

RUSSIAN ACADEMY OF SCIENCES
FERSMAN MINERALOGICAL MUSEUM

VOLUME 49

New Data on Minerals

FOUNDED IN 1907

MOSCOW
2014



New Data on Minerals. 2014. Volume 49. 154 pages, 105 photos, drawings, and schemes.

Edited by V.K. Garanin, Professor, Doctor in Science.

Published by the Fersman Mineralogical Museum, Russian Academy of Sciences.

This volume contains description of emmerichite, a new lamprophyllite group mineral from the Eifel volcanic region in Germany, nanocrystals of native molybdenum, iron, and titanium found from impact glasses of lunar regolith, and Si-rich zeolite yugawaralite discovered from the Fersman outcrop at the Oshurkovskoe apatite deposit in Buryatia, Russia. The new data for betalomonosovite from the Khibiny massif and allanite (orthite) from Verkhoturye in the Middle Urals are given. Mineralogy of plutogenic gold-quartz ores in the Northern Kazakhstan is discussed in detail. The results of studying structures of veatchite polytypes and related pentaborates are given; the crystallization products of melts in the Cu-Fe-S system with admixture of Pt, Pd, and Sn are described.

The section *Mineralogical Museums and Collections* reports new exhibits in the Ore-Petrography Museum at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences; exhibition Bauxites in the Fersman Mineralogical Museum; and mineralogical collection of V.I. Stepanov stored in this museum. The paper in the section *Persons* is devoted to the 90th anniversary of the birth of V.I. Stepanov. Here, biography of D.A. Golitsyn, Russian diplomat and collector is given. The journal publishes two brief notes devoted to the 130th anniversary of the birth of A.E. Fersman: addition to biobibliography of this outstanding scientist and mineral fersmanite named in his honor. This volume is completed by the article about mineral aggregates from the *Prometheus* Cave near Tsqaltubo, Western Georgia.

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

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Authorized for printing by Fersman Mineralogical Museum, Russian Academy of Sciences

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Published by

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



EMMERICHITE, $\text{Ba}_2\text{Na}(\text{Na}, \text{Fe}^{2+})_2(\text{Fe}^{3+}, \text{Mg})\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, A NEW LAMPROPHYLLITE-GROUP MINERAL FROM THE EIFEL VOLCANIC REGION, GERMANY¹

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Emmerichite, $\text{Ba}_2\text{Na}(\text{Na}, \text{Fe}^{2+})_2(\text{Fe}^{3+}, \text{Mg})\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, a new lamprophyllite-group mineral has been found in the Rother Kopf and Graulay basalt quarries, Eifel volcanic region, Rhineland-Palatinate, Germany in late assemblages consisting of nepheline, augite, melilite, götzenite, lileyite, fluorapatite, as well as (in Rother Kopf) leucite, phlogopite, magnetite, perovskite, and günterblässite. Emmerichite occurs as lamellar crystals up to $0.05 \times 0.3 \times 0.5$ mm in size and epitaxial intergrowths with lileyite. The new mineral is brown, with vitreous luster. It is brittle, the Mohs' hardness is 3–4; cleavage is perfect parallel to {100}. The calculated density is 3.864 g/cm^3 . Emmerichite is biaxial, (+), $\alpha = 1.725(4)$, $\beta = 1.728(4)$, $\gamma = 1.759(4)$. The chemical composition (electron microprobe $\text{Fe}^{2+}/\text{Fe}^{3+}$ estimated from X-ray structural analysis, wt.%) is as follows: Na_2O 5.44, K_2O 1.03, CaO 1.98, SrO 3.23, BaO 25.94, MgO 3.13, MnO 2.22, FeO 4.85, Fe_2O_3 6.73, TiO_2 15.21, ZrO_2 0.52, Nb_2O_5 1.32, SiO_2 27.13, F 3.54, $-\text{O} = \text{F}_2$ -1.49, total is 100.78. The empirical formula is $\text{Ba}_{1.49}\text{Sr}_{0.27}\text{K}_{0.19}\text{Na}_{1.54}\text{Ca}_{0.31}\text{Mn}_{0.275}\text{Mg}_{0.68}\text{Fe}_{0.59}^{2+}\text{Fe}_{0.74}^{3+}\text{Ti}_{1.67}\text{Zr}_{0.04}\text{Nb}_{0.09}\text{Si}_{3.97}\text{O}_{16.36}\text{F}_{1.64}$. The crystal structure has been refined on a single crystal to $R = 0.044$. The new mineral is monoclinic $C2/m$, $a = 19.960(1)$, $b = 7.098(1)$, $c = 5.4074(3)\text{Å}$, $\beta = 96.368(1)^\circ$, $V = 761.37(12)\text{Å}^3$, $Z = 2$. Emmerichite is isostructural with other monoclinic minerals of the lamprophyllite group. Its crystal chemical formula is $[\text{Ba}, \text{Sr}, \text{K}]_2[(\text{Na}, \text{Ca})(\text{Na}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_2(\text{Fe}^{3+}, \text{Mg})](\text{Ti}, \text{Fe}^{3+}, \text{Nb}, \text{Zr})_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{F}, \text{O})_2$. The strongest lines in the X-ray diffraction pattern [d , Å (l , %) (hkl)]: 9.97 (55) (200); 3.461 (65) (510, 311, 401); 3.312 (40) (220, 600); 2.882 (38) (22-1, 420); 2.792 (100) (221, 511); 2.670 (56) (002, 601, 20-2); 2.629 (45) (710, 42-1); 2.140 (57) (131, 022, 621, 22-2). The type specimen is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia.

7 tables, 6 figures, 26 references.

Keywords: emmerichite, new mineral, layered titanosilicate, lamprophyllite group, Rotter Kopf, Graulay, Eifel, alkali basalt.

Late pneumatolitic mineral assemblages related to alkali basalt of the Eifel paleovolcanic region, Rheinland-Pfalz, Germany, are characterized by the wide diversity of mineral species (Blass *et al.*, 2008; 2011) the list of which is expanding every year (Blass *et al.*, 2009₁, 2009₂; 2011; Chukanov *et al.*, 2011₁; 2011₂; 2012₁; 2012₂; 2013). More than ten minerals known from there including titanite, götzenite, fresnoite, fersmanite, batisite, no-

onkanbachite, lamprophyllite group members (lileyite, fluorine analog of barytolamprophyllite), schüllerite related to the lamprophyllite group, and emmerichite, a new member of this group reported in this paper are titanosilicates.

Emmerichite was named in honor of Franz-Josef Emmerich (b. 1940), German amateur mineralogist and mineral collector for his contributions to the mineralogy of the

¹ – A new mineral species emmerichite and its name approved by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society and by the Commission on New Minerals, Nomenclature, and Classification of Minerals of the International Mineralogical Association (September 2, 2013, IMA no. 2013-064).

Eifel region. In particular, he was initiator and publisher of the first Eifel CD with multiple photos and detailed data on minerals from the Eifel region (Blass *et al.*, 2011).

The type specimen is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia; the number in the systematic collection is 94122.

Occurrence

Specimens with emmerichite were found in two operating basalt quarries located in the Western Eifel volcanic region, Rheinland-Pfalz, Germany.

The holotype specimen originates from the Rother Kopf Quarry located 20 km WSW of the town Gerolstein near the settlement Roth. In this locality emmerichite occurs as flattened crystals frequently intergrown with altered götzenite and günterblässite (Fig. 1). Associated nepheline, leucite, augite, phlogopite, ekermanite, götzenite, lileyite, fluorapatite, magnetite, and perovskite are pneumatolitic minerals crystallized in cavities within alkali basalt. In some cavities, these minerals are overgrown by late hydrothermal chabasite-K, chabasite-Ca, phillipsite-K, and calcite. Günterblässite is a transformation mineral species formed as a result of partial leaching of cations and anions from the earlier hydrogen-free mineral of the günterblässite group (Chukanov *et al.*, 2012_c) that is probably related to umbrianite (Sharygin *et al.*,

2013). Götzenite and ekermanite in this assemblage are usually altered by superimposed hydrothermal processes (up to complete replacement of these minerals with amorphous hydrous silicates).

Cotype specimen of the new mineral was found in the Graulay quarry (other spelling is Graulai, Grauley, Graulei) near the settlement Hillesheim, where the new mineral is associated with nepheline, augite, Ti-rich andradite, titanite, noonkanbahite, lileyite, fresnoite, melilite, götzenite, batiferrite, barite, and late alumohydrocalicite. In this assemblage, emmerichite epitaxially overgrows crystals of lileyite forming rims up to 50 μm in thickness with sharp boundary between these two minerals (Figs. 2, 3).

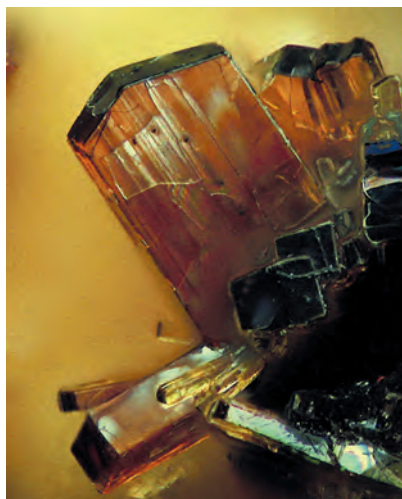
Morphology and physical properties

Emmerichite occurs as thin lamellar to tabular flattened and occasionally lath-shaped crystals up to $0.05 \times 0.3 \times 0.5$ in size and aggregates of these crystals up to 1 mm across. The major habit form is $\{100\}$; $\{110\}$ and faces of belt $\{h0l\}$ are minor. The new mineral is brown of various tints with vitreous luster and white streak. Emmerichite is brittle; the Mohs' hardness is 3–4; the cleavage is perfect parallel to (001). The calculated density is 3.864 g/cm^3 .

Emmerichite is biaxial, positive, $\alpha = 1.725(4)$, $\beta = 1.728(4)$, $\gamma = 1.759(4)$; $2V_{\text{meas.}} = 80(5)^\circ$, $2V_{\text{calc.}} = 79^\circ$. The dispersion of optical axes is medium, $r > v$. Optical orientation is:

Fig. 1. Lamellar crystals of emmerichite (brown) with günterblässite (colourless) from Rother Kopf. Field of view 1.5 mm. Photo: Volker Betz.

Fig. 2. Emmerichite (dark zones) epitaxially overgrowing lileyite crystals from Graulay. Field of view: 0.8 mm. Photo: Fred Kruijen.



$X = a$; the axes Y and Z are parallel to the (100) plane; the axis Y is parallel to the elongation of the crystals. Pleochroism is moderate: Z (brown) $\geq Y$ (light brown) $> X$ (greenish gray).

The infrared absorption spectrum of emmerichite (Fig. 4) was obtained using an ALPHA FTIR Bruker Optics spectrometer in the range $360 - 3800 \text{ cm}^{-1}$ with the resolution of 4 cm^{-1} . The powdered mineral was prepared as a pellet pressed with anhydrous KBr; a similar pure KBr pellet was used as a standard. The wavenumbers of absorption bands in the IR spectrum of emmerichite and their assignment are as follows (cm⁻¹, s – strong, w – weak, and sh – shoulder): 1055sh, 1038s, 954s, 907s, 853s (Si-O stretching vibrations), 686w, 658w (O-Si-O bending vibrations of Si₂O₇ groups), 580sh, 536 (combinations of stretching vibrations of TiO₃ and Fe³⁺O₆ polyhedra), 458s, 400s (combinations of Si-O-Si bending vibrations and stretching vibrations of MO₆, octahedra where $M = \text{Fe}, \text{Mg}, \text{Mn}, \text{Ca}$). The IR spectrum of emmerichite is similar to those of the other minerals of the lamprophyllite group (Fig. 4), especially the

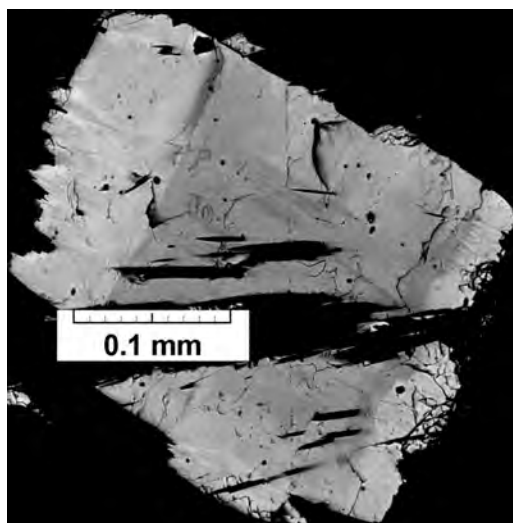


Fig. 3. Back-scattered electron image of emmerichite (light gray zones) with the empirical formula $(\text{Ba}_{1.46}\text{Sr}_{0.26}\text{K}_{0.16}\text{Na}_{0.02})_{1.90}\text{Na}(\text{Na}_{0.60}\text{Fe}_{1.10}\text{Mg}_{0.76}\text{Mn}_{0.27}\text{Ca}_{0.27})_{3.00}(\text{Ti}_{1.71}\text{Fe}_{0.13}\text{Nb}_{0.08}\text{Zr}_{0.08})_{2.00}(\text{Si}_{3.97}\text{Al}_{0.03})\text{O}_{16.33}\text{F}_{1.67}$, epitactically overgrowing lileyte (dark gray) with the empirical formula $(\text{Ba}_{1.59}\text{Sr}_{0.19}\text{K}_{0.19}\text{Na}_{0.06})_{1.94}\text{Na}(\text{Na}_{1.00}\text{Mg}_{0.75}\text{Fe}_{0.54}\text{Ca}_{0.46}\text{Mn}_{0.16}\text{Ti}_{0.05}\text{Nb}_{0.02}\text{Zr}_{0.02})_{3.00}\text{Ti}_{2.00}\text{Si}_{4.00}\text{O}_{16.37}\text{F}_{1.63}$. Graulay quarry.

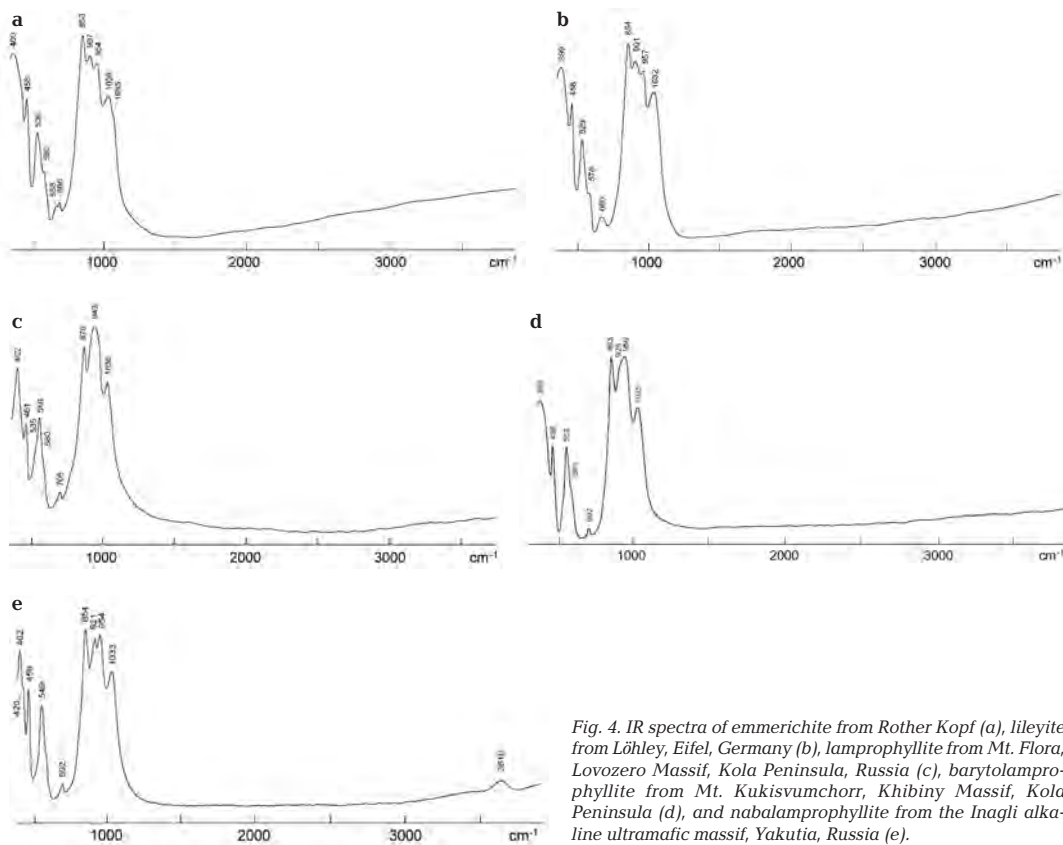


Fig. 4. IR spectra of emmerichite from Rother Kopf (a), lileyte from Löhley, Eifel, Germany (b), lamprophyllite from Mt. Flora, Lovozero Massif, Kola Peninsula, Russia (c), barytolamprophyllite from Mt. Kukisvumchorr, Khibiny Massif, Kola Peninsula (d), and nabalamprophyllite from the Inagli alkaline ultramafic massif, Yakutia, Russia (e).

Table 1. Chemical composition of emmerichite

Component	Average content, wt. %	Range of content	Standard
Na ₂ O	5.44	5.20–5.78	Albite
K ₂ O	1.03	0.95–1.13	Microcline
CaO	1.98	1.86–2.07	Wollastonite
SrO	3.23	3.02–3.48	SrF ₂
BaO	25.94	25.50–26.23	BaSO ₄
MgO	3.13	3.05–3.28	Diopside
MnO	2.22	2.04–2.43	MnTiO ₃
FeO*	4.85		
Fe ₂ O ₃ *	6.73	10.75–11.16**	Fe ₂ O ₃
TiO ₂	15.21	15.05–15.45	MnTiO ₃
ZrO ₂	0.52	0.33–0.78	Zr
Nb ₂ O ₅	1.32	1.04–1.53	Nb
SiO ₂	27.13	26.92–27.38	SiO ₂
F	3.54	3.35–3.74	CaF ₂
O = F	-1.49		
Total	100.78		

Notes: * – Total iron content (corresponding to 10.91 wt. % FeO) was apportioned between FeO and Fe₂O₃ in the ratio Fe²⁺:Fe³⁺ = 0.60:0.75 taking into account structural data (cation-ligand distances and bond valence calculations for cationic sites). ** – For total iron considered as FeO.

Mg-dominant analogue of emmerichite, lile-yite, Ba₂Na(Na,Fe²⁺,Ca)₂(Mg,Fe³⁺)Ti₂(Si₂O₇)₂O₂F₂ (Chukanov *et al.*, 2012₁; Fig. 4b). The difference between the two minerals is pronounced in the range 520–690 cm⁻¹. Bands with wavenumbers above 1100 cm⁻¹ (that could correspond to stretching vibrations of H-, B- or C-bearing groups) are absent in the IR spectrum of emmerichite.

Chemical composition

The chemical composition of emmerichite was determined using Oxford INCA Wave 700 electron microprobe operated at accelerating voltage 20 kV, current intensity 20 nA, and beam diameter 0.6 μm. Five point analyses were carried out. Average contents of components and ranges of contents are given in Table 1.

The contents of P, S, Al, V, Cr, Ni, Zn, Y, Ln, Th, and U in the mineral are below their detection limits by electron microprobe. Iron was apportioned between Fe²⁺ and Fe³⁺ taking into account structural data (see below). CO₂ and H₂O were not determined. The bands corresponding to H₂O, hydroxyl groups and carbonate anions are absent in the IR spectrum of emmerichite.

The empirical formula of emmerichite calculated on the basis of 18 O + F atoms pfu is Ba_{1.49}Sr_{0.27}K_{0.19}Na_{1.54}Ca_{0.31}Mn_{0.275}Mg_{0.68}Fe_{0.59}²⁺Fe_{0.74}³⁺

Ti_{1.67}Zr_{0.04}Nb_{0.09}Si_{3.97}O_{16.36}F_{1.64}. The simplified formula Ba₂Na₃Fe³⁺Ti₂(Si₂O₇)₂O₂F₂ requires (wt.%) Na₂O 10.31, BaO 34.02, Fe₂O₃ 8.86, TiO₂ 17.72, SiO₂ 26.65, F 4.21, -O = F₂ -1.77, total is 100.00.

X-ray crystallography

The X-ray powder diffraction pattern of emmerichite (Fig. 2) was recorded using a Stoe IPDS II single-crystal diffractometer with an image plate detector, MoKα radiation, an accelerating voltage of 45 kV, and a current of 30 mA. The experiment has been carried out using the Gandolfi method by rotation over two axes (ω and φ), the distance between sample and detector was 200 mm; the measurement time was 40 min. The X-ray powder diffraction pattern of emmerichite is readily indexed in monoclinic unit cell with the following unit cell dimensions refined by the least squares method: *a* = 19.93(3), *b* = 7.11(1), *c* = 5.407(8) Å, β = 96.5(1)°, *V* = 760(3) Å³.

Single-crystal X-ray diffraction data were collected with an Xcalibur S CCD diffractometer using MoKα radiation. The monoclinic unit cell dimensions (space group *C2/m*) refined from these data are as follows: *a* = 19.960(1), *b* = 7.098(1), *c* = 5.4074(3) Å, β = 96.37(1)°, *V* = 761.37(1) Å³, *Z* = 2.

The crystal structure of emmerichite was solved using 5201 unique reflections with $|F| > 3\sigma(F)$ to *R* = 0.044. The detailed structural data of emmerichite is reported by Aksenov *et al.* (2014); here only its brief characteristic is given.

The structure of the new mineral (Figs. 5, 6, Tables 3, 4), like the structure of other lamprophyllite-group members, is based on a triple-layered *HOH* packet (module). Inner *O* layer consists of edge-shared octahedra *M1*, *M2*, and *M3*. Outer heteropolyhedral *H* layers are composed of five-coordinated cations polyhedra *LO*₅ and silicate groups Si₂O₇. Large cations (Ba, Sr, K) occupy in the space between the packets.

Based on the *e*_{ref} values, coordination numbers, interatomic distances, character of the distortion of polyhedra, bond-valence calculations and displacement parameters, the occupancy of the sites is:

- Ba site – Ba with some Sr and K;
- Ti site – Ti with some Fe³⁺, Nb and Zr;
- M1 site – Na with subordinate Ca;
- M2 site – Na with subordinate Fe²⁺, Mn²⁺ and Mg;
- M3 site – Fe³⁺ with subordinate Mg;

Table 2. X-ray powder diffraction data for emmerichite

$I_{\text{meas.}}$	$d_{\text{meas.}}$	$I_{\text{calc.}^*}$	$d_{\text{calc.}^{**}}$	hkl
55	9.97	39	9.919	200
4	6.68	4	6.683	110
2	4.946	2	4.959	400
2	4.509	3	4.519	201
19	4.119	27	4.114	111
36	3.752	54	3.750	31-1
65	3.461	36, 53, 10	3.463, 3.459, 3.458	510, 311, 401
40	3.312	22, 29	3.341, 3.306	220, 600
27	3.044	45	3.048	51-1
38	2.882	24, 22	2.886, 2.886	22-1, 420
100	2.792	100, 28	2.791, 2.791	221, 511
56	2.670	16, 15, 38	2.687, 2.686, 2.669	002, 601, 20-2
45	2.629	37, 29	2.632, 2.614	710, 42-1
8	2.469	4, 1, 4, 3	2.481, 2.477, 2.466, 2.461	40-2, 421, 71-1, 112
5	2.427	4, 5	2.434, 2.419	31-2, 620
3	2.355	10	2.353	80-1
6	2.269	10	2.272	312
13	2.222	10, 6, 8	2.230, 2.228, 2.209	51-2, 330, 60-2
57	2.140	9, 26, 19, 22	2.142, 2.142, 2.142, 2.133	131, 022, 621, 22-2
15	2.093	16, 6	2.105, 2.086	910, 33-1
28	2.032	8, 22, 4, 13	2.033, 2.032, 2.031, 2.030	42-2, 530, 331, 512
13	1.982	18, 4, 9	1.985, 1.981, 1.961	71-2, 602, 82-1
5	1.934	7, 3	1.937, 1.932	53-1, 10.0.-1
2	1.894	6	1.893	911
3	1.865	8	1.866	531
6	1.813	13	1.816	730
20	1.774	28	1.774	040
8	1.748	5, 3, 3	1.749, 1.748, 1.747	91-2, 11.1.0, 33-2
4	1.715	6, 5	1.717, 1.714	11.1.-1, 113
5	1.654	9, 3, 1	1.658, 1.654, 1.652	51-3, 60-3, 241
4	1.638	7	1.637	313
26	1.601	10, 21, 15	1.604, 1.603, 1.599	22-3, 10.2.1, 023
6	1.560	1, 2, 9	1.563, 1.557, 1.557	640, 71-3, 73-2
2	1.527	2, 4	1.532, 1.523	513, 64-1
27	1.479	24, 8, 4, 3, 2, 17	1.482, 1.481, 1.481, 1.480, 1.479, 1.478	12.2.-1, 042, 641, 423, 13.1.-1, 24-2
5	1.453	11, 2	1.457, 1.452	732, 242
6	1.435	10, 4	1.435, 1.434	93-2, 13-3
6	1.414	3, 2, 2	1.417, 1.415, 1.410	84-1, 133, 10.0.-3
1	1.375	3, 1, 2, 2	1.383, 1.381, 1.372, 1.371	53-3, 803, 841, 333
5	1.354	3, 3, 6	1.356, 1.352, 1.351	11.3.1, 35-1, 20-4
11	1.341	6, 10, 1, 6, 3	1.343, 1.343, 1.337, 1.336, 1.336	004, 12.0.2, 550, 351, 932
6	1.310	2, 5	1.310, 1.309	10.2.-3, 55-1
2	1.291	4, 2	1.287, 1.286	823, 551
2	1.249	2, 2, 2, 2	1.250, 1.249, 1.249, 1.245	71-4, 42-4, 152, 35-2
2	1.224	2, 2	1.223, 1.222	10.4.-2, 13.3.1
3	1.213	1, 1, 3, 2, 3, 1	1.217, 1.215, 1.214, 1.213, 1.211, 1.210	62-4, 55-2, 514, 13.1.-3, 12.2.-3, 64-3
3	1.190	3, 3, 3	1.193, 1.191, 1.189	950, 91-4, 10.2.3
2	1.178	1, 3	1.179, 1.177	552, 16.0.-2
2	1.174	2	1.175	260
2	1.150	2, 2, 2	1.150, 1.150, 1.149	951, 714, 643

Notes: * – For calculated X-ray pattern, only reflections with intensities ≥ 1 are given.

** – Calculated with single-crystal unit cell parameters.

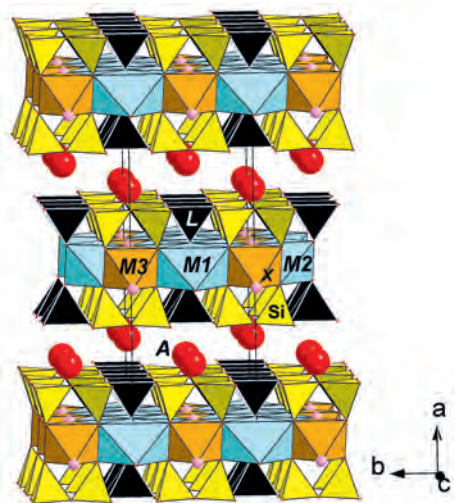


Fig. 5. The crystal structure of emmerichite projected onto the (ab) plane.

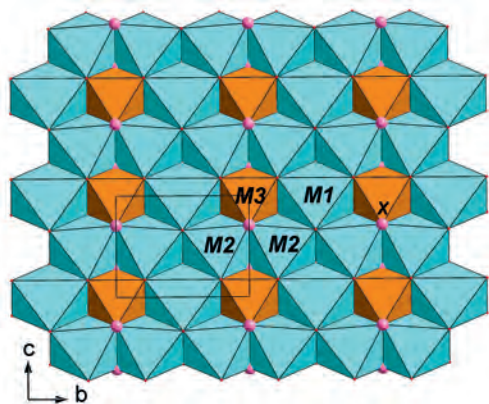


Fig. 6. Octahedral sheet in the structure of emmerichite.

Table 3. Interatomic distances (Å) in coordination polyhedra of emmerichite

Ba—O1	2.761(2)	M2—O5	2.222(2) × 2
Ba—O3	2.761(2) × 2	M2—F	2.283(2) × 2
Ba—O4	2.861(2)	M2—O2	2.322(2) × 2
Ba—O4'	2.870(2)	Mean	2.276
Ba—O3'	2.901(2) × 2		
Ba—O1'	2.909(2) × 2		
Mean	2.848		
L—O2	1.703(3)	M3—F	2.003(4) × 2
L—O1	1.977(2) × 2	M3—O5	2.063(2) × 4
L—O3	1.980(2) × 2	Mean	2.043
Mean	1.923		
M1—O2	2.267(3) × 2	Si—O5	1.603(2)
M1—O5	2.473(2) × 4	Si—O3	1.624(2)
Mean	2.404	Si—O1	1.627(2)
		Si—O4	1.669(1)
		Mean	1.631

L site — Ti with some Fe^{3+} , Nb, and Zr.

The ions F^- occupy the site at joint of M3 octahedron and two M2 octahedra.

Discussion

The lamprophyllite group is referred to the bafertisite mero-pleistotype series that in turn belongs to the heterophyllosilicate family (Ferraris *et al.*, 2001; Ferraris, Gula, 2005). The structures of all these minerals are based on triple-layered packet HOH, where O sheet consists of octahedra MO_6 ($M = \text{Ti, Nb, Fe}^{2+}, \text{Mn}^{2+}, \text{Na}$ and other) and H is heteropolyhedral sheet composed of tetrahedra SiO_4 (forming groups Si_2O_7) and various six- or five-coordinated high-force-strength cations (Ti, Nb, Zr, Fe^{3+}) (L-cations). The general formula of the bafertisite series minerals is $\text{A}_2\{\text{M}_4[\text{L}_2\text{X}_{2+p}(\text{Si}_2\text{O}_7)_2]\text{Y}_2\}\text{W}$, where A are cations with low-force-strength characteristics (as a rule, cations of alkali and alkali-earth elements with coordination numbers higher than 6); M are cations of the octahedral sheet, X and Y are O^{2-} , F^- or OH^- ; W are water molecules or polyatomic anions (PO_4^{3-} , SO_4^{2-} , CO_3^{2-}), $p = 0-2$.

In the lamprophyllite group members, W-constituents are absent, $p = 0$, the site Y is occupied with O^{2-} , and L-cations (Fe^{3+} in ericssonite and ferroericssonite or Ti^{4+} in the other members of the group) have the coordination number 5. The general crystal chemical formula of these minerals is $^{[10-11]}\text{A}_2[^{[6]}\text{M1}^{[6]}\text{M2}_2^{[6]}\text{M3} \text{X2}] [^{[5]}\text{L}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$. In Ti-dominant (with Ti at site L) members of the group, the octahedra M1 and M2 are predominantly occupied with Na. Monoclinic minerals (space group $\text{C2}/m$, the polytype 2M) are predominant among studied lamprophyllite-group members. Orthorhombic varieties (space group Pnmm , the polytype 2O), with the unit cell dimensions varying in the ranges $a = 19.1-20.3$, $b = 7.0-7.1$, $c = 5.3-5.4\text{Å}$ are known for lamprophyllite, barytolamprophyllite, and ericssonite (Moore, 1971; Matsubara, 1980; Krivovichev *et al.*, 2003; Sokolova, Hawthorne, 2008).

The predominance of Fe^{3+} in the small octahedron M3 is the major difference of emmerichite. In the other members of this group, this site is predominated by Ti (in lamprophyllite, barytolamprophyllite, and nabalamprophyllite), Mg (in lileyite), Mn^{2+} (in ericssonite), or Fe^{2+} (in ferroericssonite). In addition to the valence of Fe, emmerichite differs from ferroericssonite in the predominance of Ti in the L site and two Na-dominated octa-

Table 4. Bond valence calculations for emmerichite

Site	Ba	L	M1	M2	M3	Si	V _i
O1	0.28 ^{(x2)↓}	0.65 ^{(x2)↓}				1.00 ^{↓→}	1.93
	0.28 [→]	0.65 [→]					
O2		1.37 [↓]	0.27 ^{(x2)↓}	0.19 ^{(x2)↓→}			2.02
		1.37 [→]	0.27 [→]				
O3	0.28 ^{(x2)↓} + 0.19 [↓]	0.64 ^{(x2)↓}				1.00 ^{↓→}	2.11
	(0.28 + 0.19) [→]	0.64 [→]					
O4	(0.21 + 0.21) [↓]					0.89 [↓]	2.20
	0.21 ^{(x2)→}					0.89 ^{(x2)→}	
O5			0.17 ^{(x4)↓}	0.24 ^{(x2)↓}	0.40 ^{(x4)↓}	1.06 ^{↓→}	1.87
			0.17 [→]	0.24 [→]	0.40 [→]		
F				0.21 ^{(x2)↓→}	0.48 ^{(x2)↓}		0.90
					0.48 [→]		
V _i	1.73	3.95	1.22	1.28	2.56*	3.89	

Notes: * – The value V_i for M3 site of 2.56 was calculated for the F site occupied by F. In case of O in the F site, corresponding value of V_i = 2.56.

Table 5. Comparative data for emmerichite and other monoclinic titanium lamprophyllite-group minerals

Mineral	Emmerichite	Lileyite	Barytolamprophyllite	Lamprophyllite	Nabalamprophyllite
Formula	Ba ₂ Na(Na,Fe ²⁺) ₂ (Fe ³⁺ ,Mg)Ti ₂ (Si ₂ O ₇) ₂ O ₂ F ₂	Ba ₂ (Na,Fe ²⁺ ,Ca) ₃ (Mg,Fe ³⁺)Ti ₂ (Si ₂ O ₇) ₂ O ₂ F ₂	Ba ₂ (Na,Fe ²⁺ ,Mn) ₃ Ti ₃ (Si ₂ O ₇) ₂ O ₂ (O,OH,F) ₂	Sr ₂ (Na,Fe ²⁺ ,Mn) ₃ Ti ₃ (Si ₂ O ₇) ₂ O ₂ (O,OH,F) ₂	Ba(Na,Ba)Na ₃ Ti ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂
Space group	C2/m	C2/m	C2/m	C2/m	P2/m
a, Å	19.960	19.905	19.833	19.431	19.741
b, Å	7.098	7.098	7.089	7.086	7.105
c, Å	5.407	5.405	5.393	5.392	5.408
β, °	96.37	96.35	96.66	96.75	96.67
Z	2	2	2	2	2
Strong lines of the X-ray powder-diffraction pattern:	9.97 (55)	3.749 (45)	3.447 (70)	3.73 (40)	9.87 (96)
d, Å (I %)	3.461 (65)	3.464 (76)	3.294 (50)	3.43 (55)	3.75 (65)
	3.312 (40)	2.792 (100)	2.801 (100)	3.27 (40)	3.45 (90)
	2.792 (100)	2.672 (54)	2.153 (90)	2.874 (40)	3.275 (78)
	2.670 (56)	2.624 (43)	1.790 (70)	2.773 (100)	3.040 (41)
	2.629 (45)	2.140 (52)	1.601 (80)	2.130 (45)	2.797 (100)
	2.140 (57)		1.482 (90)	1.477 (45)	2.610 (43)
Optical data:					
α	1.725	1.718	1.735-1.743	1.733-1.751	1.750
β	1.728	1.735	1.741-1.754	1.740-1.760	1.755
γ	1.759	1.755	1.767-1.778	1.769-1.781	1.799
Optical sign, 2V_v	+30	+86	+30 – +45	+21 – +43	+40
Density, g/cm³	3.864	3.776	3.62–3.66	3.44–3.53	3.65
References	This study	Chukanov et al., 2012 ₁	The-Chung Peng, Chien-Hung Chang, 1965; Zhizhong Peng et al., 1984; Rastsvetaeva et al., 1995; Feklichev, 1989	Vlasov et al., 1959; Safyanov et al., 1983; Rastsvetaeva et al., 1990; Feklichev, 1989	Chukanov et al., 2004

hedral sites. The crystal chemical formula of emmerichite is [Ba,Sr,K]₂[(Na,Ca)(Na,Fe²⁺,Mn²⁺,Mg)₂(Fe³⁺,Mg)] [(Ti,Fe³⁺,Nb,Zr)₂(Si₂O₇)₂O₂](F,O)₂ (interblock cations, cations of the O sheet, and the H sheet are in brackets).

The unit cell parameters for emmerichite and other monoclinic members of the lamprophyllite group are given in Table 5.

The chemical composition of phyllo- and heterophyllosilicates from pneumatolitic assemblages related to alkali basalt of Eifel – oxyphlogopite KMg₂Ti(Si₃AlO₁₀)O₂, schüllerite Ba₂Na(Mn²⁺,Ca)(Fe³⁺,Mg,Fe²⁺)₂Ti₂(Si₂O₇)₂O₂(F,O)₂, and lamprophyllite group members – are characterized by the absence of hydrogen distinguishing these minerals from their analogues (micas and lamprophyllite group

members) from agpaitic intrusive rocks and pegmatites. Low content of the OH groups is typical also for other primary minerals from the Eifel basalt (amphiboles, fluorapatite, and others). This is evidently caused by the combination of some genetic factors including degassing of magma, high temperature of crystallization and high fugacity of oxygen and fluorine (Chukanov *et al.*, 2008).

Acknowledgements

This study has been supported by the Russian Foundation for Basic Research (project no. 14-05-00190-a).

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NANOCRYSTALS OF NATIVE MOLYBDENUM, IRON AND TITANIUM WITHIN IMPACT GLASSES OF LUNAR REGOLITH

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This paper discusses the results of study of the impact glass fragments from the Mare Fecunditatis and Mare Crisium regolith samples brought on the Earth by the Soviet Automatic stations Luna-16 and Luna-24. Nano-inclusions of native molybdenum, iron and titanium were found in the samples with scanning and transmission electron microscopy (SEM, TEM). It is shown that these inclusions are single crystals. A natural high pressure native ω -titanium was identified for the first time. The composition and structure of glass matrix of the regolith samples indicates its extreme micro and nano heterogeneity. The probable formation mechanisms of the studied nanocrystals are discussed.

3 tables, 10 figures, 26 references.

Keywords: native molybdenum, native iron, native ω -titanium, nanophases, single crystals, impact glasses, lunar regolith, Mare Fecunditatis, Mare Crisium.

The main goal of the investigation of minerals from lunar regolith (average fine lunar matter) was determination of the composition and structure of microphases reflecting specific character of mineral-forming processes at high temperature and pressure gradient in oxygen-free and anhydrous atmosphere. The impact events determining chemical and physical properties of lunar regolith made a substantial contribution to the formation of these phases. However, large grains of native metals have not been found on the Moon yet. These are fine particles up to 150 μm in size (Fron del, 1975), that predetermined methods of our study.

Particularly, native molybdenum as thin films and spherical submicron grains was frequently found in the Mare Fecunditatis and Mare Crisium regolith samples studying with SEM (Bogatikov *et al.*, 2001; Mokhov *et al.*, 2007; Kartashov *et al.*, 2010).

Iron is the most abundant metal on the Moon; it occurs as oxidized and native species (Fron del, 1975). Irregular-shaped, ribbon-like, spherical, and drop-like particles of native iron are the most abundant in lunar regolith (Mokhov *et al.*, 2007).

Nonvalent iron, aluminum, silicon and titanium were identified with the X-ray photo electron spectroscopy studying condensate glass film coating the lunar regolith samples from the Mare Fecunditatis (Yakovlev *et al.*, 2009). However, these data only indirectly verify metallic titanium in lunar glass and do not provide reliable information on its structure.

Therefore, the aim of this study is investigation of structure and formation mechanisms of metal inclusions in lunar glasses.

Analytical techniques

Glass fragments of the regolith samples from the Mare Fecunditatis and Mare Crisium brought to the Earth by AS Luna-16 and Luna-24 were examined with transmission (TEM) and scanning (SEM) analytical electron microscopy using a JEM-2100 microscope equipped with an IETEM spectrometer INCA-250 and a JSM-5610LV scanning electron microscope equipped with an INCA-450 EDS.

Supporting of purity and prevention of contamination by foreign phases has been regarded in the preparation of fine-dispersed samples of lunar glasses for the SEM analysis. A conductive double-sided tape in whose composition only carbon and oxygen were detected (within detection limits of EDS) was stuck on ordinary aluminum tables. A tape-free surface of the table was coated with graphite glue to avoid a fluorescence of aluminum. Immediately after opening, regolith sample was spread as a thin layer on the inner side of the tape with removed protective film and the table with the prepared sample was enclosed in clear Petri dish and was placed in a special storage till the start of electron microscopic study. Thus, a contamination of sample by artifacts is eliminated as far as possible. Minerals and metals already

Table 1. Compositions of glasses and pyroxene (wt.%) in samples of studied lunar regolith

Analysis	1	2	3*	4	5	6	7	8
Na ₂ O	3.9±0.5	2.3±0.4	—	—	—	4.2±0.5	1.4±0.4	—
MgO	1.3±0.2	2.3±0.2	6.7±0.3	14.8±0.3	4.9±0.3	2.7±0.3	—	6.21±0.3
Al ₂ O ₃	7.3±0.3	24.5±0.5	18.0±0.4	—	13.0±0.4	22.8±0.5	25.6±0.6	13.6±0.4
SiO ₂	53.9±0.5	58.1±0.7	43.2±0.6	51.9±0.7	36.7±0.5	54.0±0.8	61.7±0.8	42.4±0.6
K ₂ O	—	—	—	—	0.3±0.2	3.7±0.6	—	—
CaO	5.8±0.2	5.2±0.3	14.6±0.4	8.2±0.3	17.4±0.4	—	11.3±0.4	14.4±0.4
TiO ₂	0.9±0.1	—	—	—	5.6±0.3	—	—	4.2±0.2
FeO	26.8±0.5	5.1±0.3	17.1±0.5	25.1±0.4	22.1±0.6	12.6±0.5	—	19.1±0.4
BaO	—	2.6±0.4	—	—	—	—	—	—

Notes: Total is normalized to 100%. *— Contents of Na₂O, K₂O, and Cl below 0.2 wt.%. Analysts A.V. Mokhov and T.A. Gornostaeva.

analyzed were prepared according to the procedure of Lapina and Mokhov (1995) for using as reference samples.

A possible contamination of the samples with foreign matter is the most dangerous in these studies and put in question these findings. It refers first of all to micro and nanoparticles, which could easily contaminate a sample. We confidently can state that the phases studied are not impurities only if they were coated with glass or shallowly sank into it. Frequently, these phases are sufficiently contrasted to be detected because back-scattered electrons are generated and drift out of the sample from the relatively great depth. To demonstrate that the particles are coated with glass layer an imaging in secondary electrons is used because these electrons drift out of the sample from quite shallow depth and allow obtaining information of the morphological features of the sample regardless its mean atomic weight.

Samples were prepared for TEM according to suspension method of Gritsaenko (1969). This method is the most common because it is very informative and simple. A glass fragment nearly hundred microns or larger in size was placed into clear test microtube. Then, the test tube with a piece of glass in few amount of distilled analytically pure water was placed into sonicator for disintegration. A sample crushed by ultrasound in water drop was placed on a special cooper grid with film of formovar and collodion and then was dried at 35°C in drying box.

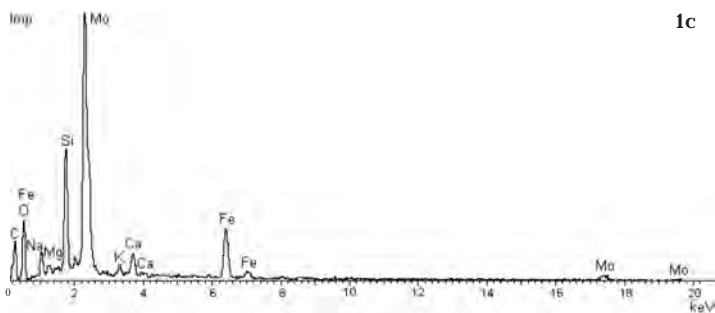
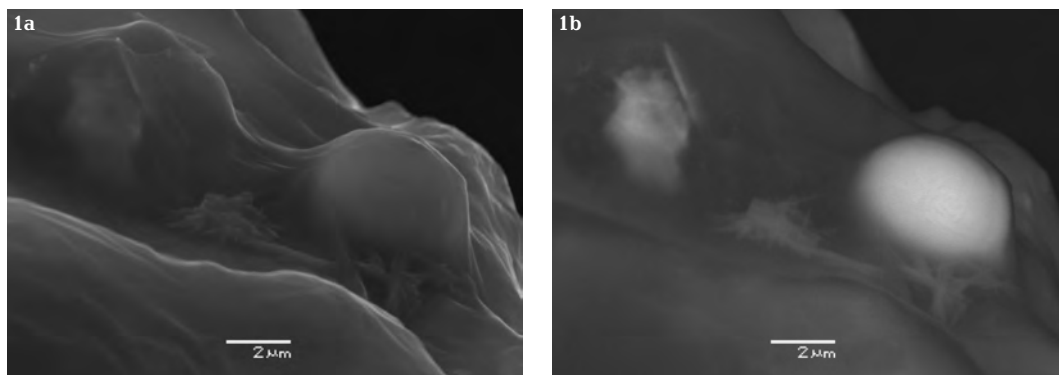
Results

As a result of the SEM study massive spherules of native molybdenum (Fig. 1) were identified in glass of the Mare Crisium regolith samples with average composition

given in Table 1 (an. 1). Secondary and back-scattered electron images (Figs. 1a, 1b) clearly show a glass coating that eliminates contamination of sample by man-made molybdenum. However, because of glass coating, the identified inclusions did not show electron backscattered diffraction (EBSD) patterns. These patterns (Fig. 2) supporting metallic state of molybdenum grains (Table 2) were obtained only after ion beam cutting of the glass coat.

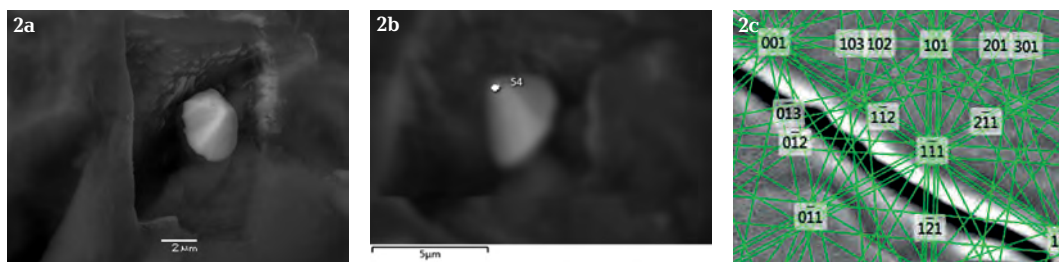
Nanocrystals of native molybdenum (Fig. 3), which occur as chains to form tri-chord structures (Fig. 4) in glass or as massive segregations also in glass (Fig. 5) were identified as a result of the TEM study. In the first case, the microdiffraction patterns show low intensive discrete-ring reflections of native molybdenum, whereas in the second case, the microdiffraction patterns are absent because of great thickness of the samples. The composition of glass is close to that determined with SEM (Table 1, an. 1), however, the higher content of silica, much lower concentration of Fe, and small amount of Ba were measured (Table 1, an. 2).

Numerous micro- and nano-inclusions of native iron were found in the Mare Fecunditatis glass samples with SEM and TEM. Matrix glass containing these inclusions inhomogeneous even in scanning electron microscope is moreover inhomogeneous in transmission electron microscope with the composition significantly different from that determined with SEM (Table 1, an. 3). Numerous fragments of this glass contain both spherical nanoparticles and larger irregular-shaped particles. Point TEM analysis showed that these larger irregular-shaped microinclusions are different in composition corresponding to the rock-forming silicates (plagioclase, pyroxene, olivine), whereas nano-in-

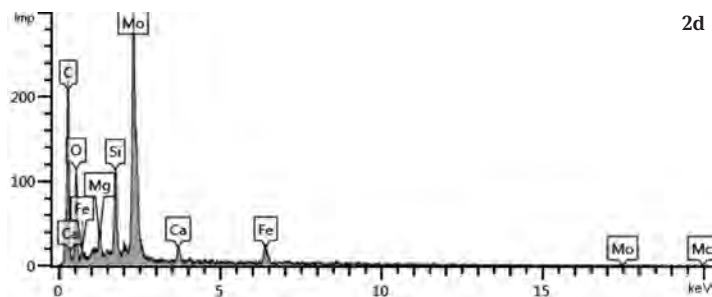


1c Fig. 1. Native molybdenum coated with film of glass.

(a) Secondary electron image,
(b) backscattered electron image,
(c) energy-dispersive spectrum.



2d Fig. 2. A particle of native molybdenum. (a) After ion beam etching; (b) analyzed point; (c) electron backscattered diffraction patterns; (d) energy-dispersive spectrum (contains glass elements peaks induced by fluorescence).



clusions are enriched only in Fe in comparison with glass.

Figure 6 shows the glass fragment containing large irregular-shaped inclusion whose composition given in Table 1 (an. 4) corresponds to pigeonite $(Mg_{0.85}Fe_{0.81}Ca_{0.34})_2(Si_2O_6)$. In addition, many spherical nano-inclusions are shown in Fig. 6. The elemental distribution patterns within one of the glass frag-

ments containing the largest inclusions of this type were obtained to determine the exact composition of these globules. The patterns obtained verified an absence of oxygen and appreciable contents of other elements than iron in globules. The microdiffraction pattern registered for such globule contained weak reflections 110 of cubic native α -iron with a of 0.28 nm and space group $Im\bar{3}m$.

High resolution imaging revealed a periodicity of structure with step of 0.2 nm that corresponds to d -spacing characteristic of this type reflections (Fig. 7).

The irregular-shaped inclusions of native titanium (Fig. 8a) of a few to a few tens nanometers in size were found in a glass fragment similar to titanite in composition (Table 1, an. 5). The microdiffraction patterns confirmed that native titanium is high-pressure hexagonal ω -modification with a 0.462 nm and space group $P6/mmm$. Fig. 8b shows the microdiffraction pattern of this phase in plane (001) . The diffraction modeling of the structure of the native titanium ω -modification using the eMap software package supported the identity of model obtained and microdiffraction pattern.

High resolution imaging has identified $hk0$ type planes of native titanium with 2D picture with d -spacing 0.23 nm corresponding to 11.0 reflections being recorded in one case. In the other cases, only 1D structure has been displayed because of inexact match of structural planes with transmitting electron beam.

It should be noted that glass fragments in the Mare Fecunditatis and Mare Crisium

Table 2. Result of automatic identification of phase according to the EBSD data based on Inorganic Crystal Structure Database

Name	Mo
Symmetry	Cubic
Laue class	11
Space group	$Im-3m$ (229)
Unit cell	
a	3.15 Å
b	3.15 Å
c	3.15 Å
α	90.00°
β	90.00°
γ	90.00°

samples are remarkably variable in compositions as it follows from the high resolution measurements. It is the most pronounced in TEM with resolution of 5 to 10 nm. Glasses close in composition to silicate phases are frequent. For example, the glass fragments with the compositions satisfactorily recalculated on formulas of sodium feldspar, olivine and pyroxenes were found. Also a few fragments of Si-rich glasses containing only 2–7 wt.% Al_2O_3 in addition to SiO_2 . Heterogeneity of glasses was presented even at nanoscale level.

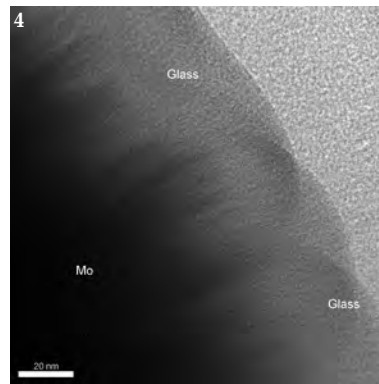
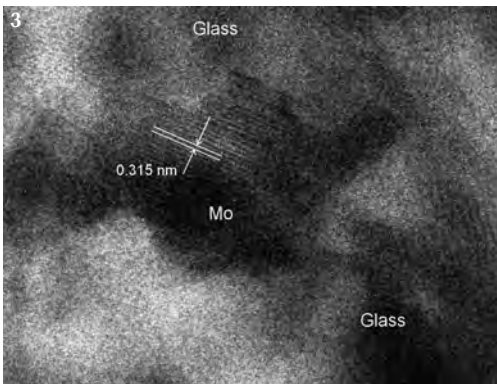


Fig. 3. Transmission electron microscopy image of native molybdenum nanocrystal in glass.

Fig. 4. Transmission electron microscopy image of native molybdenum coated with glass layer.

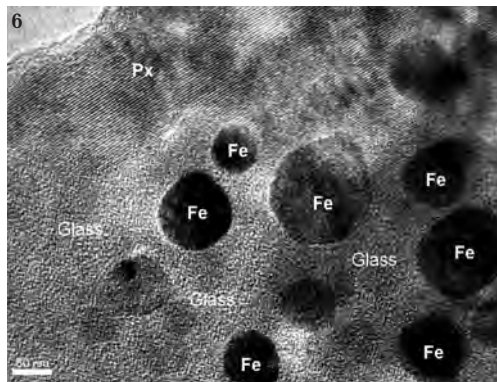
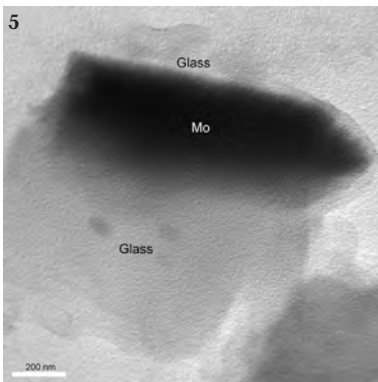


Fig. 5. Transmission electron microscopy image of aggregate of native molybdenum coated with glass layer.

Fig. 6. Transmission electron microscopy image of glass of the AS "Luna-16" regolith with inclusions of iron spherules and pyroxene.

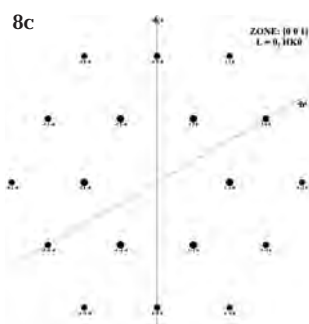
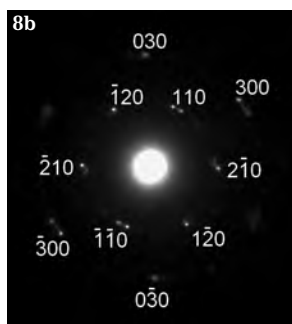
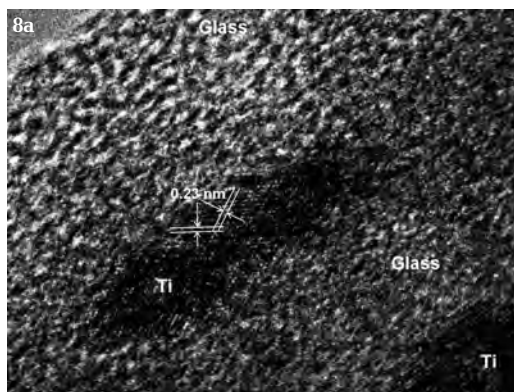
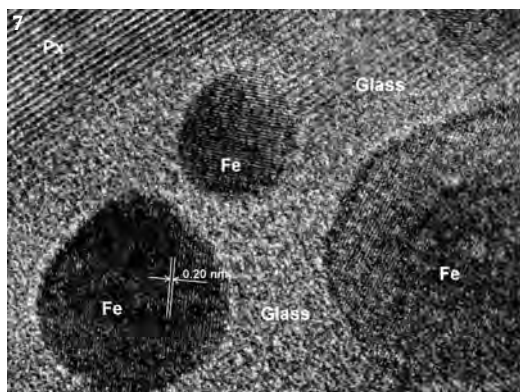


Fig. 7. Transmission electron microscopy image of single crystal spherules of native iron.

Fig. 8. Single crystal grains of native ω -Ti in pyroxene glass.

(a) Transmission electron microscopy image of separate nanocrystal of native ω -Ti; (b) its microdiffraction pattern; (c) model developed in eMap.

For example the structure of pyroxene composition glass is heterogeneous in size and distribution of structural clusters. The fragment of glass tough and homogeneous in the core is characterized by larger disordered clusters in the rim. The composition of this external unconsolidated glass film (Table 1, an. 6) substantially differs from that of matrix (Table 1, an. 5).

Thin glass layer of 5 to 30 nm thick different in composition from matrix is frequently observed on the TEM images. It coats as hardly distinguishable layer both mineral phases of different composition and other glasses. Native molybdenum in such glass is shown in Fig. 4 and a thin glass layer of other density (Table 1, an. 7) coating massive glass (Table 1, an. 8) similar to that shown in Fig. 8a is seen in Fig. 9.

Coating glasses are variable in composition that differs from that of matrix both quantitative and qualitative. In particular, barium traces were measured in glass coating native molybdenum and small sodium peaks were recorded in glass coating native iron and titanium.

Of special note are high resolution images of glass coating native iron, molybdenum and titanium demonstrating single crystal and nano-sized character of their grains.

Discussion

It should be noted that native molybdenum has been previously found with SEM by Bogatkov *et al.* (2001) and Kartashov *et al.* (2010), but no any structure characteristics were obtained. Currently, as a result of the EBSD and TEM study, not only native state of molybdenum was confirmed, but its formation as aggregates of nano-sized single crystals was established. In other words, the distinction of lunar molybdenum crystallized in the cubic system from hexamolybdenum phase discovered in C chondrites (Ma *et al.*, 2009) not only in composition, but in structure was confirmed. Native molybdenum was found on the Earth as an inclusion in carbonado (Silaev *et al.*, 2004) although no structural data were given.

As a result of previous TEM study of lunar glasses, nanoinclusions of iron ranging from a few to a few hundreds nm in size were found (James *et al.*, 2002). These iron-bearing inclusions were interpreted as native iron, but reliable evidences about presence of these particles as metallic species were not reported. We did not find any information on the crystallinity degree of these grains (Keller, McKay, 1993; Thompson, Christoffersen, 2010). However, now we have established

monocrystalline character of these nanograins.

Nonvalent titanium has been identified in glasses of the Moon studied with X-ray photoelectronic spectroscopy (Dickov *et al.*, 1977; Yakovlev *et al.*, 2009). Native titanium was found on the Earth many times. For the first time it was mentioned by Trunilina *et al.* (1988), who reported the millimeter-size lamellae of native titanium in crushed leucogranite samples from the Bezhymyanni Pluton in the northeastern Yakutia. Then titanium as micrograins in association with other native metals, carbides and carbons was found in fumarole exhalations of The Great Tolbachik Fissure Eruption occurred in 1975 (Glavatskikh and Gorshkov, 1992). In the last case, its structural parameters were determined with electron microdiffraction. This proved an existence of titanium as α -species and polycrystalline nature of found aggregate. The resolution of used transmission electron microscope was insufficient for determination of size and shape of single crystals in these aggregates.

Finally, native titanium was approved as mineral species on material from the Luobusha chromite massif in Tibet (Fang *et al.*, 2013), where it is associated with native metals, intermetallic compounds, alloys, diamonds, and various carbides and silicides. Associations and direct intergrowths of titanium with the high-pressure phases allowed estimating pressure range of 2.8 to 4 GPa under which it can be formed. Nevertheless, a common low-pressure α -titanium with $P6_3/mmc$ space group was found there (Fang *et al.*, 2013).

We identified natural high-pressure ω -titanium polymorph with $P6/mmc$ space group for the first time. According to Jamieson (1963), α -titanium transits to ω -species at 6 GPa.

How do we explain the presence α -titanium the high-pressure mantle assemblage in Tibet? The answer is found in the same paper by Jamieson (1963). Annealing of ω -titanium at 110°C for 17 h causes transition of ω - to α -modification. Obviously, initially high pressure ω -titanium transited to α -modification as a result of retrograde metamorphism of host chromitite in the upper crust. At the same time, lunar ω -titanium resulted from high-energy impact event (possibly during the formation of diaplectic glass after titanite crystal) was quickly quenched owing to rapidity of an impact process. Indeed, colossal PT values exists only during

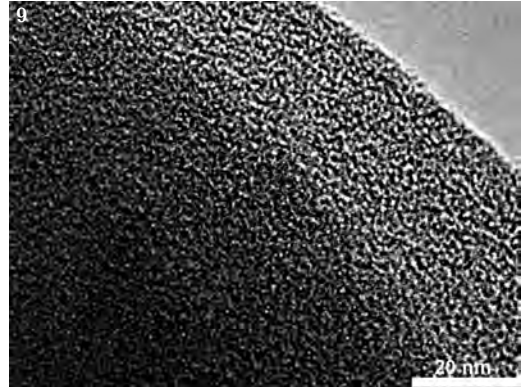


Fig. 9. Transmission electron microscopy image of glass coated with thin layer of another glass.

microseconds at impact. Apparently, the sample studied was not annealed after being formed and quenched and it was preserved in initial state in glass to recent time.

In general, the data obtained indicate a significant heterogeneity of low-Si matrix glasses. Frikh-Khar *et al.* (1988) were the first who noticed heterogeneity of lunar glasses at submicron level studying with scanning electron microscope. The compositional heterogeneity of glasses from regolith samples collected in area of AS Luna-16 landing have been earlier detected by Dikov *et al.* (1998, 2002) using layer by layer analysis performed with X-ray photoelectron spectroscopy. As a result, variable compositions both between layers and within individual layer in lateral direction were established. The Na-rich nano-size coarse-cluster layer of glass could be explained by vapor condensation out of impact cloud. The fragments of more refractory high-Si glass consolidating before low-Si glass are emplaced into liquid low-Si matrix

Table 3. Minimum value (min), median (Me), arithmetical mean (m), maximum value (max) of component contents in glasses

Components, wt.%	min	Me	m	max	n*
SiO ₂	30.71	54.39	63.84	97.67	78
TiO ₂	0.05	0.68	0.84	5.86	34
Al ₂ O ₃	0.96	4.50	8.88	34.08	77
FeO	0.06	13.37	12.81	35.35	55
MgO	0.05	5.39	6.63	32.40	61
CaO	0.15	6.45	7.14	25.83	73
Na ₂ O	0.09	1.62	3.78	25.41	55
K ₂ O	0.13	0.49	1.53	8.27	42

Notes: * – 78 observations in total, n – denotes number of observations with the component content higher above detection limit.

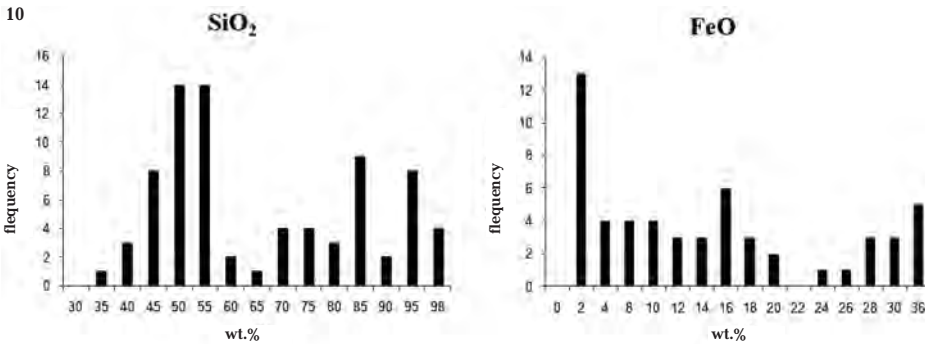


Fig. 10. Histograms of SiO₂ and FeO contents obtained studying lunar regolith glasses with high resolution.

as solids. Microfragments of diaplectic glasses are also emplaced in it. In addition, nanoparticles of some mineral (crystalline) phases were emplaced into studied low-Si glass. Thus, a few versions regard to the origin of native iron inclusions in glass are suggested. Two mechanisms are believed to be major.

According to the first, the drops of native iron resulted from impact and immediately crystallized were emplaced into liquid glass. This mechanism is supported by the presence of large pyroxene single crystal probably raised up from the surface as a result of explosion and trapped by the glass. Apparently, this mechanism explains the presence of molybdenum nanocrystals and other mineral phases in glass (Mokhov *et al.*, 2007; Kartashov *et al.*, 2010; Mokhov *et al.*, 2011; Gornostaeva *et al.*, 2012).

According to the second mechanism that is very popular among researchers, Fe⁰ is resulted from impact melting and reduction of silicate Fe²⁺ as affected hydrogen implanted by solar wind (Housley *et al.*, 1973; Wang *et al.*, 2012).

Massive (exceeding a few unit cells in volume) particles of native iron are thought to be unlikely resulted from disproportionate reaction in impact cloud (Yakovlev *et al.*, 2009).

The data of high-resolution elemental analysis obtained with SEM and TEM were processed to estimate a degree of homogeneity of glass. Only values higher than detection limits were taken into account; therefore, numbers of element measurements are different. Results are given in Table 3 as follows: minimum value, median, arithmetical mean (AM), maximum value, and number of observations. Dispersion between minimum and maximum concentration along with differences in median values and arithmetical means indicate heterogeneity of the ma-

terial. Histograms demonstrate this vividly. For example, Fig. 10 shows histograms of SiO₂ and FeO contents which exceed 60% of in the chemical composition of the glasses examined. Multimodal distribution of these constituents indicates quite obviously heterogeneity of the material studied.

Of special note is the isolating role of glass or more likely condensate film coating nearly all mineral microparticles with nanosize layer in the studied regolith samples and preventing native phases from oxidation and interaction with other phases.

Conclusions

1. Aforementioned native metals are nanocrystals or aggregates of nanocrystals implying short period of crystallization. This corresponds conditions of impact events on the Moon.

2. The presence of glasses dramatically different in composition, physical properties (particularly in melt temperature and fugacity of constituents), and structure of their aggregates in the same regolith particle allows to assume significant difference in the energy range of impact events, which caused their formation. In other words, regolith samples studied are a product of multiple impacts with different energy, i.e. with different masses and velocities of impactors.

3. Both native metals and many other mineral phases in the samples studied are usually coated with thin sometimes nano-thick condensate films of glass. It supports an authenticity of these inclusions and explains the inoxidability of lunar native iron (probably also other minerals) in the Earth environment conditions that is alternative to explanation of inoxidability caused by long bombardment by protons of solar wind (Vinogradov *et al.*, 1972; Vinogradov *et al.*, 1979).

Acknowledgements

This study was supported by the Russian Foundation for Basic Research (project no. 12-05-00624a).

