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This volume contains articles on new mineral species, among them — Faizievite, Guimarã esite, a rocherite-group mineral from Brazil, and Ferroskuterudite, arsenide of iron and cobalt from the Norilsk ore field; the description of new finds of recently discovered minerals — Pertsevite and Megacyclite with the structure of the last one; new data on mineralogical assemblages with bituminous matter in pegmatites of the Khibiny massif, on the features of occurrence of noble metals in ores and oxidized zone of the Onega deposits in South Karelia; the results of studying of Grossular, Vesuvianite and Achtrandite of the Talnakh region; the results of research of transformation of mineral paragenetic assemblages from copper sulfide ores of the Krasnov hydrothermal field; the nomenclature of the Loellingite-group diarsenides.

The paper of the chairman and vice-chairman, Subcommittee for Unnamed Minerals, IMA Commission on New Minerals, Nomenclature and Classification, published earlier in Canadian Mineralogist journal, is reproduced here in brief version by request of the Commission in order to introduce the new and approved coding system as widely as possible.

"*Mineral Museums and Collections*" section contains information on mineral collections of Fersman Mineralogical Museum: on art things of masters from the Urals on mineral collections of the Tsesarevichs and of General G.P. Chernik; on the story of one exhibit from the Museum — a black basalt with a golden monogram; and also there is in this section a description of the mineralogical collection of the GeoMuseum, Cologne University, Germany.

"*Personalities*" section includes the article on the exhibition "Jubilees and Their Heroes"; this exhibition was devoted to 290 years of Fersman Mineralogical Museum and other jubilees concerning with the Museum. Two more articles are devoted to Professors Alexander A. Godovikov and Georgiy P. Barsanov who had leaded this Museum in different periods.

In "*Mineralogical Notes*" section two articles are published. First, on carbonates in metakimberlite, Zamitsa pipe, and second, on the twisted filiform magnesian calcite from rocks at Russian platform.

The volume is interesting for mineralogists, geochemists, geologists, curators of Natural History museums, and collectors.

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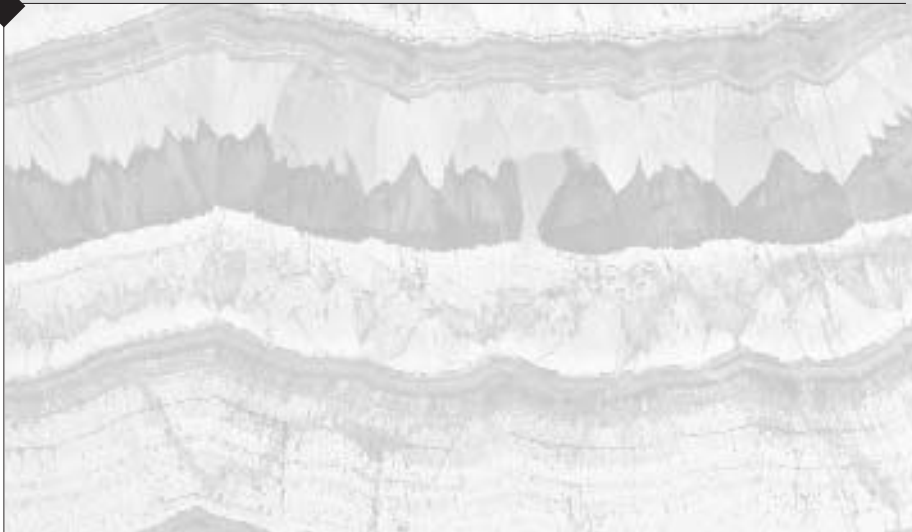
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**New Minerals
and Their Varieties,
New Finds of Rare
Minerals,
Mineral Paragenesis
Assemblages**



FAIZIEVITE, $K_2Na(Ca_6Na)Ti_4Li_6Si_{24}O_{66}F_2$ – A NEW MINERAL SPECIES*

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Faizievite, a new sodium-potassium-calcium-lithium titanosilicate, was found in a quartz boulder in association with pectolite, baratovite, aegirine, polyolithionite, leucosphenite, fluorite, etc. on a moraine of the Darai-Pioz glacier, Tadjikistan. It is colourless with a strong vitreous lustre, forms tabular plates without vicinal forms, and up to 0.3 cm in maximum dimension. Mohs hardness is 4–4.5, measured density is 2.83(2) g/cm³, calculated density is 2.819 g/cm³. Faizievite is optically positive, biaxial, $n_p = 1.651(2)$, $n_m = 1.655(2)$, $n_g = 1.657(2)$, $2V_{meas.} = -72(2)^\circ$, $2V_{calc.} = -70.4^\circ$. The crystal structure was refined to an R index of 7.5%. Faizievite is triclinic, space group $P-1$, cell dimensions: $a = 9.8156(9)\text{\AA}$; $b = 9.8249(9)\text{\AA}$; $c = 17.3087(16)\text{\AA}$; $\alpha = 99.209(2)^\circ$, $\beta = 94.670(2)^\circ$, $\gamma = 119.839(1)^\circ$, $V = 1403.7(4)\text{\AA}^3$, $Z = 1$. The strongest lines of the X-ray powder diffraction pattern are as follows: [d , \AA , (I , %), (hkl)]: 5.60 (9) (0 0 3), 4.25 (60) (0 -2 1), 3.35 (100) (0 0 5), 3.14 (20) (1 -3 2), 3.06 (90) (-1 -2 3), 2.885 (55) (-2 1 5), 2.870 (10) (-2 3 2), 1.868 (17) (-1 4 4). The strongest lines of the IR absorption spectra are as follows: 1211, 1178, 1130, 1022, 940, 783, 683, 651, 557, 534, 460 cm⁻¹. The chemical composition (microprobe, excepting data for Li₂O, Rb₂O, BaO, SrO – which was obtained by ICP OES, wt.%): SiO₂ – 60.65, CaO – 14.52, TiO₂ – 13.44, Nb₂O₅ – 0.11, SrO – 0.72, BaO – 0.24, K₂O – 3.93, Na₂O – 1.99, Li₂O – 3.76, Rb₂O – 0.13, F – 1.30, -O=F₂ – -0.55, total – 100.24. The empirical formula of faizievite is $(K_{1.98}Rb_{0.03})_{2.01}(Na_{0.90}\square_{0.10})_{1.00}(Ca_{6.16}Na_{0.63}Sr_{0.17}Ba_{0.04})_{7.00}(Ti_{4.00}Nb_{0.02})_{4.02}Li_{5.98}Si_{24}O_{66.00}(F_{1.63}O_{0.36})_{1.99}$. The ideal formula is $K_2Na(Ca_6Na)Ti_4Li_6Si_{24}O_{66}F_2$. The name honors Faiziev Abdulkhak Radzhabovitch (born 1938) of Dushanbe, Tadjikistan, professor and member-correspondent of the Academy of Sciences of the Republic of Tadjikistan. He is a well-known mineralogist, and author of numerous works on the mineralogy and geochemistry of Central Asia. The sample with faizievite is stored in Fersman Mineralogical Museum, Russian Academy of Science (Moscow). 2 tables, 4 figures, 8 references

