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New Data on Minerals. 2013. Volume 48. 162 pages, 128 photos, drawings and schemes.
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This volume contains description of laptevite-(Ce), a new vicanite group mineral found in the Darai-Pioz alkaline massif, rare minerals of the baratovite-katayamalite solid solution from the Khodzha-Achkan alkaline massif in Kirgizia, listvenite-like phlogopite-magnesite gumbeites of the Berezovsky gold deposit in the Urals, polycrystalline diamond aggregates from the Lomonosov deposit in the Arkhangelsk diamond province, and gypsum segregations from the bottom of the Okhotsk and Japan Seas. The results of fine investigation of trace elements in the crystal structure of molybdenite and experimental modeling of Pt and Pd sulfide crystallization during cooling in the central part of the Cu-Fe-S system are given.

Separate section is devoted to *150th anniversary of the birth of V.I. Vernadsky*. It contains papers about geochemical mineralogy of V.I. Vernadsky, his activity in nuclear power, and mineralogical taxonomies suggested by V.I. Vernadsky, J.D. Dana, A.G. Betekhtin, I.N. Kostov, G.P. Barsanov, and A.A. Godovikov.

In the section *Mineralogical Museums and Collections*, the first information on products of Chinese stone-cut art in the collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, brief historical review of the collection of diamond crystals of the same museum, and detail information on the new acquisitions in the museum in 2011–2012 are given.

Mineralogical Notes are represented by brief paper about findings of giant minerals in the South Urals.

This journal is of interest for mineralogists, geochemists, geologists, staff of natural history museums, collectors, and amateurs of stones.

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Mineralogical Museums and Collections

Mineralogical Notes

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

LAPTEVITE-(Ce) $NaFe^{2+}(REE_7Ca_5Y_3)(SiO_4)_4(Si_3B_2PO_{18})(BO_3)F_{11}$ – NEW MINERAL[1] OF THE VICANITE GROUP FROM THE DARAI-PIOZ ALKALINE MASSIF, TAJIKISTAN

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Laptevite-(Ce) is a new mineral of the vicanite group. It was found in a calcite-bafertisite-aegirine-microcline rock in association with stillwellite-(Ce), calcibeborosilite-(Y), fluorite, polylithionite and other minerals at the Darai-Pioz glacier moraine (Tajikistan). Color is dark-brown, in thin plates is transparent. Vitreous luster. It occurs as poorly formed crystals up to 1 cm in size. Mohs' hardness 4.5–5. $D_{meas.} = 4.61(2)$ g/cm^3, $D_{calc.} = 4.619$ g/cm^3. Optically uniaxial negative, $n_o = 1.741(3)$, $n_e = 1.720(3)$. It is partially metamict. Crystal structure has been refined with R = 3.61%. Hexagonal symmetry, space group $R3m$, $a = 10.804(2)$Å; $b = 10.804(2)$Å; $c = 27.726(6)$Å; $V = 2802.7(2)$Å^3, Z = 3. Most intense X-ray powder data lines are as follows [*d*, (I), (*hkl*)]: 7.70 (19) (012); 4.41 (29) (202); 3.13 (26) (214); 3.03 (100) (027); 2.982 (85) (125); 2.954 (60) (033); 2.689 (40) (-240); 1.979 (31) (330); 1.770 (21) (-555). IR spectrum (strongest absorption bands, cm^{-1}) 1623, 1437, 1300, 945, 930, 877, 758, 637, 570, 531. Chemical composition (microprobe analysis, wt.%): SiO_2 – 15.67, TiO_2 – 0.28, ZrO_2 – 0.01, ThO_2 – 0.38, UO_2 – 0.65, FeO – 1.48, CaO – 11.64, MnO – 1.02, SrO – 0.95, Y_2O_3 – 11.30, La_2O_3 – 14.51, Ce_2O_3 – 16.93, Pr_2O_3 – 2.76, Nd_2O_3 – 5.16, Sm_2O_3 – 0.98, Eu_2O_3 – 0.10, Gd_2O_3 – 1.56, Tb_2O_3 – 0.29, Dy_2O_3 – 1.37, Tm_2O_3 – 0.17, Yb_2O_3, – 0.28, B_2O_3 – 4.98, P_2O_5 – 1.51, Na_2O – 1.05, F – 8.53, $-O=F_2$ – 3.59, total – 100.46. The simplified formula is $NaFe^{2+}(REE_7Ca_5Y_3)(SiO_4)_4(Si_3B_2PO_{18})(BO_3)F_{11}$. The mineral is named in honor of Tatyana Mikhaylovna Lapteva (1928–2011), the Soviet geologist, petrographer, who made a major contribution to geological study of Central Asia.
3 table, 4 figures, 13 references.

Keywords: laptevite-(Ce), vicanite group, Darai-Pioz alkaline massif.

Laptevite-(Ce) was found in a fenitized rock 1 × 0.8 × 0.4 meter in size, from the Upper Darai-Pioz alkaline massif, which occurs in moraine deposits of the same name glacier (Tajikistan). The Darai-Pioz massif has an isomeric form; it is located on a joint of the Zeravshansky, Alaisky and Turkestansky ridges in the upper part of the Darai-Pioz river. A considerable part of the massif is overlain by a glacier, and primary rock exposures on the massif are hardly accessible. In this regard, mineralogy and petrography of the Upper Darai-Pioz alkaline massif are done on material from moraine deposits. Many publications are devoted to geology and mineralogy of this alkaline massif (Moskvin, 1937; Dusmatov *et al.*, 1963; Dusmatov, 1968; 1971; Semenov *et al.*, 1963; Belakowski, 1991; etc.). The mineralogy of the Upper Darai-Pioz alkaline massif, as well as the majority of alkaline massifs, is extremely variable and unique in many respects. As a rule, almost all alkaline massifs have characteristic geochemically distinct features. One feature of the Upper Darai-Pioz alkaline massif is the large variety of B and *REE* minerals: stillwellite-(Ce), tadzhikite-(Ce), tadzhikite-(Y), kapitsaite-(Y), calcibeborosilite-(Y), byzantievite. Almost all these minerals, except stillwellite-(Ce), were

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[1] – It is considered and recommended for publication by the Commission on New Minerals and Names of Minerals of RMO and approved by the Commission on New Minerals, the Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA) on December 2, 2011.

discovered and described from rocks of this massif.

The leucocratic rock in which laptevite-(Ce) was found, consists of calcite, bafertisite, aegirine and microcline, has uneven granular texture, from fine- to coarse-grained, often with a spotty texture. This texture is caused by the uneven distribution of accu-mulations of microcline, aegirine, calcite, bafertisite, quartz, calcibeborosilite-(Y), stillwellite-(Ce) and laptevite-(Ce). Microcline consists of coarse idiomorphic grains 1 – 6 cm in size; the color is grayish to yellow-white. Aegirine forms prismatic, often deformed, black crystals up to 3 cm long. Quartz forms icy, translucent, light gray, coarse-grained agregates, 2 – 3 cm in size. One characteristic feature of this association is the presence of relatively large plates of brown-red bafertisite; tetragonal, poorly formed calcibeborosilite-(Y) crystals to 2 cm of a dark gray color and aquant grains of light pink stillwellite-(Ce), to 3 cm, without visible faces. Minor minerals are fluorite, polylithionite and albite. Most often, laptevite-(Ce) grows together with bafertisite, calcibeborosilite-(Y) and stillwellite-(Ce).

Physical properties

Laptevite-(Ce) occurs as poorly formed crystals to 1 cm (Fig. 1), commonly with metamict cores. It is brown, with yellowy-brown cores. In thin splinters, it is transparent. The luster is vitreous, often greasy, fracture is uneven, cleavage is absent. The Mohs hardness is 4 – 4.5. Microhardness VHN = 453 (ave. on 15 measurements, the range is VHN = 443 to 485); measurements were made at the PMT-3, calibrated on NaCl at loading of 50 g. The measured density is 4.61(2) g/cm^3, it was determined by equilibration in aqueous solution of Clerici liquid. The calculated density is 4.619 g/cm^3. Refractive indices of laptevite-(Ce) measured by the immersion method (at 589 nm) are as follows: $n_o = 1.741(3)$, $n_e = 1.720(3)$, mineral is optically negative, uniaxial. Laptevite-(Ce) is water-insoluble, dissolves poorly in HCl (1:1) at room temperature. The infrared spectrum was measured on an Avatar IR-Fourier spectrometer of Thermo Nicolet with a KBr microtablet (Fig. 2). The strongest absorption bands of laptevite-(Ce) are as follows (cm^{-1}): 1623, 1437, 1300, 945, 930, 877sh, 758, 637, 570, 531.

Chemical composition

The chemical composition of laptevite-(Ce) was determined in two laboratories: at Fersman Mineralogical Museum RAS, Moscow and at the Geological Sciences Department, University of Manitoba, Winnipeg, Canada, by EMPA with both wave dispersive and energy dispersive spectrometers (WDS and EDS). Eight grains of a laptevite-(Ce) were studied and 42 analyses were determined for them. In A.E. Fersman Mineralogical Museum analyses were obtained with a JCXA-733 of JEOL electron microprobe using (Si-Li) EDS and INCA analysis system at 20 kV accelerating voltage, 2 nA probe current and 1 µm probe diameter. The following standards were used: microcline USNM143966 (Si), anorthite USNM 137041 (Ca), ilmenite USMN 96189 (Ti, Fe), Mn (Mn), $SrTiO_3$ (Sr), YPO_4 (Y), $LaPO_4$ (La, P), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $SmPO_4$ (Sm), $EuPO_4$ (Eu), $GdPO_4$ (Gd), $TbPO_4$ (Tb), $DyPO_4$ (Dy), $TmPO_4$ (Tm), $YbPO_4$ (Yb), omphacite USNM 110607 (Na), MgF_2 (F). At the University of Manitoba, analyses were done using a Cameca SX-100 electron microprobe, equipped with WDS at 15 kV accelerating voltage, 20 nA probe current and 5 µm probe diameter. The following standards

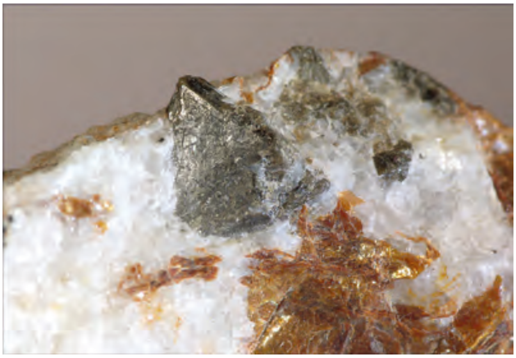

Fig. 1. A brown crystal of laptevite-(Ce) with bafertisite in calcite with microcline. Slanting light. Width of a view field is 5 cm.

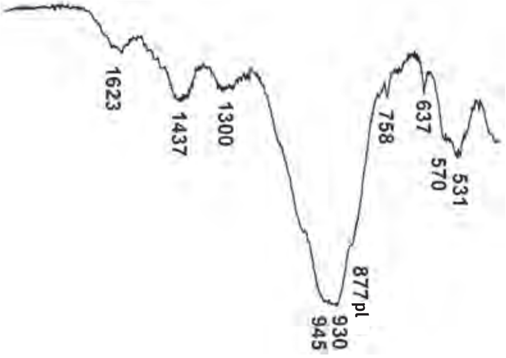

Fig. 2. IR spectrum of a laptevite-(Ce), obtained at the Avatar IR-Fourier spectrometer of Thermo Nicolet from a tablet with KBr.

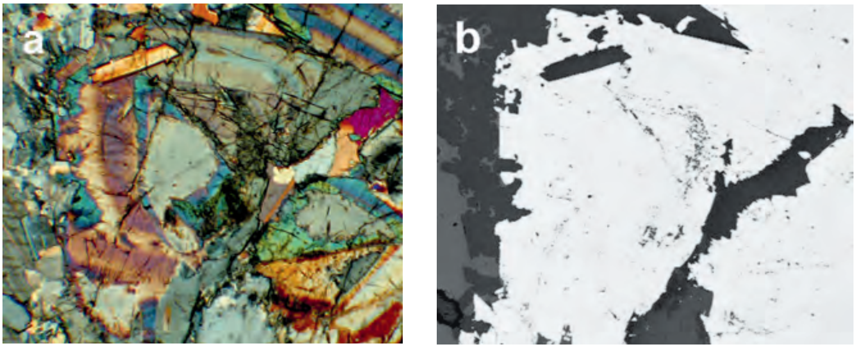

Fig. 3. Accretion of zoned laptevite-(Ce) crystals with albite and calcite:
a — the transparent polished section in transmitted light (nicols are crossed);
b — the same fragment in the back-scattered electrons contrast mode on average atomic number (BSE). Width of a vision field is 2.6 mm.

Table 1. **Chemical composition of laptevite-(Ce) (wt.%)**

Component	1		2
	Average	Range	
SiO_2	15.67	14.54 – 15.98	15.58
TiO_2	0.28	0.18 – 0.53	0.30
ZrO_2	0.01	0.00 – 0.05	0.10
ThO_2	0.38	0.17 – 0.56	0.43
UO_2	0.65	0.44 – 0.71	0.70
FeO	1.48	1.31 – 1.66	1.59
CaO	11.64	11.12 – 12.01	11.83
MnO	1.02	0.82 – 1.07	0.84
SrO	0.95	0.81 – 1.60	1.46
Y_2O_3	11.30	11.07 – 11.73	11.21
La_2O_3	14.51	13.20 – 15.01	13.86
Ce_2O_3	16.93	16.20 – 17.92	17.58
Pr_2O_3	2.76	2.43 – 3.97	2.90
Nd_2O_3	5.16	4.37 – 5.58	5.10
Sm_2O_3	0.98	0.77 – 1.26	1.03
Eu_3O_3	0.10	0.04 – 0.34	0.16
Gd_2O_3	1.56	1.19 – 1.69	1.40
Tb_2O_3	0.29	0.16 – 0.25	0.21
Dy_2O_3	1.37	1.24 – 1.67	1.47
Tm_2O_3	0.17	0.09 – 0.26	0.13
Yb_2O_3	0.28	0.20 – 0.39	0.35
B_2O_3	4.98	3.79 – 5.40	4.71
P_2O_5	1.51	1.35 – 1.58	1.47
Na_2O	1.05	0.86 – 1.26	0.98
F	8.53	8.05 – 9.47	8.44
Total	103.56		103.83
$-O=F_2$	−3.59		−3.55
Total	99.97		100.28

Note. 1 — the average and variation limits of 42 microprobe analyses for 8 grains are executed by means of JCXA-733 equipped with INCA EDS (U = 20 kV, I = 2 nA, probe diameter at 1 μm), 10 analyses has performed with Cameca SX-100 equipped with WD (U = 15 kV, I = 20 nA, 5 μm probe diameter), B_2O_3 determined by the ICP OES method (3 analyses); analysts A.A. Agakhanov, L.A. Pautov, Panseok Yang.
2 — the analysis of grain, on which crystal structure of a mineral was solved (from the same sample); performed with Cameca SX-100 equipped with WD (U = 15 kV, I = 20 on, probe diameter at 5 μm), (Uvarova et al., 2013).

were used: titanite (Ti), zircon (Zr), ThO_2 (Th), UO_2 (U), pyrope (Fe), spessartine (Mn), strontianite (Sr), YPO_4 (Y), $LaPO_4$ (La, P), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $SmPO_4$ (Sm), $EuPO_4$ (Eu), $GdPO_4$ (Gd), $TbPO_4$ (Tb), $DyPO_4$ (Dy), $TmPO_4$ (Tm), $YbPO_4$ (Yb), datolite (B), jadeite (Na), fluorite (F), diopside (Si, Ca).

For the determination of Li, Be, B and *REE*, three analyses by ICP-OES were made. In order to do this, a grain of laptevite-(Ce), previously checked by EDS, was digested in polypropylene bottles in 40% HF with addition of HNO_3 and were evaporated to wet salts. After which, HNO_3 was repeatedly added to sample and evaporated to a solid residue for full removal of all fluorides. Further, the residue was dissolved in HNO_3, and then diluted to 2% HNO_3. The resultind solution was analyzed with a VISTA Pro instrument of Varian. Concentrations of Be and Li, measured by the ICP-OES method in the new mineral does not exceed trace amounts. The data for B and *REE* by ICP-OES method are correlate well with those, obtained by EPMA.

Crystals of laptevite-(Ce) are often cracked and include intergrowths of other phases (Figs. 3, 4). They also show zonality, generally connected with isomorphous substitutions of La, Ce and Y (Fig. 4).

The average composition from electron microprobe and ICP-OES methods (Table 1, an. 1) was recalculated (on a base of total anions (O + F) = 48 apfu), giving the empirical formula $(Na_{0.88}\mathit{REE}_{0.12})_{\Sigma 1.00}(Fe_{0.54}Mn_{0.37}Ti_{0.09})_{\Sigma 1.00}(\mathit{REE}_{6.79}Ca_{5.40}Y_{2.60}Sr_{0.24}U_{0.06}Th_{0.04})_{\Sigma 15.13}(SiO_4)_4(Si_{2.78}B_{2.68}P_{0.55}O_{17.33}F_{0.67}(B_{1.05}O_3)F_{11}$, at this $\mathit{REE} = Ce_{2.68}La_{2.32}Nd_{0.80}Pr_{0.44}Gd_{0.22}Dy_{0.19}Sm_{0.15}Yb_{0.04}Tb_{0.04}Tm_{0.02}Eu_{0.01}$.

The simplified formula of laptevite-(Ce) is $NaFe^{2+}(\mathit{REE}_7Ca_5Y_3)(SiO_4)_4(Si_3B_2PO_{18})(BO_3)F_{11}$. The analysis of a grain fragment, from which crystal structure of a mineral was studied, is also given in table 1 (an. 2). The compatibility in-

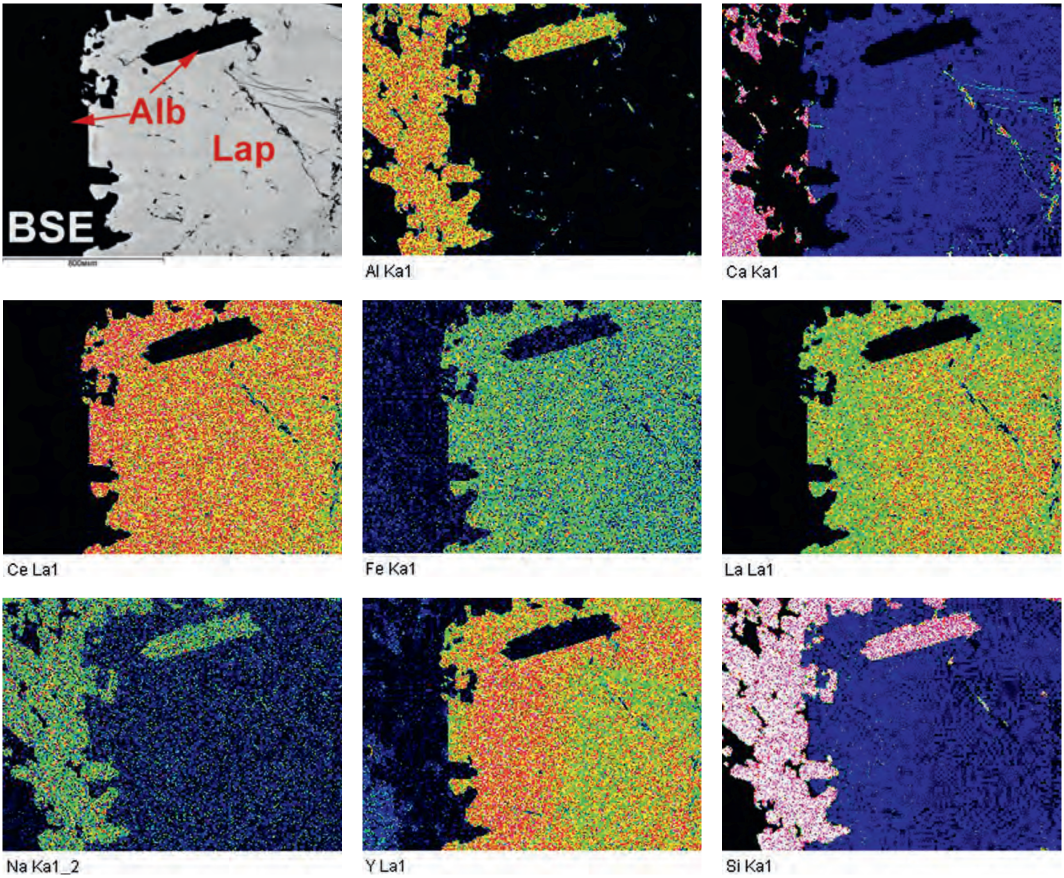

Fig. 4. A fragment of laptevite-(Ce) crystal (Lap); intergrowth with albite (Alb). BSE image mode and X-ray maps of distribution of the specified elements.

dex $(1 - K_p/K_c) = 0.004$, that corresponds to its highest degree (superior).

X-ray data

At the initial stage of this investigation, X-ray powder data of this phase were measured. After this, grains for single crystal work were selected, but they appeared metamict. Further fractions of the mineral were extracted from five samples and attempts to measure X-ray powder data were made, but those fractions also were metamict. This problem was solved by heating the mineral. The fragments of crystals, selected for tempering contained yellow-brown, more transparent cores and dark cracked rims. The compositions of both zones in the extracted crystal fragments were checked using EDS. Tempering was done in a tubular furnace at 800°C in a stream of argon. The central parts of the laptevite-(Ce) crystals turned into a white porcellanous X-ray-amorphous substance, and the external rim of the crystals remained without visible changes and gave X-ray powder data identical to those obtained at the beginning of the investigation for non-heated material. All further measurements were obtained on the heated material.

X-ray powder data of a laptevite-(Ce) (Table 2) were recorded on the DRON-2 instrument with a graphite monochromator (Cu$K\alpha$ radiation). Quartz was used as the internal standard. The powder data are well indexed in hexagonal cell, space group $R3m$: $a = 10.779(2)$, $c = 27.864(4)$Å, $V = 2803.6(3)$Å^3, $Z = 3$. Unit cell parameters and powder data of laptevite-(Ce) are very close to those of the vicanite group minerals (Table 3). The structure of laptevite-(Ce) was refined on 924 independent reflections to an R-factor = 3.87%. A mineral hexagonal, space group $R3m$, $Z = 3$. Cell dimensions are as follows: $a = 10.804(2)$, $c = 27.726(6)$Å, $V = 2802.6(2)$Å^3 (Bruker P4

Table 2. **X-ray powder diffraction data for laptevite-(Ce)**

observed		calculated		*hkl*
I	*d*, Å	*I*	*d*, Å	
5	9.24	7	9.216	0 0 3
19	7.70	17	7.755	0 1 2 1 -1 2 -1 0 2
2	5.38	3	5.394	1 1 0 -2 1 0
6	4.73	4	4.767	0 1 5 1 -1 5
29	4.41	38	4.428	2 0 2 -2 2 2 0 -2 2
4	3.62	7	3.650	1 0 7 -1 1 7
13	3.59	5	3.579	2 0 5 0 2 5 -2 2 5
7	3.53	7	3.513	-1 -1 6
4	3.48	2	3.508	2 1 1
6	3.41	3	3.427	-1 3 2
5	3.20	3	3.249	0 1 8
26	3.13	37	3.149	2 1 4 3 -1 4 -2 3 4
19	3.11	14	3.123	-3 3 0 0 3 0 3 0 0
4	3.08	11	3.081	0 0 9
100	3.03	100	3.023	0 2 7 -2 0 7 2 -2 7
85	2.982	41	2.980	1 2 5 -1 3 5 3 -2 5
60	2.954	51	2.955	0 3 3 3 0 3 -3 3 3
10	2.750	15	2.782	2 0 8
40	2.689	38	2.701	-2 4 0 -4 2 0 2 2 0
13	2.610h	10	2.638	2 1 7
		2	2.593	2 2 3
6	2.553	8	2.550	3 1 2
3	2.430	4	2.431	3 -4 4
8	2.202h	5	2.216	4 0 4
		13	2.191	0 3 9 3 0 9
11	2.171	9	2.172	3 -4 7 -4 1 7 -3 -1 7
15	2.154	9	2.155	4 -4 5 0 4 5 -4 0 5
3	2.142	2	2.140	3 2 1
13	2.117	10	2.121	2 3 2 -2 5 2 5 -3 2
2	2.079	4	2.080	0 -1 13 1 0 13 -1 1 13
11	2.049	11	2.050	3 2 4 -2 -3 4 2 -5 4
13	2.030	12	2.031	-2 -2 9 2 2 9 -2 4 9
10	2.012	6	2.012	4 0 7 -4 4 7 0 -4 7
8	2.003	17	2.002	2 3 5 3 -5 5 -5 2 5
14	1.990	16	1.994	4 1 3 -1 5 3 5 -1 3
3	1.942	6	1.940	-4 0 8 0 4 8 4 -4 8
4	1.885	5	1.887	-5 3 7 -3 5 7 3 2 7
8	1.869	6	1.868	1 4 6 4 1 6
18	1.845	23	1.855	0 3 12
13	1.822	16	1.824	-5 2 8 3 -5 8 2 3 8
31	1.797	19	1.801	3 3 0 -3 6 0 -6 3 0
21	1.770	15	1.773	-5 5 5 5 0 5 0 -5 5
5	1.700	8	1.698	3 2 10
7	1.683	3	1.685	-6 4 5 4 2 5
3	1.622	3	1.624	0 2 16
8	1.598	4	1.590	0 3 15
5	1.548	4	1.548	5 1 7
8	1.540	5	1.539	2 0 17 0 0 18
6	1.529	6	1.529	1 4 12
7	1.514	4	1.513	3 2 13 1 5 8 0 4 14
2	1.500	3	1.501	-7 4 4
5	1.491	2	1.491	2 4 10
14	1.477	9	1.479	-7 5 3 5 2 3 2 -7 3
2	1.424	2	1.425	7 -5 6

Note. DRON-2 diffractometer; Cu anode, graphite monochromator, counter speed is 1°/min, quartz used as internal standard. Analyst A.A. Agakhanov.

diffractometer with the CCD detector, Mo$K\alpha$ radiation) (Uvarova *et al.*, 2013).

The structure of the new mineral has the main features of minerals of the vicanite group (Ballirano *et al.*, 2002; Bioiocchi *et al.*, 2004; Raade *et al.*, 2007; 2008; Uvarova *et al.*, 2013). Basic elements of the structure are as follows: layers A (z ~ 0), B (z ~ 0.13) and C (z ~ 0.23), linked into a complex heteropolyhedral framework. There are four tetrahedral sites (*T*1-*T*4) occupied by Si, B, P and coordinated by O, a triangular *T*5 position occupied by B and coordinated by O and F, an octahedral *M*6 position = (Fe^{2+}, Mn, Ti), coordinated by O

Table 3. **Comparative characteristic of minerals: laptevite-(Ce), vicanite-(Ce), okanoganite-(Y), hundholmenite-(Y) and proshchenkoite-(Y)**

Mineral characteristics	laptevite-(Ce)	vicanite-(Ce)	okanoganite-(Y)	hundholmenite-(Y)	proshchenkoite-(Y)
Formula	$Na(Fe^{2+},Mn^{2+})(\mathit{REE}_7Ca_5Y_3)_{15}(SiO_4)_4(Si_3B_2PO_{18})(BO_3)F_{11}$	$(Ca,\mathit{REE},Th)_{15}Fe^{3+}[SiO_4]_3[Si_3B_3O_{18}][BO_3](As^{5+}O_4)(As^{3+}O_3)_x(NaF_3)_{1-x}F_7(H_2O)_{0.2}$, $x = 0.4$	$(Na,Ca)_3(Y,Ce)_{12}B_2Si_6O_{27}F_{14}$	$(Y,\mathit{REE},Ca,Na)_{15}(Al,Fe^{3+})Ca_xAs^{3+}{}_{1-x}(Si,As^{5+})Si_6B_3(O,F)_{48}$	$(Y,\mathit{REE},Ca,Na,Mn)_{15}(Fe^{2+},Mn)Ca(P,Si)Si_6B_3O_{34}F_{14}$
Space group	*R*3*m*	*R*3*m*	*R*3*m*	*R*3*m*	*R*3*m*
a, Å	10.804(2)	10.8112(2)	10.7108(5)	10.675(6)	10.7527(7)
c	27.726(6)	27.3296(12)	27.0398(11)	27.02(2)	27.4002(18)
Z	3	3	3	3	3
X-ray powder intensive lines, $D_{meas.}(I)$	7.70 (19)	7.70 (50)			
	4.41 (29)	4.42 (50)	4.38(41)	4.38 (33)	4.441 (36)
	3.13 (26)	3.13 (50)	3.11(48)	3.114 (43)	3.144 (77)
	3.03 (100)	2.993 (100)	2.970(100)	2.972 (100)	3.028 (45)
	2.982 (85)	2.950 (70)	2.939(95)	2.947 (76)	2.968 (100)
	2.954 (60)	2.698 (50)	2.926(50)	2.924 (66)	
	2.689 (40)	1.839 (50)	2.676(32)	2.681 (36)	
	1.979 (31)	1.802(50)	1.978(35)	1.978 (37)	
	1.770 (21)		1.822(32)		
			1.784(43)		1.782 (32)
					1.713 (32)
Color	brown, yellowy-brown	flavovirent	reddish-brown, light pink	pale grayish-brown to the grayish-brown	
Luster	vitreous	vitreous		vitreous, diamond	
$D_{meas.}$, g/cm^3	4.61(2)	> 4.2	4.35(4)	> 4.2	4.72
$D_{calc.}$, g/cm^3	4.619	4.73	4.96	5.206	4.955
Mohs hardness	4.5–5	5–6	4	5–6	near 5
Optical properties (sign)	uniaxial (–)	uniaxial (–)	uniaxial (–)	uniaxial (–)	uniaxial (–)
n_o	1.741(3)	1.757(2)	1.753(2)	1.7578(5)	1.734(2)
n_e	1.720(3)	1.722(2)	1.740(2)	1.7487(5)	1.728(2)
	Our data	Maras *et al.*, 1995; Ballirano *et al.*, 1991	Boggs, 1980	Raade *et al.*, 2008	Raade *et al.*, 2008

atoms, and six positions with coordination from 7 to 10: *M*1-*M*5 positions occupied by Ca and *REE*, and *M*7 occupied by Na and *REE*. *M*1-*M*6 positions are coordinated generally by oxygen, to a lesser extent by F.

In the **A layer**, T1 and T4 tetrahedra are linked into a complex anion, which is characteristical for vicanite minerals group; it's composition is $(Si_3B_2PO_{18})^{-17}$ in laptevite-(Ce), unlike other minerals of group where the composition of this anion is $(Si_3B_3O_{18})^{-15}$. Other units of the A layer are M6 clusters, formed by octahedra, which are connected with SiO-tetrahedra (T1, T2) and the polyhedron $^{[9]}M(1) = (\mathit{REE}, Ca)$.

The **B layer** in laptevite-(Ce) consists of isolated Si-O T3 tetrahedra $(B_{0.84}\square_{0.16})$, triangles and also $^{[10]}M2 = (\mathit{REE}, Ca)$ and $^{[8]}M4 = (Ca, \mathit{REE}, U, Th)$ polyhedrons. The BO_3-triangular groups are present only in one mineral of the group – vicanite-(Ce). In other minerals, this position is vacant.

The **C layer** is formed by M3 polyhedra = (Ca, Sr, *REE*), M5 = (Y, *REE*) and M7 = (Na, *REE*). Tetrahedra and polyhedral of all layers, connect with each other and create a single frame work. The formula of laptevite-(Ce) is (recalculation on O + F = 48 apfu): $(Fe_{0.58}Mn_{0.31}Ti_{0.10}Zr_{0.02})_{\Sigma 1.01}[(Ce_{2.80}La_{2.22}Nd_{0.79}Pr_{0.46}Dy_{0.21}Gd_{0.20}Sm_{0.15}Yb_{0.05}Tb_{0.03}Eu_{0.02}Tm_{0.02})_{\Sigma 6.95}Ca_{5.52}Y_{2.60}Na_{0.83}Sr_{0.37}U_{0.07}Th_{0.04}]_{\Sigma 16.38}Si_{6.78}B_{3.54}P_{0.54}O_{36.39}F_{11.61}$, and the ideal formula is $NaFe^{2+}(\mathit{REE}_7Ca_5Y_3)(SiO_4)_4(Si_3B_2PO_{18})(BO_3)F_{11}$.

The populations of the majority of the 14 sites in the structures of laptevite-(Ce) and the other minerals of the vicanite group are identical. Therefore it is hard to say, which of a minerals of the group has the greatest similarity to laptevite-(Ce) (Uvarova *et al.*, 2013). Structurally laptevite-(Ce) is closest to vicanite-(Ce), due to presence of BO_3-triangles, which are absent in other minerals of the group, although between vicanite-(Ce) and laptevite-(Ce), the major differences in composition are as follows in vicanite-(Ce): the M5 polyhedron is occupied by thorium, theT3 tetrahedron by arsenic, and the anion position, occupied in laptevite-(Ce) by fluorine, in general is vacant (Ballirano *et al.*, 2002).

The holotype sample of laptevite-(Ce) is stored in the Fersman Mineralogical Museum (Moscow, Russian Federation), registration number 4195/1.

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BARATOVITE–KATAYAMALITE MINERALS FROM THE HODZHA–ACHKAN ALCALINE MASSIF (KIRGIZIA)

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The baratovite $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$ – katayamalite $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH)_2$ mineral series is found in pyroxene-feldspar fenites at the northern contact of the Hodzha-Achkan alkaline massif in Taldy-Bulak valley (a northern slope of the Alaysky ridge, Batkensky Region, Kyrgyzstan). The baratovite-containing rocks have a spotty, striate texture, consertal structure, and a changeable color index that is caused by uneven distribution of the main and minor minerals: hedenbergite – aegirine pyroxenes, microcline, albite, wollastonite, miserite (REE_2O_3 to 5.5 wt.%), calcite (SrO to 1.1 wt.%), quartz. Accessory minerals are: titanite, fluorite, andradite, zircon, turkestanite, ekanite, thorite, tadzhikite-(Ce), britholite group minerals, stillwellite-(Ce), datolite, bazzirite, gittinsite, fluorapatite, barite, galena, molybdenite, pyrite, and pyrrhotite. Baratovite-katayamalite forms lamellar individes to 3 cm with a pinkish color. In short-wave UV-radiation the color is bluish-white. VHN microhardness = 670 (5–6 on the Mohs scale). $D_{meas.} = 2.92(2)$, $D_{calc.} = 2.91$ g/cm^3. Biaxial, optically positive, 2V from 70º to 90º, dispersion strong, $r > v$; $n_g = 1.674(2)$, $n_m = 1.671(3)$, $n_p = 1.666(3)$. IR spectrum (intensive bands, cm^{-1}): 1082, 972, 695, 598, 570, 541, 521, 478, 448, 412. The X-ray powder data obtained by photomethod (Guinier camera), and diffractometry are given. Parameters of a cell (photomethod): $a = 16.93(1)$, $b = 9.742(5)$, $c = 20.92(2)$Å, $\beta = 112.51(5)^\circ$, $V = 3187(5)$A^3. Chemical composition of baratovite/katayamalite (wt.%): SiO_2 51.29/51.01; Al_2O_3 0.20/0.06; TiO_2 8.87/7.97; ZrO_2 2.22/3.71; Nb_2O_5 0.00/0.23; SnO_2 1.01/1.87; Fe_2O_3 0.60/0.44; CaO 26.72/26.72; Li_2O^* 3.20/3.17; K_2O 3.17/3.07; Na_2O 0.15/0.23; F 1.75/0.94; H_2O^* 046/0.84; $-O=F_2$ –0.73/–0.39; total 98.91/98.87 (* – calculated). Most analyses belong to the middle of series between baratovite and katayamalite (F 0.70–1.30 apfu, electron microprobe analysis). The described rocks are close to quartz-albite-aegirine with baratovite-miserite from the Darai-Pioz (Tajikistan), where there is a similar list of accessory minerals (tadzhikite-(Ce), turkestanite, stillwellite-(Ce), bazirite), but there are also some differences: at Hodzha-Achkan, andradite, ekanite, minerals of britholite group are found; pyroxenes are slightly less alkaline, and there are albite pertites in large microcline grains. This occurrence of baratovite is the second in the world and katayamalite the third.

8 tables, 11 figures, 76 references.
Keywords: baratovite, katayamalite, Hodzha-Achkan, Darai-Pioz, Matchaisky intrusive complex.

Introduction

During field work on the Hodzha-Achkan massif (Kyrgyzstan) in 1993, we found samples containing the baratovite-katayamalite mineral series. In 2011, additional material was collected on the same massif, which allowed us to characterize in more detail the minerals of this series, as well as rocks bearing this mineralization.

Baratovite $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$ and its hydroxyl analogue – katayamalite $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH)_2$ – are very rare layered titanosilicates with six-membered isolated rings of SiO-tetrahedrons, known earlier only from the type localities. Baratovite was firstly discovered by V.D. Dusmatov and colleagues on the Darai-Pioz (Tajikistan) alkaline massif in the form of nacreous-white lamellar forms to 5 × 2 × 0.5 cm in quartz-albite-aegirine pegmatite streaks connected with quartz-containing aegirine syenites, and in albitites of these syenites (Dusmatov *et al.*, 1975). Later the mineral was found in the same massif in other associations: in agrellite-wollastonite-feldspar rocks, in pyroxene-quartz-feldspar rocks with polylithionite (the largest forms of baratovite, up to 7 cm in size, are found there), and in silexytes with leucosphenite, sogdianite, pectolite, polylithionite and reedmergnerite. Katayamalite was described by Nobihude Murakami and coauthors as a new mineral from Ivagi island, Ekhime Pref., in the southwest of Japan, in aegirine syenite, in which it consists of 0.3–0.5 vol.% of the rock. It forms fine tabular grains of white color to 0.5 mm in association with albite, pectolite, wollastonite and sugilite (Murakami *et al.*, 1983). Comparison of associations of the baratovite group minerals from the Darai-Pioz, Ivagi and Hodzha-Achkan are shown in table 1.

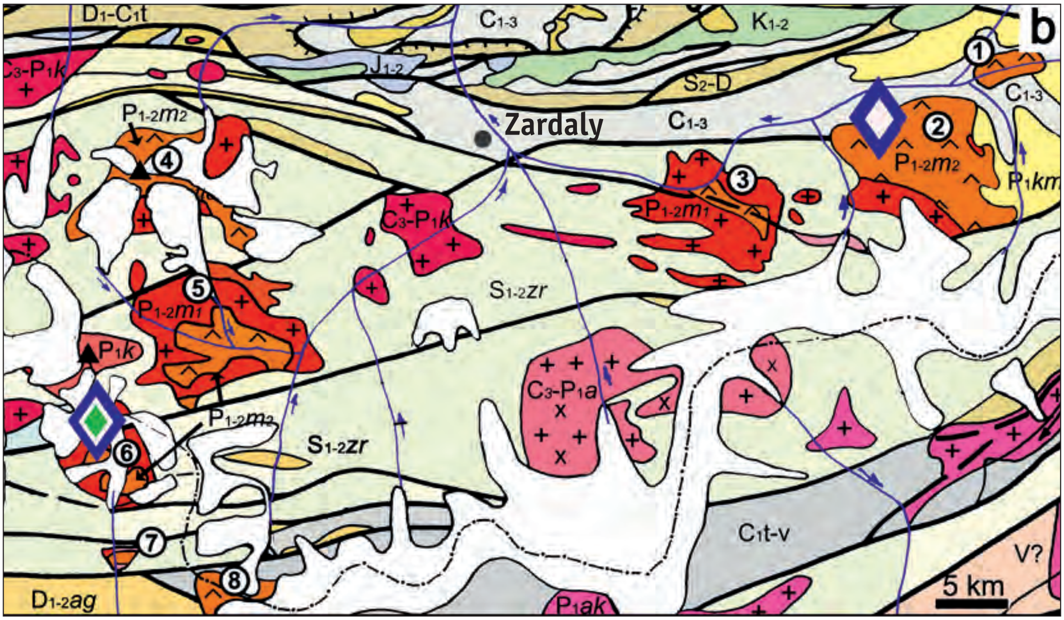
Methods of investigation

The mineralogical composition of the baratovite-containing rocks was studied in polished and transparent-polished sections and in crushed samples. Indices of refraction were measured by theodolitic-immersion method with V.G. Feklichev's PPM-1 stage. Both De-

Fig. 1. The geographic location (a) and the geological map (b) of the Turkestano-Alay alkaline massifs (drawn using the Geological map of Tajik SSR and adjacent territories (1984), the Geological map of Kirgiz SSR (1980), and field materials of A.V. Berezansky and V.M. Nenakhov. The rectangle in figure (a) shows the area of the geological map. Digits in circles are the designated massifs, as follows:

1 — Dzhilisu;
2 — Hodzha-Achkan;
3 — Kulpsky;
4 — Utrensky;
5 — Matchinsky;
6 — Upper Darai-Pioz (Darai-Pioz itself);
7 — Middle Dara-Pioz;
8 — Tutek.

The names of intrusive complexes are shown in the map legend according to V.M. Nenakhov et al. (1987).



Symbols in the geological map:

Sediment formations:

$K_{1\text{-}2}$	*Lower — Upper Cretaceous. Speckled sandstones, conglomerates, clays, marls, limestones, gypsums*
$J_{1\text{-}2}$	*Lower — Middle Jurassic. Speckled sandstones, conglomerates, coals, clays*
P_1km	*Lower Permian, kumbel series. Red sandstones, conglomerates, rarely — schists*
$C_{1\text{-}3}$	*Lower — Upper Carbon. conglomerates Sandstones, gravelites, aluerolites, soapstones*
$C_1t\text{-}v$	*Lower Carbon. Tournai — Vise. Conglomerates, sandstones, limestones, schists*
$D_1\text{-}C_1t$	*Lower Devonian — Lower Carbon (Tournai). Limestones, dolomites.*
$D_{1\text{-}2}ag$	*Lower — Middle Devonian, agbalyiskaya series. Tuffs, aluerolites, sandstones, limestones*
$S_2\text{-}D$	*Upper Silurian — Devonian. Schists, sandstones, limestones, flintstones, porphyrites, tuffs*
$S_{1\text{-}2}\,zr$	*Lower—Silurian, zeravshan series. Sandstones, coal-silicious schists, chlorite schists*
V?	*Vendian(?) Greenschists metamorphites*

Intrusive formations:

^ ^ $P_{1\text{-}2}m_2$	*Matchaisky complex. Phase 2. Alkaline and nepheline syenites, syenites, their dikes*
+ + $P_{1\text{-}2}m_1$	*Matchaisky complex. Phase 2. Alkaline and nepheline syenites, syenites, their dikes*
+ × P_1k	*Karakyzsky complex. Granodiorites, quartz diorites*
+ + P_1ak	*Achikalminsky complex. Granites*
+ + $C_3\text{-}P_1k$	*Karavshinsky complex. Leucogranites , adamellites and their pegmatites*
× + $C_3\text{-}P_1a$	*Archabashinsky complex. Granodiorites, quartz monzonites*
	Glaciers
▲	*Mountains*
1. ◆ 2. ◇	*Baratovite mineral group locations:* *1 — Darai-Pioz; 2 — Hodzha-Achkan*

bye-Scherrer and Guinier photomethods (with RKD-57.3, DKS-60 and Huber 621 cameras), and diffractometry (DRON-2) were used for X-ray powder data.

The chemical composition of baratovite and of minerals from the baratovite-containing rocks was studied both by electron probe analysis (using wave-dispersive [WDS] and energy-dispersive [EDS] spectrometers) and by wet chemistry. EDS analyses were performed with the CamScan-4D scanning electron microscope, equipped with an EDS (Si-Li) detector (U = 20 kV, I = 4 nA for metallic Co; ISIS Oxford analysis system) and with a JCXA-733 Superprobe JEOL electron microanalyzer, equipped with an EDS (Si-Li) detector with a thin ATW-2 window (U = 20 kV, I = 2 nA; INCA Energy Oxford analysis system). WDS analyses were performed with a JCXA-733 JEOL Superprobe electron microanalyzer with five spectrometers and a Camebax-microbeam with four spectrometers. Measurement conditions on the Camebax-microbeam are as follows: an accelerating voltage of 15 kV; probe current of 20 nA; counting time for main elements is 10 sec at peak, 5 sec at background; counting time for Rb*L*α, Sr*L*α, F*K*α is 40 sec at peak, 20 sec at background. Calculation of concentrations was carried out by means of the of PAP correction program from the device software. The analysis on WDS of JCXA-733 Superprobe JEOL was carried out at an accelerating voltage of 15 kV and 20 kV and probe current of 20 nA. The analysis on fluorine (TAP crystal) and boron (STE crystal) were carried out at an accelerating voltage of 10 kV and probe current of a 30 nA with the beam defocused to 20 microns. The counting time of main elements is 20 sec at the peaks and 10 sec at background; counting time for Rb*L*α, Sr*L*α, Sn*L*α, Hf*M*α is 50 sec at peak and 20 sec at background; counting time for F*K*α, B*K*α is 200 sec at the peaks and 100 sec at background. Standards used are as follows: Si*K*α, Ca*K*α – NMNH 164905 Cr-augite; Ti*K*α, Mn*K*α – $MnTiO_3$; Zr*L*α – USNM 117288-3 zircon; Sn*L*α – SnO_2; Fe*K*α – Fe_2O_3; Zn*K*α – ZnO; Mg*K*α – USNM 143968 pyrope; Sr*L*α – $SrSO_4$; Cs*L*α – $Cs_2Nb_4O_{11}$; Rb*L*α – $Rb_2Nb_4O_{11}$; K*K*α, Al*K*α – STD 107 microcline; Na*K*α – jadeite; F*K*α – fluor-phlogopite; B*K*α – danburite and stillwellite-(Ce). Calculation of concentrations was carried out by means of ZAF correction, for F and B – with full PAP correction.

Li and Rb were measured by a flame photometry method (FMD-4 spectrometer of Opton) and optical-emission spectrometry with the inductive coupled plasma method (ICP-OES MPX of Varian). For flame-photometric determination of rare alkalis an acid digestion ($HF + H_2SO_4$) of mineral weights, solubilized at a nitric acid solution has performed. Cs with 1000 ppm of final concentration in solutions was used as the ionization buffer.

F was determined by potentiometer method with an ion-selective electrode. For opening of weights of samples fusion with NaOH in nickel crucibles was used. Water amount was determined from micro-weights by the method of elemental analysis with chromatographic completion (Carlo-Erba 1106 CHN analyzer, carrier gas – helium for chromatography, reactor temperature – 1030°C, a filler of a chromatographic column is Porapak QS). In order to study accessory minerals from crushed samples of rock, the fraction – 100 μm was separated in formyl tribromide (D = 2.89 g/cm^3), and then exposed to magnetic separation. Both EDS qualitative analysis method and powder X-ray methods were used for mineral diagnostics.

Fig. 2. Hodzha-Achkansky massif: a – a general view of the massif from the lower reaches of the Gaumysh river; in the foreground the south-east part of the Dzhilisu massif is visible; b – Taldy-Bulak valley, cutting a contact of syenites with slates in the northern part of the Hodzha-Achkan; the baratovite group minerals are found in its debris cones. Photo: L.A. Pautov.

Mode of occurence

The Hodzha-Achkan massif is at the near-watershed part of the northern slope of the Alaisky ridge at elevations from 2900 to 5100 m (Batken oblast, Kyrgyzstan). The massif is exposed on the left bank of the Hodzha-Achkan River at the headwaters (Fig. 1, 2) between its two left branches (Loisu and Tilbe). It is possible to reach the bottom of the massif by foot from Aidarken (Khaidarkan) settlement through the Gaumysh pass and further down the valley of the Gaumysh river to its confluence with the Hodzha-Achkan river, or from Zardaly (Korgon) kishlak (village), located on confluence of the Ak-Terek and Hodzha-Achkan Rivers. Because of the rugged terrain, the massif is difficult to access (Fig. 2).

The first data on the massif were published by V.N. Weber based on the results of field work in 1910 (Weber, 1934). A detailed description of the Hodzha-Achkan massif was written by A.V. Moskvin and A.A. Saukov based on studies from 1928 as a part of the Pamir expedition of the Academy of Sciences of the USSR (Moskvin, Saukov, 1931; Moskvin, 1932). Subsequently, numerous researchers have been engaged in studying the massif (Dorfman, Timofeev, 1939; Omelyanenko, 1960; Perchuk, Omelyanenko, Shinkarev, 1961; Perchuk, 1964; Shinkarev, 1966; Ilyinsky, 1970; Ifantopulo, 1975; *et al.*), as well as crews from the Southern-Kyrgyz Geological Prospecting Expedition.

The Hodzha-Achkan massif is located in the area of a joining of the Zeravshansky anticlinorium with the Surmetash folded zone which are separated by the Turkestan regional break of deep underlay (Ilyinsky, 1970; Nenakhov *et al.*, 1987). In the plan the massif is close to isomeric, with abruptly falling contacts. In the north the massif breaks through limestone-slate thickness of upper Carbonian, in the east, poorly metamorphized upper Carbonian — lower Permian conglomerates with lenses of sandstones and limestones; in the west, Silurian sand-slate thickness, metamorphized in amphibolite facies; in the south the massif is limited to tectonic contact with Silurian amphibolites (Ilyinsky, 1970).

The Hodzha-Achkan massif is formed by rocks of three phases of implementation. Rocks of the first phase are widespread mainly in the southwest part of the massif. They are composed of leucocratic granites (often tourmalinized) and quartz syenites. Alkaline syenites and nepheline syenites of the second intrusive phase are predominant and distributed throughout the area (up to 75%). Biotite varieties which contact with country rocks are prevalent and pass into aegirine-augite nepheline syenites.

Rocks of the third intrusive phase are composed of leucocratic biotite granites and make up the small dykes in the host rocks and syenites of the central part of the massif (The stratified..., 1982; Nenakhov *et al.*, 1987). According to V.M. Nenakhov and coauthors (1987), the Hodzha-Achkan massif belongs to the matchaisky Permian intrusive complex, which includes also the Darai-Pioz massif,the type location of baratovite (Dusmatov *et al.*, 1975), as well as the Dzhilisuisky, Kulpsky, Matchasuisky, Gerezsuisky, Utrensky, and Tuteksky alkaline massifs (see the map in fig.1). All the massifs mentioned are characterized by a three-phase structure, with the following sequence of rocks: leucocratic granites (frequently tourmalinized), syenites and quartz syenites (nepheline and alkaline syenites), and, last, quartz-bearing syenites and granites. The increased amounts of Li, Ta, Nb, Zr, Be, Sn, Mo, Th and U in comparison with clarks (Dusmatov, 1971; Nenakhov *et al.*, 1987) is a characteristic feature of the matchaisky intrusive complex massifs. The origin of massifs was followed by development of altered rock haloes with infiltration-metasomatic zonality; this was studied at the Hodzha-Achkan and Dzhilisu massifs by L.L. Perchuk, B.I. Omelyanenko and other researchers (Omelyanenko, 1958; 1960; 1961; Perchuk *et al.*, 1961; Perchuk, 1964). Processes of K-Na metasomatism led to the origin of fenitized rocks, with various mineral compositions and textural — structural features (pyroxenes — feldspar, albite — microcline, wollastonite — feldspar).

Description of the baratovite–bearing rocks

Baratovite-bearing rocks were found in the debris cone of the Taldy-Bulak valley, cutting the northern contact of syenites with slates (Fig. 2). The external appearance and mineral composition of these rocks at Hodzha-Achkan is quite close to those baratovite- and miserite-containing quartz-albite-aegirine rocks, most widespread on the Darai-Pioz, in which baratovite was discovered (Fig. 3) and described later in detail (Dusmatov *et al.*, 1975; Reguir *et al.*, 1999), and to baratovite-containing agrellite-wollastonite-pectolite-microcline rocks from the same massif (Semenov, Dusmatov, 1989). As shown below, despite the similarities, there

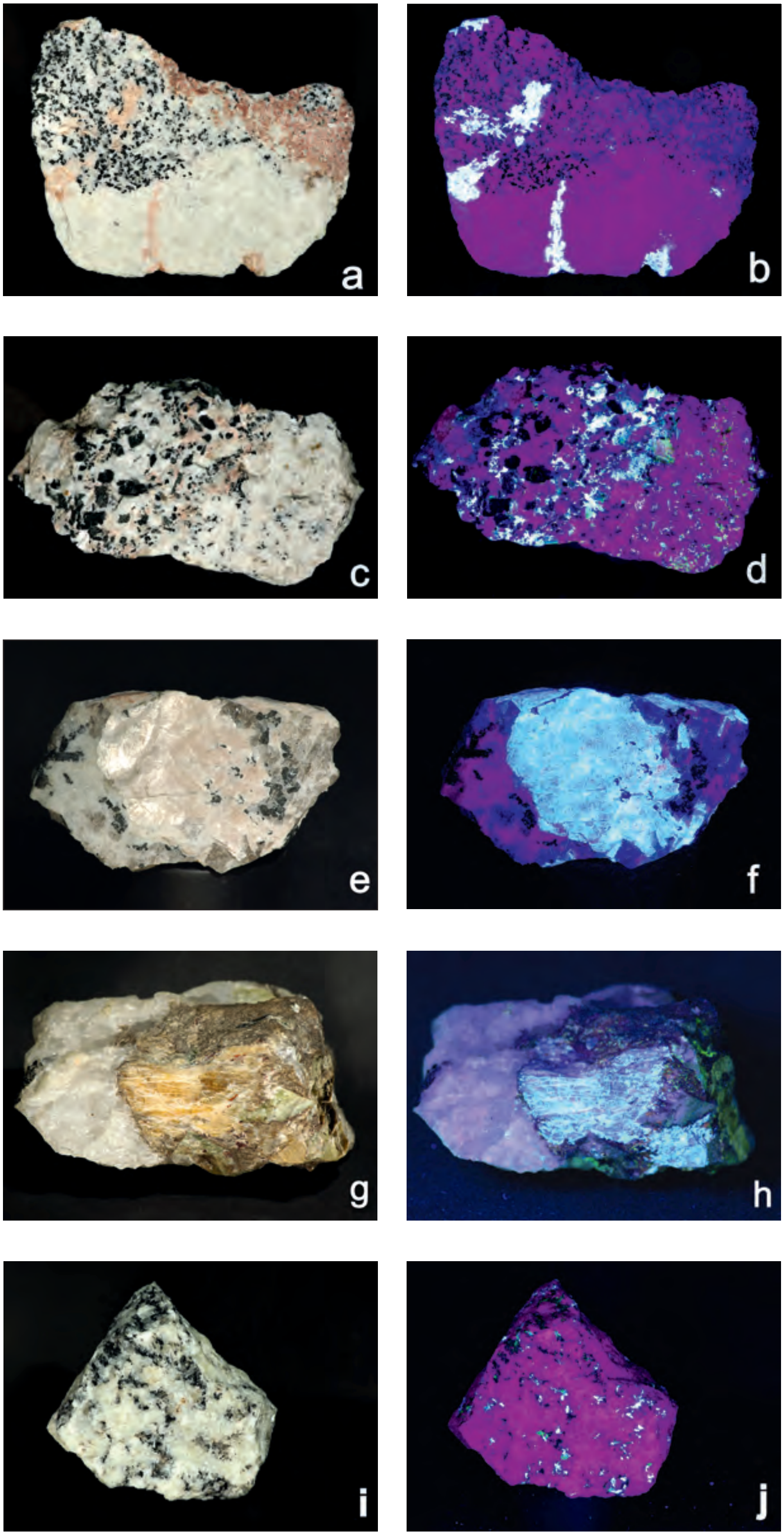


Fig. 3. Baratovite-katayamalite containing rocks: a–d – Hodzha-Achkan (Kyrgyzstan); e–h – Darai-Pioz (Tajikistan) (e, f – baratovite from miserite-pyroxene-feldspar rocks; g, h – baratovite in a silexyte with leucosphenite (green), pectolite agregate (brown). A sample from FMM's funds No. 80873); i – Ivagi (Japan); sample provided by Kotaro Watanabe. On the left – a photo under normal light (pinkish with pearly luster – baratovite, red – miserite); on the right – a photo under short-UV (bluish-white luminescence indicates baratovite group minerals); field of view – 11 cm.

Table 1. **The list of the minerals associated with baratovite and katayamalite**

List of minerals	Formula	Hodzha-Achkan, Kyrgyzstan	Darai-Pioz, Tajikistan Mineral associations					Ivagi, Japan
			Albite - mizerite	Agrellite	Sogdianite - polylithionite	Silexite	Carbonatite	
		1	2	3	4	5	6	7
Zircon	$ZrSiO_4$	+						+
Thorite	$ThSiO_4$	+						
Titanite	$CaTiSiO_5$	+	+	+	+	+	+	+
Andradite	$Ca_3Fe_2(SiO_4)_3$	+						+
Epidote	$Ca_2Al_2Fe^{+3}(SiO_4)_3(OH)$							+
Allanite-(Ce)	$Ce_2Al_3(SiO_4)_3(OH)$							+
Aegirine-hedenbergite	$NaFe^{3+}Si_2O_6$ - $CaFeSi_2O_6$	+++	+++	++	+++	++	++	++
Agrellite	$NaCa_2Si_4O_{10}F$			+++				
Wollastonite	$CaSiO_3$	+++*	+	+++				
Miserite	$(K,\square)_{1.5}(Ca, REE)_6[Si_8O_{22}](F,OH)_2 \cdot nH_2O$	++*	++	++			++	
Pectolite	$NaCa_2Si_3O_8(OH)$	+ ?		++	++	++		++
Turkestanite	$Th(Ca,Na)_2(K_{1-,}\square_X) Si_8O_{20} \cdot nH_2O$	+	+	+	+	+		
Ekanite	$ThCa_2Si_8O_{20}$	+						
Datolite	$CaBSiO_4(OH)$	+	+		+			
Fluorcalciobritholite	$(Ca, REE)_5(SiO_4,PO_4)_3F$	+						
Fluorbritholite-(Ce)	$(Ce,Ca)_5(SiO_4,PO_4)_3F$	+						
Tadzhikite	$Ca_3(REE,Y)_2TiB_4Si_4O_{16}O_{22}(OH)_2$	+	+		+	+		
Eudialyte (group)					+	++		
Stillwellite-(Ce)	$CeBSiO_5$	+	+		+	++	+	
Baratovite	$KCa_7Ti_2Li_3Si_{12}O_{36}(F,OH)_2$	+	+	+	+	+	+	
Katayamalite	$KCa_7LiTi_2(Si_6O_{18})_2(OH,F)_2$	+	+ ?	+ ?	+ ?		+	+
Aleksandrovite	$KCa_7Sn_2Li_3Si_{12}O_{36}F_2$						+	
Faizievite	$K_2Na(Ca_6Na)Ti_4Li_6Si_{24}O_{66}F_2$					+		
Bazirite	$BaZrSi_3O_9$	+	+				+	
Gittinsite	$CaZrSi_2O_7$	+						
Zektzerite	$NaLiZrSi_6O_{15}$				+	+		
Sugilite	$K Li_3Na_2Fe^{3+}{}_2Si_{12}O_{30}$				+	+		++
Sogdianite	$KLi_3Zr_2Si_{12}O_{30}$				++	++	+	
Zeravshanite	$Cs_4Na_2Zr_3(Si_{18}O_{45}) \cdot (H_2O)_2$					+		
Leucosphenite	$BaNa_4Ti_2B_2Si_{30}$				++	++		
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	+						
Polylithionite	$KLi_2AlSi_4O_{10}F_2$				++	++		
Sokolovaite	$CsLi_2AlSi_4O_{10}F_2$					+		
Orlovite	$KLi_2TiSi_4O_{10}(OF)$					+		
Neptunite	$KNa_2Li(Fe,Mn)_2Ti_2Si_8O_{24}$					+		
Pekovite	$SrB_2Si_2O_8$					+		
Fluorapophyllite	$KCa_4Si_8O_{20}(F,OH) \cdot 8H_2O$					+		
Kapitsaite-(Y)	$(Ba,K)_4(Y,Ca)_2[Si_8(B,Si)_4O_{28}]F$					+		
Microcline	$KAlSi_3O_8$	+++	+++	+++	+++	++	++	++
Albite	$NaAlSi_3O_8$	+++	++	++	++	+	+	+++
Reedmergnerite	$NaBSi_3O_8$				++	++		
Quartz	SiO_2	++	+	+	+++	+++	+	++
Pyrochlore	$(Ca,Na)_2Nb_2O_6(OH)$		+		+	+	+	
Calcite	$CaCO_3$	++*	+	+	++	+	+++	
Fluorapatite	$Ca_5(PO_4)_3F$	+	+		+	+	+	+
Barite	$BaSO_4$	+						
Fluorite	CaF_2	+	+	+	++	+	+	
Galenite	PbS	+				+		
Molybdenite	MoS_2	+						
Pyrite	FeS_2	+						
Pyrrhotite	$Fe_{1-x}S$	+						
Bismuth	Bi					+		
Sphalerite	ZnS					+		
Löllingite	$FeAs_2$					+		

Note: +++ — rock forming minerals, ++ — minor, + — accessory; +++ — in different rock types the rock forming mineral can be the main species, or a minor component; ++* — in different rock types the mineral can be either minor or accessory; ? — additional diagnostics of the mineral are required.*

The chart is based on our data as well as additional references (Ryzhev, Moleva, 1960; Ulyanov, Ilyinsky, 1964; Dusmatov et al., 1975; Semenov, Dusmatov, 1989; Murakami, 1976; Murakami et al., 1983; Belakowski, 1991; Reguir et al., 1999; Agakhanov et al., 2011).

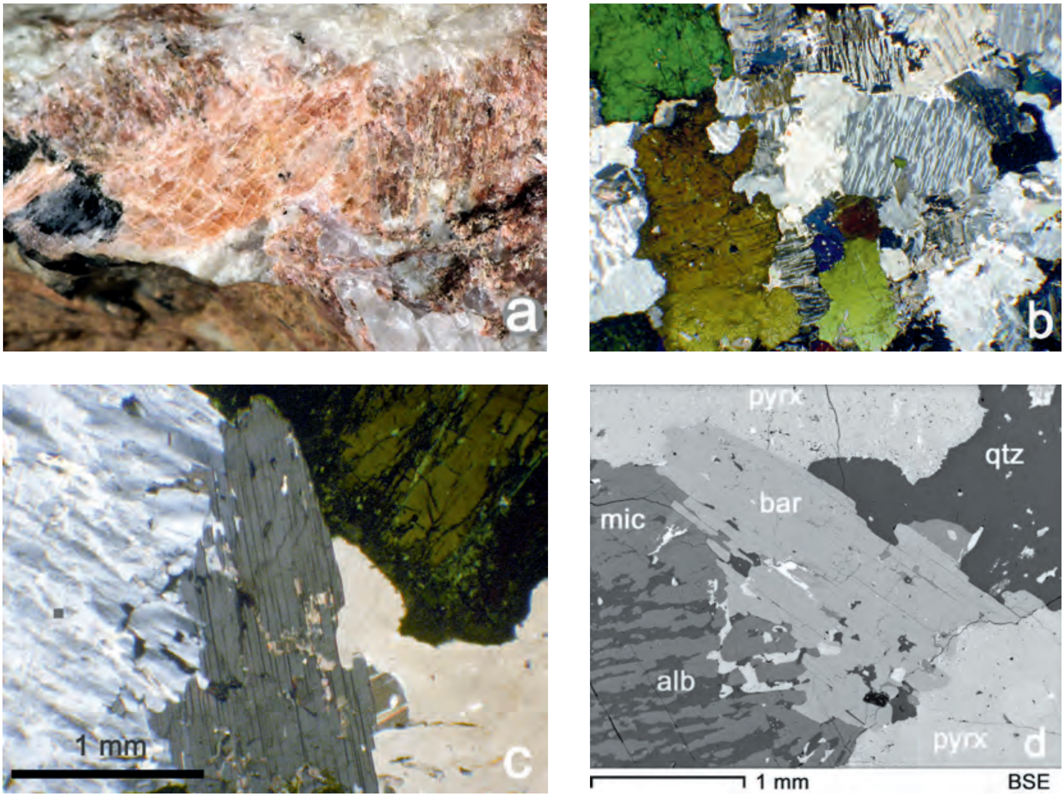


Fig. 4. Baratovite from the Hodzha-Achkan massif:
a — large lamellar form of baratovite (orange-pink) with miserite (darker, brownish-red) in microcline (light gray) with clinopyroxene (black), Taldy-Bulak valley, Hodzha-Achkan; field of view — 2.5 cm;
b — feldspar-pyroxene rock (thin section, crossed nicols). Serpiginous borders of clinopyroxene (green) and microcline-perthite accretion are visible. Grains with indigo-blue interference color are baratovite; field of view — 11 cm.
c — baratovite in feldspar-pyroxene rock (transmitted light, crossed nicols); baratovite is the bluish-grey grain in the center; on the right — microcline-perthite, dark green — clinopyroxene, with the external rim (the dark zone on the periphery of the grain) saturated with small isolated areas of garnet and more alkaline (in contrast to the host grain) pyroxene (aegirine); yellowish on the right — quartz; field of view — 2 mm;
d — the same fragment of a section, turned slightly counterclockwise, BSE mode image; bar — baratovite, pyrx — clinopyroxene; mic — microcline; alb — albite; qtz — quartz; the white extended form in baratovite — fluorcalciobritholite; light-grey grains on the left of the baratovite and microcline-perthite boundary — fluorite; light scattering in the rim zones of clinopyroxene grains — andradite, more dark scattering — aegirine.

are also differences between Hodzha-Achkan and Darai-Pioz baratovite-bearing rocks. Comparison of the mineralogical composition of baratovite- and katayamalite-containing rocks of the Hodzha-Achkan, Darai-Pioz and Ivagi are shown in table 1.

The largest and most abundant baratovite aggregates on the Hodzha-Achkan massif are found in quartz-aegirine-albite-microcline rocks, often with miserite and variable amounts of calcite, wollastonite, titanite, datolite. The color index, texture and structure of such rocks is extremely changeable even within one mass (sample). Spotty texture and, rarely, striate texture are most typical of these rocks. The textures are caused by the presence in leucocratic fine-grained quartz-albite-microcline rock (sometimes with miserite and aegirine), of segregations, consisting of more coarse-grained aggregates of the same minerals, but often in other ratios (Fig. 3). In some varieties of such rocks, miserite is not an accessory or minor mineral, but the main constituent of the rock, giving it a saturated pink color. The leucocratic fine-grained main skeleton of the rock is composed generally of *albite* and nonperthitic *microcline*, approximately in equal proportions; minor minerals include quartz and calcite. The total amount of clinopyroxene and miserite is quite variable samples both enriched and totally deprived colored minerals may be seen. The coarse-grained aggregates form isomeric, elongated or irregular clusters, which are composed of light-gray microcline-perthite tabular grains (albite perthites occupy 40–50 vol.% of individual K-feldspar grains) (Fig. 4, 5), dark green grains of clinopyroxene (Fig. 4); and variable quantities of calcite, quartz, wollastonite, and miserite. *Clinopyroxene* forms, as a rule, grains with wavy, rough borders and no evidence of crystallographic shape (Fig. 4). Pyroxene compositions (Table 2) are quite close to those from the Darai-Pioz baratovite-containing fenites and have less aegirine than Ivagi pyroxene, also considerably differing from the clinopyroxene composition of the Hodzha-Achkan syenites (Fig. 6). A characteristic feature of clinopyroxene (average composition is $Hd_{64}Aeg_{21}Di_{14}$) from coarse-grained aggregations on the contact with perthitic potassium feldspar is a zone, almost non-transparent in normal thick sections, containing numerous small pores, irregular *garnet* aggregates of andradite composition ($And_{94}Sch_3Gros_2Spes_1$) with smooth outlines and sizes to 15–20 µm (Table 2, analysis 7, 8), and segregations of pyroxene enriched with aegirine (Fig. 4, 7) which do not have crystallographic restrictions. Similar zones in the external rims of pyroxene crystals in alkaline rocks from other regions have been interpreted in the literature as a product of reactionary substitution of earlier high-calcic pyroxene against increased activity of alkalis and fugacity of oxygen (Dawson, Hill, 1988; Marks *et al.*, 2003). However, this has never been noted in baratovite-katayamalite bearing rocks of the Darai-Pioz and Ivagi. Clinopyroxenes without such rims from fine-grained quartz-albite-microcline rock from the Hodzha-Achkan are more alkaline (average composition $Aeg_{44}Hd_{36}Di_{20}$, fig. 6; table 2, analysis 5). A characteristic mineral of the baratovite-containing rocks both of Hodzha-Achkan and Darai-Pioz is miserite (Semenov *et al.*, 1973; Dusmatov *et al.*, 1975; Reguir *et al.*, 1999); as noted above, its presence is subject to considerable variation. *Miserite* at Hodzha-Achkan has been described on multiple occasions: in wollastonite-pyroxene-feldspar

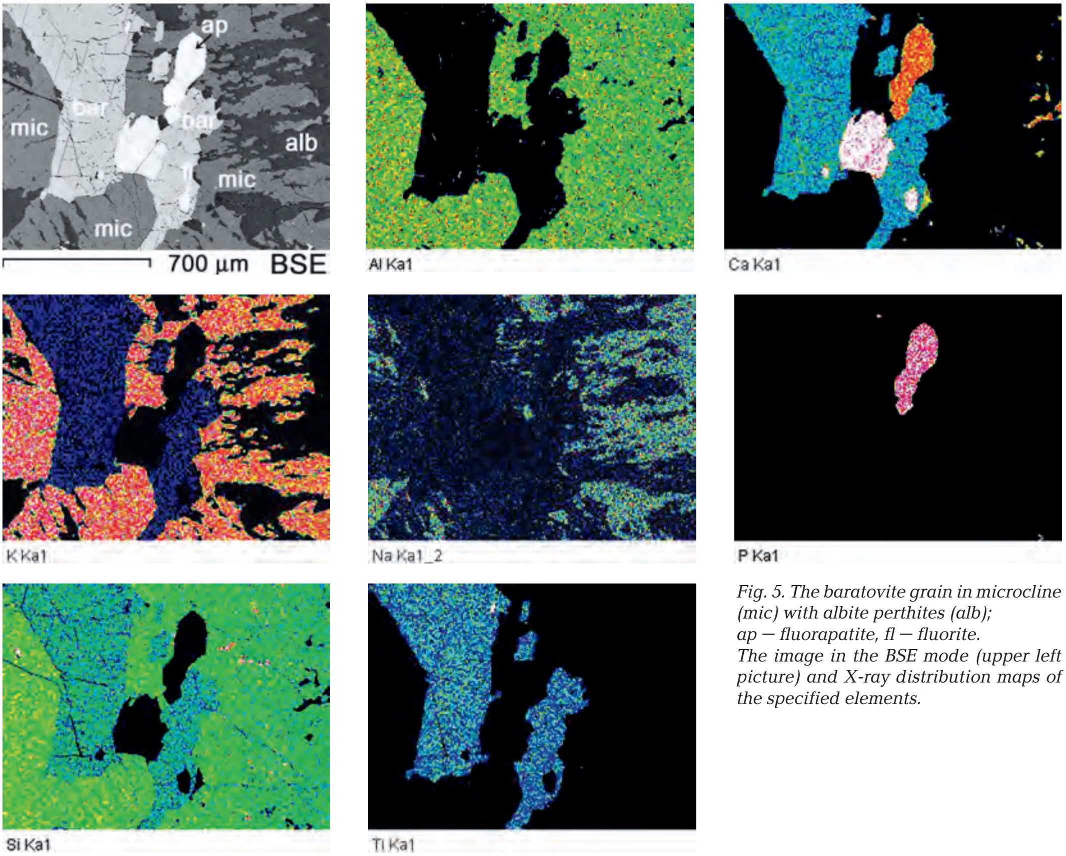


Fig. 5. The baratovite grain in microcline (mic) with albite perthites (alb); ap – fluorapatite, fl – fluorite. The image in the BSE mode (upper left picture) and X-ray distribution maps of the specified elements.