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NEW DATA ON BETALOMONOSOVITE

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The new data on compositional variations, refined crystal structure, thermal properties, and formation conditions of betalomonosovite are discussed. The results obtained assert that betalomonosovite differs from lomonosovite with which the former is identified. It has individual chemical and structural features, and distinct geological and genetic setting, and should be rehabilitated as individual mineral species.

3 tables, 6 figures, 58 references.

Keywords: lomonosovite, betalomonosovite, murmanite, crystal structure, Khibiny massif, melteigite-urtite, juvite, rischorrite, hypergpaite minerals assemblage.

The aim of this study is comparison of new data on betalomonosovite, $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{O},\text{F})_4 \cdot \text{Na}_2\text{H}_4(\text{PO}_4)_2$ results of investigation of lomonosovite $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{O},\text{F})_4 \cdot \text{Na}_6(\text{PO}_4)_2$, with which betalomonosovite is identified according to recommendation of the Commission on new Minerals and Mineral Names International Mineralogical Association in 1988, and those of murmanite $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4 \cdot (\text{H}_2\text{O})_4$ as final product of supergene alteration of lomonosovite, with which betalomonosovite is unreasonably attributed to the same solid solution series as intermediate species of similar alteration. We do not discuss other lomonosovite group minerals: vuonnemite and epistolite, Nb analogs of lomonosovite and murmanite, respectively, and quadruphite, sobolevite, and polyphite, Ca- and Mn-rich analogs of lomonosovite, although they are end-members of probable solid solution series for isomorphic admixtures typical of betalomonosovite and could be formed in similar geological environment.

Discovery

In 1890, Wilhelm Ramsay described new hydrous niobo-titano-silicate, mineral no. 3 (Ramsay, 1890) from the Lovozero tundras. In 1923, members of the Fersman expedition found this mineral in the same district and described it as violophillite. After detailed examination, Gutkova (1930) renamed it to murmanite with the refined composition $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{18} \cdot 4\text{H}_2\text{O}$ (Minerals..., 1937). Lomonosovite, anhydrous analog of murmanite, discovered from the same massif by Gerasimovsky

(1950) was studied in detail by Es'kova (1976), Vlasov *et al.* (1959), and Semenov *et al.* (1961). In contrast to murmanite, this mineral contained P and was anhydrous $\text{Na}_4\text{Ti}_4\text{Si}_4(\text{O},\text{F})_{18} \cdot 2\text{Na}_3\text{PO}_4$. In Khibiny, Dorfman (1962) found lomonosovite for the first time in the district of apatite deposits.

Betalomonosovite discussed in this article, was found and described as mineral no. 2 in 1938 by Gerasimovsky, but its detailed examination was started in 1960s (Gerasimovsky and Kazakova, 1962), when Semenov *et al.* (1961) found more representative material in the same district. In Khibiny, betalomonosovite was found at the Rasvumchorr deposit in 1958 (Sokolova, 1961; Sokolova *et al.*, 1971₂). In contrast to the previous findings, this mineral contained P and significant amount of water; betalomonosovite¹ was described by the following formulae: $\text{Na}_4\text{Ti}_4\text{Si}_4(\text{O},\text{F})_{18} \cdot (\text{Na},\text{H})_6(\text{PO}_4)_2$, $\text{Na}_4\text{Ti}_4\text{Si}_4(\text{O},\text{F})_{18} \cdot \text{Na}_2\text{HPO}_4 \cdot \text{NaH}_2\text{PO}_4$ or $\text{Na}_4\text{Ti}_4\text{Si}_4(\text{O},\text{F})_{18} \cdot \text{Na}_3[\text{PO}_4(\text{OH})\text{PO}_2(\text{OH})_2]$. To date, it is reasonably chemical, structural, and geological characterized in the context of its nature, abundance in alkaline rocks of agpaite nepheline syenite massifs and formation conditions to regard it as individual mineral species. Nevertheless, it was missinlcuded by CNMMN IMA into the list of discredited minerals (Nickel and Mandarino, 1988) that hampers its further detailed study. This forced us to carry out the new measurement of the chemical composition and crystal structure of betalomonosovite, as well as, its genetic relationship with lomonosovite and murmanite to additionally argue the reinstatement of this term.

¹ – Many researchers assumed that this name is poor because betalomonosovite is not structural modification of lomonosovite, i.e., β -species (β -lomonosovite), otherwise, term α -lomonosovite should be introduced.

Geological setting and formation conditions of murmanite, lomonosovite, and betalomonosovite

Murmanite. Murmanite is abundant accessory mineral of some peralkaline leucocratic rocks and hosted pegmatites in the Lovozero tundras. It was found at Mts. Punkaruai, Suoluai, Ninchurt, and Mannepahk; cirques Rasklak, Sengischorr, and Angvundasschorr; and in the Chinglusuai, Motchisuai, and Muruai valleys (Minerals..., 1937). According to Bussen and Sakharov (1972) referring to Gutkova (1930) and Es'kova (1959), it occurs as lenticular clusters within layers I-1 and II-2 hosted in juvite, foyaite, and urtite of the differentiated lujavrite-foyaite-urtite complex (complex III); this mineral is common in leucocratic varieties of lujavrite complex (complex IV) where it forms phenocrysts in near-contact porphyry lujavrite (tinguaite) and always occurs in porphyry murmanite lujavrite (complex V). Through all rocks, murmanite is observed with lomonosovite typically associated with apgaitic minerals: K, Na feldspar, nepheline, sodalite, aegirine, lamprophyllite, and eudialyte. Pegmatite with murmanite and lomonosovite were also hosted in porphyritic and poikilitic nepheline-sodalite syenite and tavite (complex II) (Minerals..., 1937).

In contrast to Lovozero, in Khibiny, negligible amount of altered murmanite was found only on the surface (Gutkova, 1930; Kupletsky, 1930; 1932; Minerals..., 1937; Dorfman, 1962; Tikhonenkov, 1963). Fresh murmanite was identified in mines at the Rasvumchorr, Kukisvumchorr, and Yukspor apatite deposits in pegmatites hosted in coarse-grained urtite and rischorrite hosting ore sequence, as well as, in melteigite of the upper contact zone, where it replaces lomonosovite lamellae (Sokolova, 1965; Sokolova *et al.*, 1973). The freshest pinkish white fine-flake murmanite with nacreous luster that could be assumed as newly formed phase was found as thin (up to 1 mm in thickness) stringer cutting massive urtite at the Rasvumchorr deposit (Mineralogy..., 1978).

Murmanite (associated with lomonosovite) was found in the same situation from apgaitic rocks of the Ilmaussaq massif, South Greenland (Karup-Mueller, 1983; 1986).

Lomonosovite. Es'kova (1959) studied in detail the geological setting of lomonosovite in the Lovozero massif taking into account the data of Gerasimovsky (1950) and Borneman-Starynkevich (1946). Lomonosovite and mur-

manite were established to be common in the same rocks: leucocratic varieties of rocks from the differentiated complex (III) with greater amount in foyaite than urtite and lujavrite; leucocratic lujavrite of the lujavrite complex (IV), sodalite varieties of poikilitic nepheline-sodalite syenite (II), and pegmatites hosted in these rocks. Fresh lomonosovite was observed in drill core below 250–300 m, whereas at the depth of 100–200 m below surface it was followed by the yellow and violet-pink variety; at the surface murmanite is pink. Relics of altered lomonosovite retaining morphology and optical orientation were observed everywhere in murmanite. In other words, it was proved by direct methods that murmanite is secondary after lomonosovite.

Experiments in Na and P desalination from lomonosovite using hot and cold distilled water performed by Gerasimovsky and Borneman-Starynkevich (Borneman-Starynkevich, 1946) and specified by Zabavnikova (1967) and Sokolova *et al.* (1973) using chemical and thermal analysis, and X-ray diffraction supported the probable formation of murmanite by this manner. It was established that pink-lilac color of murmanite with characteristic absorption bands at 12650, 18850, and 20600 cm^{-1} is caused by Mn^{3+} (Platonov, 1976) that is also consistent with oxidative environment in murmanite formation.

By the further investigations of Khomyakov (1990), it has become clear that in addition to the lomonosovite – murmanite pair, there are some primary minerals, which are transformed to the secondary species due to Na desalination and hydration as a result of sharply evolved alkalinity of mineral-forming medium; these minerals common close to surface as rule are: vuonnemite, $\text{Na}_{11}\text{TiNb}_2\text{Si}_4\text{P}_2\text{O}_{25}\text{F} \rightarrow$ epistolite, $\text{Na}_5\text{TiNb}_2\text{Si}_4\text{O}_{17}\text{F}\cdot 4\text{H}_2\text{O}$, parakeldyshite, $\text{Na}_2\text{ZrSi}_2\text{O}_7 \rightarrow$ keldyshite, $\text{Na}_3\text{HZr}_2(\text{Si}_2\text{O}_7)_2$, zirsinalite, $\text{Na}_6\text{CaZrSi}_6\text{O}_{18} \rightarrow$ lovozerite, $\text{Na}_3\text{CaZrSi}_6\text{O}_{15}(\text{OH})_3$, kazakovite, $\text{Na}_6\text{MnTiSi}_6\text{O}_{18} \rightarrow$ tisinallite, $\text{Na}_3\text{MnTiSi}_6\text{O}_{15}(\text{OH})_3$. They are regarded as individual mineral species or varieties with prefix "hydro", for example, delhayelite, $\text{K}_3\text{Na}_2\text{Ca}_2\text{Si}_7\text{AlO}_{19}(\text{F},\text{Cl})_2 \rightarrow$ hydrodelhayelite, $\text{KCaSi}_7\text{AlO}_{17}(\text{OH})_2\cdot 6\text{H}_2\text{O}$.

Cogenetic minerals typically associated with lomonosovite and murmanite are the same: microcline, nepheline, arfvedsonite, and sodalite. Lomonosovite inclusions are observed in albite, sodalite, cancrinite, ussingite, and natrolite; however these inclusions are transformed to murmanite only in natrolite. This not contradicts the pseudomorphous origin of murmanite and it is clear that meteoric

water or low-hydrothermal fluid is required to form it. Villiaumite is a guide mineral for lomonosovite.

In Khibiny, lomonosovite found in slightly different environment from that in Lovozero (Dorfman, 1962; Dudkin, 1959; Dudkin *et al.*, 1959; Sokolova *et al.*, 1971₁, 1973; Mineralogy... 1978) was identified in pegmatites cutting fine-grained trachitoid ijolite-urtite-melteigite, but in the first place in pegmatites hosted in massive coarse-grained urtite, apatite-nepheline sequence, and rischorrite at the Yukspor, Kukisvumchorr, and Rasvumchorr deposits. Lomonosovite is the most typical of aegirine-diopside – feldspar (microcline, adularia-like orthoclase) pegmatite, where it is associated with nepheline, lamprophyllite, delhayelite, and villiaumite. It is unknown from aegirine-diopside – nepheline pegmatites depleted in feldspar or feldspar-free. Lomonosovite is associated with microcline, aegirine, lamprophyllite, shcherbakovite, and lovozerite in pegmatites hosted in rischorrite at the top of apatite body in the Apatite cirque of Mt. Rasvumchorr.

These pegmatites are opened by mines at the significant depth below surface and deep-seated weathering profiles that favors to retaining fresh lomonosovite. It is murmanitized only along fractures cutting plates. However, lomonosovite plates occurred in dumps for a long period or in pegmatites opened in open pit are altered to the greater extent up to pinkish violet murmanite. In contrast to Lovozero, lomonosovite or replacing murmanite were found only in melteigite-urtite of the Central Arc of the Khibiny massif; they were not identified in nepheline syenite (foyaite, khibinite) rimming the arc.

Betalomonosovite. Betalomonosovite is less frequent mineral as compared with lomonosovite and murmanite. In the Lovozero massif, it was identified in association with microcline, aegirine, arfvedsonite, sodalite, zeolites, eudialyte, lorenzenite (ramsayite), lamprophyllite, neptunite, and steenstrupine in poikilitic nepheline-sodalite syenite and hosted pegmatites on the right bank of the Tulbn'yunuai river (Semenov *et al.*, 1961; Gerasimovsky and Kazakova, 1962). In the Khibiny massif, betalomonosovite was found in association with microcline, arfvedsonite, lamprophyllite, shcherbakovite, wadeite, lovozerite, and hisingerite as characteristic mineral of thin pegmatite veinlets cutting rischorrite at the top of apatite-nepheline body and in host rischorrite of the Apatite cirque at the Rasvumchorr deposit (Sokolova, 1961; Sokolova

et al., 1971₂). Sufficiently large well-shaped betalomonosovite crystals up to 5 mm in size measured with goniometer by T.A. Yakovlevskaya were recovered from gisengerite (Sokolova *et al.*, 1971₂; Mineralogy..., 1978).

Ageeva and Borutzky (1997) and Ageeva (1999, 2002) studied in detail the relationship between lomonosovite, betalomonosovite, and murmanite occurred as accessory minerals in the parental rocks of the Khibiny massif. It was established that accessory lomonosovite is common only in massive coarse-grained urtite, feldspar urtite, juvite, pyroxene rischorrite, and malignite, i.e., in the rocks of Central Arc of the massif and has different chemical composition and morphology. In urtite, it occurs as the largest (5–10 mm) grains enriched in Na, which are along with pyroxene, lamprophyllite, and aenigmatite forms poikilitic metacrysts enclosing euhedral nepheline grains (Fig. 1a). Clear smooth boundaries between lomonosovite and nepheline indicating simultaneous formation of these minerals attract attention. As K content increases from urtite to feldspar urtite, juvite, and rischorrite, lomonosovite is depleted in Na up to the composition typical of betalomonosovite and its forms resulted from orthoclase corrosion become more frequent (Fig. 1b).

In other words, as previously reported for pegmatites (Sokolova *et al.*, 1971₂), betalomonosovite is the most characteristic of rischorrite and could be resulted from the transformation of lomonosovite as primary mineral of massive coarse-grained urtite during rischorritization. It should be emphasized once more that in this process with partial removal of Na and dehydration, unlike murmanitization of lomonosovite, phosphorus is not removed and the Ti:Si:P ratio remains constant. Altered lomonosovite is observed in thin sections and attested by the electron microprobe measurement of Na and P. The alteration is usual in colorless crystal rims, whereas in the cores relict light brown-violet lomonosovite is retained (Fig. 1c).

Non-leached phosphorous indicates that this process differs from supergene or low-temperature hydrothermal transformation of lomonosovite to murmanite. The review of mineral assemblages containing betalomonosovite (K-rich adularia-like orthoclase, nepheline enriched in K, kalsilite, eudialyte enriched in K, wadeite, barium lamprophyllite, shcherbakovite) shows that it was most likely formed at one of the stages of melteigite-urtite fenitization under effect of fluids derived from nepheline syenite magma, i.e., K,Si metaso-

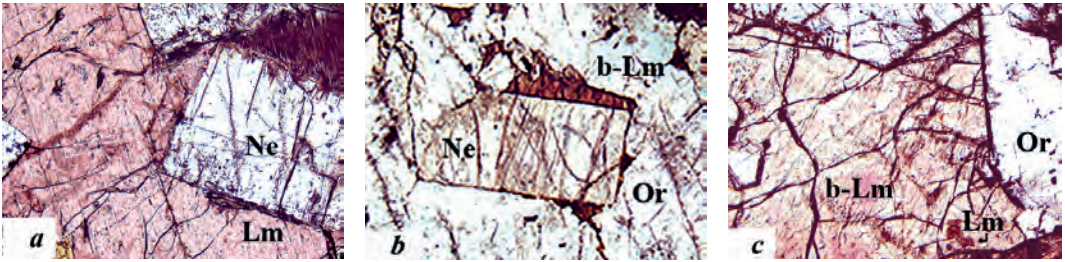


Fig. 1. Micrographs of accessory lomonosovite and betalomonosovite grains in the rocks of the urtite-juvite-rischorrite complex in the Khibiny massif: (a) poikilitic grains of lomonosovite (Lm) with euhedral nepheline phenocryst (Ne) in massive coarse-grained urtite, plane-polarized light, grain size 2×3 mm; (b) newly formed grain of betalomonosovite (b-Lm) corroded by adularia-like orthoclase (Or) on nepheline phenocryst (Ne) in rischorrite, plane-polarized light, grain size 0.4×0.8 mm; (c) lomonosovite relics (Lm) in betalomonosovite (b-Lm) in orthoclase form rischorrite, plane-polarized light, grain size 2×3 mm.

matic alteration affected primary relict rocks of Central Arc of the massif and causing the formation of high- and hyper-potassium rocks (juvite, rischorrite). The absence or low content of K in betalomonosovite is caused by that the incorporation of large K cations into the mineral crystal structure is impossible or strictly limited.

The metasomatic hypothesis of rischorrite (poikilitic nepheline syenite) origin in the Khibiny massif proposed and progressively advanced by Solodovnikova (1959), Tikhonenkov (1963), Rudenkov (1964), Titov *et al.* (1971), Mineralogy (1978), and Zotov (1989) is the most probable and elaborated because it is based on the additional results of detailed study of rock-forming and accessory minerals (Borutzky, 1988; Ageeva, 2002; Borutzky, 2010; 2012); however some details of this process remain unclear. Two conclusions are extremely important. In the first place, two types of newly formed minerals are formed: (1) replacement pseudomorphs with relics of primary minerals under conditions of non-equilibrium metasomatic process and (2) products of their recrystallization as metacrysts formed under equilibrium conditions. In the second place, the transformation of primary rocks of Central Arc of the massif urtite \rightarrow feldspar urtite \rightarrow juvite \rightarrow rischorrite started with fenetization (magmatic replacement) and as temperature and alkalinity of fluid decreased evolves to lower-temperature acidified aqueous solutions; Na minerals are replaced by Na,K minerals followed by K minerals to Na minerals again accompanied with dehydration.

Turning to betalomonosovite, we conclude that in addition to its pseudomorphs after lomonosovite forming at higher temperature than murmanite under effect of solution enriched in K in juvite, rischorrite, and pegmatites cutting these rocks, its newly formed more

perfect metacrysts overgrowing nepheline inclusions within adularia-orthoclase poikilitic crystals associated with potassium titanate and zirconosilicates: astrophyllite, wadeite, delhayelite, yuksporite, and phenacite (Fig. 2) are abundant. In contrast to pseudomorphous betalomonosovite, the crystals are colorless, optic angle decreases from $45-55^\circ$ to $27-36^\circ$ (Sokolova *et al.*, 1971₂; Ageeva, 1999). We believe that this undoubtedly indicates physicochemical equilibrium at the late stage of rischorritization, presence of individual stability field of betalomonosovite differed from that of lomonosovite that is basis for its definition as mineral species or equivalent variety.

Variation in chemical composition and typomorphism

The theoretical compositions (wt.%) are as follows: murmanite $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{18} \cdot 4\text{H}_2\text{O}$: $\text{Na}_2\text{O} - 16.40$, $\text{TiO}_2 - 42.28$, $\text{SiO}_2 - 31.79$, $\text{H}_2\text{O} - 9.53$, lomonosovite $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{18} \cdot 2\text{Na}_3\text{PO}_4$: $\text{Na}_2\text{O} - 30.63$, $\text{TiO}_2 - 31.59$, $\text{SiO}_2 - 23.75$, $\text{P}_2\text{O}_5 - 14.03$, betalomonosovite $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{18} \cdot \text{Na}_2\text{HPO}_4 \cdot \text{NaH}_2\text{PO}_4$: $\text{Na}_2\text{O} - 22.93$, $\text{TiO}_2 - 33.79$, $\text{SiO}_2 - 25.41$, $\text{P}_2\text{O}_5 - 15.01$, $\text{H}_2\text{O} - 2.86$, or $\text{Na}_4\text{Ti}_4\text{Si}_4\text{O}_{18} \cdot 2\text{NaH}_2\text{PO}_4$: $\text{Na}_2\text{O} - 20.02$, $\text{TiO}_2 - 34.64$, $\text{SiO}_2 - 26.05$, $\text{P}_2\text{O}_5 - 15.38$, $\text{H}_2\text{O} - 3.91$ (ignoring traces). The Si, Ti, P and O contents (O = 26 apfu) in lomonosovite and betalomonosovite are identical, whereas Na concentration decreases from lomonosovite to betalomonosovite as consistent with increasing content of H atoms from 10 Na at 0 H to 7 Na at 3 H apfu (first stage of transformation) to 6 Na at 4 H apfu (second stage). In murmanite with the same Si and Ti content, P is absent, H and O content is 8 and 22 apfu, respectively. Nb, Ta, Zr, Fe, Mn, Mg, Ca, K, and F are minor admixtures in these minerals.

The first researchers of the lomonosovite group minerals believed that lomonosovite

and murmanite are the products of magmatic crystallization and continuous solid solution series is between them, although murmanite containing 5.0 wt.% P_2O_5 was defined by Semenov *et al.* (1961) as betamurmanite. After pseudomorphic origin of murmanite being established, the presence of P in it was explained by relict lomonosovite. Betalomonosovite is behind this concept and variation in Na and H_2O content in its composition is determined by mineral-forming or mineral-retaining medium.

We have studied in detail using electron microprobe the chemical composition of accessory lomonosovite and betalomonosovite from the massive coarse-grained and feldspar urtite – juvite – pyroxene rischorrite selected from core of holes 1c, 2c, 4c, 1456, and 1494 drilled at the Rasvumchorr apatite deposit in Khibiny (Ageeva, 1992, 2002) and newly formed betalomonosovite from pegmatite vein hosted in rischorrite from the Apatite cirque of Mt. Rasvumchorr (specimen of M.N. Sokolova) previously examined with bulk chemical analysis (Sokolova *et al.*, 1971₂). The pegmatite sample was used for the crystal structure refinement. Electron microprobe data for lomonosovite and betalomonosovite are given in descending order of Na content in Table 1. The formulae are calculated on the basis of $Si + Al = 4$. The Na_2O content (wt.%) in the samples studied is substantially variable: 29.60–17.63 (Na 9.23–5.42 apfu; average 7.92 apfu) in feldspar urtite, 9.86–25.94 (9.69–7.99 apfu; 8.85 apfu) in juvite, and 28.98–13.57 (9.74–4.21 apfu; 6.96 apfu) in rischorrite, i.e., some features of the compositional distribution of the lomonosovite group minerals in the rocks of this complex are observed. However, overlapped compositions in the selected rock groups are established, for example, from the soda horizon within feldspar urtite (sample 61/2c, anal. 9, 38), in rischorrite (sample 50/2c, anal. 22, 35, 37, 39, 44 and sample 136/2c, anal. 5, 7, 25, 33) and malnigite (sample 502/1456, anal. 2, 19, 36). This testifies to different intensity of lomonosovite alteration, different rate of Na removal and hydration, and not achieved equilibrium during transformation of this rock complex. Accessory minerals with the most stable and closest to lomonosovite composition were observed in juvite, whereas in urtite and rischorrite, both lomonosovite (relict) and betalomonosovite (newly formed) are common, i.e., the formation of betalomonosovite corresponds to the early stage of feldspar alteration in the rocks of this complex.

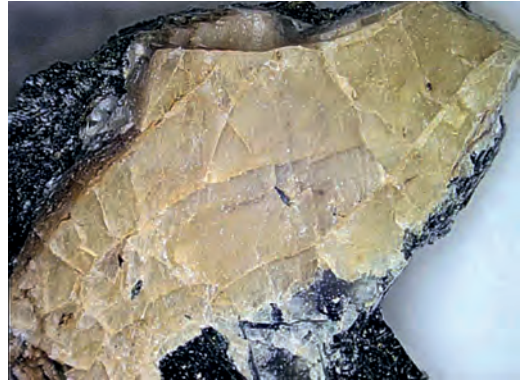


Fig. 2. Betalomonosovite from arfvedsonite-orthoclase pegmatite vein cutting rischorrite in the Apatite cirque of Mt. Rasvumchorr. Collection of M.N. Sokolova (no. 569). Grain size 3×5 mm.

The P_2O_5 content is weakly variable, wt.%: 15.15–11.59 (P 2.14–1.52 apfu; average 1.66 apfu) in feldspar urtite, 14.80–13.29 (2.07–1.79 apfu; 2.00) in juvite, and 16.95–11.91 (2.29–1.58 apfu; 1.96) in rischorrite. Assuming some uncertainty in determination of Na (elimination under beam) and P (Nb hampers its determination) we state the process differed from supergene mineralization. As is seen from Fig. 3, the lomonosovite and betalomonosovite compositions forms two different cluster close to theoretical compositions, but tend to the murmanite composition. However, parts of the same grain may correspond to both lomonosovite and betalomonosovite as illustrated by sample 87/1c from rischorrite shown as points 1 and 2 in Fig. 3 (Table 1, anal. 21, 29).

The elevated Nb_2O_5 content (wt.%) in some samples of both lomonosovite (3.76 – anal. 3, 5.18 – anal. 6, 9.00 – anal. 20) and betalomonosovite (3.82 – anal. 28) with low TiO_2

Fig. 3. A Na versus P plot for accessory minerals of the lomonosovite group in urtite-juvite-rischorrite complex in the Khibiny massif [(Lm) lomonosovite, (b-Lm) betalomonosovite, (Mmm) murmanite. (1) Core and (2) rim of the same grain (sample 87/1c) in rischorrite.

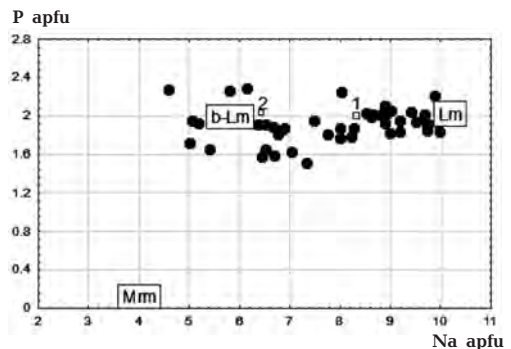


Table 1. Chemical composition (wt.%) of accessory lomonosovite and betalomonosovite in the rocks of the urtite-juvite-rischorrite complex (core samples from drill holes in the district of the Rasvumchorr apatite deposit)

No. anal.	Lomonosovite																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
No. sample	80/ 2c	502/ 1456	319/ 1456	275/ 1456	136/ 2c	477/ 1456	136/ 2c	502/ 1456	61/ 1456	309/ 1456	142/ 1c	448/ 1456	80/ 2c	306/ 1456	318/ 1456	306/ 1456	275/ 1456	76/ 1c	502/ 1456	101/ 1494	87/ 1c	50/ 2c	
SiO ₂	23.57	21.92	23.08	23.79	23.02	23.96	23.55	23.91	23.45	23.68	22.82	23.27	23.38	24.75	23.32	23.94	23.92	23.79	24.06	24.79	23.96	24.73	23.96
TiO ₂	27.36	28.92	22.55	25.84	29.87	23.42	30.18	26.32	27.10	27.21	26.60	24.97	24.27	26.94	27.84	25.02	25.85	27.77	25.32	20.73	25.80	28.90	28.90
P ₂ O ₅	13.05	14.25	12.94	14.23	13.80	13.88	12.98	14.46	13.66	14.39	13.70	14.34	14.23	14.80	13.81	14.48	13.95	14.20	14.80	15.15	13.08	16.04	16.04
Nb ₂ O ₅	0.95	1.89	3.76	1.85	0.54	5.18	0.00	1.92	0.00	0.56	0.76	0.76	1.10	0.97	0.76	3.15	0.00	0.63	0.93	9.00	0.70	0.70	0.30
Al ₂ O ₃	0.00	0.08	—	0.09	0.06	0.00	0.39	0.08	1.71	0.00	0.06	—	0.00	0.00	0.00	0.28	0.00	0.00	0.06	0.02	0.00	0.06	0.06
Fe ₂ O ₃	4.07	2.50	1.86	1.97	1.91	3.34	2.41	2.55	3.32	2.79	3.24	2.79	4.44	3.09	3.04	3.64	2.86	2.56	2.63	2.47	2.86	2.13	2.13
MnO	0.62	0.57	0.41	0.23	0.22	0.70	0.22	0.57	0.40	0.39	0.28	0.26	0.26	0.67	0.50	0.21	0.68	0.00	0.49	0.46	2.20	0.92	0.93
MgO	—	0.38	0.25	0.38	0.07	0.58	0.15	0.38	0.00	0.27	0.30	0.08	0.00	0.36	0.13	0.66	0.95	0.18	0.83	0.46	0.38	0.43	0.43
CaO	3.07	1.93	1.75	1.55	1.32	2.95	1.58	1.94	3.35	2.49	2.66	2.10	3.65	2.49	2.24	3.15	2.90	2.18	2.43	1.69	2.13	2.01	2.01
Na ₂ O	30.28	28.13	28.98	29.86	28.09	28.50	28.36	27.94	29.60	27.43	27.10	26.69	26.78	28.25	26.47	27.51	26.96	26.99	27.49	26.31	26.30	24.80	24.80
K ₂ O	0.00	0.08	0.01	0.00	0.01	0.04	0.25	0.00	0.00	0.00	0.04	0.00	0.00	0.01	0.00	0.01	0.01	0.12	0.00	0.02	0.01	0.07	0.07
Σ	102.97	100.65	95.59	99.80	98.91	102.55	100.00	100.07	102.54	99.21	98.07	95.26	98.52	102.16	97.82	102.52	97.27	99.18	99.74	102.01	96.90	99.85	99.85
Formula calculated on the basis of Si + Al = 4 apfu																							
Si	4.00	3.98	4.00	3.98	4.00	4.00	3.92	3.98	3.68	4.00	3.88	4.00	4.00	4.00	4.00	4.00	3.95	4.00	4.00	3.99	4.00	3.99	3.99
Al	0.00	0.02	0.00	0.02	0.01	0.00	0.08	0.02	0.32	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.05	0.00	—	0.01	0.00	—	0.01
Ti	3.49	3.95	2.94	3.25	3.89	2.94	3.78	3.30	3.20	3.46	3.40	3.23	3.12	3.27	3.59	3.10	3.27	3.47	3.06	2.60	3.14	3.62	3.62
Nb	0.07	0.16	0.29	0.14	0.04	0.39	0.00	0.14	0.00	0.04	0.06	0.06	0.09	0.07	0.06	0.23	0.00	0.05	0.07	0.68	0.05	0.03	0.03
Fe	0.52	0.34	0.24	0.25	0.25	0.42	0.30	0.32	0.39	0.35	0.41	0.36	0.57	0.38	0.39	0.45	0.36	0.32	0.32	0.31	0.35	0.27	0.27
Σ(Ti+Nb+Fe)	4.08	4.45	3.52	3.65	4.18	3.75	4.08	3.77	3.59	3.85	3.87	3.75	3.78	3.72	4.10	3.79	3.63	3.84	3.45	3.59	3.54	3.92	3.92
Mn	0.09	0.09	0.06	0.03	0.03	0.10	0.03	0.08	0.05	0.06	0.04	0.04	0.10	0.07	0.03	0.09	0.00	0.07	0.06	0.31	0.13	0.13	0.13
Mg	0.00	0.10	0.06	0.09	0.02	0.14	0.04	0.09	0.00	0.07	0.08	0.02	0.00	0.09	0.03	0.16	0.24	0.04	0.20	0.11	0.09	0.11	0.11
P	1.87	2.19	1.90	2.02	2.02	1.96	1.83	2.04	1.81	2.06	1.97	2.07	2.06	2.02	2.00	2.02	1.99	2.00	2.02	2.14	1.79	2.26	2.26
Na	9.96	9.91	9.74	9.69	9.43	9.23	9.16	9.03	9.01	8.98	8.93	8.90	8.88	8.85	8.80	8.79	8.79	8.70	8.58	8.51	8.25	8.00	8.00
Ca	0.56	0.38	0.32	0.28	0.24	0.53	0.29	0.35	0.54	0.45	0.48	0.39	0.67	0.42	0.41	0.56	0.52	0.39	0.42	0.29	0.36	0.37	0.37
K	0.00	0.02	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.01
Σ(Na+Ca+K)	10.52	10.30	10.07	9.97	9.67	9.76	9.51	9.37	9.55	9.43	9.42	9.29	9.55	9.28	9.21	9.35	9.31	9.12	8.99	8.80	8.61	8.38	8.38
O	26.26	21.43	25.08	25.51	26.33	25.78	25.36	25.56	24.50	25.76	25.51	25.17	25.68	25.18	25.87	25.70	25.20	25.40	24.78	25.54	24.12	25.97	25.97

Table 1. Continuation

Lomonosovite				Betalomonosovite																				
No. anal.	23	24	25	26*	27*	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	
No. sample	58/ 2c	279/ 1456	123/ 2c	69/ 2c	142/ 1456	142/ 1456	87/ 1c	142/ 1456	142/ 1456	307/ 4c	123/ 1c	136/ 2c	142/ 1456	50/ 2c	502/ 1456	61/ 2c	50/ 2c	50/ 2c	Pegm. 43/ 1c	17/ 1c	Pegm. 43/ 1c	50/ 2c	43/ 1c	
SiO ₂	26.34	24.28	26.88	25.00	25.81	24.43	25.22	25.72	24.90	23.44	25.49	25.00	24.26	25.13	24.23	25.21	26.57	25.35	24.86	26.52	25.41	25.05	24.86	24.86
TiO ₂	27.26	26.04	28.29	25.20	28.52	25.24	26.30	25.72	27.66	27.60	28.61	24.60	27.50	27.26	28.20	27.32	26.64	15.05	27.50	29.22	20.03	29.60	26.60	26.60
P ₂ O ₅	14.55	13.29	14.30	14.41	11.59	13.38	13.56	14.20	11.69	13.29	11.91	14.11	16.50	14.57	16.38	12.34	15.12	13.95	14.36	13.43	15.28	16.95	14.02	14.02
Nb ₂ O ₅	0.76	3.62	1.12	1.43	0.79	3.82	0.73	3.43	1.07	0.41	1.26	2.10	0.50	0.92	0.60	0.78	1.04	15.26	2.07	0.94	12.69	0.34	0.77	0.77
Al ₂ O ₃	0.09	0.77	0.00	0.04	0.00	0.11	0.00	0.00	0.13	0.00	0.13	0.00	0.11	0.06	0.23	0.01	0.00	0.00	0.00	0.00	0.00	0.11	0.11	0.11
Fe ₂ O ₃	3.02	2.70	2.77	5.09	2.95	3.16	2.74	3.19	3.22	4.33	3.50	3.84	2.59	2.64	2.27	3.69	2.74	3.11	2.87	2.82	2.30	1.81	1.70	1.70
MnO	0.46	0.36	0.40	0.58	0.27	3.16	0.97	0.12	0.46	0.32	0.33	0.18	1.37	0.46	0.88	0.48	0.94	2.32	0.48	0.46	0.52	0.90	0.49	0.49
MgO	0.23	0.40	0.08	0.22	0.26	0.33	0.33	0.58	0.25	0.00	0.22	0.58	0.48	0.78	0.40	0.46	0.73	—	0.13	0.35	0.58	0.38	5.65	5.65
CaO	2.38	2.59	1.79	3.15	2.36	3.04	2.34	3.25	2.56	3.18	2.52	3.33	2.60	2.42	2.25	3.04	2.59	1.15	2.11	2.88	2.25	2.00	3.05	3.05
Na ₂ O	27.26	25.94	26.88	24.20	24.40	21.80	22.2	22.28	21.54	19.90	21.34	20.68	19.20	19.06	18.40	17.63	17.82	16.98	16.20	17.17	15.38	14.90	13.57	13.57
K ₂ O	0.07	0.05	0.01	0.06	0.03	0.04	0.06	0.04	0.03	0.13	0.03	0.05	0.06	0.02	0.07	0.04	0.17	0.86	0.02	0.37	1.85	0.11	0.02	0.02
Σ	102.42	100.04	102.52	99.42	96.97	95.48	94.43	98.53	93.37	92.71	95.21	94.47	95.18	93.32	93.95	91.00	94.36	94.03	90.65	94.16	97.92	92.15	90.84	90.84
Formula calculated on the basis of Si + Al = 4 apfu																								
Si	3.98	3.86	4.00	3.99	4.00	3.98	4.00	4.00	4.00	3.97	4.00	4.00	3.98	3.99	3.96	4.00	4.00	4.00	4.00	4.00	4.00	3.98	3.98	3.98
Al	0.02	0.14	0.00	0.01	0.00	0.02	—	0.00	0.00	0.03	0.00	0.00	0.02	0.01	0.04	0.00	0.00	0.00	—	—	0.00	0.02	0.02	0.02
Ti	3.10	3.11	3.17	3.03	3.32	3.09	3.14	3.01	3.34	3.52	3.37	2.96	3.39	3.25	3.46	3.26	3.02	1.79	3.33	3.31	2.37	3.54	3.20	3.20
Nb	0.05	0.26	0.08	0.10	0.06	0.28	0.05	0.24	0.08	0.03	0.09	0.15	0.04	0.07	0.04	0.06	0.07	1.09	0.15	0.06	0.90	0.02	0.06	0.06
Fe	0.34	0.32	0.31	0.61	0.34	0.39	0.33	0.37	0.39	0.55	0.41	0.46	0.32	0.32	0.28	0.44	0.31	0.37	0.35	0.32	0.27	0.22	0.20	0.20
Σ(Ti+Nb+Fe)	3.40	3.70	3.56	3.74	3.66	3.76	3.52	3.62	3.81	4.10	3.87	3.58	3.75	3.64	3.78	3.80	3.40	3.24	3.83	3.69	3.54	3.78	3.46	3.46
Mn	0.06	0.05	0.05	0.08	0.04	0.02	0.13	0.02	0.06	0.05	0.04	0.02	0.19	0.06	0.12	0.06	0.12	0.31	0.07	0.06	0.28	0.01	0.07	0.07
Mg	0.05	0.09	0.02	0.05	0.06	0.08	0.08	0.13	0.06	0.00	0.05	0.14	0.12	0.18	0.10	0.11	0.16	0.00	0.03	0.08	0.14	0.09	1.35	1.35
P	1.86	1.79	1.80	1.95	1.52	1.84	1.82	1.87	1.59	1.91	1.58	1.91	2.29	1.96	2.26	1.66	1.93	1.86	1.96	1.71	2.04	2.28	1.90	1.90
Na	7.99	7.99	7.76	7.49	7.33	6.88	6.83	6.72	6.71	6.54	6.49	6.42	6.11	5.87	5.82	5.42	5.20	5.19	5.05	5.02	4.69	4.59	4.21	4.21
Ca	0.39	0.44	0.33	0.57	0.40	0.53	0.40	0.56	0.36	0.58	0.42	0.57	0.46	0.43	0.40	0.52	0.42	0.19	0.36	0.47	0.38	0.32	0.52	0.52
K	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.03	0.17	0.00	0.07	0.37	0.02	0.04	0.04
Σ(Na+Ca+K)	8.39	8.44	8.09	8.07	7.74	7.42	7.24	7.28	7.07	7.15	6.92	7.00	6.58	6.30	6.23	5.95	5.65	5.56	5.41	5.56	5.44	4.93	4.77	4.77
O	24.00	24.33	23.72	24.21	23.07	24.14	23.47	23.72	23.36	24.61	23.32	23.72	24.90	23.63	24.48	22.87	22.81	22.69	23.26	22.71	23.83	23.89	23.63	23.63

Notes: Analyses 9, 11, 20, 27, 31, 33, and 38 were obtained on Camebax SX-50 electron microprobe at ICGEM RAS, analyst V.V. Khangulov; analyses 1, 35, 37, 39, 40, 44 were obtained on JSM-5300 Link ISIS SEM at ICGEM RAS, analyst N.V. Trubkin; other analyses were obtained on a Cameca MS-46 at ICGEM RAS, analyst O.A. Ageeva. Host rocks: subore massive coarse-grained urtite (soda horizon) (anal. 20); feldspar urtite; with areas of fresh urtite (anal. 23), with soda horizons (anal. 9, 27, 38), with areas of juvite (anal. 6); juvite; with areas of urtite (anal. 4, 14–17, 24), with areas of rischorrite (anal. 10, 12); rischorrite; anal. 3, 5, 7, 13, 21, 22, 25, 28–30, 32–35, 37, 39, 41, 44–45, the same rock with soda horizon; anal. 1, 26; malignite; anal. 2, 8, 19, 36, the same rock with zones of rischorrite; anal. 31; pegmatites in rischorrite and malignite; anal. 11, 40, 42–43. Dash denotes that the data are absent. In number of sample, sampling depth over number of drill hole.

content comes to our attention. It is interesting that Na is partially substituted by K with high-level substitution Ti for Nb. For example, some betalomonosovites from the Mt. Yukspor pegmatite are K-Nb varieties (Nb₂O₅ 12.69 wt.%, Nb 0.90 apfu and K₂O 1.85 wt.%, K 0.37 apfu – anal. 50; Nb₂O₅ 15.26 wt.%, Nb 1.09 apfu and K₂O 0.86 wt.%, K 0.17 apfu – anal. 40).

Betalomonosovite from arfvedsonite-feldspar pegmatite vein (collection of M.N. Sokolova, sample no. 569) in the Apatite cirque of Rasvumchorr was studied in detail. Electron microprobe data together with bulk data of Sokolova *et al.* (1971) are given in Table 2. As these compositions (anal. 1–5) had been normalized to 16 cations, we recalculated them on the basis of Si + Al = 4. As is seen from Table 2, the chemical composition of betalomonosovite is more or less constant: total alkali constituents is about 6 apfu; amount of Ti and isomorphous admixtures is about 4; Si = 4; and proportion of P is about 2 apfu, but O and

H concentration ranges from 24 to 26 and 1 to 2 apfu (exceptional holotype sample from Lovozero), respectively. In general, this supports that the chemical composition of the Khibiny lomonosovite is consistent with formula: Na₄Ti₄Si₄O₁₈•2NaH₂PO₄.

Crystal structures of lomonosovite and betalomonosovite: similarity and differences

The crystal structure of lomonosovite was determined by Rastsvetaeva *et al.* (1971) and was refined by Belov *et al.* (1977). It was discussed in detail in light of the murmanite structure determined by Khalilov *et al.* (1965₁, 1965₂), Khalilov (1989), and Rastsvetaeva and Andrianov (1986), general problems of crystal chemistry and structural topology, and genetic singularities of murmanite (Belov and Organova, 1962; Belov, 1965; Khalilov and Markarov, 1966). The crystal structure of betalomonosovite was solved on samples from Lo-

Table 2. Chemical composition (wt.%) of betalomonosovite from pegmatites of various geological setting

No. anal.	1	2	3	4	5	6
SiO ₂	25.18	25.51	25.05	26.07	25.22	25.27
TiO ₂	25.01	28.80	28.58	28.77	27.64	30.43
ZrO ₂	1.89	1.00	0.52	0.71	0.54	–
P ₂ O ₅	16.12	15.12	14.31	14.55	14.86	14.49
Nb ₂ O ₅		1.10	1.70	1.16	1.17	1.01
Ta ₂ O ₅	4.78	–	0.037	0.02	0.012	–
Al ₂ O ₃	0.69	0.30	0.21	0.30	0.12	0.01
Fe ₂ O ₃	2.38	3.27	3.37	2.75	3.87	3.04
FeO	Bdl	–	0.28	–	0.16	–
MnO	1.40	0.37	0.03	0.35	0.78	0.48
MgO	0.22	0.20	0.34	0.35	0.22	0.33
CaO	0.62	2.01	2.88	2.68	3.04	3.19
Na ₂ O	17.13	18.28	17.68	17.63	16.19	19.90
K ₂ O	0.88	0.34	0.45	0.40	0.35	0.32
H ₂ O ⁺		3.90	3.83	3.80	4.95	–
H ₂ O ⁻	4.60	Bdl	Bdl	0.70	Bdl	–
F	–	0.59	0.50	0.43	0.64	0.53
-O = F ₂	–	-0.25	-0.21	-0.19	-0.27	-0.22
Total	100.90	100.54	99.55	100.49	99.67	92.48

Empirical formula calculated on the basis Si + Al = 4 apfu

1. (Na_{5.11}K_{0.17}Ca_{0.10})_{Σ=5.38}(Ti_{2.89}Nb_{0.33}Zr_{0.14}Fe_{0.28}Mn_{0.18}Mg_{0.05})_{Σ=3.87}(Si_{3.88}Al_{0.12})_{Σ=4}P_{2.10}O_{25.84}H_{4.72}
2. (Na_{5.48}K_{0.07}Ca_{0.33})_{Σ=5.88}(Ti_{3.35}Nb_{0.08}Zr_{0.08}Fe_{0.38}Mn_{0.05}Mg_{0.05})_{Σ=3.99}(Si_{3.95}Al_{0.05})_{Σ=4}P_{1.98}O_{24.74}H_{2.01}F_{0.29}
3. (Na_{5.42}K_{0.09}Ca_{0.49})_{Σ=6.00}(Ti_{3.40}Nb_{0.12}Zr_{0.04}Fe_{0.45}Mn_{0.00}Mg_{0.07})_{Σ=4.08}(Si_{3.96}Al_{0.04})_{Σ=4}P_{1.92}O_{24.83}H_{1.83}F_{0.25}
4. (Na_{5.17}K_{0.08}Ca_{0.45})_{Σ=5.70}(Ti_{3.28}Nb_{0.08}Zr_{0.05}Fe_{0.31}Mn_{0.05}Mg_{0.08})_{Σ=3.85}(Si_{3.95}Al_{0.05})_{Σ=4}P_{1.86}O_{23.59}H_{1.19}F_{0.21}
5. (Na_{4.95}K_{0.07}Ca_{0.51})_{Σ=5.53}(Ti_{3.28}Nb_{0.08}Zr_{0.04}Fe_{0.48}Mn_{0.10}Mg_{0.05})_{Σ=4.03}(Si_{3.96}Al_{0.02})_{Σ=4}P_{1.98}O_{24.31}H_{1.24}F_{0.32}
6. (Na_{4.26}K_{0.06}Ca_{0.54})_{Σ=4.86}(Ti_{3.62}Nb_{0.07}Fe_{0.36}Mn_{0.06}Mg_{0.08})_{Σ=4.10}(Si_{4.00}Al_{0.00})_{Σ=4}P_{1.94}O_{23.77}F_{0.27}

Notes: (1) Lovozero massif, Tulbn'yunuai river, pegmatite hosted in nepheline-sodalite poikilitic syenite, analyst M.E. Kazakova (Gerasimovskiy and Kazakova, 1962); (2–6) Khibiny massif, Apatite cirque of the Rasvumchorr deposit: (2) rischorrite, (3–5) arfvedsonite-feldspar pegmatite veins cutting rischorrite, analyst N.I. Zabavnikova (Sokolova *et al.*, 1971₃), (6) the same, sample no. 569, collection of M.N. Sokolova, structurally refined in this study, electron-microprobe analysis. Total of anal. 3 includes 0.024 wt. % SrO; total of anal. 5 includes, wt. %: 0.018 Li₂O, 0.013 Rb₂O, 0.0007 Cs₂O, 0.007 % SrO, analyst G.Ye. Kalenchuk. No water was analyzed in anal. 6.

vozero by Khalilov and Makarov (1966), Khalilov (1990), and Rastsvetaeva (1986, 1988, 1989) as well as sample from Khibiny (Rastsvetaeva *et al.*, 1975).

As the data on the discussed structures were obtained long enough and some new members of the lomonosovite group were discovered to date, these structures should be refined with the state methods and revision of crystal chemical features. Cámara *et al.* (2008) performed this study for the lomonosovite and murmanite structures, but the structure of betalomonosovite attributed to discredited minerals was not refined. Yakubovich *et al.* (2014) refined it and below it is compared with the structure of lomonosovite.

Unfortunately, the sample refined by Cámara *et al.* (2008) cannot be regarded as typical lomonosovite, because it was selected from fine fraction of the Lovozero bornemanite that is secondary mineral replacing lomonosovite, i.e., it is originated from different geological environment than the Khibiny lomonosovite genetically related to the discussed betalomonosovite. However, our examination of this uncommon and deficient material showed the power of modern structural methods and allowed justification of sites, their occupancies by trace elements, and determination of iron valence with the Mössbauer method. By the way, the $\text{Fe}^{2+}/\text{Fe}^{3+} = 58/42$ value of 58/42 indicates long transition from reductive to oxidative formation conditions, whereas the Lovozero murmanite was formed under oxidative conditions (iron is completely trivalent).

The empirical formula of lomonosovite with refined structure $(\text{Na}_{9.50}\text{Mn}_{0.16}\text{Ca}_{0.11})_{\Sigma 9.77}(\text{Ti}_{2.83}\text{Nb}_{0.51}\text{Mn}_{0.27}\text{Zr}_{0.11}\text{Mg}_{0.11}\text{Fe}_{0.10}^{2+}\text{Fe}_{0.06}^{3+}\text{Ta}_{0.01})_{\Sigma 4.00}(\text{Si}_{2.02}\text{O}_7)_2(\text{P}_{0.98}\text{O}_4)_2(\text{O}_{3.50}\text{F}_{0.50})_{\Sigma 2}$, calculated on the basis of 26 (O + F) anions from the composition determined on a Cameca SX100 electron microprobe is consistent with the structural formula $\text{Na}_{10}\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_4$ ($Z = 1$). The unit cell dimensions are $a = 5.4170(7)$, $b = 7.1190(9)$, $c = 14.487(2)\text{Å}$, $\alpha = 99.957(3)^\circ$, $\beta = 96.711(3)^\circ$, $\gamma = 90.360(3)^\circ$, $V = 546.28(4)\text{Å}^3$, $D_{\text{calc.}} = 3.175\text{ g/cm}^3$. Space group is $P\bar{1}$ (Cámara *et al.*, 2008).

We refined the crystal structure of the Khibiny betalomonosovite on the material from pegmatite in the Apatite cirque of Mt. Rasvumchorr. The chemical composition determined on a JEOL JXA-8200 electron microprobe (Table 2) are normalized on the basis of 4 (Si + Al) atoms to formula $(\text{Na}_{4.26}\text{Ca}_{0.54}\text{K}_{0.07})_{\Sigma 4.87}(\text{Ti}_{3.66}\text{Nb}_{0.07}\text{Fe}_{0.36}\text{Mn}_{0.07}\text{Mg}_{0.08})_{\Sigma 4.24}\text{Si}_4\text{P}_{1.96}\text{O}_{23.54}\text{F}_{0.27}$, corresponding to the crystal chemical formula

$(\text{Na}_{4.42}\text{Mn}_{0.11}\text{Ca}_{0.71}\text{K}_{0.07})_{\Sigma 5.31}(\text{Ti}_{3.63}\text{Nb}_{0.03}\text{Fe}_{0.34}^{3+})_{\Sigma 4.00}\text{O}_2[(\text{O},\text{OH})_{0.79}\text{F}_{0.21}]_2[\text{Si}_2\text{O}_7]_2[\text{H}_2\text{PO}_4]_2$. The unit cell dimensions are $a = 5.3184(3)$, $b = 7.0869(5)$, $c = 14.4490(10)\text{Å}$, $\alpha = 102.944(7)^\circ$, $\beta = 96.367(7)^\circ$, $\gamma = 90.331(6)^\circ$, $V = 527.22(6)\text{Å}^3$, $D_{\text{calc.}} = 2.91\text{ g/cm}^3$. Space group is $P\bar{1}$.

The comparison of the structures indicates.

Lomonosovite is disilicate. According to Cámara *et al.* (2008), its structure is based on the **TS** titanosilicate blocks with formula $A^p_2M^h_2M^o_4(\text{Si}_2\text{O}_7)_2X_4$, alternated along axis c with intermediate blocks **I** corresponding in composition to $\text{Na}_6(\text{PO}_4)_2$ (Fig. 4a). The **TS** block consists of octahedral layer **O** composed of close packed octahedra $M^o(2) - {}^{16}\text{Ti}^o(2)$ and ${}^{16}\text{Na}^o(2)$ as brookite-type chains $(\text{Ti}_2\text{O}_8)^{8-}$ linked with Na octahedra in similar configuration in ratio $\text{Ti}:\text{Na} = 1:1$ (Na_2Ti_2 per cell) (Fig. 5a), and heteropolyhedral layer **H** composed of M^h polyhedra $- {}^{16}\text{Ti}^h(1)$ octahedra bonded with Si_2O_7 groups and eight-fold polyhedra ${}^{18}\text{Na}^h(1)$ (Fig. 5b). Connecting **P** layer is conditionally determined because two Si_2O_7 groups are linked with the nearest ${}^{16}\text{Ti}^o(2)$ octahedra of the brookite chains via oxygen atoms (Fig. 5c) while ${}^{16}\text{Ti}^h(1)$ octahedron shares apex occupied by oxygen $X^o_M = \text{O}(8)$ with two ${}^{16}\text{Na}^o(2)$ and one ${}^{16}\text{Ti}^o(2)$ octahedra of the **O** layer (Figs. 5b, 5c). Tetrahedrally coordinated **P** bonded with Na polyhedra of three types ${}^{16}\text{Na}(3)$, ${}^{14}\text{Na}(4)$ and ${}^{15}\text{Na}(5)$ occurs in block **I** (Fig. 4a).

As aforementioned, the ideal structural formula of lomonosovite regardless isomorphic admixtures is $\text{Na}_{10}\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_4$ ($Z = 1$). The both Ti sites contain Nb, Fe, Mn, and Mg admixtures, but ${}^{16}\text{Ti}^h(1)$ octahedron is dominated by Ti. Small portion of vacancy $\square_{0.05}$ per cell occurs in eight-fold polyhedron ${}^{18}\text{Na}^h(1)$ and octahedron ${}^{16}\text{Na}^o(2)$; octahedron ${}^{16}\text{Na}(3)$ of the **I** layer contains 0.11 apfu Ca, and tetrahedron ${}^{14}\text{Na}(4)$ contains 1.71 Na + 0.16 Mn^{2+} + 0.13 \square . The calculated valence force at site $X^o_A = \text{O}(9)$ bonded with two atoms Ti(2) and atom Na(2) in the **O** layer and atom Na(1) in the **H** layer is lesser than that at site X^o_M , occupied only by O atoms and linked with Ti(1) in the **H** layer and Ti(2) and two Na(2) in the **O** layer (Fig. 5c) (1.84 against 2.05 v.u.) that is consistent with the partial substitution of F for O according to the reaction: $\text{Ti}^{4+} + \text{O}(9)^{2-} \rightarrow \text{M}^{2+} + \text{F}^-$ with the substitution of Ti at site $\text{Ti}^o(2)$ with divalent elements $\text{Mn}_{0.22}\text{Mg}_{0.11}\text{Fe}_{0.05}^{2+}$ (0.38 apfu).

The refined crystal structure of betalomonosovite (Yakubovich *et al.*, 2014) is distinguished by some features (Table 3). In the **O**

layers of the **TS** blocks, Ti sites $M2^{[6]}$ corresponding to $M^{\circ}(1) = {}^{16}\text{Ti}^{\circ}(2)$ in lomonosovite (Fig. 4b) are also completely occupied, but with Fe admixture only, whereas all-Na octahedra $M^{\circ}(2) = {}^{16}\text{Na}(2)$ of lomonosovite are transformed to seven-fold polyhedra $M5^{[7]}$ in betalomonosovite and are half occupied by Na with Ca admixture, whereas another half is vacant (Fig. 5d). In the *H* layers of the **TS** blocks the Ti dominated $M1^{[6]}$ octahedra corresponding to octahedra $M^{\text{H}} = {}^{16}\text{Ti}^{\text{H}}(1)$ in lomonosovite are also completely occupied, but only with Ti and Nb; Ca incorporates into all-Na eight-fold polyhedra $A^{\text{P}} = {}^{18}\text{Na}(1)$ depicted as $M4^{[8]}$, and nearly half polyhedra is vacant (Fig. 5e).

Therefore, Ti content in the **TS** blocks of betalomonosovite is elevated; Na is partly substituted by Ca; and nearly half Na is removed. However, the crystal chemical analysis should be careful because isomorphous admixtures in the minerals from different geological environment are compared. The additional comparison with the structure of murmanite from Lovozero (Cámara *et al.*, 2008) shows that the greatest occupancy of $\text{Ti}^{\circ}(2)$ octahedral in brookite chains with various isomorphous admixtures is common in the discussed minerals of the lomonosovite group, whereas octahedron $\text{Ti}^{\text{H}}(1)$, linked with disilicate groups Si_2O_7

is always Ti dominated. The elevated content of trace elements is observed at Na sites linked with Ti; in this case, $\text{Na}^{\circ}(2)$ contains not only Ca, but Mn, and in eight-fold $\text{Na}^{\text{P}}(1)$ polyhedra, where Cámara *et al.* (2008) found K in murmanite, Mn could be incorporated into the structures of the Khibiny lomonosovite and betalomonosovite, where elevated K and Nb contents were found (Table 1). Few vacancies are typical of these Na sites in lomonosovite and betalomonosovite. However, their amount is disparate with vacancies in the structure of betalomonosovite from Rasvumchorr that is the most important feature of the mineral studied here.

The differences in the structure of the intermediate **I** block in the structure of betalomonosovite as compared with lomonosovite highlight this feature (Table 3). All-Na five-fold polyhedron ${}^{15}\text{Na}(5)$ in lomonosovite corresponds to $M3^{[6]}$ octahedron less than half occupied and contaminated by Mn (0.762 Na + 0.118 Mn + 1.12 □) in betalomonosovite. Tetrahedron ${}^{14}\text{Na}(4)$ (1.71 Na + 0.16 Mn + 0.13 □) with similar occupancy and small vacancy was such polyhedron in lomonosovite. The ${}^{14}\text{Na}2$, polyhedron occupied with Na only for eight (0.24 Na + 1.76 □) corresponds to it in betalomonosovite. Eight-fold ${}^{18}\text{Na}1$ polyhedron that was octahedron and contained

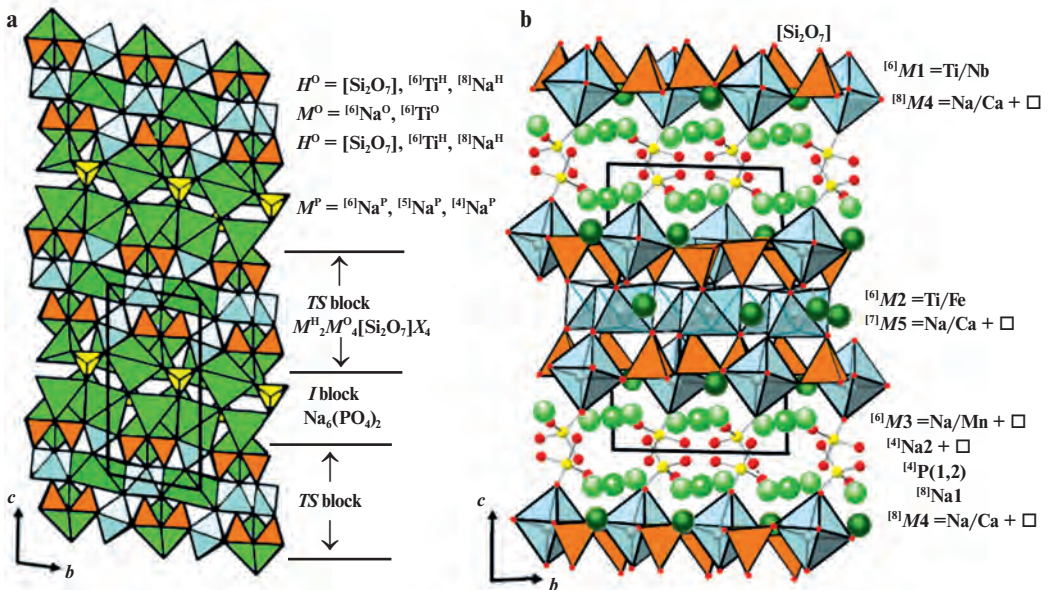


Fig. 4. Comparison of crystal structures of lomonosovite (Cámara *et al.*, 2008), and betalomonosovite (Yakubovich *et al.*, 2014): (a) structure of lomonosovite projected onto (100), titanosilicate (**TS**), heteropolyhedral (**I**), and Na-P $\text{Na}_6(\text{PO}_4)_2$ blocks alternated along axis *c*;

(b) structure of betalomonosovite, view along diagonal of the *ab* face, alternation of the same blocks along axis *c*; the unit cells are shown as rectangles; disilicate groups Si_2O_7 are red-orange; Ti-octahedra are blue; differently coordinated Na polyhedra are green; P tetrahedra are yellow; and oxygen atoms are red circles.

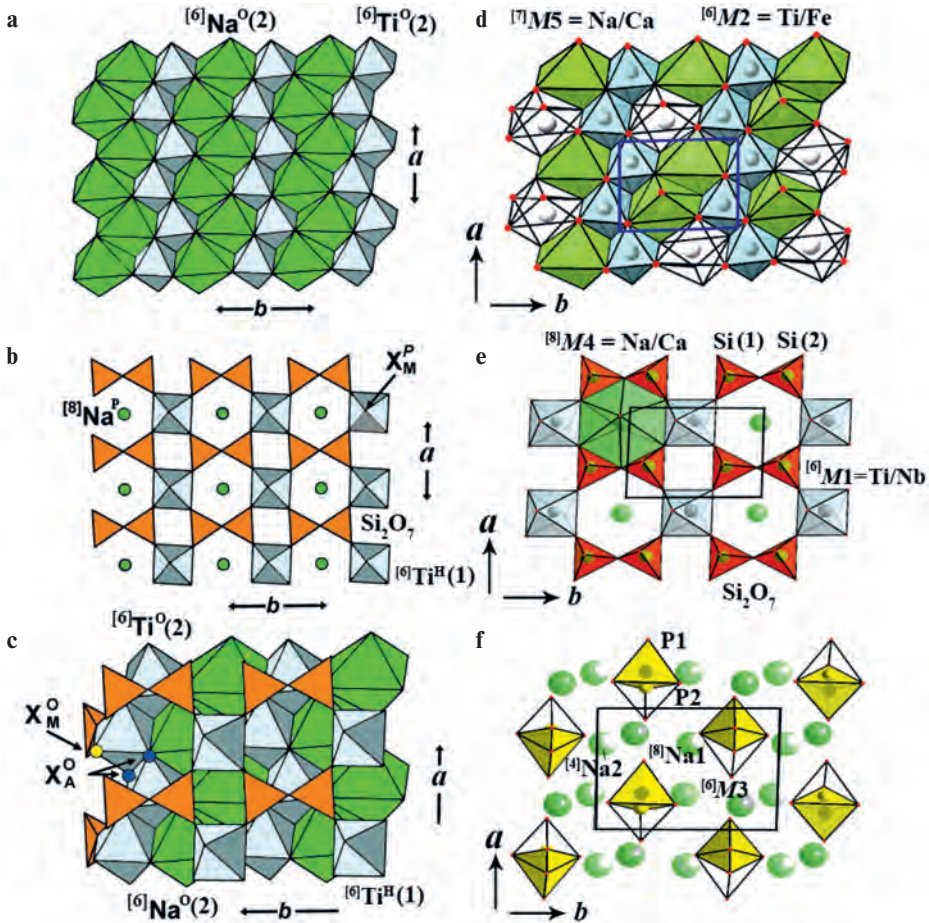


Fig. 5. Comparison of crystal structures of lomonosovite (a–c) (Cámara *et al.*, 2008) and betalomonosovite (d–f) (Yakubovich *et al.*, 2014) projected perpendicular to axis [001]:

- (a) close packed Ti and Na octahedra of octahedral O layer from TS block in lomonosovite;
 (b) disilicate groups Si_2O_7 , Ti octahedral, and Na eight-fold polyhedral of heteropolyhedral H layer from TS block;
 (c) junction of octahedral and heteropolyhedral layers in TS block, main oxygen atoms in Ti and Na polyhedra X_M^P , X_M^O and X_A^O (see text) are shown;
 (d) probable distribution of vacancies in Na polyhedra of octahedral O layer from the TS block in betalomonosovite; (e) titanosilicate "maille" of heteropolyhedral H layer from the TS block with Na eight-fold polyhedra in cavities;
 (f) defect Na-P layer $[\text{Na}_{3.00}\text{Mn}_{7.11}(\text{H}_2\text{PO}_4)_2]$ in betalomonosovite with oxocomplexes $[\text{P}_2\text{O}_6]_{0.5}\text{O}_2$ composed of two phosphate tetrahedra with different filling put into each other.

Ca ($^{[6]}\text{Na}(3) = 1.89 \text{ Na} + 0.11 \text{ Ca}$) in lomonosovite becomes all-Na. In other words, Na polyhedra are substantially reorganized: tetrahedra are retained ($\text{Na}(4) \rightarrow \text{Na}2$), whereas lomonosovite five-fold Na(5) polyhedron and octahedron Na(3) are modified to octahedron M3 and Na1 eight-fold polyhedron, respectively (Fig. 5f). According to Rastsvetaeva *et al.* (1975), two couples of Na_6 and Na_7 eight-fold polyhedra and nonpaired octahedron Na_5 disturbing centrosymmetric structure occur in this block. Thus, in I block of betalomonosovite, Na polyhedra (determined by various investigators in different ways) are signifi-

cantly rearranged and degree of their occupancy substantially decreases (proportion of vacancy increases = 2.88 □).

The split of P site is also substantial that was previously reported by Rastsvetaeva *et al.* (1975). According to their data, position of P_2 corresponded to that in lomonosovite, whereas the second P_1 was turned around that resulted in the P–O chain. Our version of the structure shows that phosphorus site is split to P_1 and P_2 at inadmissible short distance of 0.53 Å, and therefore there is a 50% chance that these positions will be occupied, as well as, two of four apices occupied by oxygen atoms

Table 3. Comparison of cation sites in the crystal structures of lomonosovite (Cámara *et al.*, 2008) and betalomonosovite (our data) as indicated by various authors and their occupancy

	Lomonosovite (Cámara <i>et al.</i> , 2008)	Betalomonosovite (Yakubovich <i>et al.</i> , 2014)
$M^O(1) = {}^{60}\text{Ti}^O(2)$	1.31 Ti + 0.22 Mn ²⁺ + 0.20 Nb + 0.11 Zr + 0.05 Fe ²⁺ + 0.11 Mg = 2.00	M2 ⁶⁰ 1.66 Ti + 0.34 Fe = 2.00
$M^O(2) = {}^{60}\text{Na}^O(2)$	1.95 Na + 0.05 □ = 2.00	M5 ⁷⁰ 0.63 Na + 0.37 Ca + 1.00 □ = 2.00
$M^H = {}^{60}\text{Ti}^H(1)$	1.52 Ti + 0.05 Mn ²⁺ + 0.31 Nb + 0.01 Ta + 0.06 Fe ³⁺ + 0.05 Fe ²⁺ = 2.00	M1 ⁶⁰ 1.97 Ti + 0.03 Nb = 2.00
$A^P = {}^{60}\text{Na}(1)$	1.95 Na + 0.05 □ = 2.00	M4 ⁸⁰ 0.78 Na + 0.34 Ca + 0.88 □ = 2.00
${}^{40}\text{P}$	2.00 P	P1 ⁴⁰ 1.00 P
		P2 ⁴⁰ 1.00 P
${}^{60}\text{Na}(5)$	2.00 Na	M3 ⁶⁰ 0.76 Na + 0.12 Mn + 1.12 □ = 2.00
${}^{60}\text{Na}(3)$	1.89 Na + 0.11 Ca = 2.00	Na1 ⁶⁰ 2.00 Na
${}^{40}\text{Na}(4)$	1.71 Na + 0.16 Mn ²⁺ + 0.13 □ = 2.00	Na2 ⁴⁰ 0.24 Na + 1.76 □ = 2.00

Notes: The site occupancy in betalomonosovite is shown for complete cell to compare with lomonosovite, i.e. it is duplicated; in this case, vacancies in its structure are better displayed.

O12 and O12A, and O13 and O13A in phosphate tetrahedra input into each other that leads to the formation of orthocomplexes [(P₂O₄)_{0.5}O₂] in average structure (Fig. 5f). The deficient valence force and overestimated O–P distance for these oxygen atoms (0.66–1.00 v.u. and 1.513–1.547Å) relative to other atoms O11 and O4 in P tetrahedral (1.61 and 1.96 v.u. and 1.497–1.508Å, respectively) suggest that they are transformed to OH groups and are donors of hydrogen bonds linking orthocomplexes and Na polyhedra.

Thus, betalomonosovite substantially differs from both lomonosovite and murmanite in the arrangement of H atoms in the structure. According to (Cámara *et al.*, 2008) in murmanite, blocks **TS** are linked through outer anions X^p_M of titanium M^H = Ti(1) octahedra and anions X^p_A of sodium A^P = Na(1) eight-fold polyhedral, in which oxygen atoms O(10) and O(11) are substituted by H₂O groups and donor-acceptor hydrogen bond arises between oxygen atoms of different oppositely oriented H₂O groups or with non-substituted oxygen atoms O(2)a and O(4)a. Hydroxyl groups are absent in the structure of murmanite.

Hydration of lomonosovite and water in the structure. Thermal analysis

The hypothesis of the secondary origin of murmanite, its formation as a result of Na leaching and hydration, was proposed for the first time by Borneman-Starynkevich (1946) and experimentally confirmed by Zabavnikova (1967); in the course of experiments, milled lomonosovite was treated by water at room temperature during one year; Na and P released from mineral as Na orthophosphate

Na₃PO₄ to complete loose of Na-phosphate constituent. The degree of replacement of lomonosovite by murmanite depended on the degree of bucking and time of water treatment. The scheme proposed by I.D. Borneman-Starynkevich and N.I. Zabavnikova is used in literature to explain pseudomorphic nature of murmanite.

Recently, Selivanova *et al.* (2008) and Selivanova (2102) performed experiments on lomonosovite hydrolysis and cation exchange, but worse carefully (the samples were soaked only 0.5–48 hours at room temperature or 1–100 hours at 74–80°C). It is surprisingly that any result has been obtained, especially when the dependence of dehydration degree on the trace element content in the structure of lomonosovite has been established. Nevertheless, Selivanova's objection of classic concept of pseudomorphic nature of murmanite as a supergene alteration product of lomonosovite caused a discussion in literature.

Lykova *et al.* (2012) repeated runs in distilled water at room temperature for 1000 hours for lomonosovite and betalomonosovite samples of 75 mg in weight crushed to 0.5–1.5 mm in size. These experiments showed that alteration is very slow in distilled water at room temperature and geological time is required to obtain the expected result. The rate of Na and P leaching from the intermediate layer in the structure of lomonosovite increases at 90°C: Na and P contents decrease from 9.5 to 5.4–3.0 apfu and from 2.0 to 0.7–0.6 apfu, respectively, i.e., the rate of Na removal is much higher than that P with *d*₀₀₁ changing from 14.2 to 12.7Å in final phase.

It is important that in the first place, the rate of Na and P leaching from betalomonosovite is half of that from lomonosovite: only 0.4% P₂O₅ and 0.5% Na₂O were leached from

fraction -0.25 to $+0.1$ mm during 6 months at room temperature, whereas from lomonosovite 2.0 and 3.3%, respectively, i.e., betalomonosovite is more persistent to affecting neutral solutions than hyperagpaitic lomonosovite. In the second place, Na is leached only from the Na-P intermediate layer of the lomonosovite structure at room temperature, but it does not remove from titanosilicate layer as established by Selivanova *et al.* (2008). The data of Lykova *et al.* (2012) support the classic conclusion that murmanitization of lomonosovite is resulted from the effect of neutral of weakly acidic low-temperature solutions although a long time is required. More stable linkage of Na-P clusters in betalomonosovite than that in lomonosovite was explained by hydrogen bonds, which are typical of acidic salts Na_2HPO_4 or NaH_2PO_4 (Sokolova *et al.*, 1971; Rastsvetaeva *et al.*, 1975). In contrast to murmanitization, lomonosovite is replaced by betalomonosovite at higher temperature in strongly alkaline medium with substantial Na removal. Our data indicate that Na is leached from both intermediate *I* layer and titanosilicate *TS* layer.

We obtained the new data on thermal behavior of the lomonosovite group minerals. Thermograms were obtained on a Q-1500D derivatograph, Hungary equipped with an Ecohrom complex for the data recording and processing within the range from 25 to 1000°C. The samples were placed into platinum crucibles and heated in air with rate of 15 degree/min; the Al_2O_3 sample of 200 mg in weight was used as reference material.

The lomonosovite thermogram (Fig. 6a) was recorded for the sample of 228 mg in weight. The DSC curve of lomonosovite exhibits one pronounced high-temperature endothermic peak at 871°C corresponding to the melting of mineral and two weak endothermic effects at 941 and 992°C not accompanied with weight loss and reflecting energy input for the processes in the lomonosovite melt. This energy was probably to be consumed for rebuilding of crystalline clusters composed of the SiO_4 and PO_4 tetrahedra. In the low-temperature region of the curve, two insignificant bends are exhibited at 248 and 250°C accompanied with insignificant weight loss of 0.68 and 0.48 wt.%. They are evidently caused by the evaporation of water and NaF.

The thermogram of betalomonosovite recorded for the sample of 227 mg in weight differs fundamentally from that of lomonosovite (Fig. 6b). The DSC curve exhibits triple endothermic effect in the range of 237 to 550° with

the bend at 271°C and minimums at 382 and 406°C followed by clear exothermic effect at 625°C corresponding to rebuilding of the mineral structure and two symmetric endothermic effects with maximum at 761 and 852°C not accompanied with weight loss and corresponding to two stage of the minerals melting. The DTG curve shows that most weight (11.01 wt.%) is lost during three stages (1.86, 3.65, and 5.50 wt.%) within the range 235–720°C. As is seen from the TG curve, at high temperature the weight is lost evenly and is not related to the high-temperature endothermic peaks on the DSC curve.

The thermogram of murmanite (Fig. 6c) recorded for the sample of 190 mg in weight differs enormously from that of lomonosovite and betalomonosovite in both shape and weight loss (27.16 wt.%). The DSC curve of murmanite exhibits strong symmetric endothermic effect at 275°C corresponding to a weight loss of 17.88 wt.% related to water removal from the mineral. This effect is followed by a pronounced curve bend at 450°C corresponding to the major stage of weight loss. The clear symmetric endothermic peak at 726°C corresponds to the mineral melting accompanied with loss of residual water (1.94 wt.%) that is exhibited as small peak at 733°C on the DTG curve. This peak is followed by a clear bend at 993°C on the DSC caused by energy consumption for the structure rebuilding in the murmanite melt. The analysis of the DTG curve reveals two types of water in the structure of murmanite: weakly bound (17.88 wt.%) quickly removed in the narrow temperature range up to 275°C with maximum at 177°C and tightly bound (7.34 wt.%) gradually released up to the mineral melting.

Thus, the minerals studied here are dramatically different in thermal curves. Total weight loss with heating increases from lomonosovite through betalomonosovite to murmanite (2.65, 14.10, and 27.16 wt.%, respectively). However, the review of thermograms does not allow consideration of betalomonosovite as an intermediate product of transformation of lomonosovite to murmanite with Na leaching and hydration. In the first place, it is indicated by the exothermic effect on the DSC curve of betalomonosovite corresponding to the rebuilding of the mineral structure accompanied with the substantial energy release. If betalomonosovite was intermediate member of the lomonosovite-murmanite series then we could observe comparable or more pronounced energy outbreak related to the end member recrystallization. However, it was obser-

ved neither in our experiments nor on the previously published DCS curves of lomonosovite and murmanite. In general, our results supplement the data of previous investigators, who terminated sample heating before mineral melting.

Status of betalomonosovite

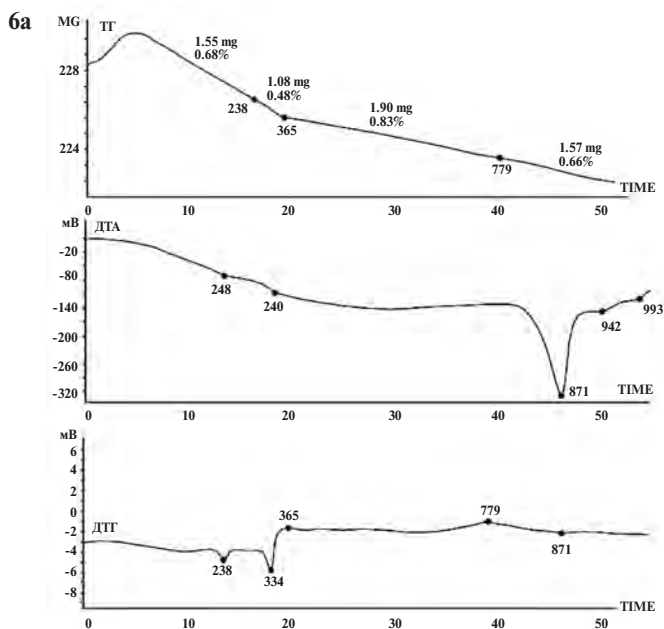
The history of the betalomonosovite discreditation is tortuous. Having acted on behalf of the Commission on New Minerals and Mineral Names of International Mineralogical Association formed in 1959 with the revision of minerals discovered in 1959–1960 and not approved by the Commission Villarroel and Joel (1967) were quite delicate in this question. They evidently understood the importance of the terms β -lomonosovite and metamurmanite and remained them with a significance of 60% or higher; however, they discredited notions metalomonosovite (= β -lomonosovite) and ortholomonosovite (= lomonosovite). In the similar publication, Nickel and Mandarino (1988) put dogmatically betalomonosovite into the list of already discredited mineral name that is surprisingly because, in the first place, this mineral was studied in detail meanwhile and this term was used in literature concerned with mineralogy of alkaline complexes; in the second place, its discreditation was argued by the references to the aforementioned article published in 1967, in which, as we know, discreditation was not discussed.

It does not matter if betalomonosovite is approved by the Commission as individual mineral species or variety of lomonosovite. It is necessary that this term should not be lost with nomenclature changes. However, we think that betalomonosovite has more reasons to be approved as mineral species than many "new minerals" recently approved by the Commission using only recommended formal chemical and crystal chemical criteria regardless genesis, i.e., analysis of formation conditions, stability field of a described mineral, and its importance for geology.

Unfortunately, well-known story of data generalization and formalization in determination of mineral species was about lomonosovite and betalomonosovite, as a result of which mineral is separated away from the parent geological system and is transformed from the real chemical compound to abstract divorced from formation conditions and field of stability within which its chemical composition, structure, and physical properties evolve during geological time in accordance with the evolution of physicochemical parameters of mineral-forming and mineral-retaining medium.

Conclusions

The novel data obtained and detailed review of this problem support necessary rehabilitation of indefinitely discredited term betalomonosovite. This mineral substantially differs in the chemical composition, structural



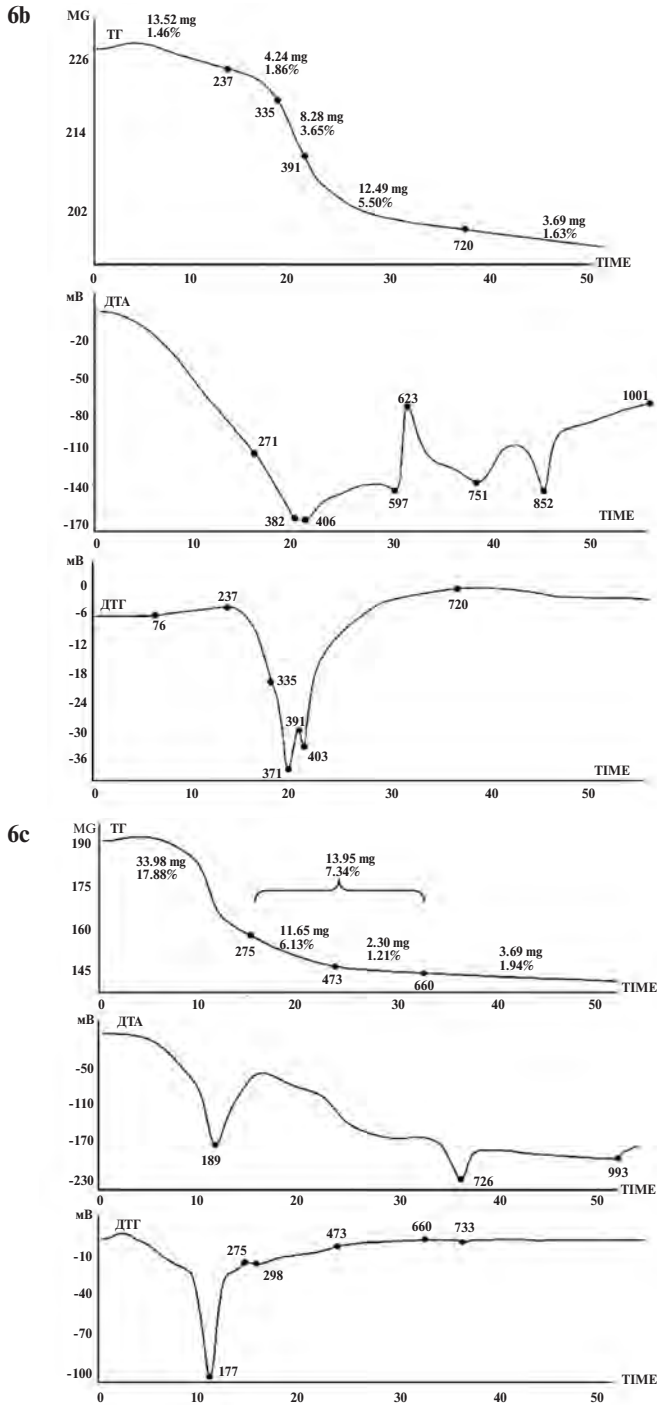


Fig. 6. Thermograms of the lomonosovite group minerals, our data:

(a) lomonosovite (weight 228 mg, weight loss 6.04 mg, 2.65 %);

(b) betalomonosovite (weight 227 mg, weight loss 32.04 mg, 14.10 %);

(c) murmanite (weight 190 mg, weight loss 57.62 mg, 27.16 %).

A Q-1500D derivatograph (MOM, Hungary), 25–1000°C, platinum crucibles, heating rate 15 degree/min, 200 mg Al₂O₃, as reference sample; measurement at air. Analyst P.M. Kartashov.

singularities, and physical properties from both lomonosovite, with which the researchers who do not know enough with nuances of mineralogy of alkaline complexes formally attempt to associate it in the recent mineralogical nomenclature, and murmanite with which it is frequently associated in the lomonosovite-murmanite solid solution, where betalomonosovite is not end-member. It is really genetically related to lomonosovite, but is a product of metasomatic alteration of lomonosovite, recrystallization and crystallization at high-temperature fenitization of rocks of alkaline magmatic complexes with variable basicity of mineral-forming fluids rather than supergene alteration like murmanite. In other words, this mineral could be defined reasonably as individual mineral species characterized by discrete chemical composition and structural singularities, with certain field of stability and studied compositional variations resulted from variable character of mineral-forming and mineral-retaining medium.

Acknowledgments

We thank M.N. Sokolova for permanent interest in our study and samples of previously studied betalomonosovite from the Rasvumchorr pegmatite kindly placed in our disposal for structure investigation.

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YUGAWARALITE FROM THE A.E. FERSMAN OUTCROP OF THE OSHURKOVSKOE APATITE DEPOSIT, BURYATIYA, RUSSIA

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During research on mineralization of the A.E. Fersman outcrop, Oshurkovskoe apatite deposit (Buryatia), the following Ca-zeolites were identified: yugawaralite $\text{Ca}[\text{AlSi}_3\text{O}_8]_2 \cdot 4\text{H}_2\text{O}$, stellerite $\text{Ca}_4[\text{Al}_2\text{Si}_7\text{O}_{18}]_4 \cdot 28\text{H}_2\text{O}$, laumontite $\text{Ca}[\text{AlSi}_2\text{O}_6]_2 \cdot 4\text{H}_2\text{O}$, heulandite-Ca $\text{Ca}(\text{Ca},\text{Na})_{2-3}\text{Al}_3(\text{Al},\text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$, and stilbite $(\text{Na},\text{K},\text{Ca})_9[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 28\text{H}_2\text{O}$. This is the first time that yugawaralite has been found in Russia. The minerals were found both in zeolitic veinlets, which are split monzodiorites, and on the surface of monzodiorite fragments in association with augite, pigeonite, diopside-hedenbergite series, ferroedenite, and almandine-spessartite series.

4 tables, 6 figures, 20 references.

Keywords: Oshurkovskoe deposit, A.E. Fersman outcrop, yugawaralite, laumontite, stellerite, heulandite-Ca, pigeonite, hedenbergite.

The Oshurkovskiy apatite-bearing massif is located in the Oshurkova and Utochkina pad'¹, on the left bank of the Selenga River 10 km to the north-west of Ulan-Ude (Fig. 1), and occupies an area of 14 km². The apatite deposit of the same name is a part of the Oshurkovskiy massif as well. The A.E. Fersman outcrop (Fig. 2) is located in the Utochkina pad' (Kislov, 2011). In 1915 A.E. Fersman studied granite pegmatites containing scapolite and zeolites in this location. The host rocks are strongly squeezed granite-gneisses, altered to amphibolites in places. The rocks of the massif are split by numerous dykes and veins of microdiorites, lamprophyres, carbonatites, granite pegmatites and aplites, and also by quartz and zeolitic veins. The general character of the veins varies, depending on the host rocks, which are mainly contact pegmatites with hornblende, titanite, and albite in the contact zones. In other veins, a gradual change of mineralization after introduction (intrusion) in amphibolite is observed. Feldspar is replaced by scapolite and hornblende, and then scapolite is replaced by zeolites (heulandite, stilbite); i.e. transition from contact pegmatite to migmatites is observed (Gavrusevich, Semenenko, 1935; Fersman, 1940).

Later research (Zanvilevich *et al.*, 1999; Semenov, 2010; Lastochkin *et al.*, 2011) showed that the massif is composed of rocks consisting of SiO_2 41–53 wt.%; the mineral composition corresponds to monzonites and monzodiorites. Alkaline – feldspar syenites occur in the massif as well, forming some small irregular bodies.

The mineral paragenesis characteristic for monzonites and monzodiorites is as follows: Ti-rich pargasite, augite, biotite, oligoclase, K-Na-feldspar, apatite, ilmenite, titanomagnetite, and titanite.

The syenites are comprised of coarse grains of alkaline feldspars, apatite, titanite, ilmenite, and titanomagnetite. There are albite-oligoclase grains in lesser amounts, as well as grains of pure albite and orthoclase in the interstices; quartz is either absent, or in quantity not exceeding 10%. Amphiboles and clinopyroxenes in the syenites are comprised of edenite and ferrous diopside (salite), respectively.

The mineral composition of dike and vein formations is more varied. Carbonatite veins are found on the left bank of the Utochkina pad' (A.E. Fersman's outcrop). Their thickness varies from 2–3 to 60 cm, averaging 30 cm. The main carbonatite mineral is a milky-white calcite (80–95%); and the minor minerals are as follows: barite, phlogopite, magnetite, titanite, and allanite. Zeolitization and silicification has been observed in the host rocks.

The granite pegmatites are comprised mainly of quartz (20–30%), potassium feldspar (40–50%), and albite (10–30%); minor minerals are as follows: biotite, beryl, muscovite, allanite, zircon, titanite, apatite, spessartite, pyrochlore, magnetite, columbite, ilmenite, rutile, fluorite, and uraninite.

The main rock forming minerals of the gabbro pegmatites are pyroxenes and feldspars. Pyroxene is present as salite; the other minerals of gabbro pegmatites include: apatite (with an increased amount of Sr), titanite, epidote (as a secondary mineral), amphibole, scapolite, magnetite, and biotite. In the east, the intrusive is overlaid by alluvial sediments.

The Oshurkovskoe apatite deposit has been studied on multiple occasions (Gavrusevich, Semenenko, 1935; Fersman, 1940; Kuznetsova *et al.*, 1995; Zanvilevich *et al.*, 1999; Semenov, 2010; Lastochkin *et al.*, 2011), but these studies

¹ – creek valleys in Siberia and Far East.

mainly focused on rock forming minerals. The mineral composition of the zeolitic veins has not yet been described in detail. According to E.V. Kislov (oral communication), the zeolitic veins are comprised of natrolite, stilbite and heulandite.

In summary, the minerals known from the Oshurkovskoe deposit are as follows: augite (including Na-augite), allanite, apatite (with increased Sr content), biotite (enriched with Ti), ilmenite, calcite, magnetite, muscovite, orthoclase, pyrochlore, plagioclases, scapolite, titanite, titanomagnetite, uraninite, zircon, and the zeolite minerals heulandite, natrolite, and stilbite. Despite considerable apatite reserves, the deposit was never developed for reasons of ecological safety, as it is in the area of the Selenga river delta at Lake Baikal.

Samples from the A.E. Fersman outcrop (Utochkina pad') of the Oshurkovskoe apatite deposit were collected in 2011 during a field trip organized for participants of the Second All-Russian Scientific and Practical Conference "Minerageny of North-East Asia" which took place in Ulan-Ude. When the samples were investigated, special attention was paid to zeolites, while amphiboles, pyroxenes, feldspars and other minerals studied earlier were not examined in detail (Kuznetsova *et al.*, 1995; Zanvilevich *et al.*, 1999; Semenov, 2010; Las-tochkin *et al.*, 2011).

Methods of investigation

The chemical composition of the minerals was determined using a JCSA-733 Superprobe JEOL microprobe analyzer (equipped with an INCA Energy Oxford analysis system, including

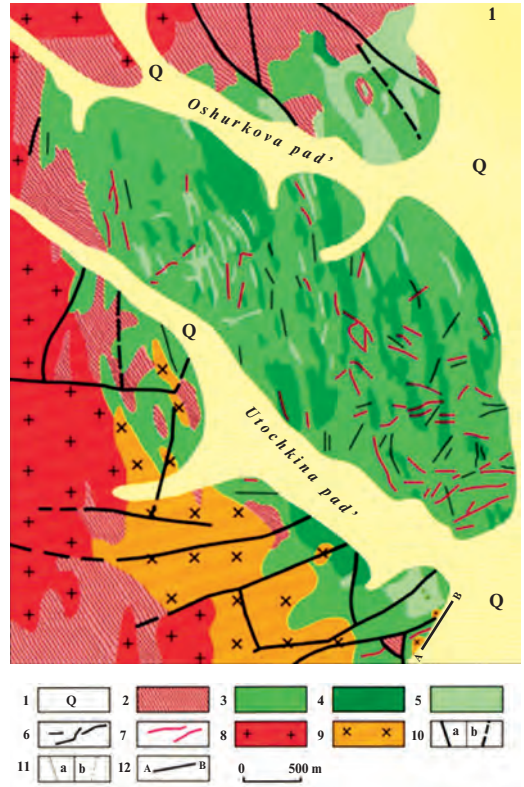


Fig. 1. The geological structure of the Oshurkovskiy massif (Kislov, 2011).

1 – quarternary sediments; 2 – gneisses and crystalline slates; 3 – alkaline melamonzonites; 4 – alkaline monzodiorites; 5 – alkaline monzonites; 6 – dikes of fine-grained monzodiorites, monzonites, lamprophyres and syenites; 7 – granite pegmatites; 8 – gneisso-granites; 9 – alkaline-feldspar syenites; 10 – main breaks; 11 – borders: a – distinct, b – uneven; 12 – A.E. Fersman outcrop.

2

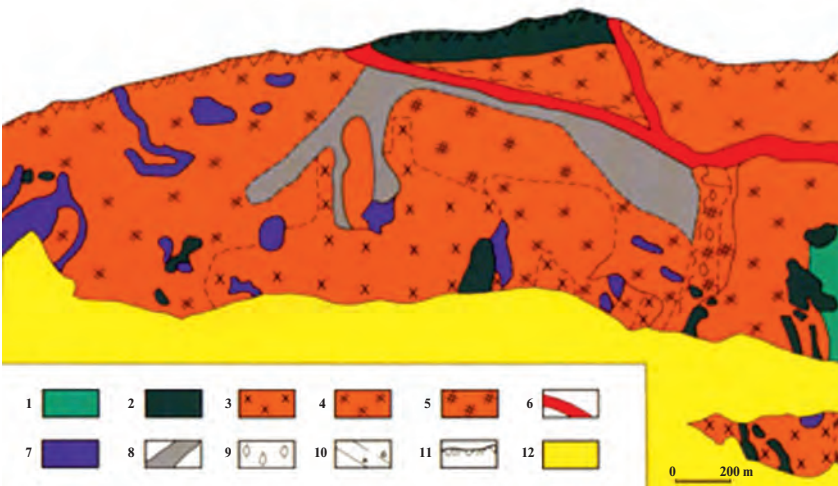


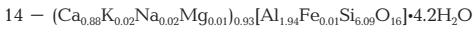
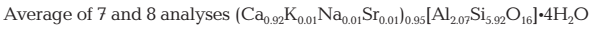
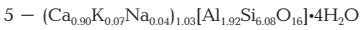
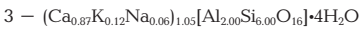
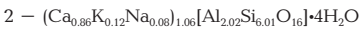
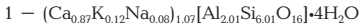
Fig. 2. Sketch of the A.E. Fersman outcrop (Kislov, 2011). Length of the outcrop is 200 m.

1 – monzonites; 2 – lamprophyre dyke; 3 – monzonites medium-grained; 4 – monzonites coarse-grained; 5 – gabbro pegmatites; 6 – granite pegmatites; 7 – vein-disseminated zeolites; 8 – carbonatites; 9 – coarse-grained apatite; 10 – contacts: a – distinct, b – gradual; 11 – soil layer; 12 – talus.

Table 1. Chemical composition (wt.%) of yugawaralite from the A.E. Fersman outcrop (1–6) and foreign locations (7–15)

Comp.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	59.96	58.82	59.63	59.16	59.04	57.59	61.44	61.47	57.94	58.44	59.58	61.14	61.81	61.74	62.30
Al ₂ O ₃	17.02	16.78	16.83	16.52	15.81	15.92	17.43	17.38	17.65	17.31	18.54	17.65	16.85	16.67	17.24
CaO	8.10	7.88	8.08	7.95	8.17	8.02	8.51	8.51	9.79	9.75	8.96	9.24	9.28	8.29	9.41
MgO				0.13		0.25	< 0.05	< 0.01	0.86	0.42				0.08	
Na ₂ O	0.41	0.38	0.30	0.27	0.22	0.58	0.07	0.06	0.38	0.38	0.19	0.08	0.05	0.11	0.10
K ₂ O	0.95	0.93	0.94	0.91	0.54	0.58	0.06	0.09	0.41	0.12	0.05	0.03		0.17	0.05
SrO							0.21	0.21				0.04			0.01
TiO ₂							< 0.01	< 0.01							
Fe ₂ O ₃							< 0.05	< 0.04	0.35	0.36	0.19	0.05		0.11	
H ₂ O ⁺							9.23	9.33			13.00	9.07			
H ₂ O ⁻							2.84	2.79	10.70	10.55		2.73			
H ₂ O									1.80	2.03			12.01	12.77	
Total	85.44	84.79	85.78	84.93	83.78	82.94			99.88	99.34	100.51	100.03	100.00	99.94	89.13
Si/Al	2.99	2.98	3.00	3.03	3.17	3.07									

Formulae, calculated on the basis of O = 16 apfu



Note. Yugawaralite from: 1–6 – A.E. Fersman outcrop (1–3 – sample 6, field 3, A-7; 4 – sample 6, field 1, B-3; 5, 6 – sample 2, B-5; our data, analyst: L.A. Pautov); 7, 8 – Chena Hot Springs, Alaska, USA (Eberlein, 1971); 9, 10 – Yugawara Hot Spring, Japan (Sakurai, Hayashi, 1952); 11, 12 – Nukabira, Hokkaido, Japan (Konno, Aoki, 1977); 13 – Khandivali quarry, India (Anthony *et al.*, 1990); 14 – Osilo, Sassari, Sardinia, Italy (Pongiluppi, 1977); 15 – Hvalfjörður, Iceland (Weisenberger, Selbekk, 2009).

a power dispersive (Si-Li) detector with an ATW-2 thin window at 20 kV accelerating voltage, 2 nA probe current). The standards used were as follows: SiK_α – quartz, AlK_α – albite, CaK_α – wollastonite, MgK_α – MgF₂, NaK_α – jadeite, KK_α – microcline, MnK_α – Mn₂SiO₄, FeK_α – FeO, TiK_α – TiO₂, BaK_α – BaSO₄, SrL_α – SrF₂. The water amount in zeolites was not determined.

X-ray powder diffraction data were obtained with Debye-Scherrer's method using a URS-50, RKD-57.3 camera, FeK_α radiation with Mn filter.

Investigation results

The zeolites found at the Oshurkovskoe deposit included yugawaralite, stellerite, lau-

montite, heulandite-Ca, and stilbite. Yugawaralite Ca[AlSi₃O₈]₂•4H₂O – a rare high-silicon zeolite with a Si:Al ratio = 3, was found in Russia for the first time.

The history of this mineral began in 1952. K. Sakurai and A. Hayashi (Sakurai, Hayashi, 1952) described yugawaralite in samples from Yugawara Hot Spring (Kanagawa prefecture, Honshu island, Japan) in association with zeolites, gyrolite, okenite, prehnite, quartz, and calcite. In 1971, yugawaralite was found in Alaska in association with quartz, laumontite, stellerite and stilbite in siliceous xenoliths in a small monzonite pluton, where colourless crystals of yugawaralite up to 8 mm long, usually covered with white powdery laumontite, has encrusted interstitial quartz (Eberlein *et al.*,

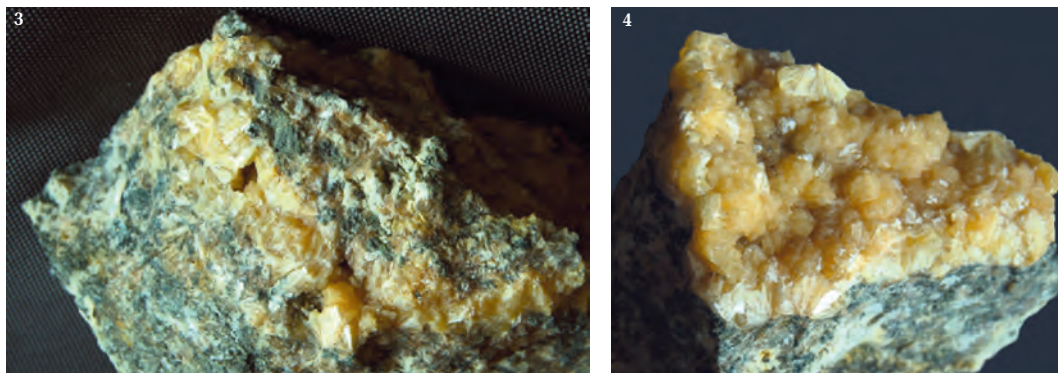


Fig. 3. A zeolitic veinlet in monzodiorite. Sample No. 5, 8 x 6.5 x 3 cm. Photo: I.A. Godovikov.



Fig. 4. Zeolite crust on a monzodiorite surface. Sample No. 2, 5 x 3.5 x 3 cm. Photo: I.A. Godovikov.

Table 2. Electron microprobe analyses (wt.%) for zeolites: laumontite (1–5), stellerite (6, 7), heulandite-Ca (8) from the A.E. Fersman outcrop, Oshurkovskoe apatite deposit

Comp.	1	2	3	4	5	6	7	8
SiO ₂	52.64	52.86	52.91	52.57	53.02	62.96	59.99	57.76
Al ₂ O ₃	21.29	21.54	21.32	21.96	21.27	15.64	14.17	16.71
CaO	11.21	11.15	11.10	11.16	10.81	8.18	7.73	4.89
Na ₂ O				0.18				
K ₂ O	0.97	0.81	0.55	0.61	1.15	0.23	0.24	2.08
SrO								4.31
BaO								0.49
Total	86.11	86.36	85.88	86.48	86.26	87.01	82.13	86.26
Si/Al	2.10	2.09	2.11	2.04	2.12	3.42	3.59	2.94

Formulae, calculated on the basis of O = 6 apfu

1 – (Ca _{0.92} K _{0.10}) _{1.02} [Al _{0.97} Si _{2.03} O ₆] ₂ •4H ₂ O
2 – (Ca _{0.92} K _{0.08}) _{1.00} [Al _{0.97} Si _{2.03} O ₆] ₂ •4H ₂ O
3 – (Ca _{0.92} K _{0.06}) _{0.98} [Al _{0.97} Si _{2.04} O ₆] ₂ •4H ₂ O
4 – (Ca _{0.90} Na _{0.02} K _{0.03}) _{0.95} [Al _{0.99} Si _{2.02} O ₆] ₂ •4H ₂ O
5 – (Ca _{0.90} K _{0.12}) _{1.02} [Al _{0.96} Si _{2.04} O ₆] ₂ •4H ₂ O
Average of 1–5 analyses (Ca _{0.91} K _{0.08}) _{0.96} [Al _{0.97} Si _{2.03} O ₆] ₂ •4H ₂ O
6 – (Ca _{0.97} K _{0.03}) _{1.00} [Al _{2.04} Si _{6.97} O _{18.00}] ₂ •28H ₂ O
7 – (Ca _{0.97} K _{0.03}) _{1.00} [Al _{1.96} Si _{7.03} O _{18.00}] ₂ •28H ₂ O
Average of 6 and 7 analyses
(Ca _{0.97} K _{0.03}) _{1.00} [Al _{2.00} Si _{7.00} O _{18.00}] ₂ •28H ₂ O
8 – (Ca _{2.46} K _{1.23} Sr _{1.19} Ba _{0.09}) _{4.97} [Al _{9.17} Si _{26.9} O ₇₂] ₂ •24H ₂ O
Ideal formulae: laumontite – Ca[AlSi ₃ O ₆] ₂ •4H ₂ O, Si/Al = 2;
stellerite – Ca[Al ₂ Si ₇ O ₁₈] ₂ •28H ₂ O, Si/Al = 3.5;
heulandite-Ca – Ca ₂ (Ca ₁ Na) _{4.6} Al ₆ (Al ₁ Si) ₄ Si ₂₆ O ₇₂ •24H ₂ O

Note. Analysed sample # 6. Analyst L.A. Pautov.

1971). In 1977 yugawaralite was found in Italy (Osilo, near Sassari, Sardinia) in altered gray-green andesite in association with laumontite, heulandite, stilbite, chabazite, mordenite, barite, calcite, ankerite and quartz (Pongiluppi, 1977). Crystals of yugawaralite from Iceland were found as plates 0.3–0.6 cm long, sometimes to 1 cm, in strongly altered andesites together with calcite, quartz, heulandite, stilbite and stellerite (Weisenberger, Selbekk, 2009). There were reports on finds of yugawaralite in the USA (Washington and Wyoming), New Zealand, Argentina, and India (Wise, 1978; Barga *et al.*, 1981; Railton, Watters, 1990; Tschernich, 1992; Leal *et al.*, 2011). Microprobe analyses of yugawaralite from the above noted deposits are shown in Table 1 (An. 7–15).

In the A.E. Fersman outcrop of the Oshurkovskoe deposit, yugawaralite was found in zeolitic veinlets, which cut monzodiorite, in association with laumontite, stellerite, heulandite, and stilbite (Fig. 3), as well as botryoidal crusts on the surface of fragments of monzodiorite (Fig. 4). The color of the zeolitic veins and crusts is light-beige, due to stilbite, which is the dominant zeolite component. Yugawaralite is found as colourless thin plates from ~ 70 × 30 to 800 × 100 microns in size. Electron-probe microanalyses of three yugawaralite grains, extracted from two different samples, are shown in Table 1 (an. 1–6). As seen in Table 1, the mineral composition is rather constant, and close to the theoretical formula: Ca[AlSi₃O₈]₂•4H₂O. The association of yugawaralite (Table 1, an. 4) with heulandite-Ca (Table 2, an. 8) and orthoclase (Table 3, an. 13) is shown in figure 5.

X-Ray powder data on yugawaralite from A.E. Fersman's outcrop, its synthetic analogue, as well as data on this mineral from other locations are shown in Table 4.

Table 3. Electron microprobe analyses (wt.%) for pyroxenes (1, 2 – augite, 3, 4 – pigeonite, 5–10 – diopside-hedenbergite), ferroedenite (11, 12), orthoclase (13), titanite (14) and ilmenite (15) from the A.E. Fersman outcrop, Oshurkovskoe apatite deposit

Comp.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	52.37	52.84	52.29	53.19	52.56	51.52	52.65	51.72	53.19	52.12	41.99	41.33	63.53	29.8	
Al ₂ O ₃	1.58	1.59	2.53	2.44	1.84	2.85	1.80	2.69	1.17	1.85	8.93	9.13	19.51	1.07	
CaO	20.15	20.55	11.89	11.92	20.61	21.18	21.58	20.86	21.05	20.14	9.49	9.61		26.32	0.67
MgO	11.30	11.16	15.41	15.15	12.14	11.85	11.76	11.74	11.59	10.91	6.39	5.81			
Na ₂ O	1.81	1.83	0.87	0.63	1.41	1.57	1.36	1.34	1.54	1.59	2.36	2.13	1.81		
K ₂ O			0.20	0.18							1.52	1.46	13.17		
BaO													1.77		
MnO	0.44	0.03		0.30	0.25		0.52		0.43	0.17	5.86	6.22			1.64
TiO ₂	0.29	0.43	0.32		0.52	0.57		0.60		0.41	0.62	0.49		36.43	45.93
FeO	12.47	11.84	13.26	13.74	10.87	11.07	10.10	10.74	10.87	11.38	21.04	21.01		1.58	48.29
Ce															0.97
Total	100.41	100.54	96.77	97.55	100.2	100.61	99.77	99.69	99.84	98.57	98.2	97.19	101.13	96.17	96.52

Formulae, calculated on the basis of: O = 6 apfu (1–10), O = 24 apfu (11, 12), O = 8 apfu (13), O = 5 apfu (14), O = 3 apfu (15)

1 – (Ca_{0.81}Na_{0.13})_{0.94}(Mg_{0.64}Fe_{0.39}Ti_{0.01})_{1.04}[Al_{0.07}Si_{1.98}]_{2.05}O₆

2 – (Ca_{0.83}Na_{0.13})_{0.96}(Mg_{0.62}Fe_{0.37}Ti_{0.01})_{1.00}[Al_{0.07}Si_{1.98}]_{2.05}O₆

3 – (Ca_{0.49}Fe_{0.42}Na_{0.06}K_{0.01})_{0.98}(Mg_{0.88}Al_{0.11}Ti_{0.01})_{1.00}[Si_{1.99}O₆]

4 – (Ca_{0.48}Fe_{0.40}Na_{0.05}K_{0.01})_{0.94}(Mg_{0.85}Al_{0.11}Fe_{0.03}Mn_{0.01}Ti_{0.01})_{1.01}[Si_{2.01}O₆]

5 – (Ca_{0.83}Na_{0.10})_{0.93}(Mg_{0.68}Fe_{0.34}Ti_{0.01}Mn_{0.01})_{1.04}[(Al_{0.08}Si_{1.97})_{2.05}O₆]

6 – (Ca_{0.85}Na_{0.10})_{0.96}(Mg_{0.66}Fe_{0.35}Ti_{0.02})_{1.03}[(Al_{0.13}Si_{1.93})_{2.06}O₆]

7 – (Ca_{0.87}Na_{0.10})_{0.97}(Mg_{0.66}Fe_{0.32}Mn_{0.02})_{1.00}[(Al_{0.06}Si_{1.98})_{2.06}O₆]

8 – (Ca_{0.84}Na_{0.10})_{0.94}(Mg_{0.66}Fe_{0.34}Ti_{0.02})_{1.02}[(Al_{0.12}Si_{1.95})_{2.07}O₆]

9 – (Ca_{0.85}Na_{0.11})_{0.96}(Mg_{0.65}Fe_{0.34}Mn_{0.01})_{1.00}[(Al_{0.05}Si_{2.0})_{2.05}O₆]

10 – (Ca_{0.82}Na_{0.12})_{0.94}(Mg_{0.62}Fe_{0.36}Mn_{0.01}Ti_{0.01})_{1.00}[(Al_{0.08}Si_{1.99})_{2.07}O₆]

11 – Na_{0.75}(Ca_{1.67}K_{0.32})_{1.99}Mn_{0.81}²⁺(Fe_{2.89}Mg_{1.56}Al_{0.61}Ti_{0.08})_{5.14}(OH)₂[(Al_{0.56}Si_{3.44})_{4.00}O₁₁]₂

12 – Na_{0.69}(Ca_{1.71}K_{0.31})_{2.02}Mn_{0.88}²⁺(Fe_{2.92}Mg_{1.44}Al_{0.67}Ti_{0.08})_{5.09}(OH)₂[(Al_{0.56}Si_{3.44})_{4.00}O₁₁]₂

13 – (K_{0.77}Na_{0.16}Ba_{0.03}Sr_{0.03}Ni_{0.02})_{1.01}[Al_{1.06}Si_{2.93}O₈]

14 – Ca_{0.96}(Ti_{0.93}Fe_{0.04}Ce_{0.01})_{0.98}O[(Si_{1.01}Al_{0.04})_{1.05}O_{3.98}]

15 – Fe_{1.08}Ti_{0.93}Ca_{0.02}Mn_{0.03}O₃

Ideal formulae are as follows: augite (Ca,Na)(Mg,Fe,Al)[(Si,Al)₂O₆], diopside CaMg[Si₂O₆], hedenbergite CaFe[Si₂O₆], pigeonite (Mg,Fe,Ca)(Mg,Fe)[Si₂O₆], ferroedenite NaCa₂(Fe²⁺,Mg)₃(OH)₂[Al_{0.5}Si_{3.5}O₁₁]₂, titanite CaTiO[SiO₄], ilmenite FeTiO₃.

Notes. 1–3 – sample 5, A-10; 4 – sample 5, A-9; 5 – sample 6, field 3, A-3; 6–8 – sample 6, field 3, A-4; 9, 10 – sample 5, A-9; 11, 12 – sample 6, field 1; 13 – sample 6, field 4; besides (wt. %) NiO 0.39, Sr O 0.97 (corresponds (apfu): Ni 0.02, Sr 0.03); 14 – sample 6, field 3; 15 – sample 5, A-10. Analyst L.A. Pautov.

Laumontite Ca[AlSi₂O₆]₂•4H₂O is found as fragile colourless acicular crystals in association with yugawaralite, and also as monomineralic crusts of colourless radial aggregates from 3 mm to 1.5 cm in diameter. The chemical composition of laumontite (Table 2, An. 1–5) is constant, and its X-Ray powder data (Tab. 4) correspond to reference literature data.

Stellerite Ca₄[Al₂Si₇O₁₈]₄•28H₂O forms small grains (to 500 × 60–70 microns), similar to yugawaralite grains. Microprobe analyses agree well with the stellerite formula (Table 2, An. 6, 7); X-Ray powder data (Table 4) correspond to those of stellerite from Sardinia.

Heulandite-Ca Ca(Ca,Na)₂₋₃Al₃(Al,Si)₂Si₁₃O₃₆•12H₂O occurs as colourless tabular crystals with a perfect cleavage, reaching 0.4 × 1 cm size. The association of heulandite-Ca (Table 2, An. 8) with yugawaralite (Table 1, An. 4) and orthoclase (Table 3, An. 13) is shown in figure 5.

Stilbite (Na,K,Ca)₆[Al₉Si₂₇O₇₂]₂•28H₂O, is a major constituent of the zeolitic veinlets and crusts, where it forms parallel-lamellar aggregates with a rounded split shape. The length of plates is up to 1.5 cm, and the color is light-beige.

The garnet found at this locality belongs to the almandine Fe₃²⁺Al₂[SiO₄]₃ – spessartite

Table 4. Continuation

Yugawaralite						Laumontite			Stellerite		
1	2	3		4	5	6	7	8	9		
<i>I</i>	<i>d_w</i> , Å	<i>I</i>	<i>d_w</i> , Å	<i>I</i>	<i>d_w</i> , Å	<i>I</i>	<i>d_w</i> , Å	<i>I</i>	<i>d_w</i> , Å	<i>I</i>	<i>d_w</i> , Å
2	2.20	5	2.197	5	2.194	—	—	—	—	—	—
2	2.16	5	2.153	5	2.151	—	—	—	—	—	—
—	—	5	1.138	5	2.137	—	—	—	—	—	—
—	—	10	2.106	5	2.105	—	—	—	—	—	—
1	2.09	25	2.092	10	2.091	—	—	—	—	—	—
1	2.02	10	2.018	5	2.017	—	—	—	—	—	—
—	—	15	2.005	10	2.004	—	—	—	—	—	—
1	1.995	10	1.997	15	1.977	—	—	—	—	—	—
2	1.944	—	—	10	1.953	—	—	—	—	—	—
—	—	20	1.934	10	1.932	—	—	—	—	—	—
1	1.904	25	1.900	5	1.907	—	—	—	—	—	—
2	1.881	5	1.883	10	1.899	—	—	—	—	—	—
—	—	—	—	5	1.874	—	—	—	—	—	—
2	1.782	5	1.788	5	1.787	—	—	—	—	—	—
1	1.745	5	1.753	5	1.752	—	—	—	—	—	—
2	1.731	20	1.735	—	—	—	—	—	—	—	—
1	1.718	—	—	15	1.722	—	—	—	—	—	—
—	—	10	1.696	10	1.698	—	—	—	—	—	—
3	1.684	5	1.681	5	1.681	—	—	—	—	—	—
2	1.644	5	1.649	5	1.648	—	—	—	—	—	—
2	1.598	5	1.613	5	1.615	—	—	—	—	—	—
1	1.562	5	1.564	5	1.567	—	—	—	—	—	—
1	1.538	15	1.538	10	1.540	—	—	—	—	—	—
2	1.528	10	1.528	5	1.524	—	—	—	—	—	—
—	—	15	1.510	10	1.512	—	—	—	—	—	—
—	—	—	—	5	1.496	—	—	—	—	—	—
1	1.473	15	1.468	10	1.470	—	—	—	—	—	—
2	1.448	10	1.453	5	1.455	—	—	—	—	—	—

Notes. Yugawaralite: 1 – A.E. Fersman outcrop, analyst L.A. Pautov; 2 – synthetic (Barrer, Marshall, 1965); 3 – Nikabira, Japan (Konno, 1977); 4 – Yugawara Hot Spring, Japan (Eberlein, 1971); 5 – Hot Spring, Alaska, USA (Eberlein, 1971). Laumontite: 6 – A.E. Fersman outcrop, analyst L.A. Pautov; 7 – (Mikheev, 1957, № 704). Stellerite: 8 – A.E. Fersman outcrop, analyst L.A. Pautov; 9 – Villanova, Monteleone, Sardinia, Italy (ASTM 25-124), its composition is as follows (wt. %): SiO₂ 59.15, Al₂O₃ 14.21, CaO 7.45, H₂O 17.79; besides there are traces of Fe, Mg, Sr, Mn, Ba, Na and K (quantities are not given), absent in stellerite from A.E. Fersman outcrop.

Mn₃²⁺Al₂[SiO₄]₃, solid solution series. It occurs as translucent bright red roundish grains up to 2 mm in size on which some faces may be visible. Microprobe analysis gave the following result (wt.%): MgO 0.42, Al₂O₃ 19.66, SiO₂ 36.34, CaO 2.91, MnO 27.82, FeO 12.42, total 99.57, which recalculates to the formula [(Mn_{0.65}Ca_{0.08}Mg_{0.02}Fe_{0.25})_{1.00}]₃[(Fe_{0.05}Al_{0.96})_{1.01}]₂[SiO₄]₃. The mineral was found in albite in association with quartz and pyroxene. An inclusion (~30 × 50 microns) with high reflection (Fig. 6) was discovered in the garnet. Its composition corresponds to the formula (Y_{2.35}Dy_{0.15}Er_{0.11}Yb_{0.08}Gd_{0.05}Ho_{0.04})_{2.78}(Fe_{1.14}Ca_{0.33}Mn_{0.12}Si_{0.11})_{1.70}[SiO₄]₃.

This rare-earth mineral was not precisely identified, and requires further study.

As noted above, the rock-forming minerals of the Oshurkovskoe apatite deposit have been studied by many researchers. We have identified the following additional pyroxenes from the A.E. Fersman outcrop: augite (Tab. 3, An. 1, 2), pigeonite (Tab. 3, An. 3, 4), and minerals of the diopside-hedenbergite CaMg[Si₂O₆] – CaFe[Si₂O₆] series (Tab. 3, An. 5 – 10). In addition, the amphibole ferroedenite was found (Tab. 3, An. 11, 12). We also performed analyses of orthoclase, sphene and ilmenite, which are shown in Table 3.

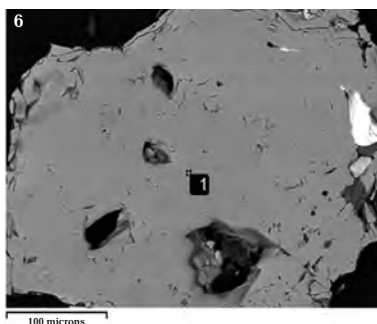
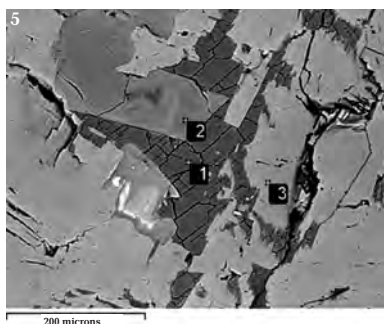


Fig. 5. Yugawaralite (tab. 1, point 1, an. 4), heulandite-Ca (tab. 2, point 2, an. 8), orthoclase (tab. 3, point 3, an. 13). Sample 6, area 1.

Fig. 6. A garnet group mineral (almandine – spessartite series) (gray) and an unidentified rare-earth silicate (bright white, ~ 50 x 30 microns). Sample 7, area 2.

Conclusions

1. Yugawaralite – a rare high-silicon zeolite with a Si/Al = 3 – was found for the first time in Russia at the A.E. Fersman outcrop in the Oshurkovskoe apatite deposit.

2. The zeolitic mineralization of this locality is described. Zeolitic veins occur in monzodiorite and as crusts on monzodiorite fragments. These contain stilbite, yugawaralite, laumontite, stellerite, and heulandite-Ca.

3. Newly recognized rock-forming minerals include: a member of almandine – spessartite solid solution series with composition $[(Mn_{0.65}Ca_{0.08}Mg_{0.02}Fe_{0.25})_{1.00}]_3[(Fe_{0.05}Al_{0.96})_{1.01}]_2[SiO_4]_3$ (25.2% of almandine and 74.8% of spessartite component), pyroxene group members (among them diopside-hedenbergite series minerals and pigeonite), and an amphibole group mineral corresponding to ferroedenite. A rare-earth phase was found as an inclusion in the garnet series mineral, which is close to $(Y,REE)_3(Fe,Ca,Mn)_2[SiO_4]_3$ in composition. The mineral requires additional investigation.

Aknowledgements

The authors thank Atali A. Agakhanov for qualitative microprobe analyses of samples and for preparation of samples for quantitative analysis, Vladimir Yu. Karpenko for help in X-Ray powder data acquisition and also Dr. M. Feinglos for English text editing.

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NEW DATA ON ALLANITE FROM VERKHOTURJE (FOR THE 180th ANNIVERSARY OF THE DISCOVERY OF ORTHITE IN RUSSIA)

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The history of the discovery of orthite in Russia (Verkhoturje, Central Ural Mountains) and the results of its investigation by A.Ya. Kupffer, G. Rose, R. Hermann, and N.I. Koksharov are briefly discussed in this article. Orthite was found as crystals in a pegmatite vein in biotite granites (Troitsky Stone). The main minerals are as follows: microcline, quartz, biotite, amphibole; minor and accessory species: allanite, magnetite, schorl, fluorapatite, zircon, epidote, calcite, chalcopyrite. New data on the composition and morphology of crystals are provided. The most developed forms are: (100), (001), (111), and (110); less developed forms are (101), (102), (103), (302), (304), (706), (221), and (112); occasionally — twins on (100) are found. Crystals are zonal and sectorial with respect to average atomic number and in the distribution of Ca, Fe, Al, REE, Th, and Ti. Orthite from Verkhoturje is allanite-(Ce); chemical composition (microprobe analysis, wt.%): SiO₂ 31.76–33.47; TiO₂ 0.10–0.23; ThO₂ 0.26–0.40; UO₂ 0.00–0.04; Al₂O₃ 16.85–20.05; Y₂O₃ 0.01–0.11; La₂O₃ 4.38–5.82; Ce₂O₃ 7.82–10.30; Pr₂O₃ 0.49–1.02; Nd₂O₃ 2.63–3.10; Sm₂O₃ 0.20–0.36; Gd₂O₃ 0.12–0.19; MgO 0.61–0.84; CaO 11.03–14.99; FeO 10.09–12.59; MnO 0.55–0.75; Na₂O 0.00–0.11; F 0.09–0.20; total 92.76–96.64. Comparison with the first analysis of R. Hermann (1848) (with La > Ce) is shown. The investigated mineral is poorly metamict, providing a reason for the underestimated totals of the analyses.

2 tables, 7 figures, 23 references.

Keywords: orthite, allanite, epidote group, pegmatites, Troitsky Stone, A. Kupffer, G. Rose, R. Hermann, N.I. Koksharov, A.E. Fersman.

Allanite a black aluminosilicate of rare earths, iron and calcium, was first described by T. Thompson and named in honor of the Scottish mineralogist Thomas Allan, who found this mineral in East Greenland (Thompson, 1810). The first find was soon followed by others: in 1818 Y. Berzelius found and described a similar mineral from Falun (Sweden) naming it "orthite" for its straight lines, and flat, radiant forms; in 1824 A. Levi discovered a black epidote near Arendal (Norway) and called it "bucklandite" in honor of the English geologist V. Buckland. There were also other numerous synonyms of allanite — orthite, reflecting properties of the mineral or its location (Armbruster *et al.*, 2006).

The discovery and investigation of orthite in Russia is connected with the names of famous Russian and European scientists and researchers — Adolf Kupffer, Gustav Rose, Rudolf Hermann, and Nikolai Koksharov.

A.Ya. Kupffer (Fig. 1), a native of Latvia, was awarded his PhD in Europe, followed by additional training in Paris (Pasetsky, 1984). In 1824 he was invited to join the faculty of Kazan University as a professor of physics, a post he held for four years. In 1828, because of his election as the academician of the Petersburg Academy of

Sciences, he moved to the capital. However, the summer before moving to St.-Petersburg, he undertook a journey across the Urals along the following route: Kazan' — Zlatoust — Yekaterinburg — Nizhnii Tagil — Kushva — Verkhoturje — Yekaterinburg — Kazan', accompanied by his colleague K. Klaus, a pharmacist and artist. Along the way, Kupffer carefully kept a diary in which he fixed the heights of ridges, their geological structure, meteoric conditions, the production and economic activity of factories and mines, and the living conditions and customs of urban and country people (Kupffer, 1833). In Verkhoturje (now a city in the Sverdlovsk oblast', Russia) Kupffer studied rocks on the bank of the Tura river around the so-called Troitsky (Trinity) Stone (Fig. 2), where he found orthite. He described the location as follows (Kupffer, 1833, p. 426): "Granites of Verkhoturje consist almost entirely of a white lamellar feldspar with a small amount of mica, and with still smaller amounts of quartz and garnet. These granites are most accessible on the left bank of the Tura River where they overhang as high cliffs. Rhomboidal prisms, with an angle of about 115°, of a black color, which melt easily in the flame of a blowpipe, and which were recognized by Mr. Berzelius as

orthite, are disseminated in this area through the right bank of the Tura river".

Kupffer provided some crystals to G. Rose, the mineralogy professor of the University of Berlin, for the further investigation of orthite from Verkhoturje. It should be noted that, before the discovery of orthite from Verkhoturje, many scientists (Thompson, Heidingen, Scherer, Breithaupt *et al.*) as well as Rose himself considered that allanite (orthite) belonged to the rhombic system due to the imperfection of the known crystals. Rose had investigated Kupffer's orthite after the completion of a famous expedition, led by Alexander von Humboldt, to the Urals and Siberia, in which he also participated (Rose, 1837). In one chapter, describing travel across the Central Ural Mountains, Rose noted a goniometrical investigation of orthite from Verkhoturje, and concluded that, as far as could be determined from, the angles of orthite that he could measure, the results were similar to those of epidote, and therefore, orthite is monoclinic. The forms found by G. Rose are *T*, *M* and *r* in the designations of Häuy for epidote (Rose, 1837), corresponding to *c* (001), *a* (100) and *r* (-101) today. Thus, Rose corrected an error of his predecessors. However, Rose did not manage to draw a full crystal of orthite: "*simple and twinned crystals occur, but, as far I can see, they are broken off at the ends*" (Rose, 1837; Koksharov, 1858). Without knowing the chemical composition of orthite, and solely on the basis of morphological features, Rose called orthite from Verkhoturje "black epidote", or bucklandite.

The chemistry of "black epidote" from Verkhoturje was established by Hans Rudolf Hermann (Fig. 3). In 1827 he left Dresden (Germany) for Moscow in order to organize a plant for production of artificial mineral waters. Subsequently, Moscow became a second home for Hermann (Trautshold, 1881; Liebman, 1956). He had



Fig. 1. Adolf Yakovlevich Kupffer (1799–1865) – the physicist, meteorologist, crystallographer, mineralogist, traveler. One of the founders of the meteorological and mineralogical services of Russia. Member of more than 20 Russian and foreign academies and societies (Pasetsky, 1984).

obtained no higher education, but, as a result of his intelligence and his enthusiasm for science, Hermann achieved amazing results. His skill in analytical chemistry of the REE, Zr, Th, U, Ta and Nb minerals is especially great. The father of modern crystallography, E.S. Fedorov, called Hermann one of founders of mineralogical science in Russia along with N.I. Koksharov and G. Rose.

In 1841 Hermann had received a sample of "chevkinite" from the Ilmen mountains for investigation. Following thorough evaluation, Hermann clearly proved its difference from chevkinite. He recognized the mineral as orthite and described it under the name uralorthite (Hermann, 1841). Thus, the Ilmen Mountains became the second location for orthite in Russia after Verkhoturje, and Hermann's chemical analysis was likely the first published for Russian orthite. Uralorthite probably originated in the No 22 pit according to M.P. Melnikov's numbering system (Popova *et al.*, 1980).

The find of "uralorthite" motivated Hermann to perform chemical analyses of other allanites,



Fig. 2. Verkhoturje. A view on the Holy Trinity Cathedral and the Troitsk Stone on the left bank of the Tura river – the locality of the initial find of orthite in Russia. Photo: S.A. Gavrilov, 2011.



Fig. 3. Rudolf Hermann (1805–1879) – scientist, mineralogist, one of the most authoritative Russian chemists-analysts of the middle of the 19th century, medicine doctor, a corresponding member of the Russian Academy of Sciences, the author of more than 180 scientific publications in Russian and German journals and transactions (Liebman, 1956).

Table 1. Composition of allanites from Verkhoturje (wt.%)

Compo- nents	Hermann,	Our data			
	1848*	1	2	3	4
SiO ₂	32.46	33.47	31.76	32.10	31.95
TiO ₂		0.10	0.16	0.19	0.23
ThO ₂		0.28	0.40	0.26	0.37
UO ₂		0.02	0.00	0.04	0.03
Al ₂ O ₃	18.09	20.05	17.10	17.46	16.85
Y ₂ O ₃	1.5	0.01	0.11	0.07	0.04
La ₂ O ₃	9.76	4.38	5.56	5.82	5.33
Ce ₂ O ₃	6.77	7.82	10.42	10.26	10.30
Pr ₂ O ₃		0.49	0.77	1.02	0.62
Nd ₂ O ₃		2.63	2.95	3.10	3.06
Sm ₂ O ₃		0.36	0.27	0.32	0.20
Gd ₂ O ₃		0.12	0.19	0.14	0.16
MgO	1.02	0.68	0.61	0.84	0.76
CaO	13.18	14.99	11.04	11.43	11.03
FeO	13.84**	10.09	11.32	12.59	11.06
MnO	traces	0.55	0.59	0.75	0.57
Na ₂ O		0.00	0.10	0.06	0.11
H ₂ O	3.40				
F		0.13	0.20	0.19	0.09
-O = F ₂		-0.05	-0.08	-0.08	-0.04
Total	100.02	96.17	93.55	96.64	92.76

Notes: * – CuO and Mn₂O₃ traces occur; ** – calc. on $\Sigma(\text{FeO} + \text{Fe}_2\text{O}_3)$.

An empty space means that component was not determined. 0.00 – component amounts are below detection limits. Analysis numbers correspond to those of the BSE image (Fig. 7); CAME-CA SX 100 microprobe analyzer. analyst V.V. Hiller.

Empirical formula of allanite (calc. on cation sum = 8 apfu, when Si > 3.05 formula normalized for Si = 3 apfu;

Armbruster et al., 2006): Hermann – (Al_{1.96}Fe_{0.89}Mg_{0.14}La_{0.11}Y_{0.01}(SiO₄)₂(Si₂O₇)O_{0.33}(OH)_{2.06};

1 – (Ca_{1.44}Ce_{0.26}La_{0.15}Nd_{0.08}Pr_{0.02}Sm_{0.01}Th_{0.01})_{1.97}(Al_{2.12}Fe_{0.76}Mg_{0.09}Mn_{0.04}Ti_{0.01})_{3.02}(SiO₄)(Si₂O₇)(O_{0.96}F_{0.04})OH_{0.70};

2 – (Ca_{1.12}Ce_{0.37}La_{0.20}Nd_{0.10}Pr_{0.03}Sm_{0.01}Th_{0.01}Gd_{0.01}Y_{0.01}Na_{0.02})_{1.88}(Al_{1.96}Fe_{0.89}Mg_{0.09}Mn_{0.05}Ti_{0.01})_{2.94}(SiO₄)(Si₂O₇)(O_{0.94}F_{0.06})(OH)_{0.35};

3 – (Ca_{1.22}Ce_{0.35}La_{0.20}Nd_{0.10}Pr_{0.03}Sm_{0.01}Th_{0.01}Na_{0.01})_{1.93}(Al_{1.92}Fe_{0.96}Mg_{0.12}Mn_{0.05}Ti_{0.02})_{3.01}(SiO₄)(Si₂O₇)(O_{0.94}F_{0.06})(OH)_{0.72};

4 – (Ca_{1.15}Ce_{0.35}La_{0.15}Nd_{0.11}Pr_{0.02}Sm_{0.01}Th_{0.01}Gd_{0.01}Na_{0.02})_{1.87}(Al_{1.86}Fe_{0.87}Mg_{0.11}Mn_{0.05}Ti_{0.03})_{2.94}(SiO₄)(Si₂O₇)(O_{0.97}F_{0.03})(OH)_{0.22}.

orthites, and "black epidotes" from Northern Europe and Verkhoturje (Hermann, 1848). There are now multiple accurate chemical composition data for orthite from Verkhoturje to compare with Hermann's (Table 1). Based on the analyses of the studied minerals and the goniometrical measurements of orthite crystals from Verkhoturje and "uralorthite" from the Ilmen mountains, performed by Rose, Hermann concluded that all the studied minerals are orthites, and members of the epidote group (Hermann, 1848). Somewhat later, N.I. Koksharov independently arrived at the same conclusion (Koksharov, 1848). Historically, the names "allanite" and "orthite" have been used to designate the tabular crystal and the prismatic metamict water-containing varieties, respectively. In 1986 the CNMMN IMA retained only the root name "allanite", and Thompson's mineral was called allanite-(Ce) (Nickel, Mandarino, 1987). Mineral species status was also assigned to allanite-(Y) and allanite-(La) (Armbruster et al., 2006). Thus, in compliance with the requirements of modern nomenclature, orthite from Verkhoturje is allanite.

During the preparation of this paper, we were unable to find any publications on the morphology of allanite from Verkhoturje. A visit by one of the authors (VAG) in 2013 to Verkhoturje did not solve the problem either, since allanite from the Troitsk Stone pegmatite veins was quite suitable for chemical analyses, but not for crystallographic measurements (Fig. 4).

Crystals of allanite from this locality, however, were found in collection of Alexander Evgenyevich Fersman. A.E. Fersman visited Verkhoturje twice as part of the Radium expedition founded by academician V.I. Vernadsky in 1911 for the study of the radioactive minerals and ores of Russia. In 1912 he visited the locality with V.I. Vernadsky, and in 1913 with the chemist-mineralogist B.A. Lindener. During the second trip, material with well-shaped allanite crystals was found, and the distribution of veins containing the mineral was also established. Fersman describes those places as follows: "In the Troitsk Stone the leucocratic veins with orthite occur, yet they are limited there, so it is not possible to extract any good material from them. But in a stone quarry in the countryside behind the Convent we succeeded in collecting excellent material. In a northwest angle of the quarry an especially rich pegmatite vein was discovered, which provided not only several chunks of rock containing this mineral, but also many regular crystals, with numerous faces and well-formed terminations" (Fersman, 1914, p. 159).



Fig. 4. Allanite crystal (1.8 cm) in a quartz-feldspar pegmatite. Verkhoturje, Troitsky (Trinity) Stone. Photo: V.A. Gubin.

Fig. 5. Allanite, a twin on {100} (1cm). Verkhoturje, a pit over the Convent. FMM, systematic collection, № 21851, collected by A.E. Fersman and B.A. Lindener, 1913. Photo: M.M. Moiseev.

Pegmatite veins containing allanite near Verkhoturje occur in a base biotite granite of the Hercynian age, without any stratification. Fersman considered these pegmatites the earliest, deep type I (allanite pegmatites subtype), corresponding to B- and C-geophases (Fersman, 1940). Pegmatites of the Troitsk Stone are mainly comprised of plagioclase; microcline, quartz, biotite and hornblende occur in lesser amounts. The list of pegmatite accessory minerals is also modest, and includes allanite, magnetite, chalcopyrite, and schorl. Additionally we have collected samples of fluorapatite (with F = 3.43 wt.%, REE = 0.35 wt.%), zircon, epidote and calcite.

After his travels Alexander Evgenyevich donated the minerals he collected to a number of Russian museums and universities, but mainly to the Mineralogical Museum of the Russian Academy of Sciences. Mineralogical collections contributed by A.E. Fersman were organized systematically recently by V.D. Dusmatov based on locations and by numbers (Dusmatov, 2003). Among them, allanite-(Ce) samples from Verkhoturje also occur, collected by A.E. Fersman and B.A. Lindener in 1913 in the above mentioned stone quarry (№№ 702 – 707 from the deposits col-

lection and №№ 21846 – 21856 from the systematic collection).

Examination of the collection shows that allanite-(Ce) crystals (both single and twins) are fresh, black, and without character "coffee color" surface of change. Fragments of crystal faces are flat, but with little luster (Fig. 5); some crystals have well shaped terminations. Crystals cataloged in the systematic collection at № 21851 are of especially high quality. The size of separate crystals reaches 2.5 x 1 cm, although the average does not exceed 1 cm. Goniometrical measurements with a Fedorov stage, mounted under binocular microscope were taken (Fig. 6).

Except for flat faces, a considerable part of the surface of the crystals is covered with simultaneous growth induction surfaces of allanite with quartz, biotite and feldspar.

X-ray investigation shows this material is poorly metamict. The powder data of one of the crystal fragments (FMM № 21851) are shown in Table 2. In contrast to typical non-metamict allanite-(Ce) (Cech *et al.*, 1972), the powder data of allanite from Verkhoturje is characterized by a small set of lines, which are partially widened and blurred.

The chemical composition of allanite samples, collected in Verkhoturje by the authors, was

Fig. 6. Crystals and twins of allanite-(Ce) from Verkhoturje (FMM systematic collection, № 21851).

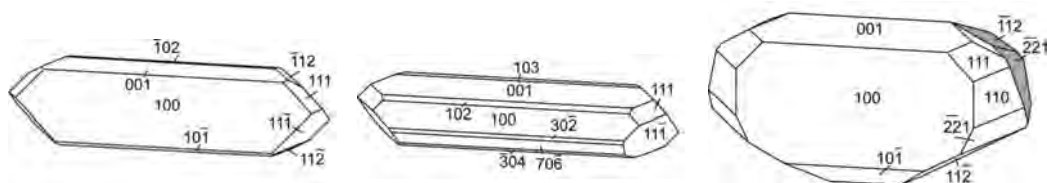


Table 2. X-Ray powder data for allanite-(Ce) from Verkhoturje, Mid. Ural, and Zambia

Verkhoturje (our data)		Luangwe, Zambia (Cech <i>et al.</i> , 1972)*		
<i>I</i>	<i>d/n</i> , Å	<i>I</i>	<i>d/n</i> , Å	<i>hkl</i>
		8	9.23	001
		11	8.11	100
		17	7.96	-101
		13	5.12	101
		10	5.02	-102
		5	4.89	011
10w	4.72	15	4.70	-110
		10	4.61	002
		1	4.06	200
		3	3.98	-202
		4	3.83	111
		8	3.79	-112
		9	3.60	012
90	3.523	45	3.53	-211
30	3.355	7	3.32	-210
		6	3.28	-212
		13	3.25	201
		2	3.17	-203
100	2.921	100	2.920	-113
30w	2.845	30	2.886	020
		16	2.829	211
		5	2.753	021
40w	2.707	65	2.714	013
		5	2.658	-303
50	2.619	40	2.627	-311
		20	2.561	202
		10	2.506	-204
10	2.462	8	2.447	022
10	2.415	14	2.413	-313
		13	2.337	-222
		8	2.301	-114
		5	2.291	-304
		2	2.233	-402
		7	2.210	122
		12	2.193	-123
		35	2.182	-401
20w	2.141	25	2.158	-403
		13	2.141	014
		19	2.135	-223
20w	2.117	11	2.105	023
		5	2.070	203
		3	2.056	322
		3	2.030	-205

Notes: w – wide line; operating conditions (allanite from Verkhoturje): photomethod, Guinier camera Huber 621 with quartz monochromator; CuK α , radiation; quartz used as internal standard, analyst V.Yu. Karpenko; * – data for *d/n* < 2.00 are omitted.

determined at the Institute of Geology and Geochemistry (Yekaterinburg) using a CAMECA SX 100 microprobe analyzer equipped with a wave dispersive spectrometer at 15 kV accelerating voltage, 100 nA probe current (Fig. 7, Table 2, analyst V.V. Hiller). The standards used were pure synthetic phosphates (*REE*)PO₄ (Y, La, Ce, Pr, Nd, Sm, Gd), Fe₂O₃ (Fe), TiO₂ (Ti), ThO₂ (Th), UO₂ (U), diopside (Si, Mg, Ca), rhodonite (Mn), jadeite (Na, Al), fluor-phlogopite (F on LPCO crystal analyzer). Maps were acquired for 260 minutes (each map) with an accelerating voltage of 15 kV and a beam current of 100 nA; scanning time for each map point was 100 ms. We analysed 15 points from which 4 typical points were chosen from different growth zones. The material we analyzed has selective-cerium composition of lanthanides with actual dominance of cerium. Thus, the mineral corresponds to allanite-(Ce). We note a rather large amount of magnesium (MgO ~ 0.9 wt.%), which can be explained by the increased Mg-content of the host granites. Weak metamictization of the mineral fixed by X-ray is probably related to the presence of trace amounts of Th. In general, modern microprobe analyses are close to that of R. Hermann (Table 1). However, in Hermann's analysis La prevails over Ce, and, according to the modern nomenclature of epidote-group minerals (Nickel, Mandarino, 1987; Armbruster *et al.*, 2006), it would be necessary to call this mineral allanite-(La). However, it may be premature to apply this label due to imperfections in the old analysis technique, as only one random section was investigated. In addition, at the time of Hermann's analysis (1848) some of the rare earth elements were not known yet, and some mixed data could lead to the corresponding result.

A wide variety of isomorphous substitutions are typical for allanites, as described by many authors (Hvostova, 1962; Kepizhinskas, Hlyostov, 1971; Gieré, Sorensen, 2004; Armbruster *et al.*, 2006; etc.). Along with the widespread scheme of heterovalent isomorphism Ca²⁺ + Al³⁺ ↔ REE³⁺ + Fe²⁺ it is necessary to specify others, as well. Some Mn, Mg and F indicates the presence of dolasseite-(Ce) and khristovite-(Ce) components and the implementation of the mechanisms Ca²⁺ + Al³⁺ ↔ REE³⁺ + (Mn, Mg)²⁺ and Al³⁺ + O²⁻ ↔ (Mn, Mg)²⁺ + F⁻ (Pecacor, Dunn, 1988; Pautov *et al.*, 1993). Th and U can enter according to the scheme (Th, U)⁴⁺ + 2M²⁺ ↔ Ca²⁺ + 2REE³⁺ (where M = Fe²⁺, Mn²⁺, Mg²⁺) (Gieré, Sorensen, 2004).

The complex growing zonality and sectoriality of an allanite crystal section observed in BSE mode does not always correlate with the

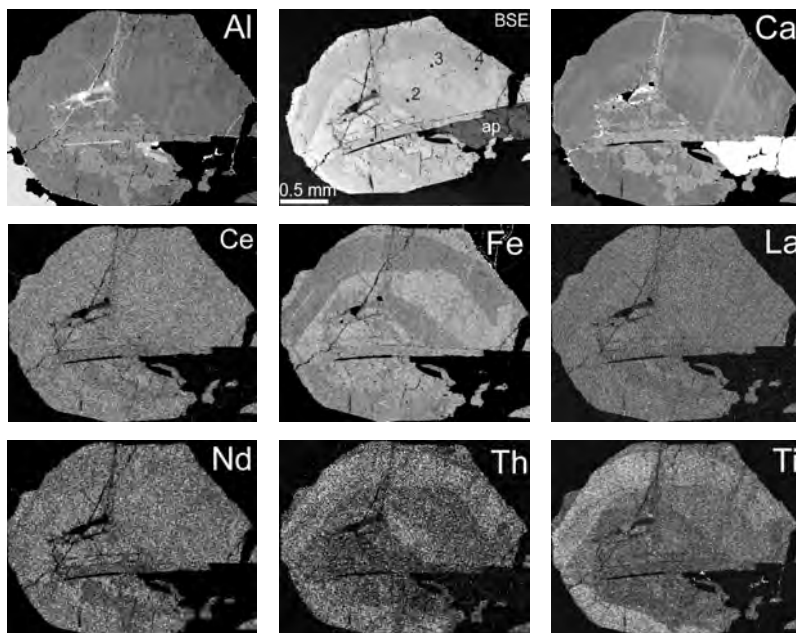


Fig. 7. Cross section of the allanite-(Ce) crystal. Back scattered electrons (BSE) and AlK α , FeK α , CaK α , TiK α , CeL α , LaL α , NdL α , ThM α X-ray radiation images. Analyst V.V. Hiller.

variability of amounts of a specific element, and most likely reflects the summary result of several schemes of isomorphous substitution (Fig. 7). In the central (lower) part of a random crystal section there are areas with an excessive amount of Ca and Al, which are close to epidote (Table 1, analysis 1). Spottiness possibly is connected with the crystal block growth there. Theoretically it is possible to find a rare-earth epidote in a full anatomic section along a crystal. Titanium and thorium both give a similar distribution picture, but their sectoriality is obviously different (Fig. 7). There is no expressed zonality for rare earth distribution in the studied sample, yet sectoriality is noticeable, especially for cerium and lanthanum. A lack of totals for analyses 2 and 4 most likely is connected with metamictization of the corresponding zones, probably caused by their enrichment with thorium; this is confirmed by the corresponding illustration (Fig. 7). A similar example can be seen for allanite-(Ce) from quartz veins of the Aldridge Formation, British Columbia, Canada (Campbell, Ethier, 1984).

The described heterogeneity of the studied crystal composition allows one to assume variations of composition of allanites both in the whole granite massif, and in the pegmatite veins.

The wide spread occurrence of allanite in the Verkhoturjsky region is has long been well known. In such a large mineralogical occurrence, considerable variations of forms and

composition of minerals in different rock phases and facies would be expected. This is confirmed by our additional research.

Verkhoturje is a region in which it is possible to study allanite typomorphism on the basis of mineralogical mapping. Allanites we have inspected from different collections, judging by induction surfaces, grew synchronously with surrounding magmatic minerals. Therefore, their typomorphism can be related to that of other minerals of the corresponding paragenesis.

The authors thank V.N. Onosova, T.B. Kochergina and Z.A. Spiridonova, library employees of Yekaterinburg, for their help in selection of historical literature, S.A. Gavrillov for a fine panoramic exposure of the Troitsk Stone, M.M. Moiseev for the twinned crystal photo, E.M. Spiridonov and L.A. Pautov for valuable advice and also Dr. M. Feinglos for English text editing.

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NEW DATA ON MINERALOGY OF DEPOSITS OF PLUTONOGENIC GOLD-QUARTZ FORMATION IN THE NORTHERN CENTRAL KAZAKHSTAN. PART I

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The formation history of mineralogy of plutogenic gold-quartz deposits of the Stepnyak group in the Northern Central Kazakhstan is discussed. Mineral facies referred to the depth of the deposit formation; mineralogical features of ore shoots, nature of ore-bearing fluids, white micas, quartz, carbonates, scheelite, pyrite, arsenopyrite, pyrrothite, gersdorffite, sphalerite, berthierite, argentotennantite, argentotetrahedrite, roshchinite, bismuth tellurides and sulfotellurides, mattagamite, Co-bearing frobergite and melonite, montbrayite, calaverite, sylvanite, petzite, petzite-hessite solid solution, and hessite are reported. The deposition sequence from Au to Ag tellurides and affinity for Te: Co > Fe, Ni > Bi, Sb > Pb > Ag, Hg > Au, Cu are improved. 10 figures, 8 tables, 60 references.

Keywords: scheelite, mattagamite, frobergite, melonite, montbrayite, calaverite, krennerite, sylvanite, petzite-hessite solid solution, affinity to Te.

Despite many reviews, current state of geology causes genetic typification of gold deposits. One of the ways is the detailed study of specific gold formations, and separate gold provinces and deposits.

Hydrothermal gold deposits are frequently referred to the three formations on the basis of the forming depth: (1) shallow (with abundant sulfides, low-fineness gold, Ag sulfosalts), (2) medium (with moderate sulfides and relatively low-fineness gold), and (3) deep (low sulfides with high-fineness gold) (Petrovskaya *et al.*, 1976). This conventional in our country classification is not up to the recent geological standards. For example, many deep-seated deposits are enriched in sulfides; low-sulfide deposits with high-fineness gold are abundant among shallow deposits; some deposits with features typical of shallow deposits were formed at the depth of 1.5–2 km; the deposits with features characteristic of deep-seated deposits were formed at the same depth. The classification of hydrothermal gold deposits on the basis of host rocks (many US researchers) or basic formations (groups of large-volume deposits of sulfide ores) is unconvincing. The classifications of Lindgren (1933), Schneiderhöhn (1941), Bilibin (1947), Ramdohr (1980), Smirnov (1982), and similar classifications of Ivensen and Levin (1975), and Spiridonov (1995; 2010) taking into account geological features of gold deposits and in particular magmatic rocks to which mineralization is related are better argued. Hydrothermal plutogenic formations of folded areas, volcanogenic formations of folded areas, arcs, and mid-oceanic ridges, volcano-plutonogenic formations, and amagmatic formations are distinguished on the basis of type of magmatic rocks, which imme-

diately predated or accompanied gold mineralization.

Plutonogenic hydrothermal gold-quartz formation. The deposits of the plutogenic gold-quartz beresite-listvenite formation are paragenetically related to tonalite-granodiorite-plagiogranite, adamellite, and monzonite-granite intrusive complexes of folded areas. These deposits are formed in closed system under elevated pressure (P). The P value is determined by the top of hydrothermal system located close to the roof of intrusives or slightly above. The lowest pressure estimated from fluid inclusions (FI) in the early quartz and carbonates of the ores ranges from 0.3 to 0.6 kbar (Spiridonov, 1995; Trumbull *et al.*, 1996) that corresponds to the shallowest formation depth of 1 to 1.5 km; the highest values reach 3.5–4 kbar (cca. 12–15 km) (Spiridonov, 1995; Hagemann and Brown, 1996; Mishra and Panigrahi, 1999; Jia *et al.*, 2000). The P values higher than 4 kbar correspond to the metamorphosed ore. The Early Archaean to Cenozoic plutogenic gold deposits were formed under relatively stable pressure at gradual temperature decreasing. Subtle (to disappearance) vertical geochemical and mineralogical zoning is typical (Smith, 1948; Naz'mova *et al.*, 1978; Spiridonov, 1995). Long vertical extension of gold mineralization is typical: 4.5 km, cca. 5 km taking into account erosion level at Kolar, India; cca. 3 km at Moro Velho, Brazil; cca. 2.5 km at Ashanti, Ghana; cca. 2 km at dozen deposits in Canada, Africa, Australia, and Kazakhstan.

North Kazakhstan gold province. The North Kazakhstan gold province localized in the western Caledonian megablock of the Northern Central Kazakhstan (Bogdanov, 1959, 1965; Shul'ga and Bulygo, 1969; Geology...

1971) comprises Stepnyak megasinclinorium (East-Kokchetav depression) and adjacent regions. In the western megablock, granitoids and metamorphic sequences with the Proterozoic granitic gneiss domes are abundant (Spiridonov, 1982); ultramafic rocks and olistostrome sequences are less common; and gold mineralization is mainly plutogenic. The Proterozoic metamorphic sequences form "granitic layer" of the Earth crust of the region that underlays in places the Archean granulite layer according to xenoliths in the Stepnyak pluton. The outlines of the ancient continental mass are marked by the chains of zircon and rutile paleoplacers hosted in the Late Riphean to Vendian quartzite-sandstone in the Kokchetav, Ishke-Ulmes, and Erementau Rises (Shlygin, 1962; Spiridonov, 1987, 1991). At the Caledonian stage, the Earth crust of the region was substantially altered. For example, in the Kokchetav Rise (middle massif) the Zerinda granodiorite-adamellite batholith with $^{86}\text{Sr}/^{87}\text{Sr} = 0.703_5$ – (Shatagin, 1994) that is age and formation analogue of the Krykkuduk Complex of the Stepnyak Depression was arisen among metamorphic sequences with $^{86}\text{Sr}/^{87}\text{Sr} = 0.716$.

In the eastern Maikain megablock, there are numerous ultramafic bodies and olistostrome sequences; granitoids are few; gold mineralization is referred to the massive-sulfide type (Geology..., 1971); this area is developed on the crust of ocean type.

The Caledonian Stepnyak megasinclinorium comprises the Stepnyak and Selety depressions (sinclinorium) and Ishke-Ulmes Rise (anticlinorium) (Shul'ga and Bulygo, 1969). Gold deposits are located within these structures close to the boundaries between them. As all over the world (Nesbitt, 1988), mesothermal gold-quartz deposits of the Stepnyak group are hosted in the upper part of continental crust within the zone of brittle deformation above isotherm 400°C.

Gold deposits of the Stepnyak group

Why this group of plutogenic gold deposits is of the greatest interest? Because these deposits are located in non-linear folded area and are not affected post-ore tectonization and metamorphism; they are located in the Caledonian folded structures. Here, there are extremely shallow to highly deep-seated coeval deposits, which are unusual in Mezo-Cenozoic and Pre-Paleozoic folded areas. All crucial deposits are opened by mines and deep drill holes because unlike Uzbekistan, no giant gold de-

posits were found here. In addition, mineralogy and geology of these deposits are studied in detail including geological, petrographic, geochemical, and mineralogical survey of 1:4000 to 1:1000 at Stepnyak down to 300 m below surface (Spiridonov, 1986), and Bestyube and Zholymbet down to 600 m (Spiridonov *et al.*, 1986₁); 3D geological, geophysical, mineralogical and geochemical survey of 1:25,000 to 1:10,000 in the Aksu ore field including deposits Kvartsitovye Gorki, North and South Aksu, and Budenovsk down to 900 m below surface (Spiridonov *et al.*, 2002).

Geological setting of the deposits. The largest Stepnyak-group deposit Bestyube is located at the joint of the Ishke-Ulmes anticlinorium and Selety sinclinorium. Large deposits Zholymbet, Kvartsitovye Gorki, and Aksu are located at the joint of the Stepnyak sinclinorium and Ishke-Ulmes anticlinorium in the zone of meridional transregional Omsk-Tselinograd deep fault, it was transected by the NW-trending faults for example the Atansor Fault and others. Large deposits are spatially related to the smallest intrusions of granodiorite formation and are distal from large intrusions.

The major Caledonian gold deposits in North Kazakhstan are related to small intrusions of the Stepnyak type, which were referred to the Stepnyak Complex (post-batholite formation of small gold-bearing diorite intrusions) (Bilibin, 1945) that is younger than the Krykkuduk Complex (tonalite-granodiorite formation). Recently it was proved that the Stepnyak-type intrusions and major gold deposits are the products of the Late Ordovician Krykkuduk Complex (Spiridonov, 1968, 1986, 1995; Spiridonov *et al.*, 1986₁, 1986₃, 2002). Small gold-bearing intrusions and dykes to which the deposits are paragenetically related belong to the inversion stepnyakite-tonalite-granodiorite formation with the age of 445 ± 5 Ma. Low and poor-sulfide deposits of the Stepnyak group Bestyube, Zholymbet, Kvartsitovye Gorki, Stepnyak, and Aksu belonging to the Late Ordovician plutogenic gold-quartz formation with the age of $445 \pm 3 - 5$ Ma are opened by mines down to 450 – 1100 m below surface and drill holes, down to 1200 – 1700 m. Other types of hydrothermal-metasomatic formations are rather developed at these deposits. There is a negative correlation between size of ore-bearing intrusion and related ore concentration that indicates deep-seated source of gold (Spiridonov, 1995).

Characteristics of plutogenic gold-quartz formation. The ore formation comprises quartz and carbonate-quartz veins and stockworks,

mineralized beresitized and listvenitized rocks including skarns and breccias of erupted hydrothermal pipe-like bodies. The structure of the deposits ranges from simple (occasional veins and lenticular stockworks) to very complex (numerous systems of ore veins, stockwork zones, and mineralized metasomatites). All deposits are root; compression and related low-amplitude gapping faults are typical; and multi-system fracture structures are common. Fractures filled by ore veins are shear with overfault movement along them. The main ore veins frequently proceed along dykes of microdiorite and spessartite. Ore stockworks occur both at contacts and within dyke-type intrusions and dykes of granitoid porphyries, within erupted hydrothermal breccias, in tectonized and listvenitized areas of skarns, and along high-amplitude feathering faults of the deep-seated Tselinograd Fault. The high angle branches of this fault are important feature of the Kvarstivoye Gorki structure. Wedges of the Paleoproterozoic and Riphean metamorphic rocks and blocks of Vendian and Cambrian terrigenous rocks and black shales occur in these faults cutting Ordovician sediments.

Like famous Kalgoorlie, at Kvarstivoye Gorki, gold mineralization is nearly complete hosted in hard rocks, which are positioners of fractures (cherty rock-phtanite at Kvarstivoye Gorki and doleritic gabbro at Kalgoorlie); adjacent black shales, carbonaceous mudstones, and siltstones host poor ores.

The reserves of the deposits do not depend on the structure. Stockwork- and mineralized metasomatites deposits contain cca. 2/3 of gold reserves; vein deposits contain cca. 1/3 of the reserves. The deposits are relatively small in area (< 2 × 2 km) and extend down to > 0.5 to > 2 km.

Forming processes of gold-quartz formation. This formation is resulted from the beresitization-listvenitization process that is medium-temperature CO₂ metasomatism (Korzhinsky, 1953; Zaraisky, 1989) one of the latest stages of post-intrusion hydrothermal activity (Spiridonov, 1995). Beresite and listvenite contain *n*.10 ppb of Au everywhere as compared with a few ppb of Au in primary rocks that unambiguously indicates introduction of Au by the beresitized fluid (like As, Sb, Ag, and Te; for example the concentration of Hg in primary rocks is < 0.04 ppb, whereas in beresite, it ranges from 0.06 to 0.17 ppb and higher). The highest PT parameters of ore deposition are 375°C, 3.3 kbar; salinity of NaCl-KCl-MgCl₂ fluid is 17 wt.% NaCl equiv., concentration of CO₂ and CH₄ is 7 and 2.5 mole/kg of solution, respectively (Spiri-

donov, 1992; Spiridonov *et al.*, 2002). Cogenetic H₂O-CO₂ and CO₂-H₂O inclusions in quartz, carbonate, and scheelite and inclusions of liquid CO₂ indicate that the ore deposition was accompanied by fluid immiscibility, boiling, and outgassing with tectonic movements. Substantial part of CO₂ incorporated into carbonates of beresite, listvenite, and ore veins. In the ore veins hosted in intrusive rocks, liquid CO₂ in the inclusions from quartz and scheelite is nearly pure, whereas that from ore bodies hosted in sedimentary sequences contains admixture of methane. According to the study of individual fluid inclusions, the highest concentration of CH₄ is 2.5 mole/kg of solution at Bestyube. Cogenetic inclusions with methane and light and medium bitumen (reason for orange-red color of scheelite) in quartz, scheelite, and carbonates indicate a migration of hydrocarbons into fracture zones that was resulted in concentrated deposition of gold. H₂S played the same role: quartz and carbonates of some deposits contain inclusions with liquid H₂S.

Weak acid (H₂CO₃) gold-bearing hydrothermal fluids with low *f*O₂ and *f*S₂ leached SiO₂, Fe, Cu, Zn, Pb, Ni, Co, and W from ore-hosting and underlying sequences, but not Mn and Mo. The ores are depleted in Mn, Ba, and Mo, and extremely poor in F, Sn, Ge, Be. Light hydrocarbons (methane) and bitumen, which migrated into fracture zones at the process of pre-ore acid metasomatism, provided the concentrated gold precipitation. The richest ores (> 2 kg/t Au) including mineralized black shales contain less than 20 ppm of Pt and Pd.

It used to be substantial part of gold in the ores is "dissolved" in sulfide minerals. Calculation showed that even in pyrite-bearing black shales at Kvarstivoye Gorki with veinlet-impregnated mineralization, 80 to 90% of Au occur as native species (Spiridonov *et al.*, 1986₃). This value is close to 100% in the rich ores at Kvarstivoye Gorki and other ores of low-sulfide deposits of the Stepnyak group.

Gold-bearing bodies of any type are composed of the following assemblages: relict minerals, scheelite-quartz (± chlorite, carbonate, sericite, graphitoid) (375–305°C, usually 330–315°C); early sulfides (pyrite, arsenopyrite ± pyrrhotite) (290–270°C); carbonate-poly-sulfide (As-rich pyrite, arsenopyrite, sphalerite, galena, pyrrhotite, cubanite, bornite, bournonite, tennantite, tetrahedrite) (270–210°C); economic (gold ± sulfides and complex sulfides of Pb, Sb, Ag, and Bi or tellurides of Bi, Pb, Ag, Ni, Fe-Co, Au-Ag, and Au) (210–155°C). The Late Ordovician post gold ore antimony mineralization was identified at some deposits. The

Table 1. Mineralogical types of the Stepanyak-group deposits in composition of economic mineral formation

Facies of formation depth of deposit	Estimated depth of formation	Economic mineral formation	Deposit
Hypabyssal	~1 km	Gold-stibnite-Ag sulfosalt	Kvartsitovye Gorki IV
	~1–2 km	Gold-galena-Ag sulfosalt	Kvartsitovye Gorki I
	~2–3 km	Gold-galena-sulfoantimonide	Bestyube
Mesoabyssal	~3–7 km	Gold-galena-sulfoantimonide with tellurides	Budenovsk Karaul-Tyube Stepnyak East Zholymbet
Abyssal	~7–>10 km	Gold-galena-telluride to gold-telluride	Zhana-Tyube Zgolymbet South Aksu North Aksu

minerals of early scheelite-quartz assemblage containing inclusions with liquid CO₂ precipitated from the CO₂-rich NaCl-KCl-MgCl₂ solutions with salinity of 9–17 wt.% NaCl equiv. The minerals of carbonate-polysulfide and economic assemblage precipitated from the solutions of the same composition with salinity of 2–11 wt.% NaCl equiv., more frequent 4–9 wt.% NaCl equiv.; liquid CO₂ was not found in inclusions; this indicates that the minerals were deposited at fluid outgassing with loss of CO₂ that could be resulted in increasing pH of the solutions and one of the reason of gold precipitation. The minerals of carbonate-poly-sulfide and economic assemblages are developed metasomatically. The gold grade in ore bodies and wall rocks metasomatites is caused by minerals of economic assemblage usually formed at 190–170°C. Therefore, the deposits are related to the small intrusions and dykes of the same age, because they had time for cooling to the required temperature. Otherwise, gold is scattered!

Depth facies of the deposits. According to geological data, the deposits were formed at the depth of 1 to 10 km and deeper. These plutogenic deposits originated in relatively close system at the background of gradual temperature decreasing that caused stable composition of ores and ore minerals along vertical extension of particular deposits and fractionation of ore matter depending on the formation depth of the deposits. As the depth increases, content of Sb, Hg, and Tl decreases, whereas that of Te and W and the Au/Ag, Te/Se (from 1–2 to 100–3000), and Au/Hg (from 1 to 200–6500) values increase. Mineralogical type determined by the mineralogy of economic assemblage corresponds to the depth facies (Table 1): hypabyssal facies (P and T at the start of mineral formation are 0.3–0.9 kbar and 310–305°C; C_{CO₂} 2–2.5 mole/kg of solution) – gold-Ag sulfosalts-stibnite with α-amalgam of gold and

gold-galena-sulfoantimonide; mesoabyssal facies (1.0–1.8 kbar and 330–315°C; C_{CO₂} 2.5–4.5 mole/kg of solution) – gold-galena-sulfoantimonide and gold-galena with tellurides; and abyssal facies (2.1–3.6 kbar and 375–325°C; C_{CO₂} 4–7 mole/kg of solution) – gold-galena-telluride and gold-telluride (Spiridonov, 1985, 1992, 1995, 2010). Telluride minerals at the deep-seated deposits are probably caused by the higher dissociation temperature of H₂Te, whereas stability of the latter is lower than that of H₂S. Width and intensity of halos of Hg strongly differ: from hundred meters and 0.n–n ppm at the hypabyssal deposits to a few meters and 0.0n ppm at the abyssal deposits.

The pressure is a function not only of the formation depth. However, the general increase of fluid pressure from gold-stibnite through gold-galena to gold telluride deposits of the Late Ordovician gold-quartz formation of the Northern Central Kazakhstan is evident. Thermobaric gradient at the deposits of this formation is specific cca. 9.5 bar/degree.

Mineralogical and geochemical zoning of the deposits. Poor vertical mineralogical and geochemical zoning was identified at all deposits (Naz'mova *et al.*, 1978; Spiridonov, 1995). Nevertheless, the economic mineralization is localized in the central part because the process of ore deposition is centripetal. The Au/Ag, Pb/Zn, and Te/Se values decrease toward margins of orebodies and deposits. At certain deposits as depth increases, content of Sb, Hg, Ag decreases, whereas that of Bi and W, and Au/Ag (vein Yanvarskaaya at South Aksu from 2.1 to 3.3), Au/Hg, and As/Sb values increase; halos of Sb and Hg become narrow; gold fineness increases while concentration of Hg in gold decreases; and concentration of Hg, Cd, and Se in sphalerite drops. Vein zones at the upper levels of the deposits are enriched in Sb-bearing minerals, whereas at the lower levels those are enriched in arsenopyrite and scheelite.

Upper levels of many ore veins are enriched in tetrahedrite and gold, intermediate levels are enriched in tennantite, and lower levels are enriched in chalcopyrite. Early mineral aggregates are retained frequently at the margins of orebodies. The study of early mineral aggregates allowed determination of distribution of berthierite (replaced pyrrhotite), chalcostibite (replaced chalcopyrite), and zinkenite (replaced galena) in the economic ores at Kvarstovoye Gorki.

Mineralogical facies of ores in the composition of ore-hosting environment. Mineralogical facies of ores and metasomatites are resulted from the composition of ore-hosting environment and concentration of sulfur in it (Spiridonov, 1998). This relationship is shown in the content of carbonates, chlorite, pyrrhotite (and its composition), Cu, Co, and Ni minerals, and formations of sulfosalts and tellurides. The orebodies hosted in black shales are enriched in carbonaceous matter, S, As, and Se. The ores hosted in basic rocks contain pyrrhotite, ilmenite, Ni and Co minerals, and are enriched in Cu minerals (chalcopyrite, bornite, cubanite, fahlores, bournonite) with Cu content reaching 1–2% that is economic. The orebodies hosted in granitoids contain galena and Pb sulfosalts. The orebodies hosted in Na gabbros, quartz diorite, tonalite, and plagiogranite are poor in Bi (Spiridonov, 1985, 1998). The ores hosted in potassium granitoid adamellite are enriched in Bi (Spiridonov, 1982; Spiridonov *et al.*, 2002).

Mineralogical and geochemical signs for gold ore shoots. Substantial part of gold reserves is concentrated in ore shoots. The ore shoots are spatially related to intraore brecciation. Vein quartz and carbonates within the shoots contain appreciable methane, bitumen, and graphitoid, while grains of gold are larger than those in common ores. The ore shoots especially their upper parts are enriched in Ag and Hg relative to Au: at Kvarstovoye Gorki I, the mean Au/Ag and Au/Hg value in the common ores is 0.8 and 1.5, respectively; in the ore shoots it is 0.5 and 0.7; and in the upper parts of the ore shoots this value is 0.2–0.3 and 0.5–0.6, respectively. Mineralogical signs of the ore shoots at the hypabyssal deposits are stibnite, Pb-Sb and Ag-Pb-Sb sulfides, Hg-bearing gold, and graphitoid; negative signs are pyrrhotite, chalcopyrite, cubanite, and bornite. Positive signs at the mesoabyssal deposits are complex Pb-Sb and Ag-Pb-Sb sulfides, tetrahedrite, tellurides, and graphitoid; those at the abyssal deposits are tellurides, fahlores, pyrrhotite, and bornite.

Nature of ore-forming fluids. Oxygen isotopic composition of scheelite, the mineral that

is stable for epigenetic isotopic exchange, is nearly uniform at the Stepyak-group deposits: $\delta^{18}\text{O} = +4 \div +6\text{‰}$ SMOW. Like oxygen and carbon isotopic composition of carbonates from ore veins, it testifies to deep metamorphic nature of $\text{H}_2\text{O}-\text{CO}_2$ fluids, which accompanied the formation of inversion stepnyakite-tonalite-granodiorite formation (Spiridonov, 1995).

Mineralogy of the Stepyak-group deposits

Light micas of beresite, listvenite, and quartz veins. Light micas of the shallow deposits are predominantly phengite, whereas at the deeper deposits these are muscovite. Both are extremely poor in F and NH_4^+ .

At Kvarstovoye Gorki, beresite and ores replacing cherty rocks with admixture of ultramafic ash contain green phengite, aluminosilicate 2M₁ with 1–2 wt.% Cr; beresite-quartzite replacing V-bearing carbonaceous cherty rocks contains phengite with 1–1.5 wt.% V; beresite replacing cherty and carbonaceous shales with kaolinite contains pyrophyllite along with phengite. Yellowish pyrophyllite at Kvarstovoye Gorki contains 0.4–0.6 wt.% Fe; according to the X-ray diffraction data, it is monoclinic pyrophyllite (Table 2). Occasional aggregate pseudomorphs composed of fine flaky muscovite – phengite with 4–9 wt.% Ba and 1–2 wt.% Na and less frequent paragonite with 1–2 wt.% Ba after plates of barite occur in beresite-quartzite replacing jasper-like rock at Kvarstovoye Gorki.

Chlorites of beresite, listvenite, and quartz veins. Chlorites are abundant in listvenite replacing basic rocks and carbonate-quartz veins hosted in them (Zhana-Tyube, South Aksu, Kvarstovoye Gorki) and less common in beresite and quartz veins hosted in them. According to electron microprobe and X-ray diffraction data, green ripidolite is the most abundant. Corundophyllite is more frequent at the deeper deposits. Al-poor Fe-rich diabantite (Al 0.8–1.1 apfu) (low-temperature) occurs in the outer zones of beresite and listvenite zonal aureoles; sheridanite and clinocllore are developed in the intermediate zones; and Al-rich ripidolite (Al 1.3–1.6 apfu) (medium-temperature) is common in the inner zones. Therefore, ore-bearing fluids reacted with cooled rocks. Pyrrhotite and/or ilmenite and less frequently rutile are associated with chlorites at the deeper deposits, whereas pyrrhotite or anatase are associated minerals at the shallower deposits.

Carbonates of beresite, listvenite, and quartz veins. Fe-rich dolomite is predominant at

Table 2. X-ray powder diffraction data of monoclinic pyrophyllite from Kavratsitovye Gorki IV (pit Flangovaya, level -270 m)

<i>hkl</i>	<i>I/I₁</i>	<i>d</i> , Å	<i>hkl</i>	<i>I/I₁</i>	<i>d</i> , Å
001	30	18.4	134	4	2.163
002	39	9.20	20-6	5	2.149
004	40	4.60	222	5	2.088
020	18	4.46	13-6	5	2.063
110	16	4.43	028	2	2.046
021	14	4.395	136	3	1.896
111	11	4.178	20-8	1	1.870
022	9	4.020	0.0.10	12	1.840
006	100	3.065	31-2	1	1.692
20-2	9	2.563	150	2	1.688
200	10	2.548	24-2	2	1.685
13-2	10	2.536	240	2	1.679
132	12	2.422	310	4	1.668
20-4	12	2.416	334	5	1.646
202	2	2.352	152	5	1.642
13-4	2	2.340	2.0-10	6	1.630
008	6	2.299	1.1.10	2	1.609

Notes: Diffractometer DRON 1.5; Co radiation. Analyst E.M. Spiridonov.

the ultrahypabyssal Kavratsitovye Gorki; siderite associated with Fe-rich pyrrhotite is frequently associated with it.

The ferrodolomite-ankerite-dolomite series is common at the hypabyssal deposits. In metasomatites and ores of the less deep Central location of the Bestyube deposit, the cation variations in carbonates of beresite and listvenite are $\text{Ca}_{50}\text{Mg}_{16-44}\text{Fe}_{6-32}\text{Mn}_{1-3}$, average $\text{Ca}_{50}\text{Mg}_{35}\text{Fe}_{13}\text{Mn}_2$; and in gold-bearing veins these are $\text{Ca}_{50}\text{Mg}_{24-46}\text{Fe}_{4-24}\text{Mn}_{1-4}$, and $\text{Ca}_{50}\text{Mg}_{37}\text{Fe}_{11}\text{Mn}_2$, respectively. In metasomatites and ores of the slightly deeper West location of Bestyube, carbonates are Fe- and Mn-poorer; compositional variations of beresite and listvenite carbonates are $\text{Ca}_{50}\text{Mg}_{26-44}\text{Fe}_{6-24}\text{Mn}_{0-3}$, average $\text{Ca}_{50}\text{Mg}_{37}\text{Fe}_{12}\text{Mn}_1$; in gold-bearing veins these are $\text{Ca}_{50}\text{Mg}_{24-44}\text{Fe}_{5-24}\text{Mn}_{0-2}$, and $\text{Ca}_{50}\text{Mg}_{38}\text{Fe}_{11}\text{Mn}_1$, respectively. Vertical zoning in the chemical composition of carbonates was established at Bestyube: direct zoning in the composition of dolomite from beresite and listvenite (the $\text{Fe}/(\text{Fe} + \text{Mg})$ value increases upward) and reverse zoning in the composition of dolomite from ore veins. The combination of beresite with ferrodolomite and gold-bearing veins with low-Fe dolomite testifies to insignificant erosion level of hypabyssal plutogenic deposits (Spiridonov *et al.*, 1995). The absence of calcite distinguishes the Bestyube beresite from classic beresite column (Zaraisky, 1989). The evolution of the carbonate-polysulfide formation at Bestyube is following: Fe-rich dolomite

($\text{Fe}/(\text{Fe} + \text{Mg})$ value 0.49–0.19) → Fe-rich dolomite (0.34–0.15) + arsenopyrite → dolomite (0.20–0.16) + chalcopyrite + galena → dolomite + bournonite + jamesonite → dolomite (0.18–0.09) + tetrahedrite + boulangérite.

Calcite is common together with dolomite and Fe-rich dolomite at the mesoabyssal deposits. Calcite is predominant in the metasomatites and ores at the abyssal deposits. Carbonates from listvenite replacing magnesian skarn at the South Aksu deposit are specific: matrix is calcite, inclusions are dolomite (after fassaite) and magnesite (after forsterite).

All types of carbonates in the gold-quartz formation are Mn-poor.

Vein quartz. Milky quartz contains numerous minute inclusions of low-saline aqueous solutions and liquid CO_2 . These inclusions cause milky color of quartz. According to ESR data, the content Al centers in vein quartz corresponds to 13–24 ppm of isomorphous Al; concentration of isomorphous Ti and Ge does not exceed 1 ppm and 0.1 ppm, respectively. These feature is resulted from low temperature of quartz formation involving moderate acidic fluid poor in F.

Scheelite. Scheelite is a typical mineral of plutogenic gold-quartz deposits, because W is mobile at beresitization. Scheelite occurs as nests up to 40 cm across in vein quartz. Average content of scheelite in the Zholymbet gold-quartz veins is 0.5 vol.% sometimes up to 5 vol.% (Spiridonov *et al.*, 1986₁).

The reddish orange color of scheelite (Fig. 1) is caused by microinclusions of bitumen (up to 0.5 wt.%). The superimposed gold mineralization results in elimination of bitumen and gradual disappearance of color (Fig. 2). In the gold-rich quartz veins, scheelite poorly differs from quartz. The color of scheelite is indicator of gold grade.

The feature of scheelite is abundant Eu, whose amount sometimes higher than that of other lanthanides. For example, scheelite in one specimen from the Stepnyak gold field contains, ppm: 153 Eu, 99 Ce, 58 La, and 37 Nd. According to spectroscopic study, more than 90% Eu is Eu^{2+} that corresponds to reductive environment of gold deposition. Average contents of trace elements in scheelite of variable facies of depth deposits: hypabyssal (Bestyube ore field, 10 analyses) – mesoabyssal (Stepnyak ore field, 8 analyses) – abyssal (Zholymbet ore field, 15 analyses), are different, ppm: Sr 7050–3200–650; Mo 3–152–240; Y 22–231–275; total REE 122–619–1016; La 12–47–65; Ce 20–52–127; Nd 18–152–240;



Fig. 1. Impregnation of bright colored scheelite in calcite-quartz vein. 103 × 84 mm. Central location of the Zholymbet deposit.
Fig. 2. Pockets of light scheelite within gold-bearing quartz vein. 77 × 77 mm. Central location of the Bestyube deposit.

Sm 25–98–150; Eu 26–59–103; Gd 10–76–120; Dy 5–52–94; Ho 1–14–26; Er 2–11–20 and Yb 2–12–21 (Spiridonov *et al.*, 1998). Thus, the contents of Sr, Mo, Eu, Y, Nd, Sm, and Gd in scheelite could be indicators of the formation depth of Au deposits. The indicative Sr/Mo value in scheelite decreases from higher than 2000 in hypabyssal through cca. 20 in mesoabyssal to 3–6 in abyssal gold deposits.

Early sulfides – pyrite, arsenopyrite, and pyrrhotite, of beresite, listvenite, and carbonate-quartz veins. As a rule, pyrite is stoichiometric with p-type conduction. Its crystals reach 35 mm in size, commonly, less than 10 mm. Pyrite is extremely irregular distributed in quartz veins. For example, in many long veins of 50–120 cm thick at the Bestyube deposit, segments up to 40–60 m in length with the content of pyrite ranging from trace to 0.5% alternate with segments up to 2.5 m in length nearly completely composed of coarse-crystalline pyrite and the content of Au lower than 1–3 g/t; therefore no any such nests were mined.

Pyrite is usually accompanied by minor S-rich arsenopyrite overgrowing crystal of pyrite. In beresite and listvenite replacing black shales, and also quartz veins, and beresite replacing dykes of granitoid porphyry hosted in these rocks, contents of pyrite and arsenopyrite are approximately equal; arsenopyrite is frequently predominant (Fig. 3a). At the East location of the Bestyube deposit, crystals of arsenopyrite reaches 13 mm in size; usual size is less than 3 mm. The crystals of arsenopyrite are fine-zoned with the variable S/As value: rims are enriched in S (direct zoning). S-rich arsenopy-

rite with the S/As value 1.08 to 1.10 are abundant at the most deposits. Arsenopyrite with reverse zoning occurs at Kvartsitovye Gorki; rims of the crystals are enriched in As and contain up to 0.4–1 wt.% Sb.

In the ore veins and listvenite hosted in mafic rocks – quartz gabbro and gabbro-anorthosite (Central location of Zholymbet), magnesian skarn (South Aksu), olivine basalt (Kvartsitovye Gorki), and its tuff (Zhana-Tyube), Fe-rich pyrrhotite frequently associated with cubanite and ilmenite is found together or instead of pyrite (Spiridonov *et al.*, 1974; Spiridonov and Shapur Khamid, 1978). Fine-lamellar intergrowths of pyrrhotite of variable composition (from Fe₉S₁₀ to Fe₁₆S₁₇), and texture of Fe-rich pyrrhotite exsolved to troilite FeS and monoclinic pyrrhotite Fe₇S₈ are observed in quartz-chlorite-calcite veins and listvenite at South Aksu and Zhana-Tyube. The composition of Fe-rich pyrrhotite associated with siderite, cubanite and magnetite in listvenite at the western flank of Kvartsitovye Gorki ranges from Fe₉S₉ to Fe₂₀S₂₁, average Fe₁₁S₁₂. The composition of pyrrhotite in the chlorite-calcite-quartz veins and listvenite at the Central location of Zholymbet ranges from Fe₉S₁₀ to Fe₁₀S₁₁.

Pyrite of carbonate-polysulfide assemblage. Pyrite is fine crystalline nonstoichiometric with p-type conduction; it is precipitant of Au. The mineral occurs as fine-grained split spherulitic aggregates with 4–9 wt.% As and 1–5 wt.% Sb in metasomatites and small quartz veins at hypabyssal Kvartsitovye Gorki. At the deeper deposits, it contains cca. 0.5 wt.% As; in association with gersdorffite, it contains up to 2 wt.% Ni and 1 wt.% Co.

Arsenopyrite of carbonate-polysulfide assemblage. Usually, it is p-type conduction enriched in S; the mineral is a good precipitant of Au. In the mineralized metasomatites and small quartz veins at Kvartsitovye Gorki, arsenopyrite occurs as aggregates of fine crystals with reverse zoning (Fig. 3b).

Gersdorffite of carbonate-polysulfide assemblage. Fine zonal crystals of gersdorffite are associated with late pyrite and chalcopyrite in the ore veins and listvenite hosted in basic rocks at Zholymbet, South Aksu, and Kvartsitovye Gorki. Usually they are located in the rims of chalcopyrite grains. The composition of gersdorffite corresponds to the formula $(\text{Ni}_{0.56-0.97}\text{Fe}_{0.07-0.31}\text{Co}_{0.01-0.04}\text{Cu}_{0.01-0.03})_{0.97-1.08}\text{As}_{0.98-1.09}\text{S}_{0.88-0.97}$. The cores of its crystals are enriched in Ni, while rims are enriched in Fe. Some crystals are rimmed by Ni-bearing arsenopyrite $(\text{Ni}_{0.15}\text{Fe}_{0.89}\text{Co}_{0.01}\text{Cu}_{0.03})_{1.07}\text{As}_{1.03}\text{S}_{0.90}$.

Pyrrhotite of carbonate-polysulfide assemblage occurs as metasomatic inclusions in the crystals of pyrite. Compositionally, it is S-rich stable monoclinic pyrrhotite Fe_7S_8 . This pyrrhotite is easily replaced by gold creating false impression of gold inclusions in pyrite.

Sphalerite of carbonate-polysulfide assemblage is common mineral; size of its nests reaches 15 cm, but usually it occurs as fine impregnation. Not less than three generations are distinguished everywhere: (1) early dark brown to black $(\text{Zn}_{0.82-0.90}\text{Fe}_{0.10-0.18})\text{S}$ with cca. 0.05 wt.% Cd, (2) later brown $(\text{Zn}_{0.94-0.96}\text{Fe}_{0.04-0.06})\text{S}$ with cca. 0.2 wt.% Cd, and (3) the latest light brown $(\text{Zn}_{0.96-0.98}\text{Fe}_{0.02-0.04})\text{S}$ with cca. 0.3–0.4 wt.% Cd. Early sphalerite from abyssal South Aksu contains 100–200 ppm In and traces of Hg and Se. At hypabyssal Kvartsitovye Gorki, this mineral is In-free; it contains Hg and Se: in late sphalerite content of these elements reaches 0.6–1 and 0.4 wt.%, respectively.

Sulfides and complex sulfides of Pb and Sb.

The ores of the ultrahypabyssal Kvartsitovye Gorki are enriched in Sb. Stibnite is abundant in economic assemblage, where the earlier mine-

erals with reactive Fe, Cu, and Pb are absent. Mn-free berthierite after pyrrhotite, jamesonite after pyrrhotite and galena, zinkenite after galena, bournonite after chalcopyrite and galena, chalcostibite and tetrahedrite after chalcopyrite and bornite, and chalcostibite and pyrite after cubanite were resulted from the Sb-bearing fluids affected these minerals. Therefore, pyrrhotite, chalcopyrite, bornite, and cubanite are absent in the ore shoots at Kvartsitovye Gorki. In some places of the shoots, the content of berthierite is comparable with that of stibnite (Fig. 4), while in the other places, zinkenite, jamesonite, or Ag-tetrahedrite are abundant.

The following series were formed in the ores of the deeper deposits Bestyube and Stepnyak as affected by the Sb-bearing fluids: in acidic rocks (plagiogranite, arcose) – primary galena → bournonite + galena → bournonite + semseyite → jamesonite + zinkenite; in medium rocks (quartz diorite, tonalite, polymictic rocks) – primary chalcopyrite + galena I → bournonite + tennantite-tetrahedrite I → tetrahedrite II + galena II ± bournonite → Ag-tetrahedrite III + jamesonite; and in mafic rocks (greywacke, gabbroic) – primary chalcopyrite → tennantite-tetrahedrite I → tetrahedrite II → Ag-tetrahedrite III. The Pb/Cu value determined by the composition of host environment did not evolve unlike minerals of Pb and Cu.

Small amount of tetrahedrite replacing chalcopyrite was formed in the ores of the deepest Zholymbet and Aksu as affected by the Sb-bearing solutions.

Complex sulfides of Pb and Bi. The ores of the Ishke-Ulmes deposit are skarn that is listvenitized and contains superimposed veinlet-disseminated Au mineralization. The deposit is related to the Seletinsky intrusion of potassium granitoid – adamellite, and therefore is enriched in Bi. The aikinite-group mineral gladite, $\text{CuPbBi}_5\text{S}_9$, is abundant in the ores; size of its grains reaches 9 mm (Spiridonov, 1982₂).

The fahlores-group minerals. The fahlores-group minerals are named according to (Spiri-

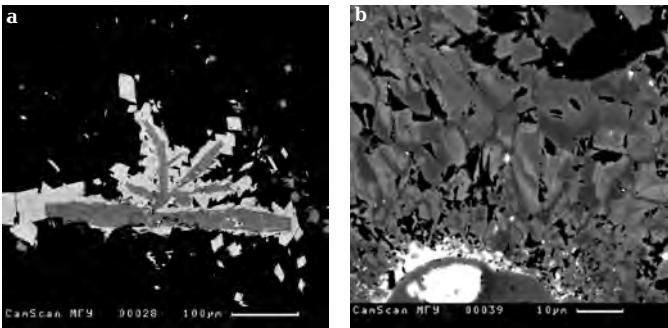


Fig. 3. Back-scattered electron images of arsenopyrite from Kvartsitovye Gorki:

(a) rims and isolated crystals of arsenopyrite (light gray) around lamellae of pyrite (gray) in listvenite, pyrite probably replaced lamellae of pyrrhotite;

(b) aggregate of fine complexly zoned crystals of arsenopyrite whose rims are enriched in As (lighter); spherulite of pyrite penetrated by late jamesonite at the bottom of image.

donov, 1984). Fahlores $(\text{Cu}^{1+}, \text{Ag}, \text{Tl})_{10}(\text{Zn}, \text{Fe}, \text{Cu}^{2+}, \text{Hg}, \text{Cd})_2(\text{As}, \text{Sb}, \text{Bi}, \text{Te})_4(\text{S}, \text{Se})_{13}$ are sensitive indicators of ore genesis; these minerals are the major carriers of Ag and Hg at many hydrothermal deposits. $\text{Sb}/(\text{As} + \text{Sb})$ and $\text{Cu}^{2+}/(\text{Zn} + \text{Fe} + \text{Cu}^{2+} + \text{Hg} + \text{Cd})$ values are their characteristics. Fahlores of the economic assemblage are of the great interest. These are poor in Te and Bi and have the low $\text{Cu}^{2+}/(\text{Zn} + \text{Fe} + \text{Cu}^{2+} + \text{Hg} + \text{Cd})$ value. The crystals are smooth zoned everywhere (Spiridonov *et al.*, 2009).

Zn-rich As-tetrahedrite and Sb-tennantite containing up to 5 wt.% Ag are the early generations at the ultrahypabyssal Kvarstitovye Gorki. At the shallowest Kvarstitovye Gorki IV, these minerals contain, wt.%, up to 7 Hg, 0.9 Se, 0.4 Cd, and 0.2 Tl. Evolution of ore-forming process resulted in the decreasing Hg concentration in fahlores; Hg fractionated into Hg-rich gold. The later generation of fahlores is As-poor freibergite (Ag-tetrahedrite containing up to 25 wt.% Ag); argentotetrahedrite poor in As and containing trace Hg is the latest (Spiridonov, 1984, 1987₂; Filimonov and Spiridonov, 2005). All these fahlores are associated with the minerals enriched in Sb: from stibnite, zinkenite, and jamesonite to andorite, roshchenite, and miargyrite.

In the deeper orebody at Kvarstitovye Gorki I, content of Ag increases, while the $\text{Sb}/(\text{As} + \text{Sb})$ value decreases from the early to late fahlores; the latest generation is Sb-argentotennantite and As-argentotetrahedrite (up to 39 wt.% Ag) (Spiridonov *et al.*, 1986₂; Spiridonov, 1987₂).

At Bestyube and mesoabyssal Stepnyak, Budenovsk, and East Zholymbet, the early generation of fahlores is Zn-rich tetrahedrite and tennantite containing < 1.5 wt.% Hg and up to 3 wt.% Ag; the late generation is tetrahedrite (up to 10 wt.% Ag) and occasional freibergite (up to 21 wt.% Ag and 1 wt.% Cd) (Spiridonov *et al.*, 1996, 2002, 2009). At abyssal Zholymbet and Aksu, fahlores are Fe-rich tennantite and tetrahedrite poor in Ag (< 0.5 wt.%) and Hg (< 0.01 wt.%) (Spiridonov, 1985). Thus, the composition of fahlores of the economic formation at the plutogenic gold deposits is additional criterion of the formation depth of deposit.

Ag and Sb sulfides and complex sulfides.

The ores of ultrahypabyssal Kvarstitovye Gorki are enriched in Ag and Sb. The economic assemblage contains a series of minerals with conventional increasing content of Ag: freibergite (Ag-tetrahedrite) → andorite $\text{AgPbSb}_3\text{S}_6$ → roshchinite $\text{Ag}_{19}\text{Pb}_{10}\text{Sb}_{51}\text{S}_{96}$ → miargyrite AgSbS_2 (Spiridonov *et al.*, 1990, 2002; Spiridonov, 2010)

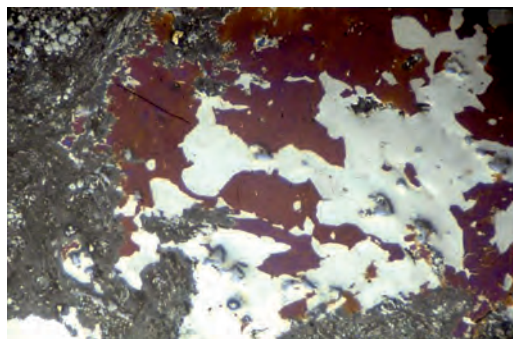


Fig. 4. Photomicrograph of aggregate of berthierite (coated by red film resulted from air etching) and antimonite (light) in listvenite, Kvarstitovye Gorki IV. Width of image 6 mm. Reflected plane polarized light.

and latest rare pyrargyrite Ag_3SbS_3 → argentite Ag_2S . The andorite-group minerals Me_5S_6 , or $\text{Me}_{20}\text{S}_{24}$, andorite in the first place, are developed at many hydrothermal deposits enriched in Ag and Sb (Sveshnikova, 1975; Moëlo, 1983; Moëlo *et al.*, 1989). Roshchinite, specific mineral of the andorite group associated with andorite is the feature of plutogenic hypabyssal Kvarstitovye Gorki (Fig. 5). The composition of roshchinite $(\text{Ag}, \text{Cu})_{19}\text{Pb}_{10}(\text{Sb}, \text{As})_{51}\text{S}_{96}$ (Fig. 6) registers special conditions of late stage ore deposition at Kvarstitovye Gorki IV: abundant Sb and Ag and relative deficiency of Pb. The structure of roshchinite differs from that of the other andorite-group members and is particular type (Fig. 7).

The Bestyube and Stepnyak ores contain few owyheite $\text{Ag}_3\text{Pb}_{10}\text{Sb}_{11}\text{S}_{28}$. Ag-Sb sulfosalts are absent at the deeper deposits.

Tellurides. According to uniform association of tellurides and native gold, these were resulted from the reaction of Au-Te-bearing solutions with the early minerals in ore veins. For example, in the pyrrhotite-rich ores of Zhana-Tyube hosted in basic rocks, numerous metacrysts of frobergite with inclusions of gold are enclosed in pyrrhotite (Fig. 8a). The probable reaction is: $2\text{FeS} + \text{Au}_{\text{fluid}} + 2\text{Te}_{\text{fluid}} \rightarrow \text{FeTe}_2$ (frobergite) + Au + FeS_2 . In this case, almost the whole Te incorporated into frobergite, therefore native gold was developed rather than gold tellurides. In the pyrrhotite-free quartz veins hosted in silicic rocks at Zhana-Tyube, frobergite and melonite are absent. Native gold is also absent in these veins, because all Au incorporated into tellurides.

Tellurobismuthite, Sb-rich tellurobismuthite, and other Bi tellurides. The intergrowths of native gold and Bi tellurides, which are tellurobismuthite and/or tetradyrite, are the most abundant; the intergrowths with tsumoite and

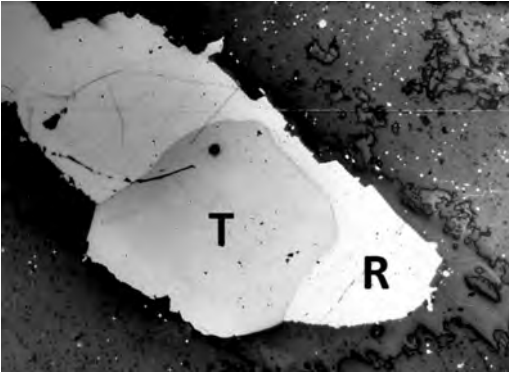


Fig. 5. Photomicrograph of intergrowth of roshchinite (R) and Ag-tetrahedrite (T) in carbonate nest within quartz vein, Kvarstsitovye Gorki IV. Width of image 3 mm. Reflected plane polarized light.

other tellurides are less frequent. Like all over the world, Bi tellurides at the Stepyak-group deposits contain admixture of Pb and trace Sb (Spiridonov *et al.*, 1978₂), because Sb incorporated into the earlier fahlores.

Galena and fahlores are unstable as affected by Au-Te-bearing fluids. The relationship of galena and replacing altaite PbTe indicates intensity of such affect. In the most ore veins of Zholymbet and South Aksu, galena is predominant. In some veins enriched in gold, altaite is predominant; in the same veins, Sb-rich tellurobismuthite is developed rather than usual tellurobismuthite; the former contains Sb that is product of fahlore decomposition. This is Sb-rich tellurobismuthite of South Aksu containing up to 8 wt.% Sb (Table 3). The ores of the small but very gold-rich Zhana-Tyube deposit is distinguished by abundant tellurides including Sb-rich tellurobismuthite (up to 11 wt.% Sb, Table 4), absence of galena and fahlores, and presence of late arsenopyrite associated with tellurides. These distinctions are caused by effect of abundant Au-Te-bearing solutions. Galena was replaced by altaite and fahlores were replaced by Sb-rich tellurobismuthite, chalcopyrite, and arsenopyrite: $\text{PbS} + \text{Cu}_{10}\text{Fe}_2\text{SbAs}_3\text{S}_{13} + 13\text{FeS} + 7\text{Te}_{\text{fluid}} + 3\text{Bi}_{\text{fluid}} \rightarrow \text{PbTe} + 2(\text{Bi}_{1.5}\text{Sb}_{0.5})_2\text{Te}_3 + 3\text{FeAsS} + 10\text{CuFeS}_2 + 2\text{FeS}_2$.

The South Aksu orebodies hosted in intrusive rocks poor in S predominantly contain tellurides – tellurobismuthite, tsumoite, and others. Polyminerals clusters of tellurides were found in them: earlier pilsenite Bi_3Te_2 and wehrlite Bi_4Te_3 , later tsumoite Bi_2Te_2 , then tellurobismuthite Bi_2Te_3 , and the latest sulfotelluride – tetradymite $\text{Bi}_2\text{Te}_2\text{S}$ (Table 5). In the South Aksu orebodies hosted in hornfels after

black shales enriched in S, tetradymite is predominant.

Fe-Co-Ni tellurides – frobergite, mattagamite, and melonite. According to Veits *et al.* (1971), N.P. Krikunova found frobergite in the Zhana-Tyube ores for the first time. The author of this article has established that in some places of chalcopyrite-pyrrhotite-chlorite-calcite-quartz veins hosted in listvenitized melanobasaltic tuffs with limestone cement the content of frobergite reaches 1–3 vol.% and frobergite enriched in Co has been identified (Spiridonov *et al.*, 1974, 1978₁). This mineral is stoichiometric in composition; admixtures are, wt.%: up to 0.5 Sb and Se, up to 0.2–1 Ni, and 0.0n Co, Cu, Ag, and Au.

The zoned crystals of frobergite are frequent in the Zhana-Tyube ores. Co-rich frobergite ($\text{Fe}_{0.6-0.5}\text{Co}_{0.4-0.5}\text{Te}_2$) is in the cores of these crystals. Occasionally, in the cores of these crystals content of Co is higher than that of Fe; these small places with the composition ($\text{Fe}_{0.48-0.49}\text{Co}_{0.52-0.51}\text{Te}_2$) correspond to mattagamite. This is the first finding of mattagamite at the plutogenic gold deposits. Intermediate zones of the zoned crystals are composed of frobergite with 1–6 wt.% Co. Sometimes, the zones of Co-bearing frobergite alternate with the zones of Co-free frobergite. The composition of rims corresponds to frobergite with 0.0n wt.% Co. The composition of minerals of the mattagamite-frobergite series is given in Table 6 and Fig. 8b.

Melonite and associated altaite were identified in the Zholymbet ores (Borishanskya, 1952; Naz'mova *et al.*, 1978). According to Veits *et al.* (1971), in the ores of Zhana-Tyube, N.P. Krikunova found melonite for the first time. The author of this paper has established abundant melonite in the pyrrhotite ores of Zhana-Tyube and Co-rich melonite in these ores. The size of nests of melonite intergrown with frobergite reaches 6 mm. Melonite and Co-bearing frobergite paragenese from Zhana-Tyube contains traces of Co; the isolated grains of melonite contain 0.5 wt.% Co as usual, occasionally up to 5.5 wt.% Co. Co-rich melonite occurs as crystal cores; also it contains up to 3 wt.% Fe (Table. 7; Fig. 8b). Thus, the affinity of Co for Te is higher than that of Fe and Ni for Te.

Au-Ag tellurides – montbrayite, calaverite, krennerite, sylvanite, and others. Montbrayite, $\text{Au}_2(\text{Te,Sb,Pb,Bi})_3$, rare early telluride occurs in the pyrrhotite ores with melonite, frobergite, and high-fineness gold (Zhana-Tyube, South Aksu, Central location of Zholymbet). It contains up to, wt.%: 3 Ag, 0.5 Cu, 1.5 Sb, and 4.5 Pb (Table 8). Calaverite, AuTe_2 is relatively

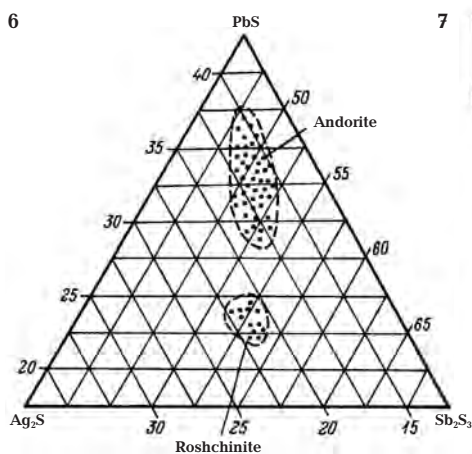
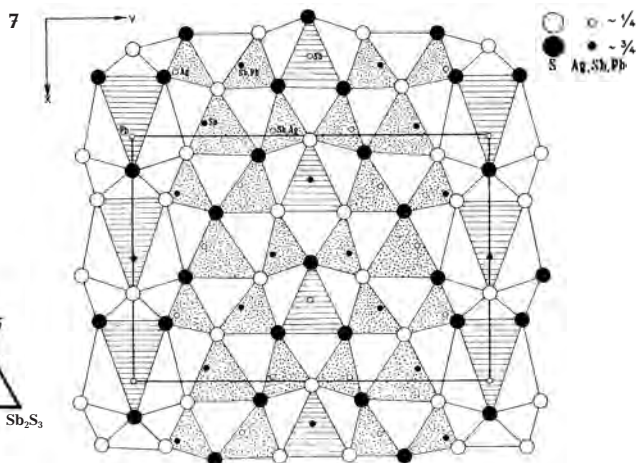


Fig. 6. Ternary diagram $Ag_2S - Sb_2S_3 - PbS$ with the compositional fields of roshchinite from Kvartsitovye Gorki (author data), andorite (Sveshnikova, 1975; Moëlo, 1983; Moëlo et al., 1989).

Fig. 7. Crystal structure of roshchinite projected onto axis c according to I.V. Petrova.



rare early telluride in the central parts and deep levels of gold veins and stockworks. The mineral is associated with high-fineness gold (970–992), altaite, and melonite (Zholymbet), extremely high-fineness gold (990–1000) and tellurobismuthite (North Aksu), and tsumoite (South Aksu). It contains, wt.%: from traces to 3 (usually < 0.5) Ag, cca. 0.5 Se, and 0.0n Hg, Sb, Cu, and Bi. The extremely high-fineness gold in the North Aksu ores is evidently caused by cogenetic calaverite in the same formation (Table 8) that incorporated residual Ag from the ore-bearing fluids.

Krennerite, $Au_3(Au,Ag,Cu)Te_8$, is common relatively early telluride is developed in the central parts and deep levels of ore veins and stockworks. At Zhana-Tyube, it is the third most important Au carrier; the mineral is abundant in the pyrrhotite ores, where it commonly occurs within frohbergite enclosed in pyrrhotite (Fig. 9a) or as clusters with frohbergite in pyrrhotite (Fig. 9b); native gold or petzite are frequently observed with these minerals. Krennerite is also abundant in the pyrite-

quartz veins at Zhana-Tyube, where it forms small intergrowth with altaite, petzite, and Sb-rich tellurobismuthite. The composition of krennerite ranges from $AuTe_2 \Delta_0 Au_3AgTe_8$; the content of Ag varies from 0.5 to 6.5 wt.%, usually 3–5 wt.%. The mineral contains 0.0n wt.% Sb and 0.0n wt.% Hg and Cu. Krennerite replacing bornite at the Central location of Zholymbet contains up to 1.5–2 wt.% Cu. The mineral is frequently cogenetic with high-fineness gold (945–960) (Spiridonov, 1985). In the Zhana-Tyube pyrite-quartz ores it is replaced by sylvanite.