Type Locality and Association

Faizievite was discovered in rocks collected on a moraine of the Darai-Pioz glacier, Tadjikistan. The glacier is located in the upper reaches of the Darai-Pioz river and crosses the Darai-Pioz alkaline massif, which is widely known for its unique mineralization. Many publications are devoted to the mineralogy and geology of this alkaline massif (Dusmatov, 1968, 1971, Belakovskiy, 1991, etc.). As is the case for many other alkaline massifs, there is an important role for elements substituting for aluminium in minerals: titanium, zirconium,

niobium, beryllium and boron. In particular, there is major enrichment in boron. The wide variety of titanium minerals is also a characteristic geochemical feature of the massif. Titanium is a dominant element in one-fifth of all Darai-Pioz mineral species. Ring titanosilicates are of special interest here. Together with zirconosilicates, this group at Darai-Pioz has unusual and unique features. Many of these minerals were first described from Darai-Pioz, and practically all of them are abundant here, e.g., **baratovite**, $KCa_7(Ti, Zr)_2Li_3Si_{12}O_{36}F_2$ and **sogdianite** $K(\square, Na)_2(Zr, Ti, Fe^{3+})_2Li_3Si_{12}O_{30}$, are often

* Faizievite is recommended for the publication by the Commission on New Minerals and Mineral Names of the Russian Mineralogical Society, and was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association on December 4, 2006

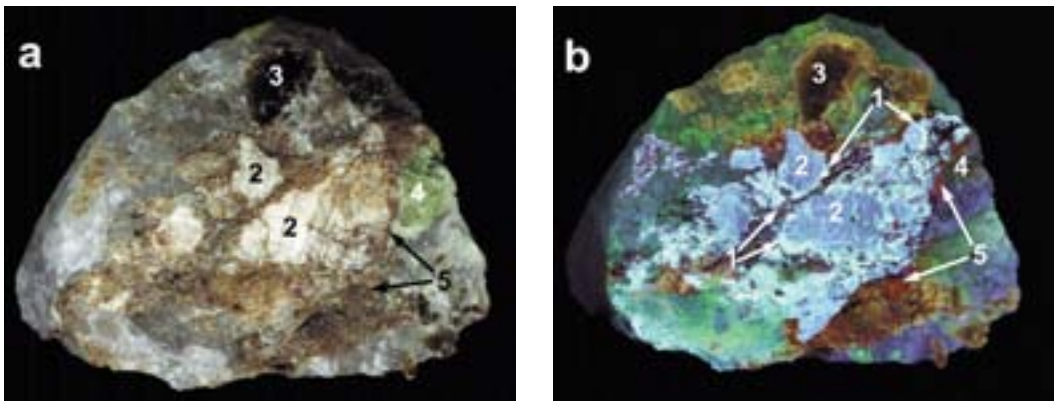


Fig. 1. A general view of the quartz boulder in which faizievite was found (a) in normal light, and (b) in short-wave ultraviolet light.
 1 – faizievite,
 2 – baratovite,
 3 – polyolithionite,
 4 – leucospheinite,
 5 – pectolite.

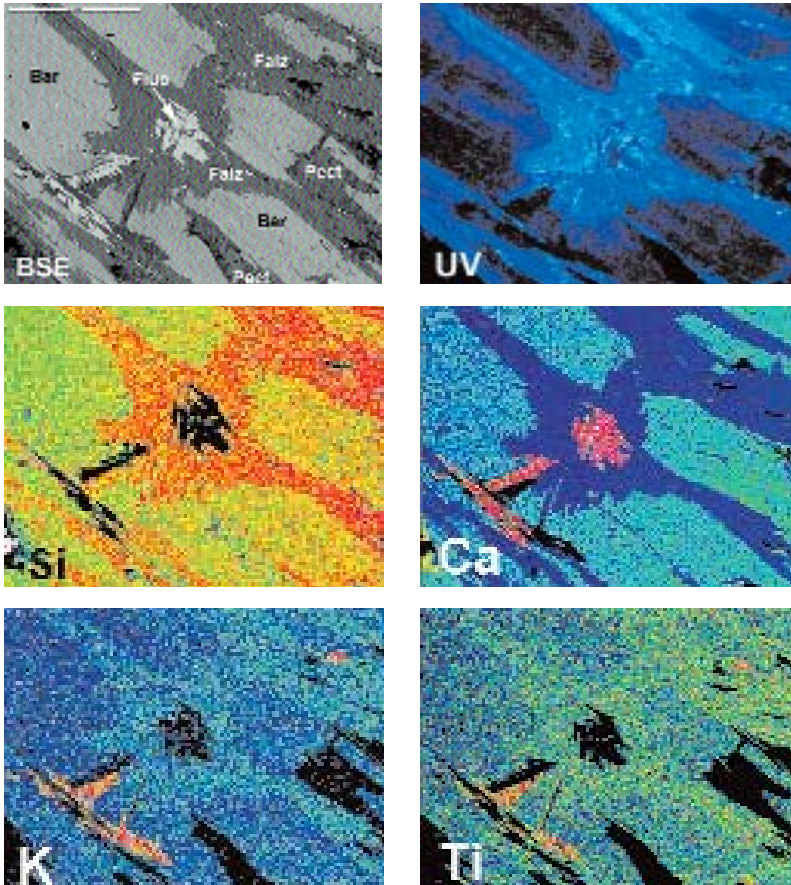


Fig. 2. Intergrowth of faizievite (Faiz) and baratovite (Bar), fluorite (Fluo), pectolite (Pect) imaged in BSE mode, short-wave ultraviolet and characteristic X-rays. Scale bar is 200 μm .

rock-forming minerals. Many ring titanosilicates are also present, e.g., **baotite**, **berezanskite**, **tienshanite**, **titantaramellite** and **faizievite**. As will be shown below, the structure of faizevite is derived from the structures of baratovite and berezanskite. (Minerals first described at Darai-Pioz are noted in bold

above).