Table 2. **Chemical composition of clinopyroxenes (1–5), wollastonite (6), andradite (7, 8), datolite (9) from the baratovite – containing rocks, Hodzha-Achkan**

Component	1	2	3	4	5	6	7	8	9
SiO_2	50.32	50.93	52.51	53.14	51.75	51.52	35.76	34.62	36.79
TiO_2	0.00	0.15	0.00	0.00	0.11	0.00	0.18	0.00	0.00
Al_2O_3	0.37	0.26	0.27	0.54	0.35	0.00	2.47	0.95	0.00
Fe_2O_3	7.85	7.21	18.55	31.81	14.65	0.00	27.53	31.24	0.00
FeO	18.29	18.84	4.03	1.08	9.94	0.74	0.00	0.00	0.36
MnO	0.60	0.60	1.24	0.17	1.38	0.31	0.38	0.11	0.00
MgO	2.45	2.30	4.47	0.00	3.36	0.00	0.00	0.00	0.00
CaO	18.82	17.64	12.75	0.34	13.25	47.47	33.01	33.38	34.07
Na_2O	2.76	3.21	7.16	13.34	5.97	0.00	0.00	0.00	0.00
Total	100.67	100.41	99.12	97.23	99.29	100.04	99.57	99.93	98.06
Calculated on the basis of:									
	O = 6 apfu					O = 3 apfu	O = 12 apfu		
Si^{+4}	1.98	2.01	1.99	2.02	2.00	1.00	3.00	2.93	
Al^{+3}	0.02	0.01	0.01	0.02	0.02	0.00	0.24	0.10	
Ti^{+4}	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	
Fe^{+3*}	0.23	0.21	0.53	0.91	0.43	0.00	1.74	1.99	
Fe^{+2*}	0.60	0.62	0.13	0.03	0.32	0.01	0.00	0.00	
Mn^{+2}	0.02	0.02	0.04	0.01	0.05	0.01	0.03	0.01	
Mg^{+2}	0.14	0.13	0.25	0.00	0.19	0.00	0.00	0.00	
Ca^{+2}	0.79	0.74	0.52	0.01	0.55	0.99	2.96	3.02	
Na^{+}	0.21	0.25	0.53	0.99	0.45	0.00	0.00	0.00	
O^{-2}	6.00	6.00	6.00	6.00	6.00	3.00	12.00	12.00	

*Note: * – Fe^{+2}/Fe^{+3} calculated.*
In the following, if there are no special comments analysis was performed by EPMA EDS.
1 – 4 – clinopyroxene from coarse-grained areas of the rock:
1, 2 – the central part of grains; 3 – aegirine isolates from the external rims; 5 – clinopyroxene from fine-grained sites; 6 – wollastonite from coarse-grained wollastonite-pyroxene-feldspar rock; 7, 8 – andradite (calculated on O = 12 apfu): 7 – apple-green grains in the matrix of a rock; analysis sum includes Nb_2O_5 = 0.24 wt. % (corresponds to Nb = 0.01 apfu); 8 – andradite from garne-aegirine rims of a coarse-grained clinopyroxene; 9 – datolite (calculated on the basis of total cations = 2 apfu): $(Ca_{0.99}Fe_{0.01})BSiO_4(OH)$, calculated amounts (wt. %): B_2O_3 = 21.31, H_2O = 5.53.
In the following tables, 0.00 means that the component amount is lower than the limit of detection.

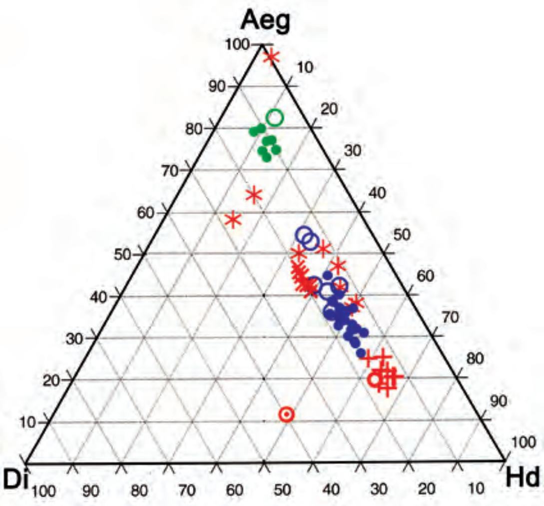


Fig. 6. Chart of clinopyroxene compositions (mol. %) from the baratovite – containing rocks from Hodzha-Achkan:
+ – coarse grains,
✱ – alkaline pyroxene segregations from the external rim of those grains,
× – small grains from fine-grained areas of the feldspar rock (our data);
○ – from quartzless syenites (Perchuk, 1964),
⊙ – from quartz syenites (Perchuk, 1964);

Darai-Pioz (miserite – bearing quartz-albite-microcline rocks):
● – our data,
○ – (Reguir et al., 1999);

Ivagi (aegirine syenite):
● – our data;
○ – Murakami et al., 1983.

Ternary tops correspond to:
Di – diopside, Hd – hedenbergite, Aeg – aegirine.

rocks in the east area (the left bank of the Loisu river) (Ryzhev, Moleva, 1960); in the northwest part of the massif (the valley of Karagach-Dzhilga) at the contact of nepheline syenites with native slates (Ul'yanov, Ilyinsky, 1964); and in albite-pyroxene metasomatites from a talus at the northern contact of the massif (Enikeeva *et al.*, 1987). Aside from Hodzha-Achkan and Darai-Pioz, miserite is known from other massifs of the matchaisky complex: Matchinsky, Kulpsky, Dzhilisuisky (Ilyinsky, 1970; Ifantopulo, 1975). Miserite in other regions of the world is also found in alkaline metasomatites (fenites) with potassium specialization, in alkaline intrusions, or in carbonatites. Other occurrences of miserite include: the contact of metamorphized slates and nepheline syenites in Wilson Springs, Arkansas, USA (Shaller, 1950); aegirine-albite-microcline metasomatites at Chergilen, Khabarovsky krai, E. Siberia (Kupriyanova, Vasilyev, 1961); the contact of dykes of alkaline rocks with limestones at Talassky ridge, Kyrgyzstan (Kozlova, 1962); aegirine — microcline metasomatites in the Yakokutsky massif, Yakutia (Kravchenko, Bykova, 1967); Kipawa carbonatites with wollastonite, orthoclase, aegirine, agrellite, Canada (Berry *et al.*, 1971; Scott, 1976); and fenites of the Murunsky complex, Yakutia (Lazebnik, Lazebnik, 1981; Konev *et al.*, 1996). Miserite at Hodzha-Achkan forms both separate acicular crystals and radial or fanlike aggregates up to 3 cm in size in rock. The color of miserite ranges from pink to saturated henna-red, and is related to the degree of manganese enrichment (MnO to 1.3 wt.%) (Fig. 3a, c). Miserite is the most important concentrator of *REE* in baratovite — bearing rocks at Hodzha-Achkan. Unlike miserite at Darai-Pioz, which is characterized by an increased dominance of yttrium *REE*, Hodzha-Achkan miserite is poor in yttrium and highly enriched in light lanthanides (Table 3). All microprobe analyses of miserite, as a rule, has a low totals, connected with the presence in the mineral of variable amounts of molecular water (Scott, 1976; Rozhdestvenskaya, Evdokimov, 2006). Very difficult mechanisms of isomorphous substitutions occur in miserite, and the idealized formula $KCa_5\square(Si_2O_7)(Si_6O_{15})(OH)F$, proposed by J. Scott (Scott, 1976), and sometimes seen elsewhere in the mineralogical literature, is not electroneutral, and carries a (-3) charge.

Table 3. **Chemical composition of miserite from Hodzha-Achkan (1–3) and Darai-Pioz (4, 5) massifs (wt.%)**

Component	Hodzha-Achkan			Darai-Pioz	
	1	2	3	4	5
SiO_2	50.30	50.26	49.80	49.16	49.93
TiO_2	0.00	0.22	0.12	0.22	0.30
ZrO_2	0.00	0.00	0.63	0.38	0.31
Nb_2O_5	0.00	0.00	0.31	0.77	0.54
Al_2O_3	0.00	0.00	0.06	0.00	0.00
Y_2O_3	0.00	0.00	0.44	0.59	0.93
La_2O_3	1.29	0.33	0.26	1.16	0.32
Ce_2O_3	3.06	0.90	0.68	2.25	1.20
Pr_2O_3	0.55	0.23	0.00	0.00	0.00
Nd_2O_3	0.59	0.51	0.32	0.45	0.31
MnO	0.00	0.42	0.48	0.15	0.14
FeO	0.25	0.30	0.35	0.20	0.28
CaO	32.88	35.08	34.13	32.18	33.46
Na_2O	0.00	0.16	0.00	0.00	0.00
K_2O	5.99	6.43	6.34	5.94	6.19
F	2.68	2.48	2.79	2.93	3.15
$-O=F_2$	–1.12	–1.04	–1.17	–1.23	–1.32
Total	97.59	97.32	96.71	96.38	97.06
Calculated on the basis of Si + Al = 8 apfu					
K^+	1.22	1.31	1.30	1.23	1.27
Na^+	0.00	0.05	0.00	0.00	0.00
Σ	1.22	1.36	1.30	1.23	1.27
Ca^{+2}	5.60	5.98	5.87	5.61	5.74
Mn^{+2}	0.00	0.06	0.07	0.02	0.02
Fe^{+2}	0.03	0.04	0.05	0.03	0.04
Y^{+3}	0.00	0.00	0.04	0.05	0.08
La^{+3}	0.08	0.02	0.02	0.07	0.02
Ce^{+3}	0.18	0.05	0.04	0.13	0.07
Pr^{+3}	0.03	0.01	0.00	0.00	0.00
Nd^{+3}	0.03	0.03	0.02	0.03	0.02
Nb^{+5}	0.00	0.00	0.02	0.06	0.04
Ti^{+4}	0.00	0.03	0.01	0.03	0.04
Zr^{+4}	0.00	0.00	0.00	0.03	0.02
Σ	5.95	6.22	6.14	6.06	6.09
Si^{+4}	8.00	8.00	7.99	8.00	8.00
Al^{+3}	0.00	0.00	0.01	0.00	0.00
ΣT	8.00	8.00	8.00	8.00	8.00
F^-	1.35	1.25	1.42	1.51	1.60
O^{-2}	22	22	22	22	22
$(OH)^{-*}$	0.17	0.72	0.41	0.42	0.28

*Note: * — values calculated based on compensation of charge. Analysis sum includes:*
1 — ThO_2 0.69 wt. % (corresponds to Th = 0.02 apfu);
3 — MgO 0.11 wt. % (corresponds to Mg = 0.03 apfu).

Other minerals which in some rock varieties become rock-forming are wollastonite, calcite, and quartz. *Wollastonite* consists of less than 1 vol.% in one type of rock, while in the others

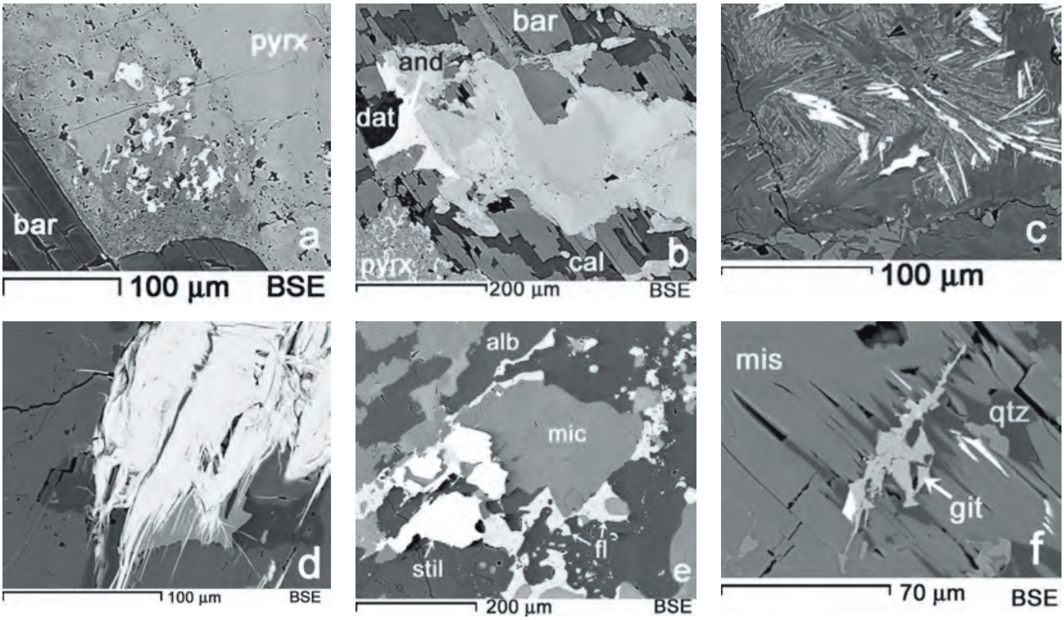


Fig. 7. Accessory minerals from baratovite-containing rocks of Hodzha-Achkan:
a — andradite — aegirine rim on the fringe of a coarse clinopyroxene grain (pyrx): bar — baratovite; light isolations — andradite; areas, enriched with aegirine component — darker in comparison with the less alkaline host pyroxene grains; black spots are cavities in the rock;
b — a zoned titanite crystal with baratovite (bar); pyrx — pyroxene grain near the aegirine — garnet rash; and — andradite; cal — calcite; dat — datolite;
c — ekanite: a deformed thin prismatic crystals in baratovite;
d — a mineral of hellandite group with Fe>> Ti: a thin — lamellar aggregate in baratovite;
e — stillwellite-(Ce): grains with microcline (mic), albite (alb), fluorite (fl);
f — gittinsite (git): isolated in miserite (mis); qtz — quartz; white grains — Ca-Ce-silicate.

it is a rock-forming mineral. It forms white to light gray board-like crystals up to 4 cm long. Its composition is close to stoichiometrical (Table 2, an. 6). *Calcite* in described rocks from Hodzha-Achkan, as well as in baratovite-containing quartz-albite-aegirine rocks from the Darai-Pioz (Reguir *et al*., 1999), is enriched in strontium (SrO to 1.1 wt.%), similar to calcite in intrusive carbonatites. The accessory minerals (table 1) of the described rocks are similar to those in baratovite-containing quartz-albite-aegirine rocks from Darai-Pioz (Dusmatov *et al*., 1975; Reguir *et al*., 1999), although there are some differences. One of the most widespread accessory minerals not only at Hodzha-Achkan, but also in other alkaline massifs of a matchaisky complex, including the Darai-Pioz massif, is *titanite* (Omelyanenko, Sirotinina, 1959; Ilyinsky, 1970; Ifantopulo, 1975; Reguir *et al*., 1999). The mineral forms wedge-shaped crystals to 5 mm in yellow-brown "flowers"; some segments demonstrate zonality and sectoriality and some of the zones are enriched in Sn, Nb, or *REE* (Fig. 7b, table 4, analysis 7).

The other widespread accessory minerals in the rocks described are *fluorbritholite-(Ce)* and the recently described *fluorcalciobritholite* (Pekov *et al*., 2007) (Fig. 4d, table 4, an. 2). Their forms (to 300 microns) are often met in baratovite, miserite. Minerals of the britholite group are very rare at Darai-Pioz and were not seen in the baratovite rocks. *Garnets* (mainly of andradite composition) are another characteristic accessory mineral group in the Hodzha-Achkan rocks which were not found in baratovite-bearing rocks at Darai-Pioz. Except for isolated andradite in clinopyroxene external rims, as noted above, garnet forms isomeric apple-green grains (0.1 — 4 mm) in leucocratic varieties of rock (Table 2, an. 7). Sulfides often associated with garnet include *molybdenite*, *galena*, and *pyrite*.

Other accessory minerals at Hodzha-Achkan are *ekanite* (frequently seen) and *turkestanite* (more rare), the structures of which are similar (Fig. 7c, table 4, an. 4, 5). They form thin-prismatic (up to 0.2 mm long), often deformed, bent crystals and are intergrown with miserite and baratovite. Turkestanite, unlike

Table 4. **Chemical composition (wt.%) of the accessory minerals from baratovite – containing rocks of Hodzha-Achkan: stillwellite-(Ce) (1), fluorcalciobritholite (2), fluorapatite (3), turkestanite (4), ekanite (5), tadzhikite-(Ce) (6), titanite (7), gittinsite (8), bazirite (9)**

Component	1	2	3	4	5	6	7	8	9
SiO_2	21.63	19.06	0.75	54.63	53.85	24.86	29.94	39.49	37.45
TiO_2	0.00	0.00	0.00	0.00	0.00	3.86	33.24	0.39	0.35
ZrO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.64
SnO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.31
ThO_2	2.44	5.25	0.00	0.00	20.16	5.07	0.00	0.00	0.00
UO_2	0.00	0.00	0.00	0.00	10.08	0.99	0.00	0.00	0.00
P_2O_5	0.00	5.23	39.88	0.00	0.00	0.00	0.00	0.00	0.00
Nb_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	1.68	2.07	0.00
B_2O_3	13.11*	n.d.	n.d.	n.d.	n.d.	14.31**	n.d.	n.d.	n.d.
Al_2O_3	0.00	0.00	0.00	0.22	0.12	0.44	1.48	0.00	0.00
Fe_2O_3	0.09	0.00	0.00	0.00	0.00	2.60	4.52	0.00	0.00
Y_2O_3	0.20	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00
La_2O_3	23.35	14.62	0.69	0.00	0.00	6.25	0.65	0.00	0.00
Ce_2O_3	27.22	22.14	0.77	0.68	0.00	11.75	0.77	0.00	0.00
Pr_2O_3	1.16	1.84	0.00	0.00	0.00	0.85	0.00	0.00	0.00
Nd_2O_3	4.63	6.12	0.00	0.00	0.00	3.44	0.61	0.00	0.00
Sm_2O_3	0.19	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00
Gd_2O_3	0.44	0.81	0.00	0.00	0.00	0.11	0.00	0.00	0.00
Tb_2O_3	0.50	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SrO	0.38	0.48	0.90	0.00	0.00	0.00	0.00	0.00	0.00
CaO	1.66	19.29	53.41	9.18	12.48	20.78	27.51	18.71	0.23
MnO	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	33.22
PbO	0.19	0.00	0.00	0.59	0.74	0.04	0.00	0.00	0.00
K_2O	0.00	0.00	0.00	2.73	0.00	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	1.81	0.09	0.00	0.00	0.00	0.00
F	0.00	2.22	4.18	0.00	0.00	0.00	1.24	0.00	0.00
$-O=F_2$	0.00	0.00	−1.75	0.00	0.00	0.00	−0.58	0.00	0.00
Total	**98.67**	**99.58**	**100.58**	**99.00**	**95.45**	**96.16**	**101.74**	**99.99**	**97.20**

*Note: "n.d." means that the component was not detected. 1 – stillwellite-(Ce) $(Ce_{0.44}La_{0.38}Ca_{0.08}Mg_{0.07}Nd_{0.07}Th_{0.02}Pr_{0.02}Gd_{0.01}Tb_{0.01}Sr_{0.01})_{3.11}B_{0.99}Si_{0.95}O_5$, formula calculated on the basis of O = 5 apfu, analysis sum includes (wt. %): MgO 1.12, Tm_2O_3 0.24; * – B_2O_3 is measured using WDS with STE crystal, U = 10 кV, I = 70 nA; 2 – fluorcalciobritholite $(Ca_{2.64}Sr_{0.04}Ce_{1.04}La_{0.69}Nd_{0.28}Pr_{0.09}Gd_{0.03}Tb_{0.03}Dy_{0.02}Th_{0.15}U_{0.05})_{5.02}(SiO_4)_{2.43}(PO_4)_{0.57}(F_{0.89}OH_{0.38})$, formula calculated on the basis of Si + P = 3 apfu, analysis sum includes (wt. %): Dy_2O_3 0.24; H_2O 0.45 (calculated); 3 – fluorapatite-(CaF) $(Ca_{4.97}Sr_{0.05}Ce_{0.02}La_{0.02})_{5.06}(PO_4)_{2.93}(SiO_4)_{0.07}F_{1.15}$, formula calculated on the basis of Si + P = 3 apfu; 4 – turkestanite $(Th_{0.92}U_{0.04}Ce_{0.04})_{1.00}(Ca_{1.43}Na_{0.51})_{1.94}(K_{0.51}Pb_{0.02})_{0.53}(Si_{7.96}Al_{0.04})_{8.00}O_{19.93}$, formula calculated on the basis of Si+Al = 8 apfu; 5 – ekanite $(Th_{0.68}U_{0.33})_{1.01}(Ca_{1.98}Pb_{0.03}Na_{0.03})_{2.04}(Si_{7.96}Al_{0.02})O_{20}$, formula calculated on the basis of O = 20 apfu; 6 – tadzhikite-(Ce) $Ca_2(Ca_{1.58}Y_{0.04}K_{0.04})_{1.66}(Ti_{0.47}Fe_{0.32}Al_{0.08})_{0.87}(Ce_{0.69}Pr_{0.05}La_{0.37}Nd_{0.20}Sm_{0.01}Gd_{0.01}Th_{0.19}U_{0.03})_{1.55}B_4Si_4O_{21.31}$, average of 3 analyses, formula calculated on the basis of Si = 4 apfu; ** B_2O_3 – calculated; 7 – titanite $(Ca_{0.96}Na_{0.01})_{0.97}(Ti_{0.82}Fe_{0.11}Al_{0.06}Nb_{0.02}Sn_{0.01}La_{0.01}Ce_{0.01}Nd_{0.01})_{1.05}Si_{0.98}O_{4.87}F_{0.13}$, formula calculated on the basis of cations sum = 3 apfu; 8 – gittinsite $(Ca_{1.00}Mn_{0.02})_{1.02}(Zr_{0.95}Nb_{0.05}Ti_{0.01})_{1.01}Si_{1.97}O_{7.00}$, formula calculated on the basis of O = 7 apfu; 9 – bazirite $(Ba_{1.03}Ca_{0.02})_{1.05}(Zr_{0.99}Sn_{0.01}Ti_{0.02})_{1.01}Si_{2.96}O$, formula calculated on the basis of O = 9 apfu.*

ekanite, is widespread at Darai-Pioz, where it is seen in many associations. In the Dzhilisuisky massif, neighboring Hodzha-Achkan, it is the main thorium concentrator (Ginzburg *et al.*, 1965; Pautov *et al.*, 1997; Reguir *et al.*, 1999). Among additional accessory minerals of the Hodzha-Achkan baratovite-bearing rocks are rare borosilicates of the hellandite group, including *tadzhikite-(Ce)* (Table 4, an. 6) and a poorly studied mineral, whose composition and X-ray powder data are close to those of tadzhikite, but with Fe>> Ti (Fig. 7d). These minerals are found as single grains, and as groups of flattened prismatic crystals up to 500 μm long as well as spherolites; their color is different shades of brown. It should be noted that at Darai-Pioz (which is the type locality for tadzhikite) (Efimov *et al.*, 1970), the mineral is a widespread accessory mineral, including an association with baratovite (Reguir *et al.*, 1999). Darai-Pioz's tadzhikite is not selective in *REE*, and two species of the tadzhikite subgroup – tadzhikite-(Y), and tadzhikite-(Ce) – are found there. Problems with crystal chemistry, rare earth distribution in the crystal structure of these minerals, and their nomenclature are discussed in a number of works (Chernitsova *et al.*, 1982; Hawthorne *et al.*, 1998; Reguir *et al.*, 1999; Oberti *et al.*, 1999; 2002). Unlike Darai-Pioz, at Hodzha-Achkan only cerium-dominant members of hellandite group are found. One additional accessory rare-earth borosilicate found in pyroxene-feldspar fenites with baratovite at Hodzha-Achkan is *stillwellite-(Ce),* which is found in the form of separate irregular grains (Fig. 7e; table 4, an. 1) up to 150 μm in size. Stillwellite-(Ce) is a very characteristic mineral of some Darai-Pioz rocks (Dusmatov *et al.*, 1963; Dusmatov 1964; 1971). On occasion it forms sharp crystals to several centimeters in diameter (Belakowski, 1991). In baratovite-containing quartz-albite-aegirine rocks at Darai-Pioz, stillwellite-(Ce) is described as crystals less than 50 μm in size, filling cracks and blebs in earlier formed minerals (Reguir *et al.*, 1999). Zirconium minerals in the baratovite rocks from the Hodzha-Achkan massif include gittinsite, bazirite, and zircon. *Gittinsite* is one of the late minerals; it is found in gap cracks in miserite crystals together with quartz (Fig. 7f, table 4, an. 1). At Darai-Pioz we found gittinsite only as a constituent part of eudialyte pseudomorphoses. At other locations where this mineral is found (the Kipava agpaitic complex in Canada (Ansell *et al.*, 1980) and the Khan-Bogdo rare-metal pegmatites in Mongolia (Tsareva *et al.*, 1993), it also occurs pseudomorphing minerals of the eudialyte group. *Bazirite* is a very rare mineral in baratovite-containing rocks of Hodzha-Achkan. It is found as single grains with hexagonal outlines to 50 μm (Table 4, an. 9). At Darai-Pioz, bazirite is seen with baratovite in association with titanite, filling in cracks in baratovite and aegirine (Reguir *et al.*, 1999), in pegmatites as a part of polymineral pseudomorphosis of eudialyte (Pautov, Khvorov, 1998), and in carbonatites with baratovite and aleksandrovite (Pautov *et al.*, 2010). *Zircon* is not a characteristic accessory mineral in baratovite-containing rocks of Hodzha-Achkan and Darai-Pioz; it is found in rare single grains. *Molybdenite* is the most typical sulfide mineral in the rocks of Hodzha-Achkan, with lamellar grains to 1.5 mm in diameter.

Baratovite description. Physical properties

Minerals of the baratovite-katayamalite series forms grains flattened on (001), thin lamellar grains, as a rule, without signs of crystallographic faces, sometimes forming fan-like aggregates, and more often random. The size of individual grains ranges from 0.02 mm to 2–3 cm, and the thickness of plates from 0.01 mm up to 1.0–1.5 mm (Fig. 4). The largest forms of baratovite are found in aegirine-feldspar rocks with miserite; baratovite in wollastonite rocks usually forms fine single grains (1–2 mm). Thin lamellar grains are transparent and colorless, while in larger grains pink coloring is observed. The luster is generally vitreous, although pearly on perfect cleavage planes. The mineral is very brittle, with perfect cleavage on (001). Two directions of cleavage are found, crossing the basal plane. In transparent sections in transmitted light baratovite is colorless, although cuts parallel to (001) have dark gray interference colors, and in slanted cuts abnormal indigo-blue interference colors are observed. The mineral is biaxial, optically positive, with 2V changeable from 70° to 90°, dispersion strong, $r > v$. The indices of refraction measured on the rotating spindle are as follows: $n_g = 1.674(2)$, $n_m = 1.671(3)$, $n_p = 1.666(3)$.

The microhardness of baratovite was measured in two sections (PMT-3 microdurometer, calibrated on NaCl, loading 100 g): in the basal plane and perpendicular to it. Microhardness in the basal plane is VHN (kg/cm^2) = 615 (average of 10 measurements, dispersion 490–710). For cuts perpendicular

Table 5. **Cell dimensions of baratovite minerals group**

Name	*a*, Å	*b*, Å	*c*, Å	β, °	*V*, A^3	Location	Reference
Baratovite	16.93(1)	9.742(5)	20.92(2)	112.51(5)	3187(5)	Hodzha-Achkan, Kyrgyzstan	Our data (photomethod)
Baratovite	16.93(2)	9.733(5)	20.94(2)	112.49(7)	3187(7)	Hodzha-Achkan, Kyrgyzstan	Our data (diffractogramm)
Baratovite	16.90(2)	9.73(1)	20.91(2)	112.30	3179	Darai-Pioz, Tajikistan	Dusmatov *et al.*, 1975
Baratovite	16.953(5)	9.752(3)	20.916(6)	112.46(2)	3195.8	Darai-Pioz, Tajikistan	Sandomirsky *et al.*, 1976
Baratovite	16.941(3)	9.746(2)	20.907(3)	112.50(10)	3189.1	Darai-Pioz, Tajikistan	Menchetti, Sabelli, 1979
Katayamalite*	16.923(3)	9.721(2)	20.909(3)	112.40(10)	3180	Ivagi, Japan	Baur, Kassner, 1992
Aleksandrovite	17.01 (2)	9.751(6)	21.00(2)	112.45(8)	3219(7)	Darai-Pioz, Tajikistan	Pautov *et al.*, 2010

Note. * — α=89.98(10); γ=89.94(10) (Baur, Kassner, 1992)

to the basal plane poor 1st sort hardness anisotropy was observed (average of 17 measurements): across cleavage cracks VHN = 725 (dispersion 500—835); along cleavage cracks VHN = 620 (dispersion 495—700). The microhardness of baratovite from Darai-Pioz measured in similar conditions (on 10 measurements) is VHN = 615 both for sections (001) and cross-sections. The values found for microhardness of baratovite in both the Hodzha-Achkan samples and those from Darai-Pioz correspond to 5—6 on Moh's scale, which is higher than the original value of $3^1/_2$ noted in the original description of the mineral (Dusmatov *et al.*, 1975).

The mineral density measured in Clerichi solution by the equitation method for separate grains is $D_{\text{meas.}} = 2.92(2)$ g/cm^3. The calculated density based on the cell parameters, obtained from the X-ray space dimensions (Table 5) and average composition (Table 6, an. 1), is $D_{\text{calc.}} =$ 2.91 g/cm^3.

The baratovite-group minerals from Hodzha-Achkan, as well as baratovite from Darai-Pioz and katayamalite from Ivagi (Fig. 3), have a bright white-bluish fluorescence in short-wave UV-radiation. Heterogeneity of fluorescence intensity is observed among individual grains of baratovite. This effect is seen more intensely in the cathodoluminescence mode after excitation by an electron probe (Fig. 8). According to B.S. Gorobets and A.A. Rogozhin (2001), photoluminescence of Darai-Pioz baratovite is related to O*- and Fe^{+3}-luminescence centers. Subsequently, luminescence of baratovite from Darai-Pioz and katayamalite from Ivagi was studied by A. Sidike and coauthors (Sidike *et al.*, 2010), who related it to Ti—O$_6$ centers.

The IR spectrums of baratovite both from Darai-Pioz and Hodzha-Achkan are similar (Fig. 9), and have a strong double absorption band in the range of 900—1100 cm^{-1}, which is characteristic of ring silicates with sextuple rings of Si—O$_4$ — tetrahedrons, less strong bands in the range of 520—540 and 470—480 cm^{-1}, connected to ν_4 oscillation of Si—O$_4$, and an absorption band of 685—695 cm^{-1}, connected with ν_3 oscillation of Ti—O$_6$ (Povarennykh, 1979).

The chemical composition of baratovite

Only a few number of chemical analyses of baratovite and katayamalite have been published (Dusmatov *et al.*, 1975; Murakami *et al.*, 1983; Reguir *et al.*, 1999; Sidike *et al.*, 2010; Pautov *et al.*, 2010). Of these, the most complete is the analysis of katayamalite published by Nobihude Murakami with colleagues (1983). Other analyses do not provide data for all possible elemental components (i.e., there are no data for one or several of the following components: Li, F, OH). The most complete analysis of baratovite is found in the original description (Dusmatov *et al.*, 1975); it is calculated on the formula $KLi_2Ca_8Ti_2Si_{12}O_{37}F$, in contrast to $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$, as obtained from the structural analysis (Sandomirsky *et al.*, 1976; Menchetti, Sabelli, 1979). However, because data on water content are not shown in the first baratovite analysis (Dusmatov *et*

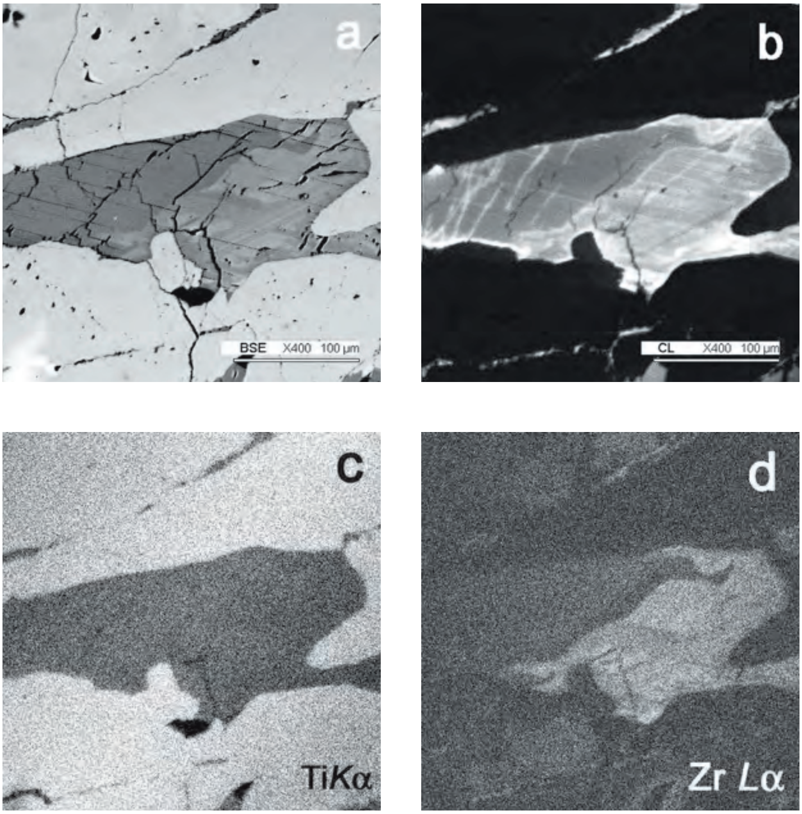


Fig. 8. Baratovite grain in titanite from miserite-aegirine-microcline rock, Hodzha-Achkan: a — BSE mode: grey — baratovite, light grey — titanite; b — cathodoluminescence mode; c, d — the X-ray image shows characteristic emission of TiKα (c) and ZrLα (d). The BSE image (fig. 8a) shows that there is complex inhomogeneity of the baratovite grain within the average atomic number; correlation with zirconium distribution (fig. 8d) is easily visible. The image in cathodoluminescence mode (fig. 8b) is much more complex: the general motif mirrors both the BSE image and the X-ray map of Zr distribution, but it is complicated by presence of areas, linear zones with a more intensive luminescence, possibly caused by deformations and an increased number of defects. Images are obtained by Camebax-microbeam with operating conditions: U = 15 kV, I = 20 nA.

al., 1975), and the fluorine content (Table 6, an. 5), after recalculation from the structural formula, is F = 0.79 apfu (which is less than half the number of additional anions in the formula), the legitimacy of katayamalite as a distinct mineral species has been questioned. Werner H. Baur and Dethard Kassner (1992), having reviewed the results of interpretation of the katayamalite structure $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH)_2$, showed that this mineral, previously described as triclinic (Kato, Murakami, 1985), within experimental error can be well described by a monoclinic cell with space group *C*2/*c*. This is the same as baratovite, and baratovite's formula, considering the insufficient amount of fluorine according to the first analysis, should be written down as $KLi_3Ca_7(Ti,Zr)_2[Si_6O_{18}]_2(OH,F)_2$ (Baur, Kassner, 1992). Both the formulas $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$ (Clark, 1993; Anthony *et al.,* 1995; Minerals, 1996; Krivovichev, 2008), and $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH,F)_2$ (Back, Mandarino, 2008) are published for baratovite in different handbooks. Based on our work, we consider that baratovite is the fluorine dominant mineral, while katayamalite is the hydroxyl dominant species. Since we were unable to find in the literature any analysis of baratovite in which fluorine and water were determined at the same time, except an electron probe analysis of the mineral (in which, along with other components, fluorine was defined), we attempted to obtain analytical data on the composition of the baratovite group minerals both from Hodzha-Achkan and from Darai-Pioz, including direct determination of F, OH, and Li.

Two samples of baratovite with large plates (one sample from Hodzha-Achkan and the other from Darai-Pioz, from miserite-bearing quartz-albite-aegirine rocks) were chosen for study. Pure material, free from visible inclusions, was separated under a binocular microscope in short-wave ultraviolet light. The weights of samples for determination of Li and Rb by ICP-OES method were 40 — 50 mg and by flame photometry 20 mg, for F determination by potentiometer method 20 — 30 mg, and for water determination by element analysis with chromatographic completion 2 — 7 mg (Table 6, analyses 1, 4). In the analyses of the mineral from Hodzha-Achkan, F (apfu) is

Table 6. **Chemical composition (wt.%) of baratovite and katayamalite from Hodzha-Achkan, Darai-Pioz and Ivagi**

Component	Hodzha-Achkan			Darai-Pioz				Ivagi		
	baratovite		katayamalite	baratovite			katayamalite	katayamalite		
	1	2	3	4	5	6	7	8	9	10
SiO_2	51.15	51.29	51.01	51.44	50.46	51.57	49.63	51.84	52.31	51.75
TiO_2	9.76	8.87	7.97	9.89	9.51	10.55	6.01	10.70	10.99	11.13
ZrO_2	1.74	2.22	3.71	1.18	2.28	0.90**	6.08	0.76	–	0.15**
SnO_2	0.46	1.01	0.87	0.87	–	>0.13**	2.04	0.17	0.00	0.06**
Nb_2O_5	0.04	0.00	0.23	0.18	0.72	>0.14**	0.00	0.04	–	0.07**
Al_2O_3	0.06	0.20	0.06	0.00	–	0.02	0.07	0.04	0.00	0.00
Fe_2O_3	0.39	0.60	0.44	0.46	0.50	0.31	0.29	0.23	0.29	0.26
CaO	27.48	26.72	26.72	27.12	30.36	27.36	26.67	27.00	28.25	28.58
MgO	0.03	0.00	0.00	0.03	–	0.00	0.00	0.01	0.00	0.01
MnO	0.11	0.00	0.00	0.10	0.50	0.34	0.15	0.20	0.22	0.07
K_2O	3.03	3.17	3.07	3.01	2.96	2.89	3.03	3.09	2.89	2.85
Na_2O	0.20	0.15	0.23	0.29	0.70	0.36	0.15	0.23	0.22	0.36
Li_2O	3.14	3.20*	3.17*	3.15	2.05	–	3.10*	3.22*	3.25	–
Rb_2O	0.12	n.d.	n.d.	–	–	0.075**	0.00	n.d.	–	0.023**
F	1.51	1.75	0.94	1.45	1.05	2.51	1.02	0.25	0.34	0.53
H_2O	0.61	0.46*	0.84*	0.68	–	–	0.76*	1.12*	1.21	–
$-O=F_2$	−0.63	−0.73	−0.39	−0.61	−0.44	–	−0.43	−0.11	−0.14	–
Total	**99.18**	**98.91**	**98.87**	**99.24**	**100.31**	–	**98.58**	**98.67**	**99.83**	–
Calculated on the basis of Si + Al = 12 apfu										
K^+	0.91	0.94	0.92	0.90	0.90	0.86	0.93	0.91	0.85	0.84
Na^+	0.09	0.07	0.10	0.13	0.32	0.16	0.07	0.10	0.10	0.16
Rb^+	0.02	–	–	–	–	–	–	–	–	–
Li^+	2.96	3.00	3.00	2.96	1.96	–	3.00	3.00	3.00	–
Ca^{+2}	6.90	6.67	6.73	6.78	7.74	6.82	6.90	6.69	6.94	7.10
Mg^{+2}	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{+2}	0.02	0.00	0.00	0.02	0.02	0.07	0.03	0.04	0.04	0.01
Ti^{+4}	1.72	1.55	1.41	1.73	1.71	1.85	1.09	1.86	1.90	1.94
Zr^{+4}	0.20	0.25	0.42	0.13	0.26	–	0.72	0.09	–	–
Sn^{+4}	0.04	0.09	0.08	0.08	–	–	0.20	0.02	–	–
Nb^{+5}	0.00	0.00	0.02	0.02	0.08	–	0.00	0	–	–
Fe^{+3}	0.07	0.11	0.08	0.08	0.09	0.05	0.05	0.04	0.05	0.05
Al^{+3}	0.02	0.05	0.02	–	–	0.00	0.02	0.01	–	0.00
Si^{+4}	11.98	11.95	11.98	12.00	12.00	12.00	11.98	11.99	12.00	12.00
F^-	1.12	1.29	0.70	1.07	0.79	1.84	0.77	0.18	0.25	0.39
OH^-	0.95	0.71	1.30	1.06	–	–	1.23	1.72	1.85	–
O^{-2}	35.92	35.64	35.72	35.79	37.23	–	36.02	35.78	35.78	–

Note: «–» means, that data for a component are not provided.

** – H_2O and Li_2O calculated on basis of (F + OH) = 2.00 apfu, Li = 3.00 apfu. 1 – average of 47 electron-microprobe analyses, instead: Li_2O (average from two analyses obtained both by ICP OES and flame photometry methods); Rb_2O (flame photometry); F (potentiometry); H_2O (CHN-analysis with chromatographic completion, average of 3 determinations); 2 – electron-microprobe analysis (with maximum F amount); 3 – electron-microprobe analysis (with maximum $H_2O_{calc.}$ amount); 4 – average of 11 electron-microprobe analyses (3 analyses – WDS JCXA 733, 8 analyses – EDS ISIS, CamScan-4D) instead: Li_2O (average from two analyses obtained both by ICP OES and flame photometry methods); F (potentiometry); H_2O (CHN-analysis with chromatographical completion, average of 2 determinations); 5 – «wet chemistry», analyst A.V. Bykova (Dusmatov et al., 1975); 6 – electron-microprobe analyses, ** – calculated on oxides from ICP-MS data. Besides, (ppm): Zn 240, Sr 903, Cs 168, Ba 4410, Hf 294 (data with amounts >100 ppm are given) (Sidike et al., 2010); 7 – electron-microprobe analyses (Pautov et al., 2010); 8 – electron-microprobe analyses (WDS); 9 – electron-microprobe analyses, Li_2O – flame photometry; H_2O – gravimetry; F – potentiometry) (Murakami et al., 1983); 10 – electron-microprobe analyses, ** – calculated on oxides from ICP-MS data. Besides, (ppm): Zn 340, Sr 754, Ba 2570, Ta 187 (data with amounts >100 ppm are given)(Sidike et al., 2010).*

Table 7. **Representative electron probe analyses (wt.%) data sampling for baratovite and katayamalite from the Hodzha-Achkan massif**

Component	Baratovite							Katayamalite							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	51.75	52.08	50.85	50.72	50.93	52.00	50.83	51.48	51.80	51.47	51.77	51.32	51.79	51.48	51.76
TiO_2	8.71	10.13	9.62	9.93	10.14	10.01	9.87	9.77	9.96	9.56	10.27	10.14	9.88	7.83	9.43
ZrO_2	2.25	1.12	1.38	1.27	1.28	1.61	1.97	1.65	1.22	1.44	1.50	1.80	1.22	3.68	1.78
SnO_2	1.01	0.00	0.64	0.85	0.71	0.72	0.00	0.13	0.74	0.13	0.67	0.74	0.76	0.87	1.29
Nb_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.08	0.44	0.00	0.00	0.00	0.00
Al_2O_3	0.18	0.19	0.00	0.11	0.00	0.00	0.00	0.07	0.00	0.07	0.00	0.00	0.00	0.00	0.10
Fe_2O_3	0.60	0.44	0.36	0.22	0.23	0.60	0.39	0.43	0.39	0.43	0.76	0.73	0.35	0.44	0.41
CaO	26.73	28.54	27.86	27.78	27.58	28.09	27.73	27.15	28.13	27.16	28.25	27.91	28.12	26.73	26.85
MgO	0.00	0.00	0.00	0.10	0.11	0.00	0.00	0.05	0.00	0.02	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.27	0.00	0.00	0.00	0.00	0.22	0.15	0.00	0.20	0.19	0.00	0.00	0.00	0.00
K_2O	3.17	2.83	3.20	2.90	2.85	2.95	2.95	3.03	3.14	3.06	2.96	3.13	3.14	3.07	3.03
Na_2O	0.15	0.38	0.23	0.26	0.27	0.33	0.31	0.21	0.19	0.19	0.21	0.29	0.20	0.23	0.14
Li_2O^*	3.17	3.10	3.12	3.13	3.14	3.08	3.13	3.18	3.09	3.20	3.01	3.02	3.08	3.16	3.16
F	1.76	1.64	1.56	1.53	1.41	1.47	1.36	1.25	1.25	1.24	1.22	1.06	1.07	0.98	0.97
H_2O^*	0.47	0.53	0.54	0.55	0.61	0.61	0.63	0.70	0.70	0.71	0.72	0.79	0.79	0.82	0.83
$-O=F_2$	-0.74	-0.69	-0.66	-0.64	-0.59	-0.62	-0.57	-0.53	-0.53	-0.52	-0.51	-0.44	-0.45	-0.41	-0.41
Total	99.21	100.56	98.70	98.71	98.67	100.85	98.82	98.75	100.08	98.44	101.46	100.49	99.95	98.88	99.34
Calculated on the basis of Si + Al = 12 apfu															
K^{+1}	0.93	0.83	0.96	0.87	0.86	0.87	0.89	0.90	0.93	0.92	0.88	0.93	0.93	0.91	0.89
Na^{+1}	0.07	0.17	0.11	0.12	0.12	0.15	0.14	0.09	0.09	0.09	0.09	0.13	0.09	0.10	0.06
Li^{+1}	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Ca^{+2}	6.61	7.02	7.04	7.02	6.96	6.95	7.01	6.77	6.98	6.77	7.02	6.99	6.98	6.68	6.65
Mg^{+2}	0.00	0.00	0.00	0.04	0.04	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mn^{+2}	0.00	0.05	0.00	0.00	0.00	0.00	0.04	0.03	0.00	0.04	0.04	0.00	0.00	0.00	0.00
Ti^{+4}	1.51	1.75	1.71	1.76	1.80	1.74	1.75	1.71	1.74	1.67	1.79	1.78	1.72	1.37	1.64
Zr^{+4}	0.25	0.13	0.16	0.15	0.15	0.18	0.23	0.19	0.14	0.16	0.17	0.21	0.14	0.42	0.20
Sn + 4	0.09	0.00	0.06	0.08	0.07	0.07	0.00	0.01	0.07	0.01	0.06	0.07	0.07	0.08	0.12
Nb^{+5}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.00
Fe^{+3}	0.10	0.08	0.06	0.04	0.04	0.10	0.07	0.08	0.07	0.08	0.13	0.13	0.06	0.08	0.07
Al^{+3}	0.05	0.05	0.00	0.03	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.03
Si^{+4}	11.95	11.95	12.00	11.97	12.00	12.00	12.00	11.98	12.00	11.98	12.00	12.00	12.00	12.00	11.97
F^{-1}	1.29	1.19	1.16	1.14	1.05	1.07	1.02	0.92	0.92	0.91	0.89	1.22	1.22	0.72	0.71
OH^{-1}	0.71	0.81	0.84	0.86	0.95	0.93	0.98	1.08	1.08	1.09	1.11	0.78	0.78	1.28	1.29
O^{-2}	35.43	35.92	36.02	36.08	36.09	36.04	36.13	35.75	35.99	35.64	36.4	36.4	36.02	35.54	35.63

*Notes: * – H_2O and Li_2O are calculated on the basis of (F + OH) = 2.00 apfu, Li = 3.00 apfu.*

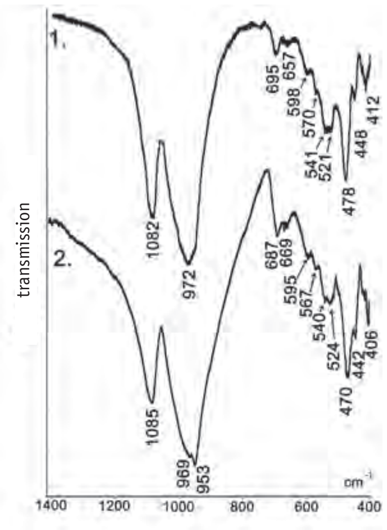


Fig. 9. Baratovite IR spectra:
1 — Hodzha-Achkan (operating conditions — microtablet with KBr, Specord-75IR);
2 — Darai-Pioz (operating conditions — tablet with KBr, Avatar 370 FT-IR Fourier spectrometer).

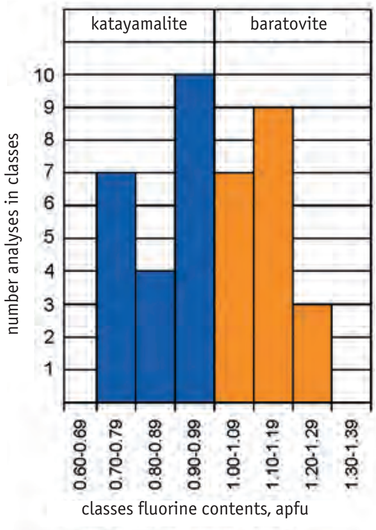


Fig. 10. A histogram of fluorine distribution in the baratovite-katayamalite mineral series from the Hodzha-Achkan massif (based on 40 analyses).

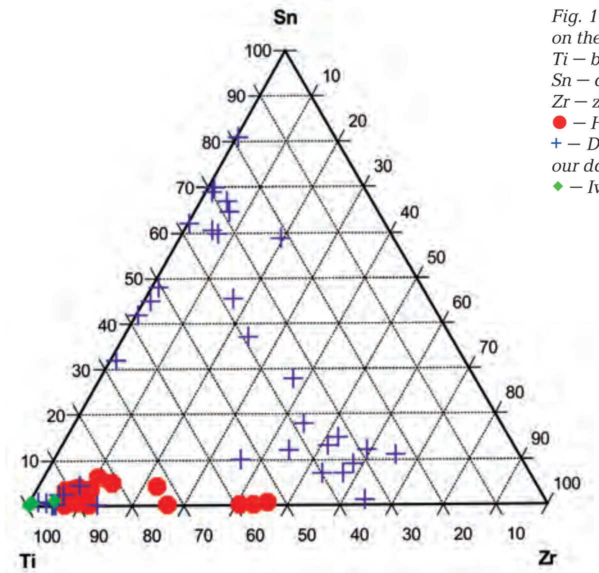


Fig. 11. Compositions (mol. %) of the baratovite mineral group on the ternary chart of end members:
Ti — baratovite and katayamalite;
Sn — aleksandrovite;
Zr — zirconium analog of baratovite:
● *— Hodzha-Achkan (by results of 48 electron probe analyses);*
\+ *— Darai-Pioz (Dusmatov et al., 1975; Reguir et al., 1999 and our data);*
◆ *— Ivagi (Murakami et al., 1983; our data).*

slightly more prevalent than OH, while this ratio is close to 1:1 for the mineral from Darai-Pioz. Because different parts of crystals, which can differ in F/OH ratio, are mixed in these samples, these analyses represent an average of the material from each locality. Localized electron probe analyses show that F amounts in the baratovite group minerals of Hodzha-Achkan and Darai-Pioz massifs are changeable and correspond to both hydroxyl- and fluorine-dominant phases. A histogram of F distribution, based on electron probe analysis, for minerals of baratovite group from Hodzha-Achkan is shown in figure 10, which also shows that most of the analyses are approximately in the middle of the baratovite-katayamalite series.

The baratovite from Hodzha-Achkan, unlike katayamalite from Ivagi, is slightly enriched in tin and zirconium, making it similar to baratovite from Darai-Pioz, where tin and zirconium are concentrated up to a tin baratovite analog (aleksandrovite) and an unnamed Zr-analog of baratovite (Fig. 11; tables 6, 7). Occupation of the *M*2 octahedral position of baratovite with zirconium is probably the result of crystallization of the mineral from high-alkaline conditions. As

Table 8. **X-ray powder diffraction data on baratovite from the Hodzha-Achkan massif**

Photo-method		Diffractogram		Calculated data					Photo-method		Diffractogram		Calculated data				
I	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*h*	*k*	*l*	*I*	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*h*	k	l
		1	9.70	3	9.663	0	0	2	20	2.106	2	2.108	10	2.107	4	2	5
20	8.34	1	8.31	6	8.269	1	1	0			2	2.095	4	2.101	-2	4	5
		2	7.70	6	7.686	-2	0	2	10	2.091			2	2.083	6	2	2
30	7.04	2	7.03	13	7.024	-1	1	2	20	2.082			10	2.079	7	1	1
10	5.74	4	5.74	12	5.735	1	1	2	10	2.078			4	2.077	3	1	7
		2	5.19	3	5.185	2	0	2	10	2.070			3	2.071	-4	2	9
		1	5.08	4	5.069	-2	0	4	20	2.043			5	2.043	-5	3	7
		2	4.83	2	4.832	0	0	4	< 10	2.027			4	2.029	5	1	5
20	4.606	4	4.599	8	4.597	3	1	0	40	2.006			14 6	2.009 2.008	1 2	3 4	7 4
20	4.354	3	4.352	8	4.350	0	2	2	10w	1.997			4	2.000	-1	3	8
10	4.266			32	4.231	-4	0	2	20	1.981			14	1.985	-5	1	10
100	4.229	23	4.234	38	4.222	-2	2	1	10	1.943			12 3	1.944 1.943	4 -7	2 3	6 3
10	4.169			8	4.166	3	1	1	10w	1.932	3	1.932	11	1.933	0	0	10
10	4.138	7	4.139	16	4.135	2	2	0	10w	1.911			2	1.911	-4	2	8
		3	4.120	14	4.114	-2	2	2	20	1.883			4	1.888	-2	4	7
90	4.088	13	4.092	43	4.090	-3	1	4	30w	1.872			6	1.863	7	1	3
80	3.889	16	3.889	43	3.885	0	2	3	20w	1.855			7	1.853	1	3	8
30	3.852	7	3.849	1 9	3.852 3.846	-2 1	2 1	3 4	10	1.849			2	1.848	6	2	4
		1	3.810	1	3.810	-1	1	5	30	1.845			26	1.846	-9	1	4
100	**3.696**	**29**	**3.697**	81	3.695	3	1	2	40	1.842	8	1.841	15 26	1.842 1.840	-9 -3	1 5	5 1
40	3.620	8	**3.621**	22	3.621	-3	1	5	10	1.838			26 24	1.839 1.838	-3 -6	5 4	2 2
10	3.555	4	3.552	2	3.550	2	2	2	10	1.832			15 20	1.834 1.832	-9 -6	1 4	3 4
10	3.513	3	3.519	4	3.512	-2	2	4	30w	1.823			11 4 5	1.825 1.822 1.822	3 -9 -7	5 1 1	0 6 10
20	3.482	4	3.486	6	3.485	-2	0	6	< 10	1.795			5	1.797	4	2	7
30	**3.433**	**19**	**3.432**	43	3.430	0	2	4	< 10	1.789			4	1.791	2	4	6
10	3.359	3	3.391						20	1.776			8	1.779	3	3	7
30	**3.260**	**9**	**3.263**	18	3.258	3	1	3	10w	1.762			2	1.763	-1	5	5
40	3.224			12	3.221	4	0	2	10	1.748			2 1	1.749 1.749	8 -2	2 2	1 11
100	**3.222**	**100**	**3.223**	100	3.221	0	0	6	20	1.742			5	1.743	-3	5	5
10	3.209			26	3.198	2	2	3	20	1.737	2	1.736	7 8	1.739 1.735	-9 6	1 2	8 5
90	**3.193**	**47**	**3.194**	94	3.192	-3	1	6	10	1.731			9	1.731	6	4	1
20	3.167	6	3.167	8	3.161	-4	2	1	10	1.716			12	1.714	-6	4	7
40	3.156			14	3.161	-2	2	5	40	1.712	2	1.713	11	1.711	9	1	0
20	3.147	11	3.149	23	3.147	-4	0	6	40	1.697			8	1.697	3	5	3
10	3.139			2	3.143	-4	2	3	20	1.687			6	1.686	-3	5	6
< 10	3.125	1	3.120	7	3.120	-5	1	1	10	1.683			4	1.682	-9	1	9
30w	3.098	**25**	**3.095**	35	3.099	1	3	1	10	1.679			1	1.676	-2	4	9
30w	3.088			48	3.087	-5	1	4	10w	1.672			2	1.674	6	4	2
30	3.051	43	3.044	75	3.049	4	2	0	10w	1.665			5	1.667	4	2	8
30	3.030	2	2.999	57	3.028	0	2	5	10	1.636			11	1.640	-3	3	11
10	2.980			5	2.978	5	1	0	20	1.629			8	1.629	6	2	6
90	**2.953**	**11**	**2.953**	99	2.953	1	3	2	20w	1.608	1	1.615	15	1.611	0	4	9

Table 8. **Continue**

Photo-method		Diffrac-togram		Calculated data					Photo-method		Diffrac-togram		Calculated data				
I	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*h*	*k*	*l*	*I*	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*h*	k	l
20	2.942			3	2.944	-1	3	3	10	1.603			2	1.604 1.601	8 0	2 6	3 2
80	**2.932**	**9**	**2.932**	92	2.932	-5	1	5	10	1.593			9	1.595	-6	2	12
80	2.882	14	2.883	78 51	2.882 2.880	4 3	2 1	1 4	10w	1.588			2 3	1.589 1.589 1.588	-8 -2 -1	4 6 3	5 2 11
< 10	2.863			11	2.868	2	2	4	10w	1.579			3	1.580	-5	1	13
10	2.837	3	2.833	7	2.834	-2	2	6	10	1.572			2 2 1	1.572 1.571 1.571	-2 -8 3	6 4 5	3 6 5
10	2.807	2	2.807	10	2.809	-3	3	1	10	1.569			4	1.570	-9	3	1
		2	2.800	4	2.801	-6	0	2	10	1.558			3 3	1.560 1.560	-3 -10	5 2	8 2
20	2.795			13	2.794	5	1	1	10	1.551			3 1	1.551 1.550	4 1	2 5	9 7
60	2.767	4	2.766	37	2.767	1	3	3	20	1.543			6 5	1.544 1.544	6 -8	4 4	4 7
20	2.757			18	2.756	-1	3	4	10	1.538			7	1.539	0	6	4
50	**2.740**	**3**	**2.742**	31	2.741	-5	1	6	10	1.531			8	1.531	6	2	7
40	**2.686**	**3**	**2.688**	19	2.687	4	2	2	30	1.523			4 5	1.524 1.522	-5 -6	3 4	12 10
10	2.655			3	2.655	3	3	1	10	1.515			9	1.518	9	1	3
20	2.641	**3**	**2.643**	13	2.643	-4	2	6	30	1.510			5 8	1.512 1.512	-2 -9	6 3	5 9
10	2.618			2	2.607	6	0	0	20	1.496			3	1.495	0	6	5
30	2.592			4	2.593	4	0	4	10	1.487			7	1.488	9	3	1
20	2.567			8	2.566	1	3	4	10	1.482			6	1.484	-1	3	12
10	2.552			7	2.555	-1	3	5	10	1.471			4 1	1.473 1.472	-4 -2	6 6	5 6
20	2.535			8	2.538	-5	1	7	10	1.463			4	1.465	7	1	7
20	2.495			2	2.496	-3	3	5	20	1.419			4	1.421	-8	4	10
10	2.485			10	2.484	4	2	3	10	1.378			7 6 3	1.381 1.380 1.378	3 0 6	1 0 6	12 14 0
30	2.441			6	2.441	-4	2	7	10	1.370			3	1.371	-6	6	6
< 10	2.431			5	2.428	-6	2	2	10	1.353			6 2 2	1.354 1.353 1.353	-12 -9 -5	2 5 3	5 4 14
40	2.412	5	2.416	4 13 17	2.416	-6 0 0	2 4 0	4 1 8	10	1.349			6 6 6	1.351 1.350 1.348	-3 -3 -9	7 7 5	1 2 3
10	2.398			7	2.392	5	1	3	10	1.342			5 3	1.343 1.343	-9 -3	5 7	6
30	2.366			5 14	2.367	3 1	3 3	3 5	20	1.336			5	1.338	-12	2	8
10	2.354			5	2.353	-1	3	6	10	1.331			4 2	1.332 1.332	3 -12	7 2	1 3
30	2.340			4	2.339	-7	1	4	20	1.326			4	1.327	6	6	2
40	2.339	3	2.339	12	2.339	-5	1	8	10	1.315			5	1.318	5	1	11
30w	2.285	**2**	**2.287**	9	2.289	4	2	4	20w	1.275			2	1.277	-2	6	10
20w	2.181	2	2.182	9	2.184	-3	3	7	10w	1.181			3 1	1.181	7 0	7 8	0 4
< 10	2.153			9	2.154	-5	1	9	10w	1.168			3 4	1.169 1.166	-2 6	8 4	5 10
< 10	2.141			2	2.145	-5	3	6	10w	1.143			6	1.145	7	7	2

Note. Photomethod: Huber 621 Guinier camera with a quartz monochromator; CuKα_1 *radiation; quartz as the internal standard. Diffractogram: DRON-2.0, CuKα radiation, Ni — filter, quartz as the internal standard. Indexes and intensities for calculated data column are taken from www.rruff.info. Lines used for calculation of cell dimensions (tab. 5) are highlighted in bold type, w — widened line.*

experimental work shows, in this case introducing zirconium into structures with coordination [6] (for example, in pyroxene, or amphibole structures), is preferable to formation of phases with a higher coordination of [7] or [8] (Jones, Peckett, 1980; Linthout, 1984; Duggan, 1988, Farges *et al.*, 1994; Piilonen *et al.*, 1998). This may explain the extreme rarity of zircon in these rocks. The problems of zirconium genetic crystal chemistry have been considered in a number of publications in detail (Pyatenko *et al.*, 1999; Pekov, 2005). The entry of tin into minerals of the baratovite, titanite, milarite and astrophyllite groups shows that tin behavior in high-alkaline systems in many respects is similar to that of titanium and zirconium.

X–ray powder diffraction data

Since X-ray powder data published in literature for baratovite (Dusmatov *et al.*, 1975) and katayamalite (Murakami *et al.*, 1983) are much poorer in reflections than calculated data, we have obtained not only the diffractogram (which can be complicated by almost inevitable texturing of material), but also powder data by photomethod in the Guinier camera (table 8). The X-ray powder diffraction data were obtained from Hodzha-Achkan samples from which material for wet chemistry determination of fluorine, water and rare alkalis was extracted. Material for powder data by Guinier method was extracted from the sample of baratovite in miserite-feldspar-aegirine rock (operating number 11HA_58). The parameters of cells calculated for both powder data, and also for baratovite, katayamalite and aleksandrovite taken from references, are shown in table 5.

Conclusions

(1) Very rare minerals of the baratovite-katayamalite series are found in fenite rocks of the Hodzha-Achkan massif (Kyrgyzstan). The find of baratovite is most likely the second, and that of katayamalite the third in the world.

(2) A complete wet chemical analysis of baratovite, including determination of Li_2O, H_2O, and F was performed for the first time. New data for minerals of the baratovite group were obtained, including more complete powder data and the mineral microhardness, which corresponds to 5 – 6 on the Moh's scale, a value higher than recorded in the previous literature.

(3) Baratovite and katayamalite, both at Darai-Pioz, and Hodzha-Achkan, has been found in pyroxene-feldspar fenites (according to fenite's classification of (Bardina, Popov, 1993)). In these rocks the minerals miserite (to 5.5 wt.% REE_2O_3), turkestanite, bazirite, and the rare boronsilicates-tadzhikite and stillwellite-(Ce) occur. However there are also differences between the fenites of Hodzha-Achkan and Darai-Pioz. First, the former is a little less alkaline, and, perhaps, of higher-temperature origin, than similar rocks at Darai-Pioz. Clinopyroxene from the Hodzha-Achkan massif fenites is poorer in aegirine in contrast to Darai-Pioz, and, especially, to Ivagi syenites. Unlike Darai-Pioz, in the Hodzha-Achkan fenites a garnet (andradite) occurs. If we compare thorium silicates, at Hodzha-Achkan ekanite, which is non-alkaline, is typical, whereas at Darai-Pioz its place is taken by alkaline turkestanite. The most important *REE* mineral is britholite, absent in Darai-Pioz's fenites. We have not excluded the possibility that katayamalite-containing rocks of Ivagi (Murakami *et al.*, 1983) are not syenites, but that they are high-alkaline fenites; yet we do not have enough of the actual material to confirm this.

(4) Baratovite and katayamalite in miserite-containing fenites of Darai-Pioz and of Hodzha-Achkan are the only lithium minerals, and are important concentrators of zirconium and tin.

(5) We believe, in contrast to Reguir and coauthors (Reguir *et al.*, 1999), that the origin of the baratovite-containing rocks of Hodzha-Achkan and Darai-Pioz is not a unique combination of several processes occurring at different times with different sources of substrate, but is a single complex process, with a common source of fenitization solutions. It is possible that carbonatites (Mayorov, Gavrilin, 1971), or syenite-carbonatites (Fayziyev *et al.*, 2010) were such sources.

(6) The Darai-Pioz mineralization, which has been represented in the past as unique, is duplicated to some extent in massifs of a matchaisky complex (and may be duplicated again in other occurrences). Our work on the baratovite-containing fenite rocks of the Hodzha-Achkan massif shows this clearly.

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COGENETIC ZIRCON, MONAZITE, XENOTIME, AND FLUORAPATITE FROM APOPICRITIC PHLOGOPITE–MAGNESITE GUMBEITES AT THE BEREZOVSKY GOLD DEPOSIT, URALS, RUSSIA

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Listvenite-like phlogopite-magnesite gumbeites, a new type of gumbeites at the Berezovsky gold deposit, Urals replaced deformed zinc chromite- and ilmenite-bearing variolitic picrite enriched in Ti, P, Ce, La, Nd, Y, U, Th, and Nb. This metasomatic rock is composed of Mn- and Ca-poor magnesite ($Mg_{83-91}Fe_{9-17}$), quartz, fluorphlogopite, potassium feldspar ($K_{94-97}Na_{3-6}$), albite ($Na_{98.5}Ca_1K_{0.5}$), muscovite enriched in F, rutile, chlorite ± dravite, dolomite, fluorapatite, monazite, zircon, xenotime, gersdorffite, siegenite, millerite, Co-bearing pyrite, and galena. Talc-magnesite altered rock of the outer zone contains hematite, hydroxylphlogopite, hydroxylapatite, and violarite. Clusters of fluorapatite, monazite, zircon and xenotime are intergrown with aggregates of rutile replacing deformed plates of ilmenite; the crystals of these minerals have compromise growth surface with quartz and magnesite. Dominant zones of zircon crystals contain 1.4 – 1.9 wt.% Hf and traces of U, Th, Y; zones enriched in U contain up to, wt.%: 3.8 U, 2.4 Hf, 1.4 Y, 0.8 Th, U/Th is 3 – 9. The composition of U-free and Th-poor (0.8 – 2.2 wt.% Th) monazite corresponds to the formula $(Ce_{0.40-0.43}La_{0.25-0.28}Nd_{0.16-0.18}Y_{0.02\text{-}0.05}Pr_{0.03}Sm_{0.02}Gd_{0.01}Eu_{0.01}Th_{0.01-0.02}Ca_{0.02})(P_{0.97-0.98}Si_{0.01-0.03})O_4$. Cores of crystals of monazite are enriched in Y; the temperature of their crystallization estimated from the Gratz-Heinrich equation (Gratz and Heinrich, 1997) is ca. 450°C, while that of rims is ca. 300°C. The composition of Th-free U-poor (0.1 – 0.8 wt.% U) xenotime corresponds to the formula $(Y_{0.71-0.74}Dy_{0.05-0.06}Gd_{0.04}Er_{0.03}Nd_{0.03}Yb_{0.02-0.03}Eu_{0.01}Tb_{0.01}Ho_{0.01}Lu_{0-0.01}Ca_{0-0.01})(P_{0.99-1}Si_{0.01})O_4$.

In the fluorapatite-monazite-zircon-xenotime assemblage, U is concentrated in zircon; Th is concentrated in monazite and to less extent in zircon; *LREE* and most Y are concentrated in monazite-(Ce) that is predominant over xenotime; the latter is a carrier of *HREE* and partially Y; fluorapatite is nearly *REE*- and actinide-free. Thus, the high-temperature gumbeites was found at the northern Berezovsky deposit for the first time.

12 tables, 15 figures, 58 references.

Keywords: apopicritic phlogopite-magnesite gumbeites, zircon, monazite, xenotime, apatite, tourmaline, Mg-rich muscovite, zincochromite.

Review of gumbeites formation

Gumbeites as a special type of hydrothermal metasomatites was reported for the first time by Korzhinsky (1953) at the Gumbeika scheelite deposits, South Urals, which were studied in detail by Matveev (1928). Like beresites, gumbeites is a product of CO_2 alteration. Quartz-carbonate-potassium feldspar assemblage is typical of gumbeites (Korzhinsky, 1953), whereas quartz-carbonate-muscovite assemblage is characteristic of beresites and listvenites (Karpinsky, 1887; Borodaevsky and Borodaevskaya, 1947; Sazonov, 1984; Spiridonov and Pletnev, 2002; Spiridonov, 1991). Sazonov (1984) suggested that beresites gradually changes downward to gumbeites. Grabezhev (1981) reported apogranitic gumbeites at the Berezovsky deposit for the first time. We established that at this deposit gumbeites and beresites occur at the same level without gradual transition; mineralogy and isotopic characteristics of gumbeites and associated ores differ from those of younger gold-bearing beresites; gumbeites replaced adamellite-porphyry; gumbeites is replaced by beresites and is cut by gold-bearing quartz veins (Spiridonov *et al.*, 1998_1; 2000).

Spiridonov *et al.* (1998_1) reported six varieties of the Ural gumbeites as temperature decreases: (1) biotite-calcite gumbeites accompanied with potassium feldspar-calcite-quartz veins and bodies with molybdoscheelite, apatite, pyrite, W-rich rutile, and monazite (ca. 450–400°), (2) biotite-calcite-dolomite gumbeites accompanied with potassium feldspar-dolomite-quartz veins with Mo-rich scheelite, pyrite, apatite, W-bearing rutile (ca. 400–370°), (3) biotite-dolomite gumbeites accompanied with potassium feldspar-dolomite-quartz veins with scheelite, pyrite, molybdenite-3*R*, apatite, and chalcopyrite (ca. 370–330°), (4) dolomite gumbeites accompanied by veins with scheelite, pyrite, chalcopyrite, galena enriched in Bi, tennantite-tetrahedrite, and Bi-Pb-Cu-Ag sulfosalts (ca. 350–290°), (5) picrophengite gumbeites accompanied with veins containing pyrite, galena, sphalerite, tennantite-tetrahedrite, meneghinite, and bournonite (ca. 310–260°), and (6) ferrophengite gumbeites accompanied with adularia-calcite-quartz veins containing pyrite, galena, cleophane, tennantite-tetrahedrite, aikinite, altaite, tetradymite, hessite, native gold, andorite, and late barite, strontianite, and witherite (< 200°) (Spiridonov *et al.,* 1998_1). Gumbeitization is expressed as influx of CO_2, K, S, and As with SiO_2 and Na partially being removed. Phosphorous is mobile at the formation of gumbeite. It is removed and input in back zones of various alteration columns of gumbeite. The mobility of P during gumbeitization is one of the reasons to form scheelite ore because P strongly stabilizes polytungsten complexes (probable transfer species of W).

High-temperature gumbeites occurs at the southwestern Berezovsky deposit at the contact with the Shartash pluton. These are quartz veins with molybdoscheelite and tourmaline, which were studied by Kutyukhin (1948). Lower-temperature gumbeites 3–6 including talc-carbonate altered rock (Spiridonov *et al.*, 2000), carbonate-sulfide-quartz veins with scheelite (Shteinberg, 1939; Kurulenko *et al.,* 1984), molybdenite (Kutuykhin, 1937), apatite (Avdonin, 1955), galena, tennantite-tetrahedrite, and sphalerite (Chesnokov *et al.,* 1975), and barren hematite-quartz veins (Spiridoniv *et al.,* 1998_1) are found in the other parts of the deposit.

Shartash granodiorite–adamellite complex

Early to Middle Carboniferous gold-bearing granodiorite complexes are located at the eastern slope of the Herzinian Urals (Sobolev, 1966; Bushlyakov and Sobolev, 1976; Ershova and Levitan, 1978; Levitan *et al.*, 1979; Fershtater, 1992; Fershtater *et al.*, 1994; Puchkov, 2010). Usually, this assemblage is regarded to orogenic. This early orogenic, more exactly inversion assemblage, accompanies and terminates the major inversion of folded area that is transition from downwarping to upwarping, termination of arc stage, and transition to orogenic stage. Geochemical and lithological zoning is typical of the granodiorite assemblage of folded areas (Spiridonov, 1995): in troughs (sinclinorium and related structures, at the upper structural level of which, folding basis is usually steep to vertical), there are Na-Ca tonalite-granodiorite-plagiogranite plutons with gold mineralization and negligible Bi content (in the studied area, these are the Upper Iset and similar intrusions); in raises (anticlinorium structures, median masses, microcontinents within folded areas, at the upper level of which folding basis is gentle to horizontal), there are K-Na-Ca granodiorite-adamellite plutons with gold mineralization and high Bi content (in the studied area, these are the Shartash and similar plutons). K-Na-Ca granitic rocks are noticeably enriched in Rb, Pb, and Ba, which are elements coherent to K; these are enriched in F and contain F-rich apatite and biotite (Fershtater *et al.*, 1994; Kholodnov and Bushlyakov, 2002). Formation of the gumbeites is related to the K-Na-Ca plutons (Spiridonov *et al.,* 1997_2; 1998_1).