Petzite, $AuAg_3Te_2$, is common telluride with the garnet-type structure (Shapur Khamid et al., 1978). In the pyrrhotite ores with frohbergite it is intimately associated with krennerite; the compromise growth surfaces are between these minerals. The fineness of gold in this formation is 930–880. In the frohbergite-free pyrite ores, petzite is associated with sylvanite and altaite. Petzite is stoichiometric in composition; admixture of Hg 0.0n–0.0n wt.% is typical. The composition of petzite at Zhana-Tyube corresponds to

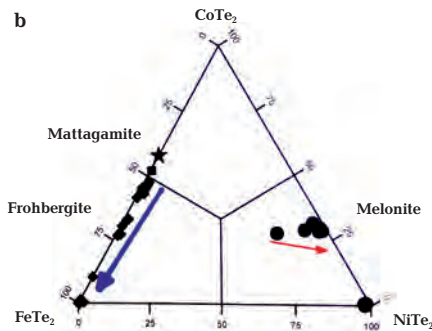
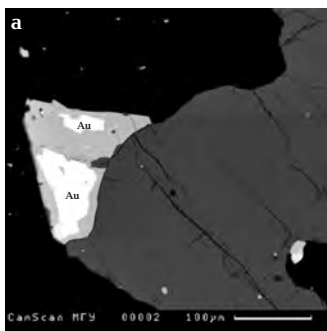


Fig. 8. Ditellurides of Zhana-Tyube:

(a) back-scattered electron image of metacryst of frohbergite (gray) with inclusions of gold (Au), matrix is composed pyrrhotite (dark gray), vein quartz is black;

(b) the composition of Fe-Co-Ni ditellurides (arrows indicate the compositional evolution of zoned crystals of frohbergite and melonite).

Table 3. Chemical composition (wt.%) of zoned Sb-bearing tellurobismuthite (anal. 1–3) from vein Yanvarskaya and Pb-Sb-bearing tellurobismuthite (anal. 4–6) from intergrowths with gold enclosed in pyrite of vein Vesennyyaya, South Aksu deposit

Comp.	1	2	3	4	5	6
	core		intermediate	rim		
Bi	41.86	47.71	50.59	46.05	46.13	42.64
Sb	7.60	3.20	1.65	1.62	1.66	1.36
Pb	b.d.l.	b.d.l.	b.d.l.	3.49	4.88	6.97
Cu	b.d.l.	b.d.l.	b.d.l.	0.12	b.d.l.	b.d.l.
Ag	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.17	0.15
Au	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.44	0.41
Te	49.62	49.65	48.93	47.71	47.37	46.48
Se	b.d.l.	b.d.l.	с.а.е.д.ы	b.d.l.	b.d.l.	b.d.l.
S	0.65	b.d.l.	b.d.l.	b.d.l.	0.47	0.32
Total	99.73	100.56	101.17	98.99	101.13	100.43
Atoms per formula unit						
Bi	1.49	1.78	1.89	1.76	1.70	1.62
Sb	0.46	0.20	0.11	0.11	0.11	0.09
Pb	–	–	–	0.13	0.18	0.27
Cu	–	–	–	0.01	–	–
Ag	–	–	–	–	0.01	0.01
Au	–	–	–	–	0.02	0.02
Total	1.96	1.98	2.00	2.01	2.02	2.01
Te	2.89	3.02	3.00	2.99	2.87	2.89
S	0.15	–	–	–	0.11	0.10
Total	3.04	3.02	3.00	2.99	2.98	2.99

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Here and after, b.d.l. denotes that the content of the element is below detection limits.

Table 4. Chemical composition (wt.%) of Sb-bearing tellurobismuthite from pyrrhotite ores of the Zhana-Tyube deposit

Comp.	7	8	9	10	11
Bi	42.04	41.14	37.99	36.56	35.90
Sb	7.50	8.80	8.94	10.14	10.95
Pb	0.21	0.01	0.02	0.08	0.14
Ag	0.17	0.43	0.41	0.66	0.61
Te	49.91	52.33	50.41	50.32	50.26
Se	0.12	traces	0.04	0.11	0.09
Total	99.95	102.71	97.81	97.87	97.97
Atoms per formula unit					
Bi	1.53	1.44	1.39	1.32	1.29
Sb	0.47	0.53	0.56	0.63	0.68
Pb	0.01	–	–	–	0.01
Ag	0.01	0.03	0.03	0.05	0.04
Total	2.02	2.00	1.98	2.00	2.02
Te	2.97	3.00	3.02	2.99	2.97
Se	0.01	–	–	0.01	0.01
Total	2.98	3.00	3.02	3.00	2.98

Notes: Cameca SX-50 electron microprobe, analyst N.N. Konovalova.

the formula $(\text{Au}_{0.98-1.02}\text{Ag}_{2.96-3.01}\text{Hg}_{0-0.01})_4(\text{Te}_{1.98-2.00}\text{Sb}_{0.01-0.02}\text{Bi}_{0-0.01}\text{Se}_{0-0.01})_2$.

Sylvanite, $\text{Au}(\text{Ag,Au})\text{Te}_{41}$, is abundant late telluride; it is the major carrier of Au in ores at Zhana-Tyube. In the stockworks and veins of the deep Central location at Zholymbet, the mineral is developed down to 1450 m below surface. At Zhana-Tyube, sylvanite occurs in the gold-free quartz veins; the size of its nests reaches up to 6 cm; the mineral is associated with altaite, Sb-rich tellurobismuthite (Fig. 9c), and occasionally with frobergite (Fig. 9d); its formula is $(\text{Au}_{1.00-1.03}\text{Ag}_{0.94-0.98}\text{Cu}_{0.01}\text{Hg}_{0-0.01})_{1.97-2}(\text{Te}_{3.97-4.00}\text{Sb}_{0.02-0.03}\text{Se}_{0-0.01})_{4-4.03}$ (Spiridonov *et al.*, 1976). The mineral uniformly contains cca. 0.1 wt.% Hg. Sylvanite at South Aksu replacing cubanite contains up to 1 wt.% Cu. Copper content in sylvanite from Zhana-Tyube is cca. 0.5 wt.%; the replaced fahlores were source for Cu. Thus, it is evident that there is natural solid solution series sylvanite AuAgTe_4 – kostovite AuCuTe_4 . At the Central, South, and North locations of Zholymbet and South Aksu, sylvanite is associated with native gold of moderate fineness (910–890). The composition of sylvanite from plutogenic gold deposits in North Kazakhstan corresponds to the formula AuAgTe_4 that is consistent with the formation temperature below 200°C according to diagram reported by Cabri (1965). Sylvanite is replaced by petzite and hessite (Fig. 10a).

Table 5. Chemical composition (wt.%) of Bi tellurides in zoned intergrowth: wehrlite (core) (anal. 12) – pilsenite (anal. 13) – tsu-moite (anal. 14) – tellurobismuthite (anal. 15) – tetradymite (rim) (anal. 16), vein Yanvarskaya, South Aksu deposit

Comp.	12	13	14	15	16
Bi	69.87	67.21	63.30	50.75	57.82
Sb	0.46	0.46	0.45	1.50	0.475
Te	27.73	30.62	36.21	46.71	35.56
S	0.14	0.14	0.15	0.07	4.66
Total	98.20	98.24	101.11	99.12	98.51
Atoms per formula unit					
Bi	2.99	3.95	2.01	1.94	1.96
Sb	0.03	0.05	0.03	0.10	0.03
Total	3.02	4.00	2.04	2.04	1.99
Te	1.94	2.95	1.93	2.94	1.98
S	0.04	0.05	0.03	0.02	1.03
Total	1.98	3.00	1.96	2.96	3.01

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Contents of Pb, Hg, Ag, Cu, Au, and Se are below detection limits.

Table 6. Chemical composition (wt.%) of zoned crystals of mattagamite (anal. 17) – Co-bearing frobergite – frobergite from pyrrhotite ores at the Zhana-Tyube deposit

Comp.	17	18	19	20	21	22	23	24	25
	core	intermediate	rim	core	intermediate	rim	core	intermediate	rim
Fe	8.57	16.10	17.97	12.28	13.07	18.05	17.79	11.03	17.91
Co	9.80	2.12	0.09	6.05	5.10	0.12	0.61	7.50	0.05
Ni	b.d.l.	0.37	3.21	–	b.d.l.	0.19	b.d.l.	0.01	0.07
Cu	b.d.l.	0.11	0.08	–	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.09
Te	81.53	81.88	81.79	81.52	81.69	82.01	82.05	81.41	82.07
Sb	0.21	0.15	0.19	0.11	0.17	b.d.l.	0.08	0.18	0.10
Bi	b.d.l.	0.14	0.11	b.d.l.	0.14	b.d.l.	b.d.l.	0.14	b.d.l.
Se	b.d.l.	0.10	0.03	0.22	0.11	0.06	0.09	0.11	0.10
Total	100.11	100.56	100.30	100.24	100.28	100.53	100.62	100.45	100.28
Atoms per formula unit									
Fe	0.48	0.89	1.00	0.68	0.73	0.995	0.98	0.62	0.99
Co	0.52	0.11	0.01	0.32	0.27	0.005	0.03	0.39	0.01
Ni	–	–	–	–	–	0.01	–	–	–
Total	1.00	1.00	1.01	1.00	1.00	1.01	1.01	1.01	1.00
Te	1.99	1.98	1.99	1.99	1.99	1.985	1.99	1.98	1.995
Sb	0.01	0.01	–	–	0.005	–	–	0.01	–
Se	–	0.01	–	0.01	0.005	0.005	–	–	0.005
Total	2.00	2.00	1.99	2.00	2.00	1.99	1.99	1.99	2.000

Notes: A Cameca SX-50 electron microprobe, analyst N.N. Korotaeva.

Table 7. Chemical composition (wt.%) of zoned (anal. 26–29) and unzoned (anal. 30–32) crystals of melonite from pyrrhotite ores of the Zhana-Tyube deposit

Comp.	26	27	28	29	30	31	32
	core	inter- mediate	inter- mediate	rim			
Ni	12.72	13.27	10.67	17.97	18.38	18.41	18.14
Co	5.08	5.07	4.71	0.31	b.d.l.	b.d.l.	b.d.l.
Fe	0.89	0.37	3.21	0.19	0.02	0.01	0.07
Cu	b.d.l.	0.11	0.08	b.d.l.	0.01	b.d.l.	0.09
Te	81.32	81.29	81.42	80.98	80.17	80.19	80.27
Sb	0.06	0.10	0.09	0.41	0.35	0.39	0.50
Bi	b.d.l.	0.05	0.07	b.d.l.	b.d.l.	0.06	0.04
Se	0.05	0.03	0.06	b.d.l.	0.11	0.09	0.12
Total	100.12	100.29	100.31	99.86	99.04	99.15	99.23
Atoms per formula unit							
Ni	0.68	0.71	0.57	0.965	0.995	0.995	0.98
Co	0.27	0.27	0.25	0.015	–	–	–
Fe	0.05	0.02	0.18	0.01	–	–	0.005
Cu	–	0.01	0.005	–	–	–	0.005
Total	1.00	1.01	1.005	0.99	0.995	0.995	0.99
Te	2.00	1.99	1.995	2.00	1.99	1.99	1.995
Sb	–	–	–	0.01	0.01	0.01	0.01
Se	–	–	–	–	0.005	0.005	0.005
Total	2.00	1.99	1.995	2.01	2.005	2.005	2.01

Notes: A Cameca SX-50 electron microprobe, analyst N.N. Korotaeva.

Fine-grained clusters of petzite and hessite with pattern typical of exsolution texture (Fig. 10b) are common in the Zhana-Tyube ores. Obviously, these are products of petzite-hessite exsolution. The average composition of the solid

Table 8. Chemical composition (wt.%) of tellurides intergrown with gold: Pb-bearing montbrayite (anal. 33–34) from vein Yanvarskaya, South Aksu deposit and calaverite (anal. 35–38) from vein Pologaya, North Aksu deposit

Comp.	33	34	35	36	37	38
	Au	46.75	44.95	44.11	43.74	43.59
Ag	3.13	3.32	0.10	0.22	0.17	0.16
Cu	traces	traces	traces	traces	traces	traces
Hg	traces	traces	traces	traces	traces	traces
Te	45.00	44.75	56.03	55.44	56.22	56.65
Se	b.d.l.	b.d.l.	0.57	0.69	0.58	0.48
Sb	1.41	1.69	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	4.41	4.45	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Total	100.70	99.17	100.81	100.09	100.56	102.50
Atoms per formula unit						
Au	1.82	1.77	1.00	1.00	0.99	1.01
Ag	0.22	0.24	0.01	0.01	0.01	0.01
Total	2.04	2.01	1.01	1.01	1.00	1.02
Te	2.71	2.72	1.96	1.95	1.97	1.95
Se	–	–	0.03	0.04	0.03	0.03
Sb	0.09	0.10	–	–	–	–
Pb	0.16	0.17	–	–	–	–
Total	2.96	2.99	1.99	1.99	2.00	1.98

Notes: Cameca SX-50 electron microprobe, analyst E.M. Spiridonov. Contents of Fe, Bi, and S are below detection limits.

solution series is $(\text{Ag}_{1.54-1.69} \text{Au}_{0.31-0.46} \text{Cu}_{0-0.01})_2 (\text{Te}_{0.99} \text{Sb}_{0-0.01} \text{Bi}_{0-0.01})_1$. These clusters overgrow grains of sylvanite, krennerite, and frobergite and in turn are overgrown by homogeneous (without exsolution texture) petzite, hessite,

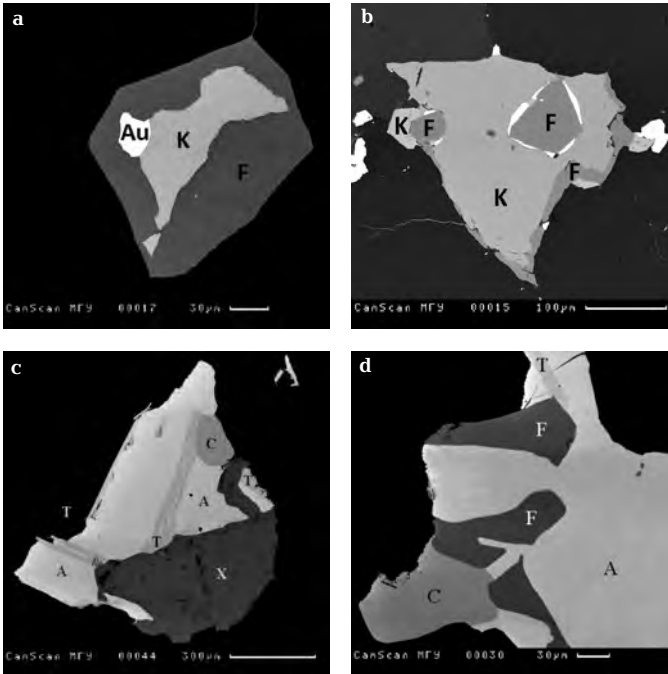


Fig. 9. Back-scattered electron images of intergrowths of tellurides from the Zhana-Tyube ores: (a, b) metasomatic krennerite (K), frobergite (F), and gold (white) enclosed in pyrrhotite,

(c) altaite (A) with lamellae of Sb-rich tellurobismuthite (T) and sylvanite (C) corrode chalcopyrite (X),

(d) intergrowth of sylvanite (C), altaite (A), frobergite (F) and tellurobismuthite (T). Vein quartz is black.

and Ag-rich gold with fineness 860–840 (Fig. 10b).

Hessite, Ag_2Te , the latest abundant telluride, occurs as isolated aggregates and intergrowths with tellurobismuthite and altaite (Fig. 10c); overgrowth and replacement rims on sylvanite and petzite, and metasomatic inclusions in pyrite, chalcopyrite, and pyrrhotite. Aggregates of hessite are mosaic of tiny grains, which are resulted from recrystallization of twins of polymorphic transition cubic \rightarrow monoclinic hessite. The composition of hessite from Zhana-Tyube complies with the formula $(\text{Ag}_{1.99-2.00}\text{Au}_{0-0.01}\text{Cu}_{0-0.01})_{2-2.01}(\text{Te}_{0.98-1.00}\text{Sb}_{0-0.01})_{0.99-1}$, that corresponds to low formation temperature. Ag-rich gold with fineness 780–810 is occasionally associated with hessite.

Thus, the succession of Au-Ag telluride deposition is following: early substantially Au tellurides (montbrayite \rightarrow calaverite \rightarrow krennerite), later Au-Ag tellurides (sylvanite, petzite), and the latest Ag tellurides (hessite).

Tellurides as indicators of deposit zoning. Au-Ag tellurides indicate zoning of orebodies: Au-rich tellurides (calaverite, krennerite) are predominant in the central parts and at the depth; Au-Ag tellurides (sylvanite and petzite) are developed in outer zones; and Ag-dominated tellurides (hessite and petzite-hessite solid solution) occur at the margins.

The contrast types of ores at Zhana-Tyube, which are pyrite ores hosted in silicic rocks and

pyrrhotite-rich ores hosted in basic rocks contain approximately equal amounts of Au, Ag, Te. Mineral species of these elements drastically differ. Frobergite is the major telluride in pyrrhotite ores; krennerite and petzite are minor; their quantitative relationship is close to 5:1:1 ($5\text{FeTe}_2 + \text{Au}_3\text{AgTe}_8 + \text{AuAg}_3\text{Te}_2$, i.e., the relationship of elements is 20Te:4Au:4Ag). Altaite and sylvanite are the major tellurides in pyrite ores; their amounts are nearly equal ($4\text{PbTe} + 4\text{AuAgTe}_4$, i.e., the relationship of the elements is the same 20Te:4Au:4Ag). The Zhana-Tyube deposit exemplifies mineralogical zoning of ores in the composition of host environment.

Affinity of chemical elements for Te. According to natural parageneses, the affinity for Te is following: $\text{Co} > \text{Fe}, \text{Ni} > \text{Bi}, \text{Sb} > \text{Pb} > \text{Ag}, \text{Hg} > \text{Au}, \text{Cu}$.

Native gold and its nanostructural characteristics as well as supergene species will be described in the second article devoted to the deposits of this group.

Acknowledgements

G.N. Naz'mova, Yu.S. Shalaev, and N.F. Sokolova are thanked for discussion of problems of formation of gold deposits in the Northern Central Kazakhstan; N.N. Korotaeva and N.N. Kononkova are thanked for the high-quality back-scattered electron images and chemical

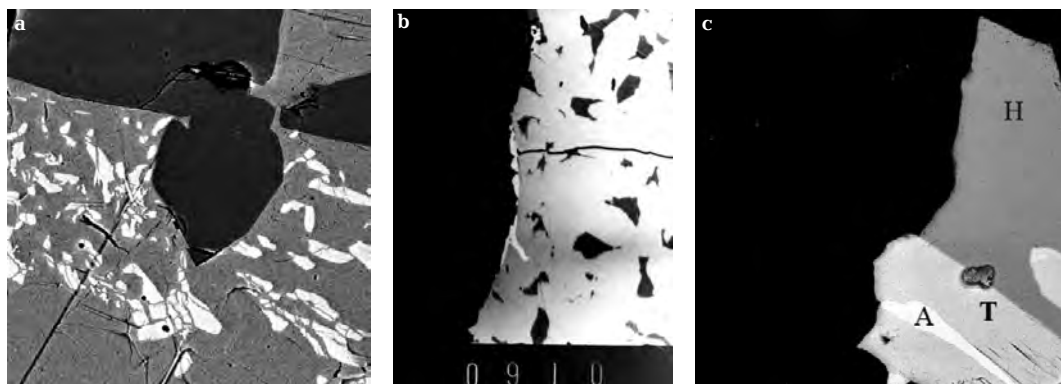


Fig. 10. Back-scattered electron images of aggregates of tellurides from quartz veins of Zhana-Tyube: (a) relics of sylvanite (white) enclosed in petzite (light gray); they are replaced by hessite (gray); (b) intergrowths of petzite (matrix) and hessite (exsolution bodies) rimmed by Ag-rich gold (white) in vein quartz, width of image 80 μm , (c) intergrowth of hessite (H), altaite (A), and Sb-rich tellurobismuthite (T) in vein quartz (black).

data obtained with electron microprobe at the laboratories of Geological Faculty, Moscow State University.

This study has been supported by the Russian Foundation for Basic Research (project no. 13-05-00839).

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



MODULAR STRUCTURE OF THE VEATCHITE POLYTYPES AND OF THE RELATED PENTABORATES

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This paper describes a crystal chemical analysis of natural and synthetic veatchite-related pentaborates based on a modular approach. The structures of three polytypes of veatchite $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, as well as similar veatchite synthetic modifications, are built up of three-layer stacks isolated from each other and formed by $\text{Ca}(\text{Sr}, \text{Ba})$ -polyhedra, connected on both sides with boron-oxygen networks. B-O-sheets are built of $[\text{B}_2^t\text{B}_3^a\text{O}_8(\text{OH})]^{2-}$, pentagroups, formed by two B-tetrahedra and three B-triangles. From the positions seen using this modular approach, the structures of the veatchite derivative pentaborates – volkovskite, biringuccite, gowerite and nasinite – have been examined. The fundamental building block (FBB or basic structure) of pentaborates is the volume unit with a formula $\{M[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2\}$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) and metric characteristics $a^* \sim 6.7\text{\AA}$, $b^* \sim 6.7\text{\AA}$, $c^* \sim 10.8\text{\AA}$, $\alpha^* \sim 105^\circ$, $\beta^* \sim 75^\circ$, $\gamma^* \sim 120^\circ$. Possible basic models of veatchite-like polytype modifications with the symmetry $P\bar{1}$, $P11n$, $P12_1$ have been derived by geometrical construction of hypothetical structures. The most probable basic structure has been defined by analysis of interatomic distances and energy testing with using a universal model of the interatomic potentials. The diversity of mineral species in the pentaborates group under consideration are associated with variations of composition, symmetry of blocks and ways of their joining in structure. 6 figures, 7 tables, 22 references.

Keywords: modular approach, a polytypism, pentaborate, veatchite, volkovskite, biringuccite, gowerite, nasinite, structural energy.

The first structural investigation of a natural strontium pentaborate – veatchite $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, published simultaneously both by Russian (Rumanova, Gandymov, 1971; Rumanov *et al.*, 1971) and American (Clark, Christ, 1971) authors, revealed two polymorphic monoclinic modifications: *p*-veatchite (sp. gr. $P2_1$) and veatchite (sp. gr. Aa). The structure of a high-calcium variety of *p*-veatchite was refined subsequently (Rastsvetayeva *et al.*, 1993). In more recent work (Grice, Pring, 2012), results of structure refinement of new finds of monoclinic *p*-veatchite and veatchite (in this publication veatchite-1*M* and veatchite-2*M*, respectively) and description of the triclinic structure of veatchite-A (veatchite-1) (Kumbasar, 1979) were presented. The currently recognized structures of 15 natural and synthetic veatchite-like and derivative pentaborates, with crystallographic characteristics, are shown in Table 1. The structural base of veatchite-like phases is comprised of three-layer stacks (Fig. 1) isolated from each other, with a central part of *M*-polyhedra ($M = \text{Ca}, \text{Sr}, \text{Ba}$), united in layers from both sides of which boron-oxygen networks occur. Building units of the network (Fig. 2) are penta-

groups $[\text{B}_2^t\text{B}_3^a\text{O}_8(\text{OH})]^{2-}$, formed of two B-tetrahedra and three B-triangles one of which is apical with an OH-group at a free vertex. The apical B-triangle is located perpendicular to the plane of a boron-oxygen sheet towards to the neighboring three-layer stack. As a result, this sheet becomes polar. Reproducing by means of horizontal translation motion, lying in the plane of a boron-oxygen sheet, pentagroups form 9-member rings of a trigonal configuration. In the center of the rings there are *M*-cations, surrounded by two types of polyhedra with ten- and eleven-vertices, which are rigidly connected with a B-polyhedra of pentaborate sheets by common edges and faces. The free vertex of the *M*1-ten-vertex polyhedron is occupied by an H_2O molecule, and *M*2-eleven-vertex polyhedron has common (OH)-edge with the additional $\text{B}(\text{OH})_3$ -triangle isolated from a boron-oxygen network of a stack. The neighboring three-layer stacks are connected along the vertical period only through hydrogen bonds, achieved by participation of H_2O -molecules and OH-groups of apical and additional B-triangles. This feature of crystal structure of veatchite explains possibility of shift and rotation of the neighboring three-

Table 1. Crystallographic characteristics of veatchite-like pentaborates

Mineral, formula	Space group Z	Unit cell parameters			Transformation			Block parameters		
		(Å, degr.)			matrixes			(Å, degr.)		
		a	b	c				a	b	c
		α	β	γ				α	β	γ
<i>p</i> -veatchite	$P2_1$	6.70	20.80	6.60	-1	0	0	6.70	6.73	10.89
$\{\text{Sr}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	2	90.00	119.15	90.00	1	0	1	103.8	73.9	121.1
					-0.55	-0.5	-0.21			
High-calcium <i>p</i> -veatchite	$P2_1$	6.686	20.614	6.594	-1	0	0	6.69	6.72	10.80
$\{(\text{Ca},\text{Sr})[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	2	90.00	119.17	90.00	1	0	1	103.8	73.9	121.1
					-0.55	-0.5	-0.21			
Veatchite-1M	$P2_1$	6.713	20.704	6.627	-1	0	0	6.71	6.75	10.85
$\{\text{Sr}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	2	90.00	119.21	90.00	1	0	1	103.8	73.9	121.0
					-0.55	-0.5	-0.21			
Veatchite	Aa	20.86	11.738	6.652	0	-0.5	-0.5	6.75	6.75	10.77
$\{\text{Sr}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	4	90.00	92.10	90.00	0	0.5	-0.5	103.6	78.4	120.9
					-0.5	-0.23	0			
Veatchite-2M	Cc	6.607	11.713	20.685	-0.5	-0.5	0	6.75	6.75	10.69
$\{\text{Sr}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	4	90.00	92.00	90.00	-0.5	0.5	0	103.6	78.4	120.4
					0	-0.23	-0.5			
Veatchite-1A	$P\bar{1}$	6.638	6.739	20.982	1	-1	0	6.74	6.74	10.90
$\{\text{Sr}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$	2	87.86	82.70	60.48	0	1	0	105.9	75.9	121.0
					0	-0.5	0.5			
$\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$ (I)	$P1$	6.665	6.617	10.605	1	0	0	6.67	6.62	10.61
	1	103.68	77.98	120.93	0	1	0	103.7	78.0	120.9
					0	0	1			
$\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}$ (II)	$P1$	6.544	6.606	10.596	1	-1	0	6.67	6.61	10.60
	1	76.66	88.48	60.94	0	1	0	103.3	78.3	120.9
					0	0	-1			
$\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{\text{H}_2\text{O}\}$	$P2_1/c$	6.530	19.613	6.530	-1	0	0	6.53	6.61	10.47
	4	90.00	119.21	90.00	1	0	1	108.9	73.6	120.4
					-0.64	0.5	-0.39			
$\{\text{Ba}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{\text{H}_2\text{O}\}$ (I)	$P\bar{1}$	6.785	6.831	10.629	0	-1	0	6.83	6.86	10.63
	2	100.07	91.98	119.46	1	1	0	102.0	79.9	120.6
					0	0	1			
$\{\text{Ba}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{\text{H}_2\text{O}\}$ (II)	$P\bar{1}$	6.781	6.901	9.737	0	-1	0	6.90	6.87	9.74
	2	102.55	91.51	119.72	1	1	0	104.1	77.4	121.0
					0	0	1			
Volkovskite	$P1$	6.50	23.96	6.62	0	0	1	6.62	6.60	10.53
$\{[\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}_2 \cdot \{\text{KCl} \cdot 2\text{H}_2\text{O}\}$	1	95.68	119.6	90.59	-1	0	-1	102.2	78.4	121.1
					0.11	0.43	0.22			
Biringuccite	$P2_1/c$	11.196	6.561	20.757	0	-1	0	6.56	6.49	10.41
$\{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{Na} \cdot \text{H}_2\text{O}\}_2$	4	90.00	93.89	90.00	0.5	0.5	0	95.4	85.9	120.4
					0	-0.11	0.5			
Gowerite	$P2_1/c$	12.882	16.360	6.558	0.5	0	0	6.44	6.56	8.52
$\{\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{[\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}\}$	4	90.00	121.62	90.00	0	0	1	103.5	75.3	121.6
					0.12	0.5	-0.18			
Nasinite	$Pna2_1$	12.015	6.518	11.173	0	-1	0	6.52	6.47	7.03
$\{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\} \cdot \{\text{Na} \cdot 2\text{H}_2\text{O}\}$	4	90.00	90.00	90.00	0	0.5	0.5	105.2	58.7	120.3
					0.5	0.56	0			

layer stacks from each other and, as a result, the formation of polytypes with a close horizontal parameters and the vertical parameter of which differing in multiples of a number.

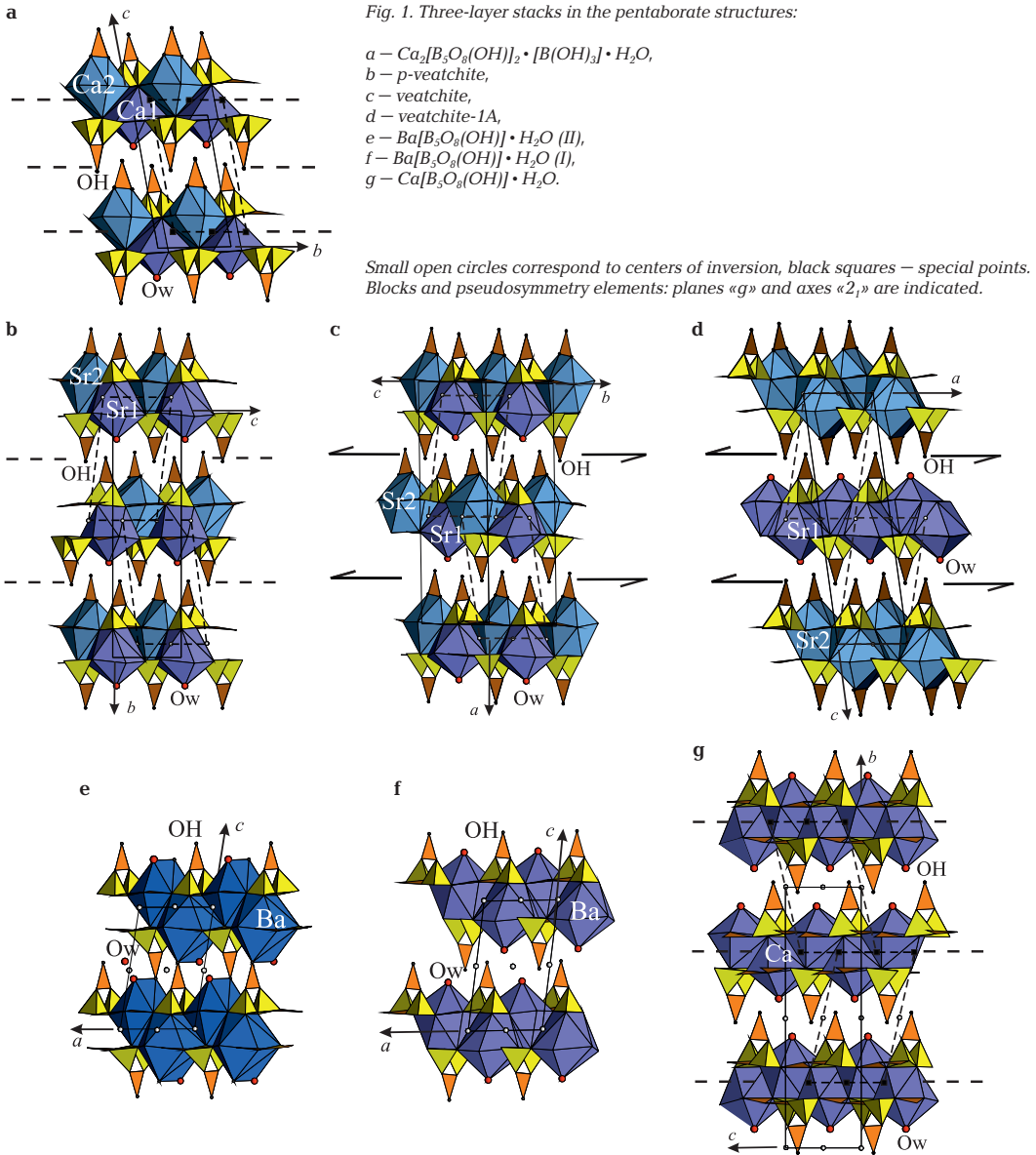
Crystal chemical investigations of the veatchite mineral group and related natural and synthetic phases, performed previously (Rastsvetayeva *et al.*, 1993; Belokoneva *et al.*, 2000; Grice, Pring, 2012), have been continued by our group (Yamnova *et al.*, 2009; Yamnova *et al.*, 2011) using a modular approach (Ferraris *et al.*, 2004; Yamnova *et al.*, 2008; Rastsvetayeva, Aksenov, 2011). As a fundamental construction unit (both of the module and basic structure) the volume block with parameters $a^* \sim 6.7\text{\AA}$, $b^* \sim 6.7\text{\AA}$, $c^* \sim 10.8\text{\AA}$, $\alpha^* \sim 105^\circ$, $\beta^* \sim 75^\circ$, $\gamma^* \sim 120^\circ$, the composition of which corresponds to a formula $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$), was separated, where the first braces corresponding to the stack occupation, and the second to the interstack space occupation. Variability of symmetry linkage between atoms within the block and variability of their composition, as well as ways of separate blocks integration into structures leads to polytype occurrence. The purpose of this work is the search of the most probable base model of veatchite-related pentaborate. For the possible hypothetical structures, built on the base of a known structure, a testing of interatomic distances, and further energetical estimation by results of calculations of interatomic potential parameters is held.

Peculiarities of symmetry linkage in structures of veatchite polytypes

Peculiarities of symmetry linkage in structures of veatchite-like pentaborates have been considered from OD-theory positions by E.L. Belokoneva with coauthors (2000) where the pseudo-symmetry elements (the center of inversion in the structure of a monoclinic veatchite and the glide plane in a veatchite related structure of volkovskite, K-Ca-pentaborate) connecting couples of boron-oxygen layers belonging to one stack were revealed. The analysis performed later by our group (Yamnova *et al.*, 2009; Yamnova *et al.*, 2011) showed existence of a new pseudo-symmetry elements connecting the layers, related to neighbor stacks: "a glide plane (g)" (Fig. 1a, b) and "screw axe 2_1 " (Fig. 1c, d). These operations are not crystallographic and are therefore in quotes. The glide component in both cases is $\sim 1/3\mathbf{T}_d$, where $\mathbf{T}_d \sim 11.7\text{\AA}$ is the b parameter of the veatchite

unit cell. Shift amplitude of the adjacent sheets in the structure of triclinic veatchite-1A is different and is $\sim 1/4\mathbf{T}_d$. The stack layers in all three veatchite polytype modifications are connected by the inversion center; further, for both monocline p -veatchite (Fig. 1b) and veatchite (Fig. 1c) those elements are pseudosymmetry elements (in so far as isolated $\text{B}(\text{OH})_3$ -triangles and H_2O molecules, located in interstitial space do not submit to them), while in the structure of veatchite-1A triclinic modification (Fig. 1d) those elements are true symmetry elements. In this case stacks of different composition have alternate in the structure: with cationic filling of Sr1 10-vertex polyhedra, coordinated by water molecules, and of Sr2 11-vertex polyhedra, coordinated by isolated $\text{B}(\text{OH})_3$ -triangles. It should be noted that in this triclinic structure the vertical glide plane, located perpendicular to $\mathbf{T}_d \sim 11.7\text{\AA}$ and broken with isolated $\text{B}(\text{OH})_3$ -triangles and water molecules, remains as pseudo-symmetry element. In the structure of monoclinic veatchite which symmetry is described by a Aa space group, this plane is true. The centers of inversion connecting sheets both for a stack and adjacent stacks in structures of two modifications of $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (II) (Fig. 1e) (Belokoneva *et al.*, 2008) and $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (I) (Fig. 1f) (Pushcharovsky *et al.*, 2000) are the true elements of symmetry, too. In the structure of synthetic $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 1g) (Yamnova *et al.*, 2003) layers of the adjacent stacks are connected by the center of inversion, and layers of one stack – with the glide plane, and in this case true symmetry has remained (space group $P2_1/c$). In the acentric structure of synthetic Ca-pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Fig. 1a) with a mixed filling of interstitial space (Yamnova *et al.*, 2009) a pair of a stack layers is connected with " g " plane noted above, but the shift vector in this case is $\sim 1/2\mathbf{T}_d$. As well as in case of veatchites, isolated $\text{B}(\text{OH})_3$ -triangles and molecules of H_2O do not submit to both operations.

The alternation and symmetry linkage of the sheets, located at four levels along the axis, perpendicular to the sheet plane in structures of three veatchite polytypes (Fig. 2a, b, c), volkovskite (Fig. 2d) (Rastsvetayeva *et al.*, 1992) and synthetic $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 2e) are shown. The layers belonging to a single three-layer stack are put into square brackets in figure: one stack in the central part of elements figure, and the others (two halves of the neighboring stacks) are in the



top and lower parts. In the same figure a module-blocks $\{M[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$ with pseudo-hexagonal section – triclinic "protocells" shown. Horizontal axes a^* and b^* are oriented in such a way that "apical" B-triangles of pentagroups are parallel to a long rhombus diagonal ($T_d \sim 11.7\text{\AA}$). In the identified blocks atoms occupy similar positions, but there are differences: 1) in symmetry linkage and filling of interstitial space within the blocks, and 2) in ways that the identified blocks consolidate along the

vertical axis. Nodes (points) of blocks are chosen in the pseudo- or true inversion centers (small white circles at Fig. 1 and 2), and also in the special points (small black squares in the figures) are linked to symmetry elements, i.e. are equidistant from pairs of *M*-positions and located on the right lines connecting them. The length of the a^* and b^* vectors are identical to horizontal translations of unit cells of the actual structures, and the c^* vector length corresponds to distance between the nodes located in the neighbor-

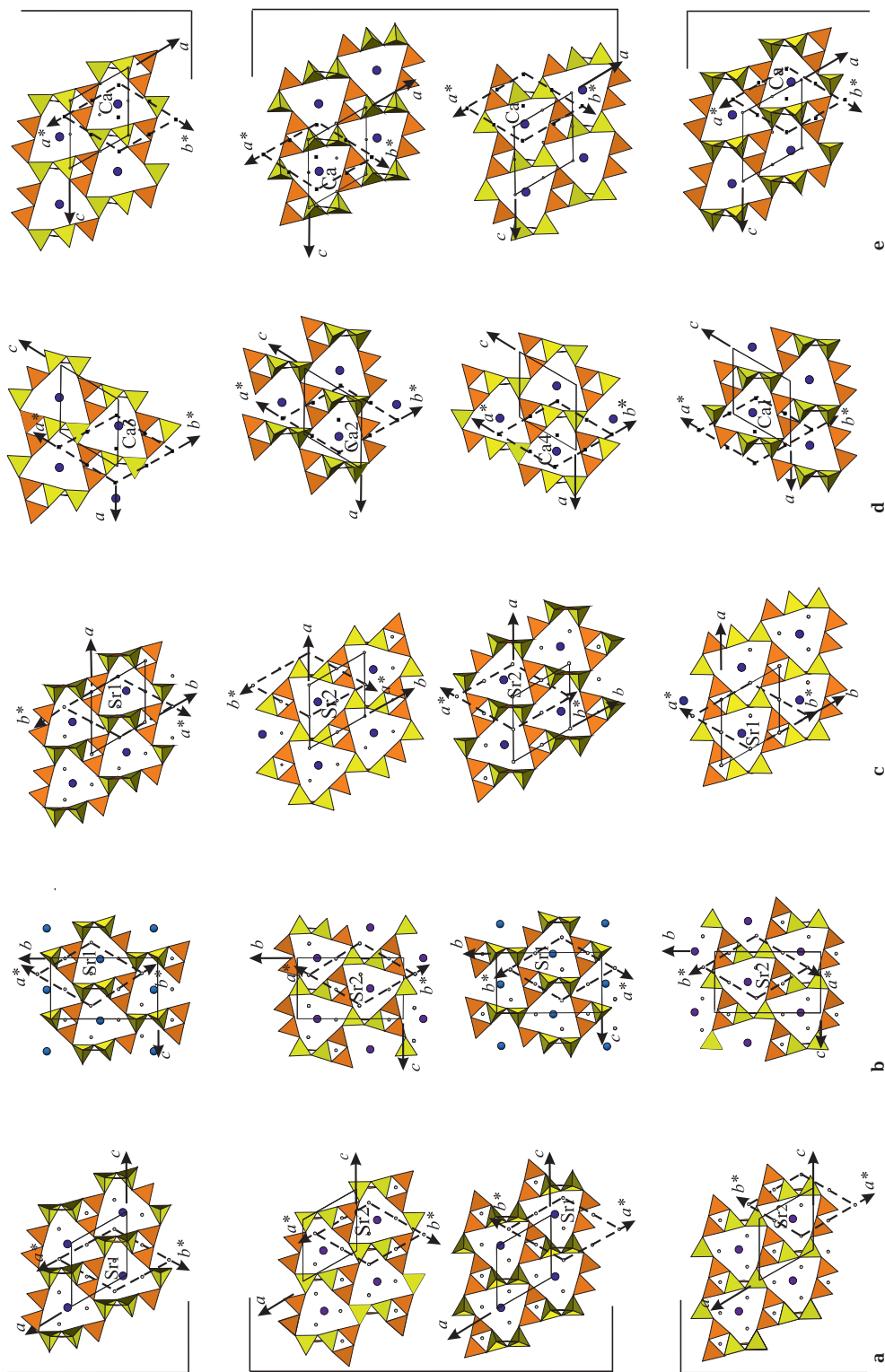


Fig. 2. Alternation of layers at four levels in the structures of pentaborates: a – p-veatchite, b – veatchite, c – veatchite -1A, d – volkovskite, and e – $\text{Ca}[\text{B}_5\text{O}_{10}(\text{OH})] \cdot \text{H}_2\text{O}$. Square brackets indicate the layers joined into stacks. Dashed lines represent blocks. Small open circles correspond to (a, b) pseudocenters of inversion and (c, e) true centers of inversion, black squares – special points.

ing three-layer stacks. In the structure of veatchite-1A (Fig. 1d; 2c) and Ba-pentaborate (Fig. 1e, f) the nodes of the blocks coincides with the true centers of inversion, in the structures of monoclinic polytypes – with the inversion pseudo-centers (Fig. 1b, c; and 2a, b). In the structures of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Fig. 1a), volkovskite (Fig. 2d) and $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 1g and 2e) the nodes of the blocks are chosen in the special points located on the glide planes. The block nodes coordinates (x, y, z) , defined for actual structures, were a basis for calculation of the transformation matrixes from unit cell of each structure to triclinic blocks (modules) which metric characteristics are provided in Table 1.

Alternation of boron-oxygen sheets based on the separated blocks in structures of the veatchite related pentaborates are schematically shown in Figure 3, where hypothetical models are constructed by combinations

both of true- and pseudo-elements of symmetry with retaining the mutual arrangement of fragment, which is similar to that of real structures. The pentagroups of boron-oxygen sheets shown as triangles on the scheme, are on borders of blocks and belongs to a three-layer stack. The structures of veatchite-like pentaborates can be divided into three types by symmetry linkage of atoms within the marked blocks. The first type – "the glide plane, g ", is found in the structures: Ca-pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ (Fig. 3a), volkovskite (Fig. 3b), p -veatchite (Fig. 3c) and hypothetical model (Fig. 3d); the second type – "a screw axes, 2_1 " – in the structures of monoclinic and triclinic veatchite (Fig. 3f), and also in two hypothetical models (Fig. 3e, g); and the third type – the center of inversion (i) – in Ba-pentaborates (Fig. 3h) structures, Ca-pentaborate $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (Fig. 3i) and in hypothetical model (Fig. 3j). Both transla-

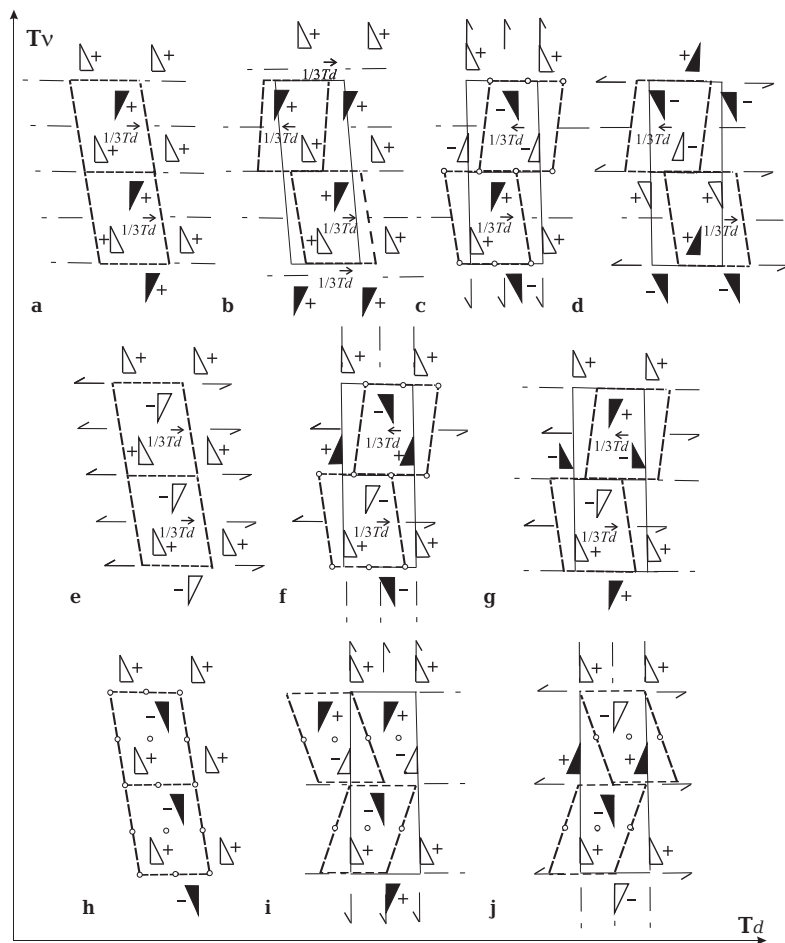


Fig. 3. Schematic diagrams illustrating the symmetry relationships between the layers in the structures of pentaborates: a – $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$, b – volkovskite, c – p -veatchite, d – hypothetical model, e – hypothetical model, f – veatchite and veatchite-1A, g – hypothetical model, h – $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (III) and $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$ (I), i – $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot \text{H}_2\text{O}$, and j – hypothetical model. Closed and open triangles represent the left and right figures (pentaborate groups of the boron-oxygen layer), respectively. Dashed lines indicate the blocks, and the letters T_v and T_d denote the vertical and diagonal translations, respectively.

Table 2. The unit cell characteristics of triclinic and monoclinic hypothetical models of pentaborates with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$ (1-1, 1-2, 1-3, 1-4) and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2\text{H}_2\text{O}$ (2-1, 2-2, 2-3, 2-4)

Unit cell parameters	Model 1-1	Model 1-2	Model 1-3	Model 1-4
	Model 2-1	Model 2-2	Model 2-3	Model 2-4
a , Å	6.665	6.665	6.665	10.430
b , Å	6.617	6.617	6.617	11.738
c , Å	10.605	10.605	10.605	6.652
α , degr.	103.68	90	90	90
β , degr.	77.98	90	90	92.1
γ , degr.	120.93	120.93	120.93	90
Symmetry	(i)	(i)	(n)	(2_1)
Transformation matrixes	x, y, z	x, y, z	x, y, z	x, y, z
	$-x, -y, -z$	$-x, -y, -z$	$x+1/2, y+1/2, -z$	$-x, y+1/2, -z$

tion-identical blocks, and those, connected by operation of true elements of symmetry of space groups of actual structures alternate along (\mathbf{T}_v), axis, perpendicular to the plane of sheets.

Geometrical construction and testing of possible basic models of veatchite polytypes

The structure models built up of blocks connected with \mathbf{T}_x , \mathbf{T}_y , \mathbf{T}_z translation are the base models of the veatchite-like structures (Fig. 3a, e, h). In this case the basic model obeying the true symmetry (space group $P\bar{1}$) (Fig. 3h), with uniform filling of the interstitial space with H_2O molecules, realized in the structures of two modifications (I, II) of synthetic $\text{Ba}[\text{B}_5\text{O}_8(\text{OH})]\cdot\text{H}_2\text{O}$, reported by E.L. Belokoneva and coauthors (Belokoneva *et al.*, 2000) as the *MDO*-polytype. Two other models have non-crystallographic (translation component $\sim 1/3\mathbf{T}_a$) symmetry of " g " (Fig. 3a) and " 2_1 " (Fig. 3e). Thus the first model is found in Ca-pentaborate structure of synthetic $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]\cdot\text{H}_2\text{O}$, as investigated by ourselves (Yamnova *et al.*, 2009) and refined later (Yamnova *et al.*, 2012), while the second model remains hypothetical.

In order to determine the probability of *MDO*-polytypes formation, the symmetry of which would result in $P\bar{1}$, $P11n$ and $P12_11$ true space groups (with translation components $1/2\mathbf{T}_a$ for monoclinic groups), the structure models of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$ and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2\text{H}_2\text{O}$ with uniform interstitial filling have been constructed. The metric characteristics and atomic coordinates of the real structure of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]\cdot\text{H}_2\text{O}$ (Yamnova *et al.*, 2009), in which H_2O molecules and $\text{B}(\text{OH})_3$ triangles alternately replace each other were used as initial model

for the building of models with symmetry (i) (space group $P\bar{1}$) and (n) (space group $P11n$) This model was chosen because of the coincidence of its metric characteristics to the basic block, and also the rather small number of parameters necessary to further carry out a power analysis. The coordinates of atoms (Clark, Christ, 1971) corresponding to a half-volume of a monoclinic veatchite cell ($a' = 1/2a = 10.4\text{Å}$) with symmetry (2_1) (space group $P12_11$) for both compositions, were used as the initial model (in a real structure of which the identified blocks possess non-crystallographic symmetry " 2_1 " with translation $\sim 1/3\mathbf{T}_a$ along the $b = 11.7\text{Å}$ axis).

Characteristics of the unit cells of the constructed models are provided in Table 2, the transformed atomic coordinates are in Tables 3–6, and "lateral" projections of hypothetical structures in Fig. 4. For models with symmetry (i), two options for the unit cell are used: triclinic "scalene", and "rectangular"; for models with symmetry (n) and (2_1) – only "rectangular" monoclinic.

The structural model of $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$ with two additional interstitial B-triangles and (i)-symmetry seems improbable, as in this case distances between the OH-tops of the isolated B-triangles and the O(OH)-tops of the apical B-triangles from the adjacent three-layer stack (those are noted with thick lines and 1 and 2 figures) are too short (1.78Å and 1.93Å for 1-1 model (Fig. 4a); 1.66Å and 1.77Å for 1-2 model (Fig. 4b)). For monoclinic models with the same composition, with symmetry (n) and (2_1) (not presented on the figure), similar distances are as follows: 1.26Å and 1.27Å (1-3 model); 1.45Å and 1.52Å (1-4 model). The same options were used for the building of hypothetical structures for $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot 2\text{H}_2\text{O}$. For triclinic models with symmetry (i)

Table 3. Atomic coordinates of the models (1-1, 1-2, 1-3) with composition $\text{Ca}_2[\text{B}_3\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$

Atom	x/a	y/b	z/c
Ca1	0.2300	0.2850	0.1150
B1	0.3320	-0.2000	0.1180
B2	-0.0950	0.6580	0.1610
B3	-0.2810	-0.0960	0.1740
B4	-0.3580	0.2130	0.1370
B5	-0.2230	-0.1850	0.3740
B6	0.1790	0.4070	0.4180
O1	-0.1010	-0.1550	0.1110
O2	0.5010	0.7290	0.1100
O3	-0.2050	0.1470	0.1520
O4	0.4020	0.0390	0.1330
O5	0.6900	0.4320	0.1250
O6	0.1080	0.6270	0.1060
O7	-0.0990	0.7090	0.3060
O8	-0.3260	-0.1040	0.3140
(OH)9**	0.1350	-0.5550	0.5510
(OH)10*	-0.2480	-0.1650	0.5070
(OH)11**	0.1340	0.5080	0.3360
(OH)12**	0.2760	0.2730	0.3480

Table 4. Atomic coordinates of the models (2-1, 2-2, 2-3) with composition $\text{Ca}_2[\text{B}_3\text{O}_8(\text{OH})]_2\cdot 2\text{H}_2\text{O}$

Atom	x/a	y/b	z/c
Ca1	0.2300	0.2850	0.1150
B1	0.3320	-0.2000	0.1180
B2	-0.0950	0.6580	0.1610
B3	-0.2810	-0.0960	0.1740
B4	-0.3580	0.2130	0.1370
B5	-0.2230	-0.1850	0.3740
O1	-0.1010	-0.1550	0.1110
O2	0.5010	0.7290	0.1100
O3	-0.2050	0.1470	0.1520
O4	0.4020	0.0390	0.1330
O5	0.6900	0.4320	0.1250
O6	0.1080	0.6270	0.1060
O7	-0.0990	0.7090	0.3060
O8	-0.3260	-0.1040	0.3140
(OH)9*	-0.2480	-0.1650	0.5070
Ow	0.1700	0.3700	0.3380

Table 5. Atomic coordinates of the models (1-4) with composition $\text{Ca}_2[\text{B}_3\text{O}_8(\text{OH})]_2\cdot 2[\text{B}(\text{OH})_3]$

Atom	x/a	y/b	z/c
Ca1	0.1100	0.0400	0.5300
Ca1-1	0.1100	0.5400	0.0300
B1	0.1500	0.3310	0.7240
B1-1	0.1500	0.8310	0.2240
B2	0.1900	0.4850	0.4850
B2-1	0.1900	0.9850	0.9850
B3	0.1500	0.2880	0.3650
B3-1	0.1500	0.7880	0.8650
B4	0.1900	0.6950	0.5140
B4-1	0.1900	0.1950	0.0140
B5	0.4100	0.5950	0.5000
B5-1	0.4100	0.0950	0.0000
B6	-0.4300	0.2100	0.0100
B6-1	-0.4300	0.7100	0.5100
O1	0.1300	0.2970	0.9190
O1-1	0.1300	0.7970	0.4190
O2	0.1300	0.4430	0.6780
O2-1	0.1300	0.9430	0.1780
O3	0.1500	0.2520	0.5690
O3-1	0.1500	0.7520	0.0690
O4	0.1500	0.4000	0.3220
O4-1	0.1500	0.9000	0.8220
O5	0.3300	0.4930	0.5060
O5-1	0.3300	0.9930	0.0060
O6	0.1300	0.5940	0.4240
O6-1	0.1300	0.0940	0.9240
O7	0.1500	0.2010	0.2330
O7-1	0.1500	0.7010	0.7330
O8	0.3300	0.6990	0.5050
O8-1	0.3300	0.1990	0.0050
(OH)9*	0.5300	0.5920	0.5070
(OH)9-1*	0.5300	0.0920	0.0070
(OH)10**	-0.5500	0.2100	0.0000
(OH)10-1**	-0.5500	0.7100	0.5000
(OH)11**	-0.3300	0.3000	0.0200
(OH)11-1**	-0.3300	0.8000	0.5200
(OH)12**	-0.3500	0.1100	0.0100
(OH)12-1**	-0.3500	0.6100	0.5100

Note: In the following tables: * – OH-group of the apical B-triangle of B-O-network; ** – OH- group of the additional B-triangle.

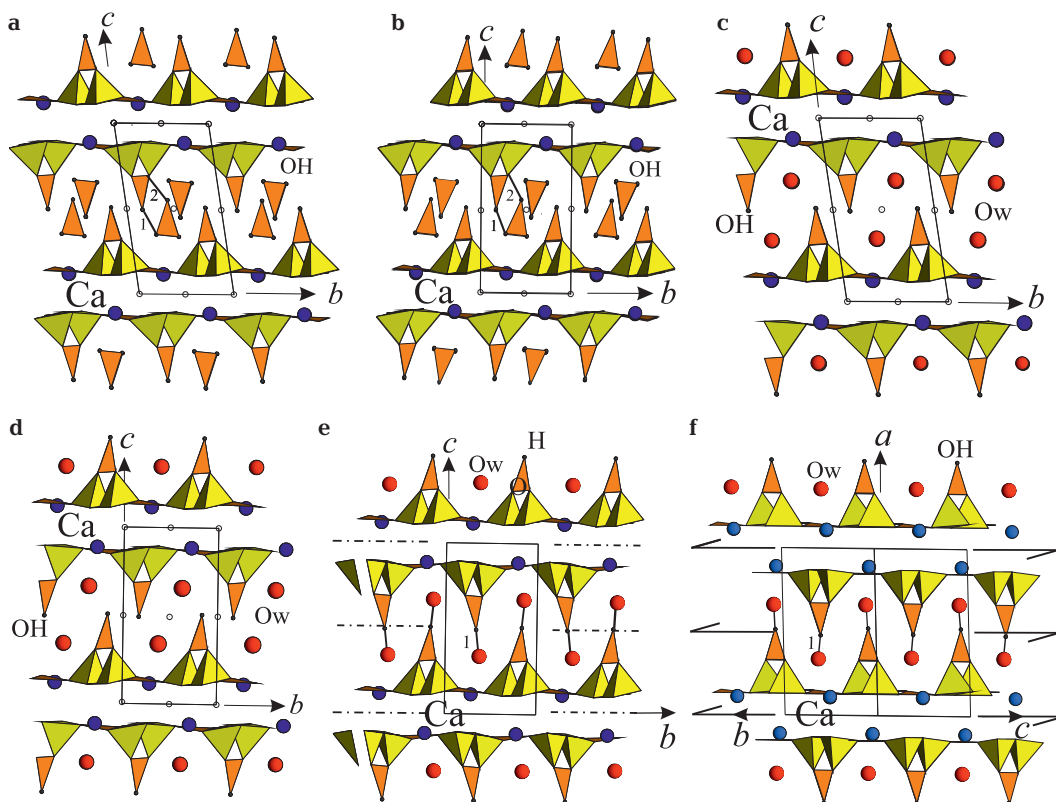


Fig. 4. Hypothetical models of the pentaborate structures with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ and $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$: a – model 1-1, b – model 1-2, c – model 2-1, d – model 2-2, e – model 2-3, and f – model 2-4. Bold lines and digits (1, 2) denote the "short" interatomic distances.

with "scalene" and "rectangular" cell an interatomic distances, the values found are not far beyond standard values (Fig. 4c, d), but for monoclinic models with symmetry (n) (Fig. 4e) and (2_1) (Fig. 4f), distances between atoms of oxygen in a water molecule and the OH-top of the apical B-triangle were inadmissible small (1.78 Å for the first model and 1.41 Å for the second). Thus, monoclinic models with a true symmetry of 2_1 and n are improbable as basic structures.

Theoretical modeling of the basic structure of veatchite polytypes

The universal set of parameters of the interatomic potentials optimized for structural modeling of borates was applied to a power analysis of possible basic structures of veatchite-like polytypes (Eremin, Urusov, 2013). In the current study to develop the potential primary model, the simplest crystal structure of CaB_2O_4 borate, containing only BO_3 triangles, was chosen. At the initial stage

of modeling, the following set was used: in addition to the Coulomb interaction of all ions, the cation-oxygen and oxygen-oxygen repulsion, described by the Buckingham potential, was considered. As result of a test calculation series we found that, 1) the B-O interaction does not allow a satisfactory description within the model with a formal charges on atoms, and 2) the Buckingham potential for this pair of atoms is also inapplicable owing to what for the description of B-O interaction in the mentioned work (Eremin, Urusov, 2013) the Morse potential was applied. In order the anions polarization effect to be included in calculation, the shell-type model was applied for oxygen atoms. Besides, an introduction of the additional contribution, described by three-particle harmonious potential, was required for the additional stabilization of valence angles coordination in boron polyhedra. The effective charges estimated from test procedures on oxygen in CaB_2O_4 were transferred without change to the other model species, SrB_4O_7

Table 6. Atomic coordinates of the models (2-4) with composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$

Atom	x/a	y/b	z/c
Ca1	0.1100	0.0359	0.5256
Ca1-1	0.1100	0.5359	0.0256
B1	0.1500	0.3310	0.7240
B1-1	0.1500	0.8310	0.2240
B2	0.1900	0.4850	0.4850
B2-1	0.1900	0.9850	0.9850
B3	0.1500	0.2880	0.3650
B3-1	0.1500	0.7880	0.8650
B4	0.1900	0.6950	0.5140
B4-1	0.1900	0.1950	0.0140
B5	0.4100	0.5950	0.5000
B5	0.4100	0.0950	0.0000
O1	0.1300	0.2970	0.9190
O1-1	0.1300	0.7970	0.4190
O2	0.1300	0.4430	0.6780
O2-1	0.1300	0.9430	0.1780
O3	0.1500	0.2520	0.5690
O3-1	0.1500	0.7520	0.0690
O4	0.1500	0.4000	0.3220
O4-1	0.1500	0.9000	0.8220
O5	0.3300	0.4930	0.5060
O5-1	0.3300	0.9930	0.0060
O6	0.1300	0.5940	0.4240
O6-1	0.1300	0.0940	0.9240
O7	0.1500	0.2010	0.2330
O7-1	0.1500	0.7010	0.7330
O8	0.3300	0.6990	0.5050
O8-1	0.3300	0.1990	0.0050
(OH)9*	0.5200	0.5920	0.5070
(OH)9-1*	0.5200	0.0920	0.0070
Ow	0.3500	0.0710	0.5320
Ow-1	0.3500	0.5710	0.0320

Table 7. Unit cell parameters and structural energy (E_{str}) of the hypothetical models $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$

Parameter	Model 2-1	Model 2-2	Model 2-3 ₁	Model 2-3 ₂
	(i)	(i)	(n)	(n)
a, Å	6.665	6.665	6.665	6.665
b, Å	6.617	6.617	6.617	6.617
c, Å	10.605	10.605	10.605	10.605
α , degr.	103.68	90	90	103.68
β , degr.	77.98	90	90	77.98
γ , degr.	120.93	120.93	120.93	120.93
E_{str} , eV	-987.56	-955.86	-896.18	-938.33

(Perloff, Cluster, 1966), used for optimization of B-O interaction in the tetrahedron of BO_4 . Thus, for preservation of electroneutrality in the unit cell, the B-charge in tetrahedral surrounding appeared above a similar charge in triangular coordination that corresponds to the crystal chemical rule of dependence of an ion charge on coordination number.

In our study, the two models of composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ and symmetry (i) in "scalene" (2-1 model) and "rectangular" (2-2 model) variants, which are the most probable basic models according the previous results, were used. For comparison with in the same unit cells with right (2-31 model) and oblique (2-32 model) corners, two structures of similar composition with symmetry (n) were tested. The structural energy (E_{str}) of all four geometrical models was estimated in the calculation mode with fixed atoms coordinates specified in Table 5. The 2-1 model with symmetry (i) and a triclinic cell (Fig. 4c) appeared to be the most energy favorable, as shown in Table 7. The other variants appeared more energy-expensive, that is why their realization is improbable. Results of comparison of structural energies of tested crystal structures confirmed data, obtained at geometrical construction of a possible basic models of veatchite-like structures.

Features of pentaborate structures related to veatchite: volkovskite, biringuccite, gowerite and nasinite

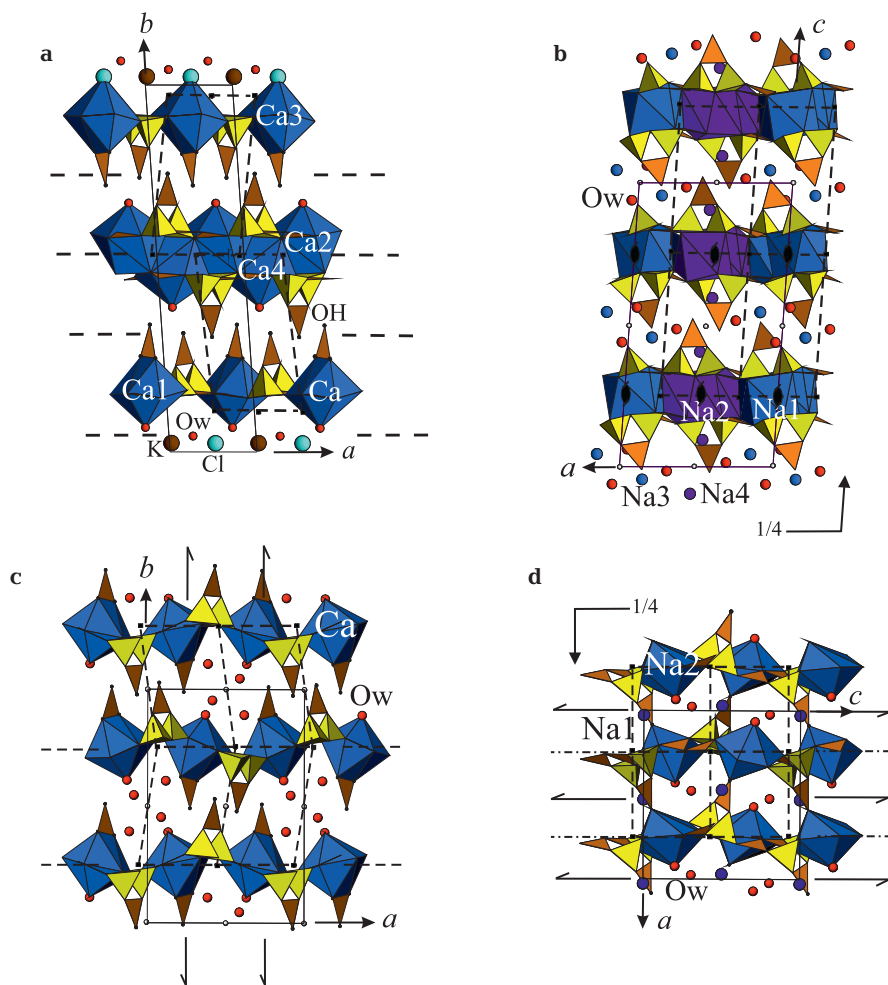
Symmetry of the separated block of composition $\{M[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{[\text{B}(\text{OH})_3], \text{H}_2\text{O}\}_2$, ($M = \text{Ca}, \text{Sr}, \text{Ba}$) defines 1) the type of bonds between boron-oxygen sheets from the neighboring three-layer stacks of the veatchite-like structures and 2) the stacks shift of the one from each other. With regard to composition, theoretically, according to the general formula of the veatchite-like species, for every two M-cations in a three-layer stack there are either two isolated $\text{B}(\text{OH})_3$ -triangles or two H_2O molecules, or single molecule of both composition. The other composition of both a three-layer stack and an interstitial space leads to distortion or change of the veatchite-like structure that is observed in natural pentaborates as follows: volkovskite $\text{KCa}_4[\text{B}_{22}\text{O}_{32}(\text{OH})_{10}\text{Cl}]\cdot 4\text{H}_2\text{O}$ (Rastvetayeva *et al.*, 1992), biringuccite $\text{Na}_4[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ (Corazza *et al.*, 1974), gowerite $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot [\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}$ (Konnert *et al.*, 1972) and nasinite $\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$ (Corazza *et al.*, 1975).

In the volkovskite structure (Fig. 5a), one of two three-layer stacks topologically completely corresponds to that described above. The second stack differs from the first by introduction of K and Cl atoms and of H₂O molecules between the top and lower half of a three-layer stack. As a result, the crystal chemical formula of the mineral can be written down as $\{[\text{Ca}[\text{B}_5\text{O}_8(\text{OH})]_2]_2 \cdot \{[\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}\}_2 \cdot \{\text{KCl} \cdot 2\text{H}_2\text{O}\}$, which corresponds to alternation along the *b* axis of two blocks and a $\{\text{KCl} \cdot 2\text{H}_2\text{O}\}$ -layer in the structure of the mineral. A symmetry linkage of boron-oxygen layers in the volkovskite structure (Fig. 2d; 3b) is similar to that in the structure of synthetic $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$: the layers of a stack are connected by the glide plane of the shift components $-1/2\mathbf{T}_a$,

and layers of the next stacks – with non-crystallographic $-1/3\mathbf{T}_a$. Thus, the positions of the H₂O-molecules and isolated B-triangles are subject to action only by the first plane. Nodes of the separated blocks are located in special points: on the glide planes, connecting calcium-boron-oxygen layers of a three-layer stack, and also equidistant from pairs of atoms Ca3 – K and Ca1 – Ow (oxygen atom of H₂O molecule). Metric characterizations of the chosen blocks and the transformation matrix for them are provided in Table 1.

In the structures of the Ca(Sr,Ba)-pentaborates previously discussed, neutrality is achieved via an equal ratio of cations and pentagroups in the three-layer stacks ($\text{M}^{2+} : [\text{B}_5\text{O}_8(\text{OH})]^{2-} = 1:1$) The same ratio is

Fig. 5. «Lateral» projections of the structures: a – volkovskite, b – biringuccite, c – gowerite, and d – nasinite. Blocks and pseudosymmetry (a) and true symmetry (b-d) elements are indicated.



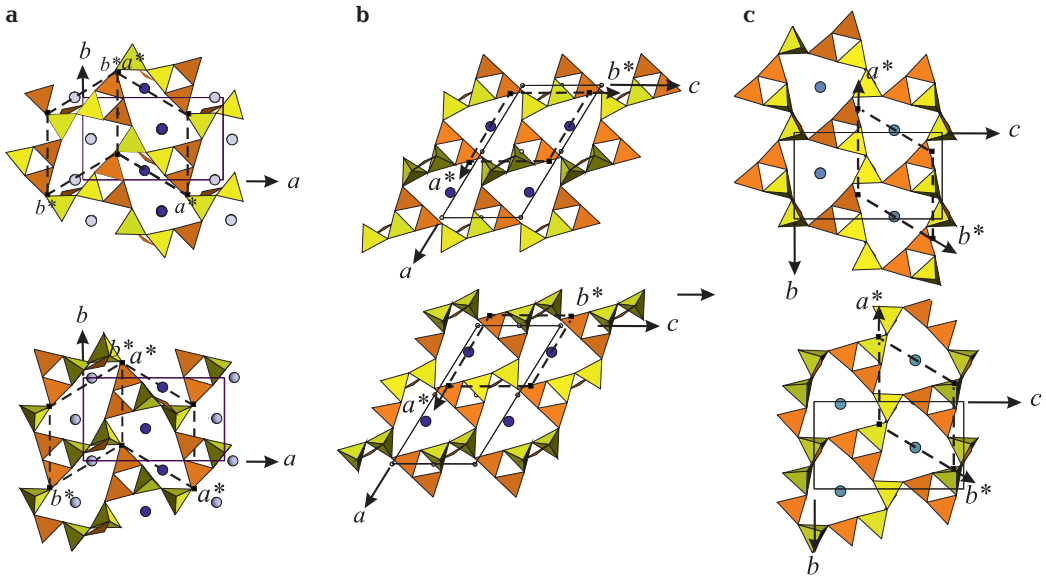


Fig. 6. Alternation of layers at two levels in the structures: *a* – biringuccite, *b* – gowerite, and *c* – nasinite. Dashed lines represent blocks.

found in the structure of biringuccite, $\text{Na}_4[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2\text{H}_2\text{O} = \{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{Na} \cdot \text{H}_2\text{O}\}_2$, the base of which (Fig. 5b) is also composed of three-layer stacks (two boron-oxygen sheets, between which Na1- and Na2-cations are enclosed). In this case the three-layer stacks have a negative charge, which is compensated for by additional Na^+ (Na3 and Na4) cations entering into the interstitial space with H_2O -molecules. As a result, the polyhedra, around the Na3 and Na4 cations are combined via common O-vertices and edges, with the Na1- and Na2-polyhedra of a three-layer stack in a three-dimensional framework. This leads to a strong distortion of the sodium-boron-oxygen network in the biringuccite structure (Fig. 6a). Unlike the structures of divalent cation pentaborates, $[\text{B}_2^t\text{B}_3^\Delta\text{O}_8(\text{OH})]^{2-}$ pentagroups in the biringuccite sheet are connected not by horizontal translations, as in the above-described structures, but by reflection in pseudoplanes (*a*), which are located on levels $y \sim 0$ and $\sim 1/2$ and which alternate with planes (*c*) of the mineral's true symmetry. Despite these differences, one can also separate a building block, similar by its metric characteristics and composition: a pseudohexagonal triclinic cell (Table 1) with the formula $\{\text{Na}[\text{B}_5\text{O}_8(\text{OH})]\}_2 \cdot \{\text{Na} \cdot \text{H}_2\text{O}\}_2$, within the mineral structure. Atoms in the separated blocks have connected with true inversion centers, while in blocks adjacent to the *a* axis, a similar arrangement of the atoms

inverts the positions of Na3-, Na4-atoms and H_2O molecules in the interstices. There are four such blocks alternating in the structure: adjacent blocks along the *b* axis have connected by translation, and those adjacent along the *a* axis, by reflection in *a* pseudoplanes.

The analysis of atomic distances which was carried out above in hypothetical structures established a small probability of a structure model with the composition $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot 2[\text{B}(\text{OH})_3]$ with two additional interstitial B-triangles. Such a ratio of cations and isolated B-triangles, together with the trebled quantity of H_2O -molecules in comparison with the synthetic pentaborate $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot [\text{B}(\text{OH})_3] \cdot \text{H}_2\text{O}$ is found in the gowerite structure $\text{Ca}[\text{B}_5\text{O}_8(\text{OH})] \cdot [\text{B}(\text{OH})_3] \cdot 3\text{H}_2\text{O}$, the basis of which is formed from a non-polar (with various orientations of apical B-triangles) calcium-boron-oxygen sheets (Fig. 5c), not connected to each other. The mechanism of such a transition from the veatchite-similar structure can be presented as follows: as H_2O -molecules and $\text{B}(\text{OH})_3$ isolated triangles are increased in the interstitial space, a reversal of some pentagroups with inversion of apical B-triangles of boron-oxygen networks occurs, leading to "destruction" of three-layer stacks and bonding of structures with non-polar sheets. In this structure, following the principles described above, it is also possible to separate the block with nodes in specific points on the planes (*a*),

corresponding to the composition $\{Ca[B_5O_8(OH)]\} \cdot [B(OH)_3] \cdot 3H_2O$, where the first part of the formula corresponds to the calcium-boron-oxygen sheet composition, and the second one to the interstitial space occupation.

There are four blocks in the gowerite unit cell, connected by symmetry elements of the $P2_1/a$ space group. Sheets, similar to those of gowerite, are also present in the structure of nasinite $Na_2[B_5O_8(OH)] \cdot 2H_2O$ (Fig. 5d), in the composition of which a doubled number of H_2O -molecules occurs, in contrast to biringuccite $Na_4[B_5O_8(OH)]_2 \cdot 2H_2O = 2 \times \{Na_2[B_5O_8(OH)] \cdot H_2O\}$. In the structure of nasinite, as well as in that of biringuccite, a negative charge of sodium-boron-oxygen networks is compensated by entry of additional Na together with two H_2O molecules to the interstitial space. As in biringuccite, sheet and interstitial Na-polyhedra forms the framework. The possible mechanism of structural transition of biringuccite – nasinite is similar to that for gowerite, as described above. In the nasinite structure, using special points on clinoplanes (n), it is possible to separate the block of composition $\{Na[B_5O_8(OH)]\} \cdot \{Na \cdot 2H_2O\}$: there are 4 blocks in the unit cell, connected by reflection in the planes (n) and (a) of the $Pna2_1$ space group. In the gowerite and nasinite structures, the hexagonal configuration of boron-oxygen layers with cations in triangular nests remains similar to veatchite, with Ca in the gowerite structure (Fig. 6b) and Na in nasinite (Fig. 6c). Metric characteristics of the blocks, separated by special points, are comparable to similar parameters in other veatchite-like structures (Table 1). In the separated blocks of the gowerite and nasinite structures, the arrangement of atoms and their quantity differs from that of the veatchite-like structures. In the gowerite and nasinite structure blocks, the volume of which is comparable with that of veatchite, there are half as many atoms in the cation-boron-oxygen network and twice as many in the interstitial space. This corresponds to a looser structures, in which cation-boron-oxygen networks do not unit into three-layer stacks, but evenly alternate with interstitial space.

Conclusions

The comparative crystal chemical analysis of minerals of the veatchite group and related natural and synthetic compounds has

allowed us to separate the module – block $\{M[B_5O_8(OH)]\}_2 \cdot \{[B(OH)_3], H_2O\}_2$ ($M = Ca, Sr, Ba$) as the fundamental construction unit with specific metric characteristics and atomic arrangement. Testing the hypothetical structures – constructed on the basis of this block has shown that theoretically the most probable basic model of the veatchite-like pentaborate polytypes with polar boron-oxygen sheets is the structure of composition $\{M[B_5O_8(OH)]\}_2 \cdot \{H_2O\}_2$ with a triclinic scalene unit cell and symmetry (i). This model, found in two Ba-pentaborate structures as the *MDO*-polytype, is the fundamental building block for synthetic Ca-pentaborate $Ca[B_5O_8(OH)] \cdot H_2O$, in which structure the blocks neighboring on horizontal axes are connected by translational motion, and those, adjacent along a vertical axis are connected by operation of true elements of symmetry. Scalene translation along the T_v direction, perpendicular to the plane of boron-oxygen sheets, providing a certain shift of three-layer stacks from each other, apparently, is a necessary condition of a stable structure obtaining (as in this case an interstitial volume, sufficient for displacement of two water molecules, has created). Therefore, the existence of monoclinic *MDO*-polytypes of a similar composition and structure, the symmetry of which follows the space group $P11n$ and $P12_11$, is improbable: there are no examples of structures built of blocks of this kind among known veatchite-like natural and synthetic phases. The structures formed of blocks $\{M[B_5O_8(OH)]\}_2 \cdot \{[B(OH)_3], H_2O\}_2$ with close metric characteristics, but with mixed interstitial filling and with "g" and "2₁" symmetry and a non-crystallographic glide component, are the most widespread. A block with "g" symmetry, found in the structure of the investigated Ca-pentaborate $Ca_2[B_5O_8(OH)]_2 \cdot [B(OH)_3] \cdot H_2O$ is a basic model for the volkovskite and *p*-veatchite structures, and a block of similar composition, with symmetry "2₁", is a basic model for the veatchite and triclinic veatchite-1A structures.

Variations in the composition of the separated block lead to transformation of the veatchite structure and the appearance of new structural types. The structures of volkovskite and biringuccite, in which polarity of boron-oxygen sheets and the "three-layer stack" character of the veatchite structure remains, can be considered as transition forms to the structures of gowerite and nasinite, with non-polar boron-oxygen sheets.

Thus, in all the structures derived from veatchite, the fundamental building block remains, which is comparable to the structure and parameters with that of veatchite, which allow to assume a genetic linkage of the specified groups minerals.

Financial support for this work was provided by the Russian Foundation of Basic Research, project No. 12-05-809a. The computations were performed in part on a "Chebyshev" SKIF-MGU supercomputer.

The authors thank Dr. M. Feinglos for English text editing.

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THE Pt-Pd-Sn ALLOYS IN THE Pt-Pd SULFIDES CRYSTALLIZATION FIELD IN THE Cu-Fe-S SYSTEM

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To understand conditions under which the unique Cu-Fe association was formed at the Norilsk Cu-Ni deposits, crystallization products of melts were studied in the Cu-Fe-S system with Pt, Pd, and Sn admixtures (1 wt.%). Pt-Pd-Sn alloys — analogues of rustenburgite Pt_3Sn , atokite Pd_3Fe and palladium rustenburgite were synthesized in phase associations with chalcopyrite, isocubanite, and mooihoekite corresponding to the stability field of Pt-Pd sulfides analogues of the naturally occurring minerals malanite $(Pt,Cu,Fe)_S$, cooperite PtS, vysotskite PdS, and braggite $(Pt,Pd)_S$. The results thus obtained testify that the presence of Sn, together with Pt and Pd, in the melts of the central part of the Cu-Fe-S system corresponding to the compositions of magmatic Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits predetermines the preferable crystallization of Pt-Pd-Sn alloys.
1 figure, 2 tables, 8 references.

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

Most Pt and Pd minerals with Sn were discovered in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits (Genkin *et al.*, 1968) and were later distinguished as a unique Sn-bearing Cu-Fe association (Nekrasov, 1984). Following the first publications and later experimental studies at temperatures corresponding to postmagmatic crystallization, most researchers connects the formation of the Pt-Pd-Sn minerals with Pt-bearing fluids after the crystallization of the ore-forming Cu-Fe sulfides. Experimental studies the features of melt crystallization in the central part of the Cu-Fe-S system corresponding to the composition of Norilsk magmatic Cu-Fe sulfide ores (50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69 with Pt and Pd admixtures or Pt, Pd, and Sn admixtures; Kravchenko, 2009) suggest that Pt-Pd minerals can crystallize before the ore-forming sulfides and that Pt-Pd-Sn minerals preferably crystallize in the stability field of Pt-Pd-Fe alloys. Materials presented in this paper demonstrate that Pt-Pd-Sn alloys also predominantly crystallize in the stability field of Pt-Pd sulfides.

Methods

The starting materials were carbonyl iron A-2, copper V-3, reagent-grade sulfur (additionally dehydrated by fusing in vacuum), metallic platinum, palladium, and tin. Pt, Pd, and Sn ((Pt, Pd)/Sn = 3/1, total concentration 1 wt.%) were added to the phase associations that were preliminarily synthesized in the Cu-Fe-S system and corresponded to the crystallization field of Pt-Pd sulfides, and to samples that have been studied previously and contained Pt-Pd sulfides (Pt + Pd = 1 wt.%, Kravchenko, 2013). The Cu/Fe ratios

(0.25, 0.43, 0.54, 0.69, 1.20, and 1.44) of these samples are not labeled by indexes in the tables. The total concentrations of admixtures in the synthesized samples were either 1 wt.% or > 1 wt.% because of a certain concentrations of Pt-Pd sulfides in the starting material. Synthesis was conducted in evacuated quartz ampoules by cooling the melt from 1200°C to room temperature. Similar to the synthesis of Pt-Pd-Sn alloys in the crystallization field of Pt-Pd-Fe-Cu alloys in the Cu-Fe-S system (Kravchenko, 2009), when cooled, all samples were held at a temperature of 600°C for two weeks and then (upon remelting) at 400°C for three months. In view of certain crystallization specifics of the Cu-Fe-S phases (Kravchenko, 2011), some of the samples were also held when cooled at 800°C for 1–10 days and/or cooled at various rates within the temperature range of 1200–850°C. The samples were cooled from 600 or 400°C to room temperature in cold water. The synthesized crystallization products were examined under an optical microscope and by X-ray diffraction techniques. Polished sections were manufactured of the halves of the samples (cut through their central parts from tops to bottoms). The chemical compositions of the samples and the distribution of minor elements in them were analyzed on a Camebax-Micro microprobe, using the RMA-96 universal computer code (Lavrent'ev and Usova, 1991), by the FeK_{α} , CuK_{α} , SK_{α} , PtM_{α} , PdL_{α} , SnL_{α} . X-ray diffraction lines, in which no overlaps occur. The standards were FeS, SnS, $CuFeS_2$, Pt, and Pd. The accelerating voltage was 20 kV, the absorbed-electron current was 40 nA, the take-off angle was 40°, the counting time was 10 s on each analytical line, and the beam diameter was 2–3 μm . The analytical errors were within $\pm 2\%$ for each

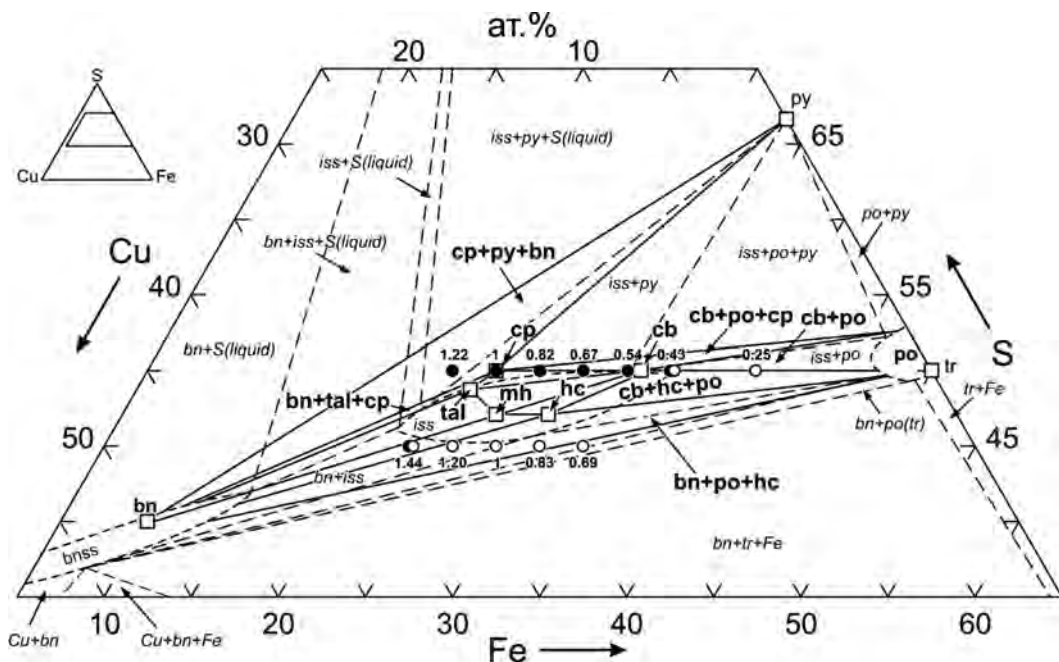


Fig. 1. Phase relations of synthesized phases (solid lines) (Kravchenko, 2011, 2012) in the central part of the Cu-Fe-S system at 600°C (dashed lines) (Cabri, 1973).

□ – stoichiometric compositions: chalcopyrite CuFeS_2 (cp), bornite Cu_3FeS_4 (bn), pyrite FeS_2 (py), troilite FeS (tr), talnakhite $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ (tal), isocubanite CuFe_2S_3 (cb), mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (mh) and haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$ (hc), iss, bns and po are the chalcopyrite, bornite and pyrrhotite solid solutions. Starting compositions of the synthesized samples: 50 at. % S, Cu/Fe = 1.22–0.25; 45 at. % S, Cu/Fe = 1.44–0.69. • – Pt-Pd sulfides; ○ – Pt-Pd-Fe-alloys.

element. The detection limits C_{\min} were calculated using the 2 δ -criterion at 99% confidence level and were as follows: Cu – 0.05, Fe – 0.03, S – 0.02, Pt – 0.06, Pd – 0.05, and Sn – 0.05. The composition of the synthesized phases was expressed in the form of chemical formulas involving all elements whose concentrations in these phases were no lower than 5 at.%; the phases were named accordingly to their analogues naturally occurring as minerals. The exceptions were the phases of haycockite composition $\text{Cu}_4\text{Fe}_5\text{S}_8$, which have a cubic *pc* structure in contrast to natural orthorhombic haycockite. In describing our results, we expressed the starting compositions of the samples synthesized in the Cu-Fe-S system and the compositions of the synthetic Cu-Fe-S sulfides in the form of the Cu/Fe ratio (in at.%) because all sulfides in the central part of the Cu-Fe-S system have variable Cu and Fe concentrations (Kravchenko *et al.*, 2012).

Results and discussion

Tables and figures below summarize the results of our experiments on the synthesis of Pt-Pd and Pt-Pd-Sn phases in the phase associations in the central part of the Cu-Fe-S system when

either Pt or Pd (alternatively) or both elements were added to the system are printed in the tables in ordinary type. The Cu/Fe ratios of the starting compositions of the synthesized samples presented of this research and their Pt-Pd phases are printed in bold type. Samples whose Cu-Fe-S are labeled with the subscript index 1 (for example, 0.43₁, 0.54₁ etc.) were cooled within the temperature range of 1200–850°C at a higher rate than samples labeled with the subscript index 2 (0.43₂, 0.54₂, etc.). The sulfides synthesized in the Cu-Fe-S system do not contain Pt, Pd, and Sn admixtures. Their compositions and phase relations are consistent with experimental data (Kravchenko, 2011; Kravchenko *et al.*, 2012; Fig. 1). The figure shows the stoichiometric compositions of chalcopyrite CuFeS_2 , isocubanite CuFe_2S_3 , mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ and haycockite $\text{Cu}_4\text{Fe}_5\text{S}_8$. The ranges of the Cu/Fe ratio for these phases are specified in the note to Table 1. Solid circles in the figure correspond to the starting compositions of samples with Pt-Pd sulfides, and open circles show the compositions of the Pt-Pd-Fe alloys (Kravchenko, 2013). As can be seen in the figure and Table 1, the crystallization fields Pt-Pd sulfides are 50 at. % S, Cu/Fe = 1.22–0.43 and 45 at. % S, Cu/Fe = 1.44, the crystallization

Table 1. Phase composition of synthesized crystallization products of Cu-Fe-S melts with Pt, Pd, and Sn admixtures

S	Starting composition, at.%, Cu/Fe			Synthesized phases		
	Cu	Fe	Cu/Fe	Cu-Fe-S, Cu/Fe*	Pt, Pd Pt(Pd)+Sn	Pt + Pd Pt+Pd+Sn
50	27.5–25	22.5–25	1.22–1	cp + bn + py	Cu(Pt,Fe) ₂ S ₄ , PdS Pt₃Sn	Cu(Pt,Fe) ₂ S ₄ , (Pt,Pd)S (Pt,Pd)₃Sn+PdS
	25–17.5	25–32.5	1–0.54	cp + cb, 0.61–0.52*	PtS, PdS Pt₃Sn	(Pt,Pd)S (Pt,Pd)₃Sn+PdS
	15	35	0.43 ₁	cb + cp 0.52–0.48*		
	15	35	0.43 ₂	mh(hc) + bn	PtS или Pt ₃ Fe, (Pd,Cu) ₁₆ S ₇ Pt₃Sn, Pd₃Sn	(Pt,Pd) ₃ Fe, (Pt,Pd) ₁₆ S ₇ (Pt,Pd)₃Sn+PdS
15	35	0.43 ₂	cb + po, 0.49–0.43* mh(hc) + bn			
45	32.5–30	22.5–25	1.44–1.20	mh(hc) + bn		
50	10	40	0.25–0.43	cb + po	Pt ₃ Fe, Pd ₃ Fe	(Pt,Pd) ₃ Fe
				0.43	Pt ₃ Sn, Pd ₃ Sn	(Pt,Pd) ₃ Sn
45	30–25	25–30	1.20–0.69	hc + bn	Pt ₃ Fe, PtFe	(Pt,Pd) ₃ Fe,
				hc + bn + po	Pd(Cu,Fe)	Pd(Cu,Fe),
				bn + po	Pt ₃ Sn, PtSn, Pt(Sn,Fe)	(Pt,Pd) ₃ (Cu,Fe) (Pt,Pd) ₃ (Sn,Fe) (Pt,Pd,Cu) ₃ (Sn,Fe)

Note: * – Cu/Fe of isocubanite, cp – chalcopyrite CuFeS₂ (Cu/Fe = 0.99–0.67), bn – bornite Cu₃FeS₄, py – pyrite FeS₂, cb – isocubanite CuFe₂S₃ (Cu/Fe = 0.61–0.43), mh – mooihoekite Cu₉Fe₉S₁₆ (Cu/Fe = 1.04–0.93), hc – cubic (pc) haycockite Cu₄Fe₅S₈ (Cu/Fe = 0.92–0.68), and po – pyrrhotite Fe_{1-x}S.

field of the Pt-Pd-Fe alloys is 50 at.% S, Cu/Fe = 0.43–0.25 and 45 at.% S, Cu/Fe = 1.20–0.69, and they are separated by the equilibrium line bornite Cu₃FeS₄ (bn) – mooihoekite Cu₉Fe₉S₁₆ (mh) – isocubanite CuFe₂S₃ (cb). The region of phase associations with isocubanite and pyrrhotite Fe_{1-x}S: cb + po, 50 at.% S, Cu/Fe = 0.49–0.43, and mooihoekite (or haycockite) and bornite Cu₃FeS₄: mh(hc) + bn, 45 at.% S, Cu/Fe = 1.44–1.20, occur between the crystallization fields of Pt-Pd sulfides and Pt-Pd-Fe alloys. In this transitional field, PtS or Pt₃Fe were synthesized together with Pd sulfides (Pd,Cu)₁₆S₇ and (Pt,Pd)₃Fe was synthesized if the melt contained both Pt and Pd. As can be seen in Table 1, the Pt₃Sn, Pd₃Sn, and (Pt, Pd)₃Sn alloys were synthesized in both the crystallization fields of Pt-Pd sulfides and the aforementioned transitional field. PdS was synthesized, together with (Pt,Pd)₃Sn, in samples containing both Pt and Pd. The compositions of the Pt₃Sn and Pd₃Sn are closely similar to the compositions of the phases synthesized previously in the crystallization field of Pt-Pd-Fe-Cu alloys, and the compositions of (Pt,Pd)₃Sn in association with PdS have lower Pd concentrations. Similar to the crystallization field of Pt-Pd-Fe alloys, the compositions of all of the synthesized Pt-Pd-Fe alloys did not vary when the samples were held at 600 and 400°C in the course of their cooling.

Table 2 presents the compositions of some samples with (Pt,Pd)₃Sn in association with PdS and samples with Pt-Pd sulfides with

Cu/Fe (0.54, 0.43, and 1.44) that were used as starting materials for the synthesis. As in Table 1, the Cu/Fe ratio of the starting samples synthesized in the course of this research and the Pt-Pd phases in them are printed in Table 2 in bold type. It can be seen in Table 2 that (Pt,Pd)₃Sn was synthesized in all Sn-bearing samples and has similar Pt and Pd ratios (Pt: 56.37–65.49 at.%, Pd: 13.48–6.36 at.%). Lower Pd concentrations (6.36 at.%) were detected in (Pt,Pd)₃Sn of sample 2 (Cu/Fe 0.54₁), which was cooled at a higher rate from 1200 to 850°C, than sample 3 (Cu/Fe 0.54₂) and other Sn-bearing samples. Samples 3 (Cu/Fe 0.54₂), sample 6 (Cu/Fe 0.43₂) and sample 8 (Cu/Fe 1.44₁), which were cooled at similar rate from 1200 to 850°C, contain (Pt,Pd)₃Sn with Pd concentrations of 9.35–13.48 at.%. This means that the Pt and Pd concentrations in (Pt,Pd)₃Sn are independent of the starting Cu-Fe-S composition of the samples. As follows from Table 2, in samples of the same starting composition, 50 at.% S, Cu/Fe = 0.43, (Cu/Fe = 0.52–0.48*; Table 1), associations of Cu-Fe sulfides of different composition were synthesized: these were isocubanite + chalcopyrite in sample 5 (Cu/Fe = 0.43₁) and mooihoekite + bornite in sample 6 (Cu/Fe = 0.43₂). Similar compositions of (Pt,Pd)₃Sn in these samples testify that the compositions of the synthesized Pt-Pd-Fe phases do not vary when the composition of the associations of Cu-Fe sulfides change during cooling.

Table 2. Chemical composition of synthesized crystallization products of Cu-Fe-S melts with Pt, Pd, and Sn admixtures

Sample	Cu/Fe, at.%, Cu-Fe-S association, admixtures, wt.%	Pt-Pd phases	Composition of Pt-Pd phases, at.%/wt.%						Σ , wt.%
			Cu	Fe	Pt	Pd	S	Sn	
1	0.54, cb + cp, Pt + Pd, $\Sigma = 1$	(Pt,Pd)S	1.93	3.06	44.11	6.50	44.40	0.00	99.60
			1.11	1.54	77.62	6.22	12.84	0.00	
		PdS	0.42	0.68	0.06	49.62	49.21	0.00	99.33
			0.38	0.54	0.18	75.84	22.66	0.00	
2	0.54 ₁ , cb + cp, (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	(Pt,Pd) ₃ Sn	3.25	0.56	65.49	6.36	0.24	24.10	100.87
			1.26	0.19	77.83	4.12	0.04	17.43	
		PdS	1.96	0.34	0.00	48.42	49.28	0.00	99.92
			1.80	0.28	0.00	74.88	22.96	0.00	
3	0.54 ₂ , cb + cp, Pt,Pd/Sn > 3/1, $\Sigma > 1$	(Pt,Pd) ₃ Sn	3.06	2.13	56.37	13.48	1.45	23.51	99.93
			1.25	0.76	70.53	9.20	0.30	17.90	
		PdS	2.33	0.05	0.00	49.98	47.64	0.00	99.79
			2.11	0.04	0.00	75.85	21.79	0.00	
4	0.43, cb + po, Pt + Pd, $\Sigma = 1$	(Pt,Pd)S	1.22	1.92	45.88	5.33	45.65	0.00	99.75
			0.70	0.96	79.94	5.07	13.08	0.00	
		PdS	0.29	0.52	0.04	50.32	48.83	0.00	99.73
			0.26	0.42	0.11	76.56	22.38	0.00	
5	0.43 ₁ , cb + po, Pt,Pd/Sn > 3/1, $\Sigma > 1$	(Pt,Pd) ₃ Sn	3.71	1.55	62.12	10.23	0.03	22.36	99.65
			1.46	0.53	74.60	6.71	0.01	16.34	
		PdS	3.57	0.50	0.00	47.28	48.65	0.00	100.68
			3.36	0.41	0.00	73.99	22.92	0.00	
6	0.43 ₂ , mh + bn, (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	(Pt,Pd) ₃ Sn	3.82	1.64	62.68	9.35	0.17	22.34	99.73
			1.50	0.56	75.20	6.13	0.04	16.30	
		PdS	2.42	0.12	0.00	49.58	47.88	0.00	100.52
			2.21	0.14	0.00	76.08	22.14	0.00	
7	1.44, mh + bn, Pt + Pd, $\Sigma = 1$	PtS	8.30	0.98	45.45	2.84	42.43	0.00	99.23
			4.71	0.49	79.18	2.70	12.15	0.00	
		(Pd,Cu) ₁₆ S ₇	17.02	0.97	0.00	52.67	29.34	0.00	99.91
			14.07	0.70	0.00	72.90	12.24	0.00	
8	1.44 ₁ , mh + bn (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	(Pt,Pd) ₃ Sn	4.43	3.16	57.52	12.46	0.81	21.62	99.28
			1.80	1.13	71.75	8.43	0.16	16.36	
		PdS	2.14	0.27	0.00	48.26	49.33	0.00	100.48
			1.99	0.22	0.00	75.14	23.13	0.00	

Note: cb – isocubanite, CuFe₂S₃, cp – chalcopyrite CuFeS₂, po – pyrrhotite Fe_{1-x}S, mh – mooihoeite Cu₉Fe₉S₁₆, hc – cubic (pc) haycockite Cu₄Fe₂S₉, bn – bornite Cu₅FeS₄.

Our results indicate that the simultaneous crystallization of Pt, Pd, and Sn, all Pt and partly Pd generates (Pt,Pd)₃Sn, and the remaining Pd crystallizes as sulfide PdS. The Pt and Pd concentrations in (Pt,Pd)₃Sn are independent of the starting Cu, Fe, and S concentrations of the samples and do not vary either when the composition of the association of Cu-Fe sulfides is varied at the crystallization temperatures of the Cu-Fe-S melts (1070–854°C) (Kravchenko, 2011) or when they are held at temperatures of 600 and 400°C in the course of cooling. This indicates that the synthesized Pt-Pd-Sn phases crystallized earlier than the Cu-Fe sulfides did.

All of the synthesized Pt-Pd-Sn alloys and all Pt-Pd phases synthesized in melts of this composition but containing no Sn (Table 1) have the same morphological features and show the same phase relations in the crystallization products of Cu-Fe-S melts as those of

corresponding natural minerals in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits.

Conclusion

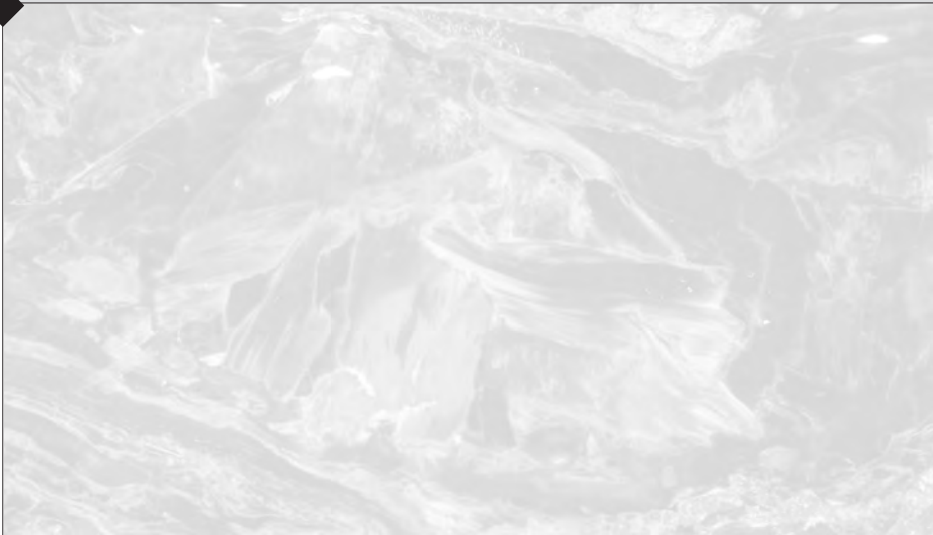
Pt-Pd-Sn alloys analogous to rustenburgite Pt₃Sn, atokite Pd₃Sn, and Pd-rustenburgite (Pt,Pd)₃Sn were synthesized in phase associations with chalcopyrite, isocubanite, and mooihoeite corresponding to the stability field of Pt-Pd sulfides that are analogues of naturally occurring minerals: malanite Cu(Pt,Fe)₂S₄, cooperite PtS, vysotskite PdS, braggite (Pt,Pd)S and an unnamed compound of the composition (Pd,Cu)₁₆S₇. Our results and the results of synthesis in the crystallization field of Pt-Pd-Fe-Cu alloys that are analogues of isoferroplatinum Pt₃Fe, Pd analogue of isoferroplatinum Pd₃Fe, tetraferroplatinum PtFe, and the unnamed compound Pd(Cu,Fe) testify to the dominant crystallization of Pt-Pd-Sn alloys when

the melts crystallize in the central part of the Cu-Fe-S system with 50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69 and with Pt, Pd, and Sn admixtures. Similarities in the composition, morphological features, and phase relations of the Pt-Pd-Sn alloys in the crystallization products of the Cu-Fe-S melts and the corresponding natural minerals in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits testify that these compounds and natural minerals were formed under similar conditions.

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Mineralogical Museums and Collections



EXHIBITION OF BAUXITES AT THE FERSMAN MINERALOGICAL MUSEUM, RUSSIAN ACADEMY OF SCIENCES

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The Fersman Mineralogical Museum exhibits a genetic collection of bauxites, which is the first exhibition of the type ever on display at such museums. According to their genesis, bauxites are classified into two major types: residual and sedimentary. The former are produced by in-situ weathering of aluminosilicate rocks and compose a portion of the laterite weathering crust that is preserved where it has been generated. The exhibition displays composite profiles of laterite weathering crusts on granites, gabbro, gabbro-amphibolites, and phyllites, with the uppermost zones of the profiles made up of bauxite. Sedimentary bauxite is formed when a laterite weathering crust suffers destruction, and its clastic material is then redeposited. Depending on the environment in which this material is redeposited, sedimentary bauxite is further classified into lagoonal, lacustrine, paludal, riverine, slope, and karst types. Almost all of these are on display at the exhibition, which demonstrates the diversity of bauxite textures. Some of them provide unambiguous evidence of the bauxite type.

9 figures, 6 references.

Keywords: bauxite, laterite, weathering crust.

Bauxite is produced by a diversity of complicated processes at the Earth's surface. These processes are very closely related to weathering (physical, chemical, and biochemical) of aluminosilicate bedrocks. The destruction of the latter and their deep transformation under certain circumstances gives rise to bauxite, which is a rock consisting mostly of such hardly soluble Fe and Al compounds as Al and/or Fe hydroxides and/or oxides: gibbsite – $\text{Al}(\text{OH})_3$, boehmite – $\gamma\text{AlO}(\text{OH})$, diaspore – $\alpha\text{AlO}(\text{OH})$, hematite – $\alpha\text{Fe}_2\text{O}_3$, maghemite – $\gamma\text{Fe}_2\text{O}_3$, goethite – $\alpha\text{FeO}(\text{OH})$ and hydrogoethite – $\alpha\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$. Bauxite sometimes additionally contains Ti oxides (anatase and rutile), kaolinite, Fe-rich chlorites, quartz, and some other minerals. The quantitative proportions of major minerals of bauxite broadly vary, up to the development of almost monomineralic bauxite varieties: gibbsite, boehmite, and diaspore bauxite.

Because bauxite is a fine-grained rock, its minerals are usually unidentifiable and indiscernible with the naked eye. Even in bauxite domains enriched in certain Al hydroxide (these rocks contain up to 70–80% aluminum hydroxide) (Fig. 1), it is very hard to identify these minerals. Visually indiscernible Al hydroxides reveal crystalline structures and specific morphologies of mineral crystals at high magnifications under a scanning electron microscope (Fig. 2).

If the content of Al_2O_3 (alumina) in a rock is not lower than 28% and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio is higher than 2.6, the bauxite can be utilized as an

Al ore, and if bauxite is dominated by Fe, it can be viewed as a Fe ore.

The exhibition of bauxites is housed in a showcase consisting of two parts. The genetic collection of bauxites is displayed in the horizontal part. The genetic types are presented in compliance with the systematics developed at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, by a research team headed by Dr. D.G. Sapozhnikov (Sapozhnikov *et al.*, 1974). The specimens are arranged corresponding to their affiliation with certain genetic types (Fig. 3). The vertical part of the showcase exhibits the most illustrative and representative bauxite specimens, and these specimens are not arranged according to their types.

In terms of their genesis, bauxites are classified into residual (lateritic) and sedimentary.

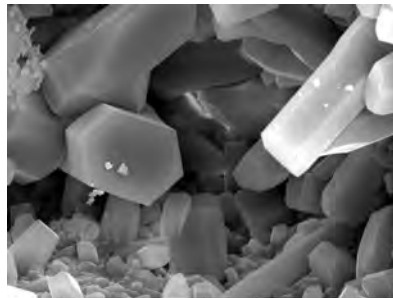
Residual (lateritic) bauxites are eluvial lateritic rocks that are formed *in situ* in bedrocks of various composition because of the accumulation of difficulty soluble products of their decomposition. Bauxites of this type are formed in a warm and humid climate. Alternating dry and rainy seasons is optimal to form bauxite. An important factor is thereby the topography of the terrain, with residual bauxite most commonly produced on plateaus raising not very high above nearby lowlands. The core meaning of the chemistry of the processes of laterite weathering is decomposition of silicates and aluminosilicates of the bedrock,



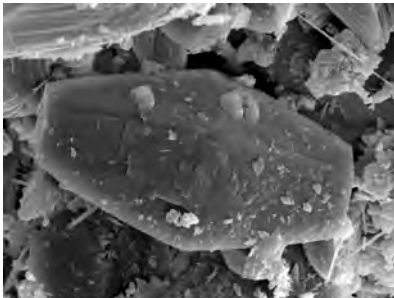
Fig. 1. Aggregates of porcelainous gibbsite in hematite and residual bauxite (developing after basalt), central India, 14.5 x 9.5 cm. FMM # 92368. Photo: M.B. Leybov.



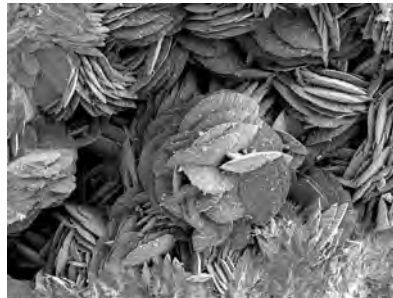
SEM HV: 20.00 kV WD: 13.95 mm VEGAII TESCAN
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SEM HV: 30.00 kV WD: 18.54 mm VEGAII TESCAN
Vac: HiVac Det: SE Detector 20 µm
Name: J-413 5 42 Date:(m/d/y): 12/24/13 Paleontology Institute RAS



SEM HV: 30.00 kV WD: 15.02 mm VEGAII TESCAN
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Name: K 292 1 3 Date:(m/d/y): 06/03/14 Paleontology Institute RAS



SEM HV: 20.00 kV WD: 19.18 mm VEGAII TESCAN
Vac: HiVac Det: SE Detector 500 µm
Name: K-7-3 21 Date:(m/d/y): 04/15/14 Paleontology Institute RAS

Fig. 2. SEM images of bauxite minerals: (a) Diaspore, Jammu and Kashmir, India; (b) gibbsite, Poços de Caldas, Brazil; (c, d) bohmite, Vislovskoe deposit, Kursk Magnetic Anomaly (KMA) area, Russia.

gradual leaching of silica and alkali-earth elements, and hydrolysis of aluminum and iron oxides, which enrich the rock.

Deposits of residual bauxites can be produced in stages or continuously. In the former instance, bauxite is formed by moderately fast tropical weathering that gradually destructs and decomposes the bedrock to form a zoned weathering crust (laterite profile), in which the decomposition intensity of the bedrock varies over the

vertical section, and the zones of the profile differ in composition. For example, such a type of weathering of feldspar, one of the dominant rock-forming minerals, proceeds as follows: feldspar → hydromica → kaolinite → gibbsite. The general trend of the process largely controls the mineralogy of the zones and the general course of transformation of the pristine bedrock into bauxite. This trend is always discernible, but the compositions of zones and their numbers in



Fig. 3. Horizontal part of the showcase. Photo: M.B. Leybov.



Fig. 4. Various crusts of weathering.

Left: gabbro-amphibolite, Novo-Burakovskoe deposit, Kazakhstan; from bottom to top: banded gabbro-amphibolite, kaolinized gabbro-amphibolite, banded gibbsite-goethite bauxite.

Right: phyllite schist, Vislovskoe deposit, KMA, Russia; from bottom to top: banded phyllite schist, kaolinized banded schist, banded hematite-boehmite bauxite, chamosite bauxite. Photo: M.B. Leybov.

individual profiles replacing various rocks may somewhat differ.

The profiles can be either complete or incomplete. The exhibition presents composite profiles, which are prepared of specimens of naturally occurring rocks, that develop after basalt, granite, gabbro-amphibolite, and phyllite schist (Fig. 4). The profiles are generally similar and reflect the aforementioned sequence of transformations of the pristine bedrock into bauxite. The only exception is the somewhat different profile on phyllite schist at the Vislovskoe deposit, which is the only one whose uppermost horizons include a zone of chamosite bauxite. This deposit deserves closer consideration because it is economic. The deposit affiliates with the Voronezh bauxite-bearing province in the iron-ore basin of the Kursk Magnetic Anomaly (KMA) and is spatially constrained to an ancient weathering crust. The bauxite deposits occur in close spatial and genetic relations with high-grade iron ores, alternate with them, and/or sometimes surround their orebodies. The very fine-grained fabrics of the schists were favorable for their replacement with bauxite because made it easier to dissolve quartz and leach silica from the weathering crust before the replacement of the rocks by kaolinite. The bauxite thus absolutely free of quartz. Because of the high alumina content of the schists, the hematite-boehmite bauxite produced by their weathering is also high in alumina and has a high quality. This crust displays iron behavior that is anomalous in the classic laterite profile. Iron ions are contained in the bauxite both trivalent and bivalent modes, the latter in chamosite $(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_3\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$, siderite, and pyrite. Such iron reduction can proceed in an reducing environment, which is ensured in this situation by bogging-up of the weathered profile during its late evolution (Nikitina, 1968).

The exhibition displays one more specimen (from the Kutch Peninsula, India) (Fig. 5) for which a change in the environment (land subsidence below the sea level and subsequent uplift) and related changes in the redox conditions resulted in berthierine ($\text{Fe}_4^{2+}\text{Fe}_2^{3+}(\text{Al}_2\text{Si}_2\text{O}_{10})(\text{OH})_8$) bauxite in submarine environments and redeposition of Fe oxides and hydroxides on land.

Capillary water ascent through the weathering crust during the dry season is associated with the ascent of elements dissolved in this water, including Fe^{2+} , which is oxidized and precipitates on the surface in the form of goethite and hematite. As a consequence, bauxite in the upper portion of the profile is enriched in iron compounds and forms compact rust-brown rocks of pisolitic texture. This rock is referred to as cuirasse (the word means armor in French). The aforementioned profiles do not contain this zone, but one specimen of cuirasse is on display.

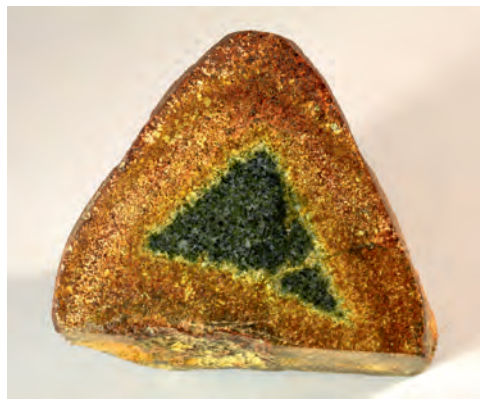
Bauxite deposits that are formed continuously occur in incomplete weathering crusts. In these instances, the bauxite layer rests immediately on fresh unaltered bedrock. An example of such a single-zone weathered profiles is relatively thin goethite-gibbsite crusts (referred to as pain d'épice in the French geological literature) that develop on fresh rocks (nepheline syenite and dolerite in Guinea, diabase in British Guiana, diabase in Cuba, etc.). Such crusts usually occur locally and make up merely a small percentage of the material of the bauxite profile. The exhibition displays a specimen of such a crust from Cuba, where it was produced via gabbro weathering (Fig. 6). Bauxite of this type can be formed only by very fast and intense weathering, when feldspar is immediately replaced by gibbsite without any intermediate products.

Sedimentary bauxites are formed by surface water that destructs and decomposes laterite weathering crusts and then redeposits their clastic material in topographic lows, often in water bodies of various type. These bauxites can be of the littoral-lagoonal type, which usually occur as layers resting on the eroded surface of reef limestone, and continental type, which comprises a large group of genetic varieties. Depending on the environment in which the terrigenous material of continental bauxites is deposited, these are classified into diluvial (accumulated on slopes), valley, riverine, lacustrine-palidal, and karst. Relations between bauxite deposits and certain landforms are schematically portrayed in Fig. 7.

The exhibition displays practically all types of sedimentary bauxites (Fig. 3), among which karst bauxite seems to be of particular interest. Bauxite of this type is formed when karst cavities and caves are filled with clayey and bauxite material. The karst cavities can be of various shape (sinkholes, karst funnels, valleys, etc.) and not only function as natural depressions able to accumulate clastic material but may also affect the latter and sometimes control its in-situ replacement by bauxite. These facts led some researchers to view these deposits as laterite-karst and distinguish them in the group of sedimentary bauxite deposits as an individual group of karst deposits. Bauxite deposits on Jamaica are interpreted by some geologists as formed on volcanic material redeposited in karst depressions and replaced there by bauxite. Also, bauxite deposits in the Northern Ural Bauxite District are also sometimes thought (Gutkin, 1978) to have been produced by redeposition of both bauxite material and the aluminosilicate material of volcanic-sedimentary rocks in karst funnels,

Fig. 5. Residual pisolitic bauxite whose composition has been twice modified in response to variations in the sea level, Kach Peninsula, India. 14 x 10 cm. FMM #VF264. Photo: M.B. Leybov.

Fig. 6. Crust of residual bauxite on fresh gabbro. Quesigua, Cuba. 9 x 7 cm. FMM #VF266. Photo: M.B. Leybov.



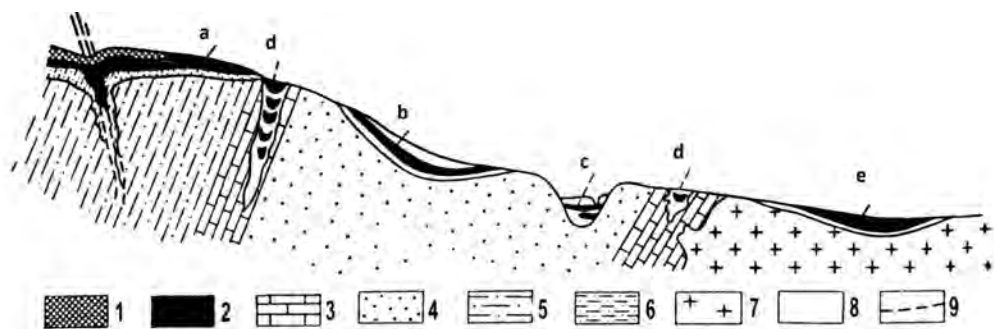


Fig. 7. Setting of bauxite deposits in relation to various landforms.

1 – duricrust; 2 – bauxites (a – residual, b – diluvial-slope, c – alluvial-fluvial and others, d – karst, e – lacustrine-paludal); 3 – limestone; 4 – sandstone; 5 – schist; 6 – weathering crust on schist; 7 – granite; 8 – (b, c, d, e) host rocks of sedimentary bauxite; 9 – faults.

with the latter type of material replaced with bauxite when in the funnels.

The principal source of alumina for sedimentary bauxites was definitely terrigenous material: residual bauxites and rocks of laterite weathering crusts. However, aluminum could also be partly transported as soluble compounds with naturally occurring organic acids, first and foremost when bauxites were formed in aquatic environments. When decomposed, these compounds precipitated aluminum in the form of hydroxides, which are then accommodated in sedimentary bauxite as its fine-grained (pelitic) constituent.

A bauxite sphere approximately 30 cm in diameter is on display on the stand near the showcase housing the exhibition (Fig. 8). This bauxite specimen was found in the Moscow area. The genesis of bauxite spatially related to a coal-bearing unit in the area is disputable, but all researchers admit that this bauxite is of chemogenic nature. According to this viewpoint, the bauxite was formed via alumina deposition from aqueous sulfate solutions, which have been generated by oxidation of pyrite, which abounds in the coal-bearing unit (Zakharova, 1974).

Contrary to what is usually thought, the bauxite collection displayed at the exhibition demonstrates that not all bauxites are alike. Although naturally occurring bauxites are dominated by brownish red types, more rare varieties (which are also exhibited) may be whitish, grayish green, gray, and even black. The fabrics of bauxites are also extremely diverse. Residual bauxites typically show relict textures and structures inherited from the bedrocks, for example, their banding (Fig. 4). Pisolite and pisolitic-clastic structures are typical of diluvial (Fig. 9a) and karst bauxites. The latter may be not only rudaceous up to breccia-like (Fig. 9b) but also massive fine-grained and resemble jasper (Fig. 9c).

When deposited in aquatic environments, bauxite material forms laminated silty and pelitic varieties of lacustrine and lagoonal genesis (Fig. 9d). Some of them may contain floral and faunal remnants replaced by bauxite material. Such specimens are also displayed at the exhibition. Pisolitic textures are known to occur in both sedimentary (including karst) (Fig. 9e) and lateritic bauxites. The original color and fabric of bauxite, as well as its mineralogy, may be modified during various episodes of bauxite lithogenesis and metamorphism after the bauxite was buried beneath sediments.

Deposits of lateritic (sedimentary) bauxite are typical of countries with a tropical climate (Guinea, Brazil, Venezuela, and India). Bauxite deposits of this type were found in Russia in the Voronezh bauxite province and in the Central Timan. Some deposits of the Chadobetsk group in the Krasnoyarsk territory also belong to this type (Slukin, 1973). For Russia, the most important bauxite deposits are of sedimentary genesis (of various types). In the broadly known Ural province, the largest deposits are concentrated in the North Ural Group (NUG) and South Ural Group. Numerous deposits are also constrained to the northern part of the Russian Platform and are combined into the North Onega, Tikhvin, and South Timan groups (Ore deposits of the USSR, 1974). Promising bauxite deposits were also discovered in the Krasnoyarsk territory (Chadobetskoe and Tatarskoe).

Bauxites are produced by complicated supergene processes that are controlled by a large number of diverse factors, so that no exhibition is able comprehensively enough to reflect the complicatedness of bauxite genesis. The exhibition at the Fersman Museum is the first in museum practice to represent a genetic collection of bauxites and display the diversity of their genetic types and their distinguishing features.



Fig. 8. Gibbsite pisolitic bauxite, Myachkovo, Moscow territory, Russia, 30 x 25 cm. FMM #88779. Photo: M.B. Leybov.

Fig. 9. Bauxite textures.

a – Clastic texture of diluvial-slope bauxite with clasts of residual bauxite. Ishkininskoe deposit, Orenburg region, Russia. 12.5 x 8 cm. FMM #VF250.

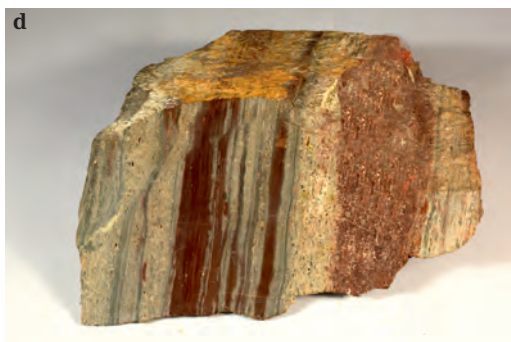
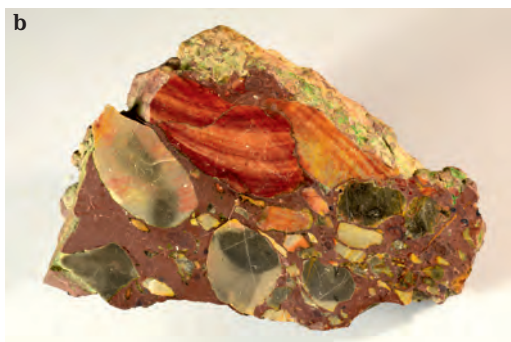
b – Brecciated texture of karst bauxite with bauxite cement of the breccia, Northern Urals bauxite region, Russia. 10 x 6.5 cm. FMM #VF271.

c – Jaspidean karst bauxite, Northern Ural bauxite region, Russia. 9.5 x 5.5 cm. FMM #VF270.

d – Laminated pelitic texture of lagoonal bauxite, Cheremukhovskoe deposit, Urals, Russia. 11.5 x 11.5 cm. FMM #VF268.

e – Pisolitic texture of sedimentary bauxite, Central deposit, Krasnoyarsk district, Russia. 15 x 10 cm. FMM #M32133.

f – Pisolitic texture of residual bauxite, Madhya Pradesh, India. 11 x 9.5 cm. FMM #VF265. Photo: M.B. Leybov.



The exhibition was made possible thanks to help of scientists studying bauxites at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, A.D. Slukin, V.M. Novikov, B.A. Bogatyrev, and Yu.Yu. Bugelsky, who provided bauxite specimens for the genetic part of the exhibition. The staff of the museum thanks these researchers for furnishing bauxite specimens for the exhibition and for valuable consultations and constructive criticism in the course of installing this exhibition.

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NEW EXHIBITIONS IN THE ORE-PETROGRAPHY MUSEUM

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The article is dedicated to new expositions of the Ore-Petrography Museum, which has systematic collection of all known types of magmatic rocks and ores. Nevertheless the museum was planned to support the institute's researchers, there are collections created for educational purposes revealing geological processes and history of geological studies of Russia.

14 figures, 3 references.

Keywords: Ore-Petrography Museum, exposition, collection, ore, mineral deposit.

Ore-Petrography Museum of the Institute of Geology of Ore deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences is the only specialized museum in Russia that is a home for a systematic collection of every magmatic rock type on the Earth. The museum has regional collections representing rocks and main ore types of most ore districts in Russia and elsewhere. It also keeps thematic collections illustrating certain features of magmatism and ore-forming processes of various geological stages and geodynamical environments that had place during the Earth evolution.

The history of the Ore-Petrography Museum started in 1930 with establishing several specialized institutions based on the Geological and Mineralogical Museum in Leningrad (currently Fersman Mineralogical Museum of the RAS in Moscow), the only academic geological organization at that time. Two specialized institutes: Mineralogy, Geochemistry and Petrography Institute (PETRIN) and Geology Institute (GIN) were formed. F.Yu Levinson-Lessing directed the Petrography Institute. He created the Petrography Museum at the Institute as a tool for scientific work as a research library of stone. The current collection was comprised mainly from gathering of the employees of several institutes, which the Petrography Museum was the part of. The Petrography Museum was located at Staromonetny Pereulok No 35 (Fig. 1) when the Academy of Sciences moved to Moscow from Leningrad in 1934.

The institutes of Mineralogy and Geochemistry merged into the Lomonosov Institute of Geochemistry, Mineralogy and Crystallography (LIGEM) in 1932 and were

lead by academician A.E. Fersman. Those institutes: LIGEM, PETRIN and GIN were united under the Institute of Geological Sciences (IGN) in the years 1937 through 1955 and then the scientific departments of this entity formed the core of the current Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM). Academician F.V. Chukhrov managed IGEM from 1956 till 1988.

The changes of the names and structures of institutes whose part the Petrography Museum was did not change the status and direction of the museum's research, because it involved a wide circle of problems, including fundamental theories of the genesis rocks and ores. Integrated expeditions were the main form of geological research at that time. The following regional integrated expeditions were formed: Tajik-Pamir, Kola, Kazakh, Urals, Caucasus, Eastern Siberian and other expeditions which worked for many years.

These expeditions discovered numerous ore-magmatic provinces and regions, metallic and non-metallic mineral deposits. The collections of the museum were flooded with a huge amount of samples of rocks and ores, so the subject of the collection went far beyond purely petrographic studies. For this reason it was renamed into Ore-Petrography Museum in 1993.

The museum comprises more than 40,000 storage units, including collections of thin and polished sections. The main types of ores and rocks, rare and unique samples are exhibited in 28 expositions including seven recent theme exhibitions devoted to various rock types and to researchers who studied them (Fig. 2). A combination of historical objects, rock and ore



Fig. 1. Building of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), in whose compass window Ore-Petrographic Museum is situated.
Photo: M.K. Sukhanov.



Fig. 2. Scenery of exhibits.
Photo: M.K. Sukhanov.

samples and minerals made the displays more vivid and informative.

Exposition: *Scientists of the Institute on the labor frontline during the Great Patriotic War*

The exposition has a center location in the museum. It catches the visitor's attention immediately and excursions around the museum start there. It creates a good reason to speak on the history of the Institute, achievements of its staff, all the more so many of them started to work during the War and later became prominent scientists. The exposition illustrate the work of D.S. Belyan-kin, V.P. Petrov, A.I. Tsvetkov, M.A. Favor-skaya, B.V. Zaleskiy, M.F. Strelkin, I.I. Gin-sburg, I.A. Preobrazhenskiy, D.I. Scherba-

kov, V.F. Morkovkina, P.I. Lebedev, O.D. Levitskiy, Ye.A. Radkevitch, S.S. Smirnov, D.S. Korzhinskiy, A.V. Pek, T.N. Shaldun, V.I. Gonshakova, V.S. Koptev-Dvornikov and others. Their photographs and most importantly the samples of ores from the deposits they studied: refractory ceramic clays in the Urals, tin, tungsten and lithium deposits in Kazakhstan, base metal and mercury deposits of Kabardino-Balkaria, Northern Ossetia and Georgia, tin deposits of the Russian Far East and many others were part of the exhibits.

Exposition: *World of Minerals*

This exposition is dedicated to the anniversary of Fedor Vasilyevich Chukhrov, who headed IGEM from 1955 till 1986. His studies



Fig. 3. Rhodochrosite $(Mn,Fe)CO_3$, Kara-Oba, Central Kazakhstan. 10 x 18 cm. OPM-IGEM # 5501, from collection of F.V. Chukhrov. Photo: M.K. Sukhanov.



Fig. 4. Crystal of fersmanite $Ca_4(Na_2Ca_2)(TiNb_3)(Si_2O_7)_2O_8F_3$ in pectolite veinlet cutting massive urtite. Khibiny massif, Kola Peninsula, Russia. Section of crystal, 1.5 x 1.5 cm. OPM-IGEM # 1341, from collection of M.N. Sokolova. Photo: M.K. Sukhanov.

of typomorphic properties of minerals, colloids in the Earth's crust, oxidation zones of sulfide deposits, weathering crusts and deposits related to them were widely recognized.

F.V. Chukhrov supervised composition of several volumes of Minerals reference book, which summarized all studies of mineral species and became a table-book for many scientists and practical geologists. Chukhrov's works significantly stimulated development of mineral resources in Kazakhstan. He was awarded an Order of Lenin and two Orders of the Red Banner of Labor, Order of the Badge of Honor, other medals and was granted the USSR State Award in 1951.

Samples which F.V. Chukhrov gathered himself are among the exhibits of the exposition: bauxite from Poços de Caldas, Brazil; Mazaugues, France; montmorillonite from Morro do Niquel; kaolin from Cornwall, England; rhodochrosite from Kazakhstan (Fig. 3). Various photos are on display with the photograph of the first graduates of the Moscow Geological Institute, later the Moscow Geological Exploration Institute (MGRI), with F.V. Chukhrov and other students who became later researchers at IGEM among them (Fig. 4). Some rare minerals are displayed: fersmanite $Ca_4(Na_2Ca_2)(TiNb_3)(Si_2O_7)_2O_8F_3$ (Fig. 5) and chukhrovite $Ca_3Al_2TR(SO_4)F_{13} \cdot 10H_2O$, which was discovered by L.P. Yermilova, a researcher at IGEM in 1960 and named after F.V. Chukhrov.

Exposition: *Non-metallic Minerals*

We celebrated the 100th years of the birth of Valeriy Petrovich Petrov (Fig. 6) in 2008.

He headed the department of Non-metallic Natural Resources at IGEM. An international conference was convened in his memory at the Institute, and a new exposition was on display to describe his life.

V.P. Petrov was the true expert in the geology of the Caucasus and Trans-Caucasus, having explored remote areas of the region on foot and on horseback. He organized the provision of a resource base for refractory ceramic industry in the Urals during the Great Patriotic War and initiated the development of the perlite industry after the War. V.P. Petrov with his colleagues and students took part in utilizing iron-free granites, alkaline kaolinites and porcelain stone, loose talc rocks in weathering crusts, brucite, wollastonite and fine mica as new materials for ceramics.

Valeriy Petrovich was awarded with three Orders of the Red Banner of Labor, the Order of the Badge of Honor, many medals, including international ones for his achievements.

The exposition shows perlite, obsidian, clays, asbestos, graphite, cut and gem stones (lazarite, nephrite, rhodonite, chrysolite, wollastonite-hedenbergite skarn) and ornamental stone (Fig. 7, 8), Petrov's bibliographical material, his photographs and scientific works are also displayed.

Exposition: *Rare-Metal Magmatism*

This exposition is devoted to magmatic rocks that host deposits and are sources of rare metals so important for the modern electronic industry. These metals include tan-



Fig. 5. First graduates of Moscow Geological Institute (present Russian State Geological Prospecting University) with their teacher professor V.I. Luchitsky, 1931.

1st row (sitting from left to right), F.V. Chukhrov, prof. V.I. Luchitsky, V.S. Myasnikov, and P.V. Kalinin;

2nd row (standing from left to right), V.P. Florensky, A.V. Sarycheva, A.V. Zak, A.M. Mamedov, N.V. Petrovskaya, A.M. Ershov. Photo from archive of N.N. Smol'yaninova.

Fig. 6. V.P. Petrov at field work (1960s). Photo from archive of V.V. Nasedkin.

talum, niobium, beryllium, lithium, rubidium, cesium, and rare earth elements. Deposits of these elements are related to certain types of granites, so-called rare-metal granites. Deeply differentiated multi-phase granite intrusive complexes usually carry such mineralization.

The latest magmatic derivative phases of the massifs are leucocratic granites of elevated alkalinity. Rare-metal lithium-fluorine granites were found in the Ladoga area, Trans-Baikalia, in Primorye, in Mongolia, the Czech Republic, France and other regions.

Vyacheslav Ivanovich Kovalenko made a big contribution to studies of these magmatic associations. He developed a theory of late magmatic rare-metal deposits, suggest-

ing quantitative assessment of rocks for potential mineralization and applied it to metallogenic analysis of the territory of Central Asia. He was one of the discoverers of rare-metal deposits in Mongolia. He was awarded with Russian Federation State Prize and many medals.

The exposition's display includes ore-bearing carbonatites, fluorite ores and samples of rare metal rocks, which were discovered, described and named by V.I. Kovalenko. One of them was ongonite (topazolite), the rocks that gave clues to understand rare metal magmatism and mineralization. Specimens of rare-metal pegmatites from Primorye from collection of M.G. Rub and her monograph "Rare-Metal Granites" are also on display.

Fig. 7. Landscape obsidian "View of the Ararat Valley". Armenia. Polished sample, 20 x 8 cm. OPM-IGEM #Gkh-16, collection of V.V. Nasedkin. Photo: M.K. Sukhanov.

Fig. 8. Wollastonite-hedenbergite skarn. Dalnegorsk, Primorsky Krai, Russia. Polished plate, 22 x 9 cm. OPM-IGEM #M1-2, collection of A.D. Babansky. Photo: M.K. Sukhanov.



Exposition: *East-African Rift*

East-African Rift is the largest of the rifts shown in the topography in the world. It stretches over 6,000 km from northern Syria to central Mozambique. The width of the rift valley is from 30 to 100 km and its depth ranges from a few hundred to thousand meters. The valley was formed as a result of geological shear faulting along the boundaries of the African and Arabian tectonic plates. It is pronounced as a huge graben with steep walls and a flat bottom partially covered with shallow lakes, swamps and salt marshes. Crystalline rock cliffs rise on the sides of the rift, and the highest in Africa volcanic structures rise on the adjacent plateaus: Kilimanjaro with Kibo peak at 5895 m and mount Kenya at 5199 m.

The Rift was formed by a meridially-trending fault system in the crust that was formed in the Mesozoic-Cenozoic and was accompanied by intense lava eruptions. Volcanic activity along the East-African rift was very intense and still continues.

The exhibition displays volcanic rocks of the region, including many alkaline rocks, labeled with local names: katungite (pyroxene free and rich in melilite olivine leucite), ugandite (melilite free melanocratic leucite basalt), limburgite (hyalo-nephelinitic basalt with plagioclase and nepheline glass as a groundmass) and also carbonatites and sodium carbonate.

The exposition was composed of specimens from the large (around 300 samples) collection of A.A. Krasnov, a former researcher at IGEM. He participated in the Soviet African Expedition with E.E. Milanovsky, N.A. Logachev, V.I. Gerasimovsky, A.P. Kapitsa and other prominent scientists.

Exposition: *Extraterrestrial Matter and Impactites*

This exposition was composed as reflecting a new avenue of research at the museum: meteorites and impact rocks. Indeed it is important to study space in the 21st century to understand the origin of our planet and its evolutionary history.

There were many people who came to the museum with a request to find out if the rock they found was a meteorite. These cases inspired the idea to form an open Russian Society of Meteoritics Enthusiasts with support from the Ore-Petrography Museum.

The main course of the society's activity was education and popularizing scientific knowledge. This public organization was registered with its equity capital as a collection of meteorites. The collection consists of 23 specimens of hondrites, iron meteorites and palassite, 10 specimens of impactites and 2 specimens of tectites. As per the agreement between the Museum and the Society the collection was kept at the museum and can be on display and studied for scientific purposes.

Meteoritic matter is represented in the collection of the museum also included new by found meteorites: Doronino found in 2003 and Pallasovsky discovered in 2004. The samples of these meteorites are kept only in two museums round the world: GEOKHI RAS and IGEM RAS (Fig. 9). The material of these meteorites was studied for the first time at IGEM (Milanovskiy *et al.*, 2003, 2005).

The history of Pallasovsky meteorite is very remarkable. P.S. Pallas, a prominent German nature scientist, was invited by Catherine the Great and worked in various areas of Russia for 20 years studying plants, fauna, geology and geography of Russia. Being in the Irkutsk region in 1771, he was informed about a boulder of iron and olivine weighing around 700 kg. He decided to transport it to St. Petersburg, and in 1777 it was delivered to the Mineral Cabinet of

Fig. 9. Fragment of Pallasovsky meteorite (pallasite), olivine crystals in nickel iron (kamacite + taenite). Sample section, 8 x 8 cm. OPM-IGEM, from collection of Russian Society of Meteoritics Enthusiasts. Photo: M.K. Sukhanov.



Kunstkamera. This boulder was named Pallas iron. Pallas himself regarded this boulder as a rare type of terrestrial iron ore. Ernst Chladni proved Pallas boulder to be of extraterrestrial origin only in 1794. It was of rare meteorite type that had only around 50 known discoveries and falls and thus called pallasite. Pallas worked in the Volga region in 1773 and made many important discoveries. A railway station was named after him and the monument was erected to his tribute later in 1904, when the railroad was built. Pallasovka became a town 200 years later and meteorite was found in its vicinity and it was surprisingly exactly of the pallasite type (Fig. 10).

The exposition shows a classification of meteorites in diagrams, photos, thin sections, monographs, and papers dedicated to lunar matter with particular emphasis on studies carried out at IGEM. The impact matter on display was derived from known impact craters: Ries, Zhamanshin and Popigay. The new specimens acquired recently were found at Glorietta Mountain in 1884 in the state of New Mexico, USA, and Tamdakht, Morocco, fell in 2008.

**Exposition: Magmatic Rocks
from Polar Siberia Collected by
E.V. Toll Expedition in 1885–1902**

The exhibition displays materials on the development of Russian Polar regions, which is especially important this time,

when the ownership of territories of the arctic shelf zones and Northern Pole is disputed in the context of the resources of these regions. The exposition shows the priority of Russian scientists in studying and exploring the Arctic.

Eduard Vasil'yevich Toll (1858 – 1902) was a Russian geologist and explorer of polar regions (Fig. 11). He took part in an expedition to the New Siberian Islands headed by A.A. Bunge, whose collection is also housed at the museum. He explored the islands of Big Lyakhovsky, Fad'yevsky, the western shore of New Siberia Island and Kotelniy Island. He headed an expedition to northern regions of Yakutia in 1893 and was the first to describe plateau between the Anabar and Popigay rivers, the mountain range between the Olenek and Anabar rivers and named it the V. Prochintsev Range. He led the expedition of the Academy of Sciences on the Zarya self-propelled schooner to the New Siberian Islands in 1902. The main purpose of the expedition was to discover the Sannikov Land, presumably the most northern island in the Siberian part of the Arctic Ocean. He performed extensive hydrographic, physical-geographic and geological research during the cruise and wintering on the north shore of the Taimyr Peninsula and the western shore of Kotelniy Island, and he was the first to conduct dredging in the Arctic Ocean. E.V. Toll and three of his companions went missing when crossing the sea on weak ice from the is-



Fig. 10. Pallasovsky meteorite and Nikolai Kharitonov with his family who found it. Photo from archive of A.E. Milanovsky.

lands of Bennett to Kotelny in November 1902. The rescue expedition headed by the military officer, who became later the famous Admiral A.V. Kolchak, was organized in 1903. The expedition found the last camp of E.V. Toll on Bennett Island, his writings and samples (Fig. 12).

The fate of samples of Toll's expedition was unknown till recently, when they were found during inventory in the Ore-Petrography Museum. F.Yu. Levinson-Lessing seems to have kept them at the museum when it was separated from the funds of Geological and Mineralogical Museum of the Academy of Sciences in the 1930s.

The exposition includes samples of rocks along with original documents: photographs, maps, letters, reports and publications (Fig. 13). E.V. Toll wrote in a draft of dismissal petition: *"I have an honor to report to Your Excellency that I have no more energy to accomplish the duties of the curator of Mineralogical Museum of the Emperor's Academy of Sciences. Having no assistants, I have the following responsibilities on my own: keeping, ordering and scientific analyzing the rich Siberian collections and bringing the museum to a higher level in general...."*

Many geographical places were named after E.V. Toll: a mountain on New Land Is-



Fig. 11. Eduard Gustav (Vasil'yevich) von Toll (1858–1902), academic curator of Mineralogical Museum of Imperial Academy of Sciences (present Fersman Mineralogical Museum). Photo from the book by P.V. Vittenburg (1960).

land, a mountain on Bennett Island, a bay on the north-western shore of the Taimyr Peninsula, a cape on Tsurcul' Island in Minin's skerries, a plateau on Kotelnii Island.

A scientific team of the Geological Institute of Academy of Sciences currently works in the areas of E.V. Toll's last expedition. This team handed newly found samples from the New Siberian Islands, geological maps, photographs, which were placed in the new section of the display named "The Research is Continued" (Fig. 14).

Fig. 12. Analcime basalt from the Bennett Island, East Siberian Sea, the last point of the Toll's route. Specimen 9 x 8 cm. OPM-IGEM# 1305. It was brought to the Mineralogical Museum of Imperial Academy of Sciences by lieutenant A.V. Kolchak, chief of rescue party on search of E.V. Toll. Photo: M.K. Sukhanov.

Fig. 13. Letter from E.V. Toll written on stationery of Russian Polar Expedition, January-February, 1901. From archive of OPM-IGEM.

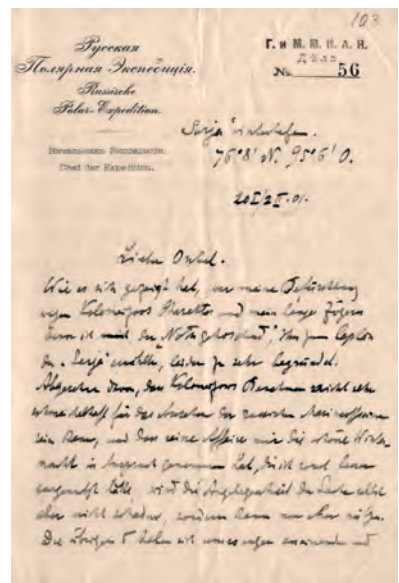




Fig. 14. Bennett Island: view of the Toll Valley and Preobrazheniya Cape, 2013. Photo: A.B. Kuzmichev.

The expositions are characterized by a combination of historical documents, samples of rocks and ores. Such an approach provides most comprehensive information and is very informative for education and in science.

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THE MINERALOGICAL COLLECTION OF VIKTOR IVANOVICH STEPANOV (1924–1988): ITS MUSEUM VALUE AND SCIENTIFIC AND SOCIAL IMPORTANCE

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V.I. Stepanov's Mineralogical Collection was assembled between 1935 and 1985 and is comparable in its importance with collections of some of Russia's largest Mineralogical Museums. Given the lack of research interest in Mineralogical Museum work and mineral collecting at the time, Stepanov developed his own methodology in working with mineralogical collections. Many of the methods developed by Stepanov proved internationally innovative. This article describes his methodology and provides statistical data on the Stepanov Collection. 3 tables, 13 figures, 11 references.

Keywords: V.I. Stepanov, Mineralogical Museum, mineralogical collection, mineral species, mineral.

It has already been over a quarter of a century since Viktor Ivanovich Stepanov (1924–1988) is no longer with us. He has left such a bright trace that it seems our acquaintance has happened only yesterday. For many of us, Viktor Ivanovich was and remains a Teacher, even beyond mineralogy. So what is the significance of his activities?

Viktor Ivanovich did not leave behind a long list of scientific publications. Assemblage of a mineralogical collection in the course of half a century has been the task of his lifetime.

The collection, now kept at the Fersman Mineralogical Museum of the Russian Academy of Sciences, rivals in its completeness, scientific and social significance with large national collections of modern Mineralogical Museums. In the extent of research and documentation, its exhibits exceed many of them.

The dedicated work of assembling this collection allowed Viktor Ivanovich to acquire tremendous mineralogical knowledge, resulting in some most interesting observations which are published in his works, but mostly written in detailed explanatory labels accompanying the mineral specimens. In working with collection's systematisation, principles of its organization, storing, methods of specimen preparation and other museum issues, Stepanov became the most qualified museum specialist, mineralogy has ever known, both in our country and perhaps even abroad. He has discovered efficient approaches of working with mineralogical collections and created his own School, whose pupils have applied his methods in

many museums across Russia. His assemblage methods have had significant impact on some high profile private mineralogical collections.

The assembly of this particular collection, its development and, on occasion, struggle for its preservation are a truly long-term feat. Viktor Ivanovich Stepanov was without any exaggeration a devotee of his craft.

History of collection

Personal collection, 1935–1963. As for many others in those years, Viktor Ivanovich's mineralogical passion began in reading Fersman's "*Popular Mineralogy*". According to his own ironic comments, after shutting the book he rushed to the cemetery where Volynian labradorite could be found among the grave stone debris. He even recalled an exact date and hour: 7 pm on 25 August 1935 (Evseev, 1998; 2014). Since then, he started his personal collection, although more serious and purposeful collecting commenced only in 1938. In 1941, Stepanov entered the Sverdlovsk Mining Institute¹. Soon he was evacuated and then signed up to the Red Army. Wounded at the frontlines, he left the hospital to continue his army service as a translator in Bulgaria until 1946 (Fig. 1). Even during his army days, Viktor Ivanovich managed to collect minerals. It is from finds of that time that the autunite and tornbernite from the outskirts of the Bukhovo Village of the Sofia Region and several specimens from the Rhodope deposits were later included into his main collection. In addition to his own collecting, he began to exchange specimens

¹ – More detailed biographical information can be found in article by I.E. Maximyuk in this issue of magazine.

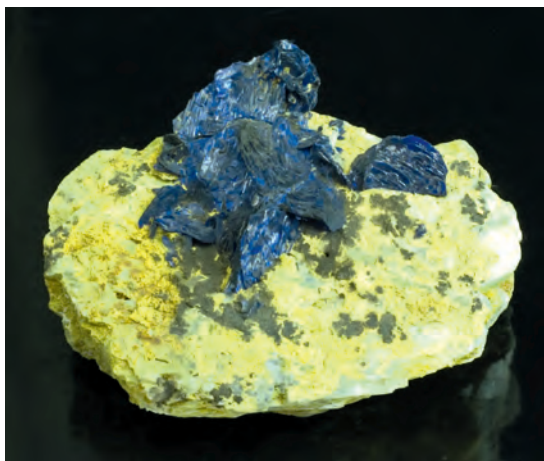


Fig. 1. Viktor I. Stepanov. Vraca, Bulgaria. October 20, 1944. From Stepanov family archive.

with the employees and post-graduate students of the Sofia University. He maintained and developed these links during his entire life. Soon after demobilisation from the army in 1946, Stepanov entered the Geology-Prospectual Faculty of the Moscow Geology-Prospectual Institute (MGRI), and in 1950, he transferred to the Geological Faculty of the Moscow State University, which he graduated in 1952. During his studies, Viktor Ivanovich continued active mineral collecting near Moscow, in Crimea (Fig. 2), and in geological expeditions. During this period, he found (for the first time for Moscow Region) delvauxite, takovite and other minerals. Later, the list of Moscow minerals substantially expanded (Feklichev, 1998).

Fig. 2. Niter rosette. Bakla Mt, near Bodrak village, Bakhchisarai district, Crimea. 5 cm. FMM #ST1334, found by V.I. Stepanov. Photo: M.M. Moiseev.

Fig. 3. Azurite. Kairakty, Central Kazakhstan. 6 cm. Found by V.I. Stepanov, 1953. FMM # ST2010. Photo: M.M. Moiseev.



Already during these years, Viktor Ivanovich not only assembled his own collection, but also granted mineral specimens to the largest Mineralogical Museums in Russia. For example, the first ones that he granted to the Mineralogical Museum of the Academy of Sciences are from Bulgaria. They were catalogued in the systematic collection in 1946, i.e., immediately after his demobilisation from the army. The specimens granted to the MGRI Museum (now Vernadskiy State Geological Museum) are dated approximately by the same year. Viktor Ivanovich continued to donate to various Museums practically throughout his entire life. It is worth mentioning, for example, that the collection of the main fund of the Fersman Mineralogical Museum received more than 1500 of its specimens from Stepanov, while the MGRI Museum – about 800. These exhibits are a separate part of his legacy and are not considered a part of his main collection.

After graduation, Viktor Ivanovich worked as a mineralogist in Central Kazakhstan (Fig. 3). Here, he acquainted himself with many unique mineralogical objects: Kara-Oba, Akchatau, Eastern Kounrad, and visited many others. He made many interesting observations and perfected his art of mineral sampling and preparation. Stepanov's archive has tremendous information on Central Kazakhstan deposits. His collection grew quickly and soon he faced the inevitable problem of its documentation and systematisation. In 1956, while still continuing to work in Kazakhstan, Stepanov became an employee of the Department of Mineralogy at the Institute

for Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) of the Academy of Sciences.

IMGRE Museum, 1964–1985. In the end of 1963, K.A. Vlasov, the founder and director of the Institute for Mineralogy, Geochemistry and Crystallochemistry of Rare Elements (IMGRE) of the Academy of Sciences, invited Stepanov to work for this institute with a special purpose of assembling its mineralogical collection. 1964 commences a new and most productive stage in the development of the Stepanov Mineralogical Collection. His personal collection served as a foundation for the IMGRE collection and was officially assigned a status of IMGRE Museum.

The transfer to IMGRE was very favourable for Viktor Ivanovich. The young employees of the newly established institute worked practically with all the most cutting edge mineralogical prospects of the USSR. This allowed Stepanov to travel to these prospects and obtain the relevant material. The analytical laboratories of the institute had supreme specialists. Administration of the institute encouraged his activity, and the majority of employees supported his work. Viktor Ivanovich had at his disposal a semi-basement floor in the building near the main edifice of IMGRE on the Sadovnicheskaya Embankment along with several other semi-basement and basement rooms nearby for his collection. He had one assistant (two at best times) and most importantly he had the freedom to fulfil the tremendous task of his daily voluntary hard work, interrupted only by Sunday cross-country skiing.

It is difficult to avoid nostalgic memories of this basement, which was visited by most curious employees from different institutes, students, pupils, and mineral collectors and stone lovers, who came far beyond Moscow. It is amazing that Viktor Ivanovich had time for everyone. He was demonstrating his collection, commenting on some specifics or on the history of findings of some minerals. He disclosed his methods, asking many questions himself, critically evaluating research or collected material. Often, he scolded his visitors, but even this scolding took such an ironic twist that it never ever had the smallest degree of anger. To those who protested against the criticism he often used to say: *"I only tell you off, because I think you can become somebody, once I understand that you are hopeless I stop wasting my time on this"*. Viktor Ivanovich did not hold back his praises, if he did like something, and it was al-



Fig. 4. Getchellite. Khaidarkan, Kirghizia. 24 cm. V.I. Stepanov donation, 1982. FMM # 81823. Photo: M.M. Moiseev.

ways a great honour to earn his compliments. He was always willing to consider newly delivered specimens for mineral assessment, enjoyed gifts and ironically encouraged his visitors to come with "a stone in their bosom". The visitors were usually willing to abide. Visiting and talking to Viktor Ivanovich, with his in-depth expertise and undying enthusiasm, was always inspiring. In A.G. Zhabin's words (Zhabin, 1992), *"Viktor Ivanich was an incarnation of a Teacher, a conscience trigger, a critic and an advisor. People would always come to see him"*. It is fascinating that his unofficial approach to people remained unaltered, whether he was talking to a school pupil or to a high level academician.

As a result, the IMGRE collection, never initially intended for public display, has acquired an exhibitory function and had quite a following, thanks to Viktor Ivanovich.

It is difficult to estimate the scale of Stepanov's collection when he joined IMGRE, but it is evident that its core collection, both in quality and scientific value, was assembled at this time. It is also during this time that Stepanov undertook the most productive field trips to the Central Asian deposits of Khaidarkan (Fig. 4), Tuya-Muyun, Chauvai, Dzhizhikrut, as well as the Moscow region (Fig. 5), Kola Peninsula, Caucasus and Crimea. Viktor Ivanovich's particular interest in cave mineralogy developed then too, result-



Fig. 5. V.I. Stepanov, collecting minerals. Podolsk, July 1975. From Stepanov family archive.

ing in a separate collection dedicated to it (Fig. 6). Key experiments and collecting methodology, to be discussed below, were developed during this period.

In 1984, A.A. Godovikov, the then recently appointed director of the Fersman Mineralogical Museum, has invited Stepanov to transfer to the Museum. The IMGRE management should be paid tribute for recognising the needs of the collection and approving Stepanov's transfer with his entire IMGRE Museum assemblage.

Already in 1984, Viktor Ivanovich was practically working at the Fersman Mineralogical Museum, being actively involved in the preparations for the International Geological Congress in the summer of the same year. His formal transfer to becoming a curator of collections and scientific inventory of the Museum's funds was documented in 1986. The collection's move took several years and was completed in 1987 (Fig. 7). Viktor Ivanovich was already seriously ill by this time. Sadly his work at the Museum was only brief. He passed away in August 1988.

So what did the Museum acquire in 1987? The main part was the most systematised and partially documented *Collection A*, consisting of ~8500 specimens. More than 10000 specimens made up the *Collection B*. The significant portion of the latter is labelled, but not catalogued. About 5000 duplicate items were

kept in the collection (Nikiforov, Shkurskiy, 1988), dedicated to the processes of cave mineralisation. This collection has not been catalogued either, with only partial detailed documentation available.

Numerous materials were moved from the basement rooms of Stepanov's former collection, where they were assembled in trays and boxes. Their number can be estimated only approximately (~15000). Only a small portion of these materials is labelled, mainly by people who collected it. It is these materials that Stepanov chose items from for his Collections A and B. Nevertheless Viktor Ivanovich kept coming back to these materials, which he considered worked out. The scale of this part of the collection turned out to be significant and remains work in progress to this day.

When the collection first joined the Fersman Mineralogical Museum, a decision, we now consider erroneous, was taken, cataloguing specimens in the same order as the Museum's other new acquisitions. About 600 specimens from Collection A were recorded this way. It is only later that a decision to catalogue Collection A as a separate memorial collection of the Museum's main fund was taken.

Key statistical characteristics of Collection A

When comparing the Stepanov Collection with those of Russia's three largest Museums based on two most important quantitative characteristics (Table 1), it is evident that despite the smaller overall number of Stepanov's mineral specimens, the number of mineral species is closely matching. About one hundred of Stepanov's mineral species was not to be found in the collections of the other three Museums mentioned in Table 1. Another 60 titles in Collection A refer to mineralogical composites as well as specimens as yet unrecognised by the Commission on New Minerals, Nomenclature and Classification (CNMNC IMA). About 30 specimens were included in the collection as potentially new mineral specimens, with some having already been recognised as such.

Collection A specimen classification is shown in Table 2. The classification largely adheres to that of a typical museum collection, indicating a highly representative nature of Collection A and its general correlation to mineral abundance in nature.

The geographic provenance of the majority of the specimens (i.e., around 75%: 6327

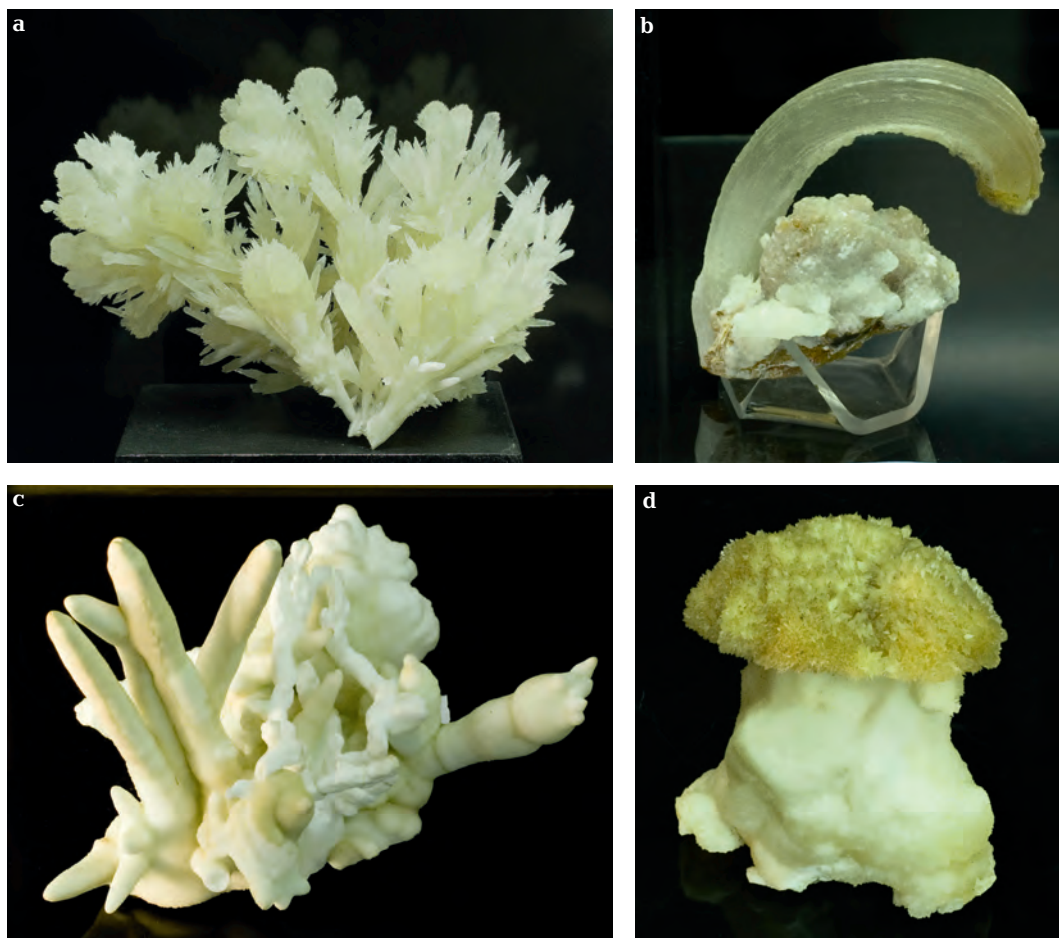


Fig. 6. Mineral aggregates of Khaidarkan caves, Kirghizia: (a) calcite, 20 cm; (b) gypsum (antolite), 8 cm; (c) calcite (helectite), 14 cm; (d) calcite (mushroom), 15 cm. V.I. Stepanov collection.
Photo: M.M. Moiseev.



Fig. 7. V.I. Stepanov in the A.E. Fersman Mineralogical Museum together with workers of Acquisition Section, 21 May 1987.
1st row (from left to right): B.B. Shkursky, V.I. Stepanov, T.I. Matrosov, Yu.S. Kobya-shev; 2nd row: D.A. Romanov, D.V. Abramov.
Photo: A.A. Evseev.

Table 1. The number of display items and mineral species in the Russian mineralogical collections as of May 1987, according to Stepanov (1989) and Stepanov et al. (1989)

	Total specimens	Total mineral species
Fersman Mineralogical Museum, Moscow	125000	1968
Museum of Plekhanov Mining Institute, St.-Petersburg	34000	1795
Mineralogical Museum, Moscow Geology-Prospectal Institute (now in collection of Vernadskiy State Geological Museum)	59000	1100
The Stepanov Collection (IMGRE Museum)	8500 Collection A 15000 Collection B	1297

specimens) is indeed from the territory of the former USSR. These are distributed across the former republics as follows: Russia – 4227, Kazakhstan – 874, Kyrgyzstan – 373, Ukraine – 331, Tajikistan – 257, Uzbekistan – 121, Georgia – 117, Azerbaijan – 103, Turkmenistan – 78, Armenia – 43, Moldova – 2, Belarus – 1.

The abundance of foreign specimens in this collection is amazing for the time (1731 specimens from 70 countries; Table 3). It is evident that rumours of Stepanov's work have reached far and wide beyond the Iron Curtain. This is probably linked to his correspondence and personal acquaintances with foreign collectors and researchers. Moreover, specimens were brought to him as gifts by fellow Soviet geologists who had travelled abroad.

We should note also that more than 300 specimens from Collection A remain unknown in provenance and location.

1350 specimens from Collection A were collected personally by Viktor Ivanovich. It is definite that 616 specimens were obtained by exchange with both national and foreign collectors and Museums. The majority of other specimens (around 6500) are donations of various nature from at least 400 researchers, collectors and stone enthusiasts. The following have contributed the most to the collection by donating 50 and more specimens: Yu.S. Kobayashv (327), E.I. Semenov (159), V.Yu. Volgin (153), A.P. Khomyakov (89), L.S. Borodin (88), B.Z. Kantor (85), A.A. Godovikov (82), A.G. Zhabin (75), V.V. Bukanov (70), R.V. Gaines (67), A.A. Evseev (66), N.N. Pertsev (51).

Stepanov's key approaches, tactics and methods of collection, systematisation and documentation are characterised below.

Assembling the collection

Personal collecting. Viktor Ivanovich was an expert of mineral specimen collecting. He gained invaluable experience of approaching a future display item without disrupting it. He was able to intuitively identify a cornerstone,

which once extracted helped dismantle a seemingly unapproachable section. The range of his tools was diverse, some of which he improved himself. This can be read about in more detail in Boris Kantor's publications (Kantor, 1982; 1988). Stepanov was tireless when it came to collecting. Even pouring rain could not put him off his work as he would put his raincoat on and rejoice in that the specimens would not need rinsing. It seems that only darkness could stop him from collecting minerals. He would always aim to get as much material as he could get and carry away, starting to prepare specimens on site (as ruined specimens could be replaced there and then, if necessary). He processed all the collected materials later (*"Do not put the best specimens separately from the others, or you would lose them"*, he would say and many would regret not heeding to his advice afterwards).

A whole separate category amongst Stepanov's personally collected specimens is the finds from dumps and, literally, bins of research institutions, whose researchers disposed of their collections (frequently with labels and analytical data) when they lost their interest after papers publications (Fig. 8, 9). In many of such cases, Stepanov would take it upon himself to take care of preserving the original research. His continuous explanatory work yielded its results, prompting such institutions as IMGRE to treat working material with more responsibility.

Revision of collections of researchers and collectors, agitation for donating of specimens to the collection. Viktor Ivanovich would systematically survey new materials of his IMGRE colleagues and staff of other Museums and institutes. He was all get-up-and-go and willing to visit collectors at their homes, even when the said collector was a mere school pupil. While observing collections he would make enquiries and interesting remarks, often revealing details about collections that the collectors would never have suspected about. Often he would automatically reach out for some paper as he spoke and write down specimen labels for the col-

Table 2. Collection A content by the mineral species, represented by five or more specimens

1. Calcite	295	55. Pyrochlore	26	109. Gibbsite	16	163. Gagarinite	11
2. Quartz	210	56. Rutile	26	110. Pyrope	16	164. Hedenbergite	11
3. Sphalerite	148	57. Phenakite	26	111. Rhodonite	16	165. Helvine	11
4. Barite	109	58. Astrophyllite	25	112. Berthierite	15	166. Lazulite	11
5. Pyrite	109	59. Gold	25	113. Wadeite	15	167. Leucophane	11
6. Fluorite	96	60. Copper	25	114. Hubnerite	15	168. Löllingite	11
7. Celestite	91	61. Mellite	25	115. Cuprite	15	169. Lomonosovite	11
8. Apatite-(CaF)	89	62. Pectolite	24	116. Livingstonite	15	170. Ludwigite	11
9. Cinnabar	69	63. Witherite	23	117. Loparite	15	171. Monticellite	11
10. Muscovite	69	64. Gypsum	23	118. Magnesite	15	172. Murmanite	11
11. Zircon	69	65. Opal	23	119. Margarite	15	173. Pyromorphite	11
12. Natrolite	68	66. Spinel	23	120. Pollucite	15	174. Ussingite	11
13. Sulphur	58	67. Augite	22	121. Prosopite	15	175. Huanghoite-(Ce)	11
14. Beryl	55	68. Bastnaesite	22	122. Rinkite	15	176. Elpidite	11
15. Malachite	54	69. Grossular	22	123. Talc	15	177. Bavenite	10
16. Molybdenite	53	70. Datolite	22	124. Anglesite	14	178. Betechninite	10
17. Antimonite	52	71. Cobaltite	22	125. Antigorite	14	179. Brookite	10
18. Diopside	52	72. Orthoclase	22	126. Danburite	14	180. Wavellite	10
19. Galena	51	73. Polyolithionite	22	127. Dravite	14	181. Variscite	10
20. Dolomite	50	74. Cyanite	21	128. Ilvaite	14	182. Villiaumite	10
21. Aragonite	49	75. Creedite	21	129. Labuntsovite	14	183. Viluite	10
22. Chalcopyrite	46	76. Mesolite	21	130. Lovozерite	14	184. Galkhaite	10
23. Siderite	44	77. Metacinnabar	21	131. Manganneptunite	14	185. Hemimorphite	10
24. Clinocllore	41	78. Silver	21	132. Realgar	14	186. Getchellite	10
25. Titanite	41	79. Smithsonite	21	133. Serandite	14	187. Canasite	10
26. Topaz	39	80. Stilbite	21	134. Scheelite	14	188. Kermesite	10
27. Eudialyte	38	81. Thomsonite	21	135. Aeschnite-Ce	14	189. Xenotime	10
28. Arsenopyrite	37	82. Wollastonite	20	136. Alunite	13	190. Cookeite	10
29. Lorenzenite	34	83. Hematite	20	137. Biotite	13	191. Laitakarite	10
30. Elbaite	34	84. Corundum	20	138. Brucite	13	192. Axinite-(Mn)	10
31. Azurite	33	85. Lamprophyllite	20	139. Vinogradovite	13	193. Manganite	10
32. Nepheline	33	86. Monazite	20	140. Wurtzite	13	194. Meionite	10
33. Prehnite	33	87. Phlogopite	20	141. Clintonite	13	195. Metavivianite	10
34. Strontianite	33	88. Bertrandite	19	142. Nenadkevichite	13	196. Mordenite	10
35. Anhydrite	32	89. Bornite	19	143. Rhabdophan	13	197. Parisite	10
36. Bismuth	32	90. Britholite	19	144. Staurolite	13	198. Powellite	10
37. Goethite	32	91. Vesuvianite	19	145. Stellerite	13	199. Antimony	10
38. Heulandite	31	92. Cancrinite	19	146. Tennantite	13	200. Fayalite	10
39. Magnetite	31	93. Rhodochrosite	19	147. Thomsenolite	13	201. Axinite-(Fe)	10
40. Chrysoberyl	31	94. Anatase	18	148. Fluorapophyllite-(K)	13	202. Chrysocolla	10
41. Albite	30	95. Cordierite	18	149. Chalcocite	13	203. Schörl	10
42. Andradite	30	96. Cerussite	18	150. Zinnwaldite	13	204. Enigmatite	10
43. Cassiterite	30	97. Andalusite	17	151. Tsumoite	13	205. Enstatite	10
44. Almandine	29	98. Bismutite	17	152. Burbankite	12	206. Anapaite	9
45. Epidote	29	99. Gearsutite	17	153. Turquoise	12	207. Willemite	9
46. Analcime	28	100. Gersdorffite	17	154. Vanadinite	12	208. Wodginite	9
47. Cryolite	28	101. Joseite A	17	155. Columbite	12	209. Vauquelinite	9
48. Perovskite	28	102. Catapleite	17	156. Laumontite	12	210. Gadolinite-(Y)	9
49. Orpiment	27	103. Pyrrhotite	17	157. Arsenic	12	211. Halloysite	9
50. Graphite	27	104. Synchronite-Y	17	158. Olivine	12	212. Hydroboracite	9
51. Sodalite	27	105. Charoite	17	159. Epididymite	12	213. Hydroxyapophyllite-(K)	9
52. Ilmenite	26	106. Chabasite	17	160. Jarosite	12	214. Gyrolite	9
53. Lepidolite	26	107. Atacamite	16	161. Adamite	11	215. Gudmundite	9
54. Microcline	26	108. Beaverite	16	162. Wulfenite	11	216. Digenite	9

Table 2. (Continuation)

217. Clinoptilolite	9	270. Hydrozincite	7	323. Hauyne	6	376. Delafossite	5
218. Cosalite	9	271. Gmelinite	7	324. Geocronite	6	377. Dumortierite	5
219. Leucosphenite	9	272. Griffithite	7	325. Hercynite	6	378. Hiortdahlite	5
220. Salammoniac	9	273. Davidite-(La)	7	326. Hureaulite	6	379. Kaliborite	5
221. Allanite	9	274. Delvauxite	7	327. Descloizite	6	380. Crandallite	5
222. Petalite	9	275. Delhayelite	7	328. Djerfisherite	6	381. Cryolithionite	5
223. Pimelite	9	276. Jadeite	7	329. Kaolinite	6	382. Cryptomelane	5
224. Pyrolusite	9	277. Calomel	7	330. Clinohumite	6	383. Cristobalite	5
225. Ralstonite	9	278. Clinozoisite	7	331. Kobellite	6	384. Cuprotungstite	5
226. Sylvanite	9	279. Colemanite	7	332. Crocoite	6	385. Linarite	5
227. Tellurobismuthite	9	280. Coronadite	7	333. Leucite	6	386. Marialite	5
228. Terskite	9	281. Xonotlite	7	334. Libethenite	6	387. Mooihoekite	5
229. Uvarovite	9	282. Cubanite	7	335. Lizardite	6	388. Neptunite	5
230. Chloritoid	9	283. Lavenite	7	336. Mountianite	6	389. Penkvilksite	5
231. Chondrodite	9	284. Marcasite	7	337. Melinophane	6	390. Pyroxmangite	5
232. Chkalovite	9	285. Metastibnite	7	338. Mimetite	6	391. Pirophanite	5
233. Eglestonite	9	286. Mitridatite	7	339. Nagyagite	6	392. Plancheite	5
234. Batisite	8	287. Nacrite	7	340. Nadorite	6	393. Rectorite	5
235. Beudantite	8	288. Narsarsukite	7	341. Natrojarosite	6	394. Rosasite	5
236. Betafite	8	289. Neotokite	7	342. Nickeline	6	395. Roselite	5
237. Bindheimite	8	290. Oligoclase	7	343. Nordite	6	396. Rockbridgeite	5
238. Brushite	8	291. Pinnoite	7	344. Pachnolite	6	397. Mercury	5
239. Bustamite	8	292. Pumpaurite	7	345. Pilsenite	6	398. Sazhinite-(Ce)	5
240. Diaspore	8	293. Pumpellyite	7	346. Pyrophyllite	6	399. Sapphirine	5
241. Idrialite	8	294. Purpurite	7	347. Proustite	6	400. Cervantite	5
242. Ilmenorutile	8	295. Piemontite	7	348. Raite	6	401. Skutterudite	5
243. Ingodite	8	296. Rancieite	7	349. Saponite	6	402. Spurrite	5
244. Covellite	8	297. Seydozerite	7	350. Semseyite	6	403. Apatite-(SrOH)	5
245. Komerupine	8	298. Senarmonite	7	351. Stannite	6	404. Suanite	5
246. Labradorite	8	299. Scolecite	7	352. Tainiolite	6	405. Thalénite	5
247. Manganotantalite	8	300. Scorodite	7	353. Gonnardite	6	406. Talnakhite	5
248. Miserite	8	301. Spessartine	7	354. Ullmannite	6	407. Tirolite	5
249. Microlite	8	302. Szaibélyite	7	355. Umangite	6	408. Tikhonenkovite	5
250. Millerite	8	303. Stibiotantalite	7	356. Whewellite	6	409. Todorokite	5
251. Paragonite	8	304. Stilpnomelane	7	357. Ferrierite	6	410. Triplite	5
252. Petzite	8	305. Taranakite	7	358. Forsterite	6	411. Tungstite	5
253. Sellaite	8	306. Thorite	7	359. Franckeite	6	412. Tungusite	5
254. Sillimanite	8	307. Fedorite	7	360. Chiolite	6	413. Tundrite	5
255. Titanclinohumite	8	308. Fersmanite	7	361. Chrysotile	6	414. Ulexite	5
256. Zoisite	8	309. Fluellite	7	362. Chromite	6	415. Fergusonite	5
257. Chamosite	8	310. Zirkelite	7	363. Euxenite-(Y)	6	416. Volborthite	5
258. Schorlomite	8	311. Ekanite	7	364. Enargite	6	417. Freibergite	5
259. Epistolite	8	312. Acanthite	6	365. Erionite	6	418. Fluorophlogopite	5
260. Altaite	7	313. Aktashite	6	366. Yuksporite	6	419. Huntite	5
261. Amblygonite	7	314. Ankerite	6	367. Baddeleyite	5	420. Apatite-(CaCl)	5
262. Anorthite	7	315. Aurichalcite	6	368. Belovite	5	421. Cyanotrichite	5
263. Bayldonite	7	316. Barytolamprophyllite	6	369. Bismoclite	5	422. Zinkenite	5
264. Birnessite	7	317. Berillite	6	370. Braunite	5	423. Churchite	5
265. Boulangerite	7	318. Betalomonosovite	6	371. Vivianite	5	424. Shcherbakovite	5
266. Bournonite	7	319. Wakabayashilite	6	372. Bismutotantalite	5	425. Euclase	5
267. Weberite	7	320. Valentinite	6	373. Harmotome	5	426. Ehlite	5
268. Vuonnemite	7	321. Galenobismutite	6	374. Hessite	5		
269. Halite	7	322. Gahnite	6	375. Danalite	5		

Table 3. Distribution of specimens beyond the former USSR in Collection A by number of items

1. USA	139	19. Brazil	26	37. Zaire	8	55. Ireland	2
2. Germany	136	20. Norway	26	38. Chile	7	56. Iceland	2
3. Bulgaria	123	21. Slovakia	25	39. Peru	6	57. Nepal	2
4. Hungary	112	22. Austria	24	40. Turkey	6	58. North Korea	2
5. China	110	23. Sweden	22	41. Bolivia	5	59. Belgium	1
6. Denmark	100	24. Great Britain	22	42. Switzerland	5	60. Burma	1
7. Czech Republic	91	25. France	19	43. Argentina	4	61. Gabon	1
8. India	62	26. Madagascar	16	44. Pakistan	4	62. Zambia	1
9. Mongolia	61	27. Namibia	16	45. Uganda	4	63. Iran	1
10. Canada	55	28. Guinea	15	46. Tanzania	4	64. Kenya	1
11. Morocco	54	29. Cuba	14	47. South Africa	4	65. Malawi	1
12. Japan	51	30. Mozambique	13	48. Vietnam	3	66. Malaya	1
13. Mexico	47	31. Finland	13	49. Greece	3	67. Sudan	1
14. Romania	45	32. Afghanistan	11	50. Zimbabwe	3	68. Taiwan	1
15. Italy	44	33. Yugoslavia	11	51. Columbia	3	69. Tunisia	1
16. Poland	40	34. Spain	9	52. Macedonia	3	70. Chad	1
17. Algeria	34	35. Serbia	9	53. Somalia	3	71. Antarctica	1
18. Congo	28	36. Australia	8	54. Sri Lanka	3	72. Indian Ocean	1

lector. This not only prompted people to give away specimens that interested him, but also made them pursue Stepanov in the future to demonstrate their collections, while many also visited him in return, bringing minerals for consultation and donation in anticipation of his evaluation and took pride, if their donations were considered worthy of inclusion in his collection. Although when talking to collectors, Viktor Ivanovich would confiscate lumps of ore that he liked and offer replacement from duplicates of his own specimens. These transactions can be hardly seen as exchanges (which he was an expert in), not only in virtue of disparity of the specimens involved, but also in intentions of both parties. It would be more accurate to see these incoming specimens as donations. A typical example is the donation to Stepanov of the

best part of Moscow Regional State Pedagogical Institute's collection, assembled by a whole group of students.

In return the institute received specimens for educational sessions. Viktor Ivanovich generally held collectors in high esteem, treating their encounters with great importance and helping them however he could, as for him collectors were "the soil on which Museums grow". This stood out amidst the infamous narrow-minded policy of some state geological institutions at the time which advocated keeping collectors out of Museums.

Exchange. When it came to purposeful exchange with Soviet collectors, specimen value rather than monetary value was at stake. Often the equivalence was not preliminarily established or traced down, especially



Fig. 8. Molybdenite (crystals up to 4 cm). Emerald Mines, Middle Urals, Russia. Found by V.I. Stepanov in waste dumps of Sverdlovsk Mining Institute, 1941. FMM #ST8138. Specimen Labels (a) left by V.I. Stepanov and (b) right – Fersman Mineralogical Museum. Photo: M.M. Moiseev.



Fig. 9. Indite. Abundant black grains in "wood tin", cassiterite. Jalinda mineral occurrence, Primorskii krai. 3.5x2 cm. G. Komarova's collection, IGEM, 1976. FMM #ST595. The label belongs to V.I. Stepanov's (left side is face, right side is reverse side). Photo: M.M. Moiseev.

in dealings with constant partners. Foreign collectors usually preferred to evaluate specimens by their market value abroad. Viktor Ivanovich was equally prepared for such transactions and was well equipped in the knowledge of foreign markets. Rare, but beneficial exchanges would take place with the very few Soviet mineral dealers. Collector Igor Bogutsky, for instance, who traded minerals in Ptichiy Flea Market in Moscow, was keen to exchange one or several valuable minerals for a multitude of less valuable once or even leftovers from specimen preparation.

Purchased items are virtually absent in Viktor Ivanovich's collection (as they were not a part of the institute's budget), except for when he used his own salary to acquire a specimen.

Preparation

Specimen moulding was a standard of preparing minerals for collections at the end of the 19th – beginning of the 20th century. Even geological field guides would recommend specimens of notable size. By the middle of the 20th century, this method had virtually disappeared in the USSR and was reinvented by Stepanov. Apart from moulding and mechanical preparation Viktor Ivanovich experimented a lot with acids and developed a series of his own methods of mineral specimen preparation. He took particular joy in watching a collector's reaction to a once discharged stone, which with some preparation had become a remarkable specimen that could make

a worthy contribution to any collection. As far as we know, Stepanov was the only museum employee and collector in the USSR to extensively apply specimen preparation, and those who used later were taught by him. Interestingly, there were some in the museum community who directly opposed any mineral preparation. The policy "to preserve everything in its original state" was often taken so far that specimens were sometimes put into Museum collections with moss and even dirt.

Diagnostics and the study of minerals

Many people who have encountered Viktor Ivanovich were most impressed by his ability to visually diagnose minerals. It is this quality that is brought up to the forefront of many memoirs and is pointed out as his key achievement, which in our opinion is not exactly accurate. This wonderful ability (Viktor Ivanovich was undoubtedly the most able and precise diagnostician) was a consequence of his in-depth knowledge of mineralogy, extensive and continuous observations, remarkable memory and persistence in working with the collection itself.

This ability allowed him to not miss any interesting and new material while working in the field or with collections and identify the material that was most worthy of further studies. He was well aware of the limitations of visual diagnostics and would always use other instrumental methods as a backup. Studied specimens were given preference when it came to assembling his collection. Viktor Ivanovich knew mineral analysis methods well and was constantly in touch with many analysts (chemists, X-ray analysis specialists and others), knew optical methods himself and had a good command of typical analytical mistakes.

More than 30 specimens are identified in the collection as "mineral X". This was how Stepanov labelled minerals, whose diagnostics led him to conclude that they could belong to new mineral species (comments to this effect are made on the label). For some of these, like khaidarkanite, his suspicions have already been confirmed. Part of these specimens is still being studied, others yet await further studying. The proportion of studied specimens in Stepanov's collection is the highest compared to Soviet Museum and private collections and it would seem, compared to foreign collections too. Moreover the potential of his collection to yield new mineral data is immense.

Systematisation of collection

Circulation of material. Incoming specimens underwent multiple filtration. The most interesting ones were selected out of the mass of collected material. From here specimens were selected for Collection A based on typology, intraspecies diversity, degree of research scrutiny and aesthetics, resulting in a systematic collection. The remaining material in the first filtration formed Collection B. Materials that did not fit either of these two categories were sometimes referred to as Collection C by Stepanov. These were the multiple duplicates and specimens considered to be of low quality in the process of filtration. After multiple investigations, they still were not dumped, even though they occupied the most space, boxed or stacked up in several basement rooms.

Stepanov would frequently come back to part C, from time to time selecting new entrants for collection A and B, as notions of mineralogical value changed over time and new information regarding them and their provenance emerged. According to Viktor Ivanovich himself, the mineral specimens that remained after filtration from collection B to collection A were more characteristic of mineral species variations, typical for their provenance. The selection logic of Collection B came to closely resemble the deposit collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences. Specimen circulation also occurred in the opposite direction $A \rightarrow B \rightarrow C$ as new collections and data came in.

Defining a specimen's place within collection. In compiling his collection, Viktor Ivanovich had a precise idea of why a particular specimen was selected, what specifics of its mineral species or its origins it reflects and what its role and place in the collection should be. Amongst other things he developed a *qualitative scale* for specimens in order to formalise these notions (Stepanov, 2001). Here, a natural specimen was to be evaluated separately based on three categories of rarity, research scrutiny and aesthetics. Every category was ranked by one to ten scale. In terms of rarity, 10 was assigned to mineral species represented by one of a kind specimen. Mineral species holotype was identified as 10 in research scrutiny scale. Ten points in the more subjective aesthetic scale relied on such criteria as a spectacular, well formed and intact crystal druse. Other scale points were also

identified and explained in detail². This approach (of identifying three numbers) made specimen evaluation significantly easier for museum staff. For Viktor Ivanovich himself however evaluation was rather intuitive. Stepanov paid most attention to systematisation of Collection A. Its mineral species were typically distributed based on the universal chemico-structural classification (although based on the storage conditions, he frequently discussed the idea of arranging them in alphabetic order). Unlike many Museum collections the order was not geographically determined within a species, but was defined by its diversity. Mineral specimens that characterised the morphological diversity of a species (Stepanov assigned immense significance to morphology as an indicator of formation conditions) were displayed first, then followed the specimens that characterised the various mineral associations of this species. This order made storage easier when new material arrived or when old material was reworked and the usefulness of additions had to be detected.

Collection documentation

Viktor Ivanovich attributed great importance to collection documentation (or, in Museum terms, scientific inventory). This made his collection one of the best documented collection of our time. Stepanov's key means of documentation was a *scientific label*. The label was not inscribed with a catalogue number, name, geographic provenance and source (all typical for Museum documentation) but also with a brief (or at times extensive) concise description of the specimen, with remarks regarding its quality and significance, time of collecting, collector, nature of acquisition, data regarding any analytical information for the specimen (and at times analysis results), the necessary conditions of storage and a series of other facts.

In other words, the label was inscribed with as much information as such piece of paper could permit (Fig. 9). To increase the label's capacity and to cut down the documentation time, Stepanov developed an advanced system of shortcut symbols. A table of these symbols was compiled. A label's capacity significantly increased, so that a stored specimen could provide efficiently obtainable data, which was often equivalent to that of a scientific article.

In fact a label became a quintessence of multi-faceted approach to a mineralogical

² – The scale is presented in full in I.E. Maximiyuk's article, published in this issue

specimen, revealing its individual peculiarities, scientific value and link to historical events, if any such was present. This was an innovative approach for Mineralogical Museum practice worldwide.

Stepanov's other means of documentation was a catalogue, so detailed that it too exceeded other Museum collections of the time, but was less scrupulous than his labels (some of Collection A specimens were not even included). Evidently, Viktor Ivanovich had no time to cover the full scope of Museum documentation work. Nevertheless, the existing catalogue is quite enough to understand how such a catalogue is to be kept according to Stepanov. Namely, it should at least consist of the data from the labels. To get some idea of the influence of his work on one of the key Mineralogical Museums in the country, one ought to compare Stepanov's own label and a typical label of the Mineralogical Museum of the Academy of Sciences at the time with a label of the same Museum after Viktor Ivanovich had worked there (Fig. 10); as well as to compare the pages of the Museum catalogue before (Fig. 11a) and after (Fig. 11b) Stepanov joined.

Another peculiar feature of Stepanov's collection is the lists (an idiosyncratic equivalent of topographic descriptions, typical for Museums), which were each placed in an individual storage tray. These lists identified the total number of specimens in the tray for each mineral species and the number of specimens that characterise a particular morphological type, specific varieties, pseudomorphs, mineral associations, deposits and such like (Fig. 12) These equally innovative means of documentations made it easier to evaluate the collection in terms of its mineral species representativeness and gaps. Each tray that started the next large taxon was supplied with a list of mineral species of this taxon and/or

its sub-division, including the location of the species' storage.

All together, this form of documentation worked as a form of database which could be used while working with the collection.

Display work

During its time as the IMGRE Museum, the collection had no permanent display. Stepanov organised separate thematic exhibitions in the institute's foyer and other venues. But even during his short stay at the Fersman Mineralogical Museum, Viktor Ivanovich had the time to prove that he was a master of his trade. In 1984, he was the key force in the Museum's preparation for the International Geological Congress alongside the Museum's then director Alexander Godovikov, creating and re-creating displays following long-term renovations. He was the author (and the chief deliverer of display items) for the permanent "Cave Mineralogy" exhibition, which, its scientific value aside, became an aesthetic asset for the Museum's exhibition hall (Fig. 13). The "Forms of Mineral Occurrence", co-created with A. Godovikov, was one of a kind exhibition, which demonstrated the systematics of individual and aggregate minerals based on the nature of their morphology and formation or transformation (Forms..., 2003). A "Diversity of Mineral Species" exhibition, based on Collection A's organisation and bearing a large part of its specimens, was created already after Viktor Ivanovich had passed away.

Speaking of Viktor Ivanovich's specimens at the Mineralogical Museum exhibitions, their quality can be evaluated according to the following criteria: the correlation between the specimens displayed to the overall total donated by Stepanov's collection is the highest amongst all other Museum donations.

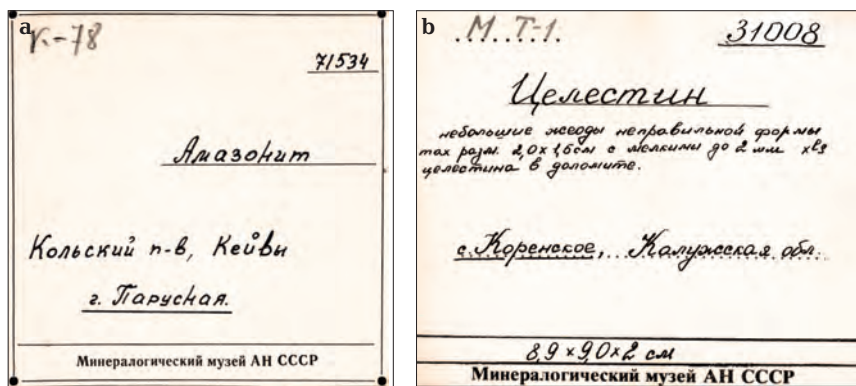


Fig. 10. Labels of the Fersman Mineralogical museum (a) until 1984 and (b) after 1984.



Fig. 13. "Mineralogy of Caves" exposition in Fersman Mineralogical Museum.

Photo: M.M. Moiseev.

cal universities. Mineralogy was no longer taught in schools. The number of amateur collectors rapidly decreased (to virtually zero, in some years). There was no interest in mineralogical specimens as a subject of collecting, even commercially. Mineralogical Museum work also decreased. Staff of scientific research institutes was largely unmotivated to preserve the already studied material. It is difficult to imagine now, the extent of spectacular mineral specimens and fascinating study material that ended up in the dumps instead of Museums and collections, just because there was no interested in collecting them. Meanwhile to obtain a specimen at the time, it was very often when all one had to do is merely bow down and pick it up.

A collection put together at such a time, which not only bears samples from deposits no longer accessible, but also contains a substantial volume of data regarding them is undoubtedly of great scientific, social and historical significance.

Equally important is that Viktor Ivanovich's personality, his collection and his ideas have all exercised a great influence on Museum work in the field of mineralogy and on the emergence of new mineral collectors. A very fair remark was made by I.V. Pekov (in his verbal presentation during the meeting at the Fersman Mineralogical Museum's, dedicated to the 90th jubilee of Stepanov's birth, January 2014) that much of what we, as Stepanov's followers today, see as obvious *a priori* givens for Mineralogical Museum, and collections work had to be first formulated and invented by him.

Viktor Ivanovich Stepanov virtually single-handedly created a collection, which is outstanding in many ways as well as developed an elegant and logical notion of museum work in the field of mineralogy at a time when it seems circumstances were least favourable. The experience that made him the most qualified and as yet unparalleled expert of mineralogical museum work is both an example, a reproach and an action plan for us, mineralogists and museum staff.

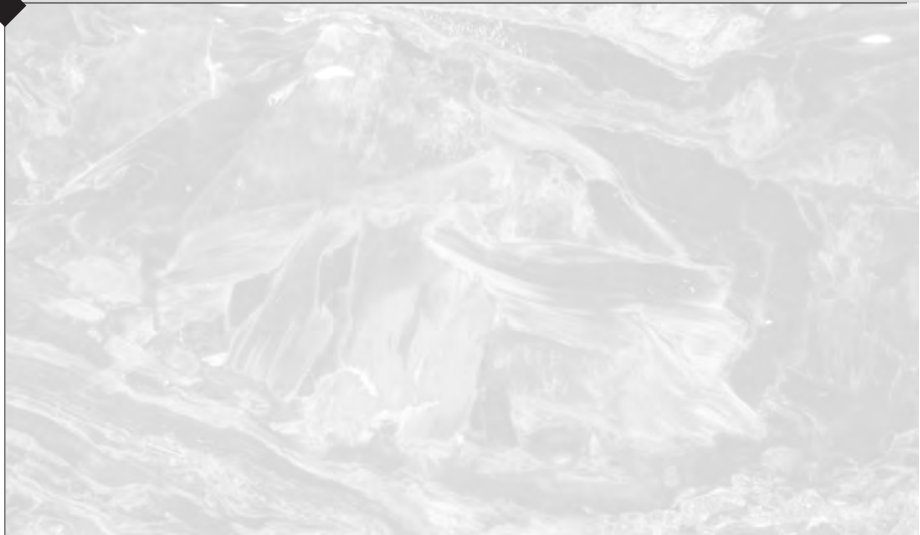
The authors express their gratitude to M.M. Moiseev, N.A. Mokhova, A.A. Evseev, D.A. Romanov and E.A. Borisova for their help in preparing this article for publication.

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Personalities



ON ADDITION TO THE BIOBIBLIOGRAPHY OF ALEXANDER E. FERSMAN

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The article supplies arguments for the necessity of publication of addition to biobibliography of academician Alexander E. Fersman, describes specifics of the material preparation to such publications. Frequency of publications dedicated to A.E. Fersman was analyzed and long-felt need of republishing of his science popularization works was emphasized.

2 figures, 17 references.

Keywords: Alexander E. Fersman, biobibliography, publications.

There were only two biobibliographies of Alexander E. Fersman (1883–1945) published. The first biobibliography was published during his lifetime in the series “*Materials to biobibliography of scientists of the USSR*” published by the Central Institute of Bibliography (Alexander Evgen'evich Fersman, 1940). The second one was published in scientific series with the same title after his 80's anniversary (Alexander Evgen'evich Fersman, 1964). The issue was not timed to coincide with the anniversary, probably to include the anniversary publications in it. 50 years passed since the day of last Fersman biobibliography publication in 2014.

The purpose of publishing bibliographies and biobibliographies of particular people is to list the work of the person and publications about him not only for the sake of cataloguing the literature on the particular person. They represent very important instrument for researcher who takes an attempt to study a subject in full depth of published material. It is clear that such a long time already is a good reason to compile bibliographical addition as A.E. Fersman works are still significant. Celebration of the scientist's 125th anniversary showed that perception of Fersman's scientific activities exposed new aspects, in the same time some of his works and achievements were forgotten. Rationalizing these facts the author started to catalog publications connected to A.E. Fersman's activities and their evaluation printed after 1964. He searched every volume of abstract journal of Geology and Geography from its establishment till present as well as catalogues of the largest Russian libraries: Russian State library (RGB), Library of the Natural Sciences (BEN RAS), Libraries of the Moscow State University (MSU) and institutions like FGUP VIMS (Fedorovskiy All-Russian Institute of Mineral Resources) and IGEM RAS (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry

of the RAS). The first results of this work were reported on the Fersman scientific session in Apatity in 2010. The list of publications accounted 228 titles devoted to A.E. Fersman and more than 30 of his own works was published in the Proceedings of the session (Ramenskaya, 2010).

Abolishing of the censorship in 1991 made sending all the published materials to the Central Institute of Bibliography not mandatory and consequently, local publications became not accessible by all of the scientific society. The author mentioned this fact in correspondence to some participants of the Fersman Anniversary lectures in 2008 with a list of found publications with request to share data they found missing in the list. However, there was no a reply to the request. Author continued the search in small libraries starting from 2010. She visited Fersman Mineralogical museum of the RAS and found there archived card catalogue of publications and public speeches of Alexander Evgen'evich himself and about him. Ekaterina Matveyevna Fersman (1902–1980), the widow of Alexander Evgen'evich, maintained the card catalogue. We were extremely grateful to T.M. Pavlova and G.A. Osolodkina, the museum employees, for the information about this catalogue. We familiarized ourselves with the four catalogue boxes by permission from directors of the museum M.I. Novgorodova and later V.K. Garanin. From the material of the boxes we found that by the 2010 we had accounted less than half of the publications. Besides the works published after 1964 there were even earlier publications. By this time the full list of articles included more than 50 works by A.E. Fersman and over 400 about him, not taking into account 170 newspaper articles, which were not included in the biobibliography of 1964. We still need to accomplish the search for publications in the period of 2011–2013 and the most labor-intensive part – to check

the titles in the list with the actual papers in libraries. Some 250 titles were possible to verify in the library of the MSU and more than 140 need to be found in other libraries. Most of them were comments on Fersman's publications and announcements of his books that did not make it to the old bibliographies. The messages about the books may not be of big interest and can be omitted, but the comments from his contemporaries after almost 70 years of the scientist's death should be documented. Not all of those references were published in special articles. Monographs, document assemblies, scientists' diaries and other fundamental publications could contain Fersman's name or assessment of his works. Correspondence of V.I. Vernadsky and B.L. Lichkov, showed an example of such reference, when Lichkov made derogatory remarks about the first and the second volumes of Fersman's *Geochemistry* and highly appreciated the third volume dedicated to the theory of geo-energy. This correspondence could not be included to Fersman's biobibliography list, as it does not fit any parameter of the genre but could be added in the appendix that lists parallel sources that a scientist can refer to by the scientist's name search only.

A bibliographer does not have to read all the material he added to the bibliography, but familiarizes with the material unwillingly. Some of the articles were impossible to leave unread. We want to inform the reader about some of the most striking materials that we collected during the work on the bibliography.

The magazine *"Chemistry and Life"* described activities of A.E. Fersman most completely and briefly: *"Mineralogist and geochemists, the organizer of the development of natural resources of Kola Peninsula, Kara Kum Desert, Urals, Transbaikaliya, the initiator of introduction of aerial photography in the scientific research, the author of fundamental works on geology, geochemistry and the writer, whose books were voraciously read by the youth..."* (Academician..., 1967). This statement was supported with quotes from Fersman's works, in which he reveals himself as an economist and coordinator of integration in mining and extraction of mineral resources, expressing care about protection of the mineral resources from high-grading.

We all know these facts about A.E. Fersman. He was the initiator of introduction of geography as one of the main school courses and became the first dean of the first Geography department in the USSR at Leningrad State University.

Few people, other than employees of Fersman Mineralogical Museum, know that Committee on Meteorites at the Presidium of Academy of Sciences had developed from the Commission on Meteorites, created by A.E. Fersman at the museum (Krinov, 1948). It is even less known, that speleological explorations in our country started under A.E. Fersman's leadership. He initiated and was on the organization committee of the First Speleological Meeting. The Meeting occurred only two years after Fersman's death (Dublyanskiy, Dublyanskaya, 1999).

The most surprising was the article published in 2006 in *Ethnographical Reports of Kola Scientific Centre of the RAS (KSC RAS)* about A.E. Fersman as an analogy of Prometheus for Saami people (Patsia, Rasumova, 2006). Fersman became a legend not only for Saami, but also for us — the readers and his admirers. He promoted this legend with his own dedication and numerous stories about life of Kola tundra and his work.

We need to give some information on the frequency of publications at the end.

Fersman's works and articles about him kept being published annually after he passed away. The curve on figure 1 illustrates the number of works published in five-year periods. It shows three peaks, two of which reflect issues of collected papers dedicated to Fersman (Alexander Evgen'evich..., 1965; Issues..., 1975; Issues..., 1976) and the third one was on his centennial anniversary, when volume of collected papers (*Development...*, 1983) was published along with journals' publications.

The collection of works issued in 1965 (Alexander Evgen'evich..., 1965) requires particular attention. It was organized in certain order as the series *"Scientists of Russia. Notes, Memoirs, Materials"* was organized and published. The first edition of the series dedicated to S.I. Vavilov was deemed to be organized by the Nobel prize laureate I.M. Frank and published in 1979 (Sergey Ivanovich..., 1979). The mentioned above paper assembly dedicated to Fersman was published in 1965 and was produced in the same way as the later first in the series on S.I. Vavilov and other in the row. D.I. Shcherbakov wrote the feature article in the book on the life and activity of the scientist. The book also contained archive letters and manuscripts of unpublished articles and more than 70 memoirs from his followers and colleagues. Thus, we could label this issue the first predecessor of the series *"Scientists of Russia..."*.

The second curve (Fig. 2) shows period from 1976 to 1988 in more details showing pub-

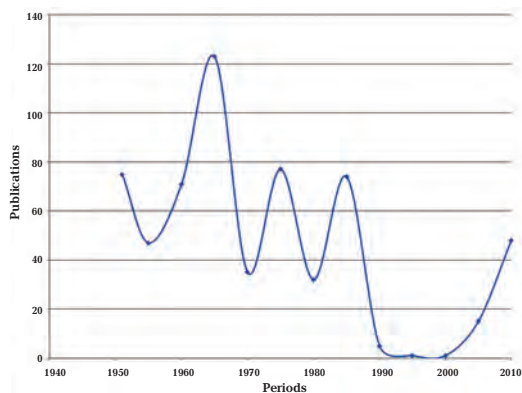


Fig. 1. Frequency of publications about A.E. Fersman during 1940–2000 in five year periods.

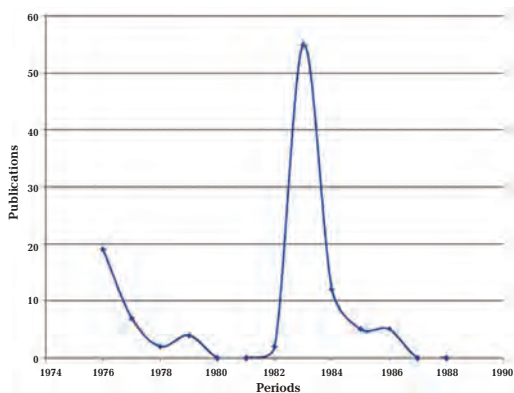


Fig. 2. Annual frequency of publications in the period of 1976–1988.

lications peaking in the centenary 1983 and declining to none later in the decade. There was no publications in 1980, nor later after the anniversary, either and in the years of Perestroika, same in the following post-Soviet times. The rise in papers in 2003 and later (Fig. 1) was due to the issuing of *"Unknown Fersman"*, published by the Mineralogical Museum (*Unknown Fersman*, 2003), Fersman sessions in Apatity and establishing of *Tietta* magazine, which had at least one article on Fersman in each issue and regularly two or three. This magazine published forgotten and unpublished works of Fersman. There was only a small collection of papers published to Fersman's 125th anniversary in Moscow (Fersmans Lectures, 2008) and articles in central newspapers apart from the journal.

The publishing pattern of Fersman's science popularization works looks less optimistic. Potential of modern publishing industry supply great options to reprint his *"Remembrance of the Stone"* and *"Popular Mineralogy"*. Almost 20 years passed since publication of the last issue of *"Remembrance of Stone"* (Fersman, 1996) and the last issue of *"Popular Mineralogy"* in Chelyabinsk (Fersman, 2000). The last issue of Fersman's *"Popular Geochemistry"* in Russian was published only in 1959! It was published later only abroad in Bulgarian and Spanish. The Spanish issue in 1972 was the last one.

We do not share the opinion that the book *"Popular Geochemistry"* was outdated. This science searched for new regularities in mineral deposit formation and gathered material on the issues that were already questioned in Fersman's time and were reflected in the book. The new geochemical data collected after Fersman's time could be placed in the appendix to the book. Only notes on the new notion

of geochemical barrier would need a special chapter.

The stories about gemstones and traveler's stories will never become outdated.

An authority leadership is needed to help our children to have their wonderful Fersman's books and articles, which helped many of us in our time to choose career path in geology.

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VIKTOR IVANOVICH STEPANOV – UNIQUE MINERALOGIST AND INEXHAUSTIBLE TOILER

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Viktor Ivanovich Stepanov (1924 – 1988) was unique expert mineralogist, encyclopedic mineralogist. He worked on deposits of various genetic types. He collected the largest mineralogical collection and donated it to Fersman Mineralogical Museum. His interest turned to speleology and mineral formation in caves during last years of his life.

1 table, 1 figure, 4 references.

Keywords: V.I. Stepanov, mineral, mineralogist, mineralogical collection, mineralogical museum.

It is hard to write about Viktor Ivanovich Stepanov after brilliant memoir sketches written by Arkadiy Grigoryevich Zhabin (Zhabin, 1992; Zhabin, 1993). I remember my first year at the university in 1949 – 1950 and my first acquaintance with Viktor. It happened after he switched job from Moscow Geological Prospecting Institute (MGRI) to Lomonosov Moscow State University (MSU) and started going to field trips in Moscow region searching for interesting specimens. He went with us, the freshman students every weekend and taught us mineralogy and also good communication. We usually sang geological songs on a train back. I remember well Podolsk open pit and wonderful druses of quartz, almost amethyst. After graduation from the University he received a job at the Institute of Geology of Mineral Deposits, Petrography, Mineralogy and Geochemistry (IGEM), where he began to study mineralogy of very complex Upper Kayraky tungsten deposit. Then he went to work with Institute of Mineralogy, Geochemistry and Crystallography of Rare Elements (IMGRE) in 1963. Viktor had a cast-iron nature and told the truth flat out, so he could not assimilate at IGEM and started to work at IMGRE. Kuzma Alekseyevich Vlasov was the director of the institute then and had a dream to create a museum of rare elements' minerals. He knew Stepanov as an excellent mineralogist and asked him to start gathering the museum. It began with small cabinets, where specimens collected by K.A. Vlasov and his colleagues in field trips and expeditions were stored. Those specimens originated from the famous vein No 3 of Koktokay pegmatite deposit in Xinjiang Region (China), specimens of vanadinite from Mibladen deposit (Morocco), uraninite from Czech deposits and other.

We need to deviate from the topic and introduce some facts from of Viktor's Ivanovich biography. He was born in town of Semenov on

Volga River (former Gorky, now Nizhii Novgorod Oblast). His family was not connected with geology at all. His parents: father Ivan Alekseyevich Stepanov and mother Capitolina Trophimovna originated from craftsmen's families. It is not clear how he became interested in mineralogy, but he was fall in it since his school years. Viktor participated in activities of regional natural history club and took participant at All-Union Agricultural exhibition in Moscow in 1939. He was admitted to Sverdlovsk Mining Institute in 1941. After the Great Patriotic War (1941 – 1945) began he was evacuated to Middle Asia. He had not finished the first year of study and worked as a worker (collector) in geological expedition. Viktor Ivanovich was called up for military service in autumn of 1942 and was sent to infantry school. After graduation he fought on 3rd Ukrainian forefront, suffered contusion, was wounded at the force a crossing of Dnestr River. When recovered from injuries he worked as a translator from German and then served as a translator from Bulgarian in Bulgaria. Upon his separation from the military, he was admitted to Moscow Geological Prospecting Institute (MGRI) and worked in expeditions in the same time. He transferred to Geological Department of the Moscow State University from MGRI and graduated from the University in 1952.

Stepanov became a junior and later senior research scientist at the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements (IMGRE). There he created Museum of Rare Elements, which in quality and quantity could compete with the largest mineralogical museums of the world. He created it with his own hands in did it in hard environment. Working in sporadically flooded basement he created systematically ordered mineral collections that contained unique specimens. Product of his creative work was a collection that had national significance. It accounted some 30000 speci-



Fig. 1. Viktor Ivanovich Stepanov in 1960-s. Photo from IMGRE archives.

mens, representing 1300 mineral species. He was extraordinary particular to the quality of specimens and elaborated his own scale of specimen quality (Table 1)*.

Deep interest to minerals was a true vocation of Viktor Ivanovich. He helped colleague at the institute to identify minerals a lot and often such consulting turned into discussions. It was hard for him to work in the dark, dump and frequently flooded basement. Nevertheless, he have never worked during only "official hours" (nine-to-five) as it felt like he lived there. I remember that he was to Equatorial Africa and washed samples in rivers and swamps as he told that "if you wash yourself, the samples also need washing". He caught some terrible infection and only thanks to the fact that the trip was held on behalf of the United Nations effective medicines were found and he recovered.

It is interesting to quote Viktor Ivanovich's report about his activities as follows:

The report of V.I. Stepanov for the period of 1979–1983.

For the reporting period intensive work on ordering and replenishing of the IMGRE collection was carried out, which took 60 % of the time.

This work included the following:

1. *Unpacking and sorting samples from the boxes brought from the closed storages (90 boxes).*
2. *Specimen preparation. Significantly improved quality of the collection – the main time consuming subject.*
3. *Writing labels on the specimens and ordering specimens of the collection.*

4. *Identification of minerals in the standard collection – the following mineral groups were sorted: bismuth tellurides, garnets, pyroxenes, amphiboles, micas, chlorites, minerals of sodalite group, zeolites, barite-celestine, Mn-hydroxides, and range of single specimens of various minerals. 110 complete microprobe analyses and 20 chemical analyses were done totaling of 600 identifications with various methods. Glaring identification mistakes were found, which according to the reference literature and collections of other museums were typical. Apparently IMGRE has the most accurate standard collection of minerals.*

5. *110 new minerals were purchased, so the total number of mineral species reached 1300 (the third place in the USSR). The collection replenished with 1100 specimens.*

6. *13 papers were published, 3 of which in foreign periodicals. Three new minerals were described and 4 first discoveries in the USSR were made.*

7. *Presentation an oral report on European conference on speleology in Sofia (Bulgaria) in 1980 and submitted written report on XIII session of International Mineralogical Association in Varna (Bulgaria) in 1982.*

Participation in giving speeches on visiting sessions of Moscow division of All-Union Mineralogical Society in Chernogolovka in 1980 and 1983. Participation in analysis of material and report writing, the chapter Mineralogical peculiarities of mercury deposit Chauvai (Kyrgyzstan) in 1980.

8. *Went to works in the field in 1980 (Chauvai deposit, Middle Asia), in 1981 (Katugin deposit, Chita region) and in 1982 (Malyshevo deposit, the Urals) for the collection of IMGRE.*

Significant part of time was spent in struggle with flooding of the working area and the museum. The archive of K.A. Vlasov, one third of my books and many valuable specimens perished in the accidental flood. The hazard of future floods has not been eliminated.

June 1, 1983. V.I. Stepanov.

Viktor Ivanovich was interested in all kinds of investigations in mineralogy. He was very educated person. As A.G. Zhabin wrote, Stepanov had "encyclopedic, wide and accurate knowledge in mineralogy" (Zhabin, 1992). His scientific activity in the last years at IMGRE and then in Fersman Mineralogical Museum was

* – This quality scale of specimens was placed as it was on the author's sketch note and we cannot completely explain his logic. His most important idea was to formalize the principles of evaluating mineralogical specimen by three most important various categories. It was not so important number of grades in each category. The most significant was the criteria, features and the system to use for qualifying a specimen to lower or higher grade in each category. It is worth noting that naturally shaped druses are more valuable than ones that were shaped by a specimen, while massive specimens were in the contrary more valuable when shaped to a standards. This rationalization of quality assessment is very functional in comparing similar specimens when it is difficult to make a choice for purchasing, exchange or sorting collection for quality of specimens and other occasions (noted by Editor).

Table 1. The Scale of Specimen quality elaborated by V.I. Stepanov in 1970-s

Grade	Aesthetic appearance	Rarity of the mineral: 1) morphological 2) by genesis 3) regional	Level of study, value to be studied (also through connection to activity of a famous scientist)
10	Spectacular immaculate druses (extrashow)	Absolute unique (a single specimen of species, unique size, morphology, coloration)	Specimen of original discovery
9	Spectacular immaculate druses with some faults	Unique in the USSR (only few specimens of a specie)	Author's material of original description; specimen belonging to historical collection
8	Druses, cabinet size specimens but not perfect shape or coloration (not picturesque)	Unique for the time of evaluation (with likelihood of another find)	Unusual chemical composition
7	Trimmed picturesque druses	Very rare (single deposit in the world)	Original specimen of the first discovery in the USSR
6	Same as 7 with minor flaws	Rare	The first discovery in the region (original specimen), or specimens of other collection from the type locality in the USSR
5	Trimmed druzes 1) Picturesque spherulitic druzes	Relatively rare	Type locality
4	Trimmed scenic polished sections: 1) Large singular (crystals); 2) Trimmed massive very attractive specimens	Infrequently occurred	Original of a specific work with the data or having published data on the similar specimens
3	Trimmed to standard size massive picturesque specimens: 1) Small separate groups of crystals; 2) Picturesque not trimmed specimens	Relatively common	Rare specimen with confirmed identification
2	Trimmed to standard size massive specimens	Common	Ordinary specimens with confirmed identification or ones with rare species without confirmed identification
1	Not trimmed or shaped regular specimens; massive regular fragments, chips, sand, thin section; trimmed unattractive specimens	Very common	Ordinary not studied specimens

connected to the new and very interesting area of the searching for criteria and means to interpret history of ore mineral aggregates' formation in open cavities. In connection with that he was absorbed in speleology and took part in International Speleological congress. V.I. Stepanov joined A.E. Fersman Mineralogical Museum in 1986 and donated his personal collection to the Museum (Nikiforov, Shkursky, 1998).

Main milestones of Viktor Ivanovich Stepanov's life were as follows:

1941 – 1942 – student of Sverdlovsk Mining Institute;

1942 – worker (collector) of Gurjivas Geological Expedition (Dushanbe);

09.1942 – cadet in Gomel infantry school;

01.1944 – 11.1944 – officer in command of infantry platoon;

11.1944 – 10.1945 – translator from German;

08.1945 – 10.1945 – student of Defense Language Institute of Red Army;

10.1945 – 03.1946 – translator from Bulgarian language;

03.1946 – 06.1946 – court secretary of the Military Tribunal;

09.1946 – 10.1950 – student of the Moscow Geological Prospecting Institute (MGRI);

05.1949 – 05.1950 – foreman geologist in Karavshin Geological Expedition MGRI;

05.1950 – 05.1952 – junior scientific researcher in Kazakhstan expedition of the Institute of Geosciences of the RAS of the USSR;

10.1950 – 06.1952 – student of geological department of Lomonosov Moscow State University;

07.1952 – 08.1955 – mineralogist in Upper Kayraky Geological Expedition;

08.1955 – 02.1956 – junior researcher in expedition No 1 at IGEM (Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the USSR Academy of Sciences);

02.1956–04.1963 – junior researcher of mineralogical department of IGEM;

05.1963–06.1973 – junior researcher at IMGRE (Institute Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements);

06.1973–04.1986 – senior researcher at IMGRE;

04.1986 – start to work at the Fersman Mineralogical Museum.

In spite of his highest mineralogical qualification V.I. Stepanov did not have many published works. List of his publications is below. He did not have titles and it was not important for him or people around him. Such experts dedicated to their work are rare and it is important that people would know them. Researchers of the Fersman Mineralogical Museum named a new mineral vistepite $[\text{Mn}_4^{2+}\text{SnB}_2(\text{SiO}_4)_4(\text{OH})_2]$ after Viktor Ivanovich (Pautov *et al.*, 1992).

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DMITRIY ALEKSEEVICH GOLITSYN – DIPLOMAT, ART CRITIC, SCIENTIST AND COLLECTOR

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The article describes Russian diplomat Dmitriy Alekseevich Golitsyn (1734–1803). Facts of his activities, scientific work, mineralogical collection are presented.

3 figures, 12 references.

Keywords: D.A. Golitsyn, mineral collection, history of science.

The history of Russian amateur mineralogists of 17–19 centuries is not yet written. There were remarkable people among them, government officials, the rich, peasant stone prospectors, mining officials and intellectual commoners. They discovered many new minerals, preserved precious and important forms of nature, our big national collections could not be composed without their efforts.

V.I. Vernadsky (Thought and notes on Goethe as a naturalist)

There was an article “*News from Yena*” published by the author in Mineralogical almanac “*In the World of Minerals*” in 2008. It was dedicated to the finding of several specimens from the collection of prince Dmitriy Alekseevich Golitsyn. The note was a part of a bigger article and now the time has come to publish the whole material on the topic.

This work is a research paper based on few primary sources of information with one major reference. We decided to introduce the paper about the man *from the past* with a story about our contemporary, Grant Konstantinovich Tsverava, the author of the book on D.A. Golitsyn's life. The unintentional analogy between the diplomat, polyglot, scientist and educator and the author of the book will be cleared below. The book of G.K. Tsverava “*Dmitriy Alekseevich Golitsyn. 1734–1803*” published in 1985 is the only complete work of biography of our prominent compatriot. The book is both serious scientific study and very absorbing reading, which rarely combine. The seriousness of the completed research can be illustrated by the bibliography list of over 400 items, most of which were archive documents in German, English and French. G.K. Tsverava wrote many other books on history of science and technology besides biography of Golitsyn. The book on French radical politician Jean-Paul Marat, Hungarian scientist Nikola Tesla, physicist Georg Wilhelm Richmann, series of articles “*From the history of Russian-Swedish Scientific relations of the 18th century, Philosophy and Physics*” and many other. Astonishing variety of topics of his

works leads us to think that he dedicated his whole life to the history of science. We would be mistaken. Surprisingly, Grant Konstantinovich his whole life worked in the field of electrical engineering at Boksitogorsk aluminum plant far away from big cities' research institutes, libraries and archives. “*It is surprising how Tsverava, living in the country, obtained unique material on the foreign scientists... his communication with foreign experts, historians, open-mindedness, clarity of ideas, wonderful memory and language skills contributed to his success*” – a person, who knew Grant Konstantinovich well wrote in memorial article about him (Sverdlova, Chistyakov, 1994).

Some facts in this paper originated from a fine article “*Dmitriy Alekseevich Golitsyn. His life and work*” by Wendell Wilson (Wilson, 1991).

All the citations from D.A. Golitsyn's correspondence and works placed here as published in Tsverava's book.

Academician Georgy Sergeevich Golitsyn, the director of Physics of the Atmosphere Institute of the RAS, provided the picture of D.A. Golitsyn portrait sculpture (Fig. 1). He carried out a big research work to find portrait of D.A. Golitsyn as there was no portraits known before his research in 2000. G.K. Tsverava wrote that no portraits of Dmitriy Golitsyn existed except for the known silhouette.

Let us return back to the 18th century...

The history of Russian mineralogy roots into the time of Peter the First and is connected to the names of Mikhail Vasilyevich Lomonosov, Peter Simon Pallas and Johann

Gottlieb Lehmann. They were the first to write works on mineralogy in the period of very intensive data acquisition in expeditions and collection gathering. Vasily Mikhailovich Severgin was usually regarded the most prominent person of the second period of mineralogy development – the period of “active analysis of collected facts and ordering them”. He became the first and the most noticeable scientist of qualitative descriptive mineralogy in Russia (Grigoryev, Shafranovsky, 1949). It is true. However, he was a successor of the author of the “*Collection of the Names in Alphabetical Order That Are Used in Mineralogy for Earths, Stones, Metals and Semi-metals and Rock Tars*”. Severgin cited complete paragraphs from that work in his “*Detailed Mineralogical Dictionary*” (Tsverava, 1985). It was diplomat prince Dmitriy Alekseevich Golitsyn who was the author of the “*The Collection of Names...*”. That work was written in French and was not well known in Russia. It was translated by American authors of “*The System of Mineralogy*” and listed among the “fundamental works” in 1946.

Biography milestones

The prince Dmitriy Alekseevich Golitsyn was born on May 15, 1734. His grandfather, Ivan Alekseevich Golitsyn was a stolnik at the court of Ivan V Alexeevich, the brother and coregent of Peter I. I.A. Golitsyn married princess A.P. Prozorovskaya. Anastasia Petrovna Prozorovskaya was a dominatrix and socially active person who moved in the circle of Peter the Great and his wife, the future Empress Catherine the First. The Golitsyns couple deceased in 1729 and was laid to rest in the Lords Epiphany Cathedral in Epiphany monastery. This monastery is one of the oldest in Moscow deemed to be found in 1296. The Epiphany Cathedral was a burial place of many noble Russian persons: Golitsyns, Dolgorukiys, Saltikovs, Yusupovs, Sheremetyevs and many others (Kondratyev, 1996).

Feodor Ivanovich and Alexey Ivanovich, sons of the Golitsyns' couple were born in Moscow. Aleksey was a warrant officer in the Butyrsky regiment. The regiment fought in all the wars Russia was involved in from the second part of the 17th and all of the 18th century. A.I. Golitsyn received family estate Spasskoye, Gubino and Gireyevo (Novogireyevo now) in Moscow County. By the petition of Ivan Golitsyn the stone church of the Holy Image of the Savior Not Made by Hand was built in the estate. The church is still there.

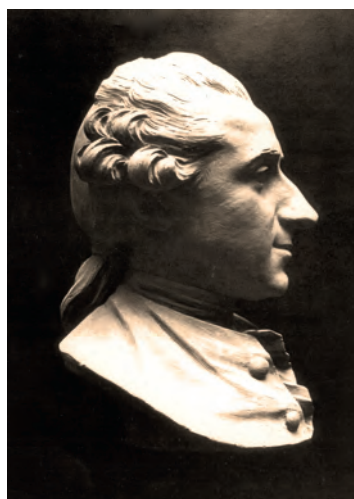


Fig. 1. Sculpture portrait of D.A. Golitsyn (Gallitzin) by Marie-Anne Collot. 1766. Terracotta.

Aleksey, the younger son of A.I. Golitsyn got married to princess Darya Vasilyevna Gagarina in this church.

Five sons: Ivan, Petr, Feodor, Aleksey, Dmitriy and a daughter Ekaterina were born to the family in the period 1729 – 1735 when Butyrsky regiment was not in a campaign. Tsverava suggested that all of them were born in their Gireyevo estate. This version is supported with fact that officer of Butyrsky regiment could not always live in Petersburg and that the Golitsyns being in disgrace during the reign of Anna Ioannovna, preferred to “take shelter in their family estates”. It is important though, that the Brockhaus and Efron dictionary and consequently later similar reference books stated that D.A. Golitsyn was born in Petersburg.

A.I. Golitsyn took part in the Russian-Turkey war of 1735 – 1739 with his regiment and died most likely in battle on 5 June 1739.

The 1730-s were very hard decade for Russia. Sergey M. Solovyov wrote that unprecedented tasteless luxury of the Court in the “very poor nation” worsened with dominance of Germans who disdained and relentlessly robbed the country (Tsverava, 1985). Other things made it even worse: reestablishment of the Secret Office of Investigation, crop failure in 1733 followed by the famine, the war with Turkey finished with adoption of the Treaty of Belgrade that brought to naught all the gains of the war.

In this situation the widow with small children was easier to survive in the estate near Moscow. However, the boys needed education and after coronation of Elisaveta Petrovna the family moved to Petersburg to the house on Vasilyevsky Island.

The widow with little wealth and many children had only possibility to educate her sons in Cadets Corps. It was established for young noblemen to become officers bypassing compulsory soldierly service.

Students of the Corps studied common educational subjects together with the military ones "since not every persons' nature is inclined only to the military". They learned mathematics, history, geography, artillery, fortification, fencing, equitation and "other sciences demanded in the military art". Also they studied German, French and Latin, writing and grammar, rhetoric, drawing, dancing, morality, heraldry and other.

It is known that all the Golitsyn brothers were officers. No documents left on this fact, but we can suggest they all had graduated from the Cadet Corps. Dmitriy Alekseevich served in army as a captain upon graduation and then was transferred to Office of Foreign Affairs the Russian central agency dealt with external politics.

Diplomatic staff rejuvenation was a crying need at the end of the reign of Elisaveta Petrovna. The writ from April 14, 1758 ordered to assign "three dignified young persons from the nobility apt to become titular counselors" to each minister (ambassador). According to the "Name list of the circulating at foreign courts..." "acting gentleman-in-waiting prince Dmitriy Alekseevich Golitsyn" was an ambassador to Paris and "the chancellor counselor Feodor Chernov, captain prince Dmitriy Alekseevich Golitsyn were appointed at his authority". This citation was dated from 1760. D.A. Golitsyn likely manifested himself as a "dignified and apt" student at the Corps and in the writ order was sent to Paris to learn diplomatic intricacies with the guidance of his relative.

Many of the Golitsyns family dedicated themselves to diplomatic career. The family was well known in Paris where young D.A. Golitsyn was directed. Alexander Mikhailovich Golitsyn was Russian ambassador to France in 1749–1755 followed by Dmitri Mikhailovich Golitsyn, who continued the service till 1761.

Dmitriy Alekseevich came to Paris in a difficult time. Russian-French relationships were not stable. They worsened when recently assumed power Peter III signed a separate peace treaty with Prussia. The French ambassador Louis Auguste Le Tonnelier, Le baron de Breteuil was recalled from Petersburg with the following withdrawal of Russian ambassador count P.G. Chernyshev from

Paris, leaving Nikolay Khotinsky as an embassy counselor in charges d'affaires. "I was not surprised that he preferred this gentleman over me", D.A. Golitsyn wrote later to the vice-chancellor A.M. Golitsyn – "neither the Golitsyns, nor other noble person... would be in Mr. Chernyshev's favor". Golitsyn ended his letter with request to authorize him in charge d'affaires. This promotion was made in August of 1762 and already in the fall of next year Catherine the Great, valuing the talents of the young diplomat, appointed him to the "minister plenipotentiary at the Versailles Court in the rank of chamber valet".

Meanwhile the relations between Russia and France worsened and at the end "prince Golitsyn was ordered to leave Paris without an audience". Golitsyn's last letter from Paris was dated 1767 and most likely he left French capital the same year.

Tsverava wrote little about Golitsyn's diplomatic activity in France, mentioning only "his intelligence, a habit of observation and high level of culture favored success of Russian external politics in the first unsecure years of reign of Catherine the Great". This activity also included an aspect, which in modern language we could name as *attaché* on issues of culture, science and technology.

The high rank and personality of the young diplomat opened him doors to Paris's saloons, where he could meet and come close with the most prominent people of the French Enlightenment. He found trust and respect from such people as creators of Encyclopedia: Denis Diderot and Jean Le Rond D'Alembert, writer Jean-François Marmontel, economists François Quesnay and Viktor Mirabeau, philosophers Claude Helvétius and Paul-Henri Holbach, historian Gabriel de Mably, sculptor Étienne Falconet. "Each of them made his own impressions in Golitsyn's mind and owed him friendly help, moral support, hospitality and at last patronage of the great Empire". Golitsyn met English historian and philosopher David Hume in Paris and translated his works into French. His activities benefited Russia in many respects.

Golitsyn participated in purchasing and delivering to Russia all the volumes of famous French "Encyclopedia or Explanatory Dictionary of Sciences, Arts and Trades" in 1773. It will be to add that the article on Russia was created with Golitsyn's participation supplying materials and information on our country.

Golitsyn persuaded Catherine the Great to purchase the library of Diderot that acco-

unted 2900 volumes. He also used to send recently published works of Voltaire to Russia with the first occasion. He had correspondence with him and they possibly met.

D.A. Golitsyn attended meetings of the Paris Academy of Science and was in the course of scientific achievements and frequently wrote about them to the Motherland. He sent in his letters drawings of 12 phases of sun eclipse of 1764, notes on bridge construction in France, successful operation on eyes of born blind adolescent and other information.

The Empress also trusted the taste of her ambassador. Golitsyn selected and purchased art masterpieces in Paris and Hague to send to Petersburg piece by piece and as entire collections. Those paintings now add to the world's fame of The State Hermitage. "Return of the Prodigal Son" by Rembrandt, "Perseus and Andromeda" and "The Landscape with a Rainbow" by P.-P. Rubens were among the paintings purchased by Golitsyn. Precious purls from Crozats' collection stand out from the other paintings: "Bacchus" and the "Portrait of Waiting Maid" by Rubens, his sketches to series of "Life of Maria Medici", five pieces from Anthony van Dyck including his "Self-Portrait", seven paintings by Rembrandt including "Danaë", "The Holy Family"; Italian Renaissance masterpieces: "Judith" by Giorgione, "Danaë" by Titian, "The Lamentation of Christ" by P. Veronese and "The Birth of St. John The Baptist" by J. Tintoretto.

Golitsyn was the one who was involved with invitation of Etienne Falcone to Russia. Falcone signed a contract to build the monument to Peter I on August 27, 1766.

D.A. Golitsyn assisted students of Petersburg Academy of Arts, who came to Paris for internship. The Academy asked Golitsyn to "look after" its alumnae in one of the letters. Well-known painters A.P. Losenko and S.F. Shchedrin, sculptors F.G. Gordeyev and F.I. Shubin, architectures I.E. Starov and V.I. Bazhenov were among of the students who were taken care of by the prince. Dmitriy A. Golitsyn was elected an Honorary Member of the Academy of Arts in admittance of his merits.

D.A. Golitsyn had to withdraw from Paris for reasons of high politics as it was mentioned. He did not want to leave the capital and tried to ask permission to stay to "continue his education" and even asked his Petersburg protégé Falcone solicit the Empress for his stay. He received the answer on November 29, 1767: "He has to leave Paris...

in the end he will have a chance to practice his God's given talents with benefit in the Patria".

Dmitriy Alekseevich did not rush back to Russia using his health issues as an excuse to go to Aachen spa. There he met Adelheid Amalie, a daughter of Samuel Graf von Schmettau, Prussian field marshal. The acquaintance grew into mutual affection and the young couple got married on August 14, 1768 in a church in Aachen. The trip to Russia became the honeymoon for the couple. The Golitsyns came to Petersburg in October, 1768 and had reception with Catherine the Great. Documented fact of Golitsyns presence in Petersburg was only that Dmitriy Alekseevich was granted a title of acting gentleman-in-waiting and a rank of secret councilor was appointed "plenipotentiary minister at General Unites provinces of Lower Netherlands". Daughter Marianna was born to the Golitsyns on the way to Hague on December 7, 1769 and son Dmitriy was born on December 22, 1770 upon the arrival to Hague.

To finish the story about the Golitsyn's family we need to tell, that the marriage happy at the start practically ended in 1780, nevertheless the couple kept friendly relationship all their life. Dmitriy Alekseevich visited his wife and children who resided in Munster in Westphalia.

The information about daughter of D.A. Golitsyn is very scarce. It is only known that Marianna-Dorothea Golitsyna (1769–1823) in marriage had name of the princess Salm-Reifferscheidt-Krautheim.

Dmitriy, the Golitsyns' son was received into Roman Catholic Church in 1787, went to Baltimore and entered Catholic Seminary. Father Demetrius was ordained on March 16, 1795 and became the second priest that was ordained on American land. Father Demetrius served 40 years as a country priest known as Augustine Smith and died in Loreto (USA) on May 6, 1840. Gallitzin, a town in Pennsylvania was named after him.

And again back to his father. D.A. Golitsyn started a new chapter in his diplomatic career in 1770. Service in Holland gave the Russian ambassador a chance to "write few new pages to the Russian diplomatic history". It was meant establishing of diplomatic relationship with United States of America that proclaimed independence in 1776. The British colonies in North America were supported in the war for independence by France, Spain and Holland. The war was lead mainly at sea and had very negative impact

on the sea trade. The diplomatic way to solve the problem was more effective. Russia declared famous declaration on armed neutrality in February 1780. It gave possibility to neutral countries to continue free sea trade during the war even with the countries participating in a war. All the interested countries including France and Spain recognized the declared right to neutral navigation. Historians still look for the answer who was the actual author of the declaration. Research of N.N. Bolkhovitinov, the most prominent Russian specialist in American studies, showed that it was "D.A. Golitsyn, who the most likely inspired and outlined if not authored the draft document" (Bolkhovitinov, 1991). Russia did not recognize the USA before the war was over in 1784. Meanwhile, Golitsyn kept in contact with the representatives of the United States who resided in the country. He did it in spite of the prohibition issued to him "to receive or visit Mr. Adams or any other person, accredited from the colonies, separated from Britain" (Bolkhovitinov, 1991). This initiative had a big cost to Golitsyn who was withdrawn in 1782 and was appointed to ambassador to Turin. It was significant career downgrade and in the end of next year of 1783 he submitted resignation and chose to reside in Holland.

Dmitriy Alekseevich wrote some works on economics. He expressed his ideas in very typical for him form of letters. At least 16 letters on economics written by Golitsyn are known. They were addressed to the vice-chancellor A.M. Golitsyn, but were directed to the attention of the Empress. Her numerous notes on the edges support this fact. These small compositions were focused on various economic issues in different periods.

Golitsyn verbalized ideas on the forms and means how to eliminate serfdom in Russia. He wrote on September 30, 1770: "By granting peasants the property I meant the following:

1) Their liberation, meaning ownership of their own personal lives, no other type of property is possible if this one does not exist;

2) Movable property, their household goods and other; and at last,

3) Permission to ones who are able to purchase land on their own and own the land as we, the masters do; which will form their land register estate with time".

The naturalist, mineralogist, collector

Golitsyn was a true man of his time, the time of encyclopedia writers and had very

wide interests: studied economics, art, history and politics and also explored the area of booming natural sciences. Natural sciences were developing more dynamically in The Republic of the United Provinces than in the rest of Europe. There were six universities and some 20 scientific societies in Holland at the time. Royal Netherlands Society of Sciences and Humanities, the oldest and the best known of them is still active. Works of Dutch scientists became recourse books for the first generation of Russian natural scientists.

D.A. Golitsyn could not be isolated from those activities. He decided to dedicate himself to natural sciences in the middle of 1770-s. His resignation followed few years later gave him free time to accomplish his dreams. "Changing his lifestyle he challenged Russian aristocracy in certain way as no one from Russian nobility did before descending "so low" to be occupied in physics or chemistry".

Golitsyn dedicated 30 years of his life to science, which put him on the same level as most prominent naturalists of the time. His interests in science were very wide: from physics, chemistry, geology, mineralogy, volcanology to medicine.

He carried out tests on nature of electricity in a laboratory and also in the field. The result of his studies was a series of works on electricity. The article "Letter on some subjects of electricity" was his first published work. It was his works with electricity that made a reason to elect D.A. Golitsyn an honorable member of Petersburg Academy of Sciences on September 13, 1778. He felt part of the highest scientific agency in the country and helped the Academy as much as he could. Brussels Academy of Science chose Golitsyn to be a foreign member in the same year.

In the spring of 1793 revolution-struck France was at war with almost all the countries in Europe including Netherlands. Russia also broke diplomatic and trade relations with France. D.A. Golitsyn in this situation had to leave Holland just before the French troops occupied the country.

A reasonable question arises about why the diplomat did not return to his country. Many facts can explain that. First of all, after Paul I coronation he was not remembered and called to the court. At second, he was close friend to French politicians and scientists, supported reformation of the serfdom law and could well fall into disgrace. At third, he did want to have opportunity to see the fami-

ly. Golitsyn moved to Braunschweig, the German town halfway between Berlin and Munster, where his wife and daughter lived. He moved there his large library, laboratory and mineralogical collection.

Now we came close to the subject matter of Golitsyn as mineralogist and collector.

Dmitriy Alekseevich Golitsyn in this period started to be more involved in mineralogy and collecting minerals. He began enjoying his new hobby already in Holland in 1780-s. As with most people, his interest started from collecting. His first mineralogical trips were to Germany. Extinct volcanoes near Bonn and Spessart plateau in Bavaria became his most popular places for mineral search. Golitsyn did not limit his activities to sample collecting. He started to immerse deeper into the new subject of his interest as a true scientist. "The zeal he utilized to acquire fundamental knowledge in all aspects of physics" was directed now to the thorough study of mineralogy, "the new discipline that was developing before his own eyes and that completely absorbed his attention and brought recognition later in his life".

D.A. Golitsyn started to study descriptive mineralogy in the time when so called naturalistic systematization approach initiated by Abraham Gottlob Werner dominated. Werner's system was based on supremacy of visual characteristics in classification. He thought that chemical composition was clearly displayed in the "exterior features, which can determine essential difference in fossil species" (Goryainov, 1835). Chemical composition exclusively could neither be a basis for an accurate classification. Jean Baptiste L. Romé de l'Isle published his "Crystallography or Description of Forms Essential to all Bodies in Mineral Kingdom" in 1783. René Just Haüy published five volumes of his "Traité de Minéralogie" in 1801, which anticipated contemporary approach in mineral classification. We need to draw reader's attention to the fact that back then "mineralogy was a voluminous science about inorganic world as a whole" (Grigoriev, Shafranovskiy, 1949) and branching of mineralogy from geology started only at the end of the 18th century.

Geosciences were blooming in those years. Many fundamental works were written then and works of D.A. Golitsyn were also noticed. He published at least 11 papers during 15 years of hard research work.

Among those he wrote two fundamental papers: "The Work on Brief Description of Minerals" (Gallitzin D. "Traite ou Description ab-

reege et methodique desmineraux", Maestricht) published in 1792 and "The Collection of the names in alphabetical order that are used in mineralogy for earths, stones, metals and semi-metals and rock tars" (Gallitzin D. "Recueil de noms par ordre alphabetique appropriés en Mineralogie aux terres et pierres. Aux mataux et au bitumen...", Brunswick) published in 1801. We will get in details of these books.

The "Traite..." had five issues published in 1792, 1796, 1801, 1808 and 1815. The work was based on the ideas of French naturalist Georges-Louis de Buffon. They met in 1760-s in Paris and Golitsyn had correspondence with Buffon for several years. He suggested systematics of minerals in his work, following Buffon's ideas which he resumed in the following: "Genesis of the bodies in mineral kingdom is the principle I prefer and will follow as long as I can. I think that it is more advantageous to others not just because it is an idea of a great person, but for it leads to the true goal. This primary goal is in the most generalized classification of objects..., reduction in number of species, which can be nothing but varieties and obstruct studying of mineralogy with multistep divisions". The author divided minerals into "8 ranks or families, which, in turn divided into classes and varieties". Down the text detailed data on almost all minerals known by that time was given in order according to the classification. The description of minerals was featured with historical facts. The names were given in Latin, French, Russia and German. The next edition was published after discovery of series of new minerals.

"The collection of Names..." was one of the last D.A. Golitsyn's works and practically was a mineralogical dictionary. It contained explicit data on known minerals and rock types. It had several editions and the second edition was published after Golitsyn had read the work of Haüy. He wrote about it: "The exceptional "The Mineralogy Course" by Mr. de Haüy... made necessary a new addition of "The Collection of names...". This "Course" helped me to realize my mistakes... I did not think twice deciding to use the guidance of this excellent work in mineral identification and comparison of minerals. I would not dare to write my opinion on the new nomenclature of the crystal shapes... when teachers speak, pupils should be silent. And I have rewritten the nomenclature... for the crystallography is the most essential part of the mentioned work and keeping in mind that it is not widely

known in Germany yet, so my work can be useful to those who would read it". One cannot underestimate the scientist's courage, modesty, his realization of his own place in science and unselfish service to the enlightenment.

Several copies of the "*Collection of names*" are kept at the Library of the Academy of Sciences in Saint Petersburg. Golitsyn sent them to Russia in August, 1801. There is no Russian translation of the book yet.

The most known Golitsyn's work besides the two works mentioned above was "*The Letter to Mr. Councilor and professor Crell*". Golitsyn's idea about amount of information one needs describing minerals mentioned in the letter is remarkable as follows: "*the bodies from mineral kingdom needs to be overviewed from every aspect... e.g. chemical analysis needs to be supplemented with data on their allocation in mountain chains, as well as with crystallization shape, their density, homogeneity, fusibility and flammability...*". Golitsyn also explains his view on origin of rocks disputing with the supporters of Verner's "neptunism". The last suggested that all rocks (including basalts and granites) were formed in result of deposition and crystallization of primordial ocean. Golitsyn was the follower of "plutonism" and supported magmatic theory of basalt formation. He wrote: "*I, honestly, do not see enough basis to exclude basalts from the generation of volcanic rocks... Basalts were formed in the depths of volcanoes and it does not matter how they formed, staying in the place of origin till some point*". Another citing from the same letter needs no comment: "*There are two approaches to the observations of minerals: one of mineralogist and the other of geologist. The first... does not achieve anything but determining and characterizing the rank, type and variety of the fossil... The physic geologist goes far beyond that: to the research of mineralogist he adds study of mode of occurrence, distribution and interrelationship of the fossils in the depths of Earth. Based on that he makes conclusions that disclose mystery of structure and composition of the globe. Pure mineralogist, no matter what place in science he has, cannot lead us to discoveries of this kind if he is not involved in geological knowledge. We would wish both sciences to come together*".

Golitsyn realized well the meaning of then actively developing analytical chemistry, mentioning particular importance of analysis of composition of minerals. Thanks

to his wide connections in scientific circles he was one of the first who learned about new sensational discoveries of new "metals and semi-metals". He kept terms with Petrus Camper, Martin Klaproth, Louis Vauquelin and many others, keeping correspondence with them and sending them samples from his collection for investigations, in particular minerals from Russia.

Golitsyn chose a phrase of French geologist Déodat de Dolomieu as an epigraph to his fundamental study: "*It is under the lead of chemistry that mineralogy could enter into internal mysteries of fossils and gain knowledge on their composition*". It is peculiar that he was very critical of works on minerals' chemistry. He wrote: "*whether the chemists have not found the best means to investigate composition of minerals yet, or of the other reasons that I do not know about, results of their analyses correspond with each other very little and we do not know how to respect all that was done and described on minerals*".

Some works of Golitsyn were dedicated to the new field of knowledge back then what now is known as volcanology. Academician S.A. Fedotov, the director of the Institute of Volcanology FEB RAS wrote: "*D.A. Golitsyn was one of the few neptunism opponents in the late 18th century. ...Most regrettably his remarkable works were forgotten and came back to attention of historians of science only in 1985*".

Golitsyn read his "*Memoirs on several extinct volcanoes in Germany*" on a session of Academy of Science of Belgium on February 18, 1785. He was amazed at that fact he was the first to study those numerous interesting volcanoes, which "were totally neglected" then. Description of the volcanoes was presented in "*The Memoirs*" and basalts, lavas and breccias were shown to be volcanic products in spite of neptunism idea of basalts being sedimentary rocks.

D.A. Golitsyn discussing the nature of volcanic activity with Italian natural scientist Lazzaro Spallanzani in 1792 came to conclusions that anticipated geological science for centuries. He wrote: "*volcanic heat*" did not originate from underground coal fires. He suggested that "*the amount of heat*" in molten rocks depended on concentration of gases in it, most importantly oxygen and sulfur compounds. Presence of the gas mixture could make "*volcanic heat*" of lower temperature than in glass making furnaces" (Fedotov, 1986).

Dmitriy Alekseevich works in natural sciences became widely known and gained him

a deserved reputation. It is enough to list titles of our compatriot to understand his position in scientific community of his time: corresponding member of Dutch Society of Sciences (1777), foreign member of Imperial and Royal Academy of Science and Letters of Brussels (1778), honorable member of Petersburg Academy of Sciences (1778), foreign fellow of Royal Swedish Academy of Sciences (1788), foreign fellow of Berlin Academy of Sciences (1793), fellow of the German Academy of Sciences Leopoldina (1795), foreign fellow of the Royal Society of London (1798), member of Free Economic Society (1798); honorable member (1799) and the president (1799) of Jena Mineralogical Society.

The last Society is of particular interest.

Town of Jena located in Duchy of Saxe-Weimar-Eisenach hosts a university founded in 1558. The university was famous by its wide and rational program in sciences. Johann Ernst Immanuel Walch was the first to introduce mineralogy in his course of natural history. His vast collection *From Three Kingdoms of Nature* (cabinet of naturals) was purchased by Karl August the Grand Duke of Saxe-Weimar-Eisenach upon initiative of J.W. Goethe in 1799 and placed in Jena ducal castle. This collection was the core of future Mineralogical Museum in Jena. Master of Philosophy Johann Georg Lenz (1748 – 1832) became the museum's custodian in the same year. Lenz introduced teaching mineralogy as an independent university course in 1872. Lenz became a chair at the University in 1794 and dedicated himself completely to mineralogy to "contribute to flourishing of this science". He found The Ducal Society of Common Mineralogy in Jena on January 7, 1796. Golitsyn's works could not be overlooked by the members of the Society and our compatriot was elected an honorable member of it in May, 1799. Goethe, Klaproth, Haüy were also honorable members of the Society.

The rule of the Society supported president and director positions. Lenz was irreplaceable director of the Society till the end of his life in 1832. The president position was offered to Dmitriy Alekseevich Golitsyn. He was elected to the president on the common meeting of the Society on June 21, 1799. Dmitriy Alekseevich could not visit Jena as for his poor health. Lenz went to meet him in Braunschweig. He was the president for four last years of his life and led frequent correspondence with Lenz. Twenty-five of his letters from that correspondence are kept in archives of Jena University. Golitsyn's activi-

ty in the Society was not limited to communication. He also transferred books and minerals including ones that came from Russia from his collection to the Society. He shared scientific news from Russia with it. For example, he told several times about A.A. Musin-Pushkin and his trip to Caucasus. He wrote that he request him to "gather a collection of beautiful minerals for our Society". He also informed that a Petersburg scientist "checked and confirmed" presence of chromium in the composition of "the red lead ore from Siberia" (crocoite). Golitsyn's works given to the Society are kept in the library of Jena University. Furthermore, Dmitriy Alekseevich continued to supply new publications and distributed new scientific information from Russia.

Meanwhile, degraded health of Dmitriy Alekseevich was complicated with financial difficulties. He started to undergo hardship as he always had little money. This situation made him think about future of his library and the mineral collection. To transport them to Russia was a risky project considering military and political situation in Europe. Need to move out from his house to a cheaper place complicated the problem. Dmitriy Alekseevich found a brilliant solution to hand his mineralogical collection and the library to the Mineralogical Society that he was heading. This gift was received with gratitude. Here is the letter composed by Goethe and signed by Duke Karl August: *"This institution [meaning the Mineralogical Society, author] that started little and reached stable life solely thanks to your care, Dear Sir, is indebted to you for the respect and brilliance distinguishing it from the rest of similar organizations. You favored to carry the burden of the president position to support the Society with your knowledge and also demonstrated superior kindness to donate magnificent collection, that interests us as both for the value and rarity of the samples and for the art of the expert who collected them"*.

It was very difficult to hand the collection and Golitsyn asked Lenz on August 8, 1802 to speed the process: *"I have to leave the house... if you receive my collection, I will leave it in the house, which I abandon..."* Dmitriy Alekseevich was informed on October 29, that all the minerals were packaged and would be the same day at expediter who would not procrastinate to send them to Jena. The collection was moved to Jena and exhibited in the old Duke's castle.

What was Golitsyns collection donated to Jena Mineralogical Society like? The information on it is fragmental and scarce. Private archive of Golitsyn that was kept in Braunschweig was destroyed during the Second World War as Tsverava mentioned. There was no catalog of the collection survived. Horst Frank, the custodian of the mineral collection of Jena University wrote about this fact to Wendell Wilson in a private letter in 1991 (Wilson, 1991).

It is known that by the time it moved from Hague to Braunschweig the mineral collection impressed the contemporaries with its quantity, variability and rarity of the samples. G. Forster who visited Golitsyn in 1790 wrote: *"The mineralogical cabinet of the prince is a collection of an expert, he gathered and kept on his own, which is rare and very didactic in its own way"*.

Golitsyn wrote: *"My collection is remarkable by the number of very large size minerals from faraway countries"*.

There is no doubt that the collection was replenishing from the numerous correspondents including ones from Russia. Visiting different cities the prince used every chance to familiarize himself with museums and private collections and purchase something interesting for himself.

The author picked all information from Tsverava book that was connected to description of the collection. There was very few things mentioning it: *"I have just received very interesting minerals from Siberia: singular aquamarines in a coat, crystal malachite, coated gold bearing pyrites, fragile gold bearing quartz, huge piece of hornblende from a*

silver mine, stone of Russian labrador and many other". He mentioned also the following: *"half a foot block of flexible Peiresc sandstone"; "peculiar set of tellurium ores, sent by abbot Arnoldi from Vena", "very beautiful hummocky malachite, weighing around a quintal (centner)", "beryl veins from the Urals and Dauria, mixed with yellow and colorless topaz"; "zeolites of all kinds"; "tourmaline group with well preserved pyramids"*.

It is known that when the collection was transferred the cargo weight sent from Braunschweig to Jena accounted 1850 kg.

V.I. Vernadsky wrote about D.A. Golitsyns collection: *"Unfortunately, the collections of Goethe, of Jena University, Golitsyn's collection and other collections were not looked through by anybody who knew mineralogy of our country. They may contain unique and new deposits that were not kept in our museums. Unfortunately, the collection was not available due to some renovations during my visit to Weimar in 1936"* (Vernadsky, 1981).

There were two opinions on the fate of the collection. Tsverava wrote in his book: *"I requested information about the mineralogical collection of Golitsyn during my visit to Jena. It was gradually dissolved in the exposition of Jena Mineralogical Museum. The Mineralogical Society came to closure in 1890-s and the collection could not find a new owner after the old castle (where it was kept) was demolished in 1908. 35 000 mineral samples are kept in one of warehouses of Jena University till now"*.

The other citing is from Wendell Wilson's article: *"Jena Mineralogical Society closed in*



Fig. 2. Slab of sandstone. 44 × 17 cm. Brazil. Mineralogical collection of Friedrich Schiller University, Jena, Germany. Photo: M.B. Leybov.

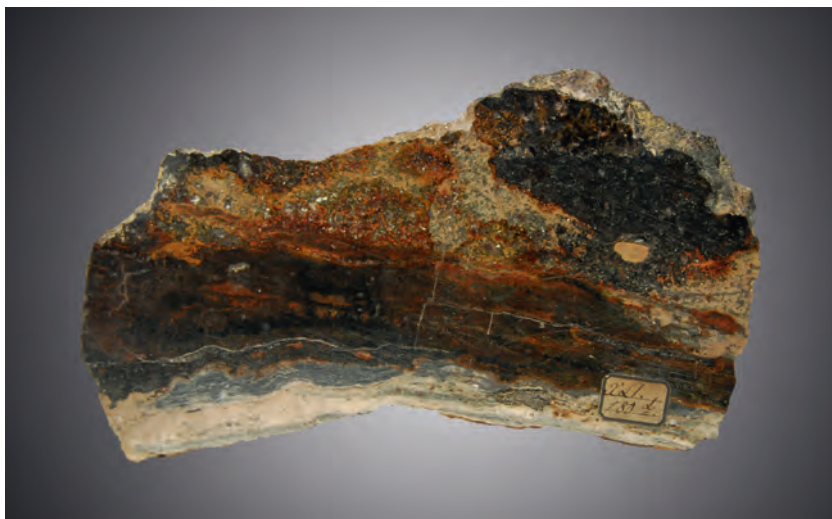


Fig. 3. Skarn with garnet and biotite 17 × 9 cm. Vesuvius, Italy. Mineralogical collection of Friedrich Schiller University, Jena, Germany. Photo: M.B. Leybov.

1890-s and the castle was demolished in 1908. Golitsyns collection, though did survive and was moved to newly build building of Mineralogical-Geological Institute where minerals were kept till 1945. They perished in bomb attack on the building" (Wilson, 1991), thus Wilson cited Tserava, whose text was a bit different.

The last known manuscript of D.A. Golitsyn was a letter to Lenz from March 8, 1803. The prince wrote that he hoped the collection was received in good condition and informed that he received a silver medal from Free Economic Society in Petersburg for "his *Collection of names...*" was recognized as the most useful for science...". That letter had the last mentioning of the collection: "I suppose, Dear Sir, that all minerals from my collection are currently unpacked and are in your disposal. I want to ask you to take care of putting them in order of Haüy system and do not worry ordering them as they were organized before. I had an honor to tell you that I had no time to change this order, nevertheless I felt an extreme necessity to change it lately".

Dmitriy Alekseevich died in Braunschweig on March 4 (March 16 by Gregorian calendar), 1803 and was laid to rest on the cemetery of St. Nicolas church.

Dr. Birgit Kreher-Hartmann prepared a report on the history of Mineralogical Museum of Jena University on 5th Mineralogical Museums Symposium in Saint Petersburg in 2005 (Kreher-Hartmann, 2005). She told about finding of at least two samples from D.A. Golitsyns collection and according description of the samples in the catalog of the University collection (mineralogical collection of Friedrich

Schiller's University, Jena) and in the catalog of Golitsyns collection (Goethe and Schiller archive, Weimar). One of the samples is a flat slab of sandstone (Fig. 2) and the second was skarn with garnet and biotite (Fig. 3).

Photographs of the samples and the catalogs were made by M.B. Leybov in 2008 with the kind permission from Brigit Kreher-Hartmann.

The founding of the samples of Golitsyns collection as well as an interest to it from our German colleagues show us that the name of our compatriot is still remembered and will stay forever in the history of mineralogy.

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Mineralogical Notes



THE BRIGHT OPTICAL FACE OF FERSMANITE

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The short characteristic of fersmanite, rare mineral of alkaline magmatites, pegmatites and hydrothermalites is given. The mineral is called in honor of Alexander Evgen'evich Fersman, the well-known mineralogist, the geochemist, the traveler, the geographer, the poet of a stone. The microphotographs showing a bright optical face of fersmanite are given.

3 figures, 10 references.

Keywords: A.E. Fersman, fersmanite, microphotographs in transmitted light.

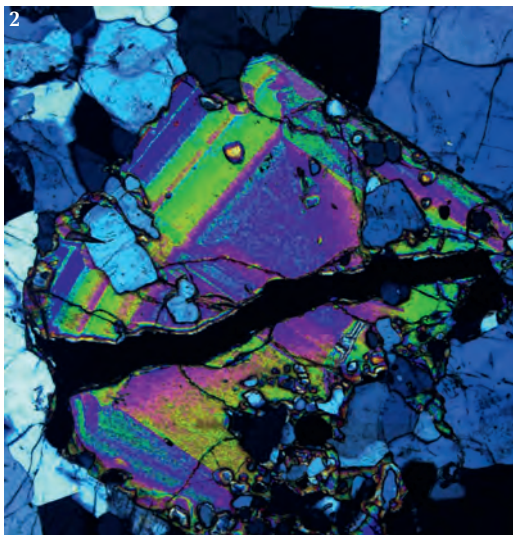
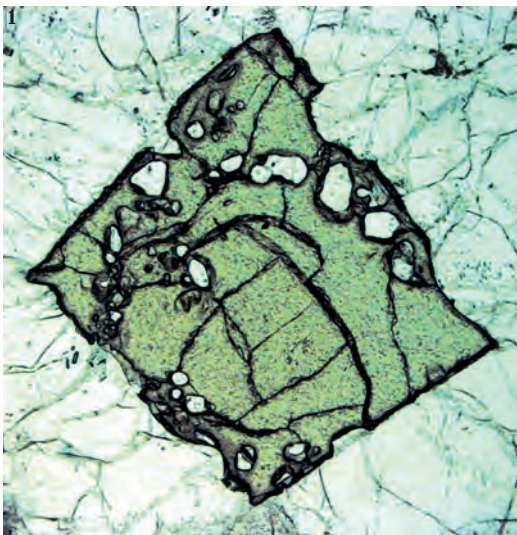
Fersmanite — the rare, but characteristic mineral of the alkaline pegmatites and alkaline hydrothermalites which are rather widely developed in the central part of the Khibiny intrusive, firstly was opened and studied by A.N. Labuntsov (Labuntsov, 1929; Labuntsov, 1933; Sokolova, 1986). The mineral is called in honor of Alexander Evgen'evich Fersman — the well-known mineralogist, geochemist, geographer, traveler, the poet of a stone. So far in addition to Khibiny Mountains fersmanite is established in alkaline formations of Brazil (Atencio *et al.*, 1999) and Rhine graben (Hentschell, 1993). Optical properties of fersmanite were defined by I.D. Borneman-Starynkevich (Starinkevitsch-Borneman, 1939). For this monocline mineral the characteristic optical properties are as follows: high relief with $n_g =$

1.91–1.94, very strong double refraction of $n_g - n_p = 0.04 - 0.05$, sometimes zonal structure, a small angle of optical axes (less than 7° is characteristic) are characteristic. The composition and structure of fersmanite were refined in 1977 (Machin, 1977). V.V. Ilyukhin with colleagues for the first time determined an accurate formula $\text{Ca}_4(\text{Na,Ca})_4\text{Ti}_3(\text{Nb,Ti})_1(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$ and solved completely the crystal structure of fersmanite from Khibiny (Morocco *et al.*, 1984). Their version of fersmanite structure and its formula is confirmed in Elena Sokolova's article (Sokolova *et al.*, 2002). Fersmanite is the tetramer, similar to batisite (Nikitin, Belov, 1962).

Thin sections with fersmanite are prepared of samples which are collected on the Eveslogchorr Mountain, in the Vuonnemiok river

Fig. 1. Relatively regular fersmanite crystal with a high relief in the nepheline – K-Na feldspar matrix. Transmitted light at a single nicol. Width of the field of view is 5 mm.

Fig. 2. A zoned fersmanite crystal. Transmitted light, crossed polars. A crack in the center of a crystal is defect of a section. Width of the field of view is 5 mm.



valley, Khibiny Mountains. Fersmanite associates with feldspar, nepheline, aegirine, pectolite. A form of crystals is various, from xenomorphic to rather regular. In transmitted light with a single nicol, fersmanite (Fig. 1) resembles titanite (sphene). A distinct zoned crystals structure of the Khibiny fersmanite and its bright optical face illustrate microphotographs in a transmitted light at crossed nicols (Figs. 2, 3).

This work was supported by the Russian Foundation for Basic Research (grant 13-05-00839).

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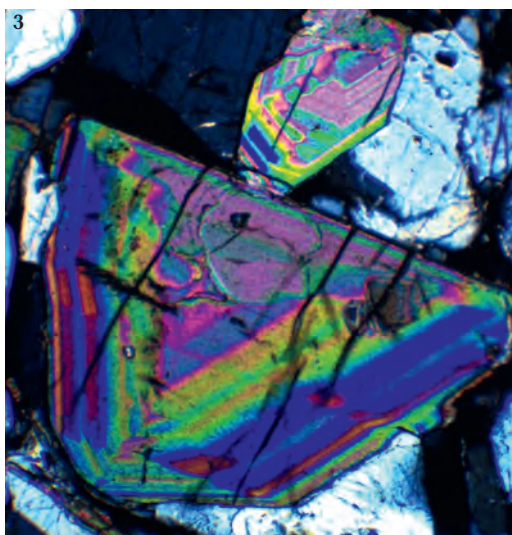


Fig. 3. Intergrowth of zoned fersmanite crystals. Transmitted light at a single nicol. Width of the field of view is 5 mm.

MINERAL AGGREGATES IN THE *PROMETHEUS* CAVE IN WESTERN GEORGIA

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In 2011 near Kutaisi in the vicinity of Tsqaltubo city within the Lower Cretaceous limestones the Prometheus cave has been opened for visitors. The main types of mineral aggregates developed within the cave have been described.

7 photos, 6 references.

Keywords: karst of Western Georgia, Tsqaltubo Plain, the Prometheus cave, mineral aggregates developed within the cave.

In September 2012 the author was happy to visit Georgia during the two-week tour with karst cave-bearing territories attending.

Due to the very often development of limestone strata belonging to the Cretaceous and Upper Jurassic periods at the Caucasus (and especially thick at the Southern slope of the Great Caucasus ridge), karst in Georgia is excellently revealed. In several regions of Georgia the total thickness of karst-able rocks varies 1200–2600 m (Geology of the USSR, 1964). This fact as well as several other favourable regional factors: hot and wet climate with abundant sediments, and active tectonic processes cause vast and various karst occurrence. Before 1990es more than 600 caves have been registered on the Georgian territory – more than two third the all known caves on the territory of the Former Soviet Union (Tintilozov, 1976). Most of caves are situated at the Western Georgia. Large Georgian limestone strip located in the intermediate place between the folded system of the Southern slope and the Georgian Block is attributed to as a large speleological province (Geology of the USSR, 1964). Novoafonskaya among the well-known caves of the Abkhazia one is the most famous was discovered in 1961 and opened for visitors only in 1975. Within the scheme of speleological regioning this cave has been attributed to the subprovince of fore-mountainous and low massifs as well as the caves of the Lower-Imeretinsky region. These caves are situated now at the territory of the modern Georgia (and the Tsqaltubo wavy plain, in particular) and similar in several features with them (Tintilozov, 1976). The lowland consists predominantly of the Lower Cretaceous limestones.

Tsqaltubo karst region is situated at the eastern wavy and hilly vicinity of the Kolkhidskaya lowland, in the valley of the Tsqaltubo River, to that from the north-east branches of the Sal'gural'sky ridge of the Great Caucasus are attached. Tsqaltubo balneological

Spa Resort located 9 km to the north-west from the Kutaisi city is known due to its thermal waters and radon-bearing springs. Before the 1990es Sataplya State Reserved Park existed here. It was found in 1935 and was famous with dinosaurs traces and a small and attractive Sataplya Cave (modest in compare with the Novoafonskaya Cave).

In 1973 a new cave was discovered by the researchers of the karstological and speleological laboratory of the Vashukhti Geographical Institute, Academy of Sciences of Georgia, in 9 km to the north-west from the Tsqaltubo in the vicinity of the Kumistavi village. During further investigation beside this cave the large system of caves jointed together by an underground river was discovered. In newest times the territory received a grandiose governmental support of tourism development in Western Georgia, and the Sataplya and Kumistavi caves have been well-developed for tourist visits. In 2011 the cave was opened for visitors under the name "*The Prometheus cave*".

The entrance to the Prometheus cave is located 100 meters above sea level. Its square is estimated as 200–250 sq kilometers, and its depth from the earth's surface – 40 meters. As it was shown during investigations, its full length of all corridors is about 20 kilometers. Now it is known that the cave consists of 17 halls, and 7 entrances-subcaves. Nowadays there is tourist route with a length of 1.6 km that is finished near the underground lake where all visitors take a boat and sail out by the underground river to the earth's surface. Constant temperature in cave is +14°C. Bats live here as well as creations adapted to live in darkness: freshwater mollusks, spiders, worms, crustaceans. Paths and stairs are arranged in such a way that tourists can visit five large cave halls (up to 35 m length and 7 m in height) (Fig. 1). Artificial lighting sometimes are coloured, together with soft romantic music evoke an atmosphere of mystery.



Fig. 1. Sight from the viewing platform. Fence 1 meter high. Photo: A. Lobachiov.



Fig. 2. Stalactitic-stalagmitic crust. Height of the «pagoda» at the right – 3 m. Photo: A. Lobachiov.



Fig. 3. Stone «waterfall», 3 m high. Photo: A. Lobachiov.



Fig. 4. Stalactitic-stalagmitic crust coloured by terrigenic admixture. Height of the ceiling up to 2.5 m. Photo: A. Lobachiov.

First of all, one may note the complicated form of the karst cavity, feature of multiple (not once) rock falls, distinct manifestation of stadiality of cave forms genesis when periods of mineral formation alternated with stoppings-interruptions, and apparently with periods of dissolution. As a whole, these features as well as giant stalactite-stalagmitic formations (Fig. 2) are similar to the Novoafonskaya cave.

Viktor I. Stepanov has investigated the Novoafonskaya cave and described characteristics of genetic stages of its development (Stepanov, 1971). It was interesting for us to compare our cave observations with Stepanov notes and describe *Prometheus* mineral aggregates based on the terms suggested by him and used during his work on "Caves" exposition in the Fersman Mineralogical museum based on the material from Central Asia caves.

As in the Novoafonskaya cave, very thick tuff stalactite-stalagmitic crust is developed within the *Prometheus* cave. In this case we mean the calc-tuff – pore calcitic rock forming the most thick gravity cave formations (Stepanov, 1971; 1998). At the steep places of blocks obstructions tuff crust makes huge «waterfalls» formations (Fig. 3).

The reason of colouring of stalactite-stalagmitic crust is terrigenic admixture (clayish, clay-sand-bearing). And very often this admixture is not distributed evenly, and we can see fragments of pure-white translucent forms (Fig. 4) of more late generations in origin.

Thus, in places one can observe calcitic stalactite-stalagmitic crust crystallization which occurred more slowly than that of a tuff crust,

and it was going without capture of terrigenic material admixture belonging to streams periodically fulfilling the cave. In places occurs uneven colouring of cave forms by ferruginous compounds in reddish-brown tones (Fig. 3), and locally – in yellow and merely bright (result of bacterial activity?) as well as in black colour with metallic luster apparently due to the admixture of manganese compounds (vad $MnO_2 \cdot nH_2O$?).

Stalactites (Fig. 5) here are very abundant, and more often than in the Novoafonskaya cave. There are many different forms: conical, cylindrical, and flattened. During cave development some stalactites were cut and in the centers of stalactites cross-sections we can see feeding channels with continuing process of stalactite formation droplets of sucking fluid (if there is a favourable lighting); as it may be often seen at the edge of stalactite cross-section, it becomes the place of overgrowing by new generations of small stalactites (Fig. 6).

Linear ensembles of stalactites are very common if they are developed along cracks of the vault (Fig. 5, 6), as well as flattened stalactites – products of linear sucking (Stepanov, 1998). Such natural mineralogical plumbs accurately following change of the location in space of the feeding surface, became more complicated in their forms, and sometimes coalescence in place forming fanciful bending drapes (Fig. 7). One should note almost transparent strips that can be distinctly seen at the background of coloured by the terrigenic clayish (Fig. 7b).

We can name these formations crystalactitic similarly to translucent drapes at the "Caves" exposition the translucent drapes at the exposi-



Fig. 5. *Stalactites*.
Photo: E. Kislova.

Fig. 6. *Stalactites and stalagmites of the same generation*.
Photo: T. Pavlova.

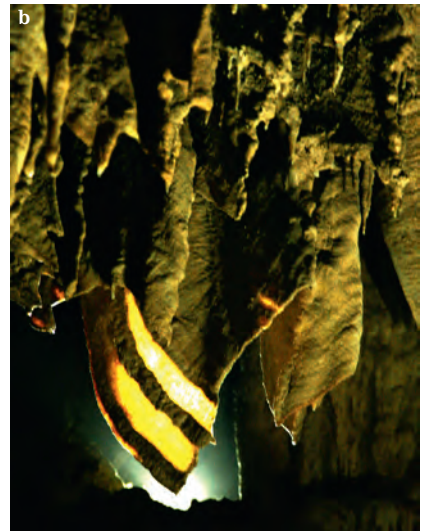
tion "Caves" due to their coarse-grained texture (Stepanov, 1998).

Stalagmites are also very variable. Vastly abundant are tuff stalagmitic crusts that arise during the surface feeding (flat gravity stream) (Stepanov, 1998). Typical crusts named "fried eggs" (Fig. 3, at the front plan) forming at the earliest stage of growth of the stalagmite itself during its axial feeding, before the moment when geometric selection acts during the former growth. Large tuffo-calcitic stalagmites (in other words, tufflagmites, according to Stepanov, 1998) are very outstanding cave formations.

They are similar to those developed in the Novoafonskaya cave, with complicated surface relief that reflects multistadiality of their origin (Fig. 2). Conical and cylindrical stalagmites in places overgrowth stalagmitic crust surface – incrustations (Figs. 4, 6) often coloured due to the admixture of clay minerals. One may observe white-snowy form with sparkling surface of numerous crystal faces.

Corallitic crust formed due to the evaporation of capillary thin films during «dry» periods is well developed in the Novoafonskaya caves (Stepanov, 1971) in side burrows, and secluded

Fig. 7a, b. *Stalactitic drapes*: a – dimension up to 0.8 m. Red lighting. Photo: A. Lobachiov.
b – Strips without terrigenous admixture, up to 4 cm wide. Photo: T. Pavlova.



corners. In the Prometheus cave, when we walked along the main route, we have seen the overgrowth of corallites onto earlier crystallization forms; these forms may be named corallactites and ensembles of corallites and stalactites similar to those known in the Khaidarkan caves and shown at the exposition in the Fersman Mineralogical museum as well as corallites and stalagmites.

Such gradual forms as transition of conical stalactites into corallites are very common. It is very typical process as a steep transition from the gravity structures to the corallitic ones parallel with diminishing of film thickness and thus its ability to move under the gravity force (Stepanov, 1998).

Helictites are fantastic twisting cylindrical branchlets (direction of growth of which are not influenced by the gravity force) arising during the crystallization on the exit from the capillary channel. We failed to detect these cave formations for sure, where as in the Novoafonskaya cave within the Helictitic hall they overgrowth onto stalactites. In order to determine properly the cave forms, one ought to investigate the character of feeding channel; in different case we may miss these forms with eccentric stalactites.

As a rule, in the *Prometheus* cave definite forms are often hardly properly characterized due to their complicated genesis, and vast distribution of such paragenetical ensembles as stalactite – drape as well as hybrid structures (Stepanov, 1998). In many cases paragenetical ensembles reveal individuality of their morphology that forces us to remember that they have been described in terms of “behaviour” analo-

gous to the characteristics of live organisms (Slyotov, 1985).

Among the products of crystallization of one of the generations in the Novoafonskaya cave a lot of gypsum aggregates occurred (Stepanov, 1971), and it is very probable to find this mineral within the *Prometheus* cave formed during the «dry» period of its life (Maltsev, 1993).

Author expresses her true gratefulness to N.A. Vaganova, A.M. Makarova and T.G. Pavlova, the leaders of the tour, as well as to our friends who gave us permission to use their photos in this publication.

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