1

Table 1.

249. Palenzonaite	1	272. Lead	1	295. Wilcoxite	1	318. Huanzalaite	1
250. Paralaurionite	1	273. Segnitite	1	296. Ulexite	1	319. Celestine	1
251. Patronite	1	274. Semseyite	1	297. Wakefieldite-(Nd)	1	320. Cerussite	1
252. Pertsevite-OH t	1	275. Serendibite	1	298. Fayalite	1	321. Jinshajiangite	1
253. Picroparmacolite	1	276. Serpentine	1	299. Fernandinite	1	322. Jixianite	1
254. Pyrope	1	277. Szmikite	1	300. Fersmite	1	323. Clindrite	1
255. Pyrrhotite	1	278. Stedindite-(Ce)	1	301. Fivegite t	1	324. Zinnwaldite	1
256. Plumbophyllite	1	279. Stronadelphite t	1	302. Phlogopite	1	325. Znucalite	1
257. Plumbosumite	1	280. Strontianite	1	303. Florencite-(Ce)	1	326. Zoisite	1
258. Proshchenkoite-(Y) t	1	281. Strontioginorite	1	304. Fornacite	1	327. Chalcocolloite	1
259. Pseudobrookite	1	282. Strontiopyrochlore	1	305. Phosphofibrite	1	328. Chevkinite-(Ce)	1
260. Pseudocotunnite	1	283. Suredaite	1	306. Phosphophyllite	1	329. Chabazite-Ca	1
261. Poudretteite	1	284. Tennantite	1	307. Foshagite	1	330. Shlykovite t	1
262. Pumpellyite-(Fe²⁺)	1	285. Tenorite	1	308. Freibergite	1	331. Spinel	1
263. Piemontite	1	286. Tetrahedrite	1	309. Friedrichbeckeite	1	332. Schröckerite	1
264. Redgillite	1	287. Tiemannite	1	310. Fluorbritholite-(Y) t	1	333. Shcherbakovite	1
265. Redledgeite	1	288. Timroseite	1	311. Fluoro-potassichastingsite	1	334. Eudialite	1
266. Refikite	1	289. Tinzenite	1	312. Fluorophosphohedyphane	1	335. Eurekadumpite t	1
267. Romanèchite	1	290. Todorokite	1	313. Chalcocite	1	336. Edgarite	1
268. Rruffite t	1	291. Thorianite	1	314. Heftetjernite t	1	337. Edenite	1
269. Santabarbaraite	1	292. Toturite t	1	315. Chloritoid	1	338. Elbrusite-Zr t	1
270. Sanjuanite	1	293. Tremolite	1	316. Holfertite	1	339. Eringaite t	1
271. Sassolite	1	294. Triplite	1	317. Chromatite	1		

cubic modification of AgI (yellowish-green crystals up to 1 mm across). Marshite and miersite were the new mineral species for the Museum and specimens of iodargyrite are of a much better quality than the specimens from deposits in Kazakhstan and Broken Hill deposit in Australia, the Museum had before. Quite a complete number of the acquired minerals which occur at this deposit (silver, beaverite, redgillite, osarizavaite, cerussite etc.) corresponds to the mineral associations described in the monograph by Igor V. Pekov and Inna S. Lykova (2011).

Following our usual way of review, we would begin it with quartz, which is almost always on the top of the table (60 specimens). Amongst new material one should note cluster of morion crystals up to 12 cm long, from pegmatites of Airtau massif in Central Kazakhstan. These are similar to the ones from Ortau massif, but terminated with more perfect and shiny faces. Interesting specimens with grayish-green on their surface, needle-like crystals, co-grown with calcite and siderite, came from the Nikolayevskiy mine, Dalnegorsk, Primorye. Quartz after apophyllite crystals up to 4 cm long, from the Krutoye deposit, Nizhnyaya Tunguska river valley, was donated by Viktor V. Levitskiy and Alexander B. Nikiforov. Among the purchased notable specimens of amethyst there are: twinned crystals by Japanese law, from the Obman deposit in Yakutia; crystal crust – a cast after calcite crystals which were dissolved later, from Rio Grande, Brazil; and new

material from Baobab mine, Kitui, Kenya – scepter crystals up to 14 cm long resembling amethyst from Vatikha, the Urals. A series of 23 agate slabs, generally from British localities, was donated by the National Museums of Scotland, Edinburgh. Besides, druses of synthetic amethyst and citrine, along with synthetic quartz twinned by various laws, synthesized in VNIISIMS, Aleksandrov town, were also cataloged.

Six specimens of calcite, out of 26, came from the Dalnegorsk deposits, Primorye. Amongst them there are autoepitaxial clusters of crystals of various habit from the 2nd Soviet mine, and also parallel pyramidal clusters, that consist of gray blocked rhombohedral crystals, covered with a fine crust of shiny quartz crystals, from the Nikolaevsky mine (fig. 6). The gem and lapidary arts collection was replenished with transparent orangy-yellow, faceted as trigon-tristetrahedron, 5 cm calcite from Nizhnyaya Tunguska river valley. To the collection of formation and transformation of minerals were added the druse of needle-like scalenohedral calcite crystals up to 4 cm long – gray, due to numerous sand inclusions, from South Dakota, USA. This specimen is similar to classic "sand calcite" from Fontainebleau, near Paris, France. To the same collection was cataloged calcite "basin" with calcite pisolites ("cave pearl") – the result of a modern mineralization in an abandoned mine at the Belorechenskoye deposit, North Caucasus, Russia (fig. 7).

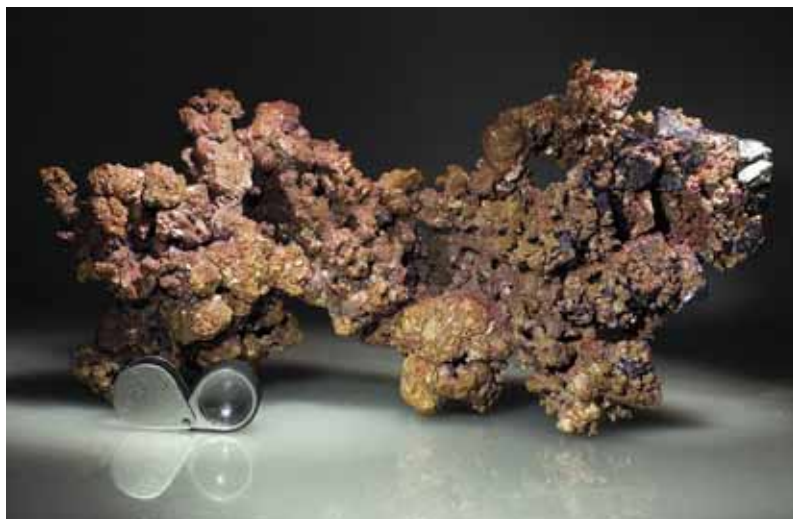


Fig. 1. Dendritic aggregate of native copper with cuprite crystals. Size 24 cm. Purchase. №93214. Photo by Mikhail Moiseev.

Fig. 2. Cuprite. Octahedral crystal modified with rhombododecahedral faces. Size 5cm. Rubtsovsk mine, Altai, Russia. Purchase. № K-5010. Photo by Mikhail Moiseev.

Fig. 3. Pseudomorph of native copper after octahedral cuprite crystals up to 1.5 cm across. Rubtsovsk mine, Altai, Russia. Purchase. № OP-2585. Photo by Mikhail Moiseev.



Fig. 4. Twinned crystal of iodargyrite 2H on limonite. Rubtsovsk mine, Altai, Russia. Donation by Igor V. Pekov. Fragment of specimen № 92960. Photo by Igor V. Pekov & Anatoliy V. Kasatkin.

Fig. 5. Marshite. Partial pseudomorph after azurite concretion. Rubtsovsk mine, Altai, Russia. Donation by Mikhail Yu. Anosov, Victor V. Levitskiy, Alexander B. Nikiforov. № OP-2577. Photo by Mikhail M. Moiseev.

Fig. 6. Parallel cluster of gray rhombohedral crystals of calcite with fine quartz crystals on its faces. Nikolayevskiy mine, Dalnegorsk. Primorye, Russia. Donation by Dmitriy I. Belakovskiy. № OP-2503. Photo by Mikhail M. Moiseev.



The majority of magnetite acquisitions, on the 3rd place by the number of specimens cataloged, is donated by the collector Boris Z. Kantor and is represented by a set of 16 genetic specimens of druses and clusters, from Dashkesan deposit in Azerbaijan and Korshunovskoye deposit in Angaro-Ilimsky region,

Russia. The cluster of small magnetite crystals on clinoclone (from Kurzshunkul, North Kazakhstan), donated by Vladimir A. Popov and Sergey G. Epanchintsev, is curious because some of these crystals are twinned along {111}.

All the specimens of marshite and majority of copper specimens, which are on the 4th

and 5th positions in the Table 1, and also specimens of azurite, beaverite, iodargyrite, native silver, miersite, osarizavaite, cuprite and smithsonite, occupying the lower positions, are from the Rubtsovsk deposit.

Among 17 specimens of fluorite the most interesting are, undoubtedly, the druses of bright-green crystals twinned along {111}, up to 4 cm, showing blue fluorescence under sunlight. These were collected by Maria S. Alferova at the classic Rogerley mine, Weardale, UK. She also donated specimens with big (up to 13 mm) harmotome crystals (# 19 in the Table) from Bellsgrove quarry, Strontian, UK.

More than half of 13 topaz specimens were collected in 2010 at the well-known locality Maynard's claim, Thomas Range, Utah, USA. These are spectacular clusters of transparent wine-colored crystals with inclusions of rhyolite (fig. 8).

11 of 12 epidote specimens are collected by Dmitriy I. Belakovskiy and Douglas Toland in 2010 at the classic deposit Green Monster Mt., Prince of Wales Island, Alaska, USA. They are represented by well-terminated dark-green twinned crystals. The biggest crystal is 5 cm in size.

Amongst the acquisitions of elbaite there are the most remarkable specimens: sectorial slabs – the cross-cuts of giant crystals from Anjanabonoina, Madagascar. These are the best specimens of the kind at the Museum.

Eight of nine specimens of aragonite are pseudohexagonal trilling hopper-crystals from Corocoro, Bolivia, in full or partially replaced with native copper. They belong to the collection of Alexander Novitskiy – Argentinean geologist, native Russian (see below). The same collection contains almost

all newly cataloged spodumene specimens, majority of hematite, goethite, sphalerite, galena and cassiterite specimens.

The most interesting specimens of corundum are bluish-gray spindle-like crystals in association with dravite, from Snezhinsk, Chelyabinsk region, the Urals, donated by Igor N. Savin.

Amongst the specimens with galena we would note a cluster of distorted crystals approximately 5 cm across on a fluorite druse, from the Belorechenskoye deposit.

Hemimorphite specimens arrived as drusy colorless split crystals from Ojuela, Durango, Mexico, and as bright-blue crusts of bud-like aggregates which incrust leaching cavities in the rocks from Wenshan, Yunnan province, China.

The most spectacular spessartine specimen is the isometric tetragon-trisoctahedron, 7.5 cm across from Morogoro, Tanzania (fig. 9), donated by Dmitriy I. Belakovskiy, Mikhail Yu. Anosov, Alexander B. Nikiforov and Viktor V. Levitskiy. Also very interesting specimens of orange-red transparent hopper-crystals of spessartine up to 3 cm from Navegadora mine in Brazil, donated by Jeffrey E. Patterson.

One of the best specimens of andradite from Dashkesan, Azerbaijan, is the druse of reddish-brown tetragon-trisectahedral crystals up to 3 cm across (fig. 10). This is one of the Museum acquisitions from the 1960s. Another variety of andradite is represented by two pieces with druses of demantoid crystals from Antetetzambato, Madagascar. This material is recent.

Among barite acquisitions there are pale blue transparent crystals from Stoneham, Weld Co., Colorado, USA.

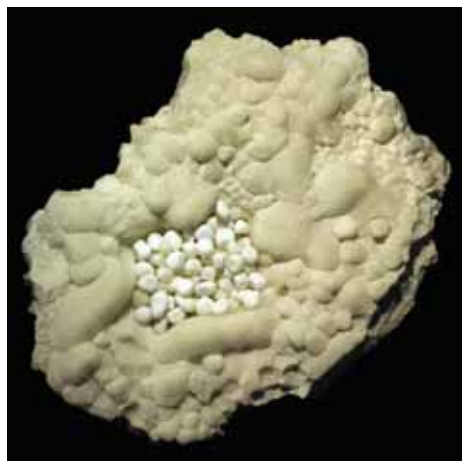


Fig. 7. Calcite pisolites (cave pearl) in calcite "basin". Formed within approximately 7 years in an abandoned mine. Belorechenskoye mine, Adygei republic, Russia. Donation by Mikhail M. Moiseev & Viktor V. Levitskiy. № OP-2501. Photo by Mikhail M. Moiseev.

Fig. 8. Topaz. Crystal cluster from rhyolites. Size 4.5 cm. Maynard's Claim, Thomas Range, Juab Co., Utah, USA. Donation by Dmitriy I. Belakovskiy. № 93039. Photo by Mikhail M. Moiseev.



Fig. 9. Spessartine. Tetragon-trioctahedron, 7.5 cm across. Nani, Loliondo, Arusha region, Tanzania. Donation by Dmitriy I. Belakovskiy, Mikhail Yu. Anosov, Viktor V. Levitskiy, Alexander B. Nikiforov. № 93063. Photo by Mikhail M. Moiseev.

The Museum was lucky to purchase one of the specimens of danburite in aggregate with datolite, found at the Borosilikatnoe in Dalnegorsk, Primorye.

The following minerals arrived in five specimens each: recently discovered mineral species oxiphlogopite from Eifel, Germany; prehnite (spherulites with epidote from Kayes, Mali and pseudostalactites from Totwa, New Jersey, USA); fluorapatite (the most remarkable one – green crystal in phlogopite from Snezhinsk, Chelyabinsk region, Urals, donated by F. Baaz, and dark-blue crystal 11 cm long from Valadares, Brazil).

The other 311 mineral species which arrived to the Museum as 1 and up to 4 samples, marked in bold in the Table, besides new for the Museum and type specimens, there should be noted tetrahedrite crystal approximately 6 cm across, in epitaxial

aggregate with blocked tetrahedral sphalerite crystals (fig. 11). Specimens of the kind occurred at the 2nd Soviet mine, Dalnegorsk, Primorye, in spring-2009. Besides, new arrivals comprise rocks, synthetic minerals, stone art pieces etc.

Geography of acquisitions

Acquisitions of 2009-2010 arrived from 62 countries and Antarctica. Their quantitative distribution among countries is given in the Table 2.

Russia (283)

The majority of Russian specimens arrived from the Altai mountains (79), from the mentioned earlier Rubtsovsk mine and some others in the same region. In addition, the number of specimens of deep purple stichtite in green serpentine from the new finds in the river Kaznakhta valley (Terektinskiy ridge, Gorny Altai), were donated by Mikhail Yu. Anosov, Viktor V. Levitskiy and Alexander B. Nikiforov.

New acquisitions from Kola peninsula got the second place and list 58 specimens; Khibina massif sourced 26, Lovozero and Kovdor massifs – 13 each, Keivy – 2 specimens. In addition to seventeen specimens of new-discovered mineral species and donated by Alexander P. Khomyakov, Igor V. Pekov, Nikita V. Chukanov, Yulia V. Azarova and Zoya V. Shlyukova, one should draw attention to the gorgeous piece with bright-red well-terminated 2 cm long crystal of manganoneptunite in gray natrolite (fig. 12). This one of the best specimens of manganoneptunite in the Museum was collected near Marchenko Peak, Khibiny Mts. It was found and donated by Gregory L. Ryabinin.



Fig. 10. Andradite. Druse of tetragon-trioctahedral crystals up to 3 cm across. In association with epidote and magnetite. Dashkesan, Azerbaijan. Purchase. № 93056. Photo by Mikhail M. Moiseev.

Table 2. Geography of acquisitions by the number of mineral specimens

1. Russia	283	17. Peru	8	33. Sweden	4	49. Burkina Faso	1
2. USA	110	18. Czech Republic	8	34. Israel	3	50. Vietnam	1
3. Bolivia	55	19. Egypt	6	35. Turkmenistan	3	51. Guinea	1
4. Argentina	42	20. Morocco	6	36. Ukraine	3	52. Spain	1
5. United Kingdom	36	21. Oman	6	37. Sri Lanka	3	53. Congo	1
6. Kazakhstan	26	22. Tanzania	6	38. Austria	2	54. Cuba	1
7. China	24	23. Australia	5	39. Belgium	2	55. Kyrgyzstan	1
8. Greece	21	24. Afghanistan	5	40. Botswana	2	56. Libya	1
9. Mexico	16	25. Canada	5	41. Venezuela	2	57. Mauritania	1
10. Brazil	13	26. Congo DR	5	42. Iran	2	58. Malawi	1
11. Germany	13	27. Tajikistan	5	43. Kenya	2	59. Nigeria	1
12. Italy	13	28. India	4	44. Mozambique	2	60. Pakistan	1
13. Azerbaijan	12	29. Mali	4	45. Nepal	2	61. Poland	1
14. Bulgaria	11	30. Namibia	4	46. Slovakia	2	62. Finland	1
15. Madagascar	11	31. Norway	4	47. RSA	2	Antarctica	1
16. Chile	11	32. Romania	4	48. Japan	2	Unknown	5

He, together with the Museum curator Mikhail M. Moiseev collected specimens of baddeleyite, forsterite, vesuvianite for the Kovdor mineral collection. Igor V. Pekov also donated specimens of spray and star aggregates of lamprophyllite from Sengischorr Mt., Lovozersky massif – of better quality than was at the Museum before. Anatoly P. Akimov donated interesting specimens of corundum from Dyadina Gora, Tedino village, Karelia.

Acquisitions from the Russian Caucasus (16) came equally from Verkhnechegemskiy plateau in Kabardino-Balkaria and Belorechenskoye deposit in Republic of Adygea. From the first locality there arrived type specimens of the new mineral species of chegemite, toturite, kumtubyte, vorlanite and also new amazing silicon-free minerals of the garnet group – bitikleite-SnAl, bitikleite-ZrFe and elbrusite. These minerals were discovered and donated by Irina O. Galuskina, Eugeny V. Galuskin and Nikolay N. Pertsev. The acquisitions from the Belorechenskoye deposit, besides the above-mentioned galena and cave pearls, are graphite, cinnabar, coronadite and schröckingerite.

Among 24 specimens from the Urals, first of all, one of the most interesting one is a crystal of redledgeite (up to 5 mm long) from the Saranovskoye deposit, donated by Mikhail M. Moiseev. This is one of the best specimens of this species. The type specimen of arsenoflorencite-(La) from the locality Grubependity, Polar Urals, was donated by Pavel M. Kartashov. The same place (Maldynyrd ridge) was the source of a large pink crystal of florencite-(Ce) up to 1.5 cm in size and xenotime-(Y), both donated by S.A. Repina. It would be worthwhile to mention coarse-grained aggregate of arsenic from the Vorontsovskoye deposit, Krasnoturyinsk,

donated by A.S. Klepikov, and a drusy fornasite up to 2 mm with crocoite – donation by A.S. Batalin and D.V. Davydov. Green apatite from Snezhinsk was mentioned before.

Siberia is represented by the minerals from the river Nizhnyaya Tunguska valley, among which we should note a big crystal of heulandite in a basalt cavity, donated by Viktor V. Levitskiy and Alexander B. Nikiforov.

Irkutsk and Baikal regions sourced 19 specimens, majority of which are magnetite and clinochlore from Korshunovskoye deposit, Angaro-Ilimskiy region. The most remarkable sample is the piece approximately 60cm in size, consisted of big buds of clinochlore. This is a good addition to a series of previous acquisitions of the cross-cuts of clinochlore stalactites and buds.

The most interesting acquisitions from Transbaikal (16 specimens) are hambergite, apatite, topaz and other minerals from pegmatites of Malkhan Ridge, Chita region, donated by Igor N. Savin.

Among a few specimens from Yakutia (7), there are holotypes of pertsevite-(OH), proshchenkoite-(Y) and eringaite, and also minerals from kimberlites and kimberlite rocks.

Almost all the acquisitions from Primorye (20) occur from the Dalnegorsk region deposits. In addition to the specimens mentioned above it is worthwhile to note clusters of needle-like slightly splitted pyrrhotite crystals with bent vertices (fig. 13). Such specimens appeared at the Nikolayevskiy mine in November 2009.

Another specimens from Russian Far East (9) are: the type specimen of the new mineral kurilite from the Prasolovskoye deposit, Kunashir island, discovered and donated by Vladimir A. Kovalenker; rare minerals meniylovite and averievite from the Tolbachik



Fig. 11. Tetrahedrite. Crystal (approximately 6 cm across) with epitaxial ingrowths of blocked sphaerite crystals. Chalcopyrite forms epitaxial overgrowths on tetrahedrite and sphaerite. 2nd Soviet mine, Dalnegorsk. Primorye, Russia. Purchase. № OP-2544. Photo by Mikhail M. Moiseev.

Fig. 12. Manganoneptunite. 2 cm long crystal within natrolite. Marchenko Peak, Khibiny Mts, Kola peninsula, Russia. Donation by Grigoriy L. Ryabinin. № 93167. Photo by Mikhail M. Moiseev.

Fig. 13. Pyrrhotite. Cluster of columnar crystals with bent apices, 9 cm. Nikolayevskiy mine, Dalnegorsk. Primorye, Russia. Donation by Dmitriy I. Belakovskiy. № OP-2504. Photo by Mikhail M. Moiseev.

volcano fumaroles, Kamchatka, resulted from an exchange; "wood tin" from the Tyrkneyskiy ore region, Chukotka (donation by Gennadiy N. Kaplenkov).

Former Soviet republics:

Kazakhstan (26)

Morion from Airtau and magnetite from Kurzshunkul were mentioned in the previous chapter. Blue topaz approximately 5 cm across, from the Ortau massif pegmatite, was purchased by the Museum. More than ten specimens of smithsonite, hemimorphite, rhodochrosite, barite and calcite from Shaimerden, Kustanay region, were donated to the Museum by Sergey G. Epanchintsev. Among rare minerals there arrived: veatchite, volkovskite, metaborite from the salt domes Shoktybay, Satimola and Chelkar (donation by Igor V. Pekov) respectively. The new mineral species *cámaraite* was discovered by Elena V. Sokolova *et al.* on the museum specimen of *bafertisitite* from the old collections.

Acquisitions from **Azerbaijan (12)** are interesting mostly by the above-mentioned number of specimens of magnetite and big cluster with andradite crystals, from the iron-ore skarns of Dashkesan deposit.

Tajikistan (5) was the source of crytohalite and stranskiite from the coal fire near the former kishlak Ravat, nordite-(Ce) from the Dara-i-Pioz massif and tyrolite from Dgani, Darbaza, Zeravshan Ridge.

Turkmenistan (3) is represented by gypsum from the Fata-Morgana cave, Gaurdak

village, and also by fragments of meteorite Kunya-Urgench (see below).

Ukraine (3) is represented by the big cluster of vivianite crystals replaced with santabarbarite, Kerch, Crimea (donated by V.A. Morozov), by prehnite with gyrolite and okenite from Trudolyubovka village, Crimea and cerussite after galena and boulangerite from Esaulovka, Nagolny Kryazh.

Only one specimen was cataloged from **Kyrgyzstan** – anthraxolite from Mednaya Gora quarry, Khaidarkan (V.I. Stepanov's old collection).

North America:

The United States of America (110)

Almost half of all the acquisitions from 16 states of the USA were collected by the Museum staff. The majority of specimens were collected in **Alaska (27)**. These are specimens from the skarn locality of Green Monster mountain, Prince of Wales Island. Besides epidote crystals and clusters, the samples collected are: 'Japanese' quartz twins, muschketowite, andradite, goethite pseudomorphs after pyrite. T. Hanna donated several specimens of pearceite-*Tac* and native silver from the Greens Creek mine, Admiralty Island.

The material collected from Utah is represented with tiemannite, dickthomssenite (new to the Museum) and 16 specimens from Thomas Range region. Sometimes clusters of topaz crystals is crowned with tetragon-trisocahedronal pseudomorph of topaz and hematite aggregate, probably, after garnet

(Fig. 14). There also occur such single "crystals" up to 3cm across. Other minerals cataloged to the Museum collection are: red beryl, pseudobrookite, holfertite and durangite – collected by Dmitriy I. Belakovskiy and Maria S. Alferova.

Maria S. Alferova also collected specimens of elbaite from the Stewart mine San Diego Co., California, crystals and small druses of diopside from the Table Mountain mine and gemmy forsterite nodules in basalts of San Carlos Indian reservation, Arizona.

Phosphates – arrojadite, whitlockite, rockbridgeite, collinsite *et al.* were collected in pegmatites Top quarry, Custer Co., S. Dakota, by Mikhail M. Moiseev, Dmitriy I. Belakovskiy and Igor V. Pekov. The same team collected manganese uvite in purple manganese tremolite (hexagonite) from the talk deposit Balmat talc mine, Lawrence Co., NY. Fragments of the co-types of auriacusite (Black Pine mine, Montana) and eurekaumpite (Centennial Eureka mine, Utah) were donated to the Museum by Stuart Mills and Igor V. Pekov respectively.

Canada (5)

Igor V. Pekov discovered the new mineral species – lecoqite-(Y), from Mont Saint-Hilaire and handed over its co-type. Mikhail N. Murashko donated jaipurite (Langis mine, Ontario) – a new mineral species for the Museum; Dmitriy I. Belakovskiy donated vlasovite with gittinsite margin within eudia-

lyte and agrellite from Kipawa complex, Quebec; also he donated fersmite from Mount Brussilof mine, British Columbia.

Mexico (16)

Among Mexican specimens the most interesting are colorless, transparent finely-terminated crystals of nifontovite up to 3.5 cm long with inclusions of probertite from San Luis Potosi. The second rank have hollow spherical clusters of creedite crystals, from colorless to bright-orange due to inclusions (fig. 15). Several big lots of the such specimens were mined during the last years from Navidad, Durango Mine. We would note pale-pink danburite crystal (14 cm long) from Charcas mine, close to San Luis Potosi, and also clusters and druses of colorless and pale-pink hemimorphite crystals from Ojuela mine, Mapimi, Durango. One should also mentioned rare minerals kinichilite and xocoolatlite – from Aztec for "chocolate" – from Bambolla, Sonora.

South America:

Bolivia (55), Argentina (42), Chile (11), Venezuela (2) – Alexander Novitskiy collection

The overwhelming majority of mineral specimens cataloged to the Museum collections in 2009–2010s from these countries, belong to the collection of ethnically Russian geologist Alexander Novitskiy, who lived in Argentina. This collection was brought together for his life-long time in Latin America, where he worked as a geologist and taught in

Fig. 14. Aggregate of topaz crystal with topaz&hematite pseudomorph after tetragon-trioctahedra crystal of, presumably, garnet group mineral. Maynard's Claim, Thomas Range, Juab Co., Utah, USA. Donation by Dmitriy I. Belakovskiy. № OP-2547. Photo by Mikhail M. Moiseev.

Fig. 15. Hollow spheroidal aggregates of creedite crystals up to 1.5 cm. Size of the specimen 27 cm. Navidad Mine, Durango, Mexico. Donation by Dmitriy I. Belakovskiy. № 92829. Photo by Mikhail M. Moiseev.



Buenos Aires. At the end of his life, he already being gravely ill, decided to donate his collection to Russia. He got in contact with the Fersman Mineralogical museum RAS via Russian diplomats. One of museum curators, Dmitriy A. Romanov traveled to Buenos Aires in 1989 to describe this collection and to prepare for shipment. Later, this collection was shipped via diplomatic channels to Russia. Unfortunately, A. Novitskiy's illness made the complete attribution of this collection impossible. In many cases it was impossible to recover geographic names. Due to this fact, in order to sort this material out, one needed a long time. At present, there described and cataloged to the main collection of the Museum 105 specimens (a little less than a half). The part of the collection cataloged comprehends many classic deposits. It is represented by phosphates, molybdates and copper sulfates from Chuquicamata, Chile; famous Bolivian copper pseudomorphs after aragonite from Corocoro; phosphophyllite, cassiterite and other minerals from Potosi; sulfosalts from San Jose near Oruro and hubnerite from Tasna. Minerals of Argentina are represented by rhodochrosite from Capillitas, spodumene from San Luis region, antimony from Cerro de Los Leones and number of others.

Acquisitions from these countries also include rare minerals suredaite and coiraite from the mining district Irquitas in Argentina, donated by Werner Paar and lithochlebite from El Dragon, Potosi, Bolivia, from Anatoly V. Kasatkin.

Brazil (13)

Amongst amethyst, spessartine and blue apatite mentioned above, one should mention: well-terminated zonal blue-green transparent kyanite crystal, 12 cm long, from Ouro Preto and fragment of strongly resorbed tabular colorless crystal of beryl. Recently discovered manganoeudialyte from Pocos de Caldos is represented by the holotype, that was donated by Nikita V. Chukanov.

Peru (8)

The most interesting specimens from Peru are: hexagonal-prismatic crystals of coquimbite, up to 3 cm long, from Javier mine, Ayacucho department; hubnerite crystals up to 5 cm long within the rock crystal druses and also new mineral species huansalaite ($MgWO_4$, wolframite group) from Huanzala and fernandinite from Ragra.

Europe:

The United Kingdom (26)

Fluorite, harmotome and agates acquired from this country were mentioned before. We

can also mention green crystals (up to 5mm) of scorodite from Hemerdon mine, Devon, donated by Jolyon Ralph.

Greece (21)

All the specimens from Greece originate from the mining district Lavrion and were donated by Igor V. Pekov. They are represented mostly by supergene minerals and also new-born minerals within antique metallurgical slag, affected by seawater. The minerals are: zincolivenite, aurichalcite, paralaurionite etc.

Germany (13)

The major part of specimens arrived belong to mineralization of alkaline basalts from Eifel region. These are mostly samples of recently discovered oxiphlogopite, donated by Nikita V. Chukanov.

Italy (13)

The material acquired from Italy originate mostly from the recent collecting in active volcanic crater La Fossa, Vulkano island. These are fumarolic minerals, such as lafossaite, adranosite, pseudocotunnite, chalcocoloite, sassolite, mozgovaite. Kaliophillite and balliranoite from Monte Somma, Vesuvius, are also volcanic.

Bulgaria (11)

This time the majority of specimens are represented with zeolites (harmotome, chabazite-Ca etc.) and collected by Svetlana N. Nenasheva at the locality Zlatolist, adjacent to Krumovgrad town.

Among the acquisitions from the other European countries there are remarkable specimens of millerite, rostitite and dickite from siderite concretions in coal from Kladno town in **Czech Republic**; specimens of cupronyite from the mining district Baita in **Romania** and chovanite from Male Zelezne в **Slovakia**, both donated by Dan Topa; new mineral species askagenite-(Nd) from Askagen в **Sweden**, and also new for the Museum stetindite-(Ce) and holotypes of hetetjernite and fluorbritholite-(Y) from **Norway**.

Africa:

The majority of 62 specimens acquired from 19 African countries originate from **Madagascar (11)**. In addition to mentioned above demantoid and slabs of zonal & sectorial cross-cuts of elbaite-liddicoatite crystals there are big and well-terminated schorl crystals up to 12 cm long from Alaotra, Ambatondrazaka, and polished specimen of iridescent labradorite from Tulear province. **Egypt, Oman, Libya, Nigeria, Mauritania, RSA and Burkina Faso** are represented, in

general, by meteorites and tectites described below. Fanciful pseudomorphs of goethite after pyrite also arrived from **Egypt**. **Morocco** had sourced calcite, variously colored with cobalt, from Bou-Azzer and holotype of nickeltalmessite; **Tanzania** – holotype of alu-moekermanite from Ol Doinyo Lengai active volcano, donated by Anatoliy N. Zaitsev, and spessartine, mentioned above; **DR Congo** – specimens of velvet malachite and heterogenite from Shaba province, and also faceted orange andesine (donated by M. Vishnevetskiy). Prehnite and epidote sets were replenished with the new specimens from Kayes region, Mali. Agates arrived from **Botswana**; stranskiite, minrecordite and maikainite – from **Namibia**. Amethyst from **Kenya** was already mentioned above.

Asia:

China (24)

The most interesting specimens added to the Museum collection from Celestial Empire are: the specimen with large hexagonal crystals of molybdenite from Guanzhou (Fig. 16) and pseudomorph of jamesonite after bournonite from Yaogangxian mine, Hunan province. The same mine provided bournonite, crystals and clusters of arsenopyrite; Wenshan mine from Yunnan province – bright light-blue hemimorphite. Gem and lapidary arts collection was supplemented with faceted triplite and dendritic 'landscape' argillite (Fig. 17).

India (4)

Selection of minerals from basaltic amygdals from Poona region was completed with specimen of stilbite and spray aggregate of okenite on a chalcedony-quartz lamellar aggregate ('settler').

Acquisitions from **Nepal (2)** are colorless orthoclase crystal from Ganesh Himal and

marialite from Dhading region donated by Oleg A. Lopatkin. The Museum collection was replenished by specimens from **Afghanistan**: afghanite crystals within calci-pyrite from Sar-e-Sang and crystals of albaite and spodumene crystals donated by Farid Wafi. **Pakistan** is represented by one specimen – big well-terminated crystal (approximately 8 cm large) chevikinite-(Ce) from Arondu, Basha Valley, Baltistan (fig. 18). Poudrettite, a new mineral species to the Museum arrived from **Sri-Lanka** as faceted stone (3 x 2 mm), donated by M. Vishnevetskiy. Large piece of marble with crystals of pink spinel (up to 3.5 cm) and green pargasite ingrowths, from Luc Yen, **Vietnam**, was acquired by the Museum (Fig. 19). K. Watanabe donated momoiite and numanoite, both from Fuka mine, **Japan** – the new mineral species for the Museum.

Australian samples are represented by the new for the Museum mineral species, including alpersite and kapundaite. Remarkable acquisitions from other countries are: bentorite and chromatite from Hatrurim Formation, **Israel**, and petrified wood – pseudomorph of chalcedony after wood – from Beaver lake, **East Antarctica** (donated by M.B. Sergeev).

Extraterrestrial acquisitions

The collection of meteorites that was compiled for the Mineralogical museum of Russian Academy of Science, in 1939 was transferred to the newly-organized Meteorite Committee (CMET). Part of this collection, along with many meteorites collected by CMET expeditions, is displayed at the Mineralogical museum, still being owned by the Museum of Extraterrestrial matter at the

Fig. 16. Molybdenite. Crystals up to 7 cm in quartz. Guanzhou, Jianxi province, China. Purchase. № 93029. Photo by Mikhail M. Moiseev.

Fig. 17. Landscape argillite with iron and manganese oxides as a decorative agent. Guilin Guangxi, China. Donation by Dmitry I. Belakovskiy. № PDK-8101. Photo by Mikhail M. Moiseev.





Fig. 18. Chevkinite-(Ce). 6 cm long chevkinite crystal. Arondu, Basha valley, Skardu district, Pakistan. Donation by Dmitry I. Belakovskiy. № 93165. Photo by Mikhail M. Moiseev.

Fig. 19. Spinel. Octahedral crystals up to 3.5 cm with ingrowths of green pargasite in marble rock. Sungate Mine, An Phu, Luc Yen, Yenbai Province, Vietnam. Purchase. № 93215. Photo by Mikhail M. Moiseev.

GEOKHI RAS. In 2008 they decided to build on the collection of meteorites, tektites and impactites within the Main collection at the Museum as: (1) meteorite matter is a subject of mineralogical study, and (2) Mineralogical museum receives new arrivals of meteorite objects. This decision was implemented and by the end of 2010 collection of meteorites contained 43 items. Amongst them there are fragments of 27 different meteorites, two types of tektites (Libyan glass and moldavite) and a sample of impactite from meteorite crater Lappajarvi in Finland. The vast majority of these arrivals are donations since 1985 till 2010 from 19 people and one organization; 4 items resulted from exchange.

The iron meteorites cataloged in the collection are: Sikhote-Alin, Seymchan, Gibeon, Canyon Diablo, Nantan, Muonionalusta, Campo del Cielo, Dronino, Morasko. Among the stony-iron meteorites there are Omolon, Seymchan, and among the stony meteorites – Kunya-Urgench, Sayh Al Uhaymir 067, Ozernoe, Gujba, Dar al Gani 400, Dhofar 935, Dhofar 007, Peekskill, Potter, Jiddat Al Harrasis 020 & 055, Gold Basin, Tamdrakht, Holbrook, El Hammani, Gao, Sulagiri (Hosur).

Type & source of acquisitions, acknowledgements

It is nice to note that number of donations among the new arrivals dramatically increased in comparison with the previous period (Belakovskiy, 2003, 2004, 2006; Belakovskiy & Pekova, 2008). At present donations make up almost 77% of all arrivals (644 specimens) including 5% (42 specimens) representing type specimens. Donations were received from 105 people and 2 organizations (Natural history museum of the North-East Interdisciplinary Science Research Institute RAS, Far East branch and National Museum of Scotland, Edinburg, UK). Amongst the donors there are 82 citizens of Russian Federation and 23 – of the USA, Canada,

Argentina, Great Britain, Germany, Czech Republic, Netherlands, Japan and Australia. Quite often donations were made by the group of people.

The donors to the Museum are (by the number of specimens donated): D.I. Belakovskiy (123), I.V. Pekov (114), A. Novitskiy (105), A.B. Nikiforov (86), M.Yu. Anosov (85), V.V. Levitskiy (85), A.V. Kasatkin (22), B.Z. Kantor (18), M.S. Alferova (15), M.M. Moiseev (14), N.V. Chukanov (14), S.G. Epanchintsev (12), I.N. Savin (12), A.P. Khomyakov (11), E.V. Galuskin & I.O. Galuskina (8), V.M. Gazeev (7), J.E. Patterson (6), M. Vishnevetskiy (6), V.N. Kalachev (6), D.V. Lisitsin (5), T. Hanna (4), D. Topa (4), F. Wafi (4), J. Watson (3), S.V. Afanasyev (3), S. Vasil'ev (3), A. E. Zadov (3), G.N. Kaplenkov (3), G.S. Nikolayev (3), N.N. Pertsev (3), L.Z. Reznitskiy (3), D.A. Sadilenko (3), S.J. Mills (2), W. Paar (2), K. Watanabe (2), A.M. Abdrakhimov (2), A.P. Akimov (2), L.B. Bulgak (2), A.G. Bushmakin (2), I.F. Gablina (2), S.V. Gritsyuk (2), A.V. Ivonin (2), K.I. Klopotov (2), O.I. Kotlyar (2), S.V. Petukhov (2), V.V. Ponomarenko (2), S.A. Repina (2), E.M. Spiridonov (2), V.M. Chalisov (2), I.V. Chaplygin (2), F. Baatz, J. Bernard, F. Burger, D. Edwards, J. Heatley, G. King, A. Langeinrich, R. Lavinskiy, P. Megaw, M. Origlieri, J. Ralph, D. Toland, Y.V. Azarova, A.S. Batalin, P.A. Beschetsnov, E.A. Borisova, A.Yu. Bychkov, V.K. Garanin, M.E. Generalov, O.I. Gritsenko, Y.D. Gritsenko, D.V. Davydov, M.D. Dorfman, A.N. Zaitsev, L.M. Ioffe, P.M. Kartashov, D.V. Kachalin, E.V. Kislov, A. S. Klepikov, A. Klyuchkin, V.A. Kovalenker, V.N. Kolesnikov, I.E. Kushnarev, O.A. Lopatkin, N.N. Mitskevich, M.P. Mogileva, V.A. Morozov, N.A. Mokhova, M.N. Murashko, L.V. Olysysh, G.N. Osipov, V.A. Popov, Y.K. Poustov, N.I. Rymaskaya, G.L. Ryabinin, N.V. Savelyev, M.B. Sergeev, E.V. Sokolova, V.I. Stepanov, E. Terekhov, V.A. Tuzlukov, N.I. Frishman, K.I. Chepizhniy, Z.V. Shlyukova.

The Museum is thankful to all who contributed to the collections; we also hope for the future collaboration. **MANY THANKS!!!**

Since 2010 the Fersman Mineralogical museum RAS awards the donors with donation certificates. These certificates were prepared for all whose donations were included in the main collections in 2009–2010 and then presented at the Museum meeting in December 2010. We plan to keep this tradition.

The acquisitions of material collected by the Museum staff include 103 specimens – 12% of the total number of acquisitions. 6 Museum curators were involved in the field collecting: Mikhail M. Moiseev (donated 43 specimens), Dmitriy I. Belakovskiy (40), Maria S. Alferova (23), Svetlana N. Nenasheva (11). Grigoriy L. Ryabinin, Igor V. Pekov, Petko Petrov and Viktor V. Levitskiy also participated in collecting. The Museum is grateful for that.

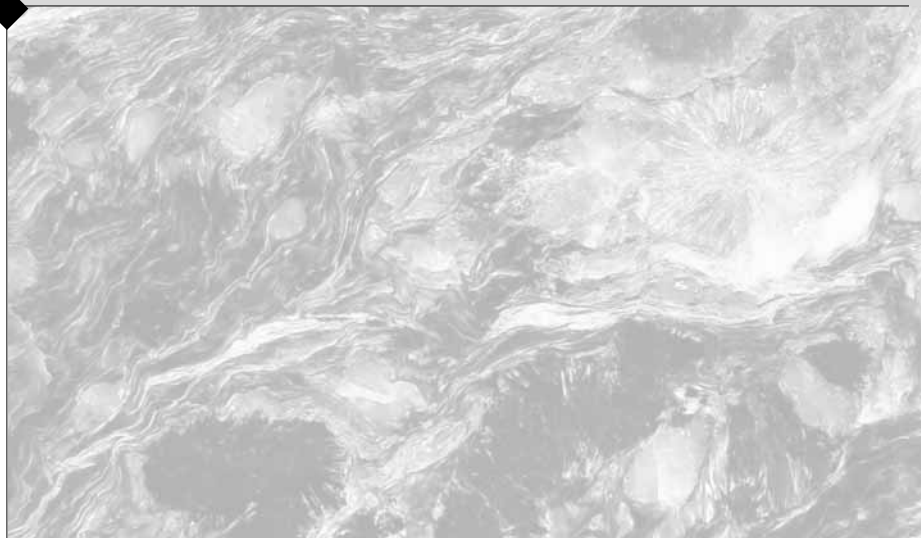
As a result of exchange with Russian and foreign collectors and organizations, the Museum acquired 54 specimens (6.5%). 26 specimens (3%) were purchased, 13 (1.5%) – arrived from a difference source.

Special thanks to Igor V. Pekov, Mikhail M. Moiseev, Alexander A. Evseev, Elena N. Matvienko and Elena L. Sokolova for assistance in compiling this review and important comments.

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Persons



ON 85th ANNIVERSARY OF YURIY L. ORLOV

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In 2011 we have celebrated 85th Anniversary of Yuriy Leonidovich Orlov. He was a talented Russian mineralogist and field researcher, expert in mineralogy of diamond. Being an exceptional expert of precious stones, he was a lead expert of the Ministry of Finance of the USSR. Yuriy L. Orlov contributed a lot in the Museum development. 2 photos and 3 references

Keywords: Yuriy L. Orlov, diamond morphology, Fersman Mineralogical museum.

Yuriy Leonidovich Orlov (1926 – 1980) was a Doctor of Geological and Mineralogical Sciences, the most prominent specialist in mineralogy of diamond and precious stones, the author of 50 published papers, including 3 monograph studies. He was a director of the Fersman Mineralogical Museum of the Academy of Science from 1976 to 1980.

Yuriy L. Orlov was born in a family of a clerk on February 4th, 1926 in Moscow. He spent his childhood in Arbat street (in the center of Moscow) where he entered a public school in 1933. Having talent in music, he was fascinated by playing accordion. He did not give up his passion with years and joined musical school in 1938. His family was evacuated to Ufa during the World Second War in 1941 – 1942. He continued musical education in the Ufa musical college. Orlov was involved to ten-grade musical school at the Moscow Conservatory after he returned to Moscow in February 1943. He graduated from school in 1945 but did not continue his musical carrier taking his father's advice to join the M.I. Kalinin Institute of noneferrous metals and gold (Figure 1). Yuriy L. Orlov graduated from the Institute in June 1950 with the Diploma of mining geologist and was commissioned as a principal geologist to geological party №41 of Vladimirskaya expedition of Union Trust №2 under the Ministry of Geology and Protection of Mineral Reserves. Then he was moved to township of Pashiya in Chusovskoy region of Perm area to work as a head of mineralogical thematic expedition №60 of the same Trust, where he worked till 1955.

Yuriy L. Orlov started his work on research programs in 1953. He collected the unique stone material on mineralogy of diamonds from the Urals, the subject he was very interested in. He was appointed to a chief of the theme geological party №44 of the

Central expedition of Union Trust №2, which carried out research on Siberian diamonds. This allowed Orlov to enlarge his area of interest and initiate comparative study of mineralogy of the two diamondiferous provinces. The new appointment made him move to Leningrad, where he started his research. He drew attention to paragenesis, morphology and inclusions in diamonds. The results of this research were published in a number of papers, which immediately became classified materials because of the topic. Orlov also led research on physical-chemical properties of various morphological types of natural diamond crystals, which was carried out in the Central expedition. The results of the study had a wide practical application.

Yuriy L. Orlov successfully obtained his Candidate thesis on inclusions in diamonds from the Urals and origin of rounded shapes of its crystals at the end of his remote post-graduate studies at M.I. Kalinin Institute of base metals and gold in January 1956. Professor Georgiy P. Barsanov, the director of Fersman Mineralogical Museum, was a scientific supervisor of this study.

Orlov, a talented scientist and experienced mineralogist, was passionate about diamond studies and all his following research was dedicated to the studies of the mineral.

Liquidation of the Union Trust №2 and lack of appropriate housing for his increased family in Leningrad, forced Orlov to move back to Moscow in April 1956. His family grew, the second son, Sergey was born in Orlov's family in June 1955, and the elder son turned 4 years old.

Professor Georgiy P. Barsanov highly valued the abilities, consistency and professionalism of young scientist and hired Orlov to



Fig. 1. Yuriy L. Orlov – 3rd year student of M.I. Kalinin Institute of nonferrous metals and gold. Moscow, 1948.

work at the Fersman Mineralogical museum of the AS as a junior scientist. Orlov continued studying diamonds from the collections of the Ministry of Finance of the USSR (MinFin), the All-Union Trust "Aerogeology" (VAGT) and Ministry of Geology of the USSR. He completed a comprehensive summary on diamonds from various deposits in Ukraine, Western Siberia, the Urals, Yakutia in collaboration with members of a theme geological party of All-Union Geological Institute (VSEGEI, Leningrad) at the time he worked at the museum. All work on diamond research by the order of the Ministry of Finance of the USSR was completely classified at that time. That is why many scientific papers written by Yuriy L. Orlov were not published for wide audience. Orlov was involved in the studies of rare metal pegmatites from Eastern Transbaikalia and Pamir during the first years of his employment at the museum at the suit of the director, professor Georgiy P. Barsanov along with diamond studies. He stressed solving problems of typomorphic properties of minerals from pegmatites and the rare earth variety of vesuvianite, discovered by him.

Yuriy Leonidovich was engaged in a museum work, took part in creation of the-

matic expositions on processes of mineral formation, precious and lapidary stones and synthetic minerals. He actively participated in teaching and popularization of science, educational work, delivering courses to university students and specialists. Orlov made a big effort in replenishing the museum's collections with precious stones and diamonds. Number of specimens increased with growth of the number of localities of their origin (Borisova, Pavlova, 2007). He led a range of research studies of natural stones and syngenetic inclusions in them with electron paramagnetic and nuclear magnetic resonance (EPR and NMR) spectroscopy with the objective to identify the original deposit and genetic type of a stone.

Besides being a well-known diamond specialist and expert in precious and lapidary stones, he also was an excellent teacher and storyteller. He could gain interest of any audience.

Apart from his research activities Yuriy L. Orlov took an active part in compiling a large reference book "Minerals" and wrote 16 articles for the chapters "Silicates" and "Haloids". He also wrote some articles for the new reference book "New Construction Materials" published by *Bolshaya Soviet Encyclopedia* Publisher.

However, studies of diamond, its' paragenesis and morphology were the main interest of Yuriy L. Orlov. He examined and studied enormous number of diamond crystals from all placer deposits of the former Soviet Union, primary deposits of Yakutia, South Africa, Congo, Brazil and other countries. He found dissolving nature of rounded diamond crystal shapes based on numerous studies. Yuriy L. Orlov investigated growth of diamond crystals and aggregates, zoned structure of aggregates, surface features of the facet dissolution as an indicator of diamond origin. He described inclusions in diamonds, correlation of mechanical properties of its crystals and their aggregate structure, morphological features of diamond crystals and more.

Yuriy Leonidovich Orlov worked very passionately and fruitfully. He published more than 50 scientific papers on diamonds in sources opened for public.

His monograph "*Morphology of Diamond*" was published in 1963. Author described pri-

mary diamondiferous rocks, various morphological types of diamond crystals and facet surface relief, compared shapes of growth and dissolution on diamond crystals, discussed his opinion on the origin of the mineral (Orlov, 1963). Yuriy L. Orlov was promoted to become a senior scientist in May of the same year.

Book "*Morphology of Diamond*" was highly valued by specialists and was awarded Alexander E. Fersman award of the Academy of Science of the USSR in 1967.

Scientific research of Yuriy L. Orlov was always connected to the needs of industrial organizations, which needed solutions of the practical problems in exploration for diamonds and their industrial application. Orlov created a scientific foundation for the instruction manual "Technical conditions for industrial classification of diamond crystals" during his work as a scientific consultant at the Central Scientific Research Laboratory of the Ministry of Finance of the USSR. This manual was used as a document to regulate the diamond grading process. He also used to head research of methods of objective identification of natural precious stones and their distinction from synthetic analogues and imitations. During the period of 1967-1968 he was awarded with three author certificates for invention to protect diamonds from corrosion during production of the diamond cutting tools. These inventions had a big positive economic effect in the industry. Yuriy L. Orlov, as a lead specialist in scientific and practical applications of a raw diamond material, actively worked on introduction of synthetic diamonds to the industry.

Yuriy L. Orlov, an experienced geologist, mineralogist and expert in solid-state physics, suggested an integrated approach to geological environment of diamond deposits, their origin and research on unique properties of the mineral. His book "*Diamonds of the Area of Lena River*" was exceptionally thorough among his fundamental works published in 1970s. He described crystal types and polycrystalline aggregates, dissolution and corrosion of crystal surface occurred during their formation and auto-metamorphism of diamond bearing rocks, syn-genetic and epigenetic inclusions in diamonds of different deposits etc.

At the same period, Yuriy L. Orlov worked on the monograph reviewing diamond mineralogy. He arose questions of crystal structure, chemical composition, crystal morphology, real structure defects, paragenesis and origin and types of deposits of the mineral. The book "*Mineralogy of Diamond*" was published as a result of this work in 1973 (Orlov, 1973). Geological and mineralogical community connected to exploration and research of the mineral welcomed it.

Yuriy L. Orlov successfully defended his thesis for degree of Doctor of Geological and Mineralogical Sciences in 1975.

Theoretical research of Orlov was closely related to his practical activity as a most experienced expert and advisor on diamond mineralogy, precious and lapidary stones. He led a large science administrative work as a scientific secretary of the Mineralogical museum since his appointment to this position on January 23, 1962. His educational activities included and were not limited by theme lectures for the staff of *SoyuzYuvelirTorg* (i.e. The State Jewelry Trade Co.) and the Ministry of Finance of the USSR, lectures on diamond mineralogy for the students of Sergo Ordjonikidze Moscow Geological Exploration Institute and work with postgraduate students. Yuriy L. Orlov was a member of Scientific Diamond Council of the State Committee on Science and Engineering at Council of Ministers of the USSR, a member of Council on Problems of Super Hard Synthetic and Natural Materials and Highly Efficient Tools with Them, Interagency Commission on material selection to the Diamond Fund of the USSR and other committees of Academy of Science and the Ministry of Finance of the USSR. He, as a member of Council of the Presidium of Academy of Science, took a regular part in organizing and holding exhibitions out of the country as a director, scientific advisor and leader of lecturer groups. He worked in Poland, Czechoslovakia, Canada, Japan, Germany, Italy, Britain, United States and France.

Research on diamond mineralogy, which was directed by Yuriy L. Orlov, was awarded with the Badge of the Honor Order for its scope, depth and practical industrial application twice in 1971 and 1973.



Fig. 2. Yuriy L. Orlov, 1976.

Yuriy L. Orlov was appointed to the director of the Fersman Mineralogical Museum by the order of Presidium of the Academy of Science in 1976 and held the position till his passing on August 30, 1980.

Yuriy L. Orlov was an outstanding scientist of his time who was able to narrow and solve significant scientific problems and was the one

of the best experts in diamond mineralogy. He proved himself as a scientist raised on the ideas of Vladimir I. Vernadsky and Alexander E. Fersman in his works, which had a great influence on the modern ideas on origin of diamonds. His monographs became classic and are used as reference books by mineralogists and specialists in a wide range of areas.

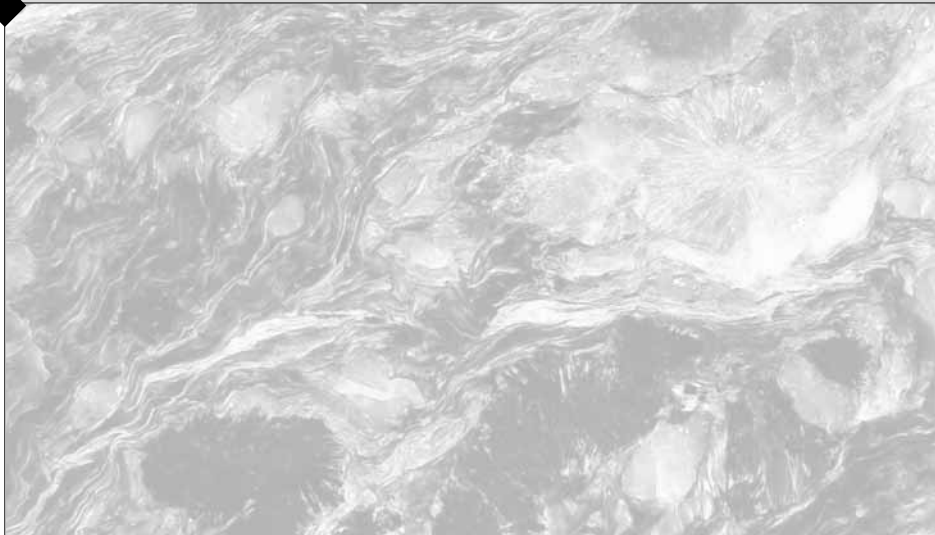
Yuriy Leonidovich Orlov worked at the Fersman Mineralogical Museum for almost 25 years. He is remembered by his colleagues not only as a talented scientist and the unique expert on diamonds and precious stones, but also as a wonderful and kind person. He had a distinct positive attitude to life, openness and big heart. Being a well-educated person, he was glad to speak about fine and applied arts, literature and, of course, had a very good knowledge of music.

Yuriy Leonidovich is remembered and valued by his colleagues and pupils. Mineralogists from the Fersman Mineralogical Museum named a mineral **orlovite** $\text{KLi}_2\text{TiS}_4\text{O}_{11}\text{F}$, recently discovered in moraine of Darai-Pioz glacier in Tajikistan, after him.

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Mineralogical Notes



THE NEW DATA OF THE FORMATION OF CALCITE SKELETAL CRYSTALS IN KARST CAVITIES

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Morphologically rare skeletal crystals of calcite from karst cavities in limestones of the Kaluga region are described. The new data of the morphology and the internal structure of skeletal crystals were obtained using a scanning electron microscope and optical methods. Acicular individuals evolves to "tower" and "bastion" aggregates of skeletal crystals; the formation model of these aggregates is proposed.

The aggregates studied here are of various shades of yellow, and less frequent pink, blue, and green. Any shade changes to dirty-white if colored specimens are stored in low-humidity environment. The relationship between calcite colour and adsorbed water is suggested.

The karst system, where skeletal crystals have been formed is of interest. Daily (5–10°C) and seasonal (30–40°C) temperature variations have been recorded, The observed significant seasonal fluctuations of the system debit are not typical of karst. It is suggested that these features account for by unusual active ventilation of this karst system.

4 figures, 9 references.

Keywords: calcite, "tower" aggregates, "bastion" aggregates, skeletal crystals, Brontsy, Kaluga region, karst, morphology of crystals.

Introduction

Skeletal growth of crystals in the nature is one of the most interesting parts of mineral ontogeny. In spite of more than semicentennial study of its laws (Shafranovsky, Mokievsky 1956), morphological features and growth conditions of skeletal crystals from rather large properties are poor documented until the present time. Previously not studied morphology and structure of skeletal segregations of calcite (Fig. 1) from the karst cavities opened by quarries near villages Kol'tsovo and Brontsy, Kaluga region are reported in this article¹.

General geology of the karst cavities near villages Kol'tsovo and Brontsy, Kaluga region

The karst cavities studied is a dense network of small (0.01–1.0 m in size) elongated jointed cavities penetrating a sequence of strongly fractured not dolomitized light limestone. The karst system ranges from 15 to 30 m in thickness; its observable extent is longer than 10 km. The whole system of the karst cavities is divided conditionally in two parts (upper and lower) separated by thin (about 10 cm) layer of dark brown clay with rare lenses of glauconite. This clay layer, being a waterproof layer in not fractured rocks, is the basis of accumulation zone of karst solutions in the lower horizon of

the upper karst system,. Solutions penetrate the lower karst system through fractures of this layer. Average thickness of each part of this system is about 15 m. The karst cavities are vertically zoned due to action of karst solutions (dissolution and precipitation of dissolved material). Active infiltration of karst-forming solutions without newly formed solid phases is typical of the upper horizons of both parts of the system.

Various newly formed calcite segregations are in the central horizons (up to 6–7 m in thickness) of the upper and lower parts of the karst system: stalactite and stalagmite, "shore ice", and echelons previously reported in the literature of karst mineral formation (Godovikov, 1961; Dorofeyev, 1979; Ikornikova, 1968; Lebedev, Stepanov, 1955; Lebedev, 1964; Moroshkin, 1984; Churakov, 1912).

Along with crystallicites and flowstones, aggregates of skeletal calcite crystals studied here were found in the both parts of the karst system.

Morphology of aggregates of calcite skeletal crystals

Aggregates of calcite skeletal crystals are formed on the roof and walls of differently sloped karst cavities. The size of individuals and aggregates varies depending upon orientation of substrate and skeletal individuals. Individuals growing vertically downwards develop more intensive. Crystallicites and

¹ — It should be noted that the article presented here has already been accepted to the publication in 1990th in journal «New data on minerals». However, owing to the break in publications of this journal, it was not issued. It is nice to own that the article is accepted by the editorial board of journal «New data on minerals», which has renewed its activity.

onyx are formed on horizontal foreparts and bottom of cavities. Skeletal individuals and aggregates are formed directly on limestone, flowstones, and earlier skeletal aggregates (second, third and subsequent generations). The structure of aggregates of calcite skeletal crystals and individuals resemble towers and fortresses; therefore, such segregations are called "tower" and "bastion" according on their shape. Skeletal segregations of the hollow polyhedron type with a gaping cavity (Shafranovsky, 1956) are attributed to the "bastions". The segregations with insignificant size of channels in comparison with the size of the individuals or without these channels are attributed to the "towers".

The aggregates are elongated along axis [0001] of calcite crystals. The cross-section of these aggregates corresponds to that of trigonal prism. "Tower" individuals reach 8 cm in length and 3 cm in diameter, and "bastion" individuals, 10 and 20 cm, respectively.

The examined material was determined as calcite according to electron microprobe and X-ray diffraction study. The X-ray diffraction patterns of its samples are similar to those given for calcite in literature.

The data of structural features and symmetry of the samples studied have been initially obtained with the Laue method. However, strong fracturing of the samples caused by numerous chips on the cleavage planes prevents unambiguous interpretation of the Laue patterns because the slightly extended arrangement of reflections corresponding to the symmetry of mineral accounts for both a displacement along cleavage planes and block structure of crystals.

The study of optical properties in oriented samples and surface features of the individuals and chips of these individuals with scanning electron microscope provides the major conclusions of the structure of skeletal individuals. Optical and scanning electron microscopy provides the distinguishing separate repeated units

of calcite individuals and aggregates of these individuals which are reflected in both internal and external structure (Fig. 2). The unit element of the structure of a skeletal crystal is an acicular subindividual elongated along axis [0001]. The size of this subindividual is 0.01 mm across and 1.0–15.0 mm in length.

Ontogeny

The study of specimens and oriented samples provides tracing of the evolution of acicular individuals. The relation of acicular crystals composing oriented parallel intergrowths is observable in the sections of individuals perpendicular to the axis of symmetry (axis of elongation). Initial acicular crystal (described above as unit element of skeletal crystal) is directly overgrown by the similar crystals. The edge of previous crystal is overgrown by subsequent parallel crystal. Next lateral subindividuals overgrow simultaneously with growth of individual along long axis. It should be noted that this growth cannot be named auto-epitactic, because newly formed and previously formed individuals are growing simultaneously (Figs. 3, 4). Cyclicity and sequence of such overgrowth is supported by separate formed areas of individuals decorated with fine clay particles (Fig. 2). It allows determination of the formation sequence of separate elements of a skeletal crystal. Nonsystematic character of such decoration accounts for heterogeneous distribution and infrequent presence of clay particles in the karst solutions. As a result of growth from a seepage solution, skeletal individuals and aggregates of the hollow polyhedron type (Shafranovskiy, 1956) are formed simultaneously with new unit crystals.

Chemical composition

According to electron microprobe measurement and semi-quantity spectral analysis, the examined calcite is extremely pure (total

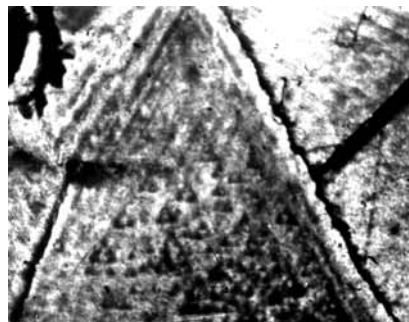
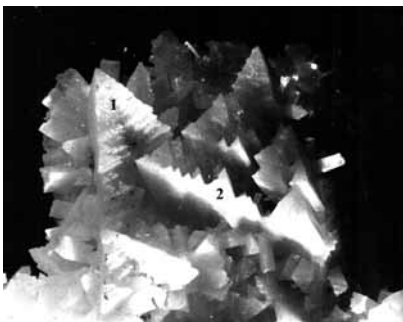


Fig. 1. Aggregate of calcite skeletal crystals (scale 1:1) from cavities of the Ferzikov quarry (Brontsy village, Kaluga region, Russia): (1) "tower" (1) and (2) "bastion".

Fig. 2. Internal structure of the "bastion" calcite. Oriented sample. Magnification $\times 25$.

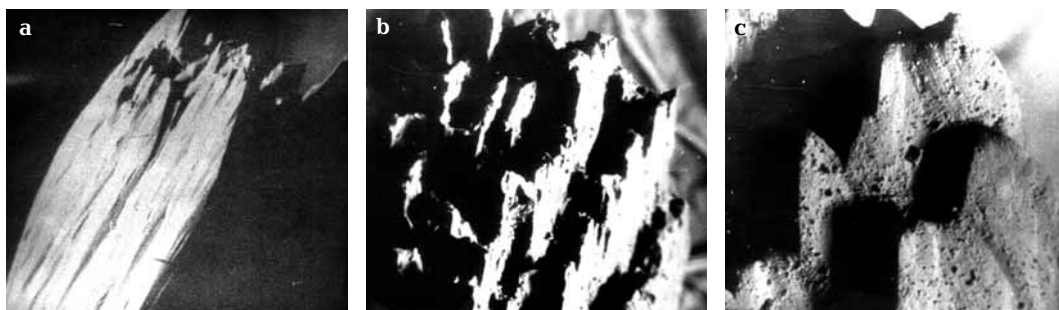


Fig. 3. Scanning electron image of rows of acicular calcite crystals on the growth front of crystal individual: (a) top of the "bastion" crystal, heads of fine acicular individuals are seen (magnification $\times 300$); (b) rows of acicular crystals (magnification $\times 300$); (c) rows of acicular crystals (magnification $\times 1000$).

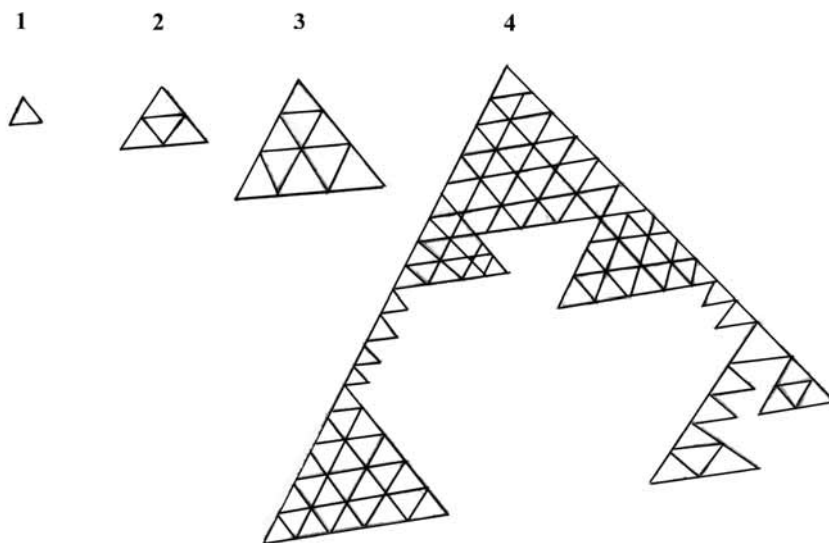


Fig. 4. Sketch of evolution of skeletal crystals from (1) acicular (1) through (2, 3) "tower" to "bastion" habit.

admixture is less than 0.01 wt.%) that is unusual for karst. According to electron paramagnetic resonance spectroscopy, neither centers nor chemical admixtures affecting color are found. However, the reported calcite segregations are characterized by unusual color changing under ambient conditions during a short period (a few hours) to dirty white. Fresh aggregates are of various yellow shades. Aggregates with pink, blue and green shades are occasional.

The samples studied, being stored at stable low humidity, do not change color for a long period (up to 15–20 days). Nevertheless, any sample becomes dirty white after this period.

In the case of long storage (one month and longer) at slowly and gradually decreasing

high humidity, yellow color of the samples was not changing. In similar environment, green shade is seldom retained, whereas pink and blue shades are never retained.

Fast change of color without artificial maintenance of the storage mode (samples are bleached for the first hours) prevents the preparation of the samples for IR-spectroscopic study. The nature of colouring of the described samples is unclear. Dependence of the aggregates color stability on humidity and storage conditions suggests that color is determined in any way by adsorbed water.

Formation conditions of skeletal crystals

Unusualness of the karst system, where the described skeletal crystals are formed is

of special interest. Daily (5–10°C) and seasonal (30–40°C) temperature variations were recorded during observation of many years. Significant seasonal fluctuations of the system debit, which are not typical of karst, were also recorded. In addition, Besides, the described karst system is characterized by an active ventilation that results in the above-mentioned features.

As is known, the crystallization from the seepage solutions is affected by fatal changes in mineral-forming system because of the temperature variations. The described calcite aggregates are formed from seeped solutions that get in the zone of crystallization as drops and aqueous films supplying the growing aggregate.

Churakov (1912) reported the similar mechanism of crystallization for stalactite in the system with constant debit and temperature. As a result of seepageinfiltration, the solution is diluted in the zone of crystallization leading to the formation of helictites and/or hollow stalactites under isothermic conditions. Strong and drastic temperature fluctuations, active ventilation, and changing debit of the systems are resulted in the formation of skeletal crystals.

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BILIBINSKITE, $(\text{Au}_{5-6}\text{Cu}_{3-2})_8(\text{Te,Pb,Sb})_5$, FROM THE CEMENTATION ZONE OF THE AGINSKOE, KAMCHATKA AND PIONERSKOE, SAYAN MOUNTAINS GOLD-TELLURIDE DEPOSITS

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The mineral assemblages and conditions of formation of bilibinskite are reported. The color photos, without which this unique Au-rich mineral is difficult to be determined, are shown for the first time. The photos illustrate extremely strong bireflectance and anisotropy of bilibinskite. The chemical composition of bilibinskite from the cementation zone of the Aginskoe and Ozernovskoe, Kamchatka, and Pionerskoe, Sayan Mountains gold-telluride deposits is refined. The chemical composition of the bilibinskite from the Aginskoe and Ozernovskoe deposits is close to $\text{Au}_5\text{Cu}_3(\text{Te,Pb})_5$, while that of Pionerskoe is close to $\text{Au}_6\text{Cu}_2(\text{Te,Pb,Sb})_5$; generalized formula $(\text{Au}_{5-6}\text{Cu}_{3-2})_8(\text{Te,Pb,Sb})_5$. Bilibinskite in the oxidation zone is the direct prospecting guide to rich endogenic gold-telluride mineralization.

Figures 4, references 16.

Keywords: bilibinskite, gold-telluride mineralization, Aginskoe deposit, Ozernovskoe deposit, Pionerskoe deposit.

Rickardite, $\text{Cu}_7\text{Te}_5\text{B}$ and weissite, Cu_2Te as pseudomorphs after gold tellurides were reported from the oxidation zone of the Kalgoorlie, Australia (Stillwell, 1931; Markham, 1960), Pervomaiskoe, Northern Kazakhstan (Borishanskaya, 1946), Pionerskoe, Sayan Mountains (Gromova, 1959; Sindeeva, 1959), and Aginskoe, Kamchatka (Andrusenko and Shchepot'ev, 1974) hydrothermal gold deposits. In reflected light, rickardite and weissite are characterized by the extremely wide range of colors, strong bireflectance and anisotropy. Therefore, the optical parameters were considered to be adequate for qualitative determination of these minerals. Hypogenic gold tellurides were unlike to be replaced by supergene copper tellurides elsewhere. The study of gold ores for the cementation zone of the Aginskoe, Pervomaiskoe, and Pionerskoe deposits did not support the presence of copper tellurides. It was established that these are Au-dominated intermetallic compounds (Spiridonov *et al.*, 1978; Spiridonov, Chvileva, 1979, 1982; Chvileva *et al.*, 1988; Spiridonov, 1991, 2010). The most abundant mineral among these compounds is bilibinskite named in memory of Yuri Alexandrovich Bilibin (1901-1952), the outstanding Russian geologist, who investigated geology of gold deposits.

In addition to the listed deposits, bilibinskite and related minerals were described from the Ozernovskoe (Kamchatka), Zod (Armenia), Zhana-Tyube, Zholymbet, Solnyshko, and Almaly (Kazakhstan), and Manka (Altai) deposits. In some places of the cementation zone of the Aginskoe and Zod deposits, bilibinskite and related minerals contain up to 10% of gold in the

ores. Bilibinskite occurs as partial or complete pseudomorphs after krennerite $\text{Au}_3(\text{Ag,Au})\text{Te}_8$, sylvanite $\text{Au}(\text{Ag,Au})\text{Te}_4$, kostovite $\text{Au}(\text{Cu,Ag,Au})\text{Te}_4$, calaverite AuTe_2 , altaite PbTe , and nagyagite $\text{AuPb}_5(\text{Te,Sb,Bi})_4\text{S}_6$, and rim hypogenic gold. It is associated with Cu-Pb and Fe-Cu-Pb tellurites. The pockets of bilibinskite are up to a few millimeters in size; radiated aggregated of the mineral are frequent. Megascopally, bilibinskite is dark brown and brown, similar to bornite. This mineral is well polished. The cleavage is absent. Conduction is metallic. The relative relief is higher than gold. $\text{VHN}_{20} = 380$ (330–420) kg/mm^2 ($n = 6$). In reflected light, this mineral is looks like bornite in one sections, whereas in the other sections, it is unique due to color changed from grey-violet to beige-cream and blood red that results in strong color bireflectance (Fig. 1). Extremely strong colored anisotropy ranges from grey and dove-color to canary yellow and fiery-red (Fig. 2). The reflectance spectra are unique, complex, and crossed (Fig. 3). According to optical parameters, the symmetry of bilibinskite is low, not high that orthorhombic.

The chemical composition of bilibinskite (determined with a Camebax electron microprobe) from the Aginskoe, Ozernovskoe, and Pionerskoe deposits is as follows, wt. %: 49.6, 50.8, 58.1 Au; 1.57, 0.99, 2.81 Ag; 9.35; 9.29, 4.53 Cu; 0.21, 0.02, 0.17 Fe; 24.6, 24.0, 23.6 Te; 12.8, 13.9, 6.35 Pb; 0.18, 0, 1.53 Bi; 0.23, 0, 3.53 Sb; and 0.34, 0, 0.13 Se, respectively; total is 98.88, 99.00, and 98.75 ($n = 13, 5, 6$), respectively. The electron microprobe data, high color strength (color purity) (close to native gold and three times more than that of rickardite), and metallic conduction

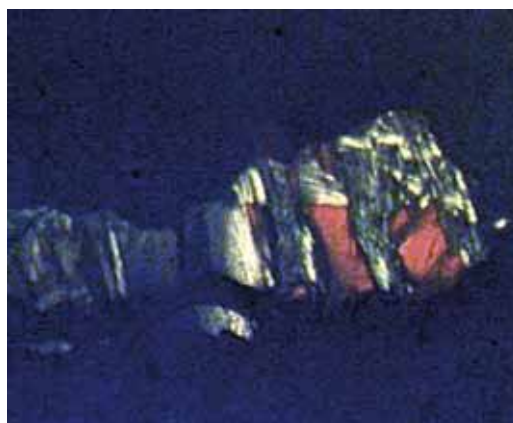


Fig. 1. Photomicrograph of bilibinskite with bright colored birefringence intergrown with Fe-Cu-Pb tellurite. Cementation zone, Aginskoe deposit, Kamchatka. Reflected light. Width of image 120 microns.

Fig. 2. Photomicrograph of bilibinskite with bright color anisotropy. Cementation zone, Aginskoe deposit, Kamchatka. Reflected light, crossed polars. Width of image 80 microns.

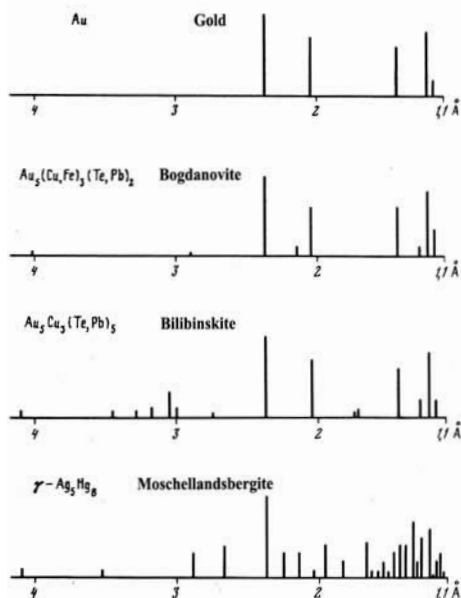
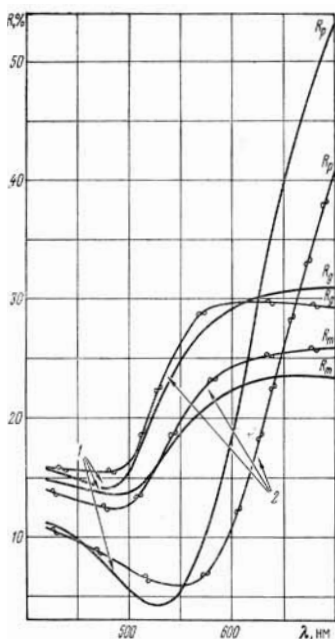


Fig. 3. Reflectance spectra of bilibinskite and Sb-rich bilibinskite in the range of 400 to 700 nm from (1) Aginskoe deposit, Kamchatka, and (2) Pionerskoe deposit, Sayan Mountains, respectively.

Fig. 4. X-ray diffraction powder patterns of gold, bogdanovite, bilibinskite, and moschellandsbergite.

are not consistent with assumption of a significant oxygen in bilibinskite.

Due to small monoblocks (less than 10–15 microns), the X-ray single crystal study and determination of the structure of the mineral were failed. The X-ray diffraction patterns of bilibinskite and related bogdanovite (Fig. 4) are different from that of gold (Berry, Thompson, 1962) in additional reflections. On the basis of this fact, these minerals are suggested to have superstructures produced from face-centered cubic lattice of gold. The dimension of the primitive pseudocubic subcell of bilibinskite is $a'_0 = 4.10 \text{ \AA}$. The X-ray powder diffraction pattern of bilibinskite shows many additional weak and medium reflections in comparison with gold that

permits the similarity to moschellandsbergite Hg_8Ag_5 with the same relation of atoms of different species. The structure of moschellandsbergite is similar to the disordered defect body-centered cubic superlattice of γ -br a ss Zn_8Cu_5 (Pearson, 1972). The X-ray diffraction data, elevated hardness, and insignificant anisotropy of hardness are not consistent with the assumption of the layered structure of the mineral.

According the X-ray diffraction data of bogdanovite, Au, Cu, Fe, and Ag are combined at one structural site Me (core of the face-centered cubic lattice), while Te, Pb, Sb, and Bi occupy another site X (interstitial atoms) (Spiridonov *et al.*, 1991). The chemical composition of bogdanovite corresponds to the formula $\text{Au}_5(\text{Cu,Fe})_3$

(Te,Pb)₂, in other words Me₄X. Therefore, bilibinskite is considered as plumbotelluride – stibio-plumbotelluride of Au and Cu with the composition of Me₈X₅.

The formulae of bilibinskite from the Aginskoe, Ozernovskoe, and Pionerskoe deposits calculated on the basis of 13 atoms are as follows:

(Au_{4.82}Cu_{2.62}Ag_{0.28}Fe_{0.07})_{7.99}(Te_{3.69}Pb_{1.18}Se_{0.06}Sb_{0.04}Bi_{0.02})_{5.01};

(Au_{5.01}Cu_{2.84}Ag_{0.18}Fe_{0.01})_{8.04}(Te_{3.66}Pb_{1.30})_{4.96};

(Au_{5.91}Cu_{1.43}Ag_{0.52}Fe_{0.06})_{7.92}(Te_{3.71}Pb_{0.61}Sb_{0.58}Bi_{0.15}Se_{0.03})_{5.08}, respectively. The composition of bilibinskite from Aginskoe and Ozernovskoe is close to Au₅Cu₃(Te,Pb)₅; from Pionerskoe, to Au₆Cu₂(Te,Pb,Sb)₅; the generalized formula of the mineral is (Au₅₋₆Cu₃₋₂)₈(Te,Pb,Sb)₅.

A mineral, AuTeO₃, with optical parameters similar to bilibinskite occurs in the cementation zone of the Aginskoe and Ozernovskoe deposits, Kamchatka. The minerals similar to bilibinskite but are different in composition and X-ray diffraction pattern occur at the Ashley deposit, Canada (Harris *et al.*, 1983).

In the oxidation zone bilibinskite (Au-Cu plumbotelluride and stibioplumbotelluride) is unstable. It is replaced by the aggregates of fine-lamellar and sponge gold, balyakinite CuTeO₃, plumbotellurite PbTeO₃, Cu-Pb oxytellurites, the cupriferous gold group minerals, and iron hydroxides.

The bilibinskite group minerals in the weathering profile are the direct prospecting guide to rich endogenic gold-telluride mineralization.

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PYRRHOTITE, PENTLANDITE AND HIBBINGITE FROM METAKIMBERLITES OF UDACHNAYA-VOSTOCHNAYA PIPE, NORTHERN YAKUTIA

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Kimberlites of numerous pre-trappean pipes and dikes of East Siberia platform have significant amount of lizardite serpentine, which associates with calcite, dolomite, amakinite or brusite, magnetite, goethite, pyrite, quartz, chalcedony, amethyst, smectites, hydrotalcite group minerals, celestine, stroncianite and some ore minerals. This paragenesis witnesses low grade metamorphism of zeolite facies which altered the rocks at various degree. Processes of regional low grade metamorphism usually occur in conditions of high oxidation potential causing formation of hematite and magnetite in metakimberlites. Patches of fresh rock can be found in Udachnaya-Vostochnaya pipe and in some places there is no goethite or magnetite present in very altered rocks. Pyrrhotite and pentlandite occur in abundance instead. Pyrrhotite and pentlandite of the studied samples are closely associated with Cl-containing lizardite and magnesian hibbingite ($\text{Fe}_{1.55}^{2+}\text{Mg}_{0.42}\text{Mn}_{0.03}^{2+}(\text{OH}_{2.88}\text{Cl}_{0.12})_{3.00}\text{Cl}_{1.00}$). Presence of hibbingite confirms our assumption that kimberlite were altered with fluids rich in chlorine. The source of them was chloride brines derived from evaporates that occur in the carbonate-terrigenous sequence hosting Udachnaya-Vostochnaya pipe.

Pyrrhotite composition has high iron content and is very close to FeS, thus the mineral is not magnetic. We need to note that studied metakimberlites do not contain magnetic minerals. Average pentlandite composition corresponds to the formula $(\text{Ni}_{4.0}\text{Fe}_{4.5}\text{Co}_{0.5})_{9.0}\text{S}_{8.0}$ with Ni/Co ratio close to the one in primary kimberlite and kimberlitic olivine and is in range from 7.7 to 9.9. Apparently, olivine was the source of Fe, Ni and Co, and sulphur derived from an hydrite-bearing carbonate-terrigenous early Paleozoic host rocks, saturated with bitumen, which often contain sulfur compounds.

3 figures, 2 tables, 16 references.

Keywords: metakimberlite, pyrrhotite, pentlandite, Cl-bearing lizardite, magnesian hibbingite, low grade regional metamorphism, Udachnaya-Vostochnaya pipe.

Kimberlite rocks of numerous pipes and dikes of Siberia platform are always in various degree altered. Practically fresh rock can be adjacent to totally altered patches of rock in the same pipe. Such kimberlites contain significant amount of lizardite serpentine in association with calcite, dolomite, amakinite or brusite, magnetite, goethite, pyrite, quartz, chalcedony, amethyst, smectites, hydrotalcite group minerals, celestine, stroncianite and some ore minerals. Our data confirms that this alteration was caused by hydrothermal metamorphic processes due to post-trappean regional metamorphism of zeolite facies conditions (Sokolova, Spiridonov, 2006; 2007; Sokolova *et al.*, 2010).

The main characteristic of low grade regional metamorphism is irregularity of its manifestations. As it was a fluid-dominated process, parts of the rocks with pores of fractures were the most altered. Metamorphic fluids had as a rule high oxidation potential and their composition was governed by mobile components of country rock and kimberlite itself.

Kimberlites of Udachnaya-Vostochnaya pipe and the host anhydrite bearing early Paleozoic carbonate-terrigenous rocks con-

taining evaporate lenses and sparsely saturated with bitumen, which often contain sulfur compounds, both are very irregularly altered with low grade metamorphism. Fresh kimberlites containing such unstable minerals as shortite can be found near to completely altered rocks.

Size of the altered zones range from tens of centimeters to several tens of meters. Primary olivine phenocrysts were altered into pseudomorphs of carbonate, carbonate-serpentine, saponite, talc-carbonate with phlogopite and tetraferriphlogopite platelets that were altered into chlorite, carbonates, vermiculite and corrensite. Cement mass contains sparse ilmenite dissemination, perovskite altered to titanite; individual apatite grains, newly formed ore minerals and so on (Lebedev, 1963; Milashev, 1963; Bobrievich *et al.*, 1964; Franzesson, 1968; Nikishova *et al.*, 1978; Kornilova *et al.*, 1981; Podvysotskiy *et al.*, 1981; Marshintsev *et al.*, 1984; Egorov *et al.*, 1991; Zinchuk, 2000; Sokolova, Spiridonov, 2006; Sokolova *et al.*, 2010). Sulfide minerals form scarce fine dissemination in the volume of altered kimberlite and fill fractures and bunnies in association with carbonates. Iron sulfides dominate: pyrite, pyrrhotite, marcasite, greigite. Some researchers report pyrite concentrations to go up to

Table 1. Chemical composition of perovskite (1), ilmenite (2), pyroilmenite (3) and titanomagnetite (4) from metakimberlites of Udachnaya-Vostochnaya pipe

Component (wt.%)	1	2	3	4
CaO	36.02	–	–	–
MgO	–	–	13.19	10.83
FeO	3.10	44.19	24.35	46.19
MnO	–	2.97	3.38	0.79
Cr ₂ O ₃	–	–	–	25.73
TiO ₂	53.12	50.99	55.87	10.20
Al ₂ O ₃	–	–	–	3.19
Nb ₂ O ₃	4.79	0.86	–	–
Total	97.03	99.01	96.79	96.93
Atomic formular coefficients based on total cations				
Ca	0.93	–	–	–
Mg	–	–	0.46	0.55
Fe ²⁺	0.06	0.94	0.47	0.43
Mn	–	0.06	0.07	0.02
Fe ³⁺	–	0.01	0.01	0.91
Cr	–	–	–	0.70
Ti	0.96	0.98	0.99	0.26
Al	–	–	–	0.13
Nb	0.05	0.01	–	–
Total	2	2	2	3

Note: Analyses were done in the laboratory of Fersman Mineralogical museum of the RAS with electron microprobe JEOL JCSA-50A. Analytical conditions: acceleration voltage 20 kV, energy dispersive spectrometer, probe current 20 nA. Standards: ilmenite USNM 96189 (Fe, Ti, Mn), metallic Nb, omphacite USNM 110607 (Ca, Mg, Al), chromite USNM 117075 (Cr). Images were taken with CamScan-4D electron microscope. Analyst A.A. Agakhanov.

1 – 2% in some parts of altered pipes and dikes. Galena, sphalerite, chalcopyrite, pentlandite, millerite, makinavite, tochilinite and other sulfides occur in much smaller amounts. Brief descriptions and single analyses of these minerals are published in some works dedicated to minerals of altered kimberlites (Ilupin, 1962; Ilupin *et al.*, 1990; Zinchuk, 2000), but their origin was not discussed.

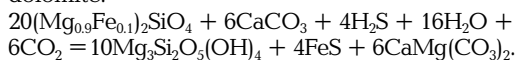
We studied drill coresamples from 430 m level, which were taken from the contact of Udachnaya-Vostochnaya kimberlite pipe with host dolomite-bearing rocks. Kimberlite was obviously altered but many small relict pieces of the primary rock can be found in it. Fine grained quenching zone 0.1 – 0.7 mm thick was found along the contact. Phlogopite platelets and long olivine phenocrysts were elongated

parallel to the contact in a narrow zone. Olivine was completely altered in the samples studied. Knitted and platy pseudomorphs of lizardite with thin inclusions of dolomite and calcite formed in place of olivine. Fringy saponite aggregate formed around the pseudomorphs (Sokolova *et al.*, 2010). The main mass of the rock is formed by metamorphic calcite, saponite, phlogopite platelets that partially were substituted with corrensite and individual grains of apatite and relicts of Nb-containing perovskite ($(Ca_{0.93}Fe_{0.06}^{2+}Nb_{0.01}^{2+})_{1.00}(Ti_{0.96}Nb_{0.04})_{1.00}O_{3.00}$ and Nb-containing ilmenite ($(Fe_{0.94}^{2+}Mn_{0.06})_{1.00}(Ti_{0.98}Fe^{3+}_{0.01}Nb_{0.01})_{1.00}O_{3.00}$, pyroilmenite ($(Mg_{0.46}Fe_{0.47}^{2+}Mn_{0.07})_{1.00}(Ti_{0.99}Fe_{0.01}^{3+})_{1.00}O_{3.00}$ (table 1), newly formed pyrrhotite and pentlandite.

Pyrrhotite rarely forms dissemination in the cementing mass of the metakimberlite (fig. 1). Its composition shown in the table 2 was averaged from analyses of 10 grains. The mineral is quite pure and corresponds to the formula $Fe_{0.982}S_{1.000}$ ($AO Fe_{0.984}S_{1.000}$). High iron pyrrhotite associated with makinavite was discovered in Udachnaya-Zapadnaya pipe (Ilupin *et al.*, 1990).

Pyrrhotite with high iron content is practically unmagnetic. Its composition reflects that activity of sulphur, which binds with iron first, was not high in the fluid. Pyrrhotite was found intergrown with primary high chromium magnesian titanomagnetite of the composition $(Mg_{0.55}Fe_{0.43}^{2+}Mn_{0.02})_{1.00}(Cr_{0.70}Al_{0.13}Fe_{0.91}^{3+}Ti_{0.26})_{2.00}O_{4.00}$ (table 1) with iron content $f = 56.3$. These minerals are in place of olivine phenocrysts totally altered into lizardite-dolomite aggregate.

Pyrrhotite formation could follow the reaction, which involved magmatic calcite. The products of the reaction were pyrrhotite, lizardite and dolomite:



Pentlandite was found much less quantity in the studies metakimberlites as crystals in cementing mass (figure 2). Composition of pentlandite was measured in 6 grains (table 2). The variation of it was not significant and content of admixtures was below the methods' detection limit. The average pentlandite composition corresponds to the formula $(Ni_{4.0}Fe_{4.5}Co_{0.5})_{9.0}S_{8.0}$, Ni/Co ratio was constantly in the range from 7.7 to 9.9, which is close to the elements' ratio in the primary rock and in olivine from kimberlites (Barmina, Frenkel, 1981). Primary olivine is deemed to be the source of Fe, Ni and Co in pentlandite. These elements were not carried out as they were not mobile and were deposited in situ in newly formed minerals. Anhydrite-bearing early Paleozoic carbonate-terrigeneous host

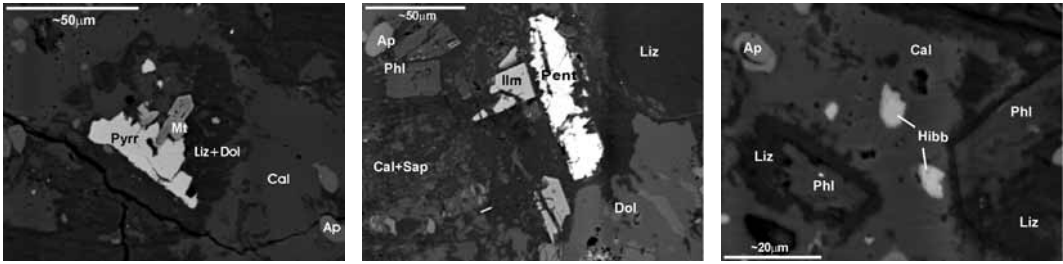


Figure 1. Metamorphic pyrrhotite (Pyrr) in intergrowth with high chromium magnesium titanomagnetite (Mt) in completely altered olivine phenocryst, replaced by lizardite-dolomite aggregate (Liz+Dol) surrounded by calcite (Cal) with individual apatite grains (Ap). Backscattered electron (BSE) image.

Figure 2. Crystal of metamorphic pentlandite (Pent) with calcite (Cal), phlogopite (Phl), ilmenite (Ilm), apatite (Ap) in carbonate-lizardite (Dol, Liz) and calcite-saponite (Cal+Sap) aggregate. Backscattered electron (BSE) image.

Figure 3. Magnesium hibbingite (Hibb) in calcite (Cal) with phlogopite (Phl), lizardite (Liz), apatite (Ap). Backscattered electron (BSE) image.

Table 2. Chemical composition of pyrrhotite (1-10) and pentlandite (11-16) from metakimberlite of Udachnaya-Vostochnaya pipe

Components (wt.%)	Fe	Ni	Co	S	Total	Formula	Ni/Co
1	62.16	—	—	36.29	98.45	Fe _{0.963} S _{1.000}	—
2	62.69	—	—	36.79	99.48	Fe _{0.960} S _{1.000}	—
3	62.53	—	—	36.48	99.01	Fe _{0.984} S _{1.000}	—
4	62.33	—	—	36.38	98.71	Fe _{0.963} S _{1.000}	—
5	61.78	—	—	36.11	97.89	Fe _{0.962} S _{1.000}	—
6	62.56	—	—	36.60	99.16	Fe _{0.961} S _{1.000}	—
7	61.71	0.01	—	35.98	97.70	Fe _{0.965} S _{1.000}	—
8	62.12	—	—	36.33	98.45	Fe _{0.961} S _{1.000}	—
9	61.77	—	—	36.10	97.87	Fe _{0.962} S _{1.000}	—
10	62.09	0.01	—	36.28	98.38	Fe _{0.962} S _{1.000}	—
11	32.98	31.07	3.18	34.13	101.36	(Ni _{4.02} Fe _{4.49} Co _{0.41}) _{8.92} S _{8.08}	9.8
12	32.80	30.93	3.20	34.10	101.03	(Ni _{4.01} Fe _{4.46} Co _{0.41}) _{8.90} S _{8.10}	9.8
13	32.55	30.38	3.96	33.16	100.05	(Ni _{4.00} Fe _{4.50} Co _{0.52}) _{9.02} S _{7.98}	7.7
14	32.48	30.35	3.87	33.89	100.59	(Ni _{3.96} Fe _{4.45} Co _{0.50}) _{8.91} S _{8.09}	7.9
15	31.92	31.56	3.43	33.50	100.41	(Ni _{4.13} Fe _{4.39} Co _{0.45}) _{8.97} S _{8.03}	9.2
16	32.78	30.21	3.11	34.02	100.12	(Ni _{3.95} Fe _{4.51} Co _{0.40}) _{8.86} S _{8.14}	9.9

Note: Pyrrhotite formulas were calculated for S=1; pentlandite formula were calculated for total of 17 atoms. Analyses were performed in the laboratory of A.Ye. Fersman Mineralogical museum of the RAS with electron microprobe JEOL JCA-50A. Analytical conditions are the same as for analyses in the table 1. Standards used: ilmenite USNM 96189 (Fe), metallic Co, NiO (Ni), barite (S). Images were taken with CamScan-4D electron microscope. Analyst A.A. Agakhanov.

rocks could be the source of sulphur. They were saturated with bitumen, which often contain sulfur compounds.

Pentlandite-millerite pair can be used as a mineral geothermometer. Lack of millerite in the studied sample indicates temperatures higher than 250°C corresponding to high temperature part of the zeolite facies.

We suppose, that pyrrhotite and pentlandite were deposited from metamorphic fluids with moderate activity of S₂. Lack of magnetite, a typ-

ical mineral of altered kimberlites, in the studied rock showed low O₂ activity during its alteration. Sulphur concentration in the fluids was low, otherwise pyrite would be formed. It's important to keep in mind possible lack of magnetic minerals in kimberlite during magnetometric prospecting.

We found elevated chlorine content up to 1.9% was a characteristic feature of lizardite in the metakimberlite (Sokolova *et al.*, 2010). Another chlorine-bearing mineral phase was

found during the study: fine grained less than 10 μm formation of magnesium hibbingite composition. Microprobe analysis of it was (in at.%): Fe 30.27, Mg 8.17, Mn 0.62, Cl 21.87, which coincide with formula $(\text{Fe}_{1.55}^{2+} \text{Mg}_{0.42} \text{Mn}_{0.03}^{2+})_{2.00} (\text{OH}_{2.88} \text{Cl}_{0.12})_{3.00} \text{Cl}_{1.00}$. Presence of the mineral confirms our suggestion that the kimberlite was altered in conditions of low grade regional metamorphism with involvement of high chlorine fluids, which derived from chloride brines. The source of the brines was evaporate lenses in the carbonate-terigenous formation hosting Udachnaya-Vostochnaya kimberlitic pipe.

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