The classic Berezovsky deposit of gold-quartz beresite-listvenite formation is located in the distal over-intrusion zone of the Shartash adamellite pluton (Borodaevsky and Borodaevskaya, 1947; Ivanov, 1948; Bellavin *et al.*, 1970; Laipanov and Mikhailova, 1982; Borodaevsky *et al.*, 1984; Sazonov, 1984). The pluton intruded Ordovician to Lower Silurian deformed sedimentary and basaltic sequences cut by dolerites, gabbro, and gabbro-pyroxenites, and hosting plates of serpentinite (Borodaevsky *et al.*, 1984; Rapoport *et al.,* 1994). Serpentinized harzburgite and other ultramafic rocks contain ferrichromite, chrome magnetite, and zincochromite, which are metamorphic products of primary aluminum chromite and magnesiochromite (Spiridonov *et al.*, 1997_1, 1998_1). Hornfelses of the shallow Shartash pluton contain andalusite and sillimanite. According to N.A. Ershova and R.S. Kurulenko, it comprises three phases of adamellite. Adamellite is cut by numerous veins and dykes of aplite, microadamellite, vein granite including pegmatoids. Adamellite is intruded by dykes of granite-porphyres, diorite-porphyrites, miscrodiorites, and lamprophyres. Dykes of granodiorite-, adamellite-, granite- and plagiogranite-porphyres are predominant. Allanite is typical accessory mineral of these rocks (Spiridonov *et al.*, 2013).

K-Ar age of the Shartash granitoids is 315 ± 15 Ma; K-Ar age of porphyry granite dykes is 316 ± 12 and 306 ± 18 Ma (Ovchinnikov et al., 1989) that is close to the boundary between Early and Middle Carboniferous. Rb/Sr age of the Shartash granitoids and granite-porphyres is 328 ± 18 Ma (Shteinberg *et al.,* 1989); U/Pb age of zircon from the Shartash adamellite and granite-porphyres is 302 ± 3 and 305 ± 7 Ma, respectively (Pribavkin *et al.,* 2012).

Pre-gold quartz-tourmaline metasomatites with Li-bearing muscovite and poor Sn mineralization, K propilite with Mo-Cu mineralization, Na propylite with epidote-quartz veins, talc-carbonate metasomatites, and gumbeites with scheelite are developed within the Berezovsky deposit (Kutyukhin, 1947, 1948; Borodaevsky and Borodaevskaya, 1947; Grabezhev, 1981; Kurulenko *et al.,* 1984; Spiridonov *et al.,* 1998_1, 2000). Quartz-tourmaline metasomatites is related to the Shartash pluton; according to Koptev-Dvornikov (1955), it is referred to the first-stage process. Propylites, gumbeites, and later beresites and listvenites are related to dykes of adamellite-porphyres, microadamellite, diorite-porphyres, and lamprophyres. These are deep-seated dykes or dykes of the second stage according to Koptev-Dvornikov (1955). These dykes terminating the Shartash granodiorite-adamellite complex and altered rocks are paragenetically related to the Shartash pluton (Ershova and Levitan, 1978; Borodaevsky *et al.*, 1984). According to our data, ^{40}Ar/^{39}Ar age of muscovite from three samples of the Berezovsky gold-bearing beresite is 306.0 ± 3.6, 312.6 ± 3.8, and 323.6 ± 3.7 Ma (Institute of Geology and Geophysics, Siberian Branch, Russian Academy of Sciences, A.V. Travin analyst). Thus, the isotopic age of post-granitoid metasomatites does not differ from that of the Shartash adamellite and adamellite-porphyres.

Listvenite–like apopicritic gumbeites of the Berezovsky deposit

Studied material. We have studied listvenite-like phlogopite-magnesite metasomatites, a new type of gumbeites developed in the central Berezovsky deposit (level -412 m, Central pit). Its precursor is variolitic picrites occurred as branched subvolcanic dykes of 0.1 to 1.5 m thick cutting foliated hurzburgitic serpentinite. Picrites and serpentinites are cut by dykes of adamellite-porphyres. Varioles range from 3 to 21 mm in size (Fig. 1); chrome spinel is frequent in the core of variole. Hand specimens up to 30 cm across were cut; thin sections, polished sections, and polished samples were prepared. According to optical microscopy, gumbeites replaced deformed picrites.

Analytical techniques. Routine bulk analyses of altered rocks were performed at chemical laboratory at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences. Content of trace elements was measured by ICP-MS at the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements. Most BSE images and electron microprobe data were obtained with a Jeol SM-6480 LV electron microscope equipped with EDS (N.N. Korotaeva analyst, Division of Petrology, Geological Faculty, Moscow State University). *REE*- and actinide-bearing minerals were examined with a Camebax-microbeam electron microprobe (I.M. Kulikova analyst, Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements). R.L. Barinsky in 1958 developed

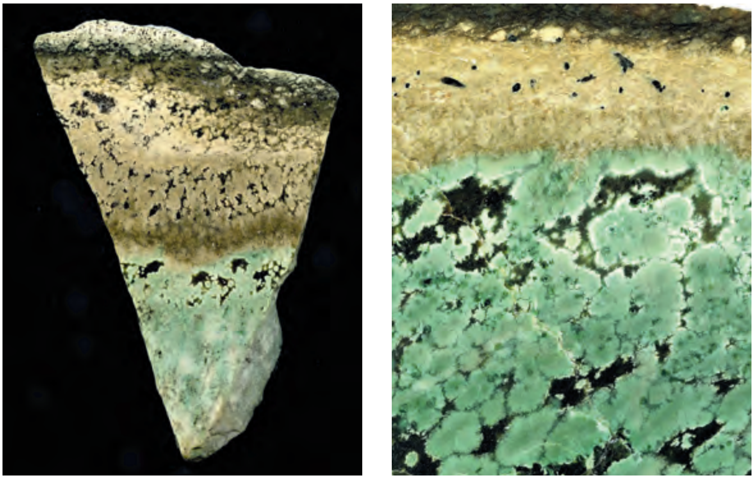


Fig. 1. Fragments of zoned column of apopicritic gumbeites:
(a) white, gray, yellow, and green zones, 168×117 mm;
(b) – gray, yellow, and green zones, 114×82 mm.
Level 512 m, Severny pit, Berezovsky deposit.

Table 1. **Chemical composition of apopicritic gumbeites, Berezovsky deposit (wt.%)**

Component	White-gray zone	Yellow zone	Green zone
SiO_2	43.25	42.64	41.34
TiO_2	1.16	1.07	1.28
P_2O_5	0.27	0.22	0.30
Cr_2O_3	0.25	0.26	0.24
Al_2O_3	6.65	7.69	6.26
Fe_2O_3	3.02	3.44	3.31
MnO	0.24	0.15	0.32
MgO	21.01	20.16	21.93
NiO	0.21	0.17	0.26
CaO	1.84	2.01	2.34
Na_2O	0.30	0.19	0.16
K_2O	3.64	2.99	2.05
CO_2	16.29	16.28	16.52
H_2O^+	1.95	2.30	2.10
S	0.12	0.10	0.02
Total	100.20	99.67	99.43
As, ppm	970	740	170

Notes: Analyses were performed at laboratory of Institute of Geology of Ore Deposits, Mineralogy, Geochemistry, and Petrography, Russian Academy of Sciences; As (ppm) was determined by quantitative spectrometry.

an X-ray technique to determine all *REE* taking into account interference of analytical lines, and effect of selective absorption and excitation of other elements. I.M. Kulikova has improved this technique for modern equipment. Operating conditions are: accelerating voltage 20 kV, current intensity 30 nA, mode of current stabilization. Fourteen *REE*, Y, Th, U, Ca, P, Si, Ti, Al, Fe, Mn, Mg, Sr, Na, Ba, and Ti were measured. The following standards were used: synthetic phosphates of individual *REE* and Y, dioxides of Th, U, and Ti, barite, celestine, and other. Counting time is 10 to 60 s. Analytical lines are measured for two stages: firstly, the relative intensities of even *REE*, Si, Y, Th, P, Ca, and Sr were measured; then the relative intensities of other elements were determined at the same points. The detection limits of *REE* are (wt.%): 0.03 La and Ce, 0.06 Pr, 0.04 Nd, 0.07 Sm, 0.08 Eu, 0.07 Gd, 0.05 Tb, 0.04 Dy, 0.10 Ho, 0.04 Er, 0.07 Tm, 0.04 Yb, and 0.08 Lu. Concentrations of 30 and more elements were calculated with the Calczaf program; ZAF or PAP correction procedure was used. Interlaboratory control attested the reliability of used technique to determine *REE* and actinides.

Metasomatic column. Picrites, precursor rock of gumbeites, contains (n = 8, ppm): 1090 Cr, 1480 Ni, 54 Co (Ni/Co = 27), 34 V, 28 Cu, 115 Zn, 8.2 Pb; this rock is enriched in Ti, P, and *REE* (ppm): 29.5 La, 38.5 Ce, 6.2 Pr, 21.9 Nd, 3.1 Sm, 0.6 Eu, 2.2 Gd, 0.26 Tb, 1.2 Dy, 0.23 Ho, 0.70 Er, 0.11 Tm, 0.26 Yb, 0.15 Lu, 6.5 Y, 178 Zr, 6.8 Hf, 47 Nb, 13.4 U, 11.6 Th, *LREE/HREE* = 17, Th/U = 0.9 (ISP-MS, N.V. Vasil'ev and L.P. Yurchenkova analysts, Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements). Content of Cr, Ni, Co, V, Cu, and Zn is typical of picrite; concentration of Zr, Nb, Hf, *REE*, and actinides is typical of alkali picrite.

The chemical composition of gumbeites from various zones of the metasomatites column (Fig. 1) is given in Table 1. Chemical variations are not great. Strong predominance of Mg over Fe and Ca characteristic of picrite retains in altered rocks. Content of Ca decreases to the inner zone, whereas that of Na, S, and As noticeably increases (Table 1).

Apopicritic gumbeites is composed of Mn-poor magnesite, F-rich phlogopite, quartz, potassium feldspar, albite, chlorite, F-rich muscovite and phengite, tourmaline (dravite), rutile (after ilmenite), to less extent dolomite, fluorapatite, monazite-(Ce), zircon, xenotime, gersdorffite, siegenite, millerite, Co-bearing pyrite, and galena. Talc-magnesite metasomatic rock with hematite, and accessory hydroxylphlogopite, hydroxylapatite, and violarite occurs in the outer zone of the column.

White inner zone of the apopicritic gumbeites column up to 2 cm in thickness (Fig. 1a) contacting with gumbeitized porphyry granodiorite or potassium feldspar-carbonate-quartz vein is composed of varigranular aggregates of magnesite, quartz and F-rich phlogopite (Fig. 2); the proportion of minerals is strongly variable from place to place; structure is massive, in some cases, it is directive, where gumbeites replaced bands of deformed picrite. Next gray zone up to 2 cm thick is composed of abundant phlogopite, quartz, and magnesite (Fig. 3) with inclusions of rare large crystals of albite and clusters of albite and potassium feldspar (Fig. 1b). Mega- and microscopically, in white and gray zones, features of primary

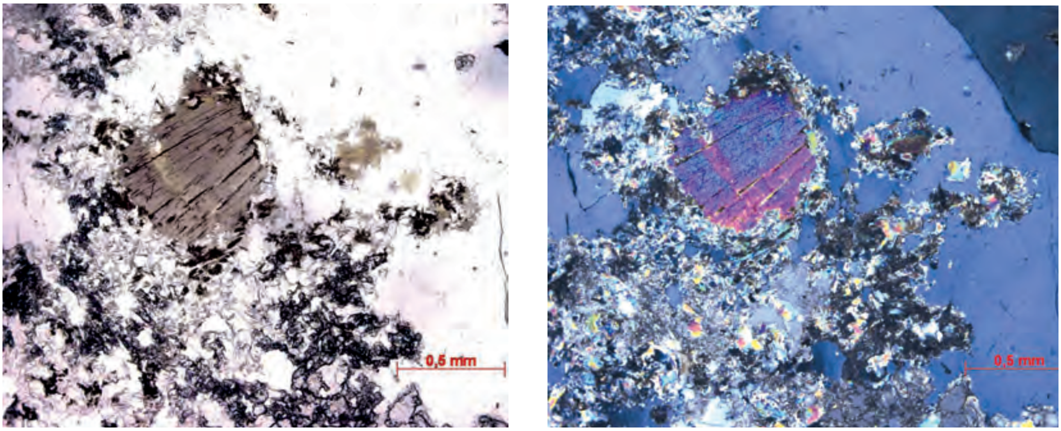
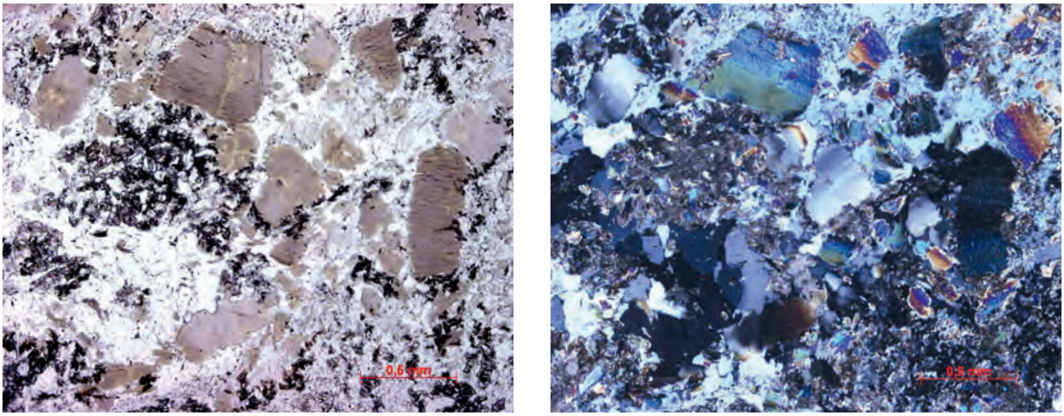


Fig. 2. Photomicrographs of white zone of apopicritic gumbeites column. Magnesite-phlogopite-quartz gumbeites. (a) Normal light, (b) crossed polars.

Fig. 3. Photomicrographs of gray zone of apopicritic gumbeites column. Quartz-magnesite-phlogopite gumbeites. (a) Normal light, (b) crossed polars.



picrite are absent; chrome spinel and ilmenite are completely dissolved. Next yellow zone ranging from 3 to 11 cm in thickness contains tourmaline and dolomite along with magnesite and does not contain green chlorite and Cr-bearing muscovite. Next green zone of 15 to 25 cm thick contains pods of green chlorite and relict chrome spinel in aggregates of Cr-bearing muscovite and phengite (Figs. 1, 4). The outer zone comprises talc-magnesite metasomatic rock with hematite; the structure is massive as usual and foliated with predominant orientation of hematite plates; crystals of dark gray magnesite are not deformed (pre-gumbeites foliation). Boundaries between zones are clear. The size of crystals of magnesite ranges from 0.0*n* to 10 – 14 mm; that of quartz, potassium feldspar and albite, and phlogopite reaches 3, 4, and 2 mm, respectively. The minerals are irregularly distributed frequently composing pockets.

Gumbeites of the yellow, gray, and white zones are enriched in Ba (average 1138 ppm, occasionally up to 3800 ppm), Rb (average 219 ppm), contains Sr (average 123 ppm), Cs (average 2.99 ppm), Ag (average 437 ppb), and Au (7.0 ppb). Thus, gumbeitization resulted in strong accumulation of Ba and Rb coherent to K and Ag, but not Au.

Relict minerals. Zincochromite is partially retained in the green zone of apopicritic gumbeites (Fig. 2). The grain size is up to 2 mm. The Ti-free, Al- and Mg-poor mineral compositionally corresponds to the formula $(Zn_{0.7-0.8}Fe^{2+}_{0.2-0.3})_1(Cr_{1.3-1.4}Fe^{3+}_{0.4-0.6}Al_{0.1-0.2})_2O_4$ ((Table 2). Spinels of similar morphology and composition occur in picrite and peridotitic serpentinite beyond gumbeites aureoles. Both zinc chromite and other spinels are the products of regional submergence metamorphism with high-alkali and high-oxidative fluids; when ultramaphic and mafic rocks are metamorphosed together, Zn from mafic rocks compensates deficiency of Fe^{2+} in spinels (Spiridonov *et al.*, 1997_1; 1998_2). Spinel is brecciated and significantly replaced by Cr-rich muscovite, phengite, and phlogopite.

Picrite in inter-variole places contained mumerous plates of ilmenite up to 2.5 × 2.5 × 0.5 mm in size. Pseudomorphs of long-prismatic rutile after deformed, curved, and twisted plates of ilmenite are abundant in the green and yellow zones of gumbeites column.

Quartz, one of the major minerals of white and gray zones, is abundant in the yellow and green zones. Its grains range from 0.0*n* to 3 mm in size. Megascopally, the mineral is light gray, opaque. It contains numerous tiny fluid inclusions with liquid CO_2. Quartz is close intergrown with phlogopite, magnesite, and potassium feldspar.

Carbonates are the major constituents of apopicritic gumbeites. Magnesite is predominant in all zones of the column. Megascopally, magnesite is black in talc-magnesite metasomatic rock of the outer zone; this mineral is white to light yellow in phlogopite-quartz-magnesite inner zone. The grains of the mineral ranges from 0.0*n* to 14 mm. Aggregates of magnesite are sufficiently abundant. The core of such aggregates is unzoned single rhombohedron rimmed by small zoned rhombohedra of Fe-rich magnesite. Magnesite is Mn-poor in all zones of the metasomatic column. The Fe/(Fe+Mg) value of the mineral from talc-magnesite rock of the outer zone ranges from 0.06 to 0.12. Magnesite from the green zone contains traced Ca and Mn, and up to 0.3 wt.% Zn; its Fe/(Fe+Mg) value is 0.13 to 0.16 (Table 3). Magnesite from the yellow zone contains traced Ca and Mn; its Fe/(Fe+Mg) value is 0.09 to 0.16 (Table 4).

Small pockets of late dolomite occur in the aggregates of magnesite of the yellow zone. In addition, dolomite heals fractures in deformed crystals of tourmaline (Fig. 5). The composition of dolomite corresponds to the formula $Ca_{0.98-1}Mg_{0.83-0.92}Fe_{0.09-0.15}Mn_{0-0.02}(CO_3)_2$.

Phlogopite, one of the major minerals of white and gray zones, occurs as lamellar and columnar crystals up to 1 to 2 mm in size. Split fan-shaped crystals of phlogopite enclosed in quartz are frequent in the white zone. Microscopically, phlogopite is light brown to brown, unzoned as usual (Figs. 3, 4). Phlogopite is F-bearing, Ti-poor and contains ca. 0.5 wt.% Cr.

Table 2. **Chemical composition (wt.%) of relict zincochromite from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	1	2	3	4	5	6	7	8	9	10
ZnO	27.46	27.01	26.26	26.54	26.68	26.26	26.41	26.04	26.01	25.52
FeO	6.48	6.89	6.68	6.48	7.47	6.98	7.28	7.32	7.00	8.39
MgO	0.30	0.32	0.46	0.62	0.30	0.55	0.28	0.62	0.81	0.56
NiO	0.34	0.19	0.26	0.28	0.22	0.49	0.25	0.19	bdl	bdl
MnO	bdl	bdl	bdl	bdl	bdl	bdl	0.43	bdl	0.37	bdl
Cr_2O_3	43.25	43.10	42.14	41.83	44.12	41.99	43.02	41.44	46.08	46.36
Fe_2O_3	18.53	18.12	18.33	19.46	19.07	20.65	19.85	20.89	13.31	13.32
Al_2O_3	3.89	4.15	3.88	3.91	3.34	3.67	3.58	4.02	5.74	5.68
Total	100.34	99.78	98.01	99.12	101.20	100.69	101.10	99.92	99.32	99.83
Atoms per formula unit										
Zn	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.71
Fe^{2+}	0.20	0.22	0.22	0.21	0.24	0.22	0.23	0.23	0.22	0.26
Mg	0.02	0.015	0.02	0.03	0.015	0.03	0.015	0.035	0.05	0.03
Ni	0.01	0.005	0.01	0.01	0.005	0.02	0.01	0.005	–	–
Mn	–	–	–	–	–	–	0.015	–	0,01	–
Total	1									
Cr	1.29	1.30	1.29	1.26	1.31	1.25	1.28	1.24	1.37	1.37
Fe^{3+}	0.53	0.52	0.53	0.56	0.54	0.59	0.56	0.58	0.38	0.38
Al	0.18	0.18	0.18	0.18	0.15	0.16	0.16	0.18	0.25	0.25
Total	2									

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst. Content of Ti and Si is below detection limit, FeO and Fe_2O_3 are calculated by stoichiometry. Here and below bdl is below detection limit.

Table 3. **Chemical composition (wt.%) of magnesite from green zone of apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	11	12	13	14	15	16	17	18	19	20
MgO	38.65	38.42	37.69	37.32	37.72	37.13	36.76	37.04	36.73	36.25
FeO	10.51	11.19	11.51	11.75	12.42	12.46	12.57	12.61	12.95	13.47
ZnO	0.18	0.17	bdl	0.19	0.24	0.23	0.19	0.25	0.31	0.21
MnO	0.10	0.12	bdl	0.12	0.13	0.13	0.14	0.08	0.11	0.17
CaO	0.10	0.12	bdl	0.10	bdl	0.09	0.15	0.09	0.10	0.14
SrO	bdl	bdl	bdl	0.10	bdl	bdl	bdl	bdl	0.09	bdl
Total	49.54	50.00	49.20	49.57	50.51	50.03	49.80	50.07	50.29	50.25
Atoms per formula unit										
Mg	0.87	0.86	0.85	0.85	0.84	0.84	0.84	0.84	0.84	0.83
Fe	0.13	0.14	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.17
Total	1									

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst.

Table 4. **Chemical composition (wt.%) of magnesite from yellow zone of apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	21	22	23	24	25	26	27	28	29
MgO	41.51	41.06	38.40	38.86	37.87	38.41	38.40	37.64	37.86
FeO	6.91	8.10	9.99	11.20	11.30	11.34	11.56	12.46	12.70
MnO	0.16	0.13	0.16	0.12	0.12	0.13	0.13	0.28	0.13
CaO	bdl	bdl	0.17	0.11	bdl	0.08	0.17	0.16	0.15
SrO	bdl	bdl	bdl	bdl	0.10	bdl	bdl	bdl	0.10
Total	48.58	49.28	48.72	50.28	49.39	49.96	50.27	50.55	50.94
Atoms per formula unit									
Mg	0.91	0.90	0.87	0.86	0.86	0.86	0.86	0.84	0.84
Fe	0.09	0.10	0.13	0.14	0.14	0.14	0.14	0.16	0.16
Total	1								

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst.

Phlogopite is frequently replaced by colorless Fe-poor chlorite or muscovite.

Potassium feldspar is abundant in gray, yellow, and green zones. Microcline without grid pattern occurs as separate grains in matrix of magnesite and quartz (± micas) and as clusters with albite. Potassium feldspar contains traces of Ca, up to 2% Ba, 3–60% of albite end-member, and 0–4% of hyalophane end-member (Table 5). Positive correlation between Ba and Na substituting K was established in the mineral.

Albite is relatively common in the gumbeites described; it is abundant in the gray zone, where albite and potassium feldspar occur as occasionally split composite crystals up to 3 mm. Crystals display predominantly albite twinning. The chemical composition of albite is as follows (anal. 38, wt.%): SiO_2 68.26; Al_2O_3 19.60; CaO 0.20; Na_2O 11.46; K_2O 0.10; total is 99.62 (N.N. Korotaeva analyst); formula is $(Na_{0.975}Ca_{0.01}K_{0.005})_{0.99}[Al_{1.01}Si_3O_8]$, or $Na_{98.5}Ca_1K_{0.5}$.

White micas. Flour-bearing (1–2.5 wt.% F) white micas are abundant in the gray and green zones of the apopicritic gumbeites column. The Cr-richest micas occur as replacement rims around zincochromite (Fig. 2; Table 5, anal. 39–44); Cr-poor micas (Table 6, anal. 45, 46) are disseminated in quartz-potassium feldspar-phlogopite-magnesite matrix. In these micas, Cr for Al chemical substitution is pronounced. Muscovite and muscovite-phengite enriched in Cr are extremely enriched in Mg. The composition of the Mg-richest F-bearing muscovite (Table 6, anal. 43) is specific; it is close to $KAlMg[(OH_{0.5}F_{0.5})_1/AlSi_3O_{10}]$. Potassium is predominant in micas; deficiency at the K site is insignificant.

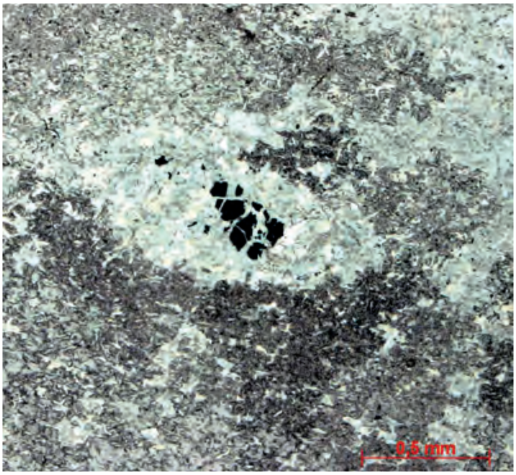
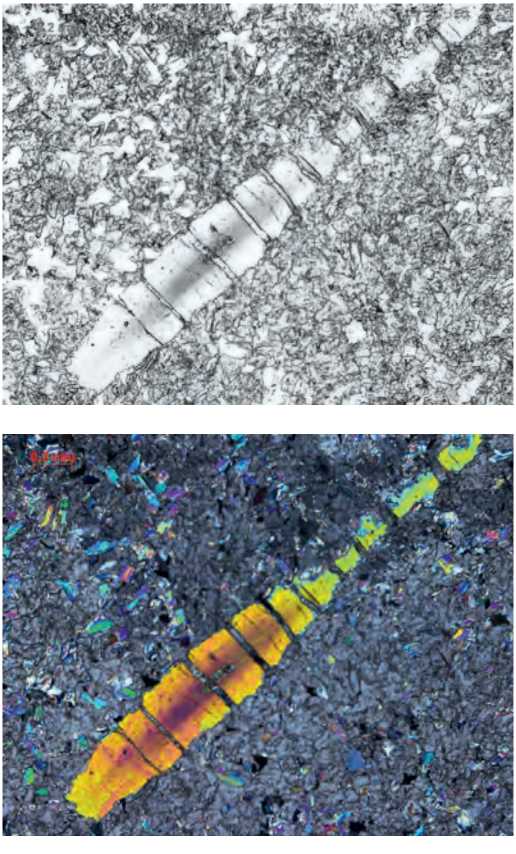


Fig. 4. Photomicrograph of green zone of apopicritic gumbeites column. Relict zincochromite (black) in aggregate of Cr-rich muscovite. Groundmass is composed of Fe-rich magnesite, muscovite, phlogopite, quartz, and potassium feldspar. Normal light.

Fig. 5. Photomicrographs of long prismatic zoned crystal of dravite in phlogopite-magnesite matrix. Crystal is deformed; parting fractures are filled by dolomite. (a) Normal light, (b) crossed polars.



F-bearing muscovite, muscovite-phengite, and phengite with noticeable content of Ti with overgrowth rims of muscovite enriched in Ba and Na are developed in the yellow zone; their compositions are given in Table 7. Ti is concentrated in muscovite and phengite, whereas Ba and Na are concentrated in low-Si muscovite.

Rutile occurs as aggregate-type pseudomorphs after plates of ilmenite (Figs. 6, 7). The composition of rutile is as follows (anal. 54, wt.%): TiO_2 98.52, Fe_2O_3 0.51, WO_3 0.13, ThO_2 0.01; total is 99.17 (I.M. Kulikova, analyst); Y, Ce, La, Nd, U, Ca, and Zr are below detection limits.

Tourmaline (dravite). Short prismatic metacrystals of tourmaline up to 4 mm in length (Fig. 5) are common in the yellow zone. The crystals are poorly zoned. Cores of some crystals are brownish green in transmit light with the Fe/(Fe+Mg) value 0.18 – 0.20; rims of these crystals are greenish and yellowish-greenish with the lower Fe/(Fe+Mg) value 0.10 – 0.16. In other crystals the zoning is reversal. Tourmaline of picritic gumbeites is Cr-free, and Ti-, Fe^{2+}, and Fe^{3+}-poor dravite (Table 8). The remarkable deficiency of Na (up to 22%) indicates high acidity of hydrothermal fluid. The composition of tourmaline corresponds to the formula $(Na_{0.8-0.9}Ca_{0-0.1}\square_{0.1-0.2})_1(Mg_{2.3-2.5}Fe^{2+}{}_{0.3-0.6}Fe^{3+}{}_{0-0.1}Al_{0-0.3})_3Al_6(BO_3)_3[(Si_{5.9-6}Al_{0-0.1})_6O_{18}](OH_{3.8-4}O_{0-0.2})_4$, value 0.10-0.20, average 0.16.

Microscopically, dravite with relict lamellae of ilmenite is green-brown to brown and contains up to 5 wt.%, up 1.5 wt.% Ti, and inclusions of acicular rutile.

Fluorapatite is abundant mineral. Clusters and aggregates of apatite grains are frequently confined to the aggregate pseudomorphs of acicular rutile after deformed plates of ilmenite (Fig. 6, 7). The size of crystals of fluorapatite is up to 0.5 mm. It forms compromise growth surface with rutile, quartz, magnesite, and potassium feldspar. The chemical composition of fluorapatite is given in Table 9 (anal. 63 – 71). The separate measurement (no. 72) with determination of *REE* was performed by I.M. Kulikova; this composition is as follows (wt.%): CaO 56.06; SrO 0.24; Na_2O 0.05; Y_2O_3 0.09; Ce_2O_3 0.07; Nd_2O_3 0.13; FeO 0.05; MnO 0.06; UO_2 0.01; P_2O_5 42.01; SiO_2 0.44; SO_3 0.28; F 3.67, total is $(-O=F_2)$ 101.61; Cl, La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th are below detection limits. Formula of this apatite is $(Ca_{4.97}Sr_{0.01}Na_{0.01}Y_{0.01})_5(P_{2.94}Si_{0.04}S_{0.02})_3O_{12}F_{0.96}$. This is all-fluorine apatite. Phosphorous in the gumbeites apatite is substituted to some extent with Si and S that testifies to the high temperature of formation and high oxidation potential (Peng *et al.*, 1997; Phosphates.., 2003).

Table 5. **Chemical composition (wt.%) of potassium feldspar from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	30	31	32	33	34	35	36	37
SiO_2	65.27	64.71	64.49	64.54	64.07	64.57	63.61	63.65
Al_2O_3	18.62	18.59	18.50	18.53	18.57	18.77	18.84	18.89
Fe_2O_3	bdl	bdl	bdl	bdl	bdl	0.15	bdl	bdl
CaO	bdl	bdl	bdl	bdl	0.11	bdl	bdl	0.16
Na_2O	0.40	0.37	0.52	0.65	0.73	0.45	0.74	0.71
K_2O	16.32	16.25	16.00	15.73	15.64	15.90	15.30	15.18
BaO	0.23	0.34	0.47	0.66	0.67	1.22	2.19	2.29
Total	100.85	100.27	99.98	100.10	99.78	101.06	100.68	100.88
Atoms per formula unit								
K	0.96	0.96	0.94	0.93	0.93	0.94	0.90	0.90
Na	0.04	0.03	0.05	0.06	0.06	0.04	0.06	0.06
Ba	-	0.01	0.01	0.01	0.01	0.02	0.04	0.04
Total	1							
Si	3.00	2.99	2.99	2.99	2.97	2.98	2.96	2.96
Al	1.00	1.01	1.01	1.01	1.03	1.01	1.04	1.04
Fe^{3+}	–	–	–	–	–	0.01	–	–
Total	4							

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst.

Table 6. **Chemical composition (wt.%) of Cr-bearing muscovite (39-45) and phengite (46) from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	39	40	41	42	43	44	45	46
SiO_2	48.16	47.60	47.54	47.27	46.61	47.47	49.40	49.61
Al_2O_3	26.38	26.65	25.13	26.11	24.96	26.67	30.83	29.43
Cr_2O_3	2.98	2.68	2.58	2.36	2.16	1.47	0.41	0.39
Fe_2O_3	1.26	1.58	1.13	1.76	1.82	1.19	0.27	0.36
MgO	5.52	3.99	7.10	5.57	8.71	6.19	3.66	3.85
Na_2O	0.18	0.12	0.15	0.17	0.25	0.18	0.21	0.22
K_2O	11.14	10.91	10.98	10.97	10.89	11.06	11.12	11.12
F	1.69	0.98	1.87	1.88	2.32	1.93	1.37	1.10
H_2O^+	5.14	6.66	4.36	4.94	2.43	4.68	6.75	7.05
Total $-O=F_2$	101.74	100.76	100.05	100.24	99.17	100.03	103.44	102.67
Atoms per formula unit								
K	0.93	0.95	0.94	0.94	0.91	0.94	0.93	0.94
Na	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.03
□	0.05	0.03	0.04	0.04	0.06	0.04	0.04	0.03
Total	1							
Al	1.24	1.38	1.11	1.23	0.96	1.25	1.61	1.59
Cr	0.16	0.14	0.13	0.13	0.11	0.08	0.02	0.02
Fe^{3+}	0.06	0.08	0.06	0.08	0.09	0.06	0.02	0.01
Mg	0.54	0.40	0.70	0.56	0.84	0.61	0.35	0.38
Total	2							
Si	3.18	3.24	3.15	3.17	3.04	3.16	3.23	3.29
Al	0.82	0.76	0.85	0.83	0.96	0.84	0.77	0.71
Total	4							
OH	1.20	1.60	1.02	1.17	0.56	1.10	1.56	1.65
F	0.39	0.21	0.39	0.40	0.48	0.41	0.28	0.23
Total	1.59	1.81	1.41	1.57	1.14	1.51	1.84	1.85

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst. Contents of Ca, Mn, and Ti are below detection limits. H_2O^+ calculated by stoichiometry.

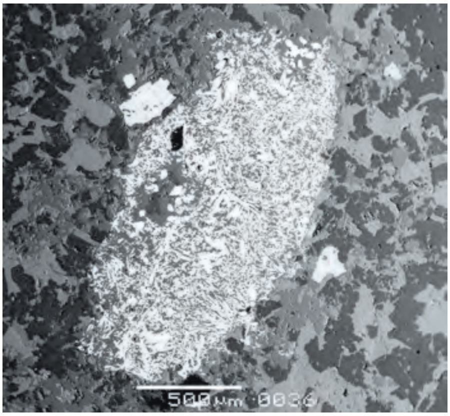
Table 7. **Chemical composition (wt.%) of muscovite (48, 50, 51), phengite (47, 49), Ba-bearing muscovite (52, 53) from yellow zone of apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	47	48	49	50	51	52	53
SiO_2	48.84	48.84	49.95	48.05	47.92	46.04	46.18
TiO_2	0.95	0.77	0.66	0.27	0.13	bdl	bdl
Al_2O_3	28.44	29.04	29.11	29.53	30.21	32.90	32.82
Fe_2O_3	1.53	1.53	0.47	1.29	2.18	1.81	1.38
MgO	3.74	4.07	4.51	4.89	4.12	2.72	2.80
Na_2O	0.17	0.19	0.19	0.20	0.21	0.41	0.35
K_2O	11.09	11.18	11.18	11.23	11.18	10.63	10.44
BaO	bdl	bdl	bdl	bdl	bdl	1.47	1.71
F	1.27	1.30	1.00	1.29	0.89	0.93	1.05
H_2O^+	6.94	6.64	6.76	5.99	6.81	6.89	6.80
Total $- O = F_2$	102.44	103.01	103.41	102.23	103.27	103.41	103.19
				Atoms per formula unit			
K	0.95	0.94	0.93	0.94	0.94	0.90	0.89
Na	0.02	0.02	0.02	0.03	0.03	0.05	0.05
Ba	–	–	–	–	–	0.04	0.04
□	0.03	0.04	0.05	0.03	0.03	0.01	0.02
Total				1			
Al	1.50	1.48	1.50	1.45	1.48	1.64	1.65
Fe^{3+}	0.08	0.08	0.03	0.06	0.11	0.09	0.07
Ti	0.05	0.04	0.02	0.01	0.01	–	–
Mg	0.37	0.40	0.45	0.48	0.40	0.27	0.28
Total				2			
Si	3.26	3.22	3.26	3.16	3.15	3.06	3.08
Al	0.74	0.78	0.74	0.84	0.85	0.94	0.92
Total				4			
OH	1.64	1.55	1.58	1.39	1.58	1.62	1.60
F	0.27	0.27	0.21	0.27	0.18	0.20	0.22
Total	1.91	1.82	1.79	1.66	1.76	1.82	1.82

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst. Contents of Cr, Ca, and Mn are below detection limits. H_2O^+ *calculated by stoichiometry.*

Fig. 6. Back-scattered electron image of grains of fluorapatite (light gray) confined to aggregate pseudomorph of acicular rutile after plates of ilmenite. Small bright white crtstal are monazite. Groundmass is composed of cluster of magnesite, quartz, phlogopite, potassium feldspar, and muscovite.

Fig. 7. Back-scattered electron image of fluorapatite (light gray) intergrown with rutile (white) in aggregate of magnesite, phlogopite, and muscovite.



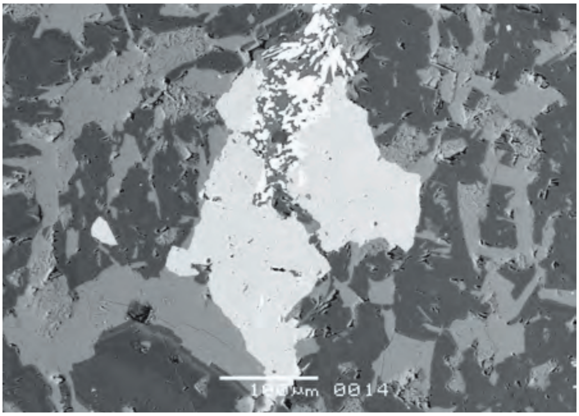


Table 8. **Chemical composition (wt.%) of tourmaline (dravite) from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	55	56	57	58	59	60	61	62
SiO_2	37.01	36.61	37.18	37.00	36.61	36.76	36.94	36.96
TiO_2	bdl	0.11	0.26	0.33	0.17	0.28	bdl	0.10
Al_2O_3	32.78	31.25	31.61	31.82	31.72	32.21	33.75	33.29
Fe_2O_3		0.42	0.07		0.57			
FeO	2.11	3.64	4.20	3.93	3.94	3.76	1.95	3.18
MgO	10.13	9.81	9.96	9.91	9.83	9.83	9.68	9.60
CaO	0.13	0.24	0.15	0.48	0.10	0.44	0.10	0.17
Na_2O	2.41	2.51	2.84	2.59	2.85	2.73	2.56	2.62
K_2O	bdl	bdl	bdl	bdl	0.10	bdl	bdl	bdl
Total	84.58	84.59	86.28	86.05	85.88	86.00	84.98	85.92
Atoms per formula unit								
Na	0.76	0.80	0.89	0.81	0.90	0.85	0.80	0.82
K	–	–	–	–	0.02	–	–	–
Ca	0.02	0.04	0.03	0.08	0.02	0.08	0.02	0.03
□	0.22	0.16	0.08	0.11	0.06	0.07	0.18	0.15
Total	1							
Al	0.27	0.04	–	0.04	–	0.09	0.40	0.26
Fe^{3+}	–	0.05	0.01	–	0.07	–	–	–
Ti	–	0.01	0.03	0.04	0.02	0.03	–	0.01
Fe^{2+}	0.28	0.50	0.57	0.53	0.53	0.51	0.27	0.43
Mg	2.45	2.40	2.39	2.39	2.38	2.37	2.33	2.30
Total	3							
Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Total	6							
Al	–	–	0.01	0.02	0.06	0.05	0.03	0.05
Si	6.00	6.00	5.99	5.98	5.94	5.95	5.97	5.95
Total	6							
O	0.07	–	–	0.08	–	0.11	0.21	0.10
OH	3.93	4.00	4.00	3.92	4.00	3.89	3.79	3.90
Total	4							

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst. Contents of Cr and Mn are below detection limits.

Zircon is a member of solid solution series $Zr[SiO_4]$ (zircon proper) – $Hf[SiO_4]$ (gaphnon) – $Th[SiO_4]$ (thorite) – $U[SiO_4]$ (coffinite) – $Y[PO_4]$ (xenotime) (Heinrich, 1962; Krasnobaev, 1986; Frondel and Collette, 1957; Gratz and Heinrich, 1997; Strunz and Nickel, 2001; Zircon..., 2004; Förster, 2006). Accessory zircon is typical of magmatic rocks from granites, granitic pegmatites, rhyolite to gabbros and basalts; baddeleite is formed instead of zircon in magmatic rocks undersaturated in silica. A lot of publications are devoted to morphology and composition of zircon from magmatic rocks (and weathered products); there is a rather complete review (Zircon.., 2004) and reviews for the Urals (Krasnobaev, 1986; Votyakov *et al.*, 2011). As a result of magmatic fractionation, Hf, U, and Th are accumulated in zircon and high-tempreature zircon is enriched in the xenotime end-member. Zirconium is established to be mobile in alkali high-temperature hydrothermal solutions; high-temperature altered rock enriched in newly formed zircon was found (albitite – mariupolite) (Frondel and Collette, 1957; Rubin *et al.*, 1993; Zircon..., 2004).

Zircon in phlogopite-magnesite gumbeites occurs as disseminated prismatic and short-prismatic crystals up to 90 μm in length, which are frequently associated with fluorapatite (Figs. 8–10). Compromise growth surfaces are frequent between zircon, quartz, magnesite, and fluorapatite. The predominant zones of zircon crystals contain (wt.%): 1.4–1.9 Hf, 0.6–1.2 P_2O_5, traces of U, Th, and Y; the zones enriched in U contain up to 3.8 wt.% U, 2.4 Hf, 1.4 Y, 0.8 Th (Table 10). Zircon from gumbeites contains 1–2% of hafnon end-member, 0–3% of coffinite end-member, 0–1% of thorite end-member, and 0–3% of xenotime end-member.

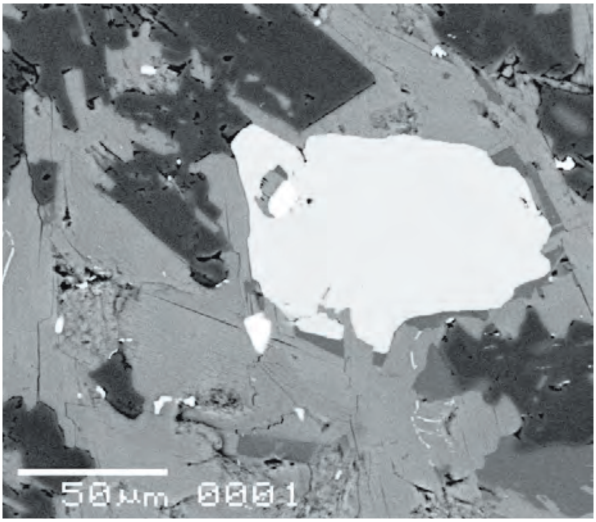
Table 9. **Chemical composition (wt.%) of fluorapatite from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	63	64	65	66	67	68	69	70	71
CaO	54.06	54.40	54.70	54.79	54.83	54.94	54.56	55.04	55.31
SrO	0.94	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ce_2O_3	bdl	0.25	bdl	bdl	bdl	bdl	bdl	bdl	bdl
FeO	0.14	0.21	0.19	bdl	bdl	bdl	bdl	bdl	bdl
MnO	bdl	bdl	0.15	bdl	bdl	bdl	bdl	bdl	bdl
P_2O_5	41.47	41.23	41.19	41.38	40.89	41.29	40.61	40.83	42.18
SiO_2	0.30	0.36	0.36	0.43	0.45	0.46	0.46	0.53	0.58
SO_3	bdl	0.30	0.11	bdl	0.29	0.10	0.45	bdl	bdl
F	3.98	3.32	3.46	3.30	3.49	3.35	3.59	3.24	3.18
Total $- O=F_2$	99.21	98.67	100.05	99.57	98.88	99.61	98.94	99.25	99.91
Atoms per formula unit									
Ca	4.94	4.98	4.98	5.00	5.00	5.00	5.00	5.00	5.00
Sr	0.05	–	–	–	–	–	–	–	–
Ce	–	0.01	–	–	–	–	–	–	–
Fe	0.01	0.01	0.01	–	–	–	–	–	–
Mn	–	–	0.01	–	–	–	–	–	–
Total					5				
P	0.97	0.95	0.96	0.96	0.94	0.96	0.93	0.96	0.95
Si	0.03	0.03	0.03	0.04	0.04	0.03	0.04	0.04	0.05
S	–	0.02	0.01	–	0.02	0.01	0.03	–	–
Total					1				
F	1.08	0.90	0.93	0.89	0.94	0.90	0.97	0.87	0.85

Notes. A Jeol SM-6480 LV electron microprobe, N.N. Korotaeva analyst.

Fig. 8. Back-scattered electron image of fluorapatite (light) intergrown with zircon (white) in matrix of magnesite (dark gray), phlogopite, potassium feldspar, muscovite (light gray), and quartz (gray).

Fig. 9. Back-scattered electron image of cluster of zircon crystals (white), two of which are large. Groundmass is composed of intergrown magnesite (dark gray), quartz (gray), phlogopite, potassium feldspar, and muscovite (light gray).



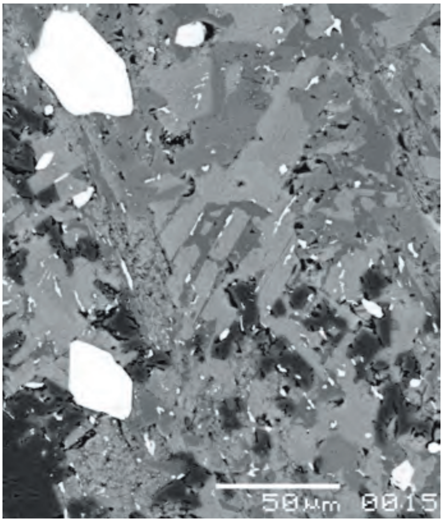


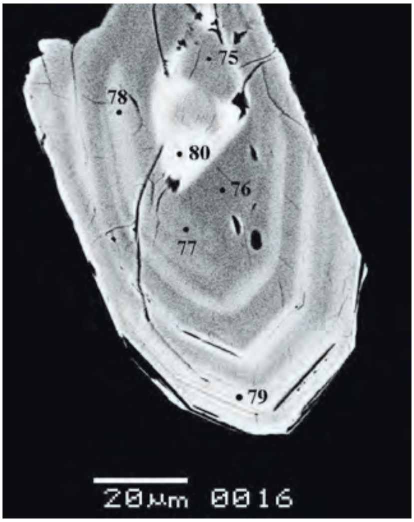
Table 10. **Chemical composition (wt.%) of zircon from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

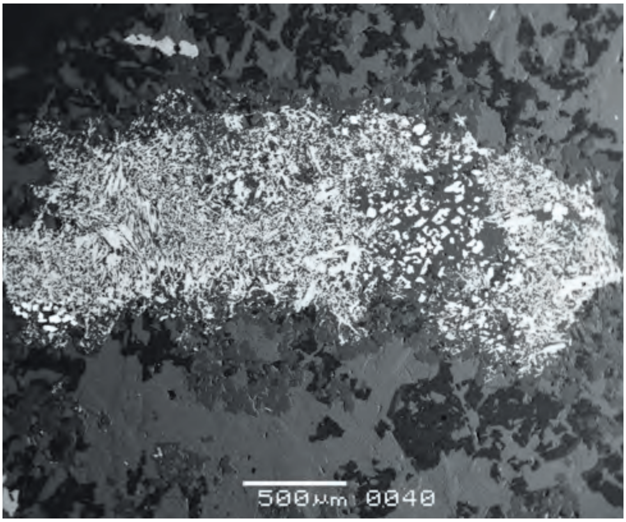
Component	73	74	75	76	77	78	79	80
ZrO_2	65.93	65.71	64.93	63.63	63.51	63.66	63.29	60.34
HfO_2	1.63	1.92	1.45	1.39	1.40	2.41	1.99	2.02
UO_2	0.01	0.02	0.01	0.02	0.03	0.59	2.19	3.88
ThO_2	bdl	bdl	bdl	0.65	0.48	0.20	0.80	0.60
Y_2O_3	bdl	bdl	0.66	1.35	1.09	0.23	0.74	0.90
Ce_2O_3	bdl	bdl	0.11	bdl	0.37	bdl	bdl	bdl
Nd_2O_3	0.05	0.06	0.05	0.15	0.20	bdl	bdl	bdl
Gd_2O_3	0.07	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Yb_2O_3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.05
SiO_2	32.38	32.19	32.32	31.39	31.15	32.03	32.07	31.07
P_2O_5	0.13	0.15	0.58	1.06	1.14	0.14	0.48	0.64
Total	100.20	100.05	100.01	99.64	99.38	99.26	101.56	99.50
Atoms per formula unit								
Zr	0.99	0.99	0.98	0.96	0.96	0.97	0.95	0.93
Hf	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02
U	–	–	–	–	–	0.01	0.02	0.03
Th	–	–	–	0.01	–	–	–	–
Y	–	–	0.01	0.02	0.02	–	0.01	0.02
Ce	–	–	–	–	0.01	–	–	–
Si	1.00	0.99	0.99	0.97	0.97	1.00	0.99	0.98
P	–	–	0.01	0.03	0.03	–	0.01	0.02

Notes. A Camebax-microbeam electron microprobe, I.M. Kulikova analyst. Contents of S, La, Pr, Sm, Er, Dy, Ho, Tm, and Lu are below detection limits.

Fig. 10. Back-scattered electron image of complexly zoned crystal of zircon. Points correspond to numbers in Table 10.

Fig. 11. Back-scattered electron image of aggregate pseudomorph of long-prismatic crystals of rutile after deformed and partly brecciated large plate crystal of ilmenite. The most deformed places are dissolved; pockets of crystals of monazite (white) are developed instead of them. Groundmass is composed of intergrown magnesite (dark gray), quartz (gray), potassium feldspar, and micas. Long fluorapatite (light gray) is above lamella.





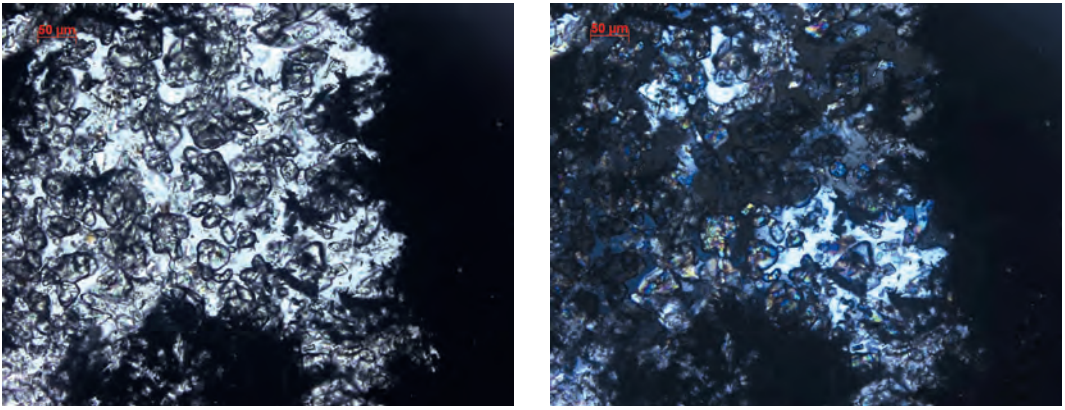


Fig. 12. Photomicrograph of pocket of monazite crystals in aggregate of acicular rutile. (a) Normal light, (b) crossed polars.

Monazite is a member of solid solution series (Ce,La,Nd...Sm)[PO$_4$] (monazite proper) – CaTh[PO$_4$]$_2$ (brabantite) – CaCe$_2$Th[PO$_4$]$_4$ (cheralite) – Th[SiO$_4$] (huttonite – gasparite (Ce,La,Nd)[AsO$_4$] with a small admixture of the xenotime end-member Y[PO$_4$] (Heinrich, 1962; Yushkin *et al.*, 1986; Pabst and Hutton, 1951; Bowie and Horne, 1953; Graeser and Schwander, 1977; Rose, 1980; Strunz and Nickel, 2001; Phosphates.., 2003). The usual Ce:La:Nd value in monazite is ~ 2:1:1, less frequent La is predominant, Nd is predominant occasionally. Monazite is typical of Ca-poor granite and syenite, granitic gneiss of normal and elevated alkalinity; it is the major carrier of *LREE*; content of Th is up to 30 wt.% and higher (Phosphates.., 2003; Philpotts and Ague, 2009). The content of U is also high in monazite of some granitic pegmatites (Gramaccioli and Segalstad, 1978). Th-free or Th-poor monazite occurs in hydrothermal rocks (Yushkin *et al.*, 1988; Phosphates.., 2003). When monazite is associated with xenotime, its composition is an indicator of temperature and pressure: at 2 kb, mole fraction of Y increases from 3 to 16% as temperature increases from 300 to 1000°C at 2 kb (Gratz and Heinrich, 1997).

Gumbeites monazite has not been studied before. In the Berezovsky gumbeite, it occurs as crystals of usual shape up to 45 μm in size, their clusters confined to deformed lamellae of ilmenite replaced by aggregates of acicular rutile (Figs. 11, 12). Monazite overgrows rutile and fill interstices between crystals of rutile (Fig. 13). It is intergrown with fluorapatite to form compromise growth surfaces. In phlogopite-magnesite gumbeite, this minerals is U-free and Th-poor (0.8–2.2 wt.% Th); Ce content is twice as much as that of La; the concentration of Nd is slightly less than that of La; content of Pr, Sm, and Dy is appreciable; small part of P is substituted by Si; content of the huttonite end-member is less than 2%. The compositions of five examined crystals of monazite are similar and correspond to the formula $(Ce_{0.40-0.43}La_{0.25-0.28}Nd_{0.16-0.18}Y_{0.02-0.05}Pr_{0.03-0.04}Sm_{0.02}Gd_{0.01-0.02}Eu_{0-0.01}Th_{0.01-0.02}Ca_{0.02})_{1-1.01}(P_{0.97-0.98}Si_{0.01-0.03})_{0.99-1}O_4$ (Table 11). These compositions are typical of monazite of high- to medium-temperature hydrothermal assemblages (Phosphates.., 2003).

The crystal cores of the Berezovsky monazite are enriched in Y (Table 11, anal. 81); the temperature of their and rims (anal. 84, 85) formation estimated from the Gratz-Heinrich equation (Gratz and Heinrich, 1997) is ca. 450°C and ca. 300°C, respectively.

Xenotime is a member of solid solution series Y[PO$_4$] (xenotime proper) – *HREE*[PO$_4$] including xenotime-(Yb) Yb[PO$_4$]. The content of the xenotime-(Y) end-member is 70–80% as usual; that of the *HREE*[PO$_4$] is 15–25%, occasionally higher than 50%; the solid solution of high-temperature xenotime contains up to 5–10% of the (Ce,La,Nd...Sm)[PO$_4$] end-member (monazite), up to 5% of the CaTh[PO$_4$]$_2$ (brabantite) – CaCe$_2$Th[PO$_4$]$_4$ (cheralite) end-member, and up to 5% of the (Th,U)[SiO$_4$] end-member (thorite-coffinite) (Heinrich, 1962; Yushkin *et al.*, 1986; Gratz, and Heinrich, 1997; Strunz and Nickel, 2001; Phosphates.., 2003; Förster, 2006). Xenotime is a typical accessory mineral of various granitoids of normal and high alkalinity; it is the major carrier of *HREE* in them. It is rather abundant in high- and medium-temperature hydrothermal assemblages (Yushkin *et al.*, 1986; Phosphates.., 2003).

Gumbeitic xenotime has not been studied before. In the Berezovsky gumbeites, it occurs as small bipyramidal crystals and anhedral grains

Table 11. **Chemical composition (wt.%) of monazite from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	81	82	83	84	85
Y_2O_3	2.40	1.41	1.33	1.18	1.04
La_2O_3	16.87	15.92	15.58	15.96	17.41
Ce_2O_3	29.58	30.73	30.36	29.43	30.60
Pr_2O_3	2.68	2.88	2.49	3.21	2.25
Nd_2O_3	11.64	12.59	13.39	12.38	12.09
Sm_2O_3	1.46	1.29	1.81	1.82	1.79
Eu_2O_3	0.36	0.23	0.27	0.10	0.16
Gd_2O_3	0.79	0.96	0.90	0.82	1.21
Tb_2O_3	bdl	0.16	0.06	0.16	0.11
Dy_2O_3	0.21	0.36	bdl	0.30	0.49
Ho_2O_3	bdl	bdl	bdl	0.16	bdl
Er_2O_3	0.18	0.15	bdl	bdl	0.15
Yb_2O_3	bdl	0.15	bdl	bdl	0.09
Lu_2O_3	bdl	0.09	0.17	bdl	0.19
ThO_2	2.20	1.41	1.41	2.23	0.83
TiO_2	0.21	0.26	0.21	0.18	0.24
UO_2	0.17	0.01	0.01	0.09	0.02
CaO	0.49	0.46	0.60	0.73	0.31
SrO	0.06	bdl	bdl	bdl	bdl
FeO	0.07	bdl	0.04	0.08	0.05
P_2O_5	30.35	30.63	30.91	30.72	30.70
SiO_2	0.66	0.37	0.50	0.48	0.34
Total	100.39	100.06	100.04	100.03	100.07
Atoms per formula unit (Total = 2)					
Y	0.05	0.03	0.03	0.02	0.02
La	0.27	0.26	0.25	0.26	0.28
Ce	0.40	0.42	0.43	0.41	0.42
Pr	0.04	0.04	0.03	0.04	0.03
Nd	0.16	0.17	0.18	0.17	0.16
Sm	0.02	0.02	0.02	0.02	0.02
Eu	0.01	–	–	–	–
Gd	0.01	0.01	0.01	0.01	0.02
Dy	–	–	–	–	0.01
Th	0.02	0.01	0.01	0.01	0.02
Ca	0.02	0.02	0.02	0.03	0.01
P	0.97	0.98	0.98	0.98	0.98
Si	0.03	0.01	0.02	0.02	0.01

Notes. A Camebax-microbeam electron microprobe, I.M. Kulikova analyst. Contents of Na and Tm are below detection limits.

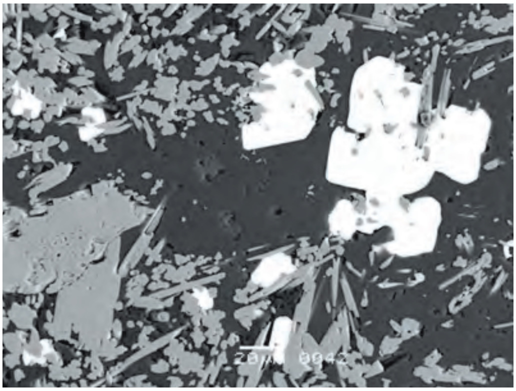


Fig. 13. Back-scattered electron image of crystal of monazite (white) in aggregate of rutile (gray), quartz, and micas (dark gray).

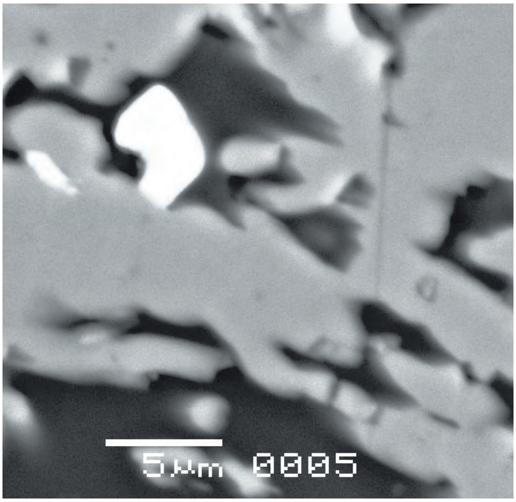


Fig. 14. Back-scattered electron image of crystal of xenotime (light) in aggregate of crystals of rutile (gray).

Fig. 15. Back-scattered electron image of anhedral xenotime (light) in aggregate of crystal of rutile (gray).

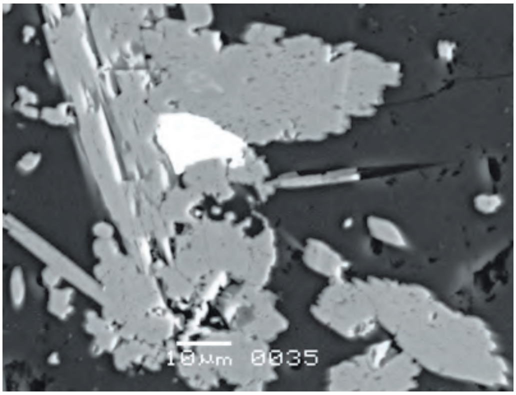


Table 12. **Chemical composition (wt.%) of xenotime from apopicritic phlogopite-magnesite gumbeites, Berezovsky deposit**

Component	86	87	88	89
Y_2O_3	42.87	41.42	39.78	39.24
La_2O_3	0.06	0.06	bdl	0.06
Ce_2O_3	0.45	0.44	0.29	0.30
Nd_2O_3	2.42	2.40	2.67	2.71
Sm_2O_3	2.07	2.05	2.51	2.55
Eu_2O_3	0.87	0.86	0.87	0.88
Gd_2O_3	3.56	3.52	5.45	3.54
Tb_2O_3	0.62	0.61	0.66	0.66
Dy_2O_3	4.45	4.43	5.09	5.17
Ho_2O_3	1.07	1.06	0.51	0.52
Er_2O_3	3.05	3.02	3.06	3.10
Tm_2O_3	0.24	0.24	0.27	0.27
Yb_2O_3	2.58	2.55	2.31	2.34
Lu_2O_3	0.40	0.40	0.54	0.55
TiO_2	0.18	0.25	0.14	0.14
UO_2	0.07	0.08	0.74	0.80
CaO	0.24	0.24	0.14	0.13
P_2O_5	35.53	35.33	34.94	34.07
SiO_2	0.24	0.22	0.31	0.22
Total	100.97	99.19	99.98	99.50
Atoms per formula unit (Total = 2)				
Y	0.75	0.74	0.71	0.71
Ce	0.01	0.01	-	-
Nd	0.03	0.03	0.03	0.03
Sm	0.02	0.02	0.03	0.03
Eu	0.01	0.01	0.01	0.01
Gd	0.04	0.04	0.06	0.06
Tb	0.01	0.01	0.01	0.01
Dy	0.05	0.05	0.06	0.06
Ho	0.01	0.01	0.01	0.01
Er	0.03	0.03	0.03	0.03
Yb	0.03	0.03	0.02	0.02
Lu	–	–	0.01	0.01
U	–	–	0.01	0.01
Ca	0.01	0.01	0.01	–
P	0.99	1.00	0.99	0.99
Si	0.01	0.01	0.01	0.01

Notes. A Camebax-microbeam electron microprobe, I.M. Kulikova analyst. Contents of Fe, Na, Sr, Pr, and Th are below detection limits.

up to 20 μm enclosed in clusters of acicular rutile (Figs. 14, 15). Xenotime in phlogopite-magnesite gumbeites is Th-free and U-poor (0.1 – 0.8 wt.% U); Y significantly predominates over *HREE*, the major of which are even with Dy≥Gd > Er > Yb. Nd and Sm are predominant of *LREE*; the content of Eu is greater than sum of Ce and La; only insignificant part of P is replaced with Si (Table 12). The composition of xenotime corresponds to the formula $(Y_{0.71\text{-}0.75}Dy_{0.05\text{-}0.06}Gd_{0.04\text{-}0.06}Er_{0.03}Nd_{0.03}Yb_{0.02\text{-}0.03}Sm_{0.02\text{-}0.03}Eu_{0.01}Tb_{0.01}Ho_{0.01}Lu_{0\text{-}0.01}Ca_{0\text{-}0.01})_{0.99\text{-}1}(P_{0.99\text{-}1}Si_{0.01})O_4$. Thus, xenotime from gumbeites contains 71 – 75% of the xenotime proper end-member, 17 – 20% of the *HREE*[PO_4] end-member, 6 – 7% of the monazite end-member, and 1% of the coffinite end-member.

Thus, in the assemblage fluorapatite-monazite-zircon, U is concentrated in zircon; Th is concentrated in monazite and to some extent in zircon; *LREE* and most Y are incorporated into monazite that is significantly predominant over xenotime; the latter concentrates *HREE* and part of Y; fluorapatite is nearly *REE*-and actinide-free.

Talc is characteristic of the outer zone of metasomatic column. This mineral is Fe-poor with appreciable Ni; its composition is as follows (anal. 90; wt.%): SiO_2 62.51; MgO 30.88; FeO 0.81; MnO 0.02; NiO 0.38, total is 94.91 (N.N. Korotaeva analyst). Formula is $(Mg_{2.94}Fe_{0.04}Ni_{0.02})_3[(OH)_2/Si_4O_{10}]$.

Gersdorffite is a typical accessory mineral of phlogopite-magnesite gumbeites. In the green zone, the composition of gersdorffite corresponds to the formula $Ni_{0.98}Fe_{0.02}AsS$; in the yellow zone gersdorffite is Co-bearing $Ni_{0.87\text{-}0.93}Co_{0.07\text{-}0.12}Fe_{0.01}AsS$.

Comparison of apopicritic and other gumbeites

The described hight-temperature gumbeites replacing picrites contains assemblage magnesite-phlogopite-quartz, whereas high-temperature apogranitic gumbeites is present calcite-biotite-quartz. Gumbeites replacing picrite contains tourmaline that is absent in granitic gumbeite.

Comparison of apopicritic gumbeites and other types of metasomatites

Unlike listvenite, apopicritic gumbeites contains assemblages magnesite-phlogopite-quartz and magnesite-potassium feldspar-quartz, and monazite-(Ce), xenotime, zircon, fluorapatite, tourmaline, F-rich and Ba-bearing muscovite.

Talc-magnesite gumbeites contains phlogopite in contrast to talc-magnesite listvenites.

Unlike porphyry copper alterations, apopicritic gumbeites contains cogenetic monazite, zircon, and xenotime and does not contain magnetite (Lowell, Guilbert, 1970; Sillitoe, 2009). In adition the described alteration is accompanied with potassium feldspar-carbonate-quartz veins with scheelite or hematite (without magnetite and molybdinite) that is not typical of the porphyry copper alterations.

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POLYCRYSTALLINE CLUSTERS OF DIAMOND FROM THE LOMONOSOV DEPOSIT, RUSSIA

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Polycrystalline aggregates of diamond from the Arkhangelsk pipe of the Lomonosov deposit have been studied with optical and scanning electron microscope, color cathode luminescence, and infrared Fourier spectroscopy. The diamonds were divided into two morphological and structural groups referred to VIII and IX varieties by the classification of Yu.L. Orlov (1984). There are diamond crystals with high N content among them, but N-poor crystals were also found. Unzoned and zoned polycrystalline clusters related to different stages of crystallization have been established.

1 table, 4 figures, 5 references.
Keywords: diamond, polycrystalline clusters of diamond, VIII variety of diamond, IX variety of diamond, admixture defects, inclusions.

As both single crystals and polycrystalline varieties of diamond (Orlov, 1984) are widely used in various industries, the origin of diamond is one of the urgent problems of geology. Morphology and structure of diamond are the source of unique information on geological processes at the depth of 150 km. Polycrystalline clusters of diamond at present are studied poorer than single crystals (Smelova, 1991). Therefore, the examination of their outer and inner morphology ensures new evidence about the conditions of diamond formation explaining actuality of this study.

Twenty samples of polycrystalline clusters of diamond of 3–4 mm in size from the Arkhangelsk pipe were examined with optical and scanning electron microscopy, color cathode luminescence (CL), and infrared Fourier spectroscopy (FTIR).

The polycrystalline aggregates studied here are composed of octahedral, combination, and dodecahedral crystallites; these crystallites are light to dark gray, greenish gray, pink, and yellow transparent or semitransparent.

Most samples studied (12 clusters) are aggregates of numerous faced small nearly equal-sized crystals. These clusters are oval and globe-shaped. Separate individuals are combination and dodecahedral. Dark granular core is in transparent clusters. This core is aggregate of irregular-shaped diamond grains, which are dark because of inclusions of graphite. The clusters are predominantly light gray and greenish gray; pink and zoned clusters also occur (Figs. 1a–c). These clusters are referred to the VIII varieties by the mineralogical classification of Yu.L. Orlov (1984).

Eight clusters of the collection studied are irregular-shaped angular pieces. Well distinguished grains composing these clusters are predominantly octahedral. The clusters are dark gray opaque. Dark irregular-shaped inclusions, which are probably graphite typical of diamond for the Arkhangelsk diamond province, are in crystallites. Significant amount of these inclusions causes black color of the crystals (Figs. 1d–f). Green pigmentation spots resulted from natural radioactive irradiation and parallel growth striation caused by layered growth of faces (Fig. 1d) are well seen on some crystallites (octahedra). Some samples show split tips indicating change of growth conditions. Polycentric growth of faces of the samples studued testified to oversaturated medium and shifted center of growing face (Kriulina, 2012). Transformation to dodecahedroid is not observed. This type of polycrystalline clusters was referred to the IX varieties by the mineralogical classification of Orlov (1984).

All diamond crystals have traces of local dissolution. Faces of separate crystals are dull, uneven and are penetrated by etch channels (Fig. 2). Matting is resulted from effect of mobile reagent that acted with equal power through all points of surface of diamond crystal and easily penetrated all pits on the crystal. In nature, such reagent was suggested to be fluid medium (Gnevushev and Shchemanina, 1975).

The CL intensity and distribution differ in the polycrystalline clusters studied (Fig. 3).

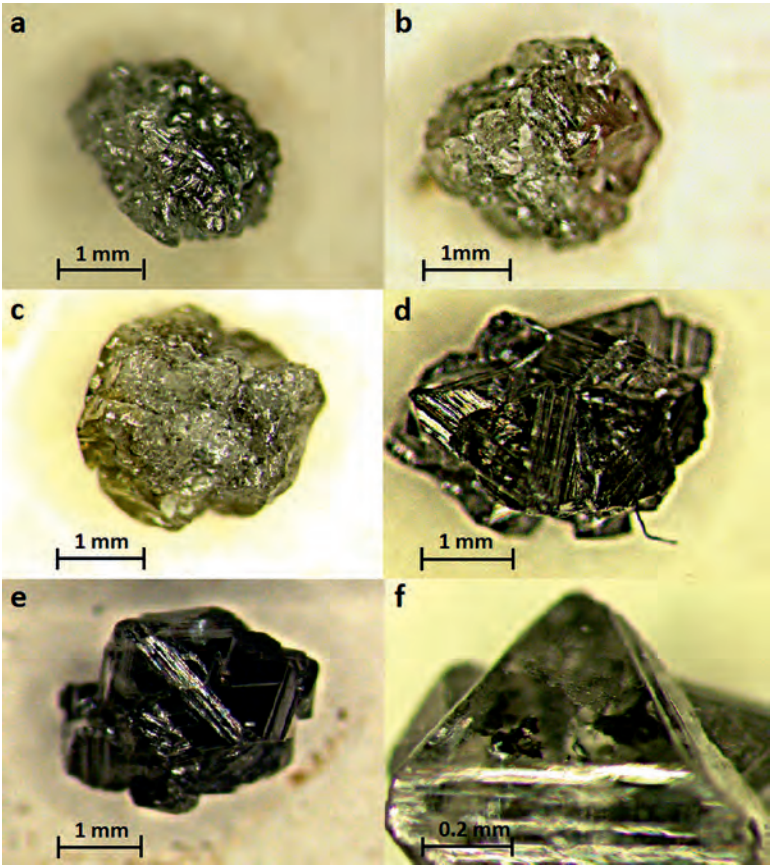

Fig. 1. Polycrystalline clusters of diamond from the Arkhangelsk pipe (transmitted light). (a) Polycrystalline clusters of the VIII variety; (b) pink crystal of diamond overgrown by small crystallites; (c) zoned polycrystalline cluster of the VIII variety; (d) cluster of octahedra with pronounced growth striation and of black color resulted from numerous inclusions, IX variety; (e) cluster with chip, IX variety; (f) irregular-shaped inclusion in crystallite of the IX-variety cluster.

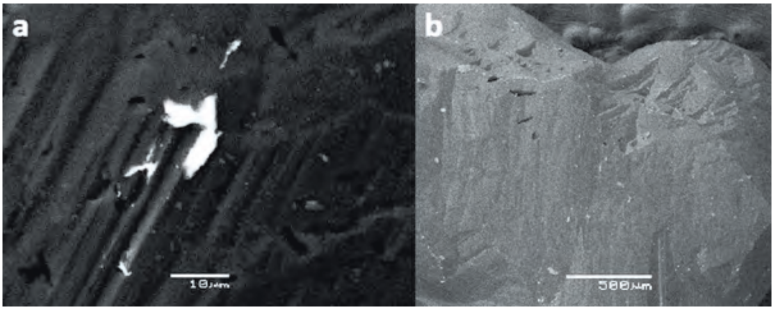

Fig. 2. Back-scattered electron image of crystallite surface. (a) Fragment of polycrystalline cluster with etch features, which are fractures, pits and rough surface; (b) fragment of polycrystalline cluster with etch caverns and negative etch pyramids.

The polycrystalline clusters studied have basically blue luminescence of varied intensity complicated with green and red lines and spots (Figs. 3a, b). The clusters, where separate crystallites with green CL are observed at the background of homogeneous blue CL (fig. 3c), were found. These crystallites are frequently complicated with blue CL spots (Fig. 3d) probably resulted from various generations and growth stages of the cluster. Zoning of crystallites is expressed as different CL of core and rims (Fig. 3b). Different CL patterns indicate testify to the different formation conditions of polycrystalline clusters.

The set of nitrogen defects in the crystal structure of diamond is extremely vast and diverse (Sobolev, 1978). According to FTIR spectroscopy, the content of nitrogen defects is higher in the studied polycrystalline clusters referred to the IX variety that that of clusters referred to the VIII variety (Fig. 4). The average content of A and B defects in the N-rich crystals is significant (1000 ppm), whereas in N-poor, that is low (260 ppm).

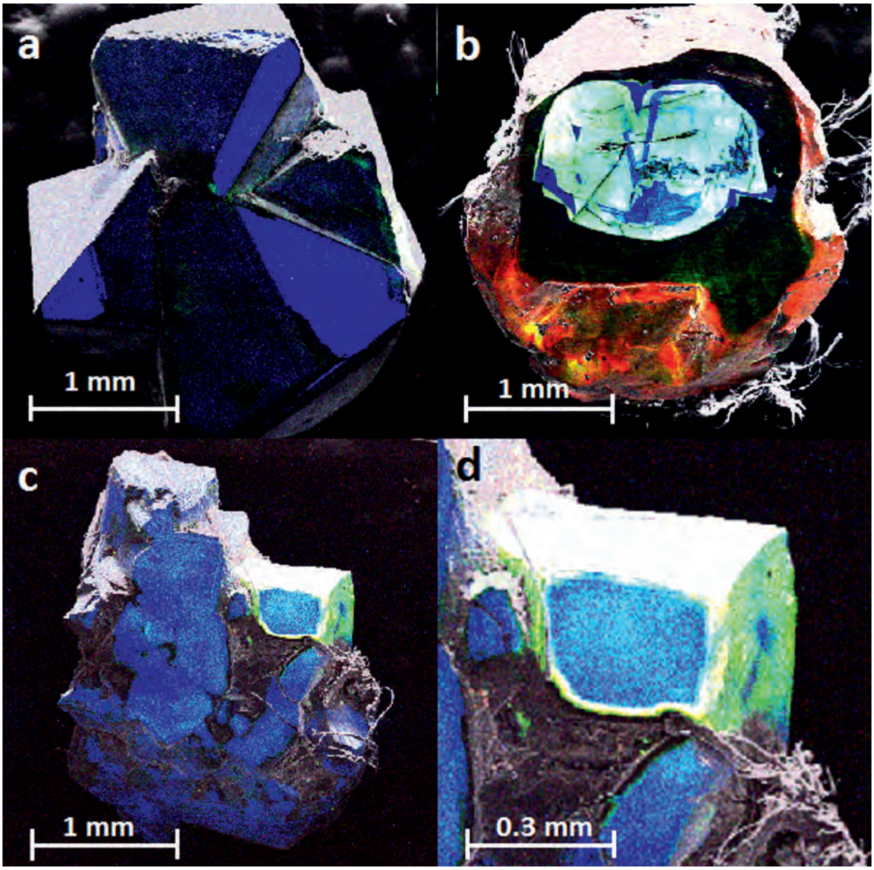

Fig. 3. Cathode luminescence pattern of diamond.
(a) monotonous blue luminescence

(b) blue luminescence complicated with lines of green luminescence;

(c) monotonous blue luminescence with green luminescence of one crystal;

(d) green luminescence of separate crystallite complicated with blue luminescence.

Table 1. **Concentration of structural defects in polycrystalline clusters of diamond from the Arkhangelsk pipe estimated from IR-Fourier spectroscopy**

Number of sample	N_{tot}, at.ppm	A, at.ppm	B1, at.ppm	B1, %	B2, cm^{-1}
1787-3-2	1002	948	54	5.39	10.36
1787-3-17	267	208	59	22.09	2.18

Notes. N_{tot} means total concentration of nitrogen in crystal; A (at. ppm) and B1 (at.ppm) are nitrogen defect A and B1 and their content; B1 (%) is content of defect B1 expressed as percent of total concentration A + B1 (aggregation of nitrogen); B2 (cm^{-1}) is concentration of defect B2 (planar defect). IR spectra were measured at National Mineral Resources University (University of Mines), St. Petersburg, Russia (V.A. Vasil'ev analyst).

C defects were not found. The aggregation of nitrogen is all polycrystalline clusters ranges from 5 to 25% with the average value 15%. The content of B2 defects ranges from 2.18 to 10.36 cm^{-1}. Average content of B2 defects in crystals with high content of nitrogen defects is 10 cm^{-1}, whereas that in the crystals with low content of nitrogen is 2.3 cm^{-1}. Both N-rich and N-poor diamond contains hydrogen.

The studied polycrystalline clusters were compared with those from the Udachanaya pipe in the Yakutia diamond province. The latter are predominantly bort (IX variety). Ellipsoidal and nearly rounded clusters, in which faced tips of diamond individuals are observed over the entire surface, indicate the growth in the medium contributing uniform influx of feed substance that is possible only in mobile medium. According to Smelova (1991), the chemical composition of cogenetic solid inclusions (olivine, richterite, magnesite, and phlogopite) and their assemblages in polycrystalline clusters attribute the latter to the ultramafic medium.

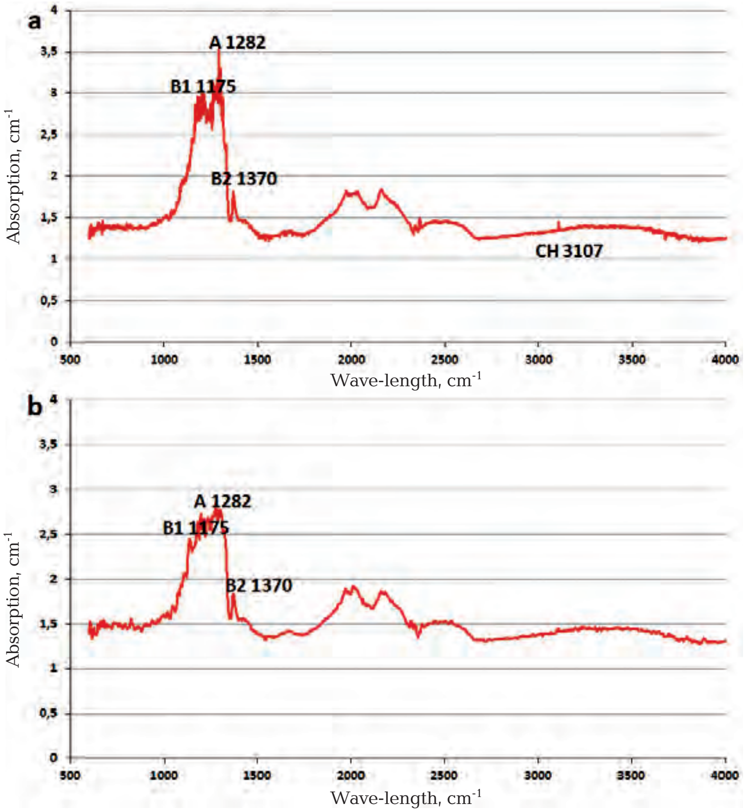

Fig. 4. IR spectra of polycrystalline varieties of diamond. (a) IR spectrum of polycrystalline cluster of the IX variety (sample no. 1787-3-2) with high content of nitrogen defects A, B, and B2 and hydrogen defect CH; (b) IR spectra of the VIII-variety cluster (sample no 1787-3-17) with low content of nitrogen defects.

Conclusions

The polycrystalline clusters studied are divided into two groups. The first group is clusters with dark gray to nearly black well-faced octahedral crystallites. Evenly distributed inclusions are typical for these clusters. These clusters belong to the IX variety by the classification of Orlov (1984). Uniform CL indicating one-stage growth of the clusters is typical of these clusters. The high content of nitrogen and low aggregation testify short post-crystallization annealing.

The second group is clusters with small nearly equal-sized predominantly octahedral and dodecahedroidal crystallites. These clusters are light gray. These samples are referred to the VIII variety by the mineralogical classification of Orlov (1984). They are characterized by heterogeneous CL, low content of nitrogen, and higher aggregation testifying to longer annealing of the clusters.

The clusters referred to the VIII variety is suggested to crystallize earlier at higher temperature than those of the IX variety. Similar morphology of polycrystalline clusters of diamond from the Arkhangelsk pipe and those from the Udachnaya pipe indicates similar conditions of formation in ultramafic medium.

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AUTHIGENIC GYPSUM IN ROCKS AT THE BOTTOM OF JAPAN AND OKHOTSK SEAS

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Morphology of authigenic gypsum occurring at the surface of the Cenozoic rocks at the floor of Seas of Japan and Okhotsk is described. The mineral looks like unusual because of morphology of mineral aggregates, shape of crystals, and conditions of formation. The formation of this type gypsum was probably determined by high concentration of Ca^{2+} and SO_4^{2-} in porous water of cristobalite-bearing rocks, lithostatic pressure, and temperature gradient between porous and sea water. Abundance of gypsum in the rocks at the slopes of submarine morphostructures of the Japan and Okhotsk Seas allows consideration of this region as a province of authigenic gypsum mineralization.

1 table, 4 figures, 24 references.
Keywords: authigenic gypsum, morphological type, rocks at the bottom of Okhotsk and Japan Seas.

The study of the Cenozoic rocks obtained from dredging of various morphostructures of marginal seas in the northwestern Pacific in 1974 – 2006 revealed authigenic gypsum in them. In the Sea of Okhotsk, gypsum was found in the rocks picked up at the western (stations 2222, 2225, and 2227; depth of dredging 1350 – 2000 m), northern (stations 2356 and 2357; depth 2600 – 2900 m), and southwestern (stations 2361, 2363, 2364, 2367, and 2368; depth 2300 – 2900 m) slopes of the Kuril Trench. In the Sea of Japan, it was found at the Primorsk continental slope (stations 1076 and 1126; depth 1500 – 1930 m), uplands Pervenets (station 1747; depth 2350 – 2460 m) and Alpatov (stations 2047 and 2212; depth 2900 – 3300 m), ridges Okushiri (stations 1708 and 1713; depth 1300 – 2500 m), Oki (stations 1270; depth 1250 – 1300 m), and South Yamato (station 1434; depth 280 – 320 m). The similar gypsum was also found at the Pacific slope of the Kuril arc system in the Vityaz Ridge (station LV 41-16; depth 1200 – 1400 m) (Fig. 1). Further, seasonal (cellar) gypsum was formed at the section of some samples dredged from the Alpatov Upland (sample 2047-2; depth 2900 – 3300 m) and Oki Ridge (sample 1296-4b; depth 350 m). Authigenic submarine gypsum occurs as rounded (close to spherical) aggregates composed of mineral individuals, which were not previously described in literature[1]. The aim of this study is examination of these aggregates and establishing their formation.

Analytical techniques

Gypsum (monomineralic sample) and cristobalite (bulk sample) were detected with a DRON 2.0 diffractometer (Cu*K*α radiation, graphite plate monochromator) operated at voltage 30 kV and current intensity 30 mA. Morphology and chemical composition of gypsum were examined on an EVO 50-XVP scanning electron microscope equipped with an INCA ENERGY 350 EDS. The samples were coated by carbon film EDVARDS E-306 high-vacuum system.

Results

Gypsum occurs as two varieties: (1) submarine variety formed under submarine conditions at the contact between Cenozoic rocks and sea water, and (2) cellar (seasonal) variety formed in storage at the section of the same rocks.

Aggregates of submarine gypsum are spheroids (0.1 – 0.5 mm in diameter, predominantly 0.2 mm) (Figs. 2, 3a, d, f) and occasional disks up to 0.2 mm thick and up to 1.5 mm in diameter (Fig. 3c). Spheroids cover the sample surface, whereas small disks are sporadic. The cellar gypsum occurs as spheroids (globe-shaper aggregates of 0.1 to 0.3 mm in diameter, predominantly 0.2 mm) which are scattered on the section of the samples (Figs. 3b, e).

The aggregates of submarine gypsum are composed of one type of mineral individuals as close aggregate of parallel lamellae of 1×0.5×70 to 4×1×70 μm in size (Figs. 4a, b, c). Globules of cellar gypsum are composed of abundant acicular (1×15×70 to 3×15×70 μm) (Fig. 4d) and tabular (2×0.5×4 to 6×1×14 μm) (Fig. 4e) crystals. Convex isometric (5×6x4 μm) segregations of gypsum are occasional between its needles (Fig. 4d).

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[1] – Below the similar aggregates are named spheroids.

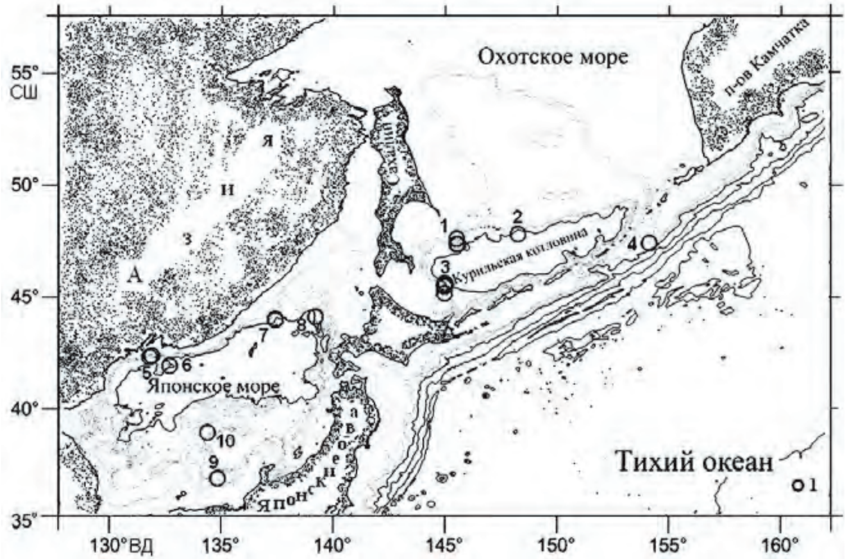

Fig. 1. Location of dredging stations. 1—3 — Slopes of Kurile Through, Sea of Okhotsk: 1 — western (stations 2222, 2225, 2227), 2 — northern (2356, 2357), 3 — southwestern (2361, 2363, 2364, 2367, 2368); 4 — Vityaz Ridge, Sea of Okhotsk (station LV 41-16); 5—10 — Sea of Japan: 5 — Primorsk continental slope (1076, 1126), 6 — Pervents Upland (1747), 7 — Alpatov Upland (2047, 2212), 8 — Okushiri Ridge (1708, 1713), 9 — Oki Ridge (1270), 10 — South Yamato Ridge (1434).

Thus, the habit of crystals of mineral individuals of submarine gypsum differs from that of cellar gypsum.

Submarine gypsum was formed at the surface of substrate that is the Cenozoic (Late Paleocene to Late Miocene) rocks. Authigenic gypsum as sporadic twins of 30×10×1 μm in size (Fig. 4f) and tables 4×5×1 μm (Fig. 4g) was found within the rocks.

The chemical composition of most part of the newly formed submarine (cores of lamellae) and cellar (surface of needles and tables) gypsum is usual (henceforward wt.%): 25.29—28.12 Ca, 21.57—23.7 S, and 46.84—48.0 O. Insignificant admixture of Si (up to 2.0), Cu (up to 0.87), and Al (up to 0.43) is frequent; Fe up to 0.53 is occasional; and Zn (0.78) and Ti (0.75) are in isolated compositions (see Table 1).

The complex composition of surface of the broad part of subsea gypsum lamellae is characterized by lowered content of Ca (16.96 wt.%) and S (16.12), elevated content of O (53.44), Si (4.98), Al (1.08), Fe (1.27), and presence of K (0.82), Na (2.49), Mg (0.59), Cl (1.42) (anal. 3). The composition of the surface of convex isometric cellar gypsum is similar. The absence of Cl in the cellar gypsum is the unique difference (anal. 6).

As aforementioned, two varieties of gypsum were found within the rocks which were basement for submarine gypsum. The chemical composition of tabular gypsum is close to theoretical, whereas that of gypsum twins is slightly different. With the same O content (48.33—48.78) and close Fe content (0.91—1.17), the latter is characterized by the lower concentration of Ca (19.66—20.35) and S (19.12—19.37), and higher content of Si (8.2—8.94) and Al (1.56—1.62); in addition, K (0.32—0.56), Na (0.55), and Mg (0.39—0.57) were measured. This composition is similar to the complex composition of the surface of the broad part of submarine lamellae and convex cellar gypsum (anal. 3, 6).

The substrate is distinguished by high (in comparison with gypsum) content (wt.%) of Si (19.93—3.64) and O (24.68—64.05); Mg (0.32—1.97), Al (1.06—9.73), S (0.32—2.34), and Fe (0.38—11.07) are constant; K (0.37—4.36), Na (0.7—2.18), Ca (1.83—2.75), Cl (0.3—1.26), and Ti (0.4—1.15) are frequent; and Cu (0.68—2.35) and Zn (0.59—0.61) are occasional (see Table 1).

Discussion

Gypsum is known to be formed in marine sediments as indicated by its frequent findings in the core of Cenozoic biogenic-siliceous rocks raised from floor of Atlantic, Indian, and Pacific Oceans (Briskin and Schreiber, 1978; Muza and Wise, 1983). Many scientists suggest that gypsum is formed at the early diagentic stage close to water/sediment interface. It precipitated (in most districts studied) in anoxic environment with involvement of anaerobic bacteria and significant amount of organic matter. The necessary concentration of Ca^{2+} is believed to be reached due to dissolution of carbonate microfossils composing sediments (Briskin and Schreiber, 1978; Muza and Wise, 1983; Schnitker *et al.*, 1980), whereas the link of SO$_4^{2-}$ with sulfate-reducing bacterial activity is proved only theoretically. Common association

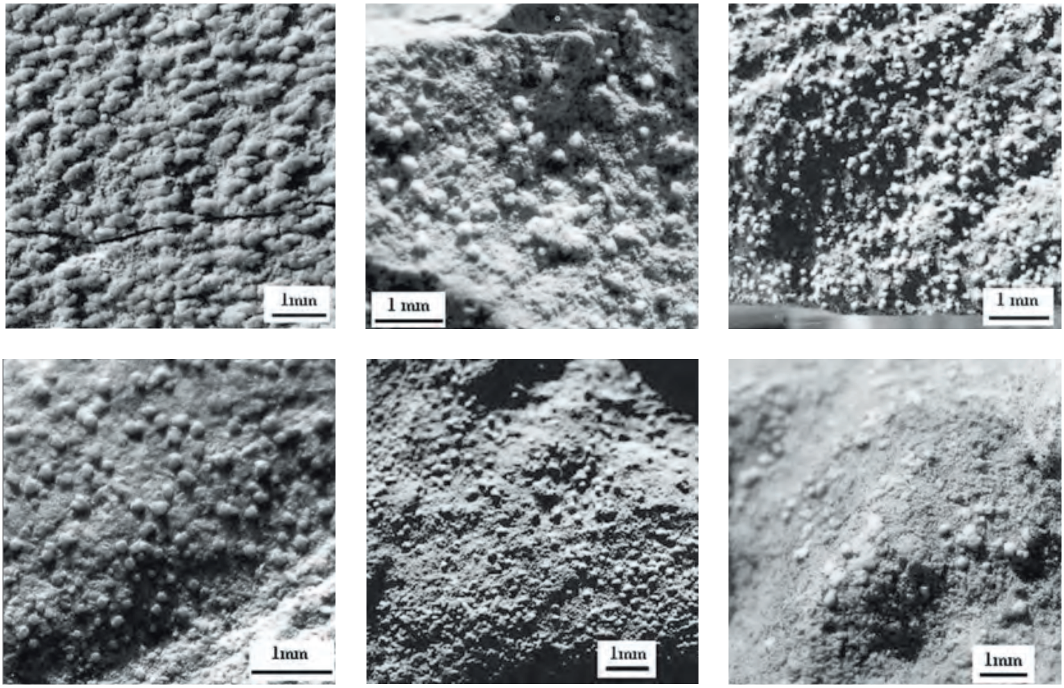

Fig. 2. Morphology of aggregates of submarine gypsum. Numbers of samples correspond to the sample locations shown in Fig. 1: a — cherty mudstone, sample 2227-a; b — diatomite, sample 2356-1; c — cherty silty mudstone, sample 2364-2; d — cherty silty mudstone, sample LV 41-16-1; e — silty mudstone, sample 1126; f — tuff stone, sample1747-2t.

Fig. 3. Morphology of aggregates of submarine (a, c, d, f) and cellar (b, e) gypsum: a — cherty silty mudstone, sample 2047-3; b — diatom clay, sample 2047-2; c — cherty rock, sample 1713-8a; d — silty mudstone, sample 1713-9; e — diatom tuff, sample 1296-4b; f — tuffdiatomite, sample 1434.

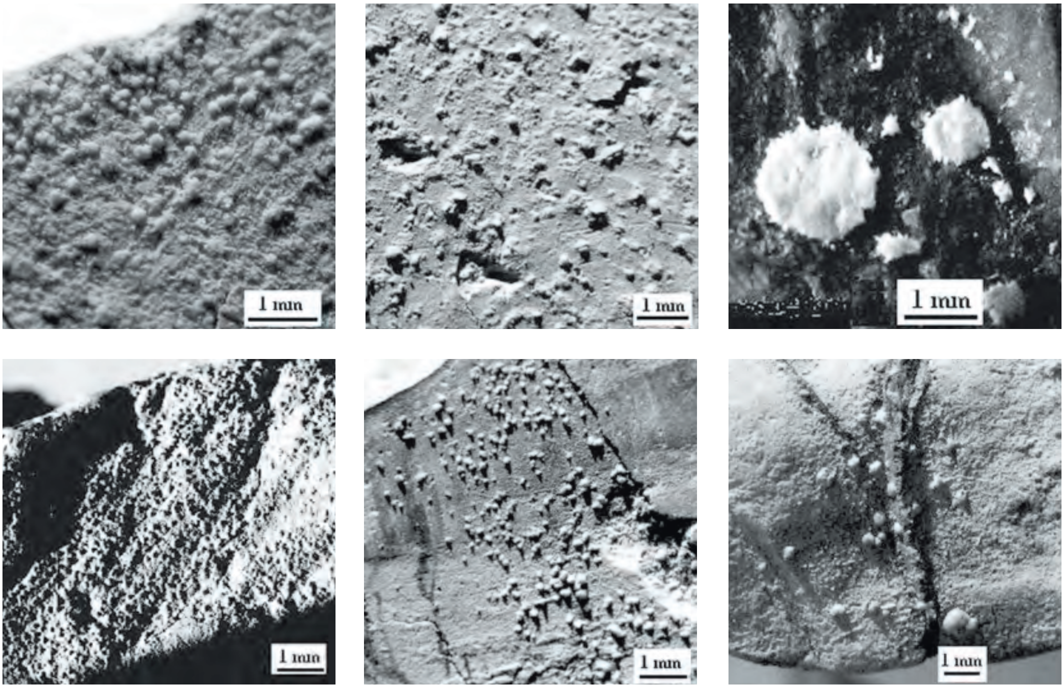

Table 1. **Composition of gypsum and substrate of Cenozoic rocks in Japan and Okhotsk Seas**

№ an.	№ sample	Location	Number of points	Content of elements (wt.%)												
				Ca	S	O	Si	Cu	Al	Fe	Zn	Ti	Mg	K	Na	Cl
Submarine gypsum																
1	2227-a	inner part of lamella	5	25.67	23.35	48.26	2.47	–	0.37	–	0.39	0.38	–	–	–	–
2	1713-8	inner part of lamella	8	25.11	24.02	46.86	0.14	0.58	–	–	0.53	0.38	–	–	–	–
		surface of lamella	2	28.64	23.62	46.98		0.36			0.39					
3	1713-8	surface of broad part of lamella	1	16.96	16.12	53.44	4.98	0.8	1.08	1.27	–	–	0.59	0.85	2.49	1.42
Cellar gypsum																
4	2047-2	surface of needle	2	25.77	23.58	47.74	1.45	0.93	0.43	–	–	–	–	–	–	–
5	2047-2	surface of plate	2	26.09	23.51	47.63	1.39	0.80	0.51	–	–	–	–	–	–	–
6	2047-2	surface of convex segregations of gypsum	1	22.75	20.05	47.59	5.54	0.81	1.47	0.46	–	–	0.42	0.37	0.55	–
Gypsum in substrate																
7	2227-a	surface of twined segregation	3	20.00	19.24	48.56	8.43	–	1.60	1.00	–	–	0.28	0.47	0.28	–
8	2047-2	surface of table	1	25.07	23.54	47.97	1.6	1.12	0.7	–	–	–	–	–	–	–
Substrate																
9	2227-a	substrate	2	0.92	1.85	55.58	30.65		4.36	2.13	–	0.2	1.29	0.76	1.62	0.62
10	2047-2	substrate	2	2.44	2.92	56.52	33.10	0.89	1.18	0.47	–	–	0.14	0.14	1.49	0.63
11	2047-a	surface of diatom	1	1.85	1.46	64.05	26.96	0.78	1.27	0.84	0.59	0.43	0.32	0.37	0.70	0.38

Notes: Scanning electron microscope equipped with integrated standards for qualitative (Point & ID) EDS analysis.
The sums obtained were normalized to 100%. N.N. Barinov, analyst.
High content of Si, Al, and Fe is resulted from rapid growth of gypsum, when it does not manage to release impurities trapped at crystallization.

of gypsum and pyrite suggests accumulation of SO_4^{2-} in interstitial water (involving gradient of diffusion) during the formation of pyrite SO_4^{2-} is probably accumulated as a result of dissimilatory sulfate-reducing to form H_2S followed by the transition of sulfide sulfur to sulfate ion by chemo- and phototrophic sulfur-bacteria and archaea (Grabovich, 1999). The available models of the SO_4^{2-} concentration in porous water do not explain the formation of authigenic gypsum (found in the rocks from drill cores deep-water holes) in oxidative environment. The model of concentration of sulfate ion in sediments as a result of its diffusion from sea-water is applicable to this sedimentation environment (Berner, 1970). SO_4^{2-} could be accumulated in both sediments enriched in oxygen and sediments enriched in H_2S.

In our case, authigenic (submarine) gypsum was formed on the rock surface rather than in sediments. Porous solutions were probable source of Ca^{2+} and SO_4^{2-} As aforementioned, gypsum studied here is divided into two types in chemical composition: usual and more complex distinguished by the admixtures of Mg, K, and Na and occasionally Cl. The qualitative chemical composition of the second type is close to the of substrate and sea water (Brownlow, 1984). The both types were found in both submarine and cellar mineralization in samples from three different districts. The geographical abundance of gypsum allows relict sea-water as common source of Ca^{2+} and SO_4^{2-}.

All samples containing gypsum are rocks displaying transformation of biogenic opal (A-opal) to CT-opal (cristobalite). In the Cenozoic rocks of the Japan and Okhotsk Seas, cristobalite was resulted from crystallization of silica of frustules dissolved in porous water (Mozherovsky *et al.*, 2001; Svinnikov, 2004). In the samples studied here, orals of diatoms are dissolved partially (semi-dissolved diatoms, sample 1296-4b) or completely (to form holes, samples 1713-9, 1747-2t, 2047-2). Crystallization of dissolved silica is shown as cristobalite that was established with the X-ray as insignificant impurity, initial transformation of A-opal (samples 1296-4b, 1434), rock-forming mineral (the process is appreciable) along with CT-opal (samples 1126, 1713-8b, 2047-3, 2227-a,

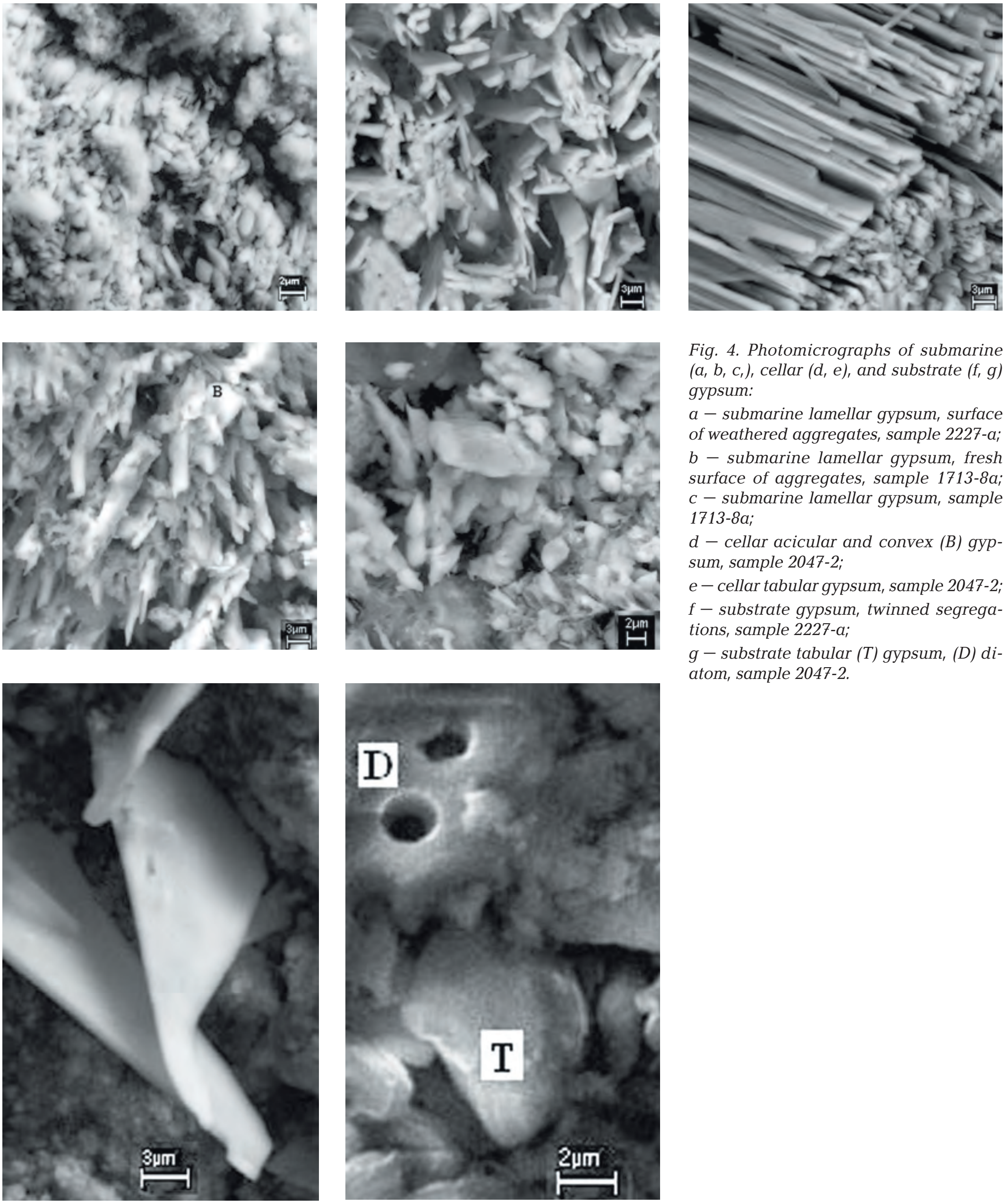

Fig. 4. Photomicrographs of submarine (a, b, c,), cellar (d, e), and substrate (f, g) gypsum:

a — submarine lamellar gypsum, surface of weathered aggregates, sample 2227-a;

b — submarine lamellar gypsum, fresh surface of aggregates, sample 1713-8a; c — submarine lamellar gypsum, sample 1713-8a;

d — cellar acicular and convex (B) gypsum, sample 2047-2;

e — cellar tabular gypsum, sample 2047-2;

f — substrate gypsum, twinned segregations, sample 2227-a;

g — substrate tabular (T) gypsum, (D) diatom, sample 2047-2.

2356-1, 2364-2, LV 41-16-1), and predominant constituent (pronounced reflection at 0.413 nm, sample 1713-8a). Thus, in the Cenozoic sediments of the Japan and Okhotsk Seas, gypsum is spatially related to the transformation boundary A-opal/CT-opal (A/CT).

The process of transformation of silica is well studied in the core of Cenozoic biogenic siliceous rocks obtained with deep-sea drilling in different districts of the World Ocean (Murray *et al*., 1992). Some publications give data of distribution of the composition of interstitial water along sections of holes crossing the A/CT boundary. Cristobalite was found at depth (thickness of sediments) ca. 200 m, drill hole 469 and ca. 150 m, drill hole 471 when the Cenozoic (Miocene to Quaternary) cover was drilled in the region of the California continental borderland

(Eastern Pacific) (Grechin *et al.*, 1981). Cristobalite was established in the Mesozoic to Cenozoic siliceous rocks at the depth ca. 300 m (Eocene-Oligocene boundary) in the Nauru depression (drill hole 462, region of Caroline and Marshall Islands, Western Pacific) (Riech *et al.*, 1981). Cristobalite was found at the depth ca. 140 m in the core of the Upper Miocene calcareous mudstone from the Barbados Ridge (drill hole 672 m, region of Lesser Antilles, Western Atlantic Ocean) (Capet *et al.*, 1990). Content of SO_4^{2-} and Ca^{2+} in interstitial water of Cenozoic rocks in these morphostructures ranges from 27.9 to 18.9 and from 29.0 to 12.14 mmol/L, respectively above the A/CT boundary. Below this boundary, the content of these ions is 24.9 to 1.6 and 29.45 to 79.2 mmol/L, respectively. The content of SiO_2 below the boundary drastically (2 – 10 times) drops (from 1030 – 1116 to 584 – 93 μmol/L) due to the formation of solid phase that is cristobalite (Gieskes, Johnson, 1981; Gieskes *et al.*, 1981; 1990).

The maximal solubility of gypsum in water without regard for effect of other components is known to be 2.05 – 2.11 g/L that corresponds to 21 mmol/L for SO_4^{2-} and 51 mmol/L for Ca^{2+} within the temperature range of 20 to 50°C. At temperature above and below these values, its solubility drastically decreases (Great Encyclopedia..., 2008). The range of temperature 36.5 to 51.0°C within cristobalite is formed (Kuramoto *et al.*, 1992) is similar. According to Gieskes, and Johnson (1981), porous water in sedimentary rocks from all holes 10 – 27 m higher than the A/CT boundary is saturated in SO_4^{2-} and undersaturated in Ca^{2+} (to form gypsum at 20 – 50°C). Below (45 – 207 m) of the A/CT boundary, porous water (drill holes 469, 462, 672) is also saturated in SO_4^{2-}; below 200 m, the content of SO_4^{2-} decreases (down to 1.1 – 0.1 g/L). The content of Ca^{2+} below the A/CT boundary gradually increase and below 200 m becomes high (drill holes 469, 672, and 462, at depth 190, 187, and 207 m, respectively). The concentration of Ca^{2+} continues to increase downward and reaches 3.1 g/L at 340 m in drill hole 672 and at 555 m in drill hole 471. At the depth below 200 m of the A/CT boundary, porous water is the maximum saturated in gypsum that is confirmed by the content of SO_4^{2-} 2.4 g/L and Ca^{2+} 2.3 g/L at 207 m in drill hole 462.

Thus, interstitial water of the Cenozoic cristobalite-bearing rocks of the Pacific and Atlantic Oceans have high content of SO_4^{2-} and Ca^{2+} at the depth ca. 200 m below the A/CT boundary. Frequent findings of gypsum resulted from drying of porous solutions in core samples of deep-sea drilling in bank of core storage supports this (Briskin and Schreiber, 1978).

The similar situation is probable in the Cenozoic rocks of the floor of the Japan and Okhotsk Seas. The assemblage of submarine gypsum and cristobalite, presence of gypsum in substrate (cristobalite), and the formation of cellar individuals on the rock surface in stone storage room indicate the high concentration of Ca^{2+} and SO_4^{2-} in the porous water of the samples studied here.

The examined gypsum was formed on the surface of primary diatom-bearing sedimentary and volcanosedimentary rocks. The sediments of the Japan and Okhotsk Seas, where transformation of A-opat to CT-opal is weak (dissolved diatoms, absence or traces of cristobalite) are weakly lithified and high porous. In most samples, transformation of silica was terminated by the formation of lithified siliceous assemblages (chert, cherty siltstone and mudstone), where cristobalite is rock-forming mineral. The rocks similar in composition are highly fractured (diagenetic and tectonic nature); because of this fracturing the common hydrodynamic system occurs in the sedimentary system (Tectonics..., 1985). It is evident that under lithostatic pressure, porous solutions should be pressed off on the outcropped rock surface.

Submarine gypsum on the rock surface indicates its formation at the contact with seawater. In the Sea of Japan, gypsum-bearing rocks were raised from the depth of 300 to 2900 m. The temperature of near-bottom water ranges from 0.14 to 1.5°C (Hydrometeorology..., 2003). In the Sea of Okhotsk gypsum-bearing rocks were raised from the depth of 1350 – 2900 m. The temperature of near-bottom water in the dredging area is 1.9 – 2.1°C (Hydrometeorology..., 1998). As aforementioned, cristobalite crystallizes at ca. 40°C. The similar bed temperature (42 – 62°C) was established in the sequences, where cristobalite is a rock-forming constituent (Tectonics..., 1985). The above data are testimony that there is a thermal gradient at the boundary between porous water (rock surface) and sea-water. Drastic drop of temperature at this boundary results in decreasing solubility of gypsum that appears to determine the mineral precipitation immediately on the rock surface.

Thus, in our opinion, the formation of submarine gypsum is determined by high concentration of Ca^{2+} and SO_4^{2-} in porous water of the rocks outcropped on the sea floor, lithostatic pressure of overlaying sequences, and thermal gradient at the boundary between porous and sea water.

In the drill core raised from the floor of Atlantic, Indian, and Pacific Oceans, gypsum usually occurs as single or twinned crystals of selenite (up to 5 mm in diameter) and gypsum rosettes (from 2 to 7.5 mm) (Muza and Wise, 1983; Briskin and Schreiber, 1978). Tabular and prismatic to acicular (Briskin and Schreiber, 1978), prismatic, and flattened (0.5×1.0×1.5 mm) (Criddle, 1974) crystals of gypsum are very seldom. According to description and photos, all these crystal types differ from those studied here in both habit and significantly larger size. Radial aggregates (spherulites) of gypsum similar in size to spheroids of cellar gypsum are formed on the surface of pebbles in continental environment. In caves, gypsum is resulted from saturated solutions filtrated through porous carbonate substrate under effect of outer (hydrostatic) pressure. This model of gypsum formation at the contact of porous substrates saturated in mineralizing solutions and air (Maltsev, 1996) is close to that of the formation of submarine gypsum proposed in this study.

In addition to the conditions governed by natural environment, the process related to human factor – deteriorating environmental situation – is known. This is sulphatization that is «disease» of marble and limestone sculptures and constructions resulted in the formation of black patina by gypsum, other authigenic minerals, and moruloids. Lamellar crystals (up to 30 μm) forming «continuous carpet» of rosettes were found in these assemblages among numerous individuals of gypsum (Timasheva *et al.*, 2007). Some individuals of this gypsum are close in size to those of submarine gypsum, but frequently differ in curved shape and disordered relationship to each other.

Conclusions

Thus, the aggregates of authigenic gypsum from the Cenozoic rocks of the Japan and Okhotsk Seas interesting in their morphology were examined. These aggregates are unusual due to their morphology, shape of individuals, and conditions of formation. The occurrence of gypsum is determined by the following reasons: high concentration of Ca^{2+} and SO_4^{2-} in porous water in the Cenozoic rocks outcropped on the floor, lithostatic pressure, and thermal gradient between porous and sea water.

The abundance of gypsum in the rocks on the slopes of submarine morphostructures of the Japan and Okhotsk Seas allows considering this region as a province (Frolov, 1992) of submarine authigenic gypsum mineralization.

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

MORPHOLOGICAL STUDY OF THE MEANS OF ACCOMMODATION OF ADMIXTURE ATOMS IN THE CRYSTAL STRUCTURE OF MOLYBDENITE

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Accommodation modes of trace elements were studied in molybdenite from porphyry copper, quartz vein greisen and other ore types by means of microprobe analysis (on a Camebax-microbeam) and morphological analysis of secondary-electron images (SEI, on a Jeol 6700F scanning electron microscope). Molybdenite is one of the main minerals concentrating Re. Our microprobe analysis do not show any differences in the Re distribution in molybdenite from deposits of different genetic types. Re concentrations above the detection limit (0.04 – 0.05 wt.%) were found only at 98 analytical spots of the analyzed 284 spots. These proportions practically do not change at Re concentrations in the specimens varying within the range of 80 – 1100 ppm. Analysis of the secondary-electron images makes it possible to identify structural defects of crystals in the examined specimens: splitting into thin sheets (0.05 – 0.50 μm thick), intense growth of dendrites and the development of screw, edge and other types of dislocations (1 – 6 μm in characteristic size). Hexagonal pits (negative crystals) geometrically corresponding to crystals of the hexagonal 2*H* molybdenite polytype testify that our specimens are dominated by this polytype, with triangular pits geometrically corresponding to crystals of the 3*R* trigonal (rhombohedral) polytype found very rarely. The accommodation modes of minor elements in the molybdenite structure are controlled first of all by structural defects and Re atoms are often concentrated at dislocations.

7 figures, 15 references.
Keywords: molybdenite, polytype, rhenium, morphological analysis, dislocation.

Introduction

Modern analytical techniques make it possible to study minerals at micro- and even nanometer scales. Molybdenite has been extensively studied by a diversity of physical (X-ray diffraction topography, electron microscopy, etc.) and chemical (calorimetric analysis, etching-pit method, etc.) techniques. This mineral is a principal concentrator of Re, an element of paramount importance for modern industry, whose individual minerals are very rare and are thus of no economic interest. Molybdenite is a semiconductor and can consequently be successfully utilized, along with silicon, in nanoelectronics to artificially separate chemically pure and structurally perfect monomolecular layers of synthetic crystals (Atuchin, 2011).

Electron properties of natural molybdenite broadly vary from sample to sample because of the structural and chemical heterogeneity of its individual crystals. Interaction of admixtures with defects in the crystal structure of the host mineral leads to the accumulation of these admixtures and development of local structured domains with elevated concentrations of these admixtures (Alekseev and Marin, 2012). Enrichment of minerals in certain chemical elements often disturbs the regularity in the atomic structures of these minerals.

Molybdenite MoS_2 is characterized by a layered crystal structure. In the planes of the sheets, Mo and S atoms are connected by strong covalent bonds, whereas chemical binding perpendicular to the layers is of the Van der Waals type, very weak and can be easily broken by even a minimal mechanical action. Molybdenite occurs in nature in two polytypes: the overwhelming majority of specimens of this mineral from 200 deposits are its hexagonal 2*H* modification (a = 3.16Å, c = 12.3Å, Z = 2)), the other, strongly subordinate, polytype is 3*R* trigonal rhombohedral (a = 3.16Å, c = 18.33Å, Z = 3) and the rest of the specimens consist of a mix of these polytypes (Khurshudyan *et al.*, 1966; Chukhrov *et al.*, 1968; McCandless *et al.*, 1983; and others). Both polytypes are stable within a broad temperature range. Literature data on the polytypes of molybdenite from high-temperature deposits is still very scarce. For example, molybdenite specimens from the Kamchab pegmatite deposit, S. Africa, contain 44 and 35% of the 3*R* polytype, which bear 700 and 1800 ppm Re, respectively (McCandless *et al.*, 1993). The content of the 3*R* polytype in molybdenite from skarn deposits (Newberry, 1979; McCandless *et al.*, 1993) ranges from 5%

(100 ppm Re) to 30 – 90% (750 ppm Re). At the same time, this mineral from Pitkjaranta, Karelia and Ak-Kezen', Kazakhstan, consists solely of the 2*H* polytype (Chukhrov *et al.*, 1968).

The principal aim of our research was to elucidate the means of accommodation of admixture atoms in the crystal structure of molybdenite. Among all admixture atoms, Re is the only one always detected in all molybdenite specimens, which contain this element in concentrations from a few ppb to 2000 ppm and even higher (Voudouris *et al.*, 2009). Elevated concentrations of Re, as well as other minor elements, such as W and Fe, are usually found in the rhombohedral 3*R* polytype of the mineral. It has been experimentally demonstrated that crystals of 3*R* molybdenite grow at spiral dislocations, which are produced in the presence of admixtures (Newberry, 1979). At the same time, structural analysis of four Re-rich (0.45 – 4.2%) molybdenite specimens from northern Greece indicates that the mineral crystallized as its hexagonal 2*H* polytype (Voudouris *et al.*, 2009). Several researchers studying Re accommodation in molybdenite explain this by isomorphism between Re and Mo (Noddack and Noddack, 1935; Pokalov, 1963; Kosyak, 1965; McCandless *et al.*, 1993; and others).

Methods

In order to elucidate the modes of Re accommodation in the crystal structure of molybdenite, we have examined molybdenite specimens from ten deposits of various genetic types in Mongolia, Magadan area, Transbaikalia and the Urals. The specimens were studied with the use of an electron microscope (BSE images) and X-ray microprobe (Maximyuk and Kulikova, 2013). The morphology of molybdenite in the specimens is very diverse: it occurs as large (0.3 – 1 cm) aggregates, individual platelets, aggregates of such platelets in quartz and as thin films in fractures (slickensides). Microprobe analysis was carried out using a Camebax-microbeam, in polished sections and epoxy pellets impregnated with molybdenite grains. Aggregates and individual platelets of molybdenite were either perpendicular or parallel to the polished surfaces of the pellets. Sites for their analysis were selected based on BSE images of the molybdenite crystals.

Mo and S concentrations in the mineral were determined using the intensities of the $L\beta_1$ and $K\alpha$ reflections, respectively, at an accelerating voltage of 20 kV and beam current of 25 – 30 nA, using a PET crystal, with regard for the contribution of the Mo line to the intensity of the $K\alpha$ line of S. Re concentrations were calculated from the intensity of the $L\alpha$ line of Re, using a LiF crystal, with regard for the overlap of the Zn line and with the amplitude discrimination of the signal (the Zn concentration was determined from the $K\beta_1$ line, with regard for the overlap of the W line). For the sake of control, we also made use of the $M\alpha$ line of Re (TAP crystal), which was complicated by the overlaps of lines of W, Pb, Si, Ca and certain other elements that are commonly found in molybdenite.

The standard for Re was high-purity metallic Re and the standards for S, Mo, Zn and W were sulvanite Cu_3VS_4, powellite $CaMoO_4$, sphalerite ZnS and scheelite $CaWO_4$. The detection limit of Re in molybdenite was 0.04%. The analytical technique is described in much detail in our earlier publication (Maximyuk and Kulikova, 2013).

Back-scattered electron (BSE) images show the microtopography of the surface of the sample. The images were acquired under a Jeol 6700F with field emission and a cold cathode at an accelerating voltage of 5 kV; crystal morphology was examined in SEI (occasionally LEI and ADD) modes. No chemical composition of mineral was determined in regions where the BSE images were taken.

Microprobe analysis

Microprobe analysis of the mineral was conducted using its specimens from molybdenum-copper porphyry and quartz-vein greisen deposits. The Re concentrations have been preliminary roughly estimated by colorimetric techniques by G.G. Lebedeva at the Institute of the Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements.

We have not detected any differences in the Re distribution in molybdenite from deposits of various genetic types and the only discernible differences were the concentrations of this element. The X-ray microprobe analysis of molybdenite crystals in planes parallel to its cleavage and perpendicular to it reveal that Re is extremely unevenly distributed in the mineral and that Re concentrations unsystematically vary. Re in concentrations higher than its detection limit (0.04%) but lower than 0.42% were detected at 98 of 284 analyzed spots (i.e., at 35% of the spots) and this proportion practically did not vary at Re concentrations in the specimens varying from

80 to 1100 ppm. The fact that Re may be concentrated within very small domains results in that this element is sometimes not detected when the beam was shifted for a few micrometers away from spots with elevated Re concentrations. Moreover, both Pb and W were determined to behave analogously to Re. An equally uneven Re distribution is also typical of poorly polishable aggregates that typically have a "hillocky" surface topography and bear the highest Re concentrations.

Our microprobe analytical data led us to suggest that the uneven Re distribution in the molybdenite crystals at Re concentrations higher than 0.04% may be explained by defects in the crystal structure of the mineral, namely, by the presence of tiny inclusions of 3*R* molybdenite in a matrix of 2*H* molybdenite. Correlations between Re concentration in molybdenite and the proportion of its 3*R* polytype were mentioned by several researchers. Judging by literature data (Gertsen *et al.*, 2003; Newberry, 1979; McCandless *et al.*, 1993; and others), in spite of the broad scatter of the data, the content of the 3*R* polytype is likely to positively correlate with their Re concentrations. Thereby the contents of the 3*R* polytype generally range from 6 to 36% of the total of both polytypes ($3R + 2H$) at Re concentrations ≤1200 ppm.

Electron microscopic data

We took BSE images of the molybdenite specimens from the Erdenet, Mongolia and Mys Pavlovich, Magadan area, Mo-Cu porphyry deposits that had been analyzed on a microprobe. The deposits are similar in mineralogy but differ in age and are hosted in different rocks.

Molybdenite is one of the principal ore minerals at the Erdenet deposit and occurs at it in a number of populations. We have studied molybdenite of the main, oldest molybdenite-quartz association. The mineral was found in the form of large (up to a few centimeters across) hexagonal tabular crystals and pockets and contains 760–1035 ppm Re. Molybdenite from the Mys Pavlovicha deposit is coarse-crystalline and is sometimes found as subhedral thick tabular crystals up to 3–5 cm across. According to chemical analyses, the mineral contains 363–393 ppm Re.

Detailed data have been previously obtained on the origin of various morphological features in a great number of various crystals, such as healing cracks (Lemmlein, 1973) and development of dislocations (Landau and Lifshitz, 1987; Novikov, 1975). Modern electron microscopic techniques make it possible to elucidate specifics of crystal growth mechanisms described by these researchers.

Our study of molybdenite at micrometer and submicrometer scales (hundreds of nanometers) indicates that molybdenite crystals can be easily split into sheets. Figure 1 shows SEM images of this splitting in naturally occurring molybdenite. The sheets are usually 0.05–0.10 μm thick and occasionally reach 0.50 μm (Figs. 1a–1f), which corresponds to 40–400 unit-cell parameters and roughly corresponds to the spacing of structural sheets. No sheet splitting have ever been observed even at magnifications as high as ×120 000 (Fig. 1f). The figures clearly show that the thin sheets warp in their margins to form hollow pipes in capillary cracks between split sheets of a crystal. The pipes are sometimes triangular (with rounded angles) in cross section (Figs. 1f, 1h). Molybdenite pipes approximately 0.4 μm in diameter and approximately 4–10 μm long often host minute (some 0.04–0.07 μm across) mineral crystals (Fig. 1b). The pipes are likely filled with solution (because some of the pipes show a meniscus) or a gas phase.

Figure 1d shows that empty space between molybdenite sheets is healed with minute aggregates (no larger than 0.10 μm across), which sometimes penetrate more than one sheet and are perpendicular to their planes. These aggregates resemble dendrites that grew between sheets and oriented them. It is known that material is deposited more rapidly closer to a tapering part of a crack. The material for the growth of the dendrite and healing cracks was mobilized via dissolving the walls of the cracks.

Molybdenite sample from the Erdenet deposit. Figure 2 displays SEM images of molybdenite specimens from the Erdenet (Figs. 1a–1d) and Kadzharan (Figs. 1e, 1f) deposits. As seen in Fig. 2a, the surface of the crystal is cut by cracks and displays numerous knobs and pits. In spite of the low magnification of the SEM image (×250) but thanks to the high resolution of the zoomed-in images, it can be seen that the knobs are spiral growth layers of the crystal on steps of the crack (shadows indicate that one side of the crack is somewhat higher than the other) that form spiral dislocations (A–C and E in Figs. 2a–2c). Some of them (B and C in Fig. 2b) show "ledges" with hexagonal sectorial crystals on their tips. Figure 3 (A–C and E, row I) displays geometrical representations of the

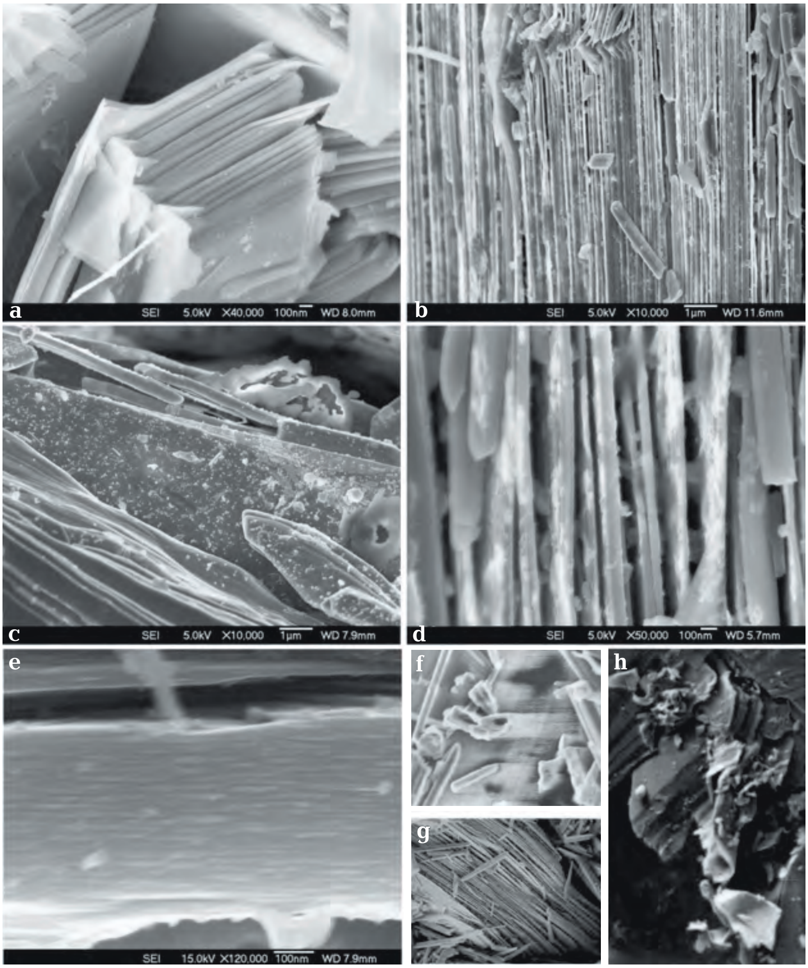

Fig. 1. Secondary-electron images (SEI) of molybdenite specimens split in thin sheets. (a, c, e) Erdenet deposit, Mongolia, (b, d, f, g), Pavlovich cape, Magadan area and (h) Kharbeiskoe deposit, Polar Urals. Magnification: a — ×40000; b — ×10000; c — ×10000; d — ×50000; e — ×120000; f — ×1000 (fragment); g — ×1000 (fragment); h — ×800 (fragment of an image taken on a Camebax-microbeam).

morphologies of the defects shown in Fig. 2. The linear dimensions of spiral sheets in Fig. 2 are equal: dislocation A is 4.4 μm (note the pronounced step of the crack), B is 8.4 μm (the hexagon is 3.1 μm), C is 3.9 μm and in E, the outer size of the hexagon is 10 μm. Dislocations B and C are geometrically similar to those in naturally occurring rosettes of molybdenite crystals.

Figure 2a displays a pit 3 μm in diameter (D), which has a hexagonal morphology (Fig. 2b, image fragment zoomed-in by a computer) and the SEM image of another sample from the Erdenet deposit shows a triangular pit (D, Fig. 3 row I). The pits were produced by dissolving molybdenite sheets where dislocations are exposed on the surface.

Defects whose distortion of structural perfectness extends to areas near a certain surface can be microscopically described as discontinuity surfaces. This linear imperfectness that defines the boundary of a displacement (slide) zone in the crystal is referred to as edge dislocation. In Fig. 1g, some sheets do not continue to the right-hand bottom portion. These are extra planes that act as a wedge and perturb the crystal lattice. Above the edge of the extra plane, the sheet spacing is lower than below the edge.

The displacement of an edge dislocation along a normal to the slide plane (climb) is related to mass transfer. The origin and displacement of edge dislocations toward a crystal margin can explain such structural defects as steps at plane margins (circled in the figure) in crystal bends (Figs. 2d — f).

Molybdenite sample from the Mys Pavlovicha deposit. Gray shades in the SEI image of molybdenite in Fig. 4 make discernible thin growth layers of the crystal. The growth front envelops various obstacles higher than the layer itself. The concentrations of

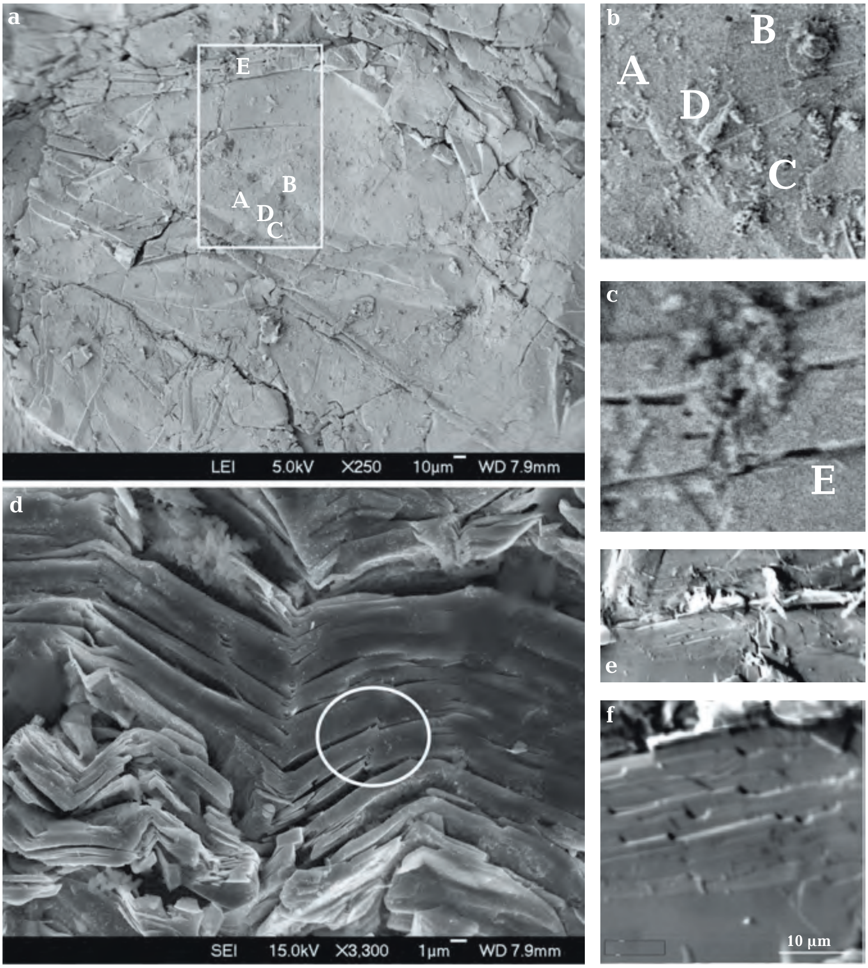

Fig. 2. SEM images of molybdenite specimens from (a — d) the Erdenet deposit, Mongolia and (e, f) Kadzharan deposit, Armenia. (a) Magnification ×250, letters A, B, C and D denote screw dislocations, D is a negative crystal. The white line contours the region of dislocations. (b, c) This region of dislocations (enlarged image); magnification: d — ×3300; e, f — ×800 and ×2000, respectively (taken on a Camebax-microbeam).

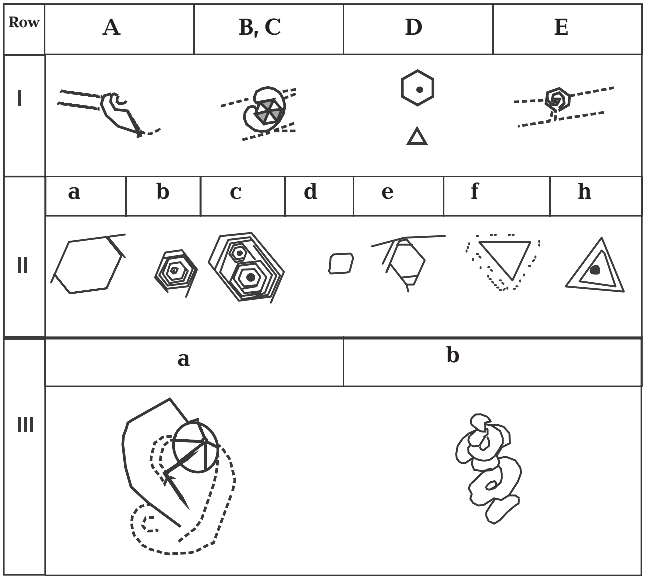

Fig. 3. Geometry of structural defects in our specimens:
row I: screw dislocations (A, B, C and E) and negative crystals (D) shown in Fig. 2a;
row II: negative crystals (a-g) shown in Figs. 5a, 5c,5 e, 5g and 5h;
row III: a — helical-layered growth contours of a crystal (Fig. 7a), arrows point to a pair of dendrite needles growing from a single center; b —contours of the screw dislocation shown in Fig. 7d.

Ca and Si admixtures (microprobe data) usually increase along the growth front of a molybdenite sheet, where clusters of minute particles are seen. The following four distinct regions are discernible in the image: (I) a region of relatively smooth surface with pits of certain morphology 2–4 μm across, (II) surface with numerous and diverse pipes up to 30 μm long and <1 μm in diameter, (III) surface with knobs up to 60 μm and (IV) region abounding in structural defects exposed at the surface and precluding the propagation of the growth layer. Smaller domains were selected for detailed studying in each of the regions.

Region I. Figure 5 presents a SEI image of this region of the molybdenite sample from the Mys Pavlovicha deposit. The geometry of the pits is shown in Fig. 3 (row II: a – e). The hexagonal pits in Figs. 5a, 5c, 5e are equant negative crystals of the hexagonal 2*H* molybdenite polytype (Figs. 5b, 5d). The geometric shapes of the pits exactly replicate the shape of the crystal itself. The negative crystals are formed via molybdenite redeposition with dissolution and evaporation of the material in a hydrothermal environment. The cavities are shaped, similar to shaping of growing crystals, by a tendency of minimizing the surface energy of the crystals. At intense evaporation and a small enough thicknesses of the surface layers, the holes go all the way through the layers (Fig. 5e), but if the layers are thick (Fig. 5c), layered spiral morphology of the negative crystals is manifested. Evaporation layers should correspond to spiral growth layers, which is explained by spiral dislocations in the crystal, which reach the crystal surface and form steps that are spiral growth centers of the crystal. It is known (Lemmlein, 1973) that layers ranging in thickness from a single unit-cell parameter to a few thousand such parameters often develop on crystals (Fig. 5c). Figures 5a and 5e show dendrites growing from beneath and seen through the holes.

Figures 5g and 5h (see contours in Fig. 3, row II, f and g) display two triangular pits with sides approximately 1 μm. The pits were found in region II. The triangular pits seem to be negative crystals similar to the molybdenite crystal of the rhombohedral 3R polytype (Fig. 5f).

Region II. As seen in Fig. 6, this region is characterized by intense growth of dendrites (the cross section of thin needles is ≤0.1 μm). During their early growth, crystals are usually not perfectly shaped and faceted but rather grow in the form of dendrites (Lemmlein, 1973). These are branching individuals that crystallize under unequilibrated conditions, when the edges and apexes of skeletal crystals split following certain laws. The resultant optically disordered subindividuals branch (see, for instance, Fig. 6b). When a little bit differently oriented branches of a single dendrite crystal merge, spiral dislocations develop at their boundary. One of such dislocations

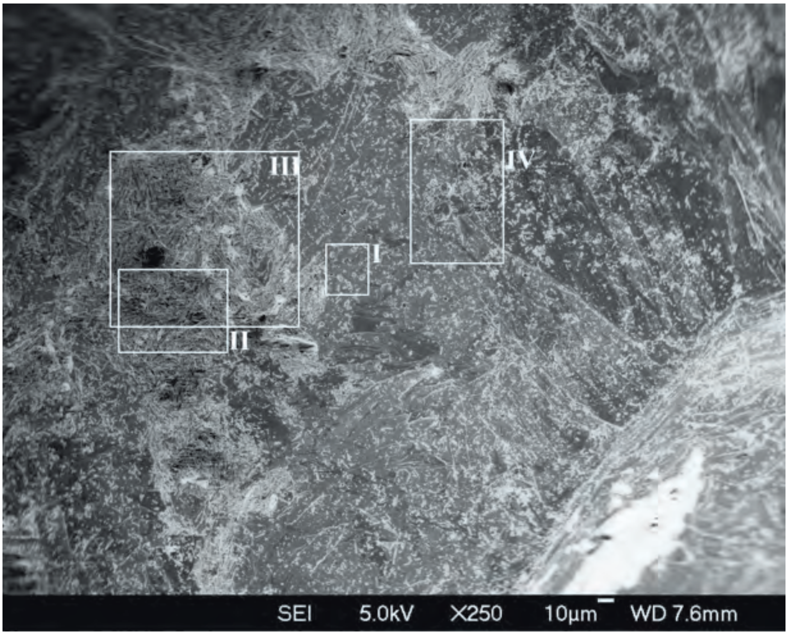

Fig. 4. SEM image of a molybdenite sample from the Pavlovich cape, Magadan area, magnification ×250. Rectangular contours outline four regions (I, II, III and IV, see text).

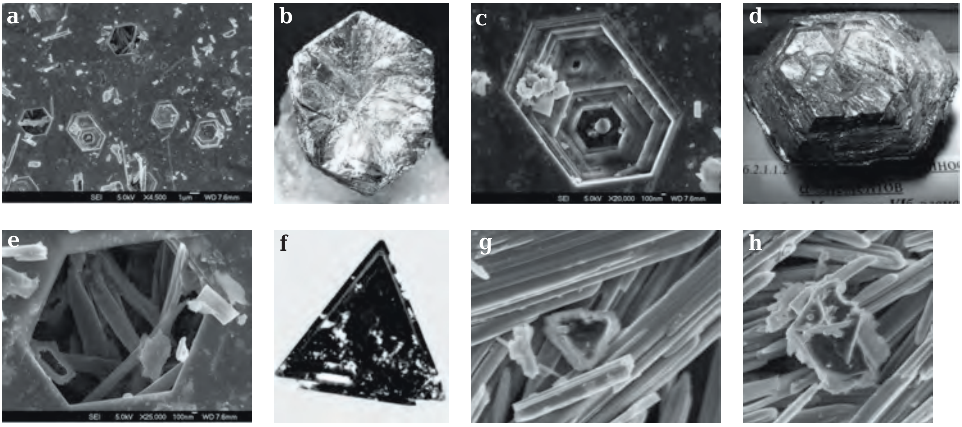

Fig. 5. SEM images of (a, c, e, g, h) negative molybdenite crystals in regions I and II (Fig. 4) from the Pavlovich cape, (b, d) molybdenite crystals, 2H polytype and (f) molybdenite crystals, 3R polytype.
Magnification: a — ×4500, c — ×20000, e — ×25000; g, h — enlarged fragments shown in Fig. 6a. Crystals: Molly Hill, Quebec, Canada (photo: Rob Lewinsky, see http://www.mindat.org/photo-20568.html); d — Selimitsa, Vitosha, Bulgaria (photo: A.A. Evseev, see http://geo.web.ru/druza/m-molib_0.htm); and f — Central Province, Zambia (photo: J. Ralf and I. Chaw, http://www.mindat.org/min-2745.html).

is displayed in Fig. 7d and the contour of this dislocation is portrayed in Fig. 3 (row III, b).

The richer the system in admixtures, the stronger the branching of the seed crystal and the higher probability that spiral dislocations are generated during further growth of the crystal (Lemmlein, 1973; Novikov, 1975). Compounds prone to crystallize in the form of dendrites commonly generate numerous dislocations (for example, metals).

Region II also shows thin sheets of the crystals rolled into pipes (some of them are exhibited in Figs. 1f, 1h). Several of the pipes are triangular in cross section, likely because of the elastic strain field of the crystal along the lines of edge dislocations. It is known that the imperfectness region of a crystal because of its edge dislocation (it is referred to as the core of dislocations) can be visualized as if enveloped by a cylindrical surface whose axis is the edge of the extra plane (Novikov, 1975; Landau and Livshits, 1987). In contrast to a screw dislocation, the strain field around an edge dislocation does not show a cylindrical symmetry (Novikov, 1975; Landau and Livshits, 1987): it has extension-gliding planes on its one side and compression on the other.

In the presence of admixture atoms, the elastic strain fields of a dislocation and an admixture atom interact and admixture atoms are accumulated at the dislocation. They are attracted to the edge of the extra plane near an edge dislocation and the concentrations of the atoms decrease away from the dislocation (Novikov, 1975). Figure 6d shows a crystal growing within a pipe under the effect of admixture atoms. In the triangular hollows of the pipes, rhombohedral 3*R* molybdenite polytype can grow in the presence of admixtures (Fig. 5f).

Free surfaces, cavities, cracks and dislocations are sources of vacancies in the crystal. The attraction of vacancies accounts for the origin of helical dislocations whose lines form geometrically regular screw (Novikov, 1975). The dislocations thereby acquire an edge component (Fig. 7c). Figure 7f shows the saw-toothed edges of the pipes shaped by geometrically regular spirals.

Region III. This region of the crystal (Fig. 4) abounds of dislocations of different types that are closely spaced (their spacing is nevertheless greater than the unit cell parameters). Such dislocations can be considered collectively and integrally (Landau and Lifshits, 1987). The concentration of dislocations commonly growths toward obstacles both in a single glide plane and in parallel planes, at a density reciprocally proportional to the square root of their distance. As the density of dislocations increases, collective effects start to play the main role, i.e., certain properties are now controlled by the interaction of several dislocation groups.

The only interacting force between homonymous edge dislocations (whose extra planes are similarly oriented relative to the gliding plane) in the same gliding plane is repulsion, whereas heteronymous dislocations, conversely, attract one another. The interacting force between parallel edge and screw dislocation is zero. It is much more dif-

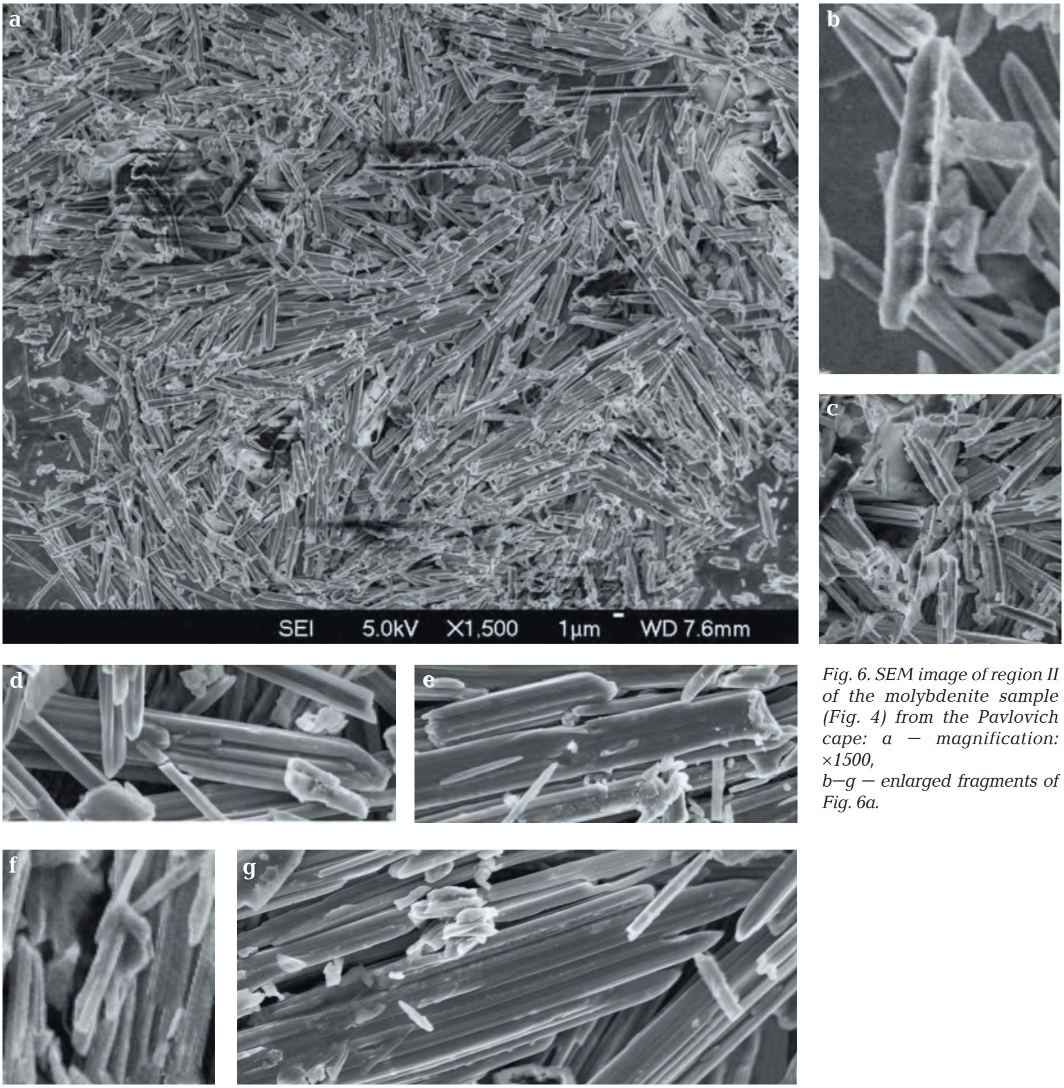

Fig. 6. SEM image of region II of the molybdenite sample (Fig. 4) from the Pavlovich cape: a — magnification: ×1500,
b–g — enlarged fragments of Fig. 6a.

ficult to evaluate the interacting force between randomly oriented dislocations.

Figure 4 displays the distribution of numerous interacting and propagating mixed dislocations. Figure 7a exhibits a fragment of Region III with discernible crystal growth contours of spiral-layer configuration (Fig. 3, row III, a). The spiral centers of this group of dislocations are spaced 50 μm apart. The spirals growing from these centers are different in their sense. The contours of the spirals are marked by dendrite needles that grow from a single center in perpendicular directions, one of which is tangent to the spiral plane. The growth directions of the needles change to opposite ones likely according to changes in the sense of the tangential and normal strain around the marginal constituent of this group of dislocations (Novikov, 1975). One of the centers of the joint dislocation group is the center of spiral growth of the layers and another center (pit) is the evaporation center of the layer and hence, only the needles of the tangential constituent can be seen in this area.

Region IV. This region in Fig. 4 (whose enlarged fragment is displayed in Fig. 7b) concentrates various dislocations: helical, which are perpendicular to the plane, are 0.5 μm across and 2 μm high; edge, which reach the surface at various angles and whose pipes are 2.5 μm in diameter; spiral, which are 2.5 μm in diameter; etc. The arrow within a group of dislocations in Fig. 7b points to a tri-

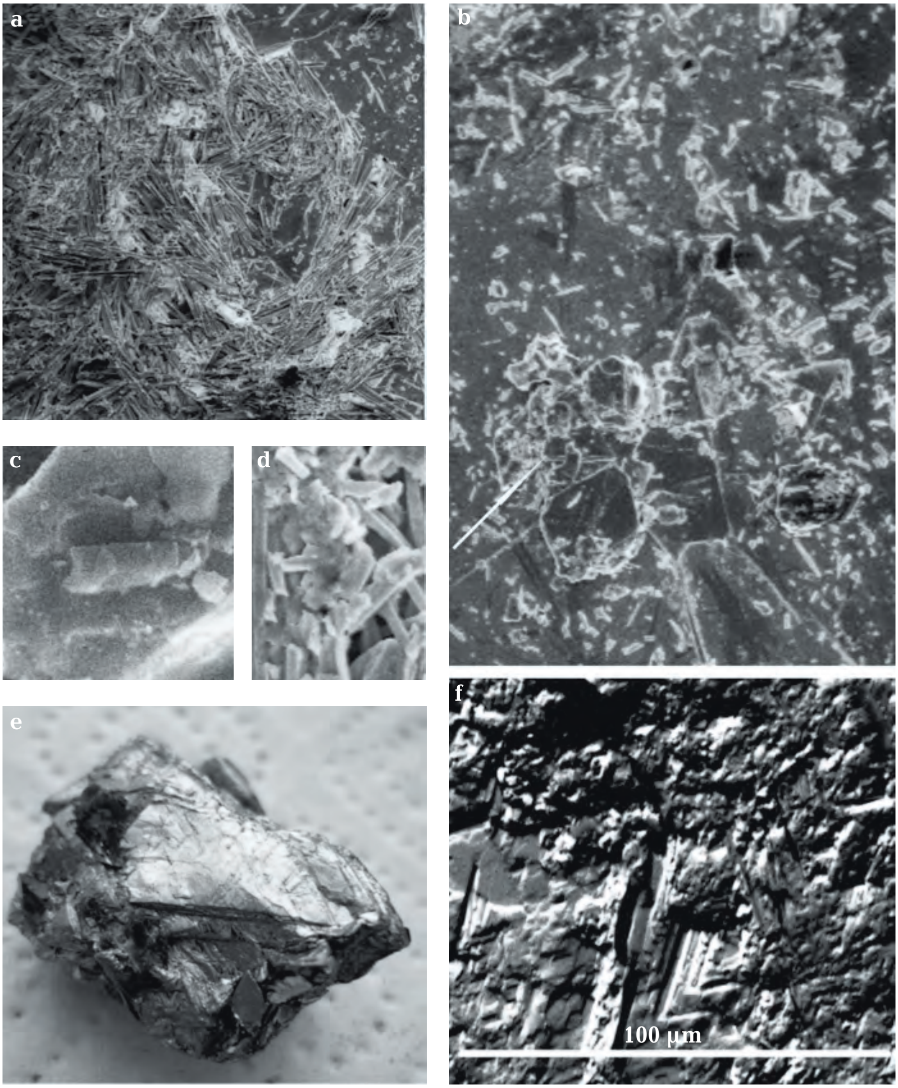

Fig. 7. Fragments of regions (a) III and (b) IV marked in Fig. 4. Dislocations: (c) helical (Fig. 2d) and (d) screw (Fig. 6a).
(f) Fragment of molybdenite image (sample from the Kharbeiskoe deposit, Polar Urals) taken on a Camebax-microbeam (all image fragments are enlarged by a computer). For comparison, the figure shows (e) 3R molybdenite polytype from the Slyudorudnik deposit, Mount Kyshtym, Chelyabinsk area, Urals (see http://форум.хитник.рф/download/file.php?id=2887&mode=view).

angular tablet (its sides are 7 µm long and its height is 0.2 µm). This minute domain resembles the triangular 3R molybdenite platelets in the sample from the Slyudorudnik deposit in the Chelyabinsk area in the Southern Urals (Fig. 7e). We have earlier obtained analogous results when studying molybdenite from the Kharbeiskoe deposit in the Polar Urals (Fig. 7f).

Discussion

Thanks to the layered structure of molybdenite, very weak bonds between its structural layers are readily broken under the effect of an even minimal force. Our X-ray microprobe and scanning electron-microscopic data demonstrate that molybdenite crystals can be easily split into thin sheets (0.05 – 0.50 µm thick), which can be readily shifted relative to one another, cracked and form voids. Defects in the crystals can be healed via intense growth of dendrites and the development of screw, edge and other dislocations. The dominant mechanisms generating dislocations in molybdenite crystals is the shift of one crystal part relative to another for a distances ranging one unit-cell parameter to hundreds and even thousands unit-cell distances. The boundary line of this shift can be seen as a line and is a structural imperfectness of the crystal at the nanometer scale. Screw dislocations observable in molybdenite are 1 – 6 µm in diameter.

Admixture atoms are concentrated at dislocations. In a group of dislocations, the greater the density of dislocations, the higher the concentration of an admixture "attracted" to them, with the concentration of the admixture rapidly decreasing away from the core of the dislocations. Surface regions of a sample with an elevated density of screw and other dislocations are usually poorly polishable. X-ray microprobe analysis of our specimens shows than molybdenite with such a characteristic knobby surface bears the highest concentrations of Re and other admixtures, such as W, Pb, Ca, Si and Fe. The accommodation of these elements in molybdenite is likely explained by their occurrence in the form of certain minerals rich in these elements: quartz, powellite, galena, scheelite, Fe oxides, etc. The admixtures are thereby concentrated within very small domains.

The loci of dislocations on the surface of a molybdenite crystal are marked by minute pits, which are negative crystals. The core of dislocations acts as a dissolution and evaporation center. The pits (2 – 6 µm across) on our specimens have clearly seen faces of negative crystals, which are often hexagonal and similar to hexagonal crystals of the 2*H* polytype of molybdenite. This led us to conclude that this polytype is dominant in our specimens. Triangular pits are negative crystals analogous to crystals of the 3*R* rhombohedral polytype of the mineral, which is very rare.

It has been experimentally demonstrated (Newberry, 1979) that crystals of 3*R* molybdenite grow on screw dislocations that are formed in the presence of admixtures. However, the occurrence of admixtures is only one of the possible reasons for the development of screw dislocations. In the vicinity of an edge dislocations, admixtures are concentrated at the edge of the extra plane. The rolling of the sheets into pipes is likely caused by the elastic strain field of the crystal along the line of edge dislocations. When a crystal grows in a pipe (which are 4 – 30 µm long, <0.40 µm in outer diameter and are sometimes triangular in cross section) because of admixture atoms, the pipe likely predetermines its structure as the 3*R* polytype.

Microprobe analyses and SEM images of molybdenite specimens make it possible to closely examine minute details in the structure of the mineral and the composition of its small fragments.

Our data indicate that admixture elements are accommodated in molybdenite at its structural defects, first and foremost, dislocations. This pertains not only to Re, an element of undoubted scientific and applied interest, but also to such elements as Si, Ca, Pb, W and Fe.

Acknowledgments

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PLATINUM AND PALLADIUM SULFIDES IN THE CRYSTALLIZATION PRODUCTS OF MELTS IN THE Cu–Fe–S SYSTEM

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To facilitate understanding conditions under which Pt and Pd sulfides were formed in Cu-Fe ores at magmatic Cu-Ni deposits of the Norilsk type, the crystallization of these minerals was experimentally modeled by cooling (from 1200 – 1100°C to room temperature) melts corresponding to the central portion of the Cu-Fe-S system doped with Pt and Pd (1 wt.%). The synthesized Pt and Pd sulfides are analogues of naturally occurring minerals: malanite $Cu(Pt,Fe)_2S_4$, cooperite PtS, vysotskite PdS and braggite (Pt,Pd)S. Their crystallization field in the examined portion of the Cu-Fe-S system (50 at.% S, Cu/Fe = 1.22 – 0.25 and 45 at.% S, Cu/Fe = 1.44 – 0.69) corresponds to the crystallization field of phase associations with chalcopyrite $CuFeS_2$ (Cu/Fe = 0.99 – 0.67), isocubanite $CuFe_2S_3$ (Cu/Fe = 0.61 – 0.48) and mooihoekite $Cu_9Fe_9S_{16}$ (Cu/Fe = 1 – 0.95). The line of the bornite Cu_5FeS_4 – mooihoekite $Cu_9Fe_9S_{16}$ – isocubanite $CuFe_2S_3$ separates the crystallization fields of Pt-Pd sulfides and Pt-Pd metallides. 2 tables, 1 figure, 18 references.

Keywords: Cu-Fe-S system, platinum, palladium, melt crystallization, Pt sulfides, Pd sulfides.

Introduction

Averaged data on the mineralogy of the Cu-Ni Norilsk ores indicate that their Pt and Pd amounts contained in minerals of these metals increase with increasing Cu content of the ores from their pyrrhotite to cubanite and then to chalcopyrite types (Dodin, 2002). It is currently generally believed that Pt-Pd minerals were formed in magmatic ores of the Norilsk type by their crystallization from magmatic fluid after the ore-forming sulfides (Genkin, 1968; Genkin *et al*., 1981; Distler *et al*., 1979, 1988, 1999). Thereby all researchers emphasized that the crystallization temperatures of several Pt-Pd minerals, such as isoferroplatinum Pt_3Fe, rustenburgite Pt_3Sn, atokite Pd_3Sn, cooperite PtS, vysotskite PdS and others, is higher than the crystallization temperatures of major ore-forming sulfides (chalcopyrite and pyrrhotite) and hence, they could have crystallized immediately from the melt. The behavior of Pt and Pd during crystallization of Pt-Pd sulfide melt is understood still inadequately poorly, largely because of our poor knowledge of the Cu-Fe-S system, whose central part corresponds to the compositions of the Norilsk Cu-Fe sulfide ores. Experimental data on the Pt and Pd speciation in the crystallization products of the central part of the Cu-Fe-S system at corresponding sulfur fugacity and 600°C (Kravchenko, Fedorova, 1996; Kravchenko, Kolonin, 1998) are consistent with data in (Evstigneeva *et al*., 1989; Evstigneeva, 1996) on isoferroplatinum and cooperite crystallization in hydrothermal systems. Similar to naturally occurring ores, the crystallization fields of Pt-Pd and Pd-Pt sulfides are separated in the phase associations of the Cu-Fe-S system (Kravchenko, 2009) and the boundary between these regions is so far uncertain. Our study was focused on experimental determining the stability field of Pt-Pd sulfides during the crystallization of the central part of the Cu-Fe-S system at 50 at.% S and Cu/Fe = 1.22 – 0.43 and 45 at.% S, Cu/Fe = 1.44. Provisional information has been obtained on phase equilibria in the central part of the Cu-Fe-S system at 50 at.% S, Cu/Fe = 1.22 – 0.25 and 45 at.% S, Cu/Fe = 1.44 – 0.69 (Fig. 1) and the composition of the respective phases: chalcopyrite $CuFeS_2$, isocubanite (cubic *fcc* cubanite) $CuFe_2S_3$, talnakhine $Cu_9Fe_8S_{16}$, mooihoekite $Cu_9Fe_9S_{16}$ and cubic *pc* haycockite Cu_4Fe_5S (Kravchenko *et al*., 2012).

Experimental

BThe starting materials were carbonyl iron A-2, copper B3, reagent-grade sulfur, which had been additionally dehydrated by fusing in vacuum, metallic platinum and palladium. Pt and Pd were added separately (1 wt.% each) or simultaneously (0.5 wt.% each) to the starting mixtures of the preparatorily synthesized samples and to the preparatorily synthesized Ce-Fe-S phase associations. The melts with Pt and Pd admixtures were cooled in the same regimes as the melts without these admixtures. The synthesis was carried out in vaccumized quartz ampoules by cooling the melt from 1200 – 1150°C to room temperature. The cooling regimes of the melts have been adjusted experimentally in order to obtain phase equilibria stable at room temperature (Kravchenko, 2011; Kravchenko *et al*., 2012; see the fig. 1). After synthesis, all crystallization

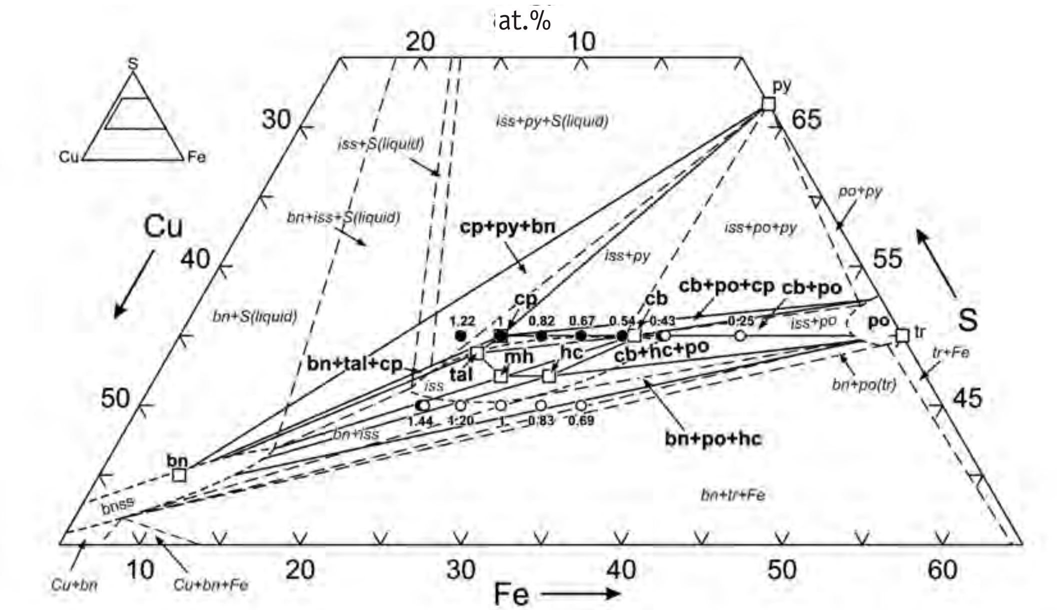

Fig. 1. Schematic representation of phase relations (solid lines according to Kravchenko, 2011, 2012) in the central part of the Cu-Fe-S system at 600°C (dashed lines according to Cabri, 1973).

□ — Stoichiometric compositions of chalcopyrite $CuFeS_2$ (cp), bornite Cu_5FeS_4 (bn), pyrite FeS_2 (py), troilite FeS, talnakhite $Cu_9Fe_8S_{16}$ (tal), isocubanite $CuFe_2S_3$ (cb), mooihoekite $Cu_9Fe_9S_{16}$ (mh) and haycockite $Cu_4Fe_5S_8$ (hc). Solid solutions: iss — chalcopyrite, bnss — bornite and po — pyrrhotite. Initial compositions of the synthesized samples: 50 wt.% S, Cu/Fe = 1.22—0.25 and 45 at.% S, Cu/Fe = 1.44—0.69. ● — Pt-Pd sulfides, ○ — Pt-Pd metallides.

products were examined under an optical microscope and by X-ray diffraction techniques. The polished sections were prepared from portions of each of the samples (which were cut along their vertical axes). The phases were analyzed for major elements and for distribution of admixtures over the whole volume of the samples on a Camebax-Micro microprobe, using the universal program (Lavrent'ev and Usova, 1991). Analysis was conducted based on the Fe$K\alpha$, Cu$K\alpha$, S$K\alpha$, Pt$M\alpha$, Pd$L\alpha$ X-ray reflections, which do not overlap. The standards were $CuFeS_2$, Pt and Pd. The operating conditions were as follows: 20 kV accelerating voltage, 40 nA absorbed electron current, 40° angle, 10 s counting time on each analytical line and 2—3 μm beam diameter. The analytical errors for all elements were within 2%. The detection limits C_{min} in compliance with the 2δ criterion at 99% confidence level were (in wt.%) 0.05 for Cu, 0.03 for Fe, 0.02 for S, 0.06 for Pt and 0.05 for Pd.

Results

As in our earlier publications (Kravchenko, 2011; Kravchenko *et al*., 2012), the composition of the synthesized samples in the Cu-Fe-S system and the compositions of the corresponding Cu-Fe sulfides are expressed in the form of Cu/Fe ratios. The synthesized phases are named according to their naturally occurring mineral analogues. We also report their generalized formulas, including elements whose concentrations in the synthetic phases are no lower than 5 at.%. The structures of the synthetic phases are mentioned when (and if) they differ from those of the natural mineral analogues. The synthesized phases of the haycockite composition $Cu_4Fe_5S_8$ have a cubic pc structure and thus differ from naturally occurring orthorhombic haycockite.

Generalized information on the accommodation of Pt, Pd and Pt together with Pd in the phase associations of the central part of the Cu-Fe-S system (50 at.% S, Cu/Fe = 1.22—0.25 and 45 at.% S, Cu/Fe = 1.44—0.69) are graphically represented in the figure and reported in Table 1. Solid circles in the figure show the composition of the samples with Pt-Pd sulfides examined in this publication and open circles display the composition of Pt-Pd metallides studied earlier (Kravchenko, 2009). The composition of phases in the region of Pt-Pd metallides that have been obtained previously and are necessary for discussing our results herein are printed in Table 1 in italics. Neither Pt nor Pd are major elements in the phases synthesized in the Cu-Fe-S system. As can be seen in Fig. 1, when the melts crystallize, Pt and Pd admixtures are contained in the same phases that crystallize from melts with admixtures of either Pt alone or Pd alone. The Pt-

Table 1. **Phase composition of the synthesized crystallization products of Cu-Fe-S melts with admixtures of Pt (1 wt.%), Pd (1 wt.%) and Pt + Pd (0.5 wt.% each)**

Starting composition (at.%) of Cu-Fe-S melts and their Cu/Fe ratios				Crystallization products of Cu-Fe-S melts with Pt, Pd and Pt + Pd admixtures			
S	Cu	Fe	Cu/Fe	Cu-Fe-S	Pt	Pd	Pt + Pd
50	27.5–25	22.5–25	1.22–1	cp + bn + py	$Cu(Fe,Pt)S_4$	PdS	$Cu(Fe,Pt)S_4$; (Pt,Pd)S
	25–17.5	25–32.5	1–0.54	cp + icb, 0.61–0.52*	PtS	PdS	(Pt,Pd)S
	15	35	0.43_1	icb, 0.52–0.48*			
			0.43_2	mh + bn, 0.95*			
			0.43_3	hc + bn, 0.90*	Pt_3Fe	$(Pd,Cu)_{16}S_7$	Pt_3Fe; $(Pd,Cu)_{16}S_7$
45	32.5	22.5	1.44_1	mh + bn, 1.00*	PtS		(Pt,Pd)S; $(Pd,Cu)_{16}S_7$
			1.44_2	mh + bn, 0.95*	Pt_3Fe		Pt_3Fe; $(Pd,Cu)_{16}S_7$
	30–25	*25–30*	*1.20–0.83*	*hc+bn, hc+bn+po, 0.90–0.68**	*Pt_3Fe*	*Pd(Cu,Fe)*	*Pd(Cu,Fe)*

*Note: bn – bornite Cu_5FeS_4; py – pyrite FeS_2; po – pyrrhotite $Fe_{1-x}S$; cp – chalcopyrite $CuFeS_2$ (Cu/Fe = 0.99–0.67); cb – isocubanite $CuFe_2S_3$ (Cu/Fe = 0.61–0.39); mh – mooihoekite $Cu_9Fe_9S_{16}$ (Cu/Fe = 1.04–0.93); hc – haycockite $Cu_4Fe_5S_8$ (Cu/Fe = 0.90–0.68). $Cu(Pt,Fe)S_4$ – malanite, PdS – vysotskite, PtS – cooperite, (Pt,Pd)S) – braggite, $(Pd,Cu)_{16}S_7$ – unnamed Pd sulfide, Pt_3Fe – isoferroplatinum, Pd(Cu,Fe) – unnamed Pd metallide. * – Cu/Fe isocubanite, mooihoekite, or haycockite. Phase compositions compiled from (Kravchenko et al., 2012) are printed in italics.*

bearing melts in samples with 50 at.% S and Cu/Fe = 1.22 – 1 crystallized the association chalcopyrite + bornite + pyrite and malanite $Cu(Pt,Fe)_2S_4$. The Pd-bearing melts crystallized cooperite PtS and the melts that contained both Pt and Pd crystallized malanite and braggite (Pt, Pd)S. In samples with 50 at.% S and Cu/Fe = 1 – 0.54, cooperite, vysotskite PdS and braggite were synthesized in association with chalcopyrite and isocubanite (Cu/Fe = 0.61 – 0.52) from melts with Pt, Pd and Pt + Pd admixtures, respectively. Isocubanite of variable composition and various Cu-Fe sulfide associations were synthesized in samples with 50 at.% S and Cu/Fe = 0.43 (see Table 1, lines 0.43_1, 0.43_2 and 0.43_3). This is explained by certain specifics of isocubanite crystallization and related traits in establishing phase equilibria during the crystallization of melts corresponding to the central part of the Cu-Fe-S system. If the cooling rate of the melt was increased, the field of Fe-enriched (Cu/Fe < 0.5) isocubanite $CuFe_2S_3$, shrank, as also did the crystallization field of Fe-enriched chalcopyrite $CuFeS_2$ (Kravchenko *et al.*, 2012). The samples with 50 at.% S and Cu/Fe = 0.43_1 obtained at different cooling rates of the melts contained isocubanite (Cu/Fe = 0.52 – 0.48) whose composition is closely similar to the stoichiometric one $CuFe_2S_3$ (Cu/Fe = 0.5) and corresponds to the bornite Cu_5FeS_4 (*bn*) – mooihoekite $Cu_9Fe_9S_{16}$ (*mh*) – isocubanite $CuFe_2S_3$ (*cb*) equilibrium (Fig. 1). The composition of the mooihoekite Cu/Fe = 1.04 – 0.93 corresponding to this equilibrium is also close to the stoichiometric composition (Cu/Fe = 1). Moreover, an increase in the cooling rate of the melt resulted in that phase associations of isocubanite, chalcopyrite and pyrrhotite (figure) gave way to phase associations of mooihoekite and haycockite with bornite and pyrrhotite. In samples with 50 at.% S, Cu/Fe = 0.43_1 and 0.43_2 isocubanite (Cu/Fe = 0.52 – 0.48) and mooihoekite (Cu/Fe = 0.95) with bornite respectively, occur in association with the same Pt-Pd sulfides (cooperite, vysotskite and braggite) as in samples with 50 at.% S and Cu/Fe = 1 – 0.54. In samples 0.43_3 with 50 at.% S and Cu/Fe = 0.43, the association haycockite (Cu/Fe = 0.90) + bornite contains synthesized isoferroplatinum Pt_3Fe and $(Pd,Cu)_{16}S_7$, which is Cu-enriched analogue of the Pd sulfide (which has no proper name) $Pd_{16}S_7$ in the Pd-S system, which crystallized at 639°C (Taylor, 1985). In samples with 45 at.% S and Cu/Fe = 1.44, the association of mooihoekite + bornite (with mooihoekite having Cu/Fe = 1) involves cooperate, $(Pd, Cu)_{16}S_7$ and braggite and this association with mooihoekite having Cu/Fe = 0.95 contains isoferroplatinum and $(Pd, Cu)_{16}S_7$. Hence, Pt-Pd sulfides were synthesized from melt with 50 at.% S and Cu/Fe = 1.22 – 0.43 in association with chalcopyrite and isocubanite (Cu/Fe = 0.61 – 0.48), whereas brom melt with 45 at.% S and Cu/Fe = 1.44 these sulfides crystallized in association with mooihoekite (Cu/Fe = 1 – 0.95) and bornite.

Table 2 reports typical compositions of the synthesized crystallization products of Cu-Fe-S melts with admixtures of Pt and Pd sulfides. The following Pt and Pd sulfides crystallized from melts with Pt and Pd admixtures: malanite, cooperite and vysotskite as single grains and as zoned aggregates (Table 2). Thereby malanite and cooperite formed the cores of the grains and vysotskite made up their outer por-

Table 2. **Composition of crystallization products of melts in the Cu-Fe-S system with admixtures of Pt (1 wt.%), Pd (1 wt.%) and Pt + Pd (0.5 wt.% each)**

Initial composition: S, at.%, Cu/Fe ratios and admixtures	Phases	Composition (at.% / wt.%) of phases					Total, wt.%
		Cu	Fe	Pt	Pd	S	
50, 1.22 – 1	cp	24.59	25.90	0.00	0.00	49.11	
		33.93	31.41	0.00	0.00	34.48	99.80
	bn	48.70	10.38	0.00	0.00	40.92	
		61.81	11.60	0.00	0.00	26.22	99.63
	py	0.37	33.26	0.00	0.00	66.37	
		0.59	46.08	0.00	0.00	52.78	99.45
Pt + Pd (each 0.5 wt.%)	Cu(Pt,Fe)S_4*	15.21	11.20	17.40	0.00	56.19	
		14.26	9.23	50.09	0.00	26.59	100.17
Pt + Pd –//–	(Pd,Pt)S**	1.18	0.55	13.59	35.43	49.25	
		0.94	0.39	33.33	47.39	19.85	101.90
Pt + Pd –//–	PdS**	1.17	0.54	0.00	49.14	49.15	
		1.08	0.44	0.00	75.46	22.75	99.73
50, 0.82	cp	23.77	26.91	0.00	0.00	49.32	
		32.82	32.66	0.00	0.00	34.35	99.83
Pt	PtS	1.54	1.00	49.39	0.00	48.07	
		0.87	0.49	85.30	0.00	13.64	100.30
Pd	PdS	0.36	0.22	0.01	50.72	48.69	
		0.33	0.18	0.04	76.89	22.24	99.68
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	2.13	2.16	44.72	5.40	45.59	
		1.22	1.09	78.42	5.17	13.14	99.04
Pt + Pd –//–	(Pd,Pt)S**	1.34	1.10	5.84	43.38	48.34	
		1.16	0.87	15.52	62.85	21.13	101.53
50, 0.67	cp	22.89	27.50	0.00	0.00	49.61	
		31.00	33.36	0.00	0.00	34.54	99.50
	cb	18.15	32.48	0.00	0.00	49.37	
		25.20	39.62	0.00	0.00	34.58	99.40
Pt + Pd (each 0.5 wt.%)	PtS*	1.25	1.13	49.70	2.02	45.90	
		0.69	0.54	83.51	1.85	12.67	99.27
Pt + Pd –//–	PdS**	0.14	0.15	0.54	49.61	49.56	
		0.12	1.12	1.49	75.42	22.20	100.35
50, 0.54	cp + cb	22.12	28.73	0.00	0.00	49.15	
		30.34	34.62	0.00	0.00	34.00	98.96
Pt	PtS	0.99	0.64	50.74	0.00	47.63	
		0.55	0.31	86.20	0.00	13.30	100.36
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	1.93	3.06	44.11	6.50	44.40	
		1.11	1.54	77.62	6.22	12.84	99.60
Pt + Pd –//–	PdS**	0.42	0.68	0.06	49.62	49.21	
		0.38	0.54	0.18	75.84	22.66	99.33
50, 0.43$_1$	cb	16.33	34.07	0.00	0.00	49.60	
	Cu/Fe = 0.48	22.86	41.91	0.00	0.00	35.03	99.80
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	1.22	1.92	45.88	5.33	45.65	
		0.70	0.96	79.94	5.07	13.08	99.75
Pt + Pd –//–	PdS**	0.29	0.52	0.04	50.32	48.83	
		0.26	0.42	0.11	76.56	22.38	99.73
50, 0.43$_2$	mh	25.84	27.18	0.00	0.00	46.98	
	Cu/Fe = 0.95	34.84	32.22	0.00	0.00	31.96	99.02
	bn	46.37	13.55	0.00	0.00	40.08	
		58.65	15.06	0.00	0.00	25.58	99.29
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	0.52	0.78	47.64	4.16	46.90	
		0.29	0.38	82.27	3.92	13.31	100.17
Pt + Pd –//–	PdS**	0.35	0.48	0.11	49.48	49.58	
		0.32	0.38	0.29	75.40	22.76	99.15
50, 0.43$_3$	hc	24.96	27.78	0.00	0.00	47.26	
	Cu/Fe = 0.90	33.68	32.94	0.00	0.00	32.18	98.80
	bn	46.37	13.55	0.00	0.00	40.08	
		13.55	15.06	0.00	0.00	25.58	99.29
Pt + Pd (each 0.5 wt.%)	Pt_3Fe	2.07	28.14	68.01	1.34	0.44	
		0.86	10.35	87.38	0.94	0.09	99.62
Pt + Pd –//–	$(Pd,Cu)_{16}S_7$	12.21	4.31	0.00	53.50	29.98	
		9.98	3.10	0.00	73.30	12.38	98.76
1.44$_1$	mh	26.94	27.00	0.00	0.00	46.06	
	Cu/Fe = 1	36.26	31.94	0.00	0.00	31.27	99.47
	bn	46.19	12.92	0.00	0.00	40.89	
		59.04	14.51	0.00	0.00	26.37	99.92
Pt + Pd (each 0.5 wt.%)	PtS	8.30	0.98	45.45	2.84	42.43	
		4.71	0.49	79.18	2.70	12.15	99.23
Pt + Pd –//–	$(Pd,Cu)_{16}S_7$	17.02	0.97	0.00	52.67	29.34	
		14.07	0.70	0.00	72.90	12.24	99.91
1.44$_2$	mh	25.86	27.20	00.0	0.00	46.94	
	Cu/Fe = 0.95	34.78	32.14	00.0	0.00	31.84	98.76
	bn	47.10	13.40	0.00	0.00	39.50	
		59.542	14.18	0.00	0.00	25.19	99.62
Pt + Pd (each 0.5 wt.%)	Pt_3Fe	2.38	27.18	69.10	0.82	0.52	
		0.99	9.92	88.04	0.58	0.11	99.64
Pt + Pd –//–	$(Pd,Cu)_{16}S_7$	15.71	0.30	0.00	54.70	29.29	
		13.00	0.22	0.00	75.80	12.22	101.24

Note: cp – chalcopyrite $CuFeS_2$; bn – bornite Cu_5FeS_4; py – pyrite FeS_2; cb – isocubanite $CuFe_2S_3$; mh – mooihoekite $Cu_9Fe_9S_{16}$; hc – haycockite $Cu_4Fe_5S_8$. Cu(Pt,Fe)S_4 – malanite, PdS – vysotskite, PtS – cooperite, (Pt,Pd)S – braggite; $(Pd,Cu)_{16}S_7$ – unnamed Pd sulfide, Pt_3Fe – isoferroplatinum.
** – cores of zoned grains, ** – margins of zoned grains.*

tions. The synthesized Pt-Pd phases exhibit crystallization features and phase relations with sulfides in the central part of the Cu-Fe-S system analogous to those of Pt-Pd and Ag-Au phases synthesized and described in much detail earlier (Kravchenko and Nigmatulina; 2009 Kravchenko, 2009): the largest grains crystallized on the surface and cavities (fractures) of the synthetic samples, crystal faces are unequally developed, crystallizing grains were often zoned, a single sample may contain different modes of occurrence of the phases, a single grain may show uneven distribution of elements and Cu-Fe sulfides are found in fractures and cavities in larger grains. These features are typical of crystallization of Pt-Pd and Au-Ag phases immediately from melts of less refractory Cu-Fe sulfides with admixtures of Pt, Pd, Au and Ag and if encountered in naturally occurring ores, are commonly regarded as evidence that these minerals crystallized after the ore-forming sulfides.

Discussion

As seen in Table 1, Pd sulfide $(Pd,Cu)_{16}S_7$ was synthesized with isoferroplatinum or with cooperite and braggite in samples whose compositions (50 at.% S, Cu/Fe = 0.43 and 45 at.% S, Cu/Fe = 1.44) are transitional from the crystallization field of Pt-Pd sulfides to that of Pt-Pd metallides. The composition point at 45 at.% S, Cu/Fe = 1.44 lies on the equilibrium line bornite (*bn*) – mooihoekite (*mh*) – isocubanite (*cb*) (Fig. 1). In sample with 45 at.% S and Cu/Fe = 1.441, Pt-Pd sulfides were synthesized with mooihoekite of stoichiometric composition $Cu_9Fe_9S_{16}$ (Cu/Fe = 1). The composition with 50 at.% S and Cu/Fe = 0.43 corresponds to the Fe-rich end member of the chalcopyrite solid solution of cubic fcc structure (Fig. 1, *iss*; Cabri, 1973). Naturally occurring analogues of the cubic *fcc* solid solution (Caye *et al.*, 1988) are referred to as isocubanite to distinguish them from natural cubanite of the stoichiometric composition $CuFe_2S_3$ (Cu/Fe = 0.5) of orthorhombic structure. The composition of the synthetic isocubanite (Kravchenko *et al.*, 2012) is closely similar to its natural analogue and varies within the Cu/Fe range of 0.61 – 0.39. The Cu-enriched isocubanite (Cu/Fe = 0.61 – 0.52) crystallizes from melt in association with chalcopyrite, whereas Fe-enriched isocubanite (Cu/Fe = 0.49 – 0.39) is formed in association with pyrrhotite and haycockite. As was mentioned above, isocubanite in association with Pt-Pd sulfides (sample 0.43_1, Table 1) has the composition (Cu/Fe = 0.52 – 0.48) close to the stoichiometric composition $CuFe_2S_3$ and corresponds to the equilibrium line bornite – mooihoekite – isocubanite. We have previously proved (Kravchenko, 2009) that melt with 50 at.% S and Cu/Fe = 0.25 crystallizes, in association with isocubanite (Cu/Fe = 0.43) + pyrrhotite, Pt_3Fe and Pd_3Fe or, in associations haycockite + bornite and haycockite + bornite + pyrrhotite (Table 1), Pt-Pd metallides: Pt_3Fe and Pd(Cu,Fe). Hence, the equilibrium line bornite Cu_5FeS_4 – mooihoekite $Cu_9Fe_9S_{16}$ – isocubanite $CuFe_2S_3$ is the boundary line between the crystallization fields of Pt-Pd sulfides (malanite, cooperite, vysotskite and braggite) and Pt-Pd metallides (Pt_3Fe and Pd(Cu,Fe)).

Our data indicate (Tables 1 and 2) that in samples 0.43_2 of the composition 50 at.% S, Cu/Fe = 0.43, Pt-Pd sulfides were synthesized (cooperite PtS, vysotskite PdS and braggite (Pt,Pd)S) in association with bornite and mooihoekite. In samples 1.44_2 of the composition 45 at.% S and Cu/Fe = 1.44, bornite and mooihoekite were synthesized with isoferroplatinum and sulfide $(Pd,Cu)_{16}S_7$, which were also synthesized in samples 0.43_3 of the composition 50 at.% S, Cu/Fe = 0.43, in association with haycockite and bornite. This testifies that the modes in which Pt and Pd are contained in the crystallization products of melts in the Cu-Fe-S system are controlled by the initial composition of the melt. These modes are independent of variations in the phase associations: isocubanite → mooihoekite + bornite and isocubanite + pyrrhotite → haycockite + bornite, which crystallized at different cooling rates of the melt.

Conclusions

1. The crystallization field of Pt and Pd sulfides, which are analogues to those of natural minerals, such as malanite $Cu(Pt,Fe)_2S_4$, cooperite PtS, vysotskite PdS and braggite (Pt, Pd)S, in the crystallization products of melts in the Cu-Fe-S system at 50 at.% S, Cu/Fe = 1.22 – 0.25 and 45 at.% S, Cu/Fe = 1.44 – 0.69 with Pt and Pd admixtures 1 wt.%) corresponds to the crystallization field of associations with chalcopyrite $CuFeS_2$ (Cu/Fe = 0.99 – 0.67), иisocubanite $CuFe_2S_3$ (Cu/Fe = 0.61 – 0.48) and mooihoekite $Cu_9Fe_9S_{16}$ (Cu/Fe = 1 – 0.95). The bornite Cu_5FeS_4 – mooihoekite $Cu_9Fe_9S_{16}$ – isocubanite $CuFe_2S_3$ equilibrium line separates the crystallization fields of Pt-Pd sulfides and Pt-Pd metallides.

2. The Pt-Pd sulfides synthesized in association with less refractory sulfides in the central part of the Cu-Fe-S system typically occur in grains similar to natural minerals and show

phase relations analogous to those of the corresponding natural minerals. This testifies that malanite, cooperite, vysotskite and braggite could have crystallized immediately from Pt- and Pd-bearing Cu-Fe-S melts of the Norilsk type before ore-forming sulfides (isocubanite, chalcopyrite and mooihoekite) crystallized from these melts.

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On the 150th anniversary of the birth of V.I. Vernadsky

MINERAL SYSTEMATICS FROM V.I. VERNADSKY TILL 21 CENTURY

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The article briefly reviews currently most widely accepted systematics of minerals that were developed in the 20th century by V.I. Vernadsky, J.D. Dana, A.G. Betekhtin, I.N. Kostov and G.P. Barsanov. A.A. Godovikov's systematic (Godovikov, 1997) is described in more detail as one reflecting currently acknowledged concepts of relationships between the chemical composition of minerals and their structures and properties. The author considers the structure of a mineral at the level of not upper but middle or even lowermost mineralogical taxons, in close relations with the chemical composition and physicochemical parameters of mineralizing systems. The upper taxons, or mineral types, are distinguished according the type of the dominate chemical bond. The basis for recognizing lower taxons, down to mineral classes, is a classification of the chemical elements. In this context, the classifications of elements suggested by V.I. Vernadsky, A.E. Fersman, A.N. Zavaritsky, A.A. Godovikov are also debated. A.A. Godovikov has more deeply explored the concepts of similarities and differences in the properties of chemical elements to put forth a more detailed mineralogical-crystallochemical systematics of the chemical elements with regard for various properties of elements that are manifested depending on other elements simultaneously occurring in a compound and on physicochemical parameters of the system. A.A. Godovikov applied this classification to distinguish taxons of order lower than type. The criteria suggested for distinguishing taxons in A.A. Godovikov's structural-chemical systematics of minerals are presented.
1 table, 11 figures, 13 references.

Keywords: systematics of minerals, classification of elements, chemical bond type, chemical composition, mineral structure, physicochemical parameters of mineralizing system.

It is often thought to be senseless to elaborate any new systematics of minerals. This opinion is most commonly shared by young researchers, who consider virtual data of minerals to be of much greater importance. However, such distinguished scientists as M.V. Lomonosov, V.M. Severgin, J.J. Berzelius, V.I. Vernadsky, J.D. Dana, A.G. Betekhtin, I.N. Kostov, A.S. Povarennykh, H. Strunz, A.A. Godovikov, J.J. Berzelius, A.R. Hoelzel and A.M. Clark created their own versions of mineral classifications. The reasons why so much importance was attached by these scientists to mineral systematics may be as follows:

1 – there is necessity to systematize different and numerous information on individual minerals. Without this it is not to get slim and scientific description;

2 – there are a lot of mineral properties which are used in their descriptions. We need to know them for mineral diagnostics and for clarification of their searching features, forming conditions of their paragenetic associations, capabilities of mineral utilization by humans;

3 – by belonging of minerals to the complete different chemical compound types; by differences and complexity of their composition;

4 – minerals are formed in completely, even in interexcluded physical-chemical conditions.

Any of mineral systematics appears to be multidementioned, because it should consider all the multitude of different mineral features. The characteristics taken as a basis for a classification should permit the possibility that the place of a mineral in it may be changed after its composition or structure are determined more accurately and/or in more detail. These characteristics should make it possible to coin new taxons for newly discovered minerals, which are chemical compounds that have not been known before to occur in nature, i.e. the classification should be evolutive system.

Because it is not possible to discuss the whole multitude of currently existing classifications in this article, below I will dwell only on the most widely accepted ones.

Vladimir Ivanovich Vernadsky – an academician of the Imperial Academy of Sciences, the Head of the Mineralogical Section of the Geological Museum at the Academy of Sciences (Fig. 1), estimated quite highly efforts to constrict mineral systematics and believed that "*establishing a natural and accurate classification concerned with the deepest comprehension of chemical and mineralogical phenomena*" (Vernadsky, 1927). V.I. Vernadsky's requirements for mineral classification were as follows.

1. The classification should be based on chemical properties of compounds and the chemical elements composing them, similarities and differences in the properties of these elements and other chemical characteristics.

2. The classification should take into account genetic and paragenetic features of min-

erals, what should be expressed in combining minerals into taxons that should comprise as many as possible mineral species similar in genesis (paragenesis) and correspond to understanding physicochemical coherence of the taxons and relations between them.

3. The structural (geometric), often named crystallochemical, traits of minerals are their secondary (follow level after chemical ones) identification features because they are determined by the chemical composition of minerals and the physicochemical parameters of their forms. They surely must be taken into account in the classification, but only at lower levels of its taxons.

V.I. Vernadsky has classified all minerals into **14 series** (Vernadsky, 1927).

I. Free elements and their mixtures (native elements).

II. Hydrogenous minerals.

III. Sulphuric and selenic compounds.

IV. Arsine and stibine derivatives.

V. Telluric compounds.

VI. Bismuthic compounds.

VII. Phosphoric, nitrogenous and carbonic metals.

VIII. Oxygenic peroxides, bases and anhydrides.

IX. Hydrates and fluoranhydrides.

X. Oxygenic salts and products of attaching to them.

XI. Oxyhaloide compounds.

XII. Haloide compounds.

XIII. Silicic compounds without clear saline nature (glasses).

XIV. УCarbonic compounds containing oxygen, without saline nature.

The series are subdivided into groups according to the character of the chemical elements in the minerals composition. When suggested, the classification comprised more than 200 groups.

Simultaneously with V.I. Vernadsky, **James Dwight Dana**, a mineralogist and geologist at the Yale University (Fig. 2), created an appropriate chemical systematics of minerals based on **Mendeleyev's Periodic Law**. J.D. Dana grouped mineral species into 8 major taxons according to the **types** of their **anions** and resemblance of elements, which followed from their position in the Periodic Table (Dana, 1892).

Type I. Native elements.

Type II. Sulfides, selenides, tellurides, arsenides, stibnides.

Type III. Sulfosalts — sulfoarsenides, sulfistibnides, sulfobismuthides.

Type IV. Halogenides — chlorides, bromides, iodides, fluorides.

Type V. Oxides.

Type VI. Oxosalts: 1 — carbonates; 2 — silicates; 3 — titanates; 4 — phosphates, arsenates, vanadates, antimonates, nitrates; 5 — borates, uranates; 6 — sulfates, chromates, tellurates; 7 — tungstenates, molybdates.

Type VII. Salts of organic acids: oxalates, mellates etc.

Type VIII. Hydrocarbons.

Anatoly Georgievich Betekhtin (Fig. 3), the author of "Mineralogy", one of the most comprehensive handbooks on mineralogy (Betekhtin, 1950). A.G. Betekhtin subdivided minerals into 6 sections according to their anions.

Section I. Native elements and intermetallic compounds.

Section II. Carbides, nitrides and phosphides.

Section III. Sulfides, sulfosalts and similar compounds.

Section IV. Haloide compounds (halogenides).

Section V. Oxides.

Section VI. Oxygen salts (oxosalts), consisting of 10 classes: 1 — iodates; 2 — nitrates; 3 — carbonates; 4 — sulfates, selenates, tellurates; 5 — chromates; 6 — molybdates and tungstenates; 7 — phosphates, arsenates and vanadates; 8 — arsenites; 9 — borates; 10 — silicates.

Ivan Nikolov Kostov (Fig. 4), a Bulgarian mineralogist and crystallographer, has created a mineral classification based on the chemical composition and paragenetic series of some elements (Kostov, 1965) and subdivided minerals into 12 classes.

Class I. Native elements.

Class II. Sulfides and sulfosalts.

Class III. Halogenides.

Class IV. Oxides and hydroxides.

Class V. Silicates.

Class VI. Borates.

Class VII. Phosphates, arsenates, vanadates.

Class VIII. Tungstenates, molybdates.

Class IX. Sulfates.

Class X. Chromates.

Class XI. Carbonates.

Class XII. Nitrates and iodates.

Georgii Pavlovich Barsanov (Fig. 5), a remarkable mineralogist and teacher, Director of the Fersman Mineralogical Museum, Academy of Sciences of the USSR (1952—1976), Vice President of the International Mineralogical Association (1960—1964), Head of the Department for Mineralogy at the Moscow State University (1953—1986). G.P. Barsanov held that the bases for classification of minerals should be:

1) types of chemical bonds in crystals;

1

2

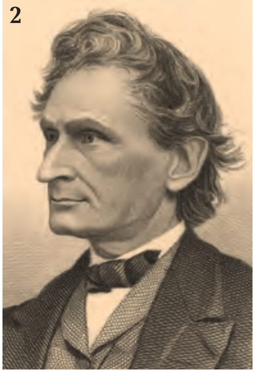

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Fig. 1. Vladimir Ivanovich Vernadsky (1863—1945).
Fig. 2. James Dwight Dana (1813—1895).

Fig. 3. Anatolii Georgievich Betekhtin (1897—1962).
Fig. 4. Ivan Nikolov Kostov (1913—2004).

2) qualitative composition of atoms in the crystal coupled via any type of chemical bond;

3) how and which are the atoms (ions) surrounded by other atoms (or ions) in the three-dimensional crystal structure, i.e. coordination, packing character, structure motif (Barsanov, 1959). G.P. Barsanov divided all minerals into 4 types according to their the chemical bond type. The types are further subdivided into classes according to the qualitative composition of the anions that make up a certain structure. The classes consist of taxons, which are distinguished depending on the presence of additional anions. Finally, a taxon next in the hierarchy is established according to the qualitative composition of the cations. G.P. Barsanov recognized 4 types as highest taxons (Barsanov, 1959).

Type I. Atomic (partly ionic) lattices with bonds of metallic or covalent type; which includes 2 classes: 1) free atoms of elements and 2) intermetallic compounds.

Type II. Ionic lattices with covalent (rarely ionic) type of bonds, with 5 classes: 1) sulfuric compounds; 2) selenides; 3) tellurides; 4) arsenides; and 5) stibnides.

Type III. Typical ionic lattices without complex anion groups in their structures. Herein 3 classes: 1) chlorides, bromides, iodides; 2) fluorides; and 3) oxides.

Type IV. Ionic lattices with complex anions. Herein 11 classes: 1) niobotantalates and niobotantalotitanates; 2) silicates; 3) borates; 4) chromates; 5) molybdates; 6) tungstenates; 7) phosphates; 8) vanadates; 9) sulfates; 10) carbonates; and 11) nitrates.

These are the most widely accepted mineral classifications suggested before the 1990s. Unfortunately, most of them postulate the formation of various taxons and show their hierarchic arrangement but do not explain the principles and sequence of this recognition , which makes it hard (if even possible at all) to apply these classifications to the newly discovered species. For this reason, several mineralogical works were recently published that describe minerals in an alphabetic order (Clark, 1993; Robert *et al.*, 1990). However, this practice does not provide the reader with any type of information on a mineral other than its characteristics. The reader remains unaware of the circumstances in which the mineral is formed and its associations and, hence, is not able to predict as to where the mineral may be searched for and how can it be used. As is known, **any hypothesis becomes a theory if it is able to predicted something that turns true in a while.**

Aleksandr Alekcandrovich Godovikov (Fig. 6) was a mineralogist of the universal style of thinking, professor, the Director of the Fersman Mineralogical Museum (1984 — 1996), renowned specialist in theoretic, descriptive, experimental and genetic mineralogy. A.A. Godovikov strove for approaching **mineralogy to the frontier where it would become not a descriptive but precise science.** Thereby he explored theoretical aspects of mineralogy aiming to create a foundation for a uniform classification of minerals based on their chemical features and genetic characteristics, with regard for their structures. These studies conducted by A.A. Godovikov (and described in 6 monogaphs) laid the basis for his *"Structural-chemical classification of minerals"* (Godovikov, 1997), in which he did his best to meet the basic requirements to systematics yet formulated by V.I. Vernadsky. In A.A. Godovikov's opinion, *"it is apparent that mineralogist will be satisfied, if systematic has on its basis chemical features which could enable to understand their connection with mineral structure and properties, mineralforming conditions and paragenesis. Features which are characterizing the structure of minerals should have not the highest*

Fig. 5. Georgii Pavlovich Barsanov (1907–1991).

Fig. 6. Aleksandr Aleksandrovich Godovikov (1927–1996).

Fig. 7. Victor Moriz Goldschmidt (1888–1947).

taxon positions, but rather middle or even inferior taxon positions, because they are in straight dependence on chemical composition and physical-chemical parameters of mineralforming systems" (Godovikov, 1997).

A classification should be natural, for "*it must able to account of not only formal features, but also of real mineral associations, their parageneses, differences of those physicochemical parameters at which minerals are formed and exist, giving preferences, in certain instances, to the latter in the classification order of minerals*".

Naturally occurring mineral associations are genuine criteria of naturality of mineral systematic. It is necessary that there were gradual transitions from one taxon to another showing their multiple interrelations.

In effort to make mineralogy closer to exact science, A.A. Godovikov introduced the concept of power characteristics (PC).

Power characteristics of atoms and ions are a measure of Coulomb's interaction between an electron (mostly a valence one) torn off the nucleus (γ). The possible power characteristics of atoms and ions in the free state and cations in ionic crystals are:

a) $\gamma_{orb.} = F/r_{orb.}$, where F is the affinity of the atom to electron and $r_{orb.}$ is the orbital radius of the atom;

b) $\gamma_{orb.}{}^{n+} = I_n/r_{orb.}{}^{n+}$, where I_n is the nth ionization potential and $r_{orb.}{}^{n+}$ is the orbital radius of the ion with valence number n+;

c) $\gamma_i = I_n/r_i$, where r_i is the effective ionic radius of the cation with valence number n+ in the ionic crystal.

Power characteristics serve as a measure of donor-acceptor (acid-alkaline) properties of atoms and ions.

As a basis for a mineral classification within chalcogenic, oxygenous and halogenic compounds, i.e. **within upper taxons of the classification (types), the dominant type of chemical bond is used.**

In the range metallides → semimetallides → chalcogenic compounds → oxygenic compounds → halogen compounds, the chemical bond changes consistently: metallic → metallic-covalent → ionic-covalent → covalent-ionic → ionic bond. The type of the chemical bond also changes according to the affiliation of compounds with elementary substances, binary compounds, or salts and is controlled by the fundamental properties of atoms composing a given mineral, namely their power characteristics (PC), atomic number Z in the Periodic System and their interrelations. The general trend manifests itself in the fact that the transition elementary compound → binary compound → salt proceeds so far as the difference ΔPC of power characteristics of consisting cations increases, i.e. according to increasing ionicity of the bond.

According to A.A. Godovikov, a **classification of chemical elements must be utilized as a basis for distinguishing taxons of order lower than type and higher than classes inclusive**. A number of geochemical classifications of elements and cations were created in the 20th century. The most widely known classifications of elements are described below.

Victor Moritz Goldschmidt (Fig. 7), a crystallographer, the director of the Geological Museum in Oslo. On the basis of crystal chemistry, he analyzed the distribution conditions of elements in various minerals and conditions of their concentration and migration. Using the dependence of the atomic volume (V) on the atomic number of the corresponding elements (Z), V.M. Goldschmidt was the first to suggest a classification of elements (Fig. 8) and devided them into 4 groups (Goldschmidt, 1937).

Siderophylic elements are located around the minima on the curves of atomic volumes as functions of atomic numbers. These elements were C, P, Fe, Co, Ni, Tc, Mo, Ru, Rh, Re, Os, Ir and Pt.

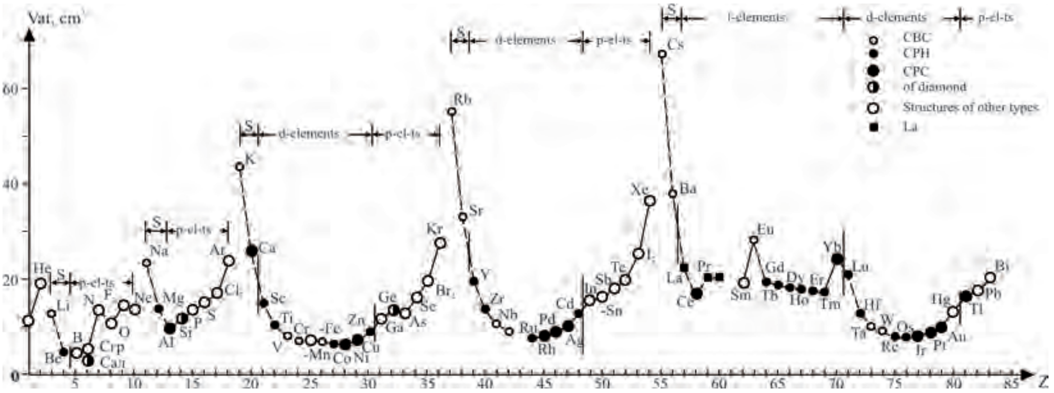

Fig. 8. Atomic volume (V) dependency on atomic number of corresponding elements (Z). Structures: space-centered cubic — CBC, hexagonal close packing CPH, cubic close packing — CPC, of diamond, structures of other types, La — structures of La type.

Chalcophylic elements correspond to ascending parts of the curves: S, Cu, Zn, Ga, Ge, As, Se, Pd (which seems to be more appropriate for the siderophile elements), Ag, Cd, In, Sn, Sb, Te, Au, Hg, Tl, Pb, Bi and Po.

Lithophylic elements cluster on descending parts: Li, Be, B, Na, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Rb, Sr, Y, Zr, Nb, Cs, Ba, Ln, Hf, Ta, W and Fr (it was not shown in the V. M. Goldschmidt's diagram), Ra, Ac, Th, Pa, U. Taking into account the common presence of O, F, Cl, Br and I in minerals of rocks and deviating from the logically formal classification of elements in favor of natural one, V. M. Goldschmidt attributed them to the same group, although they are located on ascending segments of the curves.

Atmophylic elements located on the upper parts of curves. These are He, N, Ne, Ar, Kr, Xe, Rn (Em); hereto he also referred H.

Dissatisfied with V.M. Goldschmidt's classification, A.E. Fersman and A.N. Zavaritsky have elaborated their own geochemical classifications.

Aleksandr Evgenyevich Fersman (Fig. 9), an academician and the Director of the Mineralogical Museum of the USSR's Academy of Science (starting in 1919). The sphere of his interest was extremely wide: mineralogy, crystallography, geochemistry, studying mineral resources and the processing technologies of minerals. In his systematics, A.E. Fersman segregated typical elements (i.e. elements with kainosymmetric outer and pre-outer electrons) by means of separating them from the others (in the Periodic System) with a doubled horizontal line (Fersman, 1933). The upper part of the System includes all typical elements of the first three periods and elements from K through Ni. This was done to emphasize the unusual properties of most refered ascribed to the first series of d-elements, that are kainosymmetric too, as it was discovered later.

Aleksandr Nikolaevich Zavaritsky (Fig. 10), an academician, great geologist, petrographer, specialist in ore deposits and volcanology, elaborated his geochemical classification of elements (Zavaritsky, 1950) based on the properties of elements reflected in an extended version of the Periodic System . Within the framework of the Periodic System, he distinguished 11 fields of elements:

1 — hydrogen — H;

2 — noble gases — He, Ne, Ar, Kr, Xe, Rn;

3 — rock-forming elements — Li, Na, K, Rb, Cs, Be, Mg, Ca, Al, Si;

4 — elements of magmatic emanations — B, C, N, O, P, S, F, Cl;

5 — elements of the iron group — Ti, V, Cr, Mn, Fe, Co, Ni;

6 — rare elements — Sc, Y, Ln, Zr, Hf, Nb, Ta;

7 — radioactive elements — Fr, Ra, Ac, Th, Pa, U;

8 — elements of the platinum group — Ru, Rh, Pd, Os, Ir, Pt;

9 — metallic elements (nonferrous metals) — Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb;

10 — metalloid metallogenic elements (elements of sulphoacids) — As, Sb, Bi, Se, Te, Po;

11 — heavy haloids — I, Br, At.

The elements Mo, W, Tc, Re were not ascribed to any particular fields.

As was mentioned above, classifications of elements were suggested by several mineralogists but mostly satisfy neither their authors nor their colleagues because the mineral systematics based on these classifications were not natural. These systematics did not take into account the actual associations of minerals, their parageneses and variations in the physicochemical parameters under which minerals

Fig. 9. Aleksandr Evgenyevich Fersman (1883–1945).

Fig. 10. Aleksandr Nikolaevich Zavaritsky (1884–1952).

can be formed and exist, as well as the fact that natural associations of minerals are not generated randomly but result from the grouping of elements according to all of their properties into natural associations.

Aleksandr Nikolaevich Zavaritsky's classification proved most acceptable. Unfortunately, it inherited certain disadvantates from earlier classifications.

A significantly more detailed classification of elements was put forth by V.I. Vernadsky. His classification was based on characteristics of isomorphism of elements, genesis of minerals and and parageneses. The core idea of this classification was expressed in the form of the widely known isomorphous series (Vernadsky, 1923; 1927). Vernadsky not only grouped elements similar in chemical properties but also showed how these series dependend on the genesis.

V.I. Vernadsky's isomorphous series:

1 – **Al, Fe, Cr, Mn | Ti, B, (Y), (Ce), V, In?**, where ***Al, Fe, Cr, Al, Fe, Cr, Mn,*** Al, Fe, Cr, Mn | Ti, B, (Y);

2 – **Ba, Ca, Sr, Pb**, where ***Ba, Ca, Sr, Pb, Ba, Ca, Sr***, Ba, Ca, Sr;

3 – **Br, I, Cl, F**, where ***Br, I, Cl, F, Cl, F***, Cl, F;

4 – ***V, P, As, Sb?***;

5 – **Bi, Sb, As**, where ***Bi, Sb, As***, Bi, Sb, As;

6 – **K, Na, Cs, Rb | Tl, Li, H**, where ***K, Na, Cs, Rb, K, Na, Cs, Rb | Tl, Li, H***, K, Na, Cs, Rb | Tl, Li, H;

7 – ***W, Mo***;

8 – ***Ge, Sn***;

9 – **Mg, Mn, Fe, Zn, Cd, Cu, Ni, Co, In?**, where ***Mn, Fe, Zn, Mg, Mn, Fe, Zn, Cd, Cu, Ni, Co***, Mg, Mn, Fe, Zn, Cd, Cu, Ni, Co;

10 – **Au, Ag, Hg, Cu, Pb, Tl**, where ***Pb, Tl (?), Au, Ag, Hg, Cu, Pb, Tl***, Au, Ag, Hg, Cu, Pb, Tl;

11 – Pt, Fe, Pd, Ir, Rh, Cu;

12 – Os, Ru, Rd, Ir;

13 – **Ca, Mg, Mn, Fe**, where ***Ca, Mg (?), Ca, Mg, Mn, Fe***, Ca, Mg, Mn, Fe;

14 – O, F (?);

15 – **Co, Fe, Ni**, where ***Co, Fe, Co, Fe, Ni***;

16 – **Si, Ti, Zr, Mn**, where ***Si, Ti, Zr, Mn***, Si, Ti, Zr, Mn;

17 – Th, U;

18 – Zr, Hf;

19 – Nb, Ta;

20 – **S, Se, Te?**, where ***S, Se, Te?***, S, Se, Te?

Symbols print in bold denote the whole isomorphous series and other prints select elements of various "thermodynamic shells": ***bold italic*** – material of weathered mantles (so-called weathering crusts), ***underlined bold italic*** – metamorphic, regular – magmatic shells (Vernadsky, 1927).

These isomorphous series show that similarities between elements may appear in different ways depending not only on the formation conditions (thermodynamic shells) but also on other elements constituting a given isomorphous series. At the same time, certain elements can be found in more than one of such series. For example, Fe occurs in 5 series – 1, 9, 11, 13, 15; Mn is in 4 series – 1, 9, 13, 16; and Ca is in 2 series – 2, 13, etc.

Therefore, isomorphous series attract attention to the versatility (plurality) of the chemical properties of some chemical elements, because of which such elements may simultaneously fall into a few isomorphous series. At the same time, the series cannot (for the same reason) be directly applied in a mineral classification.

This led A.A. Godovikov to alaboration more fundamental concepts of similarities and differences in properties of elements, which allowed to create a more detailed mineralogical-crystallochemical classification of elements, with regard for the variability of properties of elements that is manifested depending on other elements involved in a given compound and on the physicochemical parameters of the system. A.A. Godovikov divided all elements into 8 groups.

1. Hydrogen — H. Separating H into an individual group complies with systematics of A.N. Zavaritsky.

2. Lithophylic elements with low PC: 2.1. alkaline and alkaline-earth elements — Li, Na, K, Rb, Cs, Fr; Mg, Ca, Sr, Ba; 2.2. rare-earth and radioactive elements — Sc, Y, Ln (La — Yb), Th, U; 2.3. amphoteric elements — Be, Al, (Ga); 2.4. kainosymmetric d'-elements — Ti, V, Cr, Mn, Fe, Co, Ni. This group of elements is entirely analogous with A.N. Zavaritsky's group of iron;

3. Lithophylic elements with intermediate PC: 3.1. non-kainosymmetric d'-complex formers — Zr, Hf, Nb, Ta; 3.2. Mo and W.

4. Noble-metallic (Siderophylic) elements — Ru, Rh, Pd, Ag, Os, Ir, Pt, Au. Among them, Ag and Au are often contained in chalcophylic minerals and associations.

5. Chalcophylic elements: 5.1. chalcophylic elements with low PC — Cu, Zn, Cd, Hg, (Ga), In, Tl, Pb; 5.2. chalcophylic elements with middle PC — Ge, Sn, As, Sb, Bi, Se, Te. Groups 5.1. and 5.2. are very closely similar to, respectively, groups 9 — metallic (colored) elements and 10 — A.N. Zavaritsky's metalloid metallogenic elements (elements of "sulphoacids"), except Ge and Sn, which were referred by A.N. Zavaritsky to the group 9.

6. Light anion-forming elements — B, C, Si, N, P, O, S, F, Cl. This group of elements is completely analogous to A.N. Zavaritsky's group of elements of magmatic emanations that compose lithophile minerals as anion-forming elements (B, C, Si, N, P, S) or anions (O, F, Cl); with only S able to additionally act as an anion in chalcophylic minerals.

7. Heavy anion-forming elements — Br and I.

8. Noble gases elements — He, Ne, Ar, Kr, Xe, Rn.

This classification was later proved to also need refining, because most elements turned out to be amphoteric, with their acid-base properties defined by the properties of other elements of composition, the proportions of these elements, the physicochemical parameters of the systems in which the minerals exist or were generated. Thus, depending on its CN in a compound, a typical siderophylic or even chalcophylic element can become a crystalochemical analogue of typical lithophylic elements. This classification cannot thus form a basis for selecting taxons of order lower than **type**, because the same cations can play a cation role in different mineral types e.g. lithophylic and chalcophylic and be cations in certain minerals manifesting their alkaline properties, or anion-forming elements in other minerals and manifest acid properties. It was demonstrated to be convenient to express differences in the acid-base properties of cations with various CN by the produced PC values i.e. their PC/CN ratio, which enables one, together with the cation electronic type (*s*-, *f*-, *d*-, *p*-) and its order number, to present a classification of major mineral-forming ions in a tabular form (Fig. 1).

At the same time, A.A. Godovikov has demonstrated that the PC/CN ratio determines the role of cations in compositions but cannot be used as a strict formalized criterion, because cation properties also depend on some minute features of the atomic structure, in particular, their Z value and affiliation with kaino- or nonkainosymmetricals. However, in several instances, it elucidates not only the role of a cation in a compound but also the possibility of isomorphism between it and other cations, especially when they are similar in terms of other features. On the basis of this cation classification (Godovikov, 1997), A.A. Godovikov has worked out a more detailed grouping scheme for structural-chemical groups of elements (cations) depending on their chemical and crystallochemical properties (Godovikov, 2001).

1. H^+
2. Li^+
3. Na^+, K^+, Rb^+, Cs^+, Fr^+; Ba^{2+}(CN = 12); Pb^{2+}(CN = 12); Tl^+(CN = 12)
4. Mg^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}
5. Ca, Sr, Ba; Cu^{2+}(CN = 12); Pb^{2+}(CN = 12)
6. Sc, Y, Ln; Th, U
7. Be
8. Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, V^{3+}, Ti^{3+}
9. Ti^{4+}
10. V^{4+}, Mn^{4+}
11. V^{5+}
12. Cr^{6+}
13. Zr^{4+}, Hf^{4+}
14. Nb^{5+}, Ta^{5+}
15. Mo^{4+}, W^{4+}
16. Mo^{6+}, W^{6+}
17. Ru, Rh, Pd; Os, Ir, Pt
18. Au
19. Cu^+, Ag^+, Tl^+(CN = 2−4)
20. Zn, Cd
21. Hg
22. Ga, In, Tl^{3+}
23. Pd^{2+}(CN ≤ 12)
24. Ge, Sn
25. As^{3+}, Sb^{3+}, Bi^{3+}, Te^{4+}

Comparison of these series of cations (elements) with V.I. Vernadsky's isomorphic series show that they are mostly similar, but they is able to more completely take into account the

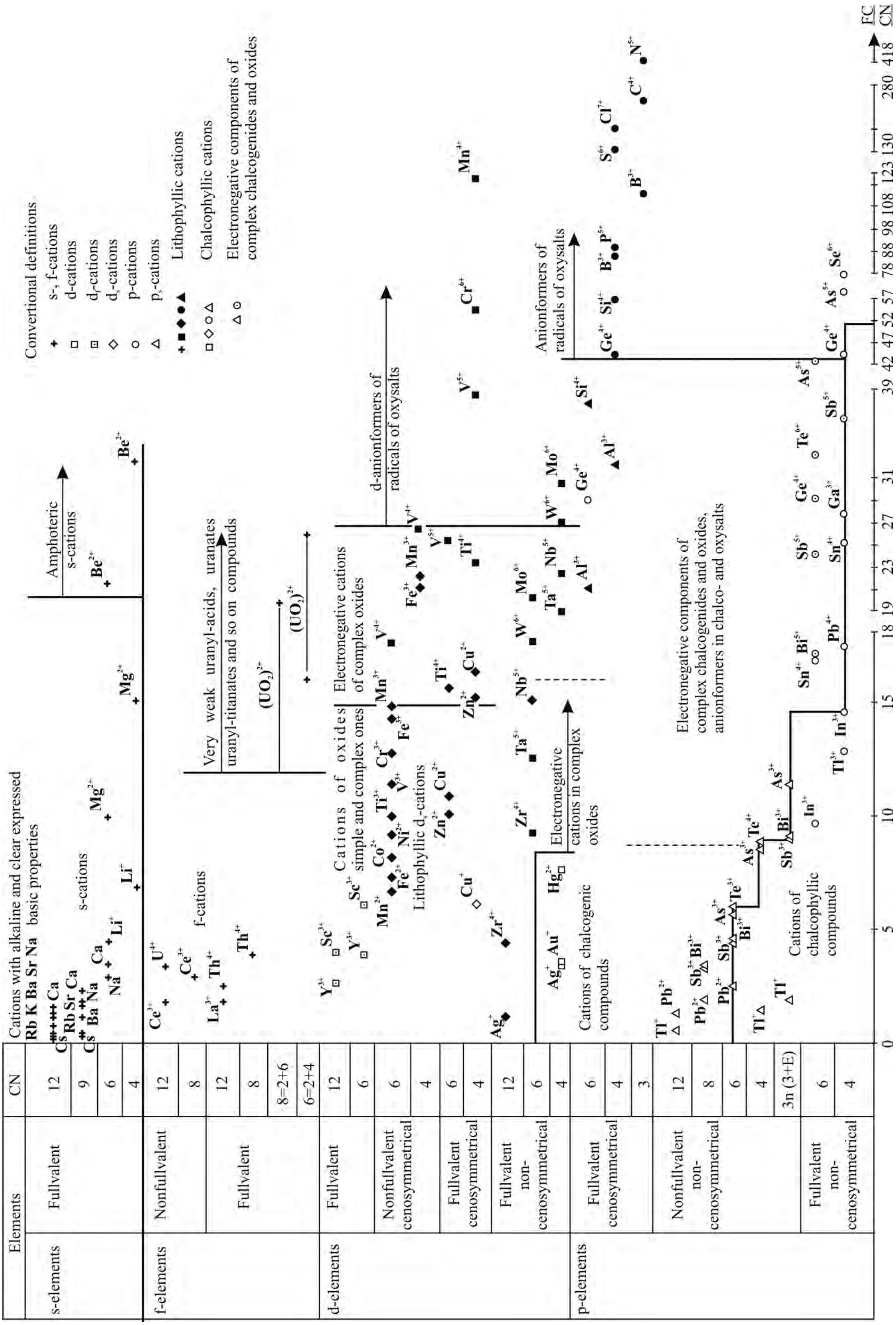

Fig. 11. Tabulated classification of main ions containing in minerals.

Table 1. **General enumeration of the taxons of structural-chemical classification of minerals**

Taxon	Feature	Examples
1	2	3
Type	It is principle type of chemical bond (but not a single type of chemical bond)	The five types are uniting all minerals species: 1. Type: Minerals with principal metallic and metallic-covalent bond — native metals and semimetals, metallides and semimetallides. 2. Type: Minerals with principal metallic-covalent and ionic-covalent bond, rare van der Waals forces — chalcogen compounds and native VIa nonmetals. 3. Type: Minerals with principal ionic-covalent and covalent-ionic bond — nonmetallides of light (typical, noncenosymmetrical) VIa element (O) — oxygen compounds. 4. Type: Minerals with principle covalent-ionic and ionic bond — halogen compounds. 5. Type: Carbon, its compounds (without carbonates) and related substances.
Quasitype*	Type of chemical bond (this taxon is divided when more higher taxon unites the minerals with three or more types of chemical bond)	There are two quasitypes at the second type of minerals with principal metallic-covalent and ionic-covalent bond, rare van der Waals forces — chalcogen compound and native VIa nonmetals: 2a. Native VIa nonmetals (van der Waals forces); 2b. Chalcogenic compounds (metallic-covalent and ionic-covalent bond rare van der Waals forces) — simple (isodesmical) → complex → chalcosalts (anisodesmical).
Subtype	1. Type of chemical bond, (only single type of chemical bond)	There are two subtypes at the 1. taxon of minerals with principal metallic and metallic-covalent bond — native metals and semimetals, metallides and semimetallides: 1.1. Metals and metallides; 1.2. Semimetals and semimetallides.
	2. Type of cation (siderophyllic, chalcophyllic or lithophyllic)	There are two subtypes at the 2b. quasitype of the second type: 2b.1. Chalcogenic compounds of sidero — and chalcophyllic cations (metallic-covalent bond); 2b.2. Chalcogenic compounds of lithophyllic cations (ionic-covalent bond).
	3. Belonging of mineral to isodesmical and anisodesmical compounds	There are two subtypes at the 3 type of minerals with principal ionic-covalent and covalent-ionic bond -nonmetallides of light (typical, noncenosymmetrical) VIa-element (O) — oxygen compounds: 3.1. Oxides and hydroxides (isodesmical); 3.2. Oxysalts (anisodesmical). There are two subtypes at the 4 type of minerals with principle covalent-ionic and ionic bond — halogen compounds: 4.1. Halogenides (isodesmical); 4.2. Halogenosalts (anisodesmical) (with hexacyanoferrates and hexatiocyanates, rhodonides).
Quasi-subtype*	1. Anion	There are two quasitypes at the 2b.1. subtype chalcogen compounds of sidero- and chalco phyllic cations (metallic-covalent bond): 2b.1a. Sulfides and sulfosalts of sidero- and chalcophyllic cations; 2b.1b. Selenides and selenosalts of sidero- and chalcophyllic cations.
	2. Type of cation and FC of cation	There are six consequently changing quasitypes at the 3.1 Subtype oxides and hydroxides (isodesmical), that are corresponding for transferal from the cations with low FC to the cations with high FC, from lithophyllic cations to chalcophyllic and to nonmetallic cations of the elements with mostly high FC: 3.1a. Oxides and hydroxides of lithophyllic cations with low FC; 3.1b. Oxides and hydroxides of lithophyllic cations with middle FC; 3.1c. Oxides and hydroxides of chalcophyllic cations (without Va- and VIa- cations); 3.1d. Oxides and hydroxides Va- cations (As, Sb, Bi); 3.1e.Oxides and hydroxides VIa- cation (Te); 3.1f. Oxides and hydroxides of nonmetals (lithophyllic) elements.
Overclass*	Cation	There are seven overclasses at the 3.1b. taxon — oxides and hydroxides of lithophyllic cations with middle FC: 3.1b.1. Oxides Zr; 3.1b.2. Oxides Ti (Ti^{4+}); 3.1b.3. Oxides and hydroxides Nb^{5+} and Ta^{5+}; 3.1b.4. Oxides and hydroxides Mo and W; 3.1b.5. Oxides and hydroxides Mn^{4+}; 3.1b.6. Oxides and hydroxides V^{4+}; 3.1b.7. Oxides and hydroxides V^{5+}.

Table 1. **Continue.**

Class	1. Type of anion (simple, complex) or compound (simple, complex)	There are two classes at the 2b.1a. quasitype — sulfides and sulfosalts of sidero- and chalcophyllic cations: 2b.1a.1. Class: Sulfides of sidero- and chalcophyllic cations; 2b.1a.2. Class: Sulfosalts of sidero- and chalcophyllic cations.
	2. Anionforming, when minerals are anisodesmical compounds	There are two classes at the 3b.1b.1. overclass — oxides Zr: 3.1b.1a. Class: Simple oxides of Zr; 3.1b.1b. Class: Complex oxides of Zr → titanates of Zr → zirconotitanates. There are eleven classes at the 3.2. subtype - Oxosalts (anisodesmical): 3.2.1. Class: Silicates; 3.2.2. Class: Borates; 3.2.3. Class: Carbonates; 3.2.4. Class: Phosphates; 3.2.4a. Class: Arsenates; 3.2.5. Class: Sulfates; 3.2.6. Class: Sulfites; 3.2.6a. Class: Selenites; 3.2.7. Class: Nitrates; 3.2.7a. Class: Iodates; 3.2.7b. Class: Rhodonates (tiocyanates).
Quasiclass	Coordination number of the anionforming	There are three quasiclasses at the 3.1b.7b. class - complex oxides and hydroxides of V^{5+}: ((6)-vanadates → (5)-vanadates → (4)-vanadates); 3.1b.7b.1. Qusiclass: (6)-vanadates; 3.1b.7b.2 Qusiclass: (5)-vanadates; 3.1b.7b.3 Qusiclass: (4)-vanadates. There are tree quasiclasses at the borates class: 1) (4)-borates; 2) (3)-borates; 3) (4)-(3)-borates: 3.2.2.1. Quasiclass: (4)-Borates; 3.2.2.2. Quasiclass: (3)-Borates; 3.2.2.3. Quasiclass: (4)-(3)-Borates.
Subclass	The size of FC	There are three subclasses at the class of silicates: 1) silicates with low FC; 2) silicates with middle FC; 3) silicates of chalcophyllic elements.
Family	The minerals of one family have similar of equal compound, single genesis or paragenesis	The family of zeolites unite the subfamilies: thomsonite, scolecite-natrolite, garronite, wairakite, gmelinite, stilbite, stellerite, mordenite. The micas family unite dioctahedral and trioctahedral micas and all polytypes.
Subfamily	Similar or equal compound and same type of structure	There are five subfamilies at the chalcopyrite family: talnakhite, actually chalcopyrite, germanite, briartite, morozeviczite. There are three subfamilies at the stannite family: stannoidite, actually stannite, rodostannite.
Series (genus)	Uninterrupted solid solutions between two or greater number of the extreme members	The forsterite genus and garnet genus among of the middle tetrasilicates.
Group	The same type of the compound or structure	The dolomite group include dolomite, ankerite, kutnohorite, benstonite, eitelite. All its minerals have one type structure, but they have not the uninterrupted solid solutions between ones.
Mineral species	There is an individual chemical compound, extreme member of the solid solutions, middle member of the uninterrupted solid solutions	a) There are three mineral species at the genus monticellite: monticellite, glaucochroite, kirnschsteinite. b) There are five mineral species at the forsterite genus: forsterite, fayalite, tephroite, liebenbergite, laihunite.

Notes: asterisks after taxon names dente taxon introduced but not named by A.A. Godovikov. Their names were suggested by S.N. Nenasheva, for exaple, quasitype*, quasisubtype*, ore overclass*.

mineralogical and crystallochemical similarity of cations (elements).

These series of cations (elements) are taken as a basis of a further classification of minerals within classes distinguished according to anions features.

Thus, **higher taxons up to classes are selected according to the prevailing type of the chemical bonds**. All minerals are grouped into **five types** (see Table 2).

In conclusion, it is pertinent to quote A.A. Godovikov: "*the fundamentals of the mineral classification elaborated by V.I. Vernadsky and their further development made it possible to construct a natural classification of minerals so much needed during his lifetime, with a firm foundation laid for this classification by V.I. Vernadsky himself*" (Godovikov, 2001).

As became evident over years that has passed since the publication of the structural-chemical classification of minerals, it enables accurate arranging newly discovered species. During this time, cells in the systematic table were found for 1457 species, most of which are newly discovered minerals and lesser part are minerals known earlier but not fit into the systematic tables proposed by A.A. Godovikov. The features assumed as the basis the of classification allow one to change the position of a mineral in this classification after more accurate and/or precise data are obtained on the composition or structure of this mineral. The classification makes it possible to distinguish new taxons for newly discovered minerals that present chemical compounds not known in the early 1990s. Thus, **this is not a frozen concept but a developing system.**

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GEOCHEMICAL MINERALOGY BY VLADIMIR IVANOVICH VERNADSKY AND THE PRESENT TIMES

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The world generally believes that *"the science of science"* about natural matter – *mineralogy* – became obsolete and was replaced by the new science – *geochemistry*, by V.I. Vernadsky. This is not true. Geochemistry was and is never separated from mineralogy – its fundament. Geochemistry studies behaviour of chemical elements mainly within the minerals, which are the basic form of inorganic (lifeless) substance existence on the Earth conditions. It also studies redistribution of chemical elements between co-existing minerals and within the minerals, by variable conditions of *mineral-forming* medium during the *mineral-forming* processes. On the other hand, owing to V.I. Vernadsky, mineralogy became geochemical mineralogy, as it took in the ideas and methods of chemistry, which enables to determine chemical composition, structure and transformation of minerals during the certain geological processes in the Earth history.
1 photo, 20 references.

Keywords: Vladimir Ivanovich Vernadsky, mineralogy, geochemistry, geology, physics of solids, mineral-forming process, paragenesis, history of science.

Vladimir Ivanovich Vernadsky's remarkable personality and his input to the Earth sciences, first of all, to mineralogy – changing it from the trendy mineral collecting hobby, observation of mineral beauty, art and culture areas into the *mineralogical science*, are not to be expressed. Even at present, over a century since, his studies impress with its full of thought, unity, systematic character and wide approach to investigation of natural objects, deep analysis of previous publications in this area. His activity amazes with unusual dedication and uncompromisingness for organization research and fight with traditional conservatism, with solution of principal issues of science and with creation of progressive scientific mineralogical school in Russia. Scientific ideas by Vernadsky are actual at present not less, but even more than 100 years ago, when not all the mineralogists could accept and understand them. According to Dmitriy Ivanovich Scherbakov's memoirs: *"Vladimir Ivanovich in his addictive aspiration forward was often taking the lead over scientific ideas of his epoch. Sometimes he was not understood and his thoughts were underestimated by his contemporaries. But his outstanding scientific intuition always lead him by the right way and his clear-sightedness helped to create the number of new leading courses with perspective future"* (Scherbakov, 1963, p. 34, 35).

Vladimir I. Vernadsky – as a mineralogist

As to the memoirs by Boris Leonidovich Lichkov (Lichkov, 1948; 1963), scientific creative work of V.I. Vernadsky could be divided into several stages. Forming his personality of scientist-mineralogist and the main input into reformation of Russian mineralogy and creation of mineralogical science in Russia are related with the early, "Moscow" stage (1988–1909). At that time, on the recommendation of professor Alexey Petrovich Pavlov, Vladimir Ivanovich was invited to occupy the post of associate professor in mineralogy at the mineralogical department at the Moscow State University, for giving lectures in mineralogy at the natural history faculty (1890). Since 1891 he became a director of Mineral cabinet and since 1892 became the head of the department and started giving lectures in mineralogy, crystallography and natural history both at the natural department of the physics-mathematical faculty and in mineralogy at the medical faculty and also (since 1901) – at the Moscow high women's courses. During that time (1891) he defended his thesis for a mastery's degree in geology and geognosy, the topic is *"On sillimanite group and the role of alumina in silicates"* (Vernadsky, 1891). Later he obtained his PhD on the theme *"Phenomena of sliding of crystal matter (physics-crystallographic study"* (Vernadsky, 1897).

The fundament of those lectures (which were later re-published as textbooks) and scientific generalizations was strict unified methodology, which was not accidental, sudden happy striking, but it resulted from the huge, purposeful work. Vernadsky analysed in detail what was done by different scientists from different countries to reveal trends in development of scientific ideas, collective input in the whole image of knowledge of construction and laws of the environment, of the Universe. We will not replicate the scientist's well-known biography facts, but will mention only those, which are necessary for the topic of this paper and our grounds for us characterizing *mineralogy* of Vernadsky as *geochemical* mineralogy and not *geochemistry*. As the basic documents we will cite scientific works by Vernadsky himself, his letters and testimonies of his contemporaries.

First of all, Vladimir Ivanovich had brilliant teachers at the Saint-Petersburg University, which he was graduated from in 1885 at the natural history department of physics-mathematical faculty. His tutors were outstanding Russian scientists, who contributed a lot into the world science. The lecturer and examiner in chemistry was Dmitriy Ivanovich Mendeleev – the creator of Periodic Table of chemical elements. Lectures in geology and mineralogy were given by Vassiliy Vassilyevich Dokuchaev – the founder of revolutionary new direction in soil science. Under his tuition Vernadsky practised in the fieldwork, studying soils of Nizhegorodskaya and Poltavskaya provinces, with geological mapping; and also actively worked in Mineralogical cabinet of the University. Still being a student, he was interested in problems of mineral genesis, which he described in Brockhaus and Efron Encyclopedic Dictionary (Vernadsky, 1892). His tutor was also Sergey Fedorovich Glinka – who supported traditional views in mineralogy, however brilliant mineral expert.

After graduating from the University, Vladimir Ivanovich obtained a position of the keeper of the Mineral cabinet and after successful passing his masters exam (1887) he was appreciated with the overseas trip (1988).

It is usually considered that he was busy with deep studying crystallography there and since that sometimes "Moscow" stage is subdivided into two: *crystallographic* and *mineralogical*. But it is not quite, as we can read from the Vernadsky's detailed autobiographical abstract to the 4th edition of his lectures he gave at the Moscow University in 1910–1912: *"Almost all mineralogy departments at the universities and high technical and medical schools were occupied with not mineralogists, but geologists... Me myself, the follower of V.V. Dokuchaev and S.F. Glinka at the Petersburg University, got the scientific training in methods of research only abroad, in Munich and Paris"* (Vernadsky, Kurbatov, 1937, p. 38). This edition was prepared in cooperation with Sergey Mikhailovich Kurbatov under the title *"The Earth silicates, aluminosilicates and their analogues"*.

Thus, Vernadsky considered western countries as providers of progressive trends in mineralogy and crystallography and new methods of research should be learnt there, in advanced as to Russian development.


Fig. 1. Vladimir Ivanovich Vernadsky. Photo 1905 year.

After a short visit at the foreign corresponding member of the Imperial Russian academy of science, professor Archangello Skakki, Vladimir Ivanovich moved to Munich for visiting well-known mineralogist and crystallographer, professor Paul Groth and physicist crystallographer Leonard Zonke. At Groth's laboratory (1888–1889) he synthesised triethyl ester of trimesic acid, which seems to have nothing in common with mineralogy. But the essentials are that Groth was the first who understood and decided to express an idea that crystal can be described simultaneously both as molecule of chemical compound (which until nowadays remains as empirical chemical formula of the mineral) and endless three-dimensional pattern with atoms in lattice points. At that time he was busy with this problem since 1870s and then was first who understood and promoted in self-founded magazine Zeitschrift für Krystallographie the works by Evgraf Stepanovich Fedorov, who was repelled in Russia and Arthur Moritz Schoenflies. Later Groth was one of the initiators of X-ray analysis application in mineralogy, after professor of physics Max von Laue proved the possibility of diffraction of X-rays on crystal lattice and in 1912 in presence of Groth and with assistance of Walter Friedrich and Paul Knipping obtained the first X-ray picture of halite.

Describing the fundamental changes in crystallography Vladimir Ivanovich wrote: *"At* *the end of the XIX and beginning of the XX century in crystallography there was formed new precise geometrical conception about crystal, which replaced the previous idea about crystal polyhedra. Crystal is considered to be an endless system of homologous points within space, which distribution meets the basic geometric characteristics of crystal polyhedra — their symmetry and the law of rational indices. The background of such ideas about crystal can be traced in XVIII century, in works by Bergman and Hahn*[1]*, general conclusions by Haüy*[2]*. Now we see that the discovery of cleavage made by Hahn, was the fundament of all the theoretical thinking of the century long. Finally, it was crowned with the complete mathematical theory of possible systems of homologous points within space, it was presented independently: analytically — by professor Evgraf S. Fedorov in St.-Petersburg (1888—1891) and geometrically — by Arthur Schönflies in Stuttgart. They both obtained the same result — 230 systems of such points, which could be brought to fractional divisions. All the crystallographic groups were found earlier (Johann F. Hessel*[3]*, 1830—1832, Auguste Bravais*[4]*, 1851—1914, L. Zonke, 1879—1885) occurred to be the subcase of this remarkable and unique mathematical construction. ... The newly created concept was not in accord with the usual but experimentally unproved belief that chemical compound must be presented with molecule. In fact, this was absolutely new approach to the scientific understanding of matter solid phase — crystal one — chemical compounds, determined or undetermined. This approach was different rather than thermodynamic ideas, the approach enabled to bring together solid phase substances to investigation of their atomic structure"* (Vernadsky, Kurbatov, 1937, p. 10).

In March 1889 Vernadsky had moved to Paris where he worked under supervision of professor of natural history and inorganic chemistry Ferdinand A. Fougué in Collège de France and of professor of general chemistry, physicist and chemist Henri Louis Le Chatelier — the author of theory of dynamic equilibrium in thermodynamics and also the discoverer of pyrometer and metallographic microscope, in École des Mines. Vernadsky studied methods of pyrometry, synthesized minerals and studied their optical properties; also he was interested in natural forms of silicon and aluminium — the most important chemical elements on Earth. The latter was the basis of his above mentioned Masters dissertation (Vernadsky, 1891) and later this investigation was the central one amongst his innovative studies of the huge group of petrologically important aluminosilicates, which resulted in explanation of relation between their structure and chemical composition.

Recalling that time in the letter to Alexander E. Fersman from Carlsbad dated 1 October 1935, Vladimir Ivanovich wrote: *"All my scientific past is going over again. Both work and wishes, failed to be fulfilled — about structural chemistry of aluminium and silicon — work with Le Chatelier and Fougué and then — interest in polymorphism where a little was done about, postponed till better times, when at the beginning of a century I left for mineralogy as dynamic discipline and then — for geochemistry"* (Letters..., 1985, № 139, p. 173—175).

However, was everything that bad at the Moscow University when Vernadsky came? What was the real level of Russian mineralogy?

The impression about this can be based on the jubilee "Geologic almanac" (2003), published to 250th anniversary of Moscow State University. The authors recall that Moscow University, founded according to the Decree of Empress Elizaveta Petrovna from 12 (25) January 1755, consisted of three faculties: faculty of law, medicine and philosophy. Department of natural sciences was within the Medical faculty and at that time it had excellent mineral cabinet. It was donated to the University by the Urals industrialist Nikita Akinfiyevich Demidov and compiled on the basis of collection acquired by Akinfiy Nikitich Demidov in Saxony, from professor of Freiberg Bergakademie Heckel. There were nearly 6000 specimens in the "Heckel mineral cabinet", supplemented with specimens from the Urals and Siberia, but in charge of this collection was not a mineralogist, but famous writer — Mikhail Matveyevich Kheraskov. At the beginning, classes in mineralogy were available at two faculties — medical and faculty of philosophy; lectures in mineralogy were given since 1758 by German professor Johann Christian Kerstens, then since 1769 — by Matvey Ivanovich Afonin, who had studied abroad, at the universities of Königsberg and Sweden.

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[1] — Otto Hahn (1879—1968) — German physicist and radiochemist, discovered nuclear isometrism and uranium fission. In 1944 was awarded with the Nobel Prize.

[2] — René Just Haüy (1743—1822) — French mineralogist, the founder of crystallography, presented the law of whole numbers and the basic law of crystallography — the law of rational intercepts.

[3] — Johann Friedrich Christian Hessel (1796—1872) — German scientist, professor of mineralogy, worked at the Marburg University.

[4] — Auguste Bravais (1811—1863) — French physicist, one of the founders of crystallography, initiated the geometrical theory of structure, established 14 Bravais lattices.

In 1804 there was established new division of physics and mathematics and another one department of mineralogy within it — the department of mineralogy and agriculture. The heads of this department were graduates of the University Anton Antonovich Prokopovich (1804—1818) and Mikhail Grigoryevich Pavlov (1820—1835). At the same time the department of natural history at the faculty of medicine was transformed into the "Demidov" department of natural history on the basis of "Semyaticheskiy mineral cabinet" donated by Czar Alexander I. This mineral cabinet was acquired from prince Yablonovskiy for 50000 Netherlands guilders and handed over by the Urals industrialist Pavel Grigaryevich Demidov, according to the family traditions, with the splendid private mineral museum, library and transferring professors position, which was occupied for 30 years (from 1804 till 1834) by German professor Johann Gotthelf Fischer von Waldheim (in Russian — Grigoriy Ivanovich). During that period he brought many innovations to the education, for instance, practical classes with students on the basis of museum specimens and excursions to the Moscow suburbs. Fischer von Waldheim wrote and published two-volume text-book in mineralogy (1812 and 1820). In 1805 he organized Moscow society of naturalists (MOIP), that became the platform for propaganda of new ideas in mineralogy by Vernadsky and Fersman and it's Magazine ("Proceedings of MOIP" — since 1806, "Memoirs of MOIP" — since 1809 and "Bulletin of MOIP" — since 1829). He was the director of Museum of natural history from 1805 till 1834. Later, the position of the Head of "Demidov" department occupied Alexey Leontyevich Lovetskiy, who gave lectures in mineralogy from 1824 till 1840 and in 1832 offered the innovative mineral classification by their chemical, physical and crystallographic features. Unfortunately, the comprehensive Mineral cabinet suffered from the Moscow fire of 1812, but in 1813 was reconstructed owing to the collection donated by Nikolay Nikolayevich Demidov.

Since 1835 the courses in mineralogy and geognosy became independent in Moscow University and after integration of two departments: of mineralogy and agriculture of the physics-mathematical division and "Demidov" of medical faculty, there occurred the new department of "mineralogy and geognosy". The head of that department was Grigoriy Efimovich Schurovskiy (until 1861) and Mineral cabinet, previously based at the Natural history museum since 1839, in 1846 became independent too and was transferred to the department of mineralogy and geognosy, under supervision of Charles Frantzévitch Roulier. Even though Schurovskiy was mostly interested in geology, his lectures in mineralogy were remarkably professional, with demonstration of facts and critical revision of existing theories. Under Schurovskiy's proposal, in 1863 department of mineralogy became independent within the division of physics and mathematics, even though it was not officially established until 1870 due to the absence of professor of mineralogy. Since 1861 lectures in mineralogy were given by Mikhail Aleksandrovich Tolstopyatov, but he was appointed to the job (on the 7th (20th) March 1870) only after he obtained his Doctoral degree in 1869; he was occupying this position will his death in 1890 (i.e. until Vladimir I. Vernadsky). He created a good collection of minerals and crystallographic models in the Mineral cabinet, his lectures in mineralogy were brilliant and also in 1887 he founded chemical laboratory at the department, for analysis of minerals; so that way he went down in history as the founder of experimental mineralogy and crystallography.

Thus, it is hard to agree with Alexander E. Fersman saying that *"all the predecessors of Vladimir Ivanovich on the post of head of geology and mineralogy department, Fischer von Waldheim, Schurovskiy and Tolstopyatov were the strangers to innovations"* (Fersman, 1946). Apparently, this reproach is unfair — the lecturers at the University took so much effort to make both mineralogy as a science and mineralogical department at the Moscow University independent, 20 years prior to Vernadsky's presence. However, in comparison with what Vladimir Ivanovich experienced in Europe, it was seemingly incomplete. He wrote: *"At the Moscow University long before me the head of the mineralogy department was M.A. Tolstopyatov (since 1868), who did not work in science, palaeontologist by education and the first professor of mineralogy, after G.E. Schurovskiy[5]. It can be said, that there was no mineralogy at the proper scientific level of that time at the Moscow University... In Moscow I found newly equipped chemical laboratory at the Mineral cabinet, which M.A. Tolstopyatov faught out from the faculty, on the initiative of his friend E.D. Kislakovskiy[6]...*

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[5] — Both theses by M.A. Tolstopyatov were on crystallography and were the summarized literature data. He was an amateur mineralogist and a brilliant lecturer, made up a good mineral collection. After his death his interesting observations of the beryl crystals morphology were published.

[6] — Yevgeniy Diodorovich Kislakovskiy — the keeper of the Mineral cabinet at the Moscow University in the time of M.A. Tolstopyatov.

V.V. Dokuchaev, one of the greatest naturalists, was a geologist and at that time was busy creating a new tendency of universal importance in soil science, where I was granted to take part in. But his lectures in mineralogy were not trivial. He stressed on the dynamic meaning of mineralogy and this was the major difference between his lectures and teaching mineralogy at home and abroad. In that respect I became his follower, bringing physics of solids — as a separate science into teaching crystallography and mineralogy — as a history of minerals of the Earth's crust, proceeding with the course by Comte de Buffon and not by Linneaus, which was dominant everywhere at that time" (Vernadsky, Kurbatov, 1937, p. 28).

In fact, Carl Linneaus was a world trend-setter at that time, who divided all the natural occurrences into three kingdoms: animals, plants and minerals, with an idea about constancy and stability of the species, which naturally led directly to creationism — an idea of divine creation. But Vernadsky was already firmly following the positions of transformism by Georges-Louis Leclerc Comte de Buffon and Jean-Baptiste Pierre Antoine de Monet Lamarck who proved variability of species under conditions of existence conditions and changes in the environment; that was explained by Charles Darwin that *"we regard every production of nature as the beginning of having a long history"*. We will add to this that in 1910 there were discovered only 82 chemical elements out of 115. Radioactivity was discovered not long ago and studies of diffraction on crystal lattice nearly began. It became apparent, that the natural form of existence of chemical elements is atoms, but their bonds within the mineral crystal structure were not determined yet. 230 Fedorov space systems deduced were not identified with the real atoms (or ions) within the structure. And the preliminary conclusion by Vernadsky about *"geochemistry that studies atoms within the Earth's crust and mineralogy — molecules"* was the gained revelation that could become the fundament for radical reformation of mineralogical science by revision of all the data accumulated.

Vernadsky's mineralogy

Vernadsky's appointment to be the head of the mineralogy department (1890 — 1911) gave start to the golden age of mineralogy and crystallography at the Moscow University. The Moscow (later the pan-Russian) mineralogical school rose from the small Mineral cabinet into the scientific centre of mineralogical research with the first-class equipment and world-level scientific achievements. One of the largest Russian mineralogical museums, replenished with Rumyantsev's collection of minerals, was organised (Geological almanac, 2003).

First of all, it was necessary to write textbooks according to the new scientific ideas and to educate new specialists in mineralogy, which Vladimir Ivanovich drew out of his students (Popov, 1963). His first students were Anatoliy Orestovich Shklyarevskiy and A.A. Aunovskiy, later — the 1897s graduates Sergey Platonovich Popov, Pavel Karlovich Alexat and Vladimir Georgiyevich Orlovskiy; Yakov Vladimirovich Samoylov from Odessa and Nikolay Nikolayevich Tikhonovich from Khar'kov; and also Yelizaveta Dmitrievna Revutskaya and Anna Boleslavovna Missuna — the graduates from the Moscow high women's courses. Later the number of the followers and staff of the Mineral cabinet rapidly increased, the new specialists were Nikolay Ivanovich Surgunov, Vladimir Vasilyevich Arshinov, Vissarion Vissarionovich Karandeev, Vladimir Victorovich Kritskiy, Konstantin Avtonomovich Nenadkevich, Leonid Lakrionovich Ivanov, Pavel Prokopyevich Pilipenko, Olga Mikhailovna Shubnikova, later — Genrikh Iosifovich Kasperovich and Alexander Yevgenyevich Fersman. The majority of the followers of Vladimir Ivanovich later had become the prominent scientists.

Vladimir I. Vernadsky creates his textbooks on the basis of his own lectures in mineralogy and crystallography, he gave to the medical and natural history students from 1891 to 1912, consequently corrected and supplemented, published on every possible occasion. What was the difference between them and the generally accepted mineralogy course at that time? Even in 1891 Vladimir Ivanovich cited some phrases from the three-volume book by Jöns Jacob Berzelius published in 1822, as an epigraph to his Masters dissertation: *"Mineralogy as a science about inorganic compounds comprising our Earth, is only a part of chemistry, which is its comprehensive and historical fundament"*.

As we know, the description of every mineral as a natural compound must include characteristics of its chemical composition, crystal structure and conditions of formation — certainly, if we consider it as an object of scientific investigation and not as an object of arts, interior or collection, which interest mostly amateurs. Such a complex description of a mineral did not exist prior to Vernadsky — mineralogy "terminated" in its evolution in detailed description of crystal faces and habitus and its physical properties (density, hardness, cleavage, color, luster, transparency). The necessity of above mentioned three major characteristics of the mineral substance was first declared by V.I. Vernadsky, even though the chemistry's key role: "*It seems to me that all the future evolution of crystallochemistry should be in close cooperation with chemical mineralogy and chemistry in general. Mineralogist and crystallochemist have to work together. ...The data of crystallochemistry and data of chemical mineralogy should correspond to each other. The data of chemical mineralogy — not only as a stoichiometric formula — should be initial for calculation the space atomic formula. Where this was not done, the space atomic formulas should be considered as undetermined and have to be refined. All the crystallochemistry is in such a state now, but for the simpler compounds this is not of big issue, however for the groups like silicates and aluminosilicates it is absolutely necessary to take this circumstance into an account as here we have minerals of completely different chemical function rather than simple saline compounds, crystallochemists believe them to be. ...The possibility to construct the space atomic lattices using the regular mathematical evaluation of X-Ray data — is the supreme achievement from chemical mineralogy. This enabled it to move this part of the science forward, as the latter was weakening and developing too slow for the last several decades. ...From such a co-operation with science field, rich in facts but poor in the modern-level ideology, both areas of mineralogy — chemical mineralogy and crystallochemistry — will benefit*" (Vernadsky, Kurbatov, 1937, p. 16).

Chemical approach to mineralogy was natural for V.I. Vernadsky, as he was an excellent chemist himself, more precisely — chemist-mineralogist like J.J. Berzelius and he worked in chemical laboratories together with such prominent Russian chemists-mineralogists as Konstantin Avtonomovich Nenadkevich, Irina Dmitrievna Borneman-Starynkevich and others. But V.I. Vernadsky interpreted "chemical mineralogy" in a greater sense rather than chemists: "*Chemical mineralogy aims for: 1) determination of chemical composition of natural compounds, minerals, 2) reconstruction of conditions of chemical reactions resulted in mineral formation, their genesis and paragenesis, 3) investigation of their alteration in various geospheres — their weathering, metamorphism (biogenic included). Chemical mineralogy is primarily based on chemistry — on synthesis and analysis of minerals, — but at the same time it is based on and is using field observation — determination of paragenesis and studying pseudomorphs. It is necessary to stress on the latter, as the study on pseudomorphs created by scientific observation, is far beyond the limits of modern chemistry, as reactions should be considered, take place within the solid matter, the crystal matter, the space lattices. ...Pseudomorphs play a great role in the study on paragenesis, which is significant for the dynamics of chemical mineral-forming process. Both the study on pseudomorphs and the study on paragenesis are still incomplete. (But) Actually, the study on paragenesis penetrates all the mineralogy. ...The main chemical problem ever existed for all the minerals, ... was the problem of understanding of digits of chemical analysis of minerals. At the beginning, it appeared that the majority of minerals dramatically do not correspond to the stoichiometric ratios of atoms which constitute the natural compound. They correspond, as solutions, to the undetermined compounds of Berthollet*[7]*. ...Eilhard Mitscherlich*[8] *mentioned that these undetermined compounds have similar shapes and compounds with analogous shapes are able to crystallise with non- stoichiometric ratios of all or part of atoms. He named this phenomenon as isomorphism — the feature corresponding to atoms and undetermined compounds crystallised — isomorphic mixtures. ...The simple solution was made mach later, at the beginning of the XX century, by Svante Arrhenius*[9]*, who pointed out that isomorphic mixtures are solid solutions, similar to liquid solutions, which comply with the similar laws*" (Vernadsky, Kurbatov, 1937, p. 16 — 19).

According to these statements V.I. Vernadsky decided to revise existing facts in mineralogy by writing the multi-volume monograph "Experience of descriptive mineralogy" (Vernadsky, 1955; 1959)[10]. In the foreword to the 1st issue of "Experience" he wrote: "*The major aim is to revise the natural chemical compounds of the*

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[7] — Claude Louis Berthollet (1748 — 1822) — French chemist, the founder of the theory of chemical equilibria.

[8] — Eilhard Mitscherlich (1794 — 1863) — German chemist, professor at Berlin University (since 1821), the founder of the theory of isomorphism and dimorphism.

[9] — Svante August Arrhenius (1859 — 1927) — Swedish physical chemist, determined dissociation of compounds and ionic composition of diluted solutions, Nobel Prize winner (1903).

[10] — Vladimir I. Vernadsky overestimated his abilities: only two volumes of "Experience of descriptive mineralogy" were published: volume 1 — Native elements, published in 5 editions (1908 — 1914) and volume 2 — Sulphury and selenite, in 2 editions (1918 and 1922). These editions are the examples of encyclopedic guidebooks and at present, almost after 100 years, are easily read as if were written recently. This definitely indicates that fundamental mineralogical data does not become out of date and can be only supplemented and revised. The further work on addition and continuation of this edition under the title "Minerals of the USSR" was performed by A.E. Fersman. However only two volumes were also prepared: volume 1 — Native elements, volume 2 — Sulphides and sulphosalts (M.-L.: AN USSR. 1940). The further work was interrupted by the Great Patriotic War and later — by death of V.I. Vernadsky and then A.E. Fersman in 1945.

Earth from the point of view of chemical processes which take place within it. This, by my opinion, is the main task of mineralogy, which is, similar to chemistry, has to study both products of chemical reaction and these very same reaction processes. This view on mineralogy and revision in this respect all the material on mineralogy took place subsequently in the early 1890s, when I gave lectures in mineralogy at the Moscow University" (Vernadsky, 1955, p. 9).

Such a grand task by means of one even though extraordinary talented and hard-working person, is unlikely to be accomplished. This can be only done by the team of experiences qualified associates, bind together with the common scientific idea, under supervision of competent respected editor or tough administrator. In this case, the attempt to write such a fundamental encyclopaedic work proceeded against private circumstances and political events. Those include the fight against traditional conservatism of colleagues-mineralogists and indolence of regal bureaucrats, who subsidised scientific research; the situation resulted from the First World war, February and October revolutions; the fight with the sudden decease after which Vladimir Ivanovich found himself in Ukraine, in Kiev (where he founded Ukrainian Academy of Science and became its president) and – in Crimea, in circumstances of civil war followed by devastation of the country. At that time he was trying to find new bonds with the new authority and to prove the importance of intensive and comprehensive mineralogical investigations for development of productive industry in the country. He struggled for discovering in Russia own ore deposits, new perspective types of mineral rough, for studying the opportunities given by atomic energy and for including science into intensive socialistic development. And, finally, he stood for mobilisation of all the forces to help the battle-front against perfidious fascist Germany (where Vernadsky in his young years learnt mineralogical science), in circumstances of Great Patriotic War (WWII). In fact, one had to be Vernadsky to be able to make all that was done for the Russian science.

Accelerated pace of the socialistic economy creation demanded the wide-range practical work in searching, prospecting, mining of ores, technologies of their extracting and separation. This resulted in publishing mineralogical hand-books of a different type – less fundamental and detailed but comprehending more mineral species with characteristics of their possible practical application and with description of the profitable deposits in the country. Thus, V.I. Vernadsky in co-operation with S.M. Kurbatov urgently revised and replenished the data of lectures Vernadsky gave at the Moscow University and that were published in 1910–1912; they publish them as a monograph characterising most important groups of minerals: simple oxides and hydroxides, silicates, aluminosilicates and their analogues (Vernadsky, Kurbatov, 1937). And the team of mineralogists of the Lomonosov institute AS USSR translated the revised and replenished text of "Descriptive mineralogy" by Edward Salisbury Dana[11] (Dana, 1937) from English into Russian under edition by Alexander E. Fersman and Olga M. Shubnikova. In the foreword for this translation Fersman wrote: *"Exceptional need for knowledge in mineralogy is obvious in the past several years. Development of mining industry, expansion and application of various mineral ores, involvement in practice both rare metals, rare compounds and various mineral bodies, widening of application of non-metallic ores and new paths of the modern mineral technology – everything demand, first of all, precise knowledge of a substance itself – a mineral, knowledge of its constants, its exact chemical composition and all the features, which can be used as a searching and prospecting markers, or have specific technological value. On the new path of geochemical analysis theoretic concepts in mineralogy has to use precise constants of minerals obtained by laborious work of crystallographers, crystallochemists and mineralogists for the last 200 years long".*

Concluding this part, it would be impossible to ignore the problem of natural forms of silicon and aluminium – the one V.I. Vernadsky was interested all his life long, starting with his Masters dissertation "On sillimanite group and the role of alumina in silicates" (1891) – investigation that resulted in real revolution in mineralogy. Later, Vladimir Ivanovich wrote about his work: *"After experimental studies of disthen andalusite and sillimanite, that were considered to be saline silicates of aluminium, the author did not find any qualities of saline in them, but pronounced features of acidic anhydrides, close to quartz. In the line of comparative analyses ... the author came to conclusion that alumina and silica play the same role in aluminosilicates and that*

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[11] – Edward Salisbury Dana (1849–1935) – son of James Dwight Dana (1813–1868), the author of the famous "System of Mineralogy", who continued its publication with supplements and revisions under the title "Texbook of Mineralogy" till the 6th edition, in 1911, with appendix-3 of 1915.

they both are acidic anhydrides[12]*. In that case, kaolinite and its analogues are silica-alumina acids and such minerals as feldspars, leucites, zeolites etc. — silica-alumina salines. Made sure experimentally that the concept about all the silicates and aluminosilicates as about silica salines, I determined aluminosilicates and their analogues as silica-alumina and analogues anhydrides... The similar ideas evolved by Swedish chemist and mineralogist Blomstrand*[13] *in the field of compounds of titanium, niobium, heavy metals; he tried to understand chemistry of more mysterious group of minerals* (Vernadsky, Kurbatov, 1937, p. 25—26).

Vladimir I. Vernadsky made a great effort and spent a lot of time for solving the problem of so-called "kaolinite core" which is considered inaccurate at present. Even in 1898—1899 he determined "existence of typical complex *$Al_2Si_2O_7$ (kaolinite core) which remains stable under endless chemical processes, natural or laboratory, sometimes taking place within solid substance. This complex (metanacrite): 1) had to have chemical character of a complex anhydride, i.e. Al_2O_3 and SiO_2 had to have similar functions of acidic anhydrides within it and 2) obviously, that within the crystal lattice they had to be distributed equally in regard to the surrounding atoms: Al and Si had to be chemically identical*" (Vernadsky, Kurbatov, 1937, p. 38). Over a period of many years Vernadsky unsuccessfully tried to refine its chemical formula to explain bonding of cations and aqua with Al, via saturated atoms of oxygen and later accepted the hypothesis by Felix Karl Ludwig Machatschki who admitted (in 1928) that "*in some aluminosilicates Al_2O_3 and SiO_2 play the same chemical role. Machatschki pointed to the possibility to avoid the problem by admitting exiting the complexes (AlO_4) and (SiO_4). These complexes occur as tetrahedra with ions Al or Si in the centre and ions of oxygen — in the corners. ... X-ray data show that in these minerals aluminium and silicon are always surrounded with atoms of oxygen, this is the closest atom amongst the others. This results in peculiar frame.*

$Al_2Si_{2+n}O_{7+2n}$ (where n can be equal to 0).

Accepted the hypothesis by Machatschki ideally resulted in understanding of the whole number of cases which could not be interpreted for a long time" (Vernadsky, Kurbatov, 1937, p. 36), i.e. finally in denial of idea about "kaolinite core".

This is the history. However we should not forget that V.I. Vernadsky was the first who drew attention to the similar chemical functions of Si and Al within the large group of minerals, later determined as *aluminosilicates* which are greatly significant for mineralogy, petrology and geology. These minerals are rock-forming and almost completely form the Earth's crust, i.e. they are the main form of mineral substance within the Earth mineral-forming processes.

Mineralogy, geochemistry or "geochemical mineralogy"?

So, who was Vladimir I. Vernadsky after all — mineralogist or geochemist? We believe that such a contraposition is absurd — those are the different sides of the same conception, the same science about natural mineral substance. However, some people used to think that Vernadsky "destroyed" Russian mineralogy by modernizing it and replacing it with "new" science — *geochemistry*. It is hardly possible to claim upon Vladimir Ivanovich that our contemporaries are that neglectful to the "*science of science*" about the mineral substance, which gave birth to crystallography, petrology and geochemistry; upon the scientist who brought up mineralogy, who determined its scientific fundaments and put it to the same level with the other natural sciences about Earth and its inhabitants. We investigated earlier what Vladimir I. Vernadsky meant by the term *mineralogy*. And what did he mean by *geochemistry*?

Vladimir I. Vernadsky, obviously, looked wider. He wanted to get to know the rules of conduct of the chemical elements both on Earth and in the Universe — the processes of their origin (by studying radioactivity), dissemination and concentration (by learning about isomorphism and solid solutions formation), re-distribution during mineral-forming processes and later alteration of minerals (by dealing with genetic or *dynamic*, according to Vladimir Ivanovich words, mineralogy).

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[12] — The further investigations of the crystal structures of the polymorphs of sillimanite, on the one hand, confirmed the ideas of V.I. Vernadsky and on the other hand, defined them dramatically. In the sillimanite structure in the chains, elongated along the c axis, aluminium occupies AlO_6 octahedra and in AlO_4 tetrahedra, alternating with SiO_4 tetrahedra (formula $Al(AlSiO_5)$). In the andalusite structure, besides the chains of AlO_6 octahedra there occur two-dimensional lattices of alternating SiO_4 tetrahedra and AlO_5 pentaredron (formula $Al_2(SiO_4)O$). In the structure of kyanite (disthen) one half of AlO_6 octahedra occupies in the chains elongated parallel to the c axis and another half — in the chains, where AlO_6 octahedra alternate with SiO_4 tetrahedra (formula $Al_2(SiO_4)O$). The bonds within the AlO_6 octahedra — ionic, within SiO_4 and AlO_4 tetrahedra — covalent (minerals, 1972; 1981). I.e. only in sillimanite Al and Si are acidic anhydrides, whereas in andalusite and disthen the function of Al — is intermediate between acidic anhydride and silicate saline.

[13] — Christian Wilhelm Blomstrand (1826—1897) — Swedish chemist and mineralogist, professor of the University in Lund (since 1862), a member of the Stockholm Academy of science.

The term "geochemistry" was not his "invention". It was applied as the "chemistry of the Earth's crust" at the end of 1830s — beginning of 1840s, by the scientist from Bazel, Christian Friedrich Schönbein. Quoting Schönbein, Vladimir I. Vernadsky reminded: "In 1842 Schönbein wrote: "*Already some time ago I publicly expressed my belief that we have to deal with geochemistry first, before speaking about the real geological science. The latter has to pay the same amount of attention to the chemical nature of masses that conclude our globe and to their origin, as to the relative age of these masses and fossilized plants and animals embedded. It can be confidently affirmed that geologists would not always follow the direction they do at present; for broaden of their science they have to search for the new supplements and then surely would introduce mineralogically chemical element into geology*" (Vernadsky, 1954, p. 20). I.e. Vladimir I. Vernadsky was obviously in accordance with that and interpreted the term *geochemistry* as *mineralogically chemical element*.

It is believed that Vladimir Ivanovich "gave life" to geochemistry in his speech at the opening ceremony of the Geology & mineralogy section at the XII Meeting of Russian naturalists and medical doctors on the 28th December 1909 (Vernadsky, 1910 — according to: Essays..., 1922). For the first time he drew attention to *paragenesis of chemical elements* in the Earth's crust: "*The ideas by de Beaumont*[14] *on paragenesis of elements as the function of geological history of their distribution and by Crookes*[15], *as the result of their dissociation — are the base tones of the modern scientific thoughts in this area. ...Ideas in natural history have to constantly grow, to change and to be created; if they would not be continually fed by the new facts, observations, experiments and specific material, then they would decay and alter and this process would finally lead to dull and dead abstraction... the mystics dissimilar to scientific reality*" (Vernadsky, 1922, p. 75—76). Then, citing the works by Johann Friedrich August Breithaupt from Freiberg, Vernadsky wrote: "*Mineral paragenesis, classifying co-existing minerals, inevitably distributes chemical elements those minerals consist of. It systematizes chemical elements of the Earth's crust. For this purpose it is sufficiently to replace "mineral" with its chemical composition*" (Vernadsky, 1922, p. 77). "*Another system was developed much later. ...That second system — about quantitative composition of the Earth's crust and its separate parts — followed two different paths, both fruitful and important. On one hand they chose the most abundant elements, trying to express numerically or orderly their relative quantity in the Erath crust... in 1888, those attempts resulted in the form, convenient for scientific work, by the American Clarke*[16] *and later were developed by his follower, well-known Norwegian scientist Vogt*[17]. *...However, merely quantitative approach of research, usual for precise chemical conclusions, is obviously not sufficient here. ...Because in the Earth's crust the order of numbers, which express distribution of different chemical elements, varies in a huge scale. Some elements are million and billion times much more abundant than the others. ...The usual and rare elements of the Earth's crust are difficult to compare. For the latter elements, the second path was developed. It was about their traces distribution within the minerals and parts of the Earth's crust, about their dissemination within the natural chemical compounds. ...The only possible explanation for the microcosmic dissemination of elements we can find in those minerals which are comparable with solutions. Due to dissemination, chemical elements form extremely diluted solid solutions — and in diluted solutions the substances solved are subject to gas laws*" (Vernadsky, 1922, p. 77—79). I.e. in this very case, geochemical conclusions are to be based on the analysis of the chemical composition of the specific minerals.

"*Mineral paragenesis is most deeply and in full comprehended by the study about isomorphic series. ...Isomorphic series for us is such a series, where similar compounds give isomorphic mixtures, i.e. are able to give mutual solutions in solid state. ...we have reliable basis for studying natural elemental paragenesis in isomorphic series. Due to them, we understand mineral formulae. The reasonable number of natural chemical compounds enables to apply*

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[14] — Jean-Baptiste Élie de Beaumont (1798—1874) — French geologist, a member of Paris Academy of science (since 1835) and its permanent secretary (since 1856), professor of École des Mines (in 1829) and Collège de France (in 1832).

[15] — William Crookes (1832—1919) — English physicist and chemist, a member and a chairman of The Royal Society of London, introduced spectral analysis in science, developed radiometer, discovered thallium.

[16] — Frank Wigglesworth Clarke (1847—1931) — the chief chemist of the Geological survey of the USA (since 1883), all his life was interested in geological problems, summarized and revised an enormous data on the content of chemical elements in the Earth's crust in the book Data of geochemistry (1908). The book was published 5 times (the ast one in 1924), one of the founders of geochemistry, professor of the University of Cincinnati (1874—1883), a member of the National Academy in Washington (since 1911).

[17] — Johan Herman Lie Vogt (1858—1932) — Norwegian petrographer and geologist, the foreign correspondence member of the Imperial Saint-Petersburg Academy of science (since 1912), professor of metallurgy at the University of Christiania (at present — Oslo) (1886—1903), professor of mineralogy and geology at the Norwegian technical high school of Trondheim (1912—1928).

the method of isomorphic series, which is awkward and inconvenient in chemistry. ...In contrast of chemical series, we would name (them) natural isomorphic series. It is extremely typical that such series are changeable due to not only the type of chemical compound itself, but to the external conditions of its formation. Isomorphic series expresses the quality of specific compounds to form solid solutions of a certain type, in the Earth conditions. Observation reveals that the isomorphic series traverse and alter under impact of temperature and pressure changes. Chemical element which is contained by one isomorphic series at a certain temperature and pressure, is not contained by it at their changed rate, but is contained by another series. At the same time, some elements which are included in some isomorphic series, cannot be included in any isomorphic series at another temperatures and pressures and become the lonely outcasts" (Vernadsky, 1922, p. 80—83).

"*Thus, the isomorphic series demands the following conditions: partially 1) geological and genetic, partially 2) physical and chemical. The latter can obviously be dependent on the former ones. Geological reasons are clear and can be traced in each separate case. ...However, sometimes the stronger influence would be not from chemical or physical properties, far from isomorphic series itself, but the very ability of the elements to make isomorphic series, i.e. — coincidence of the stability fields within the same crystal classes for the similar compounds*" (Vernadsky, 1922, p. 87).

Later, looking back at the path of geochemistry in our country, Vladimir I. Vernadsky wrote: "*The concept of geochemistry as the science about the history of the Earth atoms appeared on the basis of new atomistic ideas, new chemistry and physics, in close relationship with that specific idea about mineralogy which was accepted in the Moscow University in 1890—1911. Teaching and studying mineralogy were presented with priority of mineral history, genesis and alteration; which were normally moved to the background in the high school. In such a course of mineralogy, geochemical problems appeared to be in a higher scale level that in usual university courses of inorganic chemistry. Continually, the work at the Mineral cabinet of the Moscow University and later — Mineralogical museum of Academy of Science, became more and more geochemical. The name, given by Clarke, found the prepared contents and fertile grounds, but different from his ones*" (Vernadsky, 1954, p. 28).

All cited above clearly demonstrate that *geochemistry* — is the same *mineralogy*, but one might say, the "*higher one*" and Vernadsky's mineralogy — is mineralogy, transformed from purely descriptive and contemplative into the natural historical science, based on precise scientific methods of research. Vladimir Ivanovich introduced in it methods and methodology of both chemistry and geology; in this form it can be characterized as *geochemical mineralogy*. I.e. *geochemistry* and *geochemical mineralogy* are actually synonyms. At Vernadsky's times there was neither complete structural analysis nor modern spectroscopy — i.e. methods of research of a mineral as both a natural chemical compound and a natural physical body. Otherwise, there might appear another term — not geochemistry, but something more precise and broad, for example, "geochemphysics" or "geophyschemistry".

Concerning the tasks of mineralogy in our country, Vladimir I. Vernadsky wrote: "*In the thousand-years-long history of mineralogy, the understanding of its contents changed dramatically. ...The new content was included in the old word. This content is agile; it changes and transforms with time*" (Vernadsky, 1928, p. 21). And this is true. When characterizing modern mineral science, it is important to say, that it has experienced rather glorious but difficult way of development: once had involved the methods of structural analysis, it transformed from chemical mineralogy into crystallochemistry; on the basis of physical chemistry, thermodynamics, physical-chemical experiment and detailed natural observations — into genetic and regional-genetic mineralogy.

The hard times of mineralogy

All the above said demonstrates the huge role of Vladimir I. Vernadsky — as the reformer of the Russian and the world mineralogy, who showed its first-rate value among the other natural historical Earth sciences and who presented the actual tasks for mineralogy in our country and then successfully solved them in cooperation with the group of his followers. But the fortune of Russian mineralogy was sometimes tragic, which cannot be easily explained, yet being highly valued. It appears that in Russian and the world scientific society there existed forces which disagree with such progressive evolution of mineralogy and its enhancement among the other geological and mineralogical sciences. We believe it would be wrong to keep science about these conditions, which became public from the correspondence of V.I. Vernadsky and A.E. Fersman (Letters..., 1985).

In 1922 the physics-mathematical faculty of the Moscow University gave birth to 12 scientific research institutes, amongst which there were institute of geology (director — A.P. Pavlov) and institute of mineralogy and petrography, supervised by Ya.V. Samoylov — the follower of V.I. Vernadsky. However, they existed only until 1930, when, after reorganization of Moscow State University, geological, mineralogical and some other sciences were excluded from the University[18].

On the 10th January 1936, V.I. Vernadsky wrote to A.E. Fersman: *"Had an appointment with Bauman[19] and there I raised the question about mineralogy in our high school and about rehabilitation of mineralogy and geology departments to the Moscow University. Bauman took effort immediately and insists in urgent solution. Already on the 8th, when I was at Radium institute meeting Gabidulin, I met there also the rector of the Moscow University[20] and talked to him. You and I have to prepare short applications. I will do it tomorrow or the day after"* (Letters..., 1985, № 141, p.174).

In the letter from the 1st February 1936 Vladimir I. Vernadsky wrote about it again: *"I believe that I wrote to you that spoke to Bauman about returning mineralogy to the Moscow University. It looks like the case has moved forward. But, obviously, they are waiting for the determined arrangements from above"* (Letters..., 1985, № 142, p. 177).

And in the letter from the 13th May 1936 Vladimir I. Vernadsky was already worried about the future of mineralogy in the Academy: *"I strongly believe that you can set scientific work in mineralogy on the proper level — there is a huge work and long life in front of you. You are very, very young man, comparing to me. And it is you who only can make it: you are the head of the Lomonosov institute, where your scientific leadership is necessary and where you — and only you — can make it — can change alien to science environment that appeared there in times of your absence now and before. Now you have a giant work to do at the Academy, but the most important — the Lomonosov institute"*[21] (Letters..., 1985, № 143, p. 178).

The letter from the 24th September 1938 is already official, as if it was not a correspondence between friends, recognized world leaders, mineralogists, who did a lot for development of the mineral science in our country:

"Dear Alexander Yevgenyevich,

I ask you to discuss the problem of teaching mineralogy and geochemistry in the high school of our Union and scientific work in the same disciplines in our Academy, at the Department. Due to the reconstruction of the Academy, the situation with the scientific work can extremely retrogress in these disciplines. For more than ten years in our country the question about the state of mineralogy is on the agenda. The first All-Union conference on mineralogy in 1927[22] stressed on the hard situation with teaching and scientific work on mineralogy in our country. In 1930 the Council of People's Commissars had ceased teaching and scientific work in mineralogy and all geological sciences in the Moscow University, where they were at the high level. In 1937, the Second mineralogical meeting appealed to the government again, indicating the abnormality of the situation and damage to the country. All my attempts to make the situation better, via the Committee of the high school and media, were not successful[23]. Now the situation becomes even worse, as the scientific work in the Academy does so.

But in the meantime, the need of life demands broad development of these areas of knowledge. Their theoretical and practical application becomes more valuable... Now we need definite arrangements for enhancement of the downward scientific work on these disciplines at the Academy's Geological institute. The situation is that among the directorate staff there is no acknowledgement to these disciplines. For the plan of the 1939 — the prospecting map — the only issue is geology. However, in fact, geochemistry and mineralogy must be equal to geol-

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[18] — Department of mineralogy at the MSU was reestablished only in 1944, at the Geological-soil faculty.

[19] — K rlis (Bauman) Baumanis (1892—1937) since 1934 till his arrest and execution in 1937 was the head of the science department (est. in 1934) at the Central committee of the Bolshevik's party.

[20] — Mathematician, professor A.S. Butyagin was the director since 1934 till 1939 and rector of the MSU — since 1939 till 1943.

[21] — Lomonosov institute of geochemistry, crystallography and mineralogy (LIGEM) under leadership of A.E. Fersman, was established in 1932 by integration of Geochemical and Mineralogical institutes and Mineralogical museum of Academy of science in Leningrad. In 1934 it was moved, along with the Academy, to Moscow and in 1937 was interposed into the Institute of Geological Sciences (IGN AN USSR).

[22] — The conference took place from the 1st till the 6th January 1927 in Leningrad by the initiative of the group of the Leningrad mineralogists, who worked in the Academy of science and the Mining institute. In its work there participated president of the AN USSR A.P. Karpinskiy (chairman), academicians V.I. Vernadsky, A.E. Fersman, F.Yu. Levinson-Lessing, N.S. Kurnakov and the others. A.E. Fersman, in his talk "Mineralogy of the USSR and adjacent countries" indicated the need of the collective work of mineralogists to be resulted in the complete mineralogical description of all the territories of our country within the 10 years.

[23] — The second mineralogical meeting, which took place in Moscow on the 14th—18th of May 1937, was prepared by the Organizing bureau under management by V.I. Vernadsky. But Vladimir Ivanovich did not take part in it due to his illness. P.P. Pilipenko gave a talk "Mineralogy in the high and high-technical schools" about the wrong situation around mineralogical sciences in the high school.

ogy. As a result, all the problematic seems wrong to me. The prospecting map can be created on the basis of 3 sciences: geochemistry, geology and mineralogy. As to my knowledge, the attempt in the incomparably lower scale — the map of Switzerland by professor Niggli[24] *— was made by mineralogist. Essentially, geochemistry must occupy the eminent place. All the work of the American mining prospecting, in contrary to ours, is based on the mineralogical-geological fundament. The plan of Geological institute is based only on geological fundament. I believe, that at present in Geological institute scientific work in geochemistry is not properly set and that it is not all right as good young mineralogists (Labuntsov, for example) are moving away from it. The situation is getting more complex by creating two new departments (Geological and Chemical). Geochemistry is the chemical science by its major methodology and which is the reason of its weak position at the Geological institute, where chemical science is on the low level. We have to reconsider now such disciplines as geochemistry and geophysics at the Academy of science. They cannot belong to the Geological department. Geochemistry in a great measure was created in our country, but now we have no place for its forceful development, despite its rising application value.*

The situation looks critical to me, it demands fundamental solution. Presidium of Geological institute is not scientifically authoritative enough, as the prominent science academician Arkhangelskiy, its chairman, does not participate in it for many months and was not replaced. More than that, I reckon that the program of Geological institute cannot be approved without preliminary coordination with scientific work of the People's commissariat on the heavy industry.

Concluding all presented above, I ask you to organize the temporary Commission at the Department, for discussion the problems of teaching and scientific work on mineralogy and geochemistry in our country and at the Academy in particular. I see huge possibilities around, the new generation of mineralogists, which are unable to complete their scientific education and to apply their energy to scientific work. We have to hurry, otherwise life could lose them" (Letters..., 1985, № 156, p. 190—192).

The same situation with mineralogy was in the foreign countries. In the letters to Alexander E. Fersman from Paris (1923—1924) where Vladimir Ivanovich was sent to give lectures on geochemistry, he wrote: *"At present, the center of scientific work in our area — definitely moves to America and the most interesting publications — American ones. Comparing to that, the European literature in this area is moved to background more and more. In France there are not enough people involved in mineralogy. Departments of all the universities are occupied with crystallographers and only Georges Friedel from Strassbourgh is less strange to mineralogy. Here, Mauguin and Walletan are both crystallographers"* (Letters..., 1985, № 92, p. 107). *"In Germany, I think, it is specifically bad, especially with mineralogy. The most prominent one was Groth; Hecke, Tschermak, Niggli — are not German. And now, as it was before the war, they have no outstanding mineralogists. But in other areas they have physicists, chemists, mathematicians"* (Letters..., 1985, № 97, p. 117).

A similar pattern holds for mineralogy in our country at present. Mineralogical theme is actually excluded from the *priority* research mainstream of the Russian academy of science (see Decree of the Presidium RAS from 1st July 2003 № 233 as well as the "Plans for Fundamental Research Russian Academy of Sciences for the periods 2006—2010 and 2011—2025"). In the last part the word "mineral" exists only in one *program* № 67 as: *"Fundamental problems of development of lithogenic, magmatic, metamorphic and mineral-forming systems".* Nice but difficult to understand — as if lithogenic, magmatic, metamorphic systems are not the mineral-forming ones? In the reviewed "VAK" magazine *"Proceedings of Academy of science"* you will find neither section "mineralogy", nor "crystallography" (everything was included into "geochemistry"). Good news still that geologist are still awarded with the philosophy doctor degree of *geological-mineralogical* (and not *geochemical*) sciences, reminding with that that without the knowledge in mineralogy they cannot be the professionals in geology. Of course, at present there are no such mental giants like Vladimir I. Vernadsky or Alexander E. Fersman, but mineralogy still exists and successfully develops, taking in methods and achievements of chemistry and physics, as Vladimir Ivanovich predicted long ago.

Vladimir I. Vernadsky and the present times

Vladimir I. Vernadsky was not only the first-rate scientists but also the uncompromising social, governmental and political activist,

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[24] — Paul Niggli (1888—1953) — Swiss mineralogist, petrographer and geochemist, professor of the University of Leipzig (1915—1918), Tübingen (1918-1920) and Zürich (since 1920) and Eidgenössische Technische Hochschule (since 1920), the foreign correspondence member of the Academy of science of the USSR (since 1924).

keenly reacting to all the events in Russia and in the world; at the same time he was curating huge scientific and scientific-organizing work of a great value.

We would not recall about his emphatic retirement from the Moscow University with his students and followers: A.E. Fersman, V.V. Kandeev, G.I. Kasperovich, Ya.V. Samoylov, V.M. Tsebrikov and 126 other lecturers in protest of arrangements of the Minister of education L.A. Kasso, who broke the University's autonomy, gave it to the police arbitrariness and who discharged rector A.A. Manuylov, his assistant M.A. Menzibir and deputy rector P.A.Minakov, disagreed with that. In the same 1911 in respect with the 200th anniversary of M.V. Lomonosov's birth, Vladimir I. Vernadsky actively participated in application of the Academy to the Tsar's government to organize the Lomonosov institute[25] on the base of chemical and mineralogical laboratories and physical cabinet of the Mineralogical museum (Vernadsky, 1911). During the World War I and after the October Revolution he organized KEPS and SOPS – Commission and Counsel on investigation of the natural productive forces in Russia; he actively works at the discovering Russian own ore deposits and strategically important ores, which are necessary in war times and the further economic blockade from the side of imperialistic countries. Being involved in a research of uranium minerals and radioactivity, he organized Radium institute in Petrograd, on the base of the respective laboratory of the Mineralogical museum. Later, he insistently recommended the Soviet government to investigate in the area of nuclear energy. During the Civil war he happened to be in Ukraine, where he founded the Ukrainian Academy of science and became its president. When directing the Mineralogical museums in Moscow and St.-Petersburg-(Petrograd), he organized analytical laboratories within them, which later became scientific-research institutes etc. It is impossible to list everything. Shortly before his death in 1943 he was awarded with the Stalin's Prize of the first rank, for his scientific and organization works; this, in some extent, demonstrates recognition of his contribution in foundation and development of the Russian mineral science by the Soviet government.

We, mineralogists, do not need any proofs. In Russian and world science there hard to find a person which is comparable with Vladimir Ivanovich Vernadsky by his authority, erudition, scientific and organizing deeds, contribution in science.

But how do we respect the heritage of this ingenious scientist 100 years later? Differently, indeed. There are researchers which fairly show onto some mistakes and out-of-date solutions and ideas. And how is without it? Although Vladimir I. Vernadsky undoubtedly was far ahead of his time, he could not surpass future, eternity. Science (and also mineralogical) rapidly moves forward, despite obstacles of life, that is always full of contradiction of social-economical formations, countries, people, religions, all that interests and well-being of elite and leaders. Science has more noble and generous tasks and targets, including acquirement the knowledge about humanity, about world, about the planet Earth – its structure, composition, processes which take place on it, in it and in its far past, geological history. In this respect, Vladimir I. Vernadsky was the brightest person, the fighter for the power of the world science and the world human fairness. He was standing above strictly government, strictly political party, strictly clan interests; he was the Man of the World.

His ideas are actual at present as in the past, as they were founded on the basis of scientific methodology, which was developed alongside with the total progress of the methods of research and knowledge, in fight with conservatism, admiration of authorities and limitation of scientific schools, for omnipotence and power of objective scientific facts.

What is the situation in our mineralogy at present? Even among the prominent scientists there is an opinion that mineralogists should be involved only in mineral diagnosing, for the other sciences studying Earth, for those scientists who produce global ideas about the genesis of rocks, minerals and ore deposits. The top achievement of mineralogist should be precise diagnosing, description of the mineral phases and discovery of the new mineral species and these are exactly what is supported by various grants, projects, collector's and amateur's interest (rather than genetic mineralogy).

Vladimir I. Vernadsky taught and appealed to another idea. And, in particular, the idea that mineral, as a major form of mineral substance in nature, must be in the center of all the Earth sciences. And that on the fundament of the detailed chemical, physical, structural investigation of minerals, natural observations and physical-chemical experiments mineralogists

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[25] – In 1912 the Tsar's government formally agreed with the organizing Lomonosov institute, but the Academy did not receive neither funds, nor piece of land for its construction. It did not find any funding for it in 1912–1918 in respond to the second application of the Academy. Lomonosov institute was established only during Soviet times, but did not exist for a long period.

can and have to obtain the most valuable information about the composition, structure and features of the natural chemical compounds and can use this information in solution of genetic and applied problems. Something was achieved in this direction: genetic, regional, experimental, applied and technological mineralogy are developing. Those are the powerful arsenal of mineralogy branches which are able to provide with the detailed mineralogical description of geological objects, to reveal mineralogical indicators for search and prospecting of the ore deposits, to be the basis for choosing the method of mining, technology of processing and extraction of the ore components and finally to use structure and features of number of minerals as new and innovative materials. However, one has to have the will and skill to use it.

Instead of conclusion

More than a century ago, academician Vladimir Ivanovich Vernadsky (1863–1945) – the greatest Russian naturalist of the XIX–XX, whose 150th anniversary we celebrated this year, achieved a scientific feat – he got over misunderstanding and conservatism of the number of the "office" scientists and authorities. Resolutely and constituently, he introduce practiced new trends of the world science appeared at that time into practice of mineralogical research and teaching mineralogy at the department he was leading at the Moscow University. For a relatively short time he created brilliant Russian school of mineralogists, equipped it with scientific-research institutes and organized excellent mineralogical museums in Moscow and Petersburg. Russia is lucky to have such a Scientist, Patriot and a Man, who was able to lead mineralogy onto the first positions in the world. According to A.E. Fersman: *"There is no doubt that Vladimir Ivanovich – is the largest and the most original researcher of live and dead nature, the creator of new scientific trends, the reformer and the founder of Russian mineralogy and the world geochemistry"* (Fersman, 1946, p. 788). He *"has not only remarkable organizing talent, but also deep knowledge in the number of science areas: mineralogy, geochemistry, biogeochemistry, biology, soil science, geology, chemistry, physics, crystallography, energetics, radiogeology, radiography, hydrology, cartography, history of science, philosophy etc. Such diversity of creative thinking was combined with the rarest depth of analysis"* (Fersman, 1946, p. 789).

Unfortunately, the uncommon talent of naturalist and tutor Vladimir I. Vernadsky to predict and to understand trends of the world science, the mainstream tasks and contradictions in progress of the human civilization on Earth, deepest patriotism, the need in serving people and his fatherland, Russian science, the ability to understand the leading value of mineralogy within the Earth sciences, its role in economics, ecology, culture and human history – all these often run against one's indifference, misunderstanding and maybe envy. But Vladimir Ivanovich was unselfishly serving the science, believed in progress and power of mineralogical science, despite all the obstacles made and taught his followers and those who wanted to be one of them. Besides, he studied in detail the problem he began with, in historical aspect: what has been done in this direction by his predecessors. Alexander E. Fersman indicated: *"Vladimir Ivanovich always began to study every phenomenon with precise historical analysis. And regardless of the beginning of his treatise or description, it was always preceded with the history of a problem. Vladimir Ivanovich always required deep description of the history, from us, his students; and he made it not formally but practically, by teaching us to understand the way of a thought and the history of its development"* (Fersman, 1946, p. 790).

"In one of the letters from Italy, Vladimir Ivanovich wrote about the role of museum in the history of science. Museums, according to his opinion, had an exceptional value in development of natural sciences and culture in general... he told: "We, naturalists, have to learn from historians the deep historical methods of understanding of the mankind past. Using these methods we can become the historians of nature" (Fersman, 1946, p. 790–791).

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VLADIMIR I. VERNADSKY AND HIS ROLE IN RESOLUTION OF CHALLENGES OF NUCLEAR ENERGY UTILIZATION IN RUSSIA

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The article describes V.I. Vernadsky's activity in the area of study of natural source of radioactive decay, prospective of practical use of energy of nuclear decay. Activity of Fedorovsky All-Russian Institute of Mineral Resources in the development of mineral resources for nuclear industry in Russia is explained.
6 references.

Keywords: V.I. Vernadsky, nuclear industry, uranium ores.

150th anniversary of academician V.I. Vernadsky, a prominent Russian scientist, mineralogist, historian of science, philosopher, founder of geochemistry and many of its branches such as radiogeochemistry, biogeochemistry, cosmochemistry, geochemistry of Earths' hydrosphere and other was celebrated on March 12, 2013. He was promoted to a member of Prague and Paris Academies of Science, was granted many international awards. Majority of geologists, mineralogists and other specialists in Earth sciences in Russia and other countries employ ideas of the grand intellectual acumen of V.I. Vernadsky as the outstanding naturalist of the 20th century. His bright dynamic ideas connected all natural processes and phenomena, anticipated and defined development of Russian and the Worlds science for decades. Vernadsky gave an impulse to Russian science in many areas to contribute to the treasury of the Worlds science.

One of the most interesting areas of Vernadsky's creativity and executive scientific management was connected to his works on radioactivity, search for its natural sources and practical application of nuclear decay energy. He was one of few scientists who recognized and foresaw the new great source of energy for the humanity, the least known by the turn of the last century with hardly realized consequences of its use in the future. He mentioned in one of his first speeches "The urgent issues of radium" on the open meeting of the Academy of Science on December 25, 1910: "*We watch a revelation of such a source of energy that will make negligible power of steam, electricity, power of explosive chemical processes...., in the phenomenon of radioactivity we anticipate a source of nuclear energy which is millions of times greater than all energy sources that the mankind was dreaming of.*" His report included the following words: "*... with a thrill and expectations we direct our vision to the new power revealing for the human awareness. What will it bring us in its future development?*". He stated later: "*...with hope and concern we look into our new ally and defender*" (Vernadsky, 1954).

Amazing farsightedness of the great scientist, who could vividly describe complete meaning of the recent discovery was astonishing. Contemporary history showed that his concerns were not baseless: tragic incidents such as atomic bombs explosions on Hiroshima and Nagasaki, serious accidents at nuclear power stations: Three Mile Island, tragedies at Chernobyl, in the South Urals and Fukushima. Those episodes worsen with the problem of safe nuclear waste disposal that awaits its solution as many other ecological problems caused by careless human activities not mentioning radioactive factor. The world community started to actively address these issues, so hope for the effectiveness of the collective mind gives a space for some cautious optimism. This is why Vernadsky stated: "*The way of history is changing before our own eyes... Humankind as a whole becomes a great geologic factor. Demand to accommodate the biosphere according to the interests of freely thinking humanity as a unity arises before its mind and effort. This new state of the biosphere which we are unaware approaching is noosphere*" (Vernadsky, 1944; Armand, 2001).

Vernadsky's belief in the power and rationalism of the collective mind of humanity and subsequently his forecast of evolutionary development of human civilization with transition to the era of noosphere has been inspiring natural scientists and philosophers of various schools to dynamic research for almost half a century. Specific attention has been paid to the issue of sustained development of the civilization in the last decade. This issue is in the mainstream of the noosphere concept. Prevailing optimistic approach to the future of the humanity in the world spread out because of the great influence of V.I. Vernadsky. The scientist was convinced of the civilization stability and its regular and global development towards more sophisticated forms of structuring and collaboration in harmony with the whole biosphere. It brings natural response of optimism because he cherished this idea in the time of numerous natural, technological and social catastrophes that happened on the break of the 20th century.

There were also people who did not share the optimism of the followers of Vernadsky noosphere concept. Philosopher N.N. Moiseyev discussing the "gradual transition to the noosphere" was very cautious about this change of humanity *"... half a century ago thinkers* (Vernadsky and Teilhard de Chardin – authors note) *had more reasons to be optimistic than the people of todays' fin de siècle. They did not know about nuclear weapons and did not realize that the humankind is up to pass a harsh and severe global economic crisis. This transition will not be gradual and painless "amalgamation of the races, nature and God" as Teilhard de Chardin thought, but will be more likely bifurcation with unpredictable outcome"* (Moiseyev, 1994).

Nevertheless, let us be optimistic together with V.I. Vernadsky and based on the main law of the dialectics – the law of development and let us believe in the human mind: *"... the human had realized for the first time that he was a dweller of the planet and has to think and act in the new approach that is not limited by minding each individual, family or tribe, states or their alliances but in the light of the globe as a whole"* (Vernadsky, 1991).

Study of radioactivity was one of the main interests of V.I. Vernadsky of during all his life. Among a large group of professors he resigned from his professor position at Moscow University in 1911 in the protest to the repressive actions taken by the Tsars' government against students. He moved to Petersburg and in a year had organized Radium Expedition of the Academy of Science that explored for radioactive ores. The first results of the expedition allowed pioneering makeshift recovery of uranium and radium from ores of small Tyuya-Muyun and Taboshar deposits. Small amount of the metals was recovered from the ores for research and applied purposes.

A special chemical-mineralogical laboratory was organized at Mineralogical Museum of Academy of Science in Petersburg, which Vernadsky was leading since 1906. Mineralogy of rare and radioactive elements was studied there. Mineralogical and geochemical studies in Ilmeny Mountains in the Urals conducted by Vernadsky was a special direction of studies of that period. It was in the Urals in the Ilmens, where he started to study formation of thorium and uranium minerals yet in 1897. Radiogeochemistry was formed there as a new branch of geochemistry. Regions of Caucasus, Middle Asia, Siberia, Transbaykalia were other regions where Radium expedition worked till 1918. The researchers in the expedition gathered mineral collections to replenish funds of Saint-Petersburg Mineralogical Museum of the Academy of Science, Geological and Mineralogical museum of Peter the Great back then. The mineralogical laboratory of the museum formed upon Vernadsky's initiative in 1912, was transformed into Radium Institute of the Academy of Science in 1922.

Stepping away from the main topic of the article, I would like to present some interesting facts that linked V.I. Vernadsky and Nikolay Mikhailovich Fedorovsky. Fedorovsky later became his student and successor, then prominent mineralogist, corresponding fellow of the Academy of Science and the director of the Institute of Applied Mineralogy (All-Union from 1935 and then All-Russian Research Institute of Mineral Resources, VIMS). They met in the Ilmeny, where Fedorovsky, was sent to collect mineral collections by the owner of a store selling learning guides. Fedorovsky was previously dismissed from the university for his political activities and experienced big financial troubles. Vernadsky liked the smart and sharp-sighted young man. He involved Fedorovsky in work of his expedition, helped him to resume study at the university, which he graduated in 1914 and cultivated love of mineralogy in him. Fedorovsky had respect and gratefulness to the teacher for all his life and there friendship lasted for many years.

Fedorovsky was politically active person and became Bolshevik in 1904. He headed the Mining Council of the VSNKh (Supreme Council on National Economy) after October 1917 and executed some very important commands of the government. He got to know in the summer of 1921 that Vernadsky was arrested as an active member of Constitutional Democratic Party and an associate of a minister of the Temporary government. Fedorovsky promptly sent a telegram to narkom Lunacharsky assuring him that accusation of Vernadsky in anti-Soviet activity was baseless and demanding his immediate release. Vernadsky was freed the next day.

It was unfortunate, that Fedorovsky fell victim of defamatory accusation report as well in 1937 and was imprisoned for 15 years. Neither V.I. Vernadsky, nor V.A. Obruchev, who wrote appeals to I.V. Stalin to release Fedorovsky, could help him. Presently the Institute of Mineral Resources and streets in Nizhny Novgorod and Talnakh bear name of N.M. Fedorovsky. Soviet geologists remember the talented student of V.I. Vernadsky. Fedorovsky All-Union (All-Russian now) Institute of Mineral Resources made the essential contribution to development of the mineral resource basis for the nuclear industry of the USSR.

In 1920–30s V.I. Vernadsky paid considerable attention to the matters of nuclear reactions connected with fission of uranium nucleus with high energetic effects. He meticulously kept track of publications on the topic. Simultaneously with other soviet scientists, especially physicists, he noticed almost complete withdrawal of materials on this matter from public accessibility in the end of 1930s. It was a certain sign of concealing work on the topic because of possible weapon applications of nuclear fission. We need to note that further materials were taken from book of V.S. Gubarev (2009).

Materials gathered by Russian intelligence informed on commencing of development of nuclear weapons in England and USA. These data was delivered to the Soviet administration but at first was regarded to be disinformation determined to deviate Soviet efforts to the false direction. It was even more, that the intelligence data did not reach the people who actually worked on the nuclear program. In particular, I.V. Kurchatov was surprised when he was given helpful materials on the weapon development in England and USA in 1943. It needs mentioning, that the study on the nuclear program was carried out in several institutes of the Academy of Science even before the Second World War in spite of blunt skepticism from some scientists. There were problems with production of necessary instrumentation and obtaining radioactive materials for experiments. Vernadsky was aware of the situation.

Vernadsky knew about discovery of the effective chain fission reaction of nuclei of uranium-235 with neutrons and actively called for attention to it from the Presidium of the Academy of Science of the USSR. There were always visionaries in our nation who could foresee the future. Academicians Vernadsky and Khlopin directed a "Note on arranging uranium production" to the Presidium of the Academy of Science of the USSR. This document stated the important fundamental scientific and applied meaning of the study of nuclear reactions with energy effects. In particular it said: *"...We think, that even now, when the question of separation of U-235 isotope and utilization of nuclear fission energy meets some technical issues, which in our opinion do not have fundamental problems, urgent measures of establishing uranium exploration, mining and extraction in the USSR have to be taken. They are necessary to provide enough precious energy source material by the time when the technical issues in interatomic energy utilization will be solved. So far, the situation with such resources in the USSR is exceptionally bad. There is absolutely no resource of uranium. This metal is very scarce. There is no established recovery of the metal. Large explored deposits of it on the (Soviet) Union territory are unknown. Detailed exploration of the known deposits and searching for new ones go at very low pace, are not enough and are not connected with one big idea..."* The "Note" was discussed on the Department of the Academy of Science few days later and academicians were asked to develop a project with certain implementation plan in two-week time. Vernadsky wrote in his diary on July 17, 1940: *"There was a question on uranium on Presidium session. I presented a report that was not very successful, but the result was gained. The vast majority does not understand the historical meaning of the moment. I wonder if I'm mistaken? A note to the Government is needed..."*.

The Commission on uranium issues was formed on the meeting of Presidium of the Academy of Science of the USSR on July 30. It was a group of 14 people. There were ten academicians: Khlopin (the chairman), Vernadsky, Joffe, Fersman, Vavilov, Lazarev, Frumkin, Mandelshtam, Krzhizhanovsky, Kapitsa, professor Vinogradov and senior researchers Kurchatov, Shcherbakov, Khariton. Academicians Vernadsky and A.F. Joffe were appointed to deputy chairmen of the commission. However, the commission worked much slower than expected. It became particularly clear with the start of the Second World War. All the energy was turned to the defense. Attention to the nuclear problem increased somewhat in 1942 after the first successes of the Red Army.

Vernadsky wrote in November of 1942: *"It is necessary to seriously and extensively establish development of nuclear energy of actin-uranium. In this order the Uranium commission has to be reorganized and transformed into a flexible organization that would have two main goals: First of all, the quick discovery of rich uranium ores in our country, which is possible. In the second place, few kilograms of actin-uranium for experimental work with practical applications have to be produced promptly. We need to quickly solve the dilemma if we are indeed in the wake of a new era of the humankind, as I and many other geochemists and physicists think, the new era of application of new forms of atomic energy or we* *are not. In the light of devastation that Nazis barbarians caused to the national economy, we need to find out if it is realistic and beneficial to utilize this form of energy".*

The government made the decision creating "the Nuclear project of the USSR" on September 28, 1942. It was the direction No 2352cc of the State Committee of Defense *"On arranging work on uranium"*, signed by I.V. Stalin. This document considered organization of a special laboratory (It was laboratory No 2 from 1943), separation of materials for experimental work and providing laboratory space for atomic nucleus laboratory in the city of Kazan. A.F. Joffe was appointed to a lead resuming the study on uranium. He, in turn, insisted on transferring the duties to I.V. Kurchatov. I.V. Kurchatov was appointed the scientific chief of the work on uranium by the order of State Committee of Defense on February 11, 1943.

V.I. Vernadsky was concerned with low activity of the Uranium Commission of the Academy of Science of the USSR and addressed to the President of the Academy of Science from Borovoy, where he was evacuated. He wrote: *"I consider it is urgent to resume activities of the Uranium commission, having in mind possibility of military application of uranium as well as in quick reconstruction of the economy after devastation of the country from Hitlers barbarians. New sources of powerful energy are needed to reach these tasks."* With these words Vernadsky actually pointed to possibility of electric energy generation and anticipated design of nuclear power plants.

He wrote to the President of the Academy of Science later in personal letter criticizing his colleague: *"I'm certain that the future belongs to the atomic energy and we need to understand where uranium ores localize in our country. Our efforts in this question have been stalled for few years. Unfortunately, Ioffe does not understand or pretends that he does not understand, that to utilize atomic energy, in the first place uranium ores need to be found in significant amount. I think that it can be done during one summer campaign. Fersman and Khlopin share the same opinion as far as I know"* (Gubarev, 2009).

The Manhattan project was actively deploying in the USA from January 1943, according to the intelligence sources. It resulted in creation of the atomic bomb that killed hundreds of thousands of people in Japan in September 1945. Active work on the Atomic project, which was numerous times endorsed by Vernadsky, commenced in the USSR in the same time. We know now that its mission was accomplished successfully.

Vernadsky took part in the meeting of the Committee on geological affairs at the Sovnarkom of the USSR on October 2nd, 1943. It was chaired by I.I. Malyshev and worked out a plan for uranium exploration program and organizing a permanent Consulting Bureau on the issues of uranium resources at the All-Union Research Institute of Mineral Resources. V.I. Vernadsky was a member of the bureau.

It can be noted with satisfaction that intensive work of all exploration and mining companies, research institutes of the country quickly provided the solution for uranium resource problem. Several large deposits of radioactive ores had been discovered and the work on nuclear defense program succeeded. In very restricted time limits USSR obtained enough uranium to extract isotope U-235, the main component of weapon metal as well as fuel elements of the world's first nuclear power plants developed in the Soviet Union.

The soviet scientists, designer engineers, researchers of the nuclear industry, numerous geological parties and the whole soviet nation accomplished a great historical achievement. Monumental efforts of the soviet nation created a reliable and safe nuclear shield in unreasonably short period. The opponents who wanted to destroy Soviet Union with atomic fire were stopped in their efforts being aware of inevitability of protective retaliation.

Importance of Vernadsky's contribution to the solution of the nuclear problem in our country is gigantic. We, the grateful descendants of the great scientist will remember this accomplishment!

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Mineralogical Museums and Collections

WORKS OF CHINESE STONE-CUTTING ART AT FERSMAN MINERALOGICAL MUSEUM OF RUSSIAN ACADEMY OF SCIENCES

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This article is the first publication about Chinese stone-cutting art in a collection of Fersman Mineralogical Museum of Russian Academy of Sciences.

32 figures, 33 references.
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The collection of Fersman Mineralogical Museum of Russian Academy of Sciences began to form as a part of cabinet of curiosities, which was founded by Peter the Great in 1714. Inter alia the Mineral cabinet was created. Then, in 1836, it was reorganized into an independent Mineralogical Museum as a part of Russian Academy of Sciences. Though in the first catalogue of the collection, compiled by M.V. Lomonosov and published in 1745, there were descriptions of several small plaquettes of Florentine mosaic (Novgorodova, 2011), collecting of stone products was not included in the objectives of the Museum and their appearance in the collection (right up to the twentieth century) had an incidental character. Even in the catalogues of the 19th century mentioned only a few stone carving items and they were all Chinese, for example in Ivan Wagner's (Wagner, 1806) and Konstantin Grewingk's (Grewingk, 1846) catalogues.

In the Mineralogical Museum the current collection of the collection of ornamental and precious stones was first formed only in the 1920s, during the period of rapid nationalization of the property of the Royal family and the nobility. A huge amount of seized material was donated to various museums.

By this time among the Museum's collections, there existed several thematic sets of exhibits. It was possible to create a collection of chiselled stones, including artistically done ones. The direction of the Museum appealed to various organizations of Leningrad (the Museum moved to Moscow later in 1934) with the request to transfer the material to the new Fund. Many departments responded to the request and as a result during several years there was created a new Fund — it was a collection of ornamental and gem stones. Chinese stone-carving works received from different organizations and from a few individuals appeared in the collection, the time of the production of which in the inventory lists is marked as "new".

In following years, up to 1980–1986s, Chinese masters' works almost didn't come to the Museum. Only with the beginning of the Perestroika an opportunity of purchasing of some things and getting them through the exchange appeared. All these items are from the late 20th — early 21st century.

Unfortunately, the collection of Chinese stone carving art still almost does not attract attention of the researchers. The exception is the article written by D.D. Novgorodova. It has published two jade disks, donated to the Museum by chief curator of the Museum V.I. Kryzhanovsky in 1923 and jade "disk 3", received in 1949 from the State Historical Museum and which is not a disk, but the image of the animal is most likely as a dragon curled up in the ring (Novgorodova, 2004). The attribution of these works D.D. Novgorodova conducted on a broad historical and cultural background. We do not object to the proposed D.D. Novgorodova dates: ranging from the Ming dynasty (1368–1644 years.) until the early twentieth century for a single disk within the 19th — beginning of 20th century to another and within the second half of 17th — beginning of 20th century for the image of a coiled into a ring of the dragon. This cautious, relatively late dating is reasonable.

China is predominantly a mountainous country, except for the lower reaches of large rivers carrying their waters to the Pacific Ocean and the great plain between the Huang He and the Yangtze River. It applies not only to the southern and North-Eastern China, but to included in China vast regions of Inner Mongolia, Qinghai, Tibet and East Turkestan (present-day Xinjiang Uyghur Autonomous region). It is a vast territory with numerous deposits of various minerals. China can be called a country of stone and stone-cutting art, traditions which comprise the millennia.

The collection of the Mineralogical Museum is not an accurate reflection of the mineral resources of China. In general, this is a collection of products that were accidentally included into the Museum. They were not the main object of gathering, keeping and analysis. At the same time, the "Chinese character" of the collection as a whole meets if not the variety of produced in China ornamental stones, but preferences and tastes of Chinese stone-cutters.

About half of stored in the Museum works of Chinese stone-cutters are jade. Nephrite is one of the favorite in China stones. Its hardness can be called average (5.5 on the Mohs scale). But jade is so thick and viscous that in ancient times it was already a great material for various works.

The second place in popularity in the Chinese collection of the Museum is agalmatolite, well-known ornamental stone. Agalmatolite is a solid variety of the mineral pyrophyllite. Its name is composed of the Greek words "agalma" (a sculpture, a statue) and "lithos" (a stone) and other names of this mineral (a soapstone, a waxstone, steatite, pagodite) they say of its softness or of those beautiful products, which can be carved out of it (Korenyako, Chistyakova, 2012). The hardness of agalmatolite (1 – 3 on the Mohs scale) allows carving it with an ordinary knife and the combination of density and viscosity gives the stone plastic qualities, highly valued in stone-cutting art.

A significant number of Chinese works were carved out of quartz and its varieties like rock crystal, amethyst, chalcedony, carnelian, agate, moss agate.

There are only few instances of using fluorite and turquoise.

Malachite is also little known in Chinese stone-carving art. This mineral has bright green colour and low hardness (3.5 – 4 on the Mohs scale), it's highly valued as a striking ornamental stone in the form of a patterned kidney-shaped units.

The use of fluorite and malachite in Chinese stone-carving art has began relatively recently. In the Mineralogical Museum there is just one work of fluorite (FMM #PDK 7874) and three Chinese works of malachite. This is the reason for the late arrival of such works in the Museum (malachite – 1982, fluorite – 1998).

These are the basic data on minerals, used for the production of the caught in the Museum of Chinese carved items.

The attribution of Chinese stone-carving works is very difficult. It is connected with the rich artistic heritage of the vast country, whose artistic production is divided into elite and provincial, "folk".

Speaking about the works of the collection we should definitely mention that there are not only the Chinese ("Han") elite works which was connected with the old centers of Chinese crafts, but provincial products, too. So, we must consider China as a huge multiethnic country. Part of this state are vast territories inhabited until recent decades, not Chinese and other peoples, who had sustained centuries-old artistic traditions. This is the extreme West of China, East Turkestan, modern Xinjiang Uygur Autonomous region. The main population of East Turkistan Uighur, a Turkic-speaking Muslim people, has long been famous for carpet weaving, art metal work, embroidery. One of the areas Uighur traditional art stone carving has not been studied yet. Touch this area to some extent allow the materials of the Mineralogical Museum of the Russian Academy of Sciences.

When receiving things in the Museum quite often mineral (in this case jade) was determined and commented addition "the Murghab river, China". The use of the hydronym "Murgab in somewhat mysterious, because there is no such river in China (Xinjiang Uygur Autonomous region). Murghab is one of the main sources of the Amu Darya, the current in Gorno-Badakhshan (Tajikistan). On the Murghab River, there are deposits of jade. River valley is separated by only several tens of kilometers (including the crossing of the ridge Sarykol) from Tashkurgan – one of the artisan and trading cities of Xinjiang. Jade was supposed to go to the East across the border of the Russian Empire and Sarykol mountains. Why the source jade could not become its field in China is primarily famous since the Middle Ages jade mines Kunlun part located here in Xinjiang?

Museum documentation does not give answers to these questions. Perhaps codified the definition of "R. Murghab, China" although not quite clear, but indicates a peripheral

(Western China, East Turkestan, Xinjiang, Uighur) the area of production of jade carvings, different from the Han Chinese forms. This, at least, ten items received in the 1920s. Among them are two simple and identical in the shape of a cup, like the Central Asian cups (FMM #PDK-1583, FMM #PDK-1640). Green jade carved small hexagonal "tray" and decorated on the edge of the ellipsoidal cavities — "spoons" (FMM #PDK-1661). As "Persian" in the documents identified carved from gray "the Murghab" jade deep dish (FMM #PDK-2314). Both the internal and external surfaces it is all decorated belts of “spoons". Such decoration matches with wavy edge of the bowl. In General, the style of these products is not Chinese, but rather pointing to the morphological features of the Islamic pottery of Central Asia and the Middle East.

With this group of things we can bring together six jade beads (Fig. 1). They are large, rounded and brown (with the exception of one cut from a lighter, greenish jade). The pattern is made in the technique of inlaying with gold wire. The main part of the pattern is the triple duplicate picture plant sprigs of flowers, leaves, buds, spiral curls. These images are limited to the paired bands of zigzag lines or circuits closed diamonds. In General, the pattern, with all its technological complexity, angular, geometrized and "dry", with a noticeable number of small failures and "texture" and this makes it unambiguous attribution as Chinese ornament. We have no reason to believe these six jade beads Eastern Turkestan products. But in any case within the huge Chinese cultural space such products are the essence of "products second-rate, peripheral, provincial.

Now let us refer to the images of the animals and plants that are characteristic of Chinese art and even to some extent, are emblems of the Chinese artistic traditions.

First place in the list of such images, undoubtedly, is the dragon.

Experts on the history of Chinese culture long incline to the opinion that the image of the dragon began to emerge in the Neolithic-the late Stone Age, 8th – 3rd millennia BC. Mean stone carvings and images on clay — they are quite guessed animals with long bodies and tails, with a ferocious predator head. In these images we can see the deformed artistic imagination reptiles or amphibians, animals and fantastic animals, which combined features of reality and fiction.

The study of the origin of the image of the dragon in the East Asia and neighboring regions clearly shows that this image took shape in China and very early. In the Neolithic, we see the start of his features, in the Bronze Age in the 2nd millennia BC. it is quite obvious. China is almost indisputable homeland of the dragon image. Of course, the image of the dragon is well known and in neighboring regions (Korea, Japan, Mongolia, Tibet, Vietnam). But that all countries for which China were if not the "mother civilization", in a sense, a cultural metropolis. It is significant that India, with all the complexity of religious beliefs and a high level of art, cannot claim the role of "mother of dragons". Close to the dragon, is also fantastic and "hybrid" image of crocodile-like water monster Makara — in India it has a different origin.

The iconography of the image of the dragon "Lung" quite clearly emerged in China in the era of the first historically attested States Shang-Yin (17th – 11th centuries BC). In the era of Zhou (11th – 3rd centuries BC) dragon has purchased the kind that practically did not change in the coming era of Chinese history. Mandatory signs images of Chinese dragons: monstrous head with bulging eyes, a wide toothy mouth, moustache, beard and horns, long covered with scales torso and tail, four powerful claws.

The dragon was one of the main places in ancient mythology, religious views, picture of the world. The semantics of the dragon image is varied. He was considered a symbol of the bright male power "Yang", the Supreme power and the Emperor himself, the element of

Fig. 1. Beads. Nephritis. Inlaid with gold. From 2.7×2.65 cm to 1.8×2.9 cm. 19th – early 20th centuries. Received from the Department of nonmetallic minerals KEPS (Commission for the Study of Productive Forces) in 1925. FMM #PDK-2345.

Fig. 2. Two-part buckle with dragon. Nephrite. 7.3×5.45×2.75 cm. 19th — early 20th centuries. Purchased from Y.S. Edelstein in 1912. FMM #PDK-814.
Fig. 3. Vase with lid. Rock crystal. Support — wood. Size of the "assembly" (with cover and stand) 24.2×10.55×8.7 cm. 19th — early 20th centuries. Received from the Hermitage in 1926. FMM #PDK-1669.
Fig. 4. Part of the buckle. Nephrite. 9.1×1.8×2.5 cm. The first half of the 20th century. Purchased from B.A. Fedorovich in 1950. FMM #PDK-4911.

fire, Lord of thunder, lightning and rain (Bir, 2011; Terent'ev-Katanskiy, 2004; Fisser, 2008; Shmotikova, 2012).

In the Mineralogical Museum a few things, decorated with dragon images or an image of a dragon. This is primarily a flat image of a coiled into a ring of the dragon "disk 3", published D.D. Novgorodova (Novgorodova, 2004). In the artistic sense, this work is mindless. Decorative developing stonecutter gave so important that it even makes recognition in carved stone dragon image. Essentially, recognizable only horned head, very vaguely depicted paws and tail. You can say that they disappeared in a mass of curls and spiral elements (FMM #PDK-4662).

The plate of light grey (white) jade (FMM #PDK-6935) is also inexpressive. The plate is a delicate image of two dragons in the "heraldic" (symmetric) compositions. Quite discern only the head. All items dragon bodies efface under "pressure" excessive decoration.

More successful is a different product from light gray jade (Fig. 2) received in the Museum collection in 1912, is a two-part belt buckle. Each part of it represents the dragon: a sculpture or bas-relief head with round eyes, horns, mane and flat, enriched with decorative elements, "broken" at right angles to the body. Geometric and decorative character hampers the determination of the dragon image, but after a brief examination of the buckle this task is successfully solved.

The most spectacular in the "dragon" part of the collection of the Museum is a vase with lid, carved from colorless rock crystal (Fig. 3). This is a pretty big subject, the walls of which are covered with large, energetic bas-relief and high relief carvings, combined with cutlines: vegetative shoots, the abundance of spiral and double-spiral curls. Three deformed and stylized high relief image of dragons stretched vertically. Probably the same animal, but curled up in the ring, depicts the round sculpture on the cover of the vessel. All images are different heads, ridges and paws. But they are so deformed by styling and overloaded "plant" items, that to call them dragons can only conditionally.

Around the same time (1926), the Museum received a bottle carved from agate (FMM #PDK-1603). It is decorated with bas-relief carvings and with plane-thread. On the shoulders – a simple conditional ornament. The main surface of the body is covered with carvings with a predominance of smooth curves. This is a figure of two opposing dragons. The abundance of large and small spiral curls, turning into drawn from these scrolls branching shoots hard conceals the dragon figure.

The museum has two objects with images of dragons which are made from Kunlun light gray and slightly greenish jade. One of them – part of a belt buckles with a sculptural head and figure of a dragon (see Fig. 4). The other – the head pin is differing with the fine openwork carving. Here depicts a dragon surrounded by lace elements (FMM #PDK-4910).

Given that the Chinese collection of the Mineralogical Museum is small, it is clearly traced one very important feature: with all the clarity of the dragon's image, the attempts to implement in art differ. Peripheral or provincial level of art, the individual features of artistic skill could lead to deviations from the canons and greatly complicate the definition in the dim form of a dragon image. A similar situation apparently exists in the embodiment of a zoomorphic image – comically grotesque lion "Shijia" or "Shifo."

The origin of the fantastic image of "Shijia" is very rarely considered in the special literature (Korenyako, 1998).

It is well known that the area of the lion as a zoological species never locked in historical times the territory of China. Lions for Chinese people have always been rare exotic animals, which were delivered from time to time from the west to the imperial court, since 1st – 2nd centuries AD (Schaefer, 1981, p. 120–124; Muensterberg, 1910, S. 103). This huge distance between the visual canon and natural conformation of the animal prototype could be explained by this statement.

In the era of the Qing Dynasty (1644–1911) in the architectural decoration, sculpture, painting and arts and crafts of China dominated the iconic canon of the lion "Shijia".

"Shijia" – short-legged creature with the body as it is swollen, with disproportionately large head and with the common shortened and compressed proportions. "Shijia" cannot be confused with any other animals primarily in the face, mane and tail. His snout – it's grimacing pug's face with wide open jaws, bulged eyes, bushy eyebrows and sharply distinguished elements of facial muscles. Mane treated stressed decorative – it consists of a number of regularly spaced curls, each of which is typically a spiral, coiled into a tight cone or pineal bulge. The tail has no stem – almost behind the base of it is dissolved in a more or less lush plumes.

Qing "Shijia" in terms of zoological morphology – not lions at all, although the word itself means "lion", these images have other "lions" names like ''Korean Lion", "Lion Fo", ie "Lion of Buddha" (Williams 1941, p. 254).

Morphologically "Shijia" has little in common with the individuals of the cat family and is fully consistent with small dogs of Chinese rock "Pekingese" and "chin".

Analysis of works of Chinese art from the Han Dynasty (3rd century BC – 3rd century AD), says that the first images of lions appeared in China in the 2nd AD. They are dry, laconic, schematized embodiment of real beast. In 3rd–6th centuries, along with realistic images of the long-tailed animals, other images appear. They differ more grotesque and decorative, with thick tails in the form of sheet, festoon, blades or large curl (Lee, 1968, p. 142, 143, ill. 167; Asiatische Kunst..., 1977, S. 18, Abb. 58; Fong, 1991). The coexistence of these two styles of lions images even sharper denoted in the art of the Tang Dynasty (618–907.), The second style is developing in the direction of the canon "Shijia» (Lessing, 1936, S. 5, 14, Abb. 2; Jenins, Watson , 1980, p. 34, 89, ill. 17, 53; Miroir des arts de la Chine, 1984, p. 315, ill. 174).

Chinese lions' images of the Yuan Dynasty (1260–1368) are carried out in full accordance with the canon of "Shijia", i.e. they mark the complete victory of the grotesque ornamental style (Muensterberg, 1912, S. 262, 263, Abb. 219; Asiatische Kunst..., 1977, S. 41, Abb. 202). Approximately the same situation is for the era of the Ming Dynasty (1368–1644). However, in contrast to the Qing time, in the art of which the canon "Shijia" monopoly dominates, among Ming images of lions can be seen not only grotesque ornamental "Shijia", but also realistic images or images with realistic details, for example with a long thin tail and not the tail-plume (Muensterberg, 1912, S. 72, 146, 147, Abb. 112, 246, 250; Boerschmann, 1914, S. 48–54, Bilder 24, 25; Boerschmann, 1925, plates 24, 63—65, 81; Muensterberg 1910, S. 317, Abb. 292; Jenins, Watson, 1980, p. 96—98, ill 62, 63).

We can say that the formation of the canon "shijia" completed in China long before the Qing era (obviously, in the end 1st millennium — the first half of the 2nd millennium) that the genesis of this canon was not a simple process.

In the collection of the Mineralogical Museum there are eight products which are the pictures of the fantastic feline predator or they bear his image.

One of the earliest sculptures (in the inventory book — link to the catalog of Grewingk, 1846) — a small (2.7×2.5×1.5 cm) agalmatolite sculpture (FMM #PDK-819). Animal lying on the stand is vaguely interpreted. Many of its features do not coincide with the canon "Shijia": small ears, narrow and long tail with a brush, cutting mane, tail and sides with a simple parallel grooves. Considering the statuette, you do not come to a conclusion, that is, you cannot stop at any of the possible definitions (lion, tiger, "shijia" or a hybrid "tiger-lion").

In 1920s the Museum received a bottle which was carved from smoky, pinkish-purple agate with orange-red spots. Relief images are made of opaque dark (from brown to black) layer (FMM #PDK-1515). On one side of the flattened side bottle — stylized pine branch, on the other — a composition composed of an adult "Shijia" and "Shijia" child which is supplemented with spherical image of emblems and a long ribbon.

At the same time the museum has received a signet from different shades of red agalmatolite (see Fig. 5). Sculptures of adult animal and clung to him a baby can be roughly defined as "Shijia". It is hampered by careless simplified thread and some of the details (small ears, no relief mane with clearly recognizable neck and back because of narrow parallel grooves, "non-canonical" form of the tail). Figures of animals placed on a high and prismatic pedestal, all side and bottom faces of which are filled with Chinese characters.

More specifically discern "Shijia" in a small sculpture of a light gray jade (Fig. 6). But he has also "non-canonical" long and divided into two parts tail, on which sits a bird held by the beast.

One of the images "Shijia" made of turquoise (see Fig. 7). Green ("old") turquoise color varies in intensity and broken by dark gray, almost black spots. As eyes there are two small diamonds with the cut "rose". Most of the features of the product are characteristic for the canonical image "Shijia". However, the top of the legs are completely covered with regular rounded protuberances which resemble large scales or horny scutes, and such cutting is not typical for the Chinese canonical image "Shiji" (but there are examples to refute (see: Mongol ardyn gar urlag).

Fig. 5. Signet with a lion and the young lion "Shijia". Agalmatolite. 7.7×3.6×3.6 cm. 19th — early 20th centuries. Received from the State Museum Fund in 1926. FMM #PDK-1587.

At the beginning of the 1980s in the Mineralogical Museum came on exchange the two images "Shijia" carved from African (Congo), malachite (see Figs. 8, 9). Sculptures, obviously made by one master; similar in shape and in ornamentation and with wooden supports for them. The modeling of animals coincides with the visual canon "shijia". One adult lion fell down, holding in his mouth a long ribbon and stepped right with the front paw on the ball. Right at his side fell a child "Shijia". Another picture more succinctly, is not accompanied by any ball or baby figure, but the similarities in the details is very big.

In 1998, the museum acquired two-figure sculptural composition of polychrome fluorite from South China's Hunan Province

Fig. 6. Lion "Shijia" with bird. Nephrite. 2.25×3.85×3.45 cm. 19th — early 20th centuries. Came from the Department of nonmetallic minerals KEPS in 1925. FMM #PDK-2315.
Fig. 7. Lion "Shijia". Turquoise, diamonds. 2.4×5×2.9 cm. 19th — early 20th centuries. Came from the State Museum Fund in 1927. FMM #PDK-1612.

(FMM PDK # 7874). Transparent and translucent stone is bicolored. Between the colors here is a clear boundary, so that the higher animal has a light green color and the color of the lower animal is a combination of light green and light purple hues. Lower animal, judging by the horns, by three-toed paws and by trying to treat the rows of scales — dragon sitting and turning his head back. The second animal, perched on the "dragon", is very difficult to learn. Perhaps this is some sort of feline beast or fantastic creature. The exact definition of animals which were carved from fluorite is impossible, especially if you consider the same techniques of interpretation: both of animals are the same, ending with two swirls of their tails and large plant stems with swirls or leaf-like shapes at the ends are hanging from their maws. Generally, animalistic images and their parts are modeled succinctly and rough, which inevitably leads to an uncertain, conjectural definitions. Maybe these features are peculiar to the late and "provincial" Chinese Stone Carving Crafts products.

Pictures of other animals are rare. One of the earliest is fixed in the catalog of Grewingk (№ 351) — a small sculpture of taupe agalmatolite (see Fig. 10). It depicts schematically interpret figure of sitting tailless monkeys, not devoid of comic features like round eyes and grotesquely stretched down jaws. Emblematic role of monkey is well known and fixed in the Far Eastern culture very often. Let us recall that the monkey — one of the zoomorphic emblems of the twelve calendar cycle.

In the 1920s the museum received a cat sculpture, carved from "Murghab" light gray

Fig. 8. Lion and cub "Shijia". Malachite (Africa, the Congo). Support — wood; thread, toning, inlaid metal. Size assembly (on the stand) 7.8×10.2×5.3 cm. Late 20th century. Came from Cisneros Sh. (Miner Res. Co) in 1982. FMM #PDK-6938.
Fig. 9. Lion "Shijia". Malachite (Africa, the Congo). Support — wood; thread, toning, inlaid metal. Size assembly (on the stand) 5.3×7.7×4.15 cm. Late 20th century. Came from Cisneros Sh. (Miner Res. Co) in 1982. FMM #PDK-6939.

jade. Its shape is concise and rounded. The cat is lying, it's head is turned to the right and bending the tail on the right side; rounded and very catlike body and all the details — eyes, ears and even a mustache (see Fig. 11).

Much later, in the early 1980s, the museum acquired the jade sculpture of dog — clearly domestic, if judged by the collar with two ball-shaped pendants (FMM #PDK-6936).

Other images of mammals are not full sculptures. They are the small sculptural or relief parts of larger objects; in fact it's a zoomorphic decoration, although expressive.

Basically, these things were got in Mineralogical Museum in the 1920s except received vase in 1990 (FMM #PDK-7823). This vase of "Murghab" bright greenish-gray jade has a neck with two handles in the form of stylized heads of wild beasts or dragons. In the museum documents the vase was attributed presumably to the 18th century, but hardly worth sticking this dating of the object that is different by a perfectly preserved. Vase, apparently is a good reproduction of the Chinese artistic traditions, but it is unlikely was made before the 20th century.

Small bottle (FMM #PDK-1535) was made of a two-layer agate. Pink stone with grayish spots became the stuff for the image gourd. From white opaque layer was carved two figures which were located on a pumpkin. It's a four-legged animal like a tiger and the leaves on the stems.

Images of bats are very popular in the Chinese cultural tradition. They are placed on an agate composition of two peach fruits (FMM #PDK-1552) on a vase of carnelian (see Fig. 12) on the belt buckle of the light-gray "Murghab" jade (see Fig. 13) on the vial of yellowish-gray chalcedony (see Fig. 14), where the bat — a very small element of landscape and emblematic composition.

Fig. 10. Monkey. Agalmatolite. 3.4×1.9×2.2 cm. 18th — first half 19th centuries (?). FMM #PDK-818.

In addition to mammals, images of birds are worth noting. From transparent almost

Fig. 11. Image of a cat. Nephrite. 3.6×5.7×3.35 cm. Came from the Department of nonmetallic minerals KEPS in 1925. FMM #PDK-2317.

Fig. 12. Vase in the form of two pieces of tree trunks. Carnelian. 8.9×11.3×5.7 cm. Beginning of the 20th century. Assigned to the State Museum Fund in 1926. FMM #PDK-1600.

Fig. 13. Part of the belt buckle with images of bats. Nephrite. 6.1×4.05×1.75 cm. 19th – early 20th centuries. Received from the V.I. Kryzhanovsky in 1923. FMM #PDK-2319.
Fig. 14. Small bottle. Chalcedony. 6.3×5.9×1.85 cm. 19th – early 20th centuries. Transferred from the Hermitage in 1926. FMM #PDK-1508.

colorless quartz was cut a bottle (FMM #PDK-1511). Its surface layer was used for flat-relief carving: stylized image "rocks" and "water", a large blooming lotus and far schematic figures of heron (or crane).

Of the same transparent slightly yellowish quartz was cut a vessel ("the vase") in a shape of waterfowl, which has turned its head back with an extending from the beak beard, spectacular decorative trim with mortise lines of plane and sculptural carvings. All the bird's body is covered with curls, single and double spirals and circles (see Fig. 15).

It is much easier was done a little amethyst sculpture of waterfowl with chick (see Fig. 16). Cutting was made by carvings and devoid of decorative effects. Mortice straight lines and parallel minor cuts only schematically transmit the plumage or coloring of both birds.

Image of a bird which was carved in the Hong Kong from round agate almonds is dated from the end of the 20th century (Fig. 17). External polished surface is gray and yellow and with dark brown spots the inner part of it is composed of light-blue and blue-white layers of agate. Of the last was carved high relief (or round-sculpture) image of a prey bird with a powerful beak and clawed feet. Raising its wings, the bird is sitting on a branch of a tree and below it there are distinct curves and swirls which reflect an attempt to portray the wave water – in the stylized form and which is often found in the Far East traditional art. This is an example of modern lapidary crafts, which tends to remain in the mainstream of Chinese art traditions. Small cuts only schematically transmit the plumage or coloring of both birds.

A unique thing in the collection of the Mineralogical Museum can be considered

Fig. 15. The vessel in the form of waterfowl. Rock crystal. 7.05×12.45×6.85 cm. 19th – early 20th centuries. Came from the Hermitage in 1926. FMM #PDK-1657.
Fig. 16. Waterfowl with nestling. Amethyst. 3.65×6.4×4.2 cm. 19th – early 20th centuries. Received from the Hermitage in 1926. FMM #PDK-1654.

Fig. 17. *Eagle. Chalcedony. 9.1×9.1×3.85 cm. Late 20th century. Obtained on the exchange in 2000. FMM #PDK-7943.*

Fig. 18. *Mantis on leaves. Agalmatolite. 14.4×9.9 cm. Late 20th century. Purchased in Tucson (USA) in 1998. FMM #PDK-7876.*

the image of a leaf which was received in the 1920s. It is carved from rock crystal (FMM #PDK-1553). On the convex side of it there is a greenish stain. Master used it for small high-relief figures of frogs, it is shown schematically.

Insects are also widely reflected in the Chinese stone-cutting art. This refers primarily to the butterflies; it's very popular in traditional culture. Images of butterflies or decorated with insects objects committed to the museum in the 1920s. This is a pair of identical plate suspension from light-gray and greenish "Murghab" jade. It is made in the art of plane and openwork carving (FMM #PDK 2318). Images are simulated and geometrized.

Small, with a big mustache, more stylized not easy defined shapes of butterflies are arranged on a jade things: the suspension in the form of two elongated fruits (FMM #PDK 2344) and details of the handle (FMM #PDK-2392). In the thread on the details of the handle is quite apparent a characteristic of Chinese handicrafts – its paradoxicality. The decor was made with a confident and energetic thread and zoomorphic image itself – unintelligible, "confusing", disintegrated before the disappearance of a coherent and easy-to-guess image.

Much later modern work was acquired by the Museum in the late 1990s (Fig. 18). It is made of two-color agalmatolite. Large leaves are cut from light, pinkish-yellow stone. A pair of insects located on the leaves which are made of light yellow "amber" agalmatolite. The interpretation of them is so naturalistic that they can be easily determined. These common mantises, in any case, are members of the class of mantis.

Perhaps equally numerous in Chinese stone-cutting art images of different plants and their parts. Among the exhibits fruit are primarily can be called.

Explicit creative success – masterfully carved from translucent light, bluish-green chalcedony group of three large fruit – "palmate lemon", ordinary lemon (this definition is most likely) and pomegranate (see Fig. 19). Fruits merge with each other, entwined leaves and stems and flowers are complemented with a small pomegranate. Large fruit are hollow and open at the top, so the composition is defined as a "vase".

"Palmate lemon" with typical finger-like sprout is at least an exotic fruit, in its complex form. Mineralogical Museum has another image of it – a small yellowish agate pendant (FMM #PDK-1510).

Form of pomegranate fruit is a completely ordinary ball. Pomegranate is recognized under "disclosure" of the fetus. There is depicted a wide gap or slit of the rind with a grid filling, juicy pomegranate grains are designated in such a way. In addition to said composition, in the museum there is an image of the pomegranate fruit from "Murghab" light gray, yellow jade (FMM #PDK-1662).

There are quite a lot of images of peach fruits. Their Chinese canon is simple and easily recognizable: a round fruit with a pointed end in the form of narrow curved grooves. Of grayish-red agate was carved a couple of peaches, which was completed with images of stems, leaves, small peach, bats and flowers (FMM #PDK-1522). Amethyst bottle has a shape of single peach fruit (see Fig. 20). These things were received in 1920s. At the beginning of the 1980s the vessel in the form of a pair of peaches with a stem and leaves was

Fig. 19. The vessel in the form of fruits palmate lemon, lemon and pomegranate. Quartz. 10.9×15.15×7.4 cm. 19th – early 20th centuries. Came from the Hermitage in 1926. FMM #PDK-1502.

Fig. 20. Small bottle in the form of peach fruit. Amethyst. 5.0×5.4×3.0 cm. 19th – early 20th centuries. From the State Museum Fund in 1927. FMM #PDK-1618.

acquired. It is made of light gray, greenish jade (FMM #PDK-6937).

"Murghab" jade was a material for rectangular with rounded corners low box which was received in the 1920s. Vegetable decor fills the upper surface of the lid and the upper inner surface of the box itself. It is made by cut-lines, tinted gold pigment. The main ornamental space is filled with images of "bushes" with fruit peaches; these "bushes" grow from the symbolic "rock" among rising bubble waves.

The images of gourd from agate (Fig. 21) and a jade pair of rounded oblong fruits concern to new things of the 1920s. They merge with each other and complemented with a peony flower or rose and butterfly (FMM #PDK 2344). Of purple amethyst is made an image of two serried oblong fruits.

Its outlines were duplicated by a band or a tape with small frequent cuts (FMM #PDK-1658).

One of the earliest works of stone carving art in the Mineralogical Museum (Grewingk, 1846), can be considered a vase from reddish agalmatolite with whitish, dark gray and black spots (see Fig. 22). The vase has a widened upwardly irregular shape and cross-section in the form of a segment of a circle. Rear flat surface just polished out and the "front" occupied with a high-relief and sculptural threads – black vines, light-gray leaves and red grapes. Polychrome points out that the thread was enhanced with toning.

Fig. 21. Small bottle as a gourd. Agate. 6.6×5.1×2.7 cm. 19th – early 20th centuries. From the Hermitage in 1926. FMM #PDK-1535.

Fig. 22. A vase with decoration of grapes. Agalmatolite. 11.3×9.9×4.3 cm. 18th – first half 19th centuries. Source of unknown. Recorded in 1950. FMM #PDK-4727.

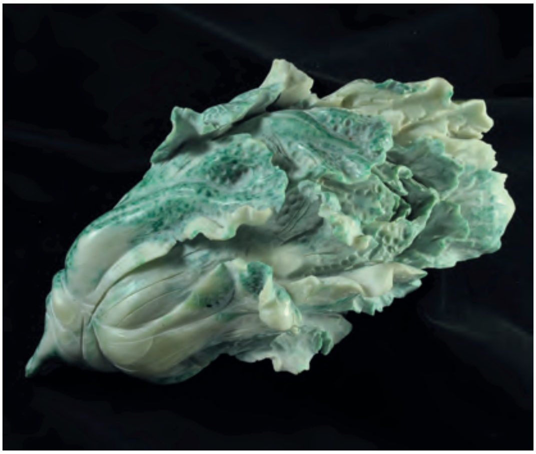

Fig. 23. Flower. Chalcedony (Brazil). 2.4×9.0×7.7 cm. End of 20th – beginning of 21st century. Present from D.I. Belakovskiy. FMM #PDK-8103.
Fig. 24. Crisp-head lettuce. Agalmatolite. 22.2×13.9×8.3 cm. Late 20th century. Purchased in Tucson (USA) in 1998. FMM #PDK-7875.

In the 1920s a box made of greenish "Murghab" jade (FMM #PDK-1660) was transferred from the Hermitage to the Mineralogical Museum. The box has four internal cells and the general shape of flower's rosette with four petals. This form is completed at the lid with carved images of the flower with four petals and four long curly leaves. The core of the flower is round ruby cabochon. Its weight is 0.15 carats in gold caste.

A much later time includes the image of the flower, arrived in 2011 (see Fig. 23). Flower with large petals is carved from a bluish chalcedony. The master used the stone excellent. He cut its cavity and opened the "center of the flower" – a flat plot of fine-grained quartz. Due to this peculiar reception, we can admire the spectacular modern stone-cutting work.

The museum's collection presented a few images of leaves. The things of the 1920s include the previously mentioned list of rock crystal with a small sitting frog (FMM #PDK-1553) and carved from light, purple-milk-yellow agate lotus leaf (FMM #PDK-1651).

Example of modern carving agalmatolite of Hunan Province is the image of crisp-head lettuce. Stone carving in light gray with large pockmarked green areas is diverse but the general interpretation is extremely naturalistic (see Fig. 24). This makes the thing in pairs for described image of two mantises on a leaf (see Fig. 18).

Incarnations of plant motifs can be considered as stone container – "vases" in which basis conditional image "pieces of trunks" or "stump" – so old, decayed or corroded by wood borers that they have become hollow, turned into a container. The collection of the Mineralogical Museum has such containers, singles and doubles. The main forms are complemented by spikes, excrescences, flowers, mushrooms, spiral curls. Material for vases served as a bright red carnelian (see Fig. 25), red with white, pink and yellow spots agate (FMM #PDK-1600), a light transparent amethyst (FMM #PDK-1656).

Fig. 25. A vase in the form of the trunk of a peach tree. Carnelian. 12.5×8.5×5.7 cm. 19th – early 20th centuries. Transferred from the Hermitage in 1926. FMM #PDK-1531.

Fig. 26. Table decoration two-part. Agalmatolite. 23.8×36.6×8.1 cm. 19th – early 20th centuries. From State Museum Fund 1926. FMM #PDK-1586.

Fig. 27. Paired vessels depicting monkeys and squirrels, eating grapes. Agalmatolite. 12×24×5.4 cm. Present from Martin Bohaty in 1988. FMM #PDK-7612.

Bamboos are often found in the works of Chinese art. In the collection of the Mineralogical Museum you can see the image of bamboo on the already described bottle which was made of rock crystal with white layer and hollow handle, carved from dark green jade (FMM #PDK-2313). Both products came to the Museum in 1920.

In a flat bottle of the same arrival time, made of yellowish-gray chalcedony with areas of milky color (FMM #PDK-1508), one side covered with Chinese characters. On the other was placed landscape and emblematic composition which was consist of images rocks, waves of water, bamboo, mushrooms, bat, "endless knot" and two or three obscure items.

An example of pure landscape composition is received in the 1930s agalmatolite table decoration (see Fig. 26). It is a large two-part thing. Lower part is a stand. It has the shape of a squat container or column base and decorated by two notches filled with openwork decoration "skew the grid." The upper part – complex sculptural image of mountain forest uninhabited landscape. In the center on a hill with a step-rise two-storey building is towering, apparently secluded temple. It is surrounded by cliffs and thick forest of pine, bamboo, willow.

The lower part of table decoration is carved from dark brown, almost black agalmatolite. Stone of the upper "landscape" half is light red with light yellow spots, but on the front side clearly localize spots of different colors from light green to black. Obviously, the decoration of carved stone was finished by coloring.

Landscape filled with animals, we see in other major agalmatolite product which was donated to the museum in 1988, by a citizen of Czechoslovakia Martin Bohaty (Fig. 27). The base of composition is two flattened, vertically arranged containers of vertical proportions. Below them and to the left — "rock", roughly interpreted "terra firma." Actually landscape areas are irregular in shape with frequent round curved places. Apparently, in such a way the stonecutter depicted vines with bunches. Active participants in the composition — three tailless monkey and two squirrels with bushy tails — they regale with juicy berries. Color of the stone is warm, terracotta-red with black and greenish-yellow spots.

Object identified as "cover" (see Fig. 28) refer to the things of the 1920s. Oval and convex, it is exquisitely carved out of the "white" (light gray) jade. In the flat and shallow relief felt certain monotony and lack of expressiveness. It can be assumed that the master was guided by traditional Chinese painting and drawing and this has affected on the style of stone-cutting work. Depicted composition is interesting and not typical for stone carving. The middle part is occupied by figures of elderly men: three of them are sitting around a game board. The fourth stands at a distance, leaning on a long staff, the fifth is on the right bottom. The rocks and boiling water are showed below. It is at the top and on the sides — stylized pine. In fact, the composition embodies the story, very popular in the classical Chinese culture: voluntary leaving of sages and scientists and thinkers of the world of dust, their staying in the gardens, groves, wooded mountains of the charming nature.

Fig. 28. Oval lid. Nephrite. 2.1×12.15×11 cm. 19th — early 20th centuries. Came from the Department of nonmetallic minerals KEPS in 1925. FMM #PDK-2367.

In the Chinese collection of the Mineralogical Museum there is a number of anthropomorphic sculptures — expressive images of people or gods in human form.

One of the earliest (18th — first half 19th centuries) anthropomorphous sculptures is agalmatolite small figure of a man sitting cross-legged on a bit of a cushion (Fig. 29). Bearded face, a large nose and round eyes, a turban or a wrapper on his head — these signs probably indicate that depicts not Chinese, but "Westerner" and probably a Muslim.

Another sculpture is image of a seated man with long beard and mustache which is carved from yellowish green agalmatolite. He is wearing a large coat (see Fig. 30). In his left hand men swatter "inshua" behind the back is the sword "jian". These attributes clearly indicate that Liuy Dong Bin was depicted there. He was one of the "Eight Immortals" ("ba xian"), Taoist deities which were once humans, but

Fig. 29. Seated man in a turban. Agalmatolite. 5.45×2.45×3.3 cm. 17th — the first half of the 21st century. From old collections. FMM #PDK-531.

Fig. 30. Chinese Taoistic deity Liuy Dong Bin. Agalmatolite. 10.7×10.5×3.8 cm. 18th — first half 19th centuries (?). From old collections. FMM #PDK-532.

Fig. 31. Chinese Taoistic deity Liu Hai. Agalmatolite. 39.0×15.0×7.5 cm. 19th – early 20th centuries. Received from the Military Medical Academy in 1931. FMM #PDK-4188.
Fig. 32. Chinese deities. Agalmatolite. 22.7×24.5×6.6 cm. 18th – first half 19th centuries (?). From old collections. FMM #PDK-4726.

because of their feats they achieved immortality and turned into spirits (Vasil'ev, 1970, p. 283 – 287; Riftin, 1980_1, 1980_2; Sidihmenov, 1987, p. 174, 175; Sychev, Sychev, 1975, p. 65, 112, fig. XIX). At first a group of gods "ba xian" led Lee Tae-guay, but then this role passed to Liuy Dong Bin. He was born at the end of 8th century AD and was canonized in 1111. Judging by the literary biography, the Liuy Dong Bin possessed supernatural powers: in adolescence, for example, he could memorize 10,000 characters per day. His life – is a series of exploits directed on taming the evil demons and help disadvantaged simple people. From here – most popularity of the Taoist deity in Taoism and folk religion, his prominent role in the traditional pantheon.

In 1931 the Mineralogical Museum was transferred from the Military Medical Academy an agalmatolite sculpture, designated in the inventory records as "image lying" Buddha "Chinese work" (see Fig. 31). In fact, this work of art has nothing to do with Buddhism. It depicts a smiling cheerful fat man standing on the left leg (right arm is raised and strongly bent at the knee). From the top of the head to the left arm is a bunch of eleven yellow coins on red cord and completes with a brush. Depicts not the Buddha and do not Buddhist deity, but Liu Hai – god of coins in the retinue of the Chinese god of wealth Tsai Shen. It is believed that Liu Hai was a real historical figure of 8th – 9th centuries and Liuy Dong Bin guided him on the path of Taoist teachings. Liu Hai, or Liu Har – a popular Chinese deity. Liu Hai necessarily accompanied by a toad, which is absent in the sculpture of the Mineralogical Museum. However, the article has a big loss – chips; because of the damage it could lose this zoomorphic details (Riftin, 1980_2, 1982_2).

Apparently, large and complex sculpture consisting of five anthropomorphic figures on a stand came to the museum relatively early (Grewingk, 1846) and can be dated within the 18th – first half 19th centuries. The material of a long narrow and with a through hole of the coasters is of agalmatolite dark brown color. The main color of agalmatolite figures – yellow-gray, but colored spots talk about coloring of the stone (see Fig. 32). The central figure depicts an elderly man in a complex tiara-like headdress, holding in his right hand a magic wand "Ruyi" head in the form of "ganoderma" – the "mushroom of immortality". This is probably the god of happiness Fu-hsing, or Fu-sheng. Lower on the right and left of the figure stand figures which are smaller with a comely adolescent faces. The right figure is a middle-aged man holding a baby in his arms – maybe god Lu-hsing (Riftin, 1882_1, 1982_4). The most expressive and recognizable is the left image – a god of longevity Shou-hsing with a staff in his right hand and a "peach of immortality" in the left (Vasil'ev, 1970; Riftin, 1982_1, 1982_3, 1982_5).

In the Mineralogical Museum is stored also other carved stone anthropomorphic images, which are not published in this article primarily because of these difficult attribution of works of art created in the country with the rule of polytheistic religions: there are only in the Taoist pantheon thousands of deities.

Work on the collection of Chinese art of stone-cutting has just begun and it is difficult to say what discoveries are waiting for us along the way.

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DIAMOND COLLECTION IN THE FERSMAN MINERALOGICAL MUSEUM OF THE RUSSIAN ACADEMY OF SCIENCES: SHORT HISTORICAL REVIEW

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Historical review on development of diamond collection of Fersman Mineralogical Museum is presented. Several chronological stages were outlined according to the history of exploration and study of new worlds diamondiferous provinces. Yu.L. Orlov's contribution to diamond studies and collection replenishment with diamond of various genesis and morphology was shown as well as his diamond classification. Several varieties of diamonds are described.

6 figures, 11 references.
Keywords: diamond, mineralogical collection, diamond genetic classification, Yu.L. Orlov.

Diamond collection of Fersman Mineralogical museum contains more than 1200 diamond crystals from placer and bedrock deposits from Russia, Brazil, Namibia, South Africa, Indonesia, USA and Australia. Its almost a century long history covers periods of discoveries and studies of Russian and foreign deposits and carries names of people who contributed to the collection.

The oldest diamond discoveries were done from placers and were made almost always by accident. It is known that bondman Pavel Popov, found the first Russian and European diamond in the basin of Koiva River near Krestovozdvizhensky gold workings in Perm government on the western slope of Ural mountains (now village Promysla of Gornozavodsk district in Perm region) on 4th of July, 1829 (Kharkiv *et al.*, 1997). There are several crystals (sample FMM #25684) from those workings that came to the museums by the merit of Pavel Vladimirovich Eremeev (1830 – 1899), professor of mineralogy and crystallography of the Petersburg Mining Institute.

Significant donations of diamonds came to the museum in 1912 – 1916 period. They derived from foreign deposits: crystals from placers in Indonesia (Kalimantan and Borneo islands), Brazil, Namibia, Australia (Bingara); Middle Urals and also bedrock diamonds from South Africa (Kimberly and Jagersfontain pipes).

The diamond findings from Kalimantan and other regions of Indonesia were known from ancient times and were dated to VI – X centuries. Those are the second oldest diamond placers after India (Smith, 1980).

The specimens from Borneo (Kalimantan) island are connected to Georgiy Prokof'evich Chernik (1865 – 1942), major general of the Russian Army, who was professionally involved in gathering and studying of minerals. He handed more than 300 samples of various minerals to the museum within 30 years starting from 1903 (Mokhova, Generalov, 2007). Those samples included diamonds from Kalimantan placers (samples FMM #11273 and FMM #11304).

Diamond deposits in Brazil were discovered in the 18th century (Smith, 1980). The worlds center of diamond mining moved from Indonesia to South America for almost one century till the discovery of bedrock deposits in South Africa. Brazil is famous by unique green colored diamonds. Black cryptocrystalline aggregates, so-called carbonados, were also found there (Orlov, 1984). Uniqueness of the black diamonds was in their origin from environment that was not suitable for typical diamond formation as kimberlitic pipes. Brazilian black diamonds were found in young sedimentary rocks, in spite to their isotopic age that was calculated to be 3 bln. years old (Mal'kov, Askhabov, 2010).

Kimberly pipe (South Africa) was discovered in 1871 and was the first bedrock body containing diamonds. That is why the diamondiferous rock was named kimberlite. Kimberly pipe was mined out by 1914 (Smith, 1980). 14.5 mln. carats of diamonds were mined during its exploitation. Diamond mining is still active in South Africa, but located in other territories and depths. Thus, studies of diamonds from historical mines and ones that are still operational at larger depths are useful to compare diamond characteristics from various deposits and trace change in their properties with depth.

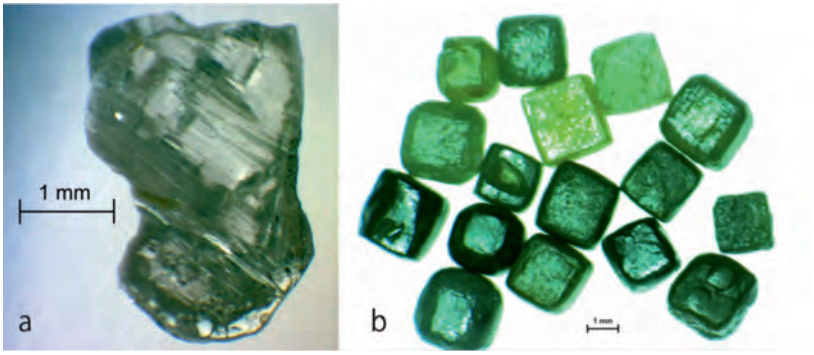


Fig. 1. Diamonds from South Africa: a — fragment, sample FMM #3; b — cubs of II, II and IV variety; sample FMM #64771. Donor: Ministry of Finance of the USSR.

South African crystals from the collection have various morphology: octahedral, cubical, combination forms, fragments and other. There are many colored stones and often are as large as around 1 carat and bigger. So-called "coated diamonds" (or diamond in diamond — *translator*) need to be mentioned as they are well presented in the collection. They belong to the IV variety according to Yu.L. Orlov classification. Referring of any diamond to a variety marked with Latinic digits in the article below was done according to this classification. "Coated" crystals represent octahedrons and cubes with dominating cubes (Fig. 1). The sample on the figure 1a is a flat fragment of indefinite shape weighed 0.4 ct. It is colorless, transparent with small dark inclusions. It fits to the variety I. Glide lines are well defined in one direction on the whole surface. South African cubic crystals of 3.48 ct total mass are shown on figure 1b demonstrating II, III and IV varieties. All of them are characterized with substantial degree of dissolution and slightly distorted shape. The crystals classify by the color into yellow, grey, black and crystals with yellow and green tint. All the cubes are dull due to the rough surface sculpture, so inclusions cannot be observed. Yellow and yellow-green specimens have etch channels on the surface.

The museums main fund is replenished from various sources. Most part of samples comes from scientific expeditions, from exchange with private people and organizations and from donations. The museum management always considered acquisition of private collections that have high historical, scientific and cultural value as a very important method to expand funds.

Academicians V.I. Vernadsky and A.E. Fersman and also the museum associate and later director of the museum V.I. Kryzhanovsky made significant contribution to the museums replenishing. Unique collection of prince Petr Arkadyevich Kochubey (1825—1892) was purchased hundred years ago, in 1913 on the initiative of Vernadsky and Fersman. The collection contained 2700 samples of minerals from Russian and foreign deposits, including fine assortment of diamond crystals from Brazil and South Africa.

The museum purchased a big mineral collection from Ilya Nikolayevich Kryzhanovsky in 1912. The gathering contained placer diamonds from Bobrovka River near Nizhniy Tagil in the Middle part of the Ural (sample FMM #22911). Those samples of museum funds were assigned to the diamond collection in 1927.

I.P. Balashovs' collection containing Brazilian diamonds was acquired with A.E. Fersman involvement in 1919.

Discoveries of numerous diamond placers mostly in Africa were made in 1920s (Kharkiv *et al.,* 1997). The largest coastal marine placers in Namibia have the highest grades of gem grade diamonds. Namibian diamonds in the collection are small (lighter than 0.3 ct) and most of them are fragments of greenish-yellow crystals with well-defined surface sculpture and dark inclusions (Fig. 2). Greenish-yellow 0.17 ct crystal of complex shape is shown on figure 2a. This diamond has medium resorption degree. One side of the sample has "lollypop" surface sculpture, which shows mechanic abrasion in the coastal zone (Posukhova, 2003). The crystal is transparent with dark inclusions. Fragment of combination shape (octahedroid) 0.26 ct crystal is shown in figure 2b. It has yellow color with smooth polished surface and deep etch channels and a negative cavern. The whole crystal is cut with dark and light fractures.

Active exploration for bedrock diamond deposits started in Siberia in 1930—40s. V.I. Vernadsky was the first who predicted possibility of kimberlite discovery in Siberia region. He recommended revising of diamond prospects

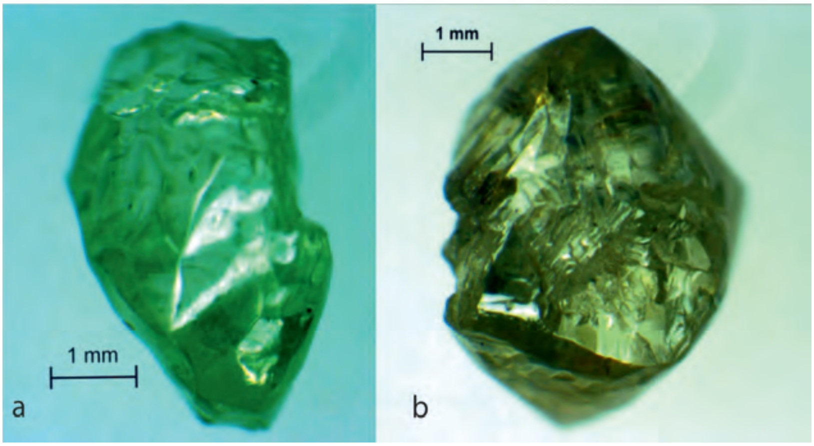


Fig. 2. Placer diamonds from Namibia: a — fragment with "lollipop" sculpture, sample FMM #999 (A.E. Fersman); b — octahedroid fragment, sample FMM #1054. (A.E. Fersman).

of the Russia's North according to results of new studies of South African deposits as early as in 1914. Diamond crystal (FMM #37711) found in the vicinity of Melnichnaya River near Eniseysk in 1897 came to the collection in 1938. It is established fact that this sample was the first diamond fount in Eastern Siberia. Vera Arsenyevna Balandina (1871—1943), a known educator, scientist and public person of her time gifted this sample to the museum.

Irkutsk Geological Survey carried out exploration in the north of Irkutsk Region, in Krasnoyarsk Territory and Yakutia. Diamond expedition of All-Union Geological Institute (VSEGEI, in Leningrad) explored foothills of Sayan Mountains. The predictions for diamond discoveries in Siberia in that period were based on geological and structural similarity with largest diamondiferous region of South Africa. Diamonds were actually found soon in terrace and riverbed sediments of Nizhnyaya Tunguska tributaries and middle reach of Angara river. Diamonds were subsequently discovered in sediments of Vilyuy and Malaya Botuobiya rivers. Those findings pointed to presence of a large diamondiferous province in Eastern Siberia.

The collection replenishes not only with Siberian diamonds during this period. The State Research Institute of Mining and Chemical Resources (GIGKhS) presented diamonds from Brazil (Minas Gerais, Diamantina, Villa Rica) and South Africa. State Archives of Ministry of Internal Affairs of the USSR gifted a collection of placer diamonds from Urals.

Part of the diamond collection was received from private donors. O.M. Shikhova passed diamonds from SAR in 1938. N.V. Kazakova donated diamonds also from South Africa in 1940. V.Ya. Burdakov handed over diamonds from Zhuravlik River area in the Middle Urals in 1941.

Fig. 3. Places of discoveries of some diamonds from the Ural mountains in the collection of Fersman Mineralogical Museum:
1 — Bobrovka river, Nizhniy Tagil, Middle Ural mountains, sample FMM #22911 (I.N. Kryzhanovskiy);
2 — Zhuravlik river, the Is river tributary, Ural mountains, sample FMM #43171 (V.Ya. Burdakov);
3 — Krestovozdvizhensky mines to northeast of Bisersk, the Middle Urals, sample FMM #25684 (P.V. Eremeev).

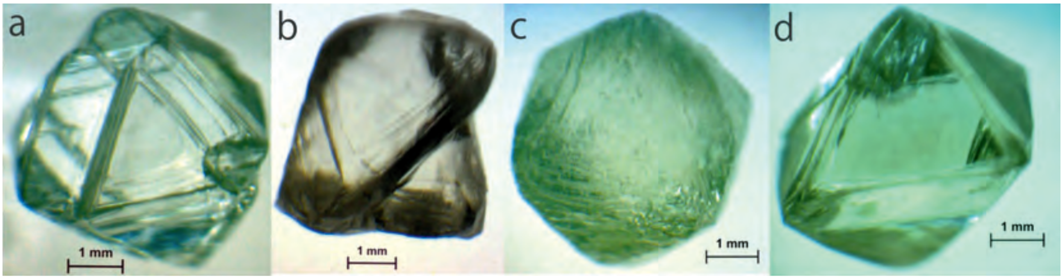


Fig. 4. Diamonds from Ayhal pipe, Yakutiya: a, c, d — octahedra with various resorption degree, sample FMM ##64723, 64726, 64725 accordingly; b — intergrowth of two crystals, sample FMM #64724. Donor: Ministry of Finance of the USSR.

Localities of placer diamonds from the Urals in the collection of the museum are marked on a map on figure 3.

Center of diamond exploration in our country moved to Yakutiya in 1950s. The work advanced with a great success very soon in 1953 when pipes Zarnitsa (1954), Mir (1955) and Udachnaya (1955) were discovered in very short period of time. These pipes are currently the biggest operating deposits in the country (Kharkiv *et al*., 1997).

Russia has the worlds biggest proven diamond reserves as a result of big exploration efforts. The major diamondiferous territories are Yakutiya and Arkhangelsk region. Yakutiya diamond province has about 1000 known kimberlite pipes, 150 of which are diamond bearing and 20 are economical. Arkhangelsk deposits are now in mine developing stage. M.V. Lomonosov deposit is in pilot production since 2000. Industrial operations of diamond placers in Perm Region in the Urals started in 1955, but showed very high operation costs per carat exceeding by several times Yakutiyan diamonds.

Diamond exploration and mining boom in Eastern Siberia gave start to growth of the museums funds. Large amount of diamonds from Russian deposits came to the museum in the second half of the 20th century. Diamonds from Aykhal, Mir and Udachnaya pipes bedrock deposits in Yakutiya compose the main part of the collection. The crystals are mostly octahedral in shape with insignificant resorption. The diamonds have high color and clarity characteristics and there are some of lower quality including brown, black and crystals with inclusions (Fig. 4, 5).

Samples from Aykhal pipe are shown on figure 4. One of them is colorless gem quality octahedral crystal of I variety (Fig. 4a). The crystal weighs 0.36 ct and has sharp steps on its faces and deep negative apexes at fourfold crystal axes. Sharp stepped surface of the faces makes difficult observation of internal structure of the crystal. Only one dark inclusion can be spotted. Colorless 0.14 ct spinel twin crystal with slight brownish tone from a thin color coat of unclear origin on the surface is depicted on figure 4b. The crystal has flat-rounded faces with medium signs of resorption. One small light inclusion is observed. Figure 4c demonstrates a 0.58 ct crystal of I variety with yellow hue. It has combination shape with dodecahedroid faces originated from stepped growth. The crystal is strongly resorbed and the faces are covered with etched trigons pits. The surface sculpture hides from view the internal structure of the diamond. Colorless 0.51 ct octahedron with brownish hue and no inclusions on figure 4d belongs to I category. Medium degree of resorption, small microlayers, etch trigons and a channel are present of the faces. Fractures are observed near tip.

Samples from Mir pipe are shown on figure 5. All of them belong to the I variety. Transparent 0.12 ct octahedron with yellowish tone and no inclusions is shown on figure 5a. The faces are flat and fully covered with pattern of small trigon etch pits that dull the crystal. Colorless 0.17 ct spinel twin crystal is shown on Fig. 5b. It is transparent and has characteristic twin seam. Small brownish diamond grown on one face of the twin. Rounded stepped 0.3 ct octahedron with little resorption is shown on figure 5c. There is significant size smaller diamond grown on an apex. Micro layers and pits are well observed on the faces of the crystal. Many black inclusions are seen and a tension zone manifested with rainbow.

Collection has also placer diamonds from Prilenskaya region in Yakutya (Motorchuna, Molodo, Irelyakh rivers). These crystals are dodecahedroids, rounded octahedrons, fragments and intergrowths. Their outlook and surface morphology are different from placer diamonds from the Urals. The last ones have characteristic shape thet allowed to distin-

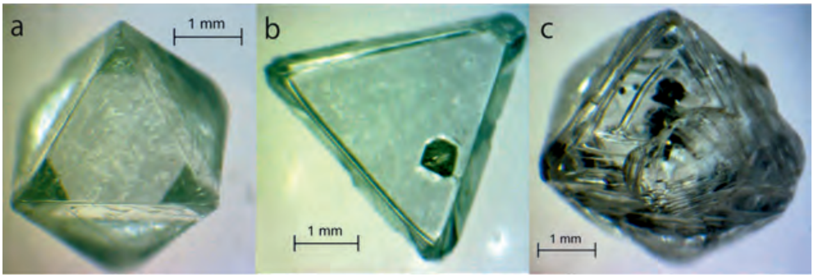


Fig. 5. Diamonds from Mir pipe, Yakutiya: a — flattened octahedron, sample FMM #74398; b — flattened spinel twin crystal with intergrown crystal, sample FMM #74398, c — rounded stepped octahedron with intergrown crystal, sample FMM #74398. Donor: Centrakademsnab.

guish a specific "Ural type dodecahedroid" which is dodecahedron with smooth faces presenting a final resorption shape (Palyanov, 1997).

Diamonds in Yakutiya placer showings are usually rounded crystals with convex crystal faces and rarely have flat surfaces. They also are larger and rounded, have rough sculpture with signs of mechanical attrition typical for placer diamonds. Surface features make the stones dull and do not allow observation of their internal structure. Placer diamonds of "Urals type" from Yakutiya are shown on figure 6 (a, b) and have residual (etch — *transl.*) relief pattern on the surface.

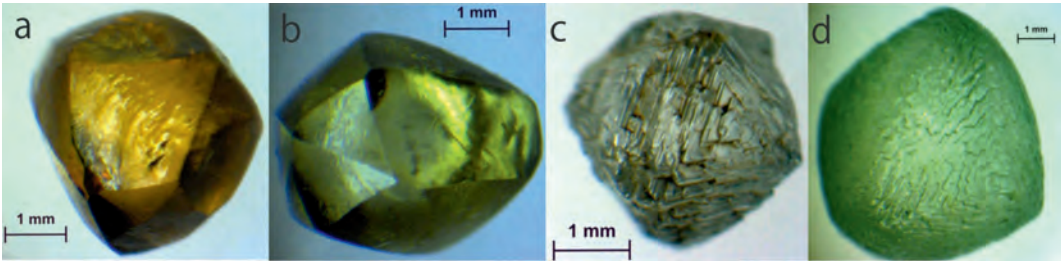
Figure 6a illustrates large 0.23 ct single dodecahedroid crystal of saturated yellow-brown color. Droplet shaped surface relief and intensive color assigns it to the II category. The crystal is semi-transparent due to surface roughness. Similar 0.07 ct dodecahedroid is documented on figure 6b. It is also yellow but less intensive with cool greenish tint, has no inclusions and was classified as I variety. Colorless 0.15 ct octahedral crystal with polynucleation facet growth is shown on figure 6c. The crystal has well defined stepped facet surface with ferrous stains on the surface features visible with stereoscope. Colorless 1.03 ct dodecahedroid with rough relief and tegular etch texture. Resorption degree of the crystal is high and thus internal features cannot be observed.

The short description of bedrock and placer diamonds of two genetic types: of Yakutiya and the Urals diamondiferous provinces from the museum collection gives an idea on morphologic features of the crystals.

Two sources of the museum collection replenishing were mentioned above. The government and various organizations: Yakutalmaz, Centracademnab, Gokhran, Institute of Experimental Mineralogy (IEM RAN) played a big role donating significant amount of samples to the museums funds. Some diamonds were received from private collections of research mineralogists: A.A. Arsenyev (samples FMM ##57215 — 57218), M.E. Yakovleva (FMM ##62181 — 62184), V.I. Stepanov (sample FMM #87470), E.M. Spiridonov (sample FMM #92005).

Yury Leonidovich Orlov (1926 — 1980), the most prominent expert in diamond mineralogy, made exclusively significant contribution to the collection. He gathered unique field specimens of the Urals diamonds as early as in 1953. He was hired as a junior researcher at the Fersman Mineralogical Museum in 1956 and continued studying diamonds, then he became the director of the museum in 1976 (Pavlova, 2011). He investigated immense amount of crystals from placers in republics of Soviet Union, South Africa, Kongo, Brazil, bedrock deposits of Yakutiya and other countries. The museums collection of diamonds and precious stones increased greatly by the efforts of Yu.L. Orlov.

Fig. 6. Placer diamonds from Russia: a, b — dodecahedron of the Ural type, Yakutiya, Molodo River, sample FMM #74404 (Donor: Centrakademsnab); c — octahedron with polynucleation character of facet growth and sharp stepping, Yakutiya, Motorchuna River, sample FMM #74405. Donor: Centrakademsnab; d — spongy dodecahedroid of Yakutian type, the Urals, sample FMM #64776. Donor: Ministry of Finance of the USSR.



Orlov's main interests were associated with diamond genesis and morphology. Yuriy Leonidovich had opportunity to collect samples from industrial concentrators and had most typical samples in the museums collection, which became the basis of his famous genetic classification. Every variety in the classification has its own typical features: forms of growth, mechanism of facet growth, color, visual transparency and other physical properties of the mineral such as light absorption in IR, visible and UV spectral range, luminescence in UV light, presence of typical color centers. All these features reflect conditions of diamond formation. Total of 11 varieties were determined and can be categorized into two groups: singular crystals – from I to V variety and polycrystalline aggregates – from VI to X variety. XI variety was distinguished separately and includes impact diamonds.

Orlovs's classification was the first well thought-out genetic diamond classification. All diamond experts in Russia use it. It is important to mention that discovery of new deposits reveals new genetic types of crystals which is hard to fit into a definite variety. Origin of diamonds of some varieties is questionable, for example V variety (Afanas'ev, 2000; Solodova *et al.*, 2008; Kriulina, 2012). Disparity between modern observations and limitations of varieties the classification surfaced nowadays. The cause of it, without going into scientific details, lays in the development of instrumental methods of mineralogical studies from 1970s when the classification was created and methods of modern micro mineralogy utilizing electron microscopy and microprobe analysis, Raman spectroscopy, methods local trace element composition and so forth. Contemporary research methods can be used to solve questionable issues and also support introduction of new genetic types developing Orlov's classification.

Description of morphological features of crystals from bedrock and placer deposits from various regions of the world, history of their exploration and information about people offered samples to the museum give an idea on the content of diamond collection of the Fersman Mineralogical Museum, its scientific and historic value.

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NEW ACQUISITIONS TO FERSMAN MINERALOGICAL MUSEUM IN 2011–2012

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Eight hundred and seventy-seven mineral specimens representing 488 mineral species from 59 countries, Antarctica, the oceanic floor, and space were catalogued into six collections of the main fund of the Fersman Mineralogical Museum, Russian Academy of Sciences, during 2011 and 2012. Among them, 160 mineral species were previously absent in the museum collection. Eighty-five of the new species are represented by type specimens (holotypes, co-types, or their fragments) of which twenty-seven minerals species were discovered by Museum staff members or with their participation. Of the new specimens, 645 (74%) were donated by 151 private persons and 3 organizations, including 104 (85 species) type specimens. The museum staff collected 85 items (10%). One hundred and twelve specimens were exchanged. Three specimens were purchased. Thirty-two mineral specimens (4%) were documented from previous acquisitions. The new acquisitions are surveyed by mineral species, geography, type of entry, and donor. Lists of new mineral species and mineral species missing in the museum are given.
4 table, 18 figures*, 10 references.

Keywords: Mineralogical museum, collection, new acquisitions, mineral species, mineral, meteorite.

Eight hundred and seventy-seven mineral specimens were catalogued into six collections of the main inventory of the museum in 2011 – 2012. The majority – 712 items – were placed into the systematic collection; 33 specimens were added to the collection of deposits; 60 items were entered into the collection of the formation and transformation of minerals (OP); 43 specimens were catalogued into the collection of crystals and synthetic compounds; 17 specimens became a part of the collection of ornamental stones and gems (PDK); and 12 specimens were catalogued into the collection of meteorites and impactites.

About 75% of items were acquired during 2011 – 2012 or shortly before this time. The remainder were acquired before, but were cataloguized later at that period after diagnostic.

The vast majority of mineral specimens (807) represent various mineral species for their morphology, properties, and other features. Seventy specimens are rocks, meteorites, impactites, mineraloids, mixtures of minerals, and other natural or partly natural phases, which are currently not approved by the Commission on New Minerals, Nomenclature, and Classification of International Mineralogical Association (CNMNC IMA) as mineral species. For example, some are products of coal waste fire or biogenic crystalline phases such as cholesterol. Stone artifacts, synthetic minerals, and other synthetic phases are included to this category.

The principles guiding the new acquisition for the collections of the main museum fund were reported in previous reviews of new acquisitions (Belakovskiy, 2001; 2003; 2004; 2006; 2011; Belakovskiy and Pekova, 2008).

Only the data on the specimens which were catalogued in the collections of the main museum fund in 2011–2012 are part of this review. Other acquisitions of this period, such as those processed for registration in inventory or assigned by the buying commission of the museum to the scientific or exchange accounts are not reported here. All given numerals refer to inventory numbers of the main fund.

Acquisitions classified by mineral species

The additions to the systematic collection during the surveyed period totalled 488 valid mineral species, 160 of which are new species for the museum. This includes 104 specimens which are type materials for 85 recently discovered new minerals (holotypes, co-types, and/or their fragments). Type materials include 27 new mineral species discovered by the museum staff or in collaboration with the museum staff.

The total number of mineral species in the museum as of December 31, 2012 is 3,450, after excluding the species received before for which the diagnostic appeared to be wrong.

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* – all specimens from Fersman Mineralogical Museum, Russian Academy of Sciences.

Table 1. **Distribution of mineral species on the number of specimens (for those taken as more than 5 specimens)**

1.	Tenorite	31	6.	Goethite	10	11.	Anhydrite	7
2.	Quartz	24	7.	Magnetite	9	12.	Kurnakovite	6
3.	Calcite	15	8.	Epidote	9	13.	Labrador	6
4.	Gypsum	11	9.	Rhodonite	8	14.	Tephroite	6
5.	Cristobalite	11	10.	Schorl	8	15.	Fluorite	6

Three hundred and sixty-eight of the 488 mineral species are represented by a single specimen. Sixty-three mineral species are represented by two specimens. Forty-two species are represented by three or four specimens. Fifteen mineral species were taken as five or more specimens (Table 1). Two specimens contained a few mineral species, which is novel for the museum.

The mineral species in this table are reviewed below.

The unusual abundance of **tenorite** resulted from collection by the museum staff in July, 2012 at the second cinder cone of the North breach of the Great Fissure Tolbachik Eruption (GOPE). In the Tenorite fumarole opened by I.S. Lykova and the neighboring fumaroles, spectacular large crystals and aggregates of tenorite extremely variable in morphology were found. Tenorite occurs as flattened-elongated skeletal crystals up to 4 cm in size, filamentous crystals and their crossed aggregates, variously split crystals, dendrites, and twinned clusters. Two or three types frequently are neighbors in the same sample. The collected specimens surpass known specimens of tenorite from Vesuvius, Italy in aesthetics and diversity. This fact and the morphological diversity of tenorite from Tolbachik caused the introduction into the systematic collection of a great number of specimens of this single mineral species, which only occasionally forms interesting collection specimens. Of the other mineral specimens collected in the same trip, very interesting items of piypite with langbeinite (Fig. 1), dolerophanite with euchlorine, anglesite (transparent crystals up to 7 mm in size) with euchlorine, hematite, and sylvite are registered at present. In addition, CNMNC IMA is considering the applications for several apparent new mineral species whose specimens were collected during this trip. A.A. Antonov, D.I. Belakovskiy, V.N. Kalachev, P.V. Kalachev, I.S. Lykova, I.V. Pekov, and A.G. Turchkova collected these minerals during this trip. Type specimens of approved new mineral species pseudolyonsite, cupromolybdite, steklite, kra-

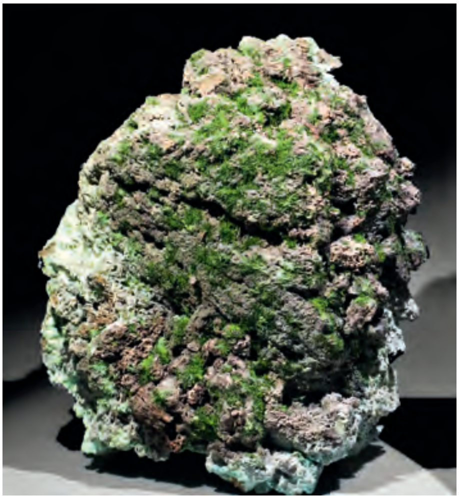


Fig. 1. Piypite. Bunches of dark green acicular crystals on volcanic cinder. Second Cinder Cone of the North Breach of GOPE, Tolbachik volcano, Kamchatka, Russia. Size of specimen 8 cm. Collected by museum. Systematic collection. FMM no. 93859. Photo: M.M. Moiseev.

Fig. 2. Pseudomorph after tree. Trunk is replaced by chalcedony. Calcite and agate are between trunk and peeled bark. Specimen was taken with fixing "Nevada, US", but most likely it came from Blue Forest, Eden Valley, Wyoming. Size of specimen 15 cm. Donation of D.I. Belakovskiy. OP collection. FMM no. OP 2611. Photo: D.I. Belakovskiy.

sheninnikovite, calciolangbeinite, starovaite and yaroshevskite found earlier by M.E. Zelensky at the second cinder cone of GOPE have already been catalogued into the museum collection.

Specimens of **quartz** and **chalcedony** catalogued into the museum collection in 2011 – 2012 are lithophyses of agate in rhyolite from Oregon and Nevada, US donated by Stephen Schuchman. Pseudomorphs of chalcedony after trees from Nevada, US, consisting of peeled pieces of bark overgrown by light bluish gray chalcedony and cemented by calcite (Fig. 2) are of interest. Pseudomorphs of chalcedony after the space between stem ossicles of crinoids in silicified limestone (followed by the dissolution of the ossicles), a novel and unusual specimen, makes a deep impression of fossilized screws (Fig. 3). This specimen, which was donated by M.M. Moiseev, came from the Komsomolsky quarry in the Donetsk area, Ukraine. A chalcedony flower carved from an agate geode and large spectacular varicolored cabochons of so called pietersite from Namibia, which is a quartz pseudomorph after a fibrous, diverse aggregate of an alkali amphibole in various tints of light blue and red, are catalogued into the PDK collection.

A cluster of parallel rhombohedra of honey calcite (gallery no. 34, Dodo, Sub-Polar Urals), a druse of Co-bearing calcite from Likasi, Democratic Republic of Congo, donated by N.N. Kamzolkin and A.F. Popov, and a transparent twinned crystal of calcite ca. 14 cm in size from the Kurunzhukul deposit, Northern Kazakhstan, donated by M.M. Moiseev, are the most interesting specimens of **calcite**. In addition, large cleavage fragments of calcite from the Peregrina mine, Guanajuato, Mexico with various fluorescence depending on the wavelength of UV light are catalogued into the collection for the exhibition Fluorescence of Minerals. An icon ultrasonically carved on nacre, designed and donated by M. Andreev, was catalogued into the PDK collection.

Gypsum. Druse of colorless and lustrous thin long-columnar crystals of gypsum from the San Timoteo mine, Portman, Cartagena, Murcia, Spain, donated by D.E. Tonkacheev, frequently draws the attention of visitors. Another specimen of gypsum from Spain (Consuelo mine, Chinchon, near Madrid) is a pseudomorph after glauberite. The author of this review brought a few clusters of colorless transparent crystals of gypsum up to 11 cm from the Naica mine, Chihuahua in Mexico. These clusters are similar in origin to gypsum from the Cave of Crystals found at this mine in 2000, where the size of crystals reaches 11 m. Spectacular clusters of pale sky blue split crystals of **anhydrite** came from the same mine.

Cristobalite was received from various localities. Spherulites up to 3 cm with fayalite enclosed in obsidian from the Cougar Mt., Modoc Co., California in the United States were donated by S. Schuchman. A specimen of cristobalite from the Libya desert in Egypt consists of snow-white spherulites up to 2 mm in size in the Libya impact glass. However, the most unusual specimens of cristobalite were acquired from the Thomas Range, Utah, USA. There, in addition to the separate spherulites, cristobalite was found as thick spherulitic crusts on quartz druses in rhyolite and breccias, in which fragments of these crusts are cemented by calcite. Specimens of tridymite and natural quartz glass lechatelierite

Fig. 3. Chalcedony after crinoids in silicified limestone. Chalcedony fills space between stem ossicles of crinoids. Stem ossicles are dissolved causing strange shape of this pseudomorph like fossilized screws. Komsomolsky quarry, Donetsk area, Ukraine. Size of specimen 26 cm. Collected by museum (M.M. Moiseev). OP collection. FMM no. OP 2613. Photo: D.I. Belakovskiy.

Fig. 4. Rhodonite. Druse of bright pink flattened crystals up to 2 cm in size with quartz and colorless fine-acicular crystals of cummingtonite. Conselheiro Lafaiete, Minas Gerais, Brazil. Size of specimen 10 cm. Donation of D.I. Belakovskiy. Systematic collection. FMM no. 93322. Photo: M.M. Moiseev.

Fig. 5. Rhodonite. Veinlets with black selvages (parsettensite) in cherty metasiltstone. South Faizulino deposit, Bashkiria, Russia. Size of specimen 12 cm. Donation of A.I. Brusnitsyn. Systematic collection. FMM no. 93917. Photo: M.M. Moiseev.

were collected from that and neighboring ancient fumaroles.

Eight of the ten catalogued specimens of **goethite** are from the Farafra Oasis, Matruh Governorate in Egypt. These are pseudomorphs after fancy concretions and pseudostalactites of pyrite and marcasite.

Of the catalogued specimens of **magnetite**, aggregates of oolites, with individual oolites up to 3 cm, from the Rudnogorsk deposit, Irkutsk area were donated by O.I. Gritsenko and "ontogenic" specimens from Dashkesan, Azerbaijan donated by B.Z. Kantor, are of the most interest.

Half of the catalogued specimens of **epidote** were collected by D. Toland and D.I. Belakovskiy from cavities in skarn at the classic locality Green Monster Mountain, Prince of Wales Island, Alaska, USA. These are dark green pinacoid-prismatic twinned crystals and sheaf-like clusters of high quality; they supplement the existing collection of epidote from this locality. The remaining specimens are tabular pseudohexagonal crystals up to 8 cm in size and isometric pseudoctahedral crystals and clusters of crystals of various habits from Kharan, Baluchistan, Pakistan. Although these new collection specimens are from the abundant find of a few years ago, the museum specimens are some of the best from this locality and the morphology of epidote is well characterized.

A cluster of bright pink flattened crystals up to 2 cm in size with quartz and finely acicular cummingtonite from Conselheiro Lafaiete, Minas Gerais, Brazil (Fig. 4) stands out among the new specimens of **rhodonite**. A series of specimens of rhodonite along with **tephroite**, pyroxmangite, braunite, caryopilite, parsettensite, alleghanyite, and other minerals typical of contact-metasomatic rhodonite deposits was donated by A.I. Brusnitsyn (mainly from the Ural deposits) and L.A. Pautov, D.I. Belakovskiy, and A.L. Galkin, who collected specimens at localities in Kirgizstan and Ukraine (Fig. 5).

Most specimens of **schorl** donated to the museum in 2011 – 2012 are from Tsitondroina, Fianarantsoa province, Madagascar. These are hoper crystals of various morphologies up to 11 cm in size with well-shaped lustrous faces. A lot consisting of few hundred specimens in 2011 at the Denver mineral show was quickly snapped up and similar specimens have not been observed since.

Most of the new specimens of very nice iridescent **labradorite** are from Madagascar. These specimens were added to the PDK collection. One zoned 8 cm crystal of labradorite acquired from Ylamaa in Finland was donated by T. and L. Holm. One specimen consists of lapilli crystals collected at cinder cones in the region of the South breach of GFTE, Kamchatka.

A group of well-shaped crystals of **kurnakovite** of various forms from Boron, Kramer District, Kern Co., California in the United States was catalogued into the collection of crystals. Size of the crystals ranges from 4 to 6 cm.

The acquired **fluorite** is from various localities. The Russian specimens are colorless, transparent rhombododecahedral and cuboctahedral crystals up to 5 cm from a ventilation shaft at the Nikolaevsk mine in the Dalnegorsk district, Primorskii krai (Fig. 6). One good specimen was received from each of the famous old deposits in Mogov, Tajikistan and Akchatau, Kazakhstan (donation of O.A. Lopatkin and N.S. Lukinykh). Y-bearing fluorite from the White Cloud pegmatite, Colorado, United States was donated by I.V. Pekov.

One of the principal acquisition priorities of the museum is to collect a systematic collection which is as complete as possible with known mineral species. The mineral species, catalogued in 2011 to 2012, which are new to the museum are given in Table 2. In this list, mineral species catalogued as type material or its fragments are marked by T; mineral species discovered by the museum staff or in collaboration with the museum staff are asterisked.

As mentioned earlier, the museum catalogue now has ca. 3400 mineral species of the ca. 5000 known species. Minerals species which are absent in the museum collection are listed at the end of this article.

New acquisitions classified by geography

In 2011 – 2012 the museum received items from 59 countries (Table 3), Antarctica, and the ocean floor; eleven specimens have no geographical reference (these are mainly synthetic minerals). In addition, four specimens originate from the Pacific floor, one is from Antarctic, and twelve are of space origin.

The domestic items are reviewed from localities from west to east. Then, the acquisitions from the republics of the Former Soviet Union are reported followed by those from other countries in descending number of specimens.

Russia

Three hundred and seventy-five domestic items (ca. 43% of total number) are distributed by regions as follows: Kola Peninsula (51), Karelia (19), Central Russia (14), Caucasus (23), Urals (77), Siberia (97), Primorskii krai (16), Magadan area (5), Kamchatka and Kurile (59). Another fourteen specimens are minerals synthesized in Russia and Russian specimens without detailed reference.

Fig. 6. Fluorite. Colorless rhombododecahedral crystal of 5 cm in size on fine-crystalline quartz. Nikolaevsk mine, Dalnegorsk, Primorsk krai, Russia. Size of specimen 12 cm. Donation of D.I. Belakovskiy. Systematic collection. FMM no. 93655. Photo: M.M. Moiseev.

The fifty-one specimens (44 mineral species) from the **Kola Peninsula** come from the following major localities of this region: 23 (17 mineral species) from **Khibiny**, 18 (18) from **Lovozero massif**, 6 (6) from **Kovdor**, and 3 (2) from **Keivy**.

Type specimens of four new mineral species (davinciite, kazanskyite, carbobystrite, ekplexite) were donated by A.P. Khomyakov and I.V. Pekov and found in Khibiny. In addition, other minerals added from Khibiny are lucasite-(Ce), orickite, chlorbartonite, and kulsonite. A crystal of eudialyte in apatite, from the former collection of A.S. Podlesny and donated by V.G. Grishin, should be highlighted among the other specimens from Khibiny. Vigrishinite, yegorovite, alluaivite, and vitusite-(Ce) are type specimens added to the museum from the Lovozero massif. Like other specimens from this massif catalogued in 2011 – 2012, these were donated by A.P. Khomyakov, I.V. Pekov, and V.G. Grishin. A very nice specimen with multicolor crystals of quintinite-2*H* in magnetite is from **Kovdor**; the species diversity of the museum collection from this massif was increased by the addition of specimens of tacharanite, gorceixite, and sodalite. A type of fluortalenite-(Y) and goethite unusual for the region from the Serpovidniy Ridge (donation of A.V. Voloshin) should be mentioned among acquisitions from the **Keivy** district.

About half of the 19 items from Karelia are specimens from old collections from the Lupikko, Pitkyranta district, among which chrysoberyl should be mentioned. Most of the other specimens from Karelia are shungite, which are better in quality than previous specimens. Menshikovite was catalogued as type material (donation of A.Yu. Barkov).

Table 2. **Mineral species novel for museum received in 2011–2012**

1. Agardite-(Nd) T
2. Aklimaite T
3. Alcaparrosaite T
4. Alexandrovaite T*
5. Alluaivite T
6. Aluminocopiapite
7. Ambrinoite
8. Ammoniomagnesiovoltaite
9. Anatacamite
10. Anorpiment T
11. Anyuite T
12. Arangasite T
13. Arhbarite
14. Bayldonite
15. Beshtauite T*
16. Bitikleite-(SnFe) T
17. Boyleite
18. Brandholzite
19. Byzantievite T*
20. Calciolangbeinite T*
21. Capgarronite
22. Carbobystrite T
23. Carlgieseckeite-(Nd) T
24. Chabazite-Mg
25. Changoite
26. Chlormayenite
27. Christofschäferite-(Ce) T*
28. Claringbullite
29. Cobaltoblodite T*
30. Cordylite-(La) T*
31. Cuprokalininite T
32. Cupromolybdite T
33. Daliranite
34. Davinciite T
35. Demicheleite -Cl
36. Demicheleite-Br
37. Dorallcharite
38. Dymkovite T
39. Edgrewite T
40. Efremovite
41. Ekplexite T
42. Eltyubyuite T
43. Fangite
44. Ferhodsite T
45. Ferrikaersutite
46. Ferrinatrite
47. Ferrotochilinite T
48. Ferrovalleriite T
49. Fluorchegemite T
50. Fluorocronite T
51. Fluoro-magnesiohastingsite
52. Fluoro-potassic-pargasite T
53. Fluororichterite T
54. Fluor-schorl
55. Galuskinite T
56. Gelosaite
57. Günterblassite T*
58. Hielscherite T
59. Hillesheimite T*
60. Hughesite
61. Hydrochlorborite
62. Hydroxylchondrodite T
63. Hydroxyledgrewite T
64. Hydroxymanganopyrochlore T
65. Irarsite T
66. Irinarssite T
67. Jadarite
68. Jonassonite
69. Juangodoyite
70. Junoite
71. Kadyrelite T
72. Kasatkinite T
73. Kazakhstanite T
74. Kazanskyite T
75. Kirchhoffite T*
76. Kobokoboite
77. Kobyashevite T*
78. Kokchetavite
79. Kottenheimite T
80. Krasheninnikovite T
81. Krasnoite
82. Kumdykolite
83. Kunatite
84. Kuzminite
85. Lahnsteinite T*
86. Langbanshyttanite T*
87. Laptevite-(Ce) T*
88. Larosite
89. Lavinskyite T
90. Lavoisierite
91. Lileyite T
92. Manganoblödite T*
93. Manganoquadratite
94. Mariinskite T*
95. Markcooperite
96. Mattheddleite
97. Megawite T
98. Mejillonesite T
99. Mendeleevite-(Ce) T*
100. Mendozavilite-NaCu
101. Menshikovite T
102. Mikasaite
103. Natropharmacoalumite
104. Nelenite
105. Nickelpicromerite T*
106. Nimite
107. Nioboaeschynite-(Ce)
108. Noonkanbahite
109. Nowackiite
110. Odintsovite T
111. Okhotskite
112. Orlovite T*
113. Osumilite-(Mg) T*
114. Oxyplumboromeite
115. Oxy-rossmanite T
116. Palmierite
117. Parvo-manganotremolite
118. Pavlovskyite T
119. Perrierite-(La) T*
120. Pertlikite T
121. Piemontite-Pb T*
122. Plimerite
123. Pseudolyonsite T
124. Pumpellyite-Al
125. Qingheiite
126. Rabbittite
127. Rauchite T
128. Rongibbsite
129. Rooseveltite
130. Rusinovite T
131. Santarosaite
132. Sarrabusite
133. Schüllerite T*
134. Scottyite
135. Souzalite
136. Starovaite T
137. Steklite T
138. Štěpite
139. Steropesite
140. Sveinbergite T
141. Švenekite
142. Tashelgite T
143. Ternesite T
144. Thermessaite
145. Thorneite
146. Tubulite
147. Uchucchacuaite
148. Umbrianite T
149. Vigrishinite T*
150. Vladykinite
151. Wesselsite
152. Whitecapsite T*
153. Willemseite
154. Windhoekite T*
155. Witzkeite T
156. Yangite T
157. Yaroshevskite T
158. Yegorovite T
159. Yttriaite-(Y) T*
160. Yuanfuliite

Acquisitions from **Central Russia** are basically minerals from the Moscow area (vivianite, chalcedony). The species diversity was increased by the addition of a few minerals. Epsomite, heulandite-Ca, and aluminocopiapite (a new species for the museum) identified in the specimens from the Gzhel quarry are among them. The minerals previously not catalogued from the Moscow area were found, identified and donated by M.M. Moiseev and I.A. Novikov. Acicular spherulites of strontianite up to 2 cm in diameter from the barren Vodino sulfur deposit near Samara (donation by T.V. Pashko) are also noteworthy.

Two specimens of honey-colored, large lamellar whewellite crystals in a marl concretion from **Krasnodar krai** were donated by S.V. Popov. These specimens are from an outcrop at the Pshish River.

Half of the items from the **Caucasus** are type specimens of recently discovered minerals from the Lakargi Mount in the Upper Chegem Ridge,

Table 3. **Distribution of new entries by countries**

1. Russia	375	21. China	8	41. Czech Republic	3
2. United States	88	22. Namibia	8	42. Switzerland	3
3. Germany	27	23. Morocco	7	43. South Africa	3
4. Mexico	24	24. Pakistan	7	44. Belorussia	2
5. Hungary	18	25. Japan	7	45. Bolivia	2
6. Kazakhstan	16	26. Austria	6	46. Great Britain	2
7. Madagascar	16	27. Norway	6	47. Dania	2
8. Ukraine	16	28. Spain	5	48. Zimbabwe	2
9. Brazil	15	29. Myanmar	5	49. Iran	2
10. Romania	15	30. Turkmenistan	5	50. Island	2
11. Chile	15	31. Democratic Republic of Congo	4	51. Poland	2
12. Egypt	14	32. Kirgizstan	4	52. Bosnia and Herzegovina	1
13. Canada	13	33. Macedonia	4	53. Greece	1
14. Tajikistan	13	34. Finland	4	54. Dominican Republic	1
15. Australia	13	35. Ethiopia	4	55. Israel	1
16. Italy	12	36. Azerbaijan	3	56. Indonesia	1
17. Bulgaria	11	37. Argentina	3	57. Niger	1
18. Sweden	11	38. Afghanistan	3	58. Serbia	1
19. Peru	9	39. Slovakia	3	59. France	1
20. India	8	40. Thailand	3		

Note: In addition, four specimens came from the Pacific floor, one is from Antarctic and twelve are of space origin.

Kabardino-Balkaria. This extremely interesting locality recently became a source of minerals found in carbonate xenoliths from ignimbrite lava. Holotypes and co-types of megawite, rusinovite, pavlovskyite, irinarssite, fluorchegemite, edgrewite, hydroxyledgrewite, aklimaite, eltyubyuite, and bitikleite-(SnFe) were catalogued into the systematic collection. Subsequently, bitikleite-(SnFe) was renamed to dzhuluite (Grew *et al.,* 2013) by CNMNC IMA. These specimens were received from I.O. Galuskina, E.V. Galaskin, A.E. Zadov and others who collected and examined them. The Belaya Rechka deposit near the settlement of Nickel is one of the traditional sources of new acquisitions. Holotypes of two new minerals, rauchite and dymkovite, donated by I.V. Pekov and V.V. Levitsky are from there. Also from this deposit is a new specimen with crystals of strontianite up to 5 cm in size on barite. A holotype of beshtauite is from the Beshtau Mount. Cuspidine and ferrimolybdite from Tyrnyauz (donation of E.M. Spiridonov and O.V. Kononov) and a large hand specimen with spectacular clusters of crystals of colorless barite on dark brown calcite within a septarian nodule from the Lower Cretaceous sediments near the Uchkeken village, Karachaevo-Cherkesia (donation of V.V. Levitsky) are noteworthy other additions from the Russian Caucasus.

The seventy-seven specimens from the **Urals** consist of forty-five mineral species, of which hydroxylchondrodite, yttriaite-(Y), kasatkinite, kobyashevite, mariinskite, nickelpicromerite, ferhodsite, and fluororichterite are holotypes. In addition, a series of unique mineral samples from burnt rocks from the waste banks of coal opencasts in the Chelyabinsk basin, South Urals comprise a new type material. These assemblages were donated to the museum by B.V. Chesnokov, a famous Ural mineralogist. Due to their partially man-caused origin, they are not approved by CNMNC IMA as a new mineral species. Nevertheless, they do exist and contribute to the study of natural mineral-forming processes which occur after human activities. In some cases, similar minerals were found in a true natural environment (for example, avdoninite and steklite). In addition, there are mineral species of this type of origin approved by CNMNC IMA before the decision to discriminate against phases with an imperfect natural origin (for example, downeyite and godovikovite.) Despite the decision of the Commission, B.V. Chesnokov published some phases with their proper names (Chesnokov *et al.,* 1998; Avdonin and Polenov, 2007). The specimens given by him were catalogued into the systematic collection under their original names. These are orthorhombic *ammonite* $Zn(NH_3)_2Cl_2$, hexagonal *ignicolorite* $FeS_2 \bullet 0.7CaCO_3 \bullet 2.8H_2O$, tetragonal *ovchinnikovite* $4FeS \bullet FeO \bullet 3CaO \bullet CaCO_3$, cubic *perkovaite* $CaMg_2(SO_4)_3$, orthorhombic *podnoginite* γ $Ca_2[SiO_4]$ (analog of calciolivine) and tetragonal *torbakovite* $3CaO \bullet Fe_2O_3 \bullet CaCl_2$. Several hand specimens of tobermorite composed of snow-white spherulitic crusts consisting of fine, acicular crystals should be mentioned among the most interesting Ural specimens. These are some of the best specimens of tobermorite (donation of A.B. Loskutov and E.A. Novgorodova). The same can be said of nioboaeschinite-(Ce), relatively recently found in mine 97, Ilmeny Mountains (Fig. 7). Separate crystals with rough lateral striations reaching 6 cm in size are combined into a near-parallel aggregate. Restoration of this specimen does not reduce its value. The series of specimens from the Ural rhodonite deposits was aforementioned.

Altai krai is represented by ten hand specimens where all but two (polished plates of dark lilac stichite replacing chromite from the Kaznakhta Valley, Terekta Ridge) originate from the Rubtsovsk deposit and supply a rather representative mineralogical collection from this interesting locality. This collection is comprised of high-quality crystals of cuprite, dendrite of native copper, and miersite. A magnificent cluster of isometric concretions of azurite donated by K.S. Berdysheva is particularly noticeable (Fig. 8).

One specimen, a holotype of tashelgite, originates from **Mountain Shoriya**.

Eight specimens were received from the **Krasnoyarsk krai**, among which are holotypes of the new species ferrotochilinite and ferrovalleriite from the Oktyabrsk mine near town Talnakh.

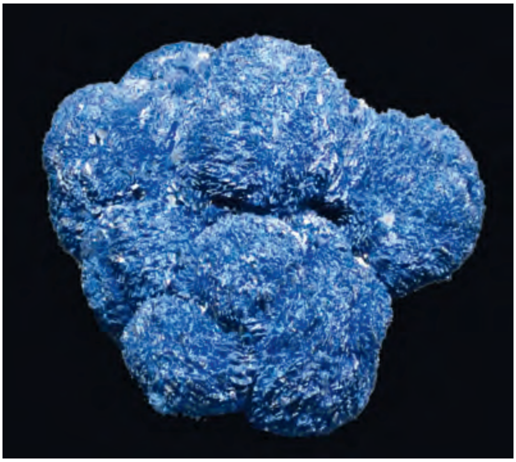
The **Republic of Tyva** (11 specimens) is basically represented by mercury minerals, consisting of kadyrelite, corderoite, lavrentievite, eglestonite, and kuzminite from the Arzak and Kadyrel occurrences (collection of V.I. Vasil'ev).

Baikal region, Irkutsk area, and Transbaikal region. Fifty five specimens (34 mineral species) were received from these regions. Cordilite-(La), cuprokalininite, odintsovite, pavlovskyite, and galuskinite brought by L.Z. Reznitsky, E.V. and I.O. Galuskin, A.A. Konev, and P.M. Kartashov are among the holotypes of mineral species. Most of the items are newly processed from old collections of A.A. Konev from the Murun massif including lamprophyllite, eudyalite, noonkanbahite (previously described as K-batisite) and kalsilite. Tausonite and recently discovered vladykinite received from N.V. Vladykin are from the same locality. Specimens of zircon, phlogopite and fluorapatite from old collections of K.I. Klopotov which were collected from various occurrences near town Slyudyanka were catalogued. He donated from his new collections a very bright specimen of agardite-(Y) from Sherlova Gora (Fig. 9). Oolites of magnetite from the Rudnogorsk deposit near town Zheleznogorsk were aforementioned.

Yakutia is represented by 19 specimens (15 mineral species). Type specimens include arangasite and fluorocronite from G.N. Gamyanin and P.M. Karatshov and yuanfuliite from the Tayoznoe deposit examined by V.V. Rudnev, but approved according to the earlier application of Chinese researchers, who

Fig. 7. Nioboaeschenite-(Ce). Cluster of columnar crystals up to 6 cm in size. Mine 97, Ilmeny Mountains, South Urals, Russia. Size of specimen 11 cm. Donation of K.A. Zakharov, S.V. Kolisnichenko and V.A. Popov. Systematic collection. FMM no. 93888. Photo: M.M. Moiseev.

Fig. 8. Azurite. Cluster of spherulitic concretions up to 5cm in size. Rubtsovsk mine, Altai krai, Russia. General size of specimen 10 cm. Donation of K.S. Berdysheva. Systematic collection. FMM no. 93817. Photo: M.M. Moiseev.



described a specimen from China. A series of specimens of innelite, harmotome, and edingtonite originate from the Inagli massif near the town of Aldan. V.V. Sharygin gave niererite, shortite, and halite from unusual assemblages in the Udachanaya East kimberlite pipe, Daldyn field. A nugget of native bismuth (donation of G.N. Gamyanin) found near the settlement of Omchinkandya on the Oimyakon River (Fig. 10) should be mentioned.

Almost all sixteen specimens (14 mineral species) from the Primorskii krai are from deposits near Dalnegorsk; most are from the Serebryanaya vein at the Nikolaevsk mine. These collections belonged to O.L. Sveshnikova. In addition to common minerals, miargirite, akantite, and andorite were catalogued from this vein. Fluorite from this locality was previously discussed.

In addition to holotypes of anyuite and rooseveltite, new mineral species for the museum, several specimens of the Seimchan meteorite were received from the **Magadan area**. One of them, donated by V.N. Kalachev, is an extremely spectacular large plate whose central part is acid-etched; this results in the well-known Widmanstatten pattern and crystals of schraibersite. The initial polishing is preserved in the 6 mm wide rim that was protected from acid (Fig. 11). This old way to prepare meteorite plates displays a difference between the etched and fresh surfaces, which frequently causes a mistaken assumption that the rim is natural.

Kamchatka turned out to be one of the leading domestic regions which supplied specimens (58) in 2011 – 2012. That was possible due to the museum collections in 2012 in the district of the Tolbachik volcano. Results of these collections were discussed above.

The **Kurile Islands** (Kunashir Island, Mendeleev volcano) is represented by one spectacular specimen of native sulfur donated by A.D. Babansky.

Republics of the Former Soviet Union

In total, 59 specimens were received from the Republics of the Former Soviet Union. These specimens were basically collected during the Soviet period, although most were recently donated. Some of them were delivered to the museum through the countries outside the CIS.

Kazakhstan (16). In addition to the specimens from the classic deposits: hoper blocky fluorite from Akchatau, cosalite from Kara-Oba, eosphorite from Ognevka in the Kalba Ridge, and picture moss agate from Pstan, Balkhash region, the systematic collection was increased by new rare minerals. Kazakhstanite (holotype) donated by E.A. Anikovich and recently found in the eclogite of the Kokshetav massif kokchetavite and kumdykolite, which are polymorph modifications of microcline and albite, respectively, are among them.

There were the same number of acquisitions from **Ukraine**. An exceptional specimen of groutite from the Zavallya graphite deposit, Kirovograd area should be the first to be mentioned. This is one of the best speci-

Fig. 9. Agardite-(Y). Green radial bunches of fine-acicular crystals. Sherlova Gora, Transbaikal region. Donation of K.I. Klopotov. Size of specimen 8 cm. Systematic collection. FMM no. 93857. Photo byM.M. Moiseev.

Fig. 10. Bismuth. Rounded nugget of native bismuth with enclosed cryatals of cassiterite. Omchikandya, Oimyakon River, Yakutia, Russia. Size of specimen 7 cm. Donation of G.N. Gamyanin. Systematic collection. FMM no. 93885. Photo: M.M. Moiseev.

Fig. 11. Meteorite Seimchan. Polished acid-etched plate. Margins were preserved against acid. Found near settlement Seimchan, Magadan area, Russia. Size of specimen 20 cm. Donation of V.N. Kalachev. Collection of meteorites and impactites. FMM no. MET 55. Photo: D.I. Belakovskiy.

Fig. 12. Sylvite after langbeinite. Crystal of langbeinite (combination of tetrahedron and cube) is replaced by sylvite. Y block 700 foot level, Mosaic mine, Carlsbad, New Mexico, US. Size of specimen 5 cm. Donation of D.I. Belakovskiy. OP collection. FMM no. OP 2640. Photo: M.M. Moiseev.

mens of this mineral species consisting of open-work aggregates of weakly split crystals up to 1 cm in size on calcite-phlogopite rock. An unusual pseudomorph of chalcedony after stems of crinoids was described above. This and specimens of rhodonite from the Glimeya deposit, Rakhiv district, Zakarpattia area were donated by A.L. Galkin.

Tajikistan (13). Holotypes of new minerals found by L.A. Pautov, A.A. Agakhanov, and V.Yu. Karpenko, the museum staff, from the Darai-Pioz alkaline massif are of the most interest. These are mendeleevite-(Ce), kirchhoffite, byzantievite, orlovite, alexandrovaite, and Laptevite-(Ce).

Specimens of gypsum, calcite, and metacinnabar from the Fata-Morgana Cave in settlement Gaurdak are from **Turkmenistan**. Four specimens of rhodonite assemblage from the Museyniy Sai near settlement Inylchek were received from **Kyrgyzstan**. Specimens of magnetite and sphalerite from the Dashkesan iron deposit originate from **Azerbaijan** and two specimens of sylvite were received from Soligorsk in **Belorussia**.

Other countries

As usual, most of the acquisitions from abroad are from the **United States** (88 specimens from 15 states; 55 mineral species). In addition to the aforementioned cristobalite and kurnakovite, very nice specimens of tunnelite, inderite, colemanite, and morphologically interesting ulexite from the Boron deposits, Kern County, and blödite and thenardite from Soda Lake, Obispo County are from **California**. The specimens of the rare mineral species markcooperite, timroseite, thorneite, fluorphosphohedyphane, hughesite, and bario-orthojoaquinite came from the same state. In total, twenty-six specimens were received from California in 2011 – 2012.

Utah (15) is the second state by number of acquisitions; in addition to the aforementioned specimens of cristobalite, holotypes of the new minerals manganblödite and cobaltoblödite discovered by A.V. Kasatkin (in collaboration with the museum staff) should be mentioned. An interesting specimen with grossular crystals to 2 cm in an aggregate of gehlenite from the Wah Wah Mts., Beaver County was donated by J. and C. Watson. Most of the specimens from **Alaska** (13) are from the Green Monster Mountain, Prince of Wales Island; in addition to the aforementioned epidote, there are magnetite and quartz. **Arizona** is represented by seven items, including specimens of the emblematic minerals of this state, wulfenite and vanadinite, from a few occurrences in the La Paz County, and rare claringbullite, cuprobismutite, and rongibbsite. A holotype of the new mineral whitecapsite, found by I.V. Pekov, is the most interesting specimen from **Nevada** (6); a pseudomorph of sylvite after a crystal of langbeinite is of the most interest from **New Mexico** (Fig. 12). One to four specimens originate from Arkansas, Colorado, Massachusetts, New Jersey, Oregon, North Caroline, South Dakota, New York, and Maine.

Many acquisitions are from other North America countries. In addition to the aforementioned crystals of gypsum and anhydrite from the Naica mine and luminescent calcite, a few specimens of moganite from Madre, Chihuahua and native tellurium from the Bamballa mine, Moctezuma, Sonora should be mentioned as specimens from **Mexico** (24). Acquisitions from the alkaline complexes at Kipawa (vlasovite, agrellite, gittinsite) and at Mont Saint Hilaire (normandite, analcime, serandite) should be highlighted among the specimens from **Canada** (13). Stillwellite-(Ce) from the new locality of Desmont Mine, Haliburton Co., Ontario was donated by W. Pinch.

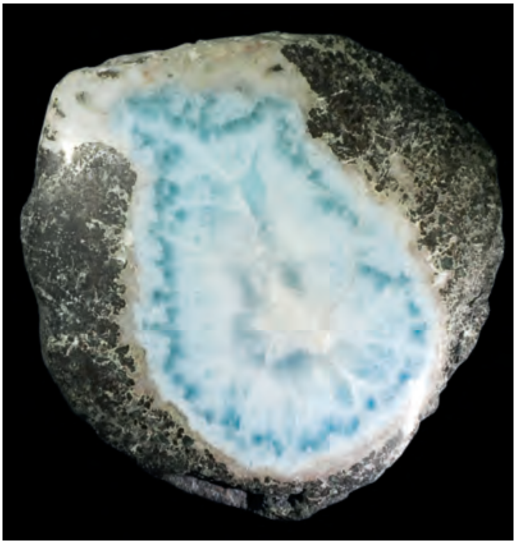
Most new acquisitions from South America are from **Brazil** (15), as usual, and are mainly from the Minas Gerais district. These are the previously discussed rhodonite cluster and flower carved from chalcedony, and also the new species for the museum, carlosbarbosaite and souzalite. In addition, a specimen from the Uruacu iron meteorite was catalogued. The same number of specimens was received from **Chile** (15). Basically, these are rare minerals which were absent in the museum collection: mejillonesite (holotype), santarosaite, anatacamite, and mendozavilite-NaCu. The new spherulitic crust of orpiment and crystals of realgar from the Palomo mine, Huancavelica Department is from **Peru** (9). Anorpiment, a recently discovered triclinic polymorph of orpiment, turned out to be in one of these specimens. The new for the museum mineral species uchucchacuaite and manganoquadratite were also received from Peru. A magnificent well-shaped crystal of andorite ca. 7 cm in size with inclusions of zinkenite from the San Jose mine, Oruro department, **Bolivia** and rare phosphate qingheite from the Santa Anna pegmatite, San Luis, **Argentina** should be mentioned. A basaltic amygdule completely filled by pastel-blue pectolite (so called larimar) was received from Sierra de Baoruco, **Dominican Republic** (Fig. 13).

The new acquisitions from Europe come from 22 countries. The acquisitions from **Germany** (27) primarily came from the Eifel volcanic district, Rheinland-Pfalz. They significantly added to the current collection of specimens from this famous district. Holotypes of 12 mineral species (schüllerite, perrierite-(La), hielscherite, kottenheimite, lileyite, günterblassite, hillesheimite, lahnsteinite, osumilite-(Mg), hydroxymanganopyrochlore, christofschäferite-(Ce), ternesite) were discovered by N.V. Chukanov with the coauthors (exceptional ternesite); museum staff members were among the group. These minerals were found in cavities within alkali basalts and carbonate xenoliths. The more common species ferrikaersutite, nosean, reunite, native nickel, chlormayenite, and scottyite were catalogued to show the entire characteristic of mineral assemblages found at Eifel. A. Ertl donated a specimen of fluorschorl from its type locality, Zschorlau, Saxony.

Most acquisitions from **Hungary** (18), **Romania** (15) and **Slovakia** (3) were obtained in an exchange with a Hungarian collector. This series of rare minerals includes mikasaite, iltisite, capgaronite, belendorffite, ammoniomagnesiovoltaite, and brandholzite from various localities. In addition, hyalite from Monok, Zempleni Mts. in Hungary with bright green fluorescence in UV light should be mentioned.

Among other European countries, many acquisitions were from **Italy** (12), **Bulgaria** (11), and **Sweden** (11). The Italian specimens are mineral species which are new for the

Fig. 13. Pectolite (larimar). Fine-fibrous concentric-zoned aggregate of pectolite completely filling amygdule cavity within volcanic rock. Sierra de Baoruco, Dominican Republic. Size of specimen 9 cm. Donation of D.I. Belakovskiy. Systematic collection. FMM no. 93766. Photo: M.M. Moiseev.



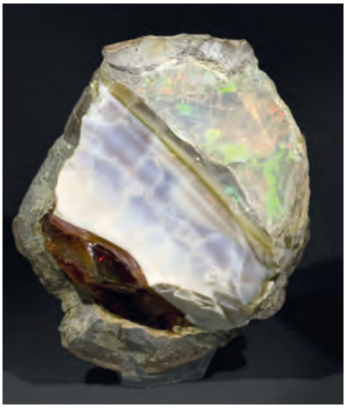


Fig. 14. Precious opal fills amygdule cavity in rhyolite. Eyhiopia. Size of specimen 9 cm. Donation of A. Volkonsky. Systematic collection. FMM no. 93882. Photo: M.M. Moiseev.

Fig. 15. Stilbite. Split sheaf-like crystal on druse of apophyllite. Poona, India. Donation of D.I. Belakovskiy. Size of specimen 10 cm. Systematic collection. FMM no. 93761. Photo: M.M. Moiseev.

Fig. 16. Ilvaite. Cluster of weakly-split crystals. Huanggang Mine, Chifeng Prefecture, Inner Mongolia, China. Donation of D.I. Belakovskiy. Size of specimen 10 cm. Systematic collection. FMM no. 93759. Photo: M.M. Moiseev.

museum, most from the volcanic condensations of the craters of La Fossa Island and Vulcano volcano (demicheleite-Cl and demicheleite-Ba, thermessaite, steropesite). A holotype of a new mineral species, umbrianite, found by Russian researchers (V.V. Sharygin *et al.*) is from Pian di Celle, Umbria. The minerals from the famous Langban deposit are predominant among Swedish specimens. An individual specimen, weighing 345 grams, of the Muonionalusta iron meteorite (collected and donated by D.A. Sadilenko) should be highlighted. Bulgarian acquisitions collected by the museum staff characterize the mineralogy of porphyry copper and base-metal skarn deposits from various districts. Among the specimens from **Austria** (6), oxy-rossmanite and olenite, minerals of the tourmaline supergroup, and eskimoite and heyrovskyite from the Hohe Tauern Mounts near Salzburg donated by A. Ertl are of the most interest. From **Norway** (6), a holotype of a new mineral sveinbergite was given by A.P. Khomyakov and some novel for the museum specimens were exchanged. Among the five specimens from **Spain**, a relatively new finding of colorless, transparent crystals of glauberite from the Consuelo mine near Madrid should be mentioned. Among the acquisitions from the other European countries particular attention should be paid to the new minerals štěpite, švenekite and krasnoite from **Czech Republic** (3), impactite Paasselkä from **Finland** (4) and holotypes examined by Russian researchers, piemontite-Pb from Nezhilovo in **Macedonia**, agardite-(Nd) from the Hilarion mine, Laurion in **Greece** and carlgieseckeite from Ilimaussaq in **Greenland**, **Dania**. We suggested that volcanic ash from the Eyjafjallajökull in **Iceland**, whose eruption disrupted air travel in Europe for a long period in spring, 2010, is of enough interest to be included in the collection.

The acquisitions from Africa are from nine countries, including **Madagascar** (16). Hoper crystals of schorl and iridescent labradorite are discussed above. The other specimens from this island are picture jaspers, crystal of betafite from Betafo, and the new for the museum species flour-potassic-pargasite.

Nearly all acquisitions from **Egypt** (14) were discussed in the previous section of this review except a specimen of the meteorite Gebel Kamil found in the Uweinat desert. **Namibia** (8), next in the number of acquisitions, is represented by the aforementioned picture pietersite and holotypes of two species new to the museum: yangite from the Combat mine and windhoekite from Aris. The latter was discovered in collaboration with the museum staff and named in honor of the capital of this country. In addition to rare minerals from the Bou Azzer deposit (wendwilsonite, smolianinovite, irhtemite), a small individual specimen of meteorite (plessite octahedrite) Taza (NWA-859) is from **Morocco** (7). A large hand specimen of heterogenite from Lubumbashi, donated by N.N. Kamzolkin, is from the Democratic Republic of the **Congo** (4). **Ethiopia** (4) is represented by fine specimens of precious opal donated by A. Volkonsky, from **France** (Fig. 14). The fragment of a new mineral species, lavinskyite, containing new minerals scottyite and wesselsite from the Wessels mine, Kalahari in **South Africa** (4) was donated by W. Pinch. The cluster of colorless to dark blue crystals of euclase is from Mwami, **Zimbabwe** (2). Niger turned out to be a new country for the museum. The fragment of trunk replaced with chalcedony from Toulouk in the South Sahara was donated by T.K. Berkeliev.

In addition to those from Russia and other republics of the Former Soviet Union, Asian acquisitions are from eight countries. Most of the specimens are from **India**, **China** (by 8), **Pakistan**, and **Japan** (by 7). We mention among them the aesthetic specimen of bowtie stilbite on a druse of crystals of apophyllite from the Poona district, India (Fig. 15), well-shaped large crystals and clusters of crystals of ilvaite (Fig. 16) recently found at the Huanggang mine, Inner Mongolia in China, and druse of small crystals of pääkkönenite from the Damingshan Mount, Guangxi province in China. The new crystals of epidote were aforementioned. A series of rare minerals from Japan were exchanged. Transparent crystals of petalite up to 3.5 cm in size from the Palelni mine (donation of I. Szegeni and O.A. Lopatkina) were brought from **Myanmar** (5). Green sodalite as clusters of rhombododecahedral crystals up to 2 cm in size from Lajuar Medam, Sar-e-Sang in Badakhshan (Fig. 17) is of particular interest among the specimens from **Afghanistan** (3). A new mineral species, daliranite, from the Zarshuran deposit in **Iran** (2) was exchanged with the British Museum in London. Tektites (indochinites) were collected in **Thailand** (3). N.S. Lukinykh donated a specimen of native sulfur from the Ijen crater in the eastern Java, **Indonesia**.

Australia is represented by thirteen specimens, of which clusters of acicular crystals of scholzite on limonite from Reaphook Hill in South Australia are noteworthy. One of the best specimens of this species (Fig. 18) were donated by I.S. Lykova. A specimen of the new mineral gelosatite donated by P.A. Williams should be mentioned.

Concluding the geographical review, variously shaped Fe-Mn concretions from the Pacific floor, which are older material brought by P.F. Andryushchenko, and a beryllium silicate surinamite, received in exchange, from the Christmas point, Enderby Land in Antarctica should be mentioned.

New acquisitions classified by type and source

Five hundred and forty-one items were donated by private persons and organizations. In addition, one hundred and four mineral specimens, which are type material of 85 new mineral species, are also attributed to donations. Thus, total donations are 645 items or ca. 74% of total acquisitions. Eighty-five mineral specimens (ca. 10%) collected by the museum staff were catalogued into the main inventory of the museum. One hundred and twelve specimens (13%) were exchanged (including earlier exchanged items, which were examined or processed). The exchange was carried out with 11 domestic and foreign col-

Fig. 17. Sodalite. Cluster of green (!) rhomododecahedral crystals up to 2 cm in size on calciphyre. Ladjuar Medam, Sar-e-Sang, Kokcha Valley, Badakhshan, Afghanistan Size of specimen 8 cm. Donation of D.I. Belakovskiy Systematic collection. FMM no. 93767. Photo: M.M. Moiseev.

Fig. 18. Scholzite. Druses of long-acicular crystals within cavities in limonite. Reaphook Hill, South Australia. Size of specimen 12 cm. Donation of I.S. Lykova. Systematic collection. FMM no. 93330. Photo: M.M. Moiseev.

lectors; 4 mineralogical companies; and Natural History Museums in London, Great Britain; Bern, Switzerland; and Uppsala, Sweden. Thirty-two mineralogical specimens (ca. 4%) were catalogued into the main inventory out of the old working materials of researchers from various organizations, which were taken when the storage was closed or after the death of the researchers. It should be noted that these acquisitions were catalogued as donations if the names of the collectors are known. Three specimens were purchased.

Donated items are from 151 private persons and 3 organizations. Most specimens were donated by 122 Russian citizens. In addition, many specimens were donated by 29 foreign citizens from 12 countries: Australia, Austria, Bulgaria, Czech Republic, France, Germany, Hungary, Japan, Kazakhstan, Netherlands, Ukraine, and United States.

More than 10 mineral specimens were donated by A.A. Antonov (47), A.I. Brusnitsyn (24), D.I. Belakovskiy (180), G.O. Vertyankin (11), E.V. and I.O. Galuskin (12), A.V. Kasatkin (19), A.A. Konev (14), V.M. Moiseev (18), I.V. Pekov (101), A.G. Turchkova (47), A.P. Khomyakov (16), N.V. Chukanov (27) and John and Claudia Watson (13). Five to ten mineralogical specimens came from M.Yu. Anosov (6), M. Bitman (5), V.I. Vasiliev (7), A.V. Voloshin (6), V.G. Grishin (5), S.G. Epanchintsev (5), B.Z. Kantor (6), K.I. Klopotov (6), V.V. Levitsky (8), A.B. Loskutov (9), A.B. Nikiforov (8), I.A. Novikov (6), L.A. Pautov (10), I.N. Savin (5), D.A. Sadilenko (7), E.M. Spiridonov (7), B.V. Chesnokov (6), A. Ertl (10), T. Hanna (9), W. Pinch (5) and S. Schuchman (5). One to four specimens were donated by A.A. Agakhanov, M. Andreev, I.P. Andreeva, P.F. Andryushchenko, E.A. Ankinovich, A.V. Antonov, L.A. Artemenko, S.V. Afanasiev, A.B. Babansky, K. Baburov, A.G. Bazhenov, A.Yu. Barkov, V.D. Begizov, S.I. Belykh, K.S. Berdysheva, N.R. Berkeliev, E.A. Borisova, G.I. Bocharova, A.V. Bulatov, B.I. Vaintrub, N.V. Vladykin, A. Volkonsky, A.L. Galkin, G.N. Gamyanin, M.E. Generalov, V.Yu. Gerasimov, O.I. Gritsenko, E.M. Degtyareva, P.Ya. Detkov, A.V. Donskov, D.N. Dubkov, Yu.V. Erokhin, S.V. Efimova, E.N. Zavyalov, A.E. Zadov, K.A. Zakharov, M.E. Zelensky, F.Sh. Iskanderov, V.N. Kalachev, N.N. Kamzolkin, V.Yu. Karpenko, P.M. Kartashev, I.K. Klochkov, A.L. Kovalev, S.V. Kolisnichenko, O.V. Kononov, L.V. Kravchuk, D.I. Krinov, O.A. Lopatkin, N.S. Lukinykh, I.S. Lykova, E.A. Lyashenko, P.A. Martynov, I.A. Mikhailov, S.V. Mudruk, I.A. Nelkin, E.A. Novgorodova, M.I. Novgorodova, V.M. Okrugin, L.V. Olysych, T.V. Pashko, N.A. Pekova, N.N. Pertsev, P. Petrov, N.M. Podgornykh, V.V. Ponomarenko, A.F. Popov, V.A. Popov, M.P. Popov, S.V. Popov, I.E. Proshenkin, L.V. Razin, L.Z. Reznitsky, V.V. Rudnev, N.I. Rymskaya, G.L. Ryabinin, L.A. Samoylov, A.B. Sandomirskiy, E.I. Semenov, A. Serafimovich, E.V. Sereda, I. Szegeni, V.L. Skvortsova, A.M. Skrigitil, M.A. Smirnova, E.V. Sokol, E.V. Sokolova, E.L. Sokolova, A.V. Stepanov, S.F. Struzhkov, T. Tatyanchenko, D.E. Tonkacheev, V.A. Tuzlukov, V.G. Tyulkin, V.V. Khiller, Yu.A. Chulzhanov, L.I. Shabynin, V.V. Sharygin, D. Allum, J. Fuller, E.S. Grew, F. Hofmann, J. Holfert, L. Holm, T. Holm, A.L. Kidwell, P. Megaw, O'Neil Cristofer, D. Toland, Gy.Varhedy, F. Wafi, S. Wall, K. Watanabe, D. Weyhersmuller and P.A. Williams.

Type specimens were obtained from 31 researchers: I.V. Pekov (23), N.V. Chukanov (19), E.V. Galuskon (12), I.O. Galuskina (12), A.P. Khomyakov (10), L.A. Pautov (7), B.V. Chesnokov (6), A.A. Agakhanov (4), M.E. Zelensky (3). L.Z. Reznitsky (3), A.G. Bazhenov (2), V.D. Begizov (2), A.V. Voloshin (2), E.N. Zavyalov (2), V.Yu. Karpenko (3), P.M. Karatashev (3), A.V. Kasatkin (2), A.A. Konev (2), Rudnev (2), E.A. Ankinovich, G.N. Gamyanin, A.Yu. Barkov, Yu.V. Yerokhin, A.E. Zadov, V.V. Levitsky, M.I. Novgorodova, M.P. Popov, L.V. Razin, E.V. Sokolova, V.V. Khiller, V.V. Sharygin.

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We are highly grateful to all donors for their assistance in adding to the museum's collection.

In 2011 – 2012, eighty-five specimens were catalogued as collected by the museum staff; most specimens (72) were collected in trips under the recent initiative. The earlier collected specimens were catalogued after identification and processing of filed materials. Ten museum researchers collected the specimens. The most specimens were collected by D.I. Belakovskiy (65), I.S. Lykova(47), O.L. Sveshnikova (9), M.M. Moiseev (4), A.A. Agakhanov, V.Yu. Averin, M.D. Dorfman, A.V. Kovalev, V.M. Chalisov, and B.B. Shkursky. The researchers of other organizations actively participated in the collections for the museum.

The researchers from other organizations which actively collected specimens for the museum are: I.V. Pekov, A.G. Turchkova, A.A. Antonov, N.N. Pertsev, Petko Petrov, and D. Toland.

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Mineralogical Notes

MINERALS-GIANTS OF THE SOUTHERN URALS

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Mineralogy of the South Urals has different variations. The set of deposits, which has been and is being mined for minerals in addition to the useful component do also often contain unique minerals, sometimes in the form of giant properly shaped crystals. The article presents information on the findings of such giants, according to the literature, on personal observations and on the oral reports of geologists.
6 figures, 10 references.

Keywords: mineral, crystal, crystal giant, deposit, South Urals.

The stone nature of Earth is generous and diverse. In it's marvelous works, it is attractive with imagination, originality and exclusivity of creations. The same mineral may have been born in different parts of the world and may look like a twin or may look fabulously dissimilar. There is no person who has never admired these masterpieces – crystals! As he admires the sunset and sea wave, or a heap of stone mountains.

Crystals have surprised human intellect at the dawn of the emergence with it's perfection and completeness of forms. Special rarity passed from person to person, from generation to generation for hundreds of years. The evidence for this are the legends about giant precious rubies and diamonds.

There are cyclops and giants in the world of mineral monsters. Not every corner of the earth has given birth to its bosom these rarities. In the South Urals so many unique crystals were found that was enough for a large narrative. Giant crystals were observed by researchers, mineralogists, geologists. Often, these creatures of nature long maintained, but more often simply destroyed during production or used as a raw material. Rare findings settled in museum collections.

Interestingly, the phrase "crystal giant" for different minerals characterizes completely different in size crystals. For example, even a meter long quartz crystal (morion) from the Urals is not a giant compare to quartz veins of Kazakhstan or Ukraine, where in pegmatites much more substantial in size individuals were mined. And at the same time, transparent quartz crystals "Diamonds" (Herkimer "Diamonds" or the South Urals Ust Katavsk "diamonds") are considered as giant with crystal size of only 3 – 5 cm! In this article there more than two dozen South Ural minerals noted, crystals which have outstanding size.

Perovskite. This mineral several times pleased Urals with its "appearance in the world". First found in the mines of the Zlatoust, Urals, he remained a "native" residents of those places. Until now, the best and large crystals of this mineral occur at perovskite mines of Chernorechenskie Mountains. The largest crystals are considered to be samples of M.P. Melnikov in 1882. It was a crystal-individuals with an edge length of 12 cm. Nowadays there are perovskites up to 5 – 6 cm in size. A rare lump has sometimes up to 30 – 40 perovskite crystals of up to 4 cm each!

Zircon. Large zircon crystals were found in the Ilmeny Mountains. One of them is a sample found in 1837: *"... in this pit [kop' number 12 – hereinafter in brackets annotations made by author] found the most enormous zircon in the Ilmeny mines, weighing 8 pounds 61 spool. It consists of several fused in a parallel position indivisible"* (Melnikov, 1883). It is extended to 22 cm splice of several individuals weighing about 3.5 kg. In the pit of academician Koksharov No. 20 *"zircons crystals differentiate – up to 1.5 inches long (6.5 cm) and met very often."* Crystals of a "fist" size caught in the Ilmeny Mountains repeatedly in syenite-pegmatite veins. Also, A.E. Fersman noted that G.G. Kitaev has presented him a similar sample (Balandin, 1982). Zircon crystal (8×6 cm) from the vicinity of Selyankino village exhibited at the exposition of Natural History Museum of the Ilmeny State Reserve.

Giant zircon crystals are constantly mined in Vishnevogorsk on the Mountain Karavay. In nepheline pegmatites of "Vein No. 5" proper shaped zircon crystals can reach sizes up to 10 cm and weight of 2 – 2.5 kg, crystals weighing 1 kg are no rarity. There were rumors that at the mine "Central" of Vishnevogorsk niobium deposits was found a crystal weighing 17 kg!

Microcline. This mineral goes alone with granitic pegmatites. Reliable data on crystals-giants are on topaz pit “Polyakov” on the

Fig. 1. Microcline crystals. Length of the longest is 0.75 m. Eremkinskaya pegmatite vein, the South Urals. Photo: S. Kolisnichenko.
Fig. 2. Morion. Crystal weight is 100 kg. Svetlinskiy pegmatite quarry, South Urals. Photo: V. Musatov.

shores of Lake Argazi in the Ilmeny Mountains and on Svetlinskiy pegmatite quarry. There were met crystals with length of about 50 cm. In 2008 pegmatite vein at the former steading Eremkin (Kochkarskiy district) was discovered area with crystal size of 60×75 cm! (Fig. 1)

Amazonite. The large-sized crystals were observed in the pits of Ilmeny Mountains. On Lobachevskaya pit No. 85 *"... Amazon stone was more than $^1/_4$ yard and actually because of this, topaz crystals reached to one pound weight".* On pit No. 82, *"the value of the pieces of the Amazon stone reached $^1/_2$ yard..."* (Melnikov, 1883). Amazonite crystals up to 30 cm were found in the pit No. 395.

Rock crystal. South Urals is characterized by particularly large size of quartz crystals. In 1967 at Svetlinskoye deposit of piezoelectric quartz at a depth of 13 meters has been discovered a crystal cellar with crystals in the vein No. 500. Two of those rock crystal from this nest weighed three tons each! They were shaped as short-prism, with developed rhombohedrons faces. The crystalls were called "Jubilee-1" and "Jubilee-2". By processing of one of them was produced 92 kg piezoelectric materials. The other crystal is kept at the entrance to the Museum "Gems" ("Samotsvety") in Moscow. On Astafyevskoye deposit large crystals reach a length of up to one meter with weight of 300 kg. There was mined a unique one – piezocrystal of 100 kg! Terensayskoye deposit of piezoquartz (Orenburg region) also excelled by giants. There was found the largest crystal cellar of Urals with capacity of 176 m^3. The largest crystals, extracted from this cellar, weighed from 350 to 750 kg. There was the famous crystal "Baby" ("Malyutka") among them, weighing 784 kg, which is stored in the Geological Museum of Ekaterinburg.

Morion. Large crystals of morion are typical for Svetlinskiy pegmatite quarry (Kochkarskiy district). Larinskaya Geological Reconnaissance Expedition worked there and removed from the cavities crystals weighing over a hundred kilograms. Usually it would be isometric crystals (with short prisms and developed rhombohedrons facets). In 1998 was mined crystal morion of one meter long and weighing 100 kg. The crystal was shaped as long-prism, obelisk form (Fig. 2). The head part of the crystal was perfectly clean and hardly shone in a bright beam of light.

Apatite. To the north-east of Vishnevye Mountains, in the city of Snezhinsk "Seven Keys" apatite crystal locality is known. Apatite crystals found in the peculiar pegmatite consisting of phlogopite, albite and apatite. Apatite appeared around phlogopite to the direction of the contact with the host rock (ultra-basic and serpentinized rocks) almost ideal crystals bottle-green with olive tinge. The largest crystal is considered to be an individual length of about 100 cm with a thickness of 20 cm. Not uncommon are the findings of crystals up to 50 cm.

Polyakovite. In the Ilmeny Mountains, at the pit No. 97 for the first time in the world was discovered and described mineral polyakovite – chrome analogue of chevkinite. In 2007, in the pits in ultra-basic pegmatite vein (richterite-phlogopite composition) were found two polyakovite crystals, which dimensions were 12×8×6 cm. They were the largest crystals in the history of the study of this mineral. Polyakovite was found in the same place in the veins of carbonatite-bearing pegmatites in association with monazite and aeschynite, but here it is only reach 6.5 cm size of the crystals (Fig. 3).

Rutile. Rutile crystals in granulated quartz veins are known to Kyshtym deposit in the vicinity of the village Slyudorudnik. Rutile crystal with length of 23 cm is kept in the Geological Museum of Ekaterinburg. This is one of the well-known large-preserved crystals. There, in the neighborhood of the vein number 126, was found accumulation of rutile crystals weighing about 10 kg, which had the largest individ crystal measuring 18×6×6 cm and found along with it cranked twins – up to 10 cm (found by the author, 1985). From rumors geologists know that there have been cases of rutile crystals finds up to 40 cm.

The longest needle crystals of rutile, representing inclusions in quartz, it is necessary to consider the discovery in 1942 at Svetlinskoye deposit of piezoelectric quartz. Needle length in excess of 40 cm pierce smoky rock crystal (Geological Museum, Ekaterinburg).

Titanite. Sphene (titanite) of South Urals is known from the pits Ilmeny Mountains. Crystals up to 15 cm have been repeatedly found there. Vishnevye Mountains spear-shaped crystal of titanite length of 15 cm were found in nepheline pegmatite vein in Svistunov log (1986). Crystal about 20 cm in size was found in a similar vein of Yushtinsk ridge to the north of the Ilmeny Mountains. White and cream titanites with sizes up to 12×18 cm with a thickness of 1 cm (Fig. 4) are known to Nicolae-Maximilian mine (village Kusinsk Magnitka).

Topaz. The largest crystals of topaz in the South Urals should be considered as samples from the Ilmeny Mountains. Here we describe the crystals of amazonite pegmatites up to 10 pounds (4 kg) weight (Melnikov, 1883). Although it is likely that it was given the weight of all the stones from the same nest. Basically, there were found the individual crystals in 1 pound. The length of the crystals up to 20 cm. Proper blue-greenish crystal weighing 720 g was found in the deposits of the Vostochniy (eastern) log on Svetlinskoye deposit of piezoelectric quartz. The largest pink topaz from the vicinity of river Kamenka has length 5.7 cm and thickness 1.1 cm (Fig. 5).

Beryl. Some large crystals of beryl from pegmatite veins reaching along the axis up to a half of meter long, have been found in the vicinity of the village Annenskiy (Kartalinskiy district). Such fractured crystals were found at opening veins of the pit No. 411 in the Ilmeny Mountains. M.P. Melnikov said that, *"Accordingly Koksharov, 5 pounds crystal stored in the museum of Mining Institute has 25 cm in length and the*

Fig. 3. Polyakovite. Crystal length of 6 cm. Mine number 97, Ilmeny Mountains, South Urals. Photo: A. Titaev.

Fig. 4. Titanite. The size of 8.5 cm. Quarry near village Stroiteley, Ilmeny Mountains, South Urals. Photo: S. Kolisnichenko.

Fig. 5. Topaz, pink. Crystal length 5.7 cm. Pit of pink topaz on the former Proroko-Ilyinskiy mine, South Urals. Photo: S. Kolisnichenko.

Fig. 6. Euclase. Crystal length 7.5 cm. Bakakinskie mines, the South Urals. Specimen: Mining Museum, St.-Petersburg State Mining Institute. Photo: A. Ilyin.

same in circumference, it is bluish-green" (Melnikov, 1983). In 2011, Eremkinskaya pegmatite vein (near Plast) in the quartz core were found proper long-prizm shaped greenish-yellow crystals of beryl length of 0.75 m! The thickness of the crystals was 12 – 15 cm.

Euclase. The Homeland of Russian euclase is "Russian Brazil", the territory is named by academician N.I. Koksharov in 1858 because of minerals assemblage of gold placers, like the Brazilian ones. Gold placers of rivers Kamenka and Sanarka in the South Urals presented to mineralogy a rare mineral euclase. The secrets of his origin and more associated with this has not yet been disclosed. The largest crystal is about 7 cm long. It was found on Bakakinsk placers by washing the rocks for gold in 1862. This euclase is gem quality, polychrome color and has a regular shape (Fig. 6). Kept in the museum of the Mining Institute in St. Petersburg.

Spinel. The largest sample of spinel in the Urals was discovered in 1882 by M.P. Melnikov at multimineral carbonatite veins in Nicolae-Maximilian mine. It is represented by proper octahedral shape, crystal weight is 21 kg. Crystal was a conjunction with smaller spinel individuals weighing between 2 and 6 kg. These exemplars are stored in the Geological Museum of the University of Kazan.

Corundum. Corundum crystals of up to 0.5 m were found on Sinarskoye deposit. Here corundum-phlogopite pegmatites located in ultrabasic rocks. The shape of crystals is spindle and barrel-like; they are pink, white or blue. Sometimes corundum crystals are zonal – the core is blue and the border is pink. Explorated and studied of this deposit in 1944, geologists noted findings of large crystals up to 50 cm and a thickness of 20 cm (Soshina, 1944). In corundum pit No. 299 was discovered tabular sapphire crystal, 17×15 cm in size (Kolisnichenko, 2006). Barrel-like crystal corundum 2 kg was found in corundum pit, Nicolskaya Mountain (Potaninskie Mountains).

Molybdenite. The crystal of molybdenite with diameter of 47 cm is described in 1957 for one of the pegmatite veins of Berkut ridge, south of the village Slyudorudnik. Fragment is located in the Geological Museum of Ekaterinburg.

Epidote. Home to the giant crystals of epidote in the South Urals is considered Zelentsovskaya pit in the village Magnitka. Known gem crystal length of one meter. Formed in carbonate rocks epidote crystals are well dissected as by the very nature of karst and by human actions in mines. Lovely large crystals of epidote sometimes intergrown with hastingsite were not uncommon.

Large discoid crystals of yttrium-containing epidote ("yttroepidot") are described in the pegmatite veins near village Slyudorudnik. In the halls of ancient tunnels there are still visible greenish-black discoid crystals with a diameter of 20 to 80 cm and a width of 5 – 10 cm.

Zoisite. The mineral zoisite is distinguished by a significant size of crystals in the veins of granulated quartz at Kyshtym deposit. There, near the village Slyudorudnik, one of the veins contained aggregates and single crystals of zoisite with length 35 cm and thickness of 4 – 5 cm. Color of mineral changed from light green at the base to bluish on the head.

Ilmenite. Crystals of ilmenite are often observed in cavities of alkaline pegmatite veins in the Vishnevye Mountains. One of the veins of Dolgaya Mountain contained about 5 tonnes of ilmenite crystals. The large crystals weighed about 25 – 30 kg. In the Ilmeny Mountains giant ilmenites were extracted from the Mountain Firsovaya and pits No. 154 – 155, the size of the crystals was about 30 – 50 cm, weight was up to 60 kg.

Nepheline. Good crystals of this mineral are rare, though it occurs often in Ilmeny and Vishnevye Mountains. In pegmatites of Kurochkin Log on the old pit "Shpat" nepheline forms meter-sized agregates. There are cavities with imperfect crystals of nepheline located in pegmatites of Dolgaya Mountain. The flattened crystal with size of 16 cm in diameter was found by the author in the nest with ilmenite and lepidomelane in nepheline pegmatite vein, exposed by trenching at the construction site of the Natural History Museum of the Ilmeny State Reserve in 1978.

Biotite (lepidomelane, black mica) is often found in the Ilmeny and Vishnevye Mountains as a large mass. The first mention of the discovery of a giant crystal black mica was made by M.P. Melnikov (1883): in the pit No. 8 in the Ilmeny Mountains *"...during a visit of Duke Maximilian of Leuchtenberg (1842) was extracted crystal 3 poods 33 pounds weight"*. In the pit No. 82 M.P. Melnikov noted *"black mica in the form of six-sided prisms up to 1.5 arshin [3.5 feet] wide"*. Plates of lepidomelane with diameter of more than 0.5 m are found in the work sites of the Vishnevogorsk deposit of pyrochlore.

Helvine. For the first time in the Urals this mineral was discovered in amazonite pegmatite vein of pit No. 63 in the Ilmeny Mountains. P.V. Eremeev in 1868 wrote that *"solid pieces reach the size of a human head and also it ingrowths into graphic (pismenny) granite. From other known deposits of helvine, Ilmeny Mountains mineral differentiate by its non-crystalline form, by being in large quantities and dark red-brown tint"* (Eremeev, 1868).

Fergusonite. In muscovitic pegmatites of Slyudyanogorsk deposit in the vicinity of the village Slyudorudnik there were findings of poorly-formated crystals in dark brown and black, which length was 20 cm (Belkovsky, 2010).

The sunstone and the moonstone (oligoclase or other feldspars). Sunstone occurs in the Ilmeny and Vishnevye Mountains. It is often found in feldspar pegmatite veins, where it forms crystals in large cavities. On Potanin quarry in 2006 the crystal of feldspar with the effect of sunstone has a size 29×13×9 cm and a weight of 5 kg. Crystal of moonstone there was 14×14×10 cm and weighing about 5 kg.

Scheelite. This mineral was actively mined in the South Urals during 30s to 50s of 20th century. Then new deposits of tungsten ores were discovered – Gumbeyskoye and Boevskoye where scheelite was the bulk of the ore. In literature it is mentioned that during the Second World War in 1941 – 1945 on Gumbeyskoye deposit there were rich scheelite veins, where the crystals of the "crystal cellars" acquired a size of 15 cm (*World of Stones*, 2001).

Monazite. The sample called "tabular zircon" was brought by I. Menge from the Razderishin pits in Ilmeny Mountains, the study proved to be monazite. The weight of this crystal was 362.25 g (Popov, Popova, 2006). Later in the Ilmeny Mountains such large monazite was not found again.

Gold. Gold crystals do not exceed a few centimeters. But we can courageously admit the biggest accumulation of this mineral, called prills. So, for Russia the largest prill is considered to be the "Big Triangle" (in the literature of the 19th century – the "World Monster"), weighing 36 kg. It was found in 1842 by Nikifor Syutkin, worker at Tsarevo-Alexander mine on a inflow of the rivers Miass – Tashkutarganka. The second largest nugget of South Urals can be considered "Midhadsky" weighing 1 poods 20 pounds (about 24 kg), which was found in the root of the ore vein near the Balkany village during the second half of the 19th century (Zavaritsky, 1926).

Limonite geode of gigantic size was found in the Bakal mines in the 1937 by famous miner G.G. Kitaev (Pronin, 1985). Its size is 2.5×1.5 m, weight is 9.5 tons! It is now on display in front of the Geological Museum in Ekaterinburg.

Multimineral secretion. Secretions composed by polymineral aggregate are known around village Kizilskoye. In one of the out-crops of volcanic rocks on the left bank of the River Ural the author has discovered secretion up to 70×50 cm, composed of quartz, chalcedon, zeolite and calcite.

Thus, the South Ural with its wealth of different mineral species is characterized by the presence of large and giant mineral agregates, including the well-faceted crystals, which certainly attract the professional mineralogists and amateur collectors.

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