The Darai-Pioz massif is difficult to access because of the complex mountain relief, including sheer walls of a trough-shaped glacial valley. Glacial sediments consists of massive transported material and outcrop. Some boulders in the moraine one can corre-

late with rocks observed in outcrop. Some of the transported rocks can be seen in outcrop, but some of the rocks in the moraine could not be established authentically until now. The quartz rocks contain rich rare-earth and rare-metal mineralization where faizievite has been found. The boulder in which faizievite was found consists dominantly of granulose and middle-large-grained clear quartz, and contains large plates of polyolithionite (up to 20 cm), microcline (crystals up to 3 cm), reedmergnerite pockets (up to 12 cm), idiomorphic crystals of aegirine (up to 5 cm), rare red-brown lenticular crystals of stillwellite-(Ce) (up to 2 cm), grass-green crystals of leucosphenite (up to 3 cm), violet-red plates of sogdianite and sugilite (up to 20 cm), dark green prismatic crystals of hydrated turkestanite with high U-content (up to 2 cm), pockets of polymineral aggregates consisting mainly of pectolite (up to 20 cm). Less common in this rock are baratovite, galena, calcite, kapitzaite-(Y), neptunite, pyrochlore, eudialite-group minerals, hyalotekite, tadhikite, bismuth, sphalerite, fluorite, fluorapatite and fluorapophillite, sokolovaite, pekovite and senkevichite. These rocks occur on a moraine as boulders of different roundness and sizes from 0.2 up to 2 m in diameter. They have not been seen in outcrop and, unfortunately, no contact with any other rock was encountered. As has already been noted, the genesis of these boulders lacks a satisfactory explanation. In order to avoid genetically inappropriate rock names, we call these "quartz boulders".

Faizievite occurs in quartz boulders (fig. 1) as platy grains with no vicinal faces, up to

3 mm across and up to 0.2 mm thick, closely intergrown with baratovite and fluorite in quartz-pectolite aggregates (Fig. 2). More commonly, faizievite overgrows baratovite, forming a thin rind between quartz and baratovite.

Physical Properties

Faizievite is colourless, transparent, with a strong vitreous lustre. In short-wave ultraviolet light, it has a bright white luminescence; in long-wave ultraviolet light, it does not luminesce. The Mohs hardness is 4–4.5. Micro-indentation VHN was determined with a 50 g load on a PMT-3 instrument, graduating on NaCl; the mean value is 445 kg/mm² (average of 20 measurements in the range 424–474 kg/mm²).

Faizievite is brittle. Density was determined in Clerici solution. The measured density is 2.83(2) g/cm³, calculated density is 2.819 g/cm³. Faizievite is biaxial positive, $2V = -72(2)^\circ$ measured on a Fedorov stage, calculated $2V = -70.4^\circ$. Indices of refraction were measured by immersion at 589 nm: $n_p = 1.651(2)$, $n_m = 1.655(2)$, $n_g = 1.657(2)$. Dispersion is medium, $r < v$. Faizievite does not dissolve in water or HCl (1:1). The infra-red spectrum of faizievite was recorded on an Avatar IR-Fourier spectrometer (Thermo Nicolet), and is characterized by the following absorption bands: 1211, 1178, 1130, 1022, 940, 783, 683, 651, 557, 534, 460 cm⁻¹. The spectrum of faizievite is individual, does not correspond to that of any known mineral (Fig. 3).

Chemical Data

The chemical composition of faizievite was determined on a JXA-50A JEOL electron microprobe and by ICP OES (Table 1). EMP analyses were done at 20 kV accelerating voltage and 2 nA probe current (for energy-dispersive analysis) and at 15 kV and 25 nA (for wavelength-dispersive analysis). Si, K, Na, Ca, Ti and Nb were analysed by EDS, and F was measured by WDS. Microcline USNM143966 (Si, K), omphacite USNM 110607 (Na), anorthite USNM 137041 (Ca), ilmenite USMN 96189 (Ti), synthetic LiNbO₃ (Nb), MgF₂ (F) were used as standards. Grains of the new mineral are homogeneous and free

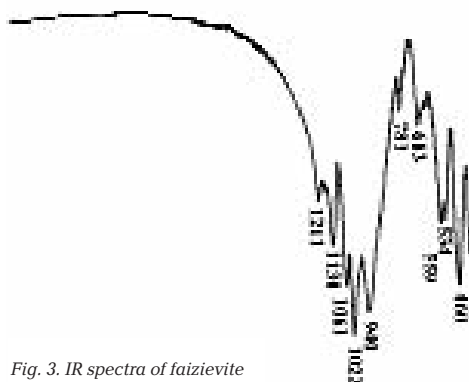


Fig. 3. IR spectra of faizievite prepared in a KBr tablet (analyt A.A. Agakhanov).

Table 1. Chemical data for faizievite (wt%)

Constituent	Content from 20 points in 6 grains	
	Average	Limits of contents
SiO ₂	60.65	58.77–62.15
CaO	14.52	13.58–15.39
TiO ₂	13.44	12.94–13.84
Nb ₂ O ₅	0.11	0.00–0.34
SrO*	0.72	
BaO*	0.24	
K ₂ O	3.93	3.68–3.97
Na ₂ O	1.99	1.81–2.07
Li ₂ O*	3.76	
Rb ₂ O*	0.13	
F	1.30	1.20–1.39
-O=F ₂	-0.55	
Total	100.24	

Note: *The data was done by the ICP OES method. Analysts: A.A. Agakhnov, L.A. Pautov.

from inclusions of other minerals. The raw data were processed by a ZAF-correction program. Li, Ba, Sr and Ba concentrations were determined by ICP OES. Mineral grains were digested in a polypropylene tube in concentrated HF with the addition of HNO₃, and the resulting solution was evaporated to wet salts. Further HNO₃ was added to the sample and was evaporated to dryness in order to remove all fluorides. The precipitate was diluted in 2 % HNO₃ and then the solution was analysed with VISTA Pro ICP OES of Varian. The average composition of the analysed grains (table 1) is recalculated for Si = 24 atoms per formula unit to give the empirical formula (K_{1.98}Rb_{0.03})_{2.01}(Na_{0.90}□_{0.10})_{1.00}(Ca_{6.16}Na_{0.63}Sr_{0.17}Ba_{0.04})_{7.00}(Ti_{4.00}Nb_{0.02})_{4.02}Li_{5.98}Si₂₄O_{66.00}(F_{1.63}O_{0.36})_{1.99}. The ideal formula of faizievite is K₂Na(Ca₆Na)Ti₄Li₆Si₂₄O₆₆F₂. The compatibility index (1-K_p/K_c) is 0.005, superior.

X-Ray Crystallography

X-ray powder diffraction data for faizievite was obtained (Table 2) with a DRON-2 instrument. To avoid preferred orientation, the X-ray powder pattern was also obtained with a RKU-114M chamber. The powder-diffraction pattern of faizievite does not correspond to any known mineral or synthetic compound. Quartz was used as an internal standard.

Table 2. Diffraction data of faizievite

Debaegram		Diffractogram		Theoretical		hkl
<i>I</i>	<i>D</i>	<i>I</i>	<i>D</i>	<i>I</i>	<i>D</i>	
			6 8.47	4 8.488		-1 1 0
			9 5.60	10 5.594		0 0 2
7	4.27	60	4.25	50 4.261		0 0 3
				42 4.249		0 -2 1
				50 4.244		-2 2 0
		4	4.16	13 4.181		0 0 4
				22 4.162		-1 -1 3
1	4.06	5	4.08	29 4.080		2 -1 2
			3.98	34 3.998		1 -2 3
		5	3.72	1 3.718		-2 2 2
				3 3.699		-2 0 3
		3	3.59	13 3.614		-1 -1 4
		4	3.46	14 3.460		2 -2 3
10	3.36	100	3.35	100 3.356		0 0 5
5h	3.14	20	3.14	12 3.164		1 -3 2
				13 3.157		-1 3 0
				15 3.136		2 1 0
				14 3.131		3 -2 1
				36 3.123		-1 -1 5
9	3.08	90	3.06	48 3.066		-1 -2 3
				51 3.064		-2 3 1
				52 3.063		3 -1 1
				43 3.061		2 -1 4
2	3.01	9	3.00	23 2.999		-1 3 1
				42 2.996		1 -2 5
8h	2.886	55	2.885	35 2.881		-2 1 5
		10	2.870	39 2.865		-2 3 2
				39 2.865		-1 -2 4
		9	2.803	41 2.864		3 -1 2
1	2.722	8	2.721	17 2.716		-1 -1 6
				10 2.708		-3 1 4
		5	2.400	13 2.398		3 -1 4
		1	2.298	2 2.297		-3 3 4
		2	2.178	8 2.179		3 -1 5
				7 2.177		-1 -2 7
		1	2.120	2 2.119		1 -4 5
				3 2.119		-1 4 2
		1	2.062	6 2.062		-4 1 5
		1	2.014	1 2.015		4 -4 3
		2	1.983	7 1.983		3 1 3
				5 1.983		-1 -2 8
				4 1.983		3 -1 6
		17	1.868	5 1.868		-1 4 4

Note: Photographic method – RKU 114 M, Fe – anode, Mn-filter, URS-50IM. Diffractometer DRON-2, Fe – anode, graphite monochromator, speed of counter 1 degree /min., internal standard – quartz. Analyst: A.A. Agakhnov

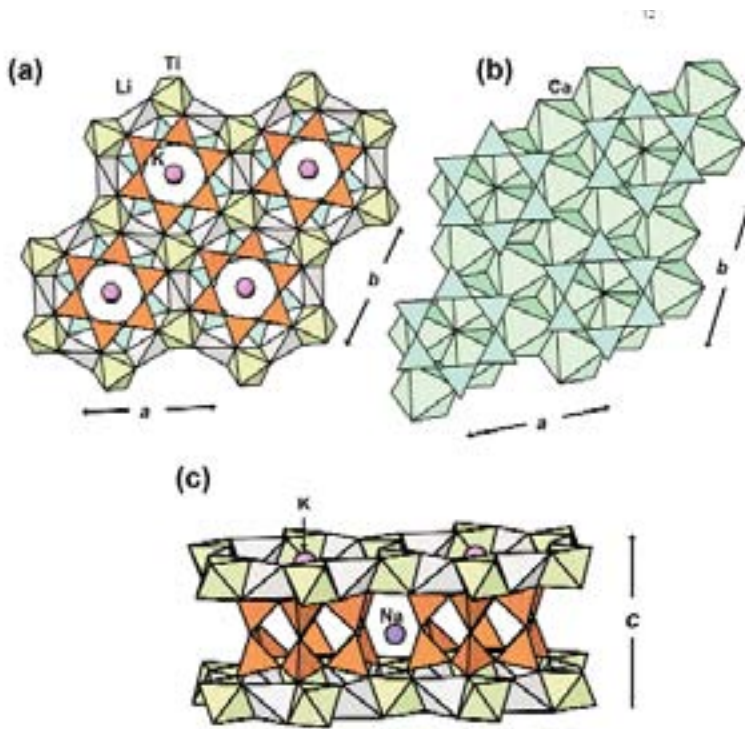


Fig. 4. The crystal structure of faizievite: (a) a fragment of the structure showing $[Si_{12}O_{30}]$ double milarite rings, $[Si_6O_{18}]$ single beryl rings, $[LiO_4]$ tetrahedra and $[TiO_6]$ octahedra viewed down $[001]$; (b) a linkage of $[Si_6O_{18}]$ single rings and Ca-dominant $M(1,2,3,4)$ octahedra viewed down $[001]$; (c) a linkage of $[Si_{12}O_{30}]$ rings and $[LiO_4]$ tetrahedra and $[TiO_6]$ octahedra viewed down $[100]$. $[SiO_4]$ tetrahedra constituting milarite and beryl rings are orange and blue, $[LiO_4]$ tetrahedra are grey, $[TiO_6]$ octahedra are honey yellow; $M(1,2,3,4)$ octahedra are green, $A(1)$ ($=Na$) and $A(2)$ ($=K$) atoms are shown as purple and pink circles.

The crystal structure of faizievite, ideally, $K_2Na(Ca_6Na)Ti_4Li_6Si_{24}O_{66}F_2$, triclinic, $a = 9.8156(9)$, $b = 9.8249(9)$, $c = 17.3087(16)$ Å, $\alpha = 99.209(2)$, $\beta = 94.670(2)$, $\gamma = 119.839(1)^\circ$, $V = 1403.7(4)$ Å³, space group $P-1$, $Z = 1$, was refined to an R_1 index of 7.5% unique reflections measured with MoK X-radiation on a Bruker P4 diffractometer equipped with a Smart 4K CCD detector (Uvarova *et al.*, 2008). There are fifteen tetrahedrally coordinated T sites, twelve of them are occupied solely by Si, with a grand $\langle Si-O \rangle$ of 1.613 Å, and three other tetrahedrally coordinated sites that are occupied solely by Li, with a grand $\langle Li-O \rangle$ of distance 1.928 Å. There are six octahedrally coordinated sites. Two of them are occupied by Ti and four of them are occupied by Ca with minor Na and Sr. The $D(1)$ site is occupied by $Ti_{2.00}$ with $\langle D(1)-O \rangle = 1.937$ Å, and the $D(2)$ site is occupied by $Ti_{2.00}$ with $\langle D(2)-O \rangle = 1.934$ Å. The $M(1)$ site is occupied solely by $Ca_{2.00}$ with $\langle M(1)-O \rangle = 2.441$ Å. The $M(2)$ site is occupied by $(Ca_{1.87}Sr_{0.13})$, with $\langle M(2)-O \rangle = 2.424$ Å. The $M(3)$ site is occupied by $(Ca_{1.55}Na_{0.37}Sr_{0.04}Ba_{0.04})$, with $\langle M(3)-O \rangle = 2.415$ Å. The $M(4)$ site is occupied by

$(Ca_{0.74}Na_{0.26})$, with $\langle M(4)-O \rangle = 2.418$ Å. There are two interstitial A sites: the $A(1)$ site is [12]-coordinated and is occupied by $(K_{1.98}Rb_{0.03})$ with $\langle A(1)-O \rangle = 3.092$ Å; the $A(2)$ site is [9]-coordinated and is occupied by $(Na_{0.90}\square_{0.10})$ with $\langle A(2)-O \rangle = 2.718$ Å.

In the structure of faizievite, Si tetrahedra share common vertices and form [6]-membered rings. Some of the rings are single, $[Si_6O_{18}]$, and some of them are double, $[Si_{12}O_{30}]$. Both types of [6]-membered rings share common vertices with $[LiO_4]$ tetrahedra and $[TiO_6]$ octahedra (Fig. 4a) and form heteropolyhedral sheets perpendicular to the c axis. $M(1,2,3,4)$ octahedra share common vertices and form octahedral sheets perpendicular to the c axis (Fig. 4b). Heteropolyhedral sheets of $[SiO_4]$, $[LiO_4]$ tetrahedra and $[TiO_6]$ octahedra alternate with octahedral sheets of $M(1,2,3,4)$ octahedra (Fig. 2). [6]-membered double- and single rings occlude interstices. K atoms are located in these interstices (Figs. 4a,c). Na atoms are located in between double [6]-membered rings (Fig. 4c)

The faizievite structure (Uvarova *et al.*, 2008) includes an interleaving of sheets of baratovite,

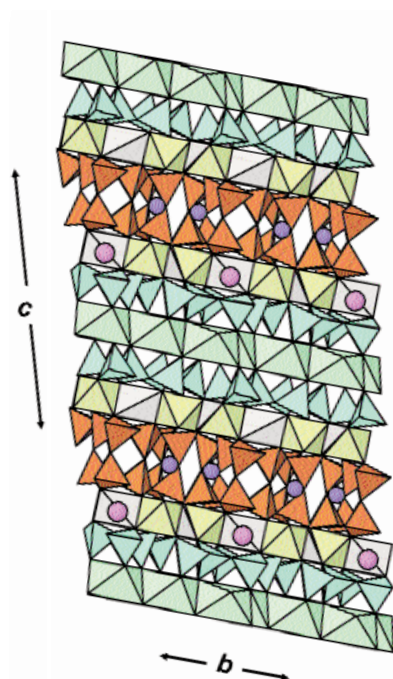


Fig. 5. The crystal structure of faizievite projected onto (011): $[SiO_4]$ tetrahedra constituting milarite and beryl rings are orange and blue, $[LiO_4]$ tetrahedra are grey, $[TiO_6]$ octahedra are honey yellow; $M(1,2,3,4)$ octahedra are green, $A(1)$ ($=Na$) and $A(2)$ ($=K$) atoms are shown as purple and pink circles

Table 3. Comparative characteristic of faizievite, baratovite and berezanskite

	faizievite	baratovite	berezanskite
Chemical formula	$K_2Na(Ca_6Na)Ti_4Li_6Si_{24}O_{66}F_2$	$KCa_7(Ti,Zr)_2Li_3Si_{12}O_{36}F_2$	$KLi_3Ti_2Si_{12}O_{30}$
Space group	Triclinic	Monoclinic	Hexagonal
	<i>P</i> -1	<i>C</i> 2/ <i>c</i> or <i>C</i> c	<i>P</i> 6/ <i>mcc</i>
a , Å	9.8156(9)	16.941(3)	9.903 (1)
b , Å	9.8249(9)	9.746(2)	14.276(2)
c , Å	17.3087(16)	20.907(3)	
α , °	99.209(2)		
β , °	94.670(2)	112.5(1)	
γ , °	119.839(1)		
V , Å ³	1403.7(4)	3189.1	1212.4(4)
Z	1	4	2
Strong lines in X-ray diffraction pattern d_{meas} (Å)			
	5.60 (9)	4.18(3)	7.15(40)
	4.25 (60)	3.54(4)	5.81(12)
	3.35 (100)	3.22(100)	4.29(50)
	3.14(20)	3.02(5)	4.07(85)
	3.06(90)	2.41(20)	3.57(80)
	2.885(55)	1.92(17)	3.16(100)
	2.870(10)	1.83(3)	2.952(50)
	1.868(17)		2.895(95)
			2.742(30)
Density, g/cm ³ (meas.)			
	2.83	2.89	2.66
	Biaxial(+)	Biaxial(+)	Monoaxial(-)
n_p	1.651	1.672	1.630
n_m	1.655	1.672	
n_g	1.657	1.673	1.635
Angle $2V$, °	-72	+60	

$KLi_3Ca_7Ti_2[Si_6O_{18}](OH,F)$ (Sandorskii *et al.*, 1976, Menchetti, Sabelli 1979) and berezanskite, $KLi_3Ti_2[Si_{12}O_{30}]$. It is remarkable that all three minerals, faizievite, baratovite (Dusmatov *et al.* 1975) and berezanskite (Pautov, Agakhanov, 1997), were described first from the Darai-Pioz alkaline massif. The characteristics of these minerals are compared in Table 3.

The holotype sample of faizievite is kept at the Fersman Mineralogical Museum of the Russian Academy of Science (Moscow).

Acknowledgements

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GUIMARÃESITE, A NEW Zn-DOMINANT MONOCLINIC ROSCHERITE-GROUP MINERAL FROM ITINGA, MINAS GERAIS, BRAZIL*

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Guimarã esite¹, Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O, monoclinic, is a new member of the roscherite-group. It occurs as a late fracture-filling mineral in a phosphate-rich granite pegmatite near the Piauí river, Itinga county, Minas Gerais, Brazil. Associated minerals are: albite, microcline, quartz, elbaite, lepidolite, schorl, eosphorite, moraesite, saleeite, zanazziite, an iron-dominant roscherite-group mineral, opal. Guimarã esite forms peripheral zones (up to 0.1 mm thick) in crystals of roscherite-group minerals. The inner zones of the crystals are Mg-rich (and correspond to zanazziite) or Fe-rich (greifensteinite and/or ruifrancoite). Its colour is brown, the streak is white and the lustre is vitreous. Guimarã esite is transparent and non-fluorescent. Density (calc.) is 2.963 g/cm³. The mineral is biaxial (-), α 1.596(2), β 1.600(2), γ 1.602(2) (589 nm). 2V(obs.) 55-75°, 2V(calc.) 70°. The optical X axis coincides with the elongation direction, dispersion: none observed. It is colourless under the microscope. The chemical composition is (wt. %, ranges are indicated in brackets; EDS mode electron microprobe): CaO 9.72 (9.61-9.79); MgO 4.00 (3.61-4.74); MnO 2.18 (0.89-3.26); FeO 2.65 (1.40-4.45); ZnO 19.06 (16.33-20.50); Al₂O₃ 1.70 (1.53-1.92); BeO (calculated) 8.975; P₂O₅ 38.20 (37.61-37.78); H₂O (calculated by difference) 13.515, total 100.00. The empirical formula based on six (PO₄) groups per formula unit is Ca_{1.93}(Zn_{2.61}Mg_{1.11}Fe_{0.41}²⁺Al_{0.37}Mn_{0.34})_{Σ4.84}Be_{4.00}(PO₄)_{6.00}(OH)_{3.90}·6.41H₂O. The strongest reflections of the powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 9.98 (90) (110), 5.98 (100) (020), 4.82 (80) (310), 3.152 (90) (-202), 3.052 (70) (-421), 2.961 (70) (040, 202), 2.841 (70) (-312), 2.708 (80) (041). Unit cell parameters refined from powder data are *a* = 15.98(1) Å, *b* = 11.84(2) Å, *c* = 6.63(1) Å, β = 95.15(15)°, *V* = 1249.4(34) Å³, *Z* = 2. The space group is *C2/c*. The name is for Djalma Guimarã es (1895-1973), in recognition of his outstanding contributions to Brazilian mineralogy and geology. Holotype specimen of guimarã esite is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Brazil, registration number DR 591. 3 tables, 3 figures and 16 references

Introduction

As it was shown in the course of recent investigations (Atencio *et al.*, 2005; Chukanov *et al.*, 2006), hydrous berylophosphates of the roscherite group are characteristic minerals of late parageneses connected with phosphorus-rich rare metal granite pegmatites. These minerals are characterized by wide variations of chemical composition reflecting diversity of local conditions of mineral formation. Now Mn-, Mg-, Fe²⁺- and Fe³⁺-dominant monoclinic roscherite-group minerals are known (respectively, roscherite, zanazziite, greifensteinite and ruifrancoite), as well as two triclinic members of this group (atencioite and footemineite). New Zn-dominant monoclinic member of the roscherite group guimarã esite, Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O described

in this publication was named in honour of the Brazilian mineralogist Djalma Guimarã es (1895-1973). He published several papers and books on geology, petrology, mineralogy and geochemistry, and is the author of the mineral arrojadite and of problematic minerals as "eschwegeite", "giannettite" and "pennaite". Djalma Guimarã es was honored with the name "djalmaite" (later renamed as uranmicrolite). The name "Guimarã esite" was improperly applied more than 50 years ago (Gagarin & Cuomo 1949) to an unnamed mineral, incompletely described by Guimarã es (1926). The new mineral has been approved by the CNMMN-IMA (vote 2006-028).

Holotype material is deposited under the number DR591 in the Museu de Geociências, Instituto de Geociências, Universidade de

* It was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association on September, 1, 2006, No 2006-028

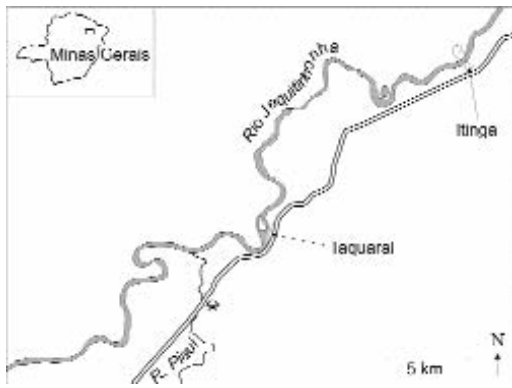


Fig. 1. Type locality of guimarã esite: sketch map

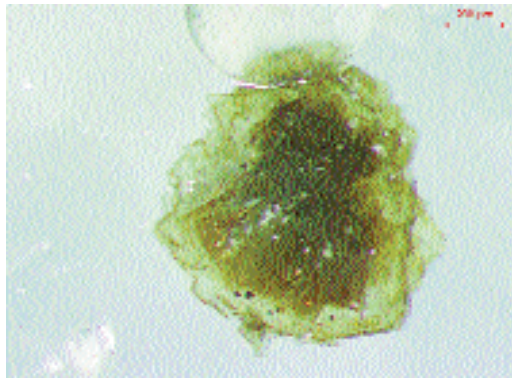


Fig. 2. Crystals of roschelite-group minerals with guimarã esite peripheral zones.

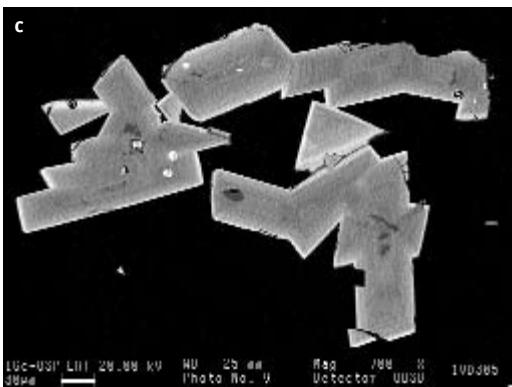
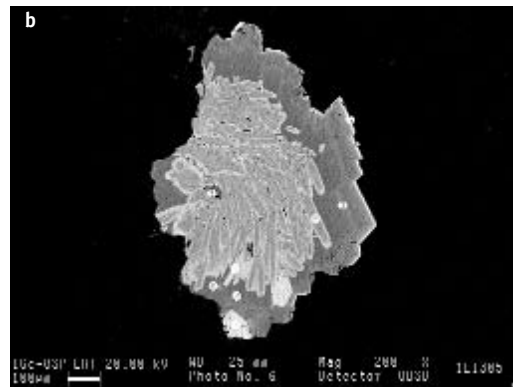
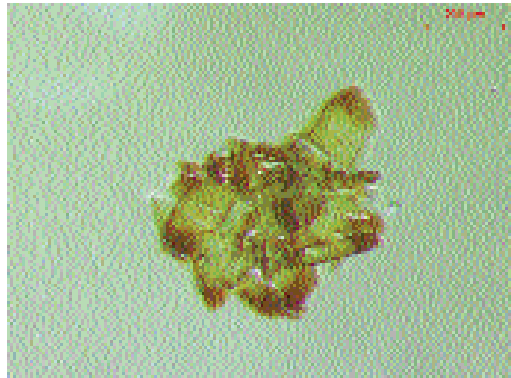


Fig. 3. Polished sections of aggregates of a roschelite-group mineral with guimarã esite peripheral zones. SEM-photos. The electron-microprobe analyses in the points 3 (on Fig. 3a), 6 (on Fig. 3b) and 4 (on Fig. 3c) correspond to guimarã esite.

Table 1. Chemical data for guimarã esite

Constituent	Wt.%,	Range	Probe Standard
CaO	9.72	9.61–9.79	Wollastonite
MgO	4.00	3.61–4.74	Diopside
MnO	2.18	0.89–3.26	MnTiO ₃
FeO	2.65	1.40–4.45	Fe
ZnO	19.06	16.33–20.50	Zn
Al ₂ O ₃	1.70	1.53–1.92	Al ₂ O ₃
P ₂ O ₅	38.20	37.61–38.78	LaPO ₄
BeO*	(8.975)		
H ₂ O*	(13.515)		
Total	(100.00)		

Notes: Calculated, see text

Sã o Paulo, Rua do Lago, 562, 05508-080, Sã o Paulo, SP, Brazil.

Occurrence, appearance and physical properties

The mineral occurs as a late fracture-filling mineral in a phosphate-rich granite pegmatite near the Piauí river, Itinga county, Minas Gerais, Brazil (16°36'47"S and 41°45'55"W), Fig.1. Associated minerals are: albite, microcline, quartz, elbaite, lepidolite, schorl, eosphorite, moraesite, saleeite, zanazziite, an Fe-dominant roscherite-group mineral, opal.

Guimarã esite forms peripheral zones (up to 0.1 mm thick) in crystals of roscherite-group minerals. The inner zones of the crystals are Mg-rich (and correspond to zanazziite) or Fe-rich (greifensteinite and/or ruifrançoite?) (Figs. 2 and 3). Its colour is brown, the streak is white and the lustre is vitreous. Guimarã esite is transparent and non-fluorescent. Mohs hardness is probably about 4.5 by analogy with other roscherite-group minerals. The mineral is brittle. Density could not be measured because of zonal grains. Density calculated with empirical formula is 2.963 g/cm³. By analogy with other roscherite-group minerals, guimarã esite should have perfect cleavage on {100} and good cleavage on {010}. Fracture is uneven. The crystals are not adequate for morphological observations. Forms are probably {100}, {001} and {010} (from prismatic habit). The crystals are tabular parallel to (100). Twinning was not observed.

Optical properties

Guimarã esite is biaxial, negative, α 1.596(2), β 1.600(2), γ 1.602(2); $2V_{\text{obs.}} = 55 - 75^\circ$, $2V_{\text{calc.}} = 70^\circ$. Orientation: the optical X axis

Table 2. X-ray powder-diffraction data for guimarã esite

$I_{\text{obs.}}$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl
90	9.48	9.50	110
10	7.93	7.96	200
100	5.98	5.92	020
20	5.30	5.29	111
80	4.82	4.84	310
30	4.41	4.41	021
60	3.358	3.345	-131
90	3.152	3.151	-202
70	3.052	3.046	-421
70	2.961	2.960	040
		2.957	202
70	2.841	2.838	-312
60	2.798	2.797	331
80	2.708	2.701	041
20	2.528	2.530	241
		2.528	-132
40	2.423	2.427	-422
		2.421	620
50	2.360	2.354	-512
60	2.272	2.274	-441
		2.268	531
70	2.223	2.227	332
		2.217	-151
60	2.161	2.162	350
		2.158	512, -242
10	2.093	2.092	242
50	2.036	2.039	-223
		3.033	-622, 351
50	1.985	1.989	800
		1.983	602
30	1.925	1.928	-641
		1.927	-133
		1.922	-152
20	1.869	1.868	-513
20	1.826		
40	1.781		
40	1.751		
30	1.699		
70	1.642		
20	1.612		
30	1.587		

coincides with the elongation direction; $Z \approx a$. The mineral shows direct extinction with respect to elongation direction. Dispersion is none observed. The mineral is none-pleochroic, colourless under the microscope.

For dark (Fe-dominant) zones of crystals

Table 3. Comparative data for guimarã esite and isostructural minerals (all monoclinic, *C2/c*)

Name	Guimarã esite ¹	Ruifrancoite ²	Roscherite ³	Zanazziite ⁴	Greifensteinite ⁵
Chemical formula	Ca ₂ (Zn ,Mg,Fe) ₅ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ □ ₂ (Fe ³⁺ ,Mn,Mg) ₄ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Mn ₃ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Mg ₃ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Fe ₅ ³⁺ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O
Unit-cell dimensions	<i>a</i> = 15.98 Å <i>b</i> = 11.84 Å <i>c</i> = 6.63 Å <i>β</i> = 95.15°	<i>a</i> = 15.92 Å <i>b</i> = 11.91 Å <i>c</i> = 6.61 Å <i>β</i> = 96.47°	<i>a</i> = 15.935 Å <i>b</i> = 11.963 Å <i>c</i> = 6.664 Å <i>β</i> = 94.77°	<i>a</i> = 15.874 Å <i>b</i> = 11.854 Å <i>c</i> = 6.605 Å <i>β</i> = 95.35(3)°	<i>a</i> = 15.903(7) Å <i>b</i> = 11.885(7) Å <i>c</i> = 6.677(3) Å <i>β</i> = 94.68°
Optical data	<i>n_p</i> = 1.596(2) <i>n_m</i> = 1.600(2) <i>n_y</i> = 1.602(2) 2 <i>V_{obs.}</i> = 55–75° 2 <i>V_{calc.}</i> = 70°	<i>n_p</i> = 1.665(3) <i>n_m</i> = 1.665(3) <i>n_y</i> = 1.682(3) 2 <i>V_{obs.}</i> = 0–10° 2 <i>V_{calc.}</i> = 0°	<i>n_p</i> = 1.624 <i>n_m</i> = 1.639 <i>n_y</i> = 1.643 2 <i>V_{calc.}</i> = 54°	<i>n_p</i> = 1.606(2) <i>n_m</i> = 1.610(2) <i>n_y</i> = 1.620(2) 2 <i>V_{obs.}</i> = 72° 2 <i>V_{calc.}</i> = 65.0°	<i>n_p</i> = 1.624(2) <i>n_m</i> = 1.634(2) <i>n_y</i> = 1.638(2) 2 <i>V_{obs.}</i> = 80(10) 2 <i>V_{calc.}</i> = 64(20)°

Note: Species-forming octahedral cations are given in bold.

¹This work; ²Atencio *et al.*, submitted; ³Rastsvetaeva *et al.*, 2005; Larsen, Berman, 1934; ⁴Leavens *et al.*, 1990; ⁵Chukanov *et al.*, 2002; Rastsvetaeva *et al.*, 2002.

mean refractive index is > 1.64 which can be connected with high content of Fe³⁺ (compare ruifrancoite, the Fe³⁺-member of the roscherite group).

Chemical data

Three point analyses were carried out by means of an electron microprobe (EDS mode, 15.7 kV, 0.5 nA, 8 μm beam diameter). The contents of K, Sr, Ba, Pb, Ni, Cr, Si, S, V, F are below their detection limits. BeO was calculated from the condition Be:P = 2:3 (the stable atomic proportion for roscherite-group minerals following from specific features of their crystal structures). H₂O was calculated by difference. Averaged analytical results are given in Table 1. The empirical formula, calculated based on six (PO₄) groups per formula unit is Ca_{1.93}(Zn_{2.61}Mg_{1.11}Fe_{0.41}²⁺Al_{0.37}Mn_{0.34})_{Σ4.84}Be_{4.00}(PO₄)_{6.00}(OH)_{3.90}·6.41H₂O. The simplified formula is Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O. The end-member formula is: Ca₂Zn₅Be₄(PO₄)₆(OH)₄·6H₂O, which requires: CaO 9.43, ZnO 34.22, BeO 8.41, P₂O₅ 35.81, H₂O 12.12, total 99.99 wt.%.

Crystallography

Single-crystal electron-microdiffraction data revealed the mineral is monoclinic, space group *C2/c*, *a* 15.9(1)Å, *b* 11.85(15)Å, *c* 6.7(1) Å, *β* 95(1)°, *V* 1258(25)Å³, *Z* = 2. X-ray

powder-diffraction data (Table 2) have been obtained for most Zn-enriched particles with sizes 0.05–0.1 mm (selected using semi-quantitative electron microprobe analysis), with RKG 86 mm diameter Debye-Scherrer camera, using CuKα irradiation. Unit cell parameters refined from powder data are *a* = 15.98(1) Å, *b* = 11.84(2) Å, *c* = 6.63(1) Å, *β* = 95.15(15)°, *V* = 1249.4(34) Å³. The *a*:*b*:*c* ratio is: 1.3497:1:0.5600. Compatibility 1-(*K_p*/*K_c*) is 0.031, excellent.

Discussion: crystal chemistry of the roscherite group

The crystal structure of all representatives of the roscherite group studied previously (Fanfani *et al.*, 1975, 1977; Rastsvetaeva *et al.*, 2002, 2004a, 2004b, 2005; Barinova *et al.*, 2004; Chukanov *et al.*, 2006), is based on a three-dimensional framework composed of tetrahedra, octahedra, and calcium seven-vertex polyhedra. The Be and P tetrahedra form infinite chains combined into a mixed framework through *M* octahedra, which, in turn, form octahedral chains by sharing edges. Calcium occurs in the framework cavities. Monoclinic members of the roscherite group are characterized by the space group *C2/c*. Their simplified crystal-chemical formula is Ca₂D₂M₄Be₄(PO₄)₆(OH)₆·4H₂O where *D* and *M* are octahedral cations Mg, Mn²⁺, Fe²⁺, Fe³⁺, Al, Zn. The site *M* is fully occupied; the site *D* con-

tains 50% vacancies, hence the total number of octahedral cations is 5. *D*-polyhedron is characterized by enhanced cation-anion distances (as compared with *M*-polyhedron) and is populated mainly by divalent cations. Monoclinic mineral species from the roscherite group are distinguished by the prevailing octahedral cation. Earlier Mn-, Mg-, Fe²⁺- and Fe³⁺-dominant members have been described (see Table 3). In guimarã esite prevailing octahedral cation is Zn. In the structurally investigated Zn-rich greifensteinite from Brazil (Barinova *et al.*, 2004), all Zn is localized in the *M* site. By analogy, one can suppose that the same takes place in guimarã esite. Among monoclinic roscherite-group minerals, guimarã esite has the largest value of the a unit-cell dimension and the lowest value of refractive index γ (see Table 3).

Triclinic members of the roscherite group form another subgroup (Fanfani *et al.* 1977, Rastsvetaeva *et al.* 2004b, Chukanov, Möckel, 2005, Chukanov *et al.* 2006). Lowering of symmetry is connected with the splitting of the sites *D* and *M* into two pairs of non-equivalent (and differently occupied) sites.

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FERROSKUTTERUDITE¹, NICKELSKUTTERUDITE, and SKUTTERUDITE FROM THE NORILSK ORE FIELD

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Co-Ni-Fe triarsenides skutterudite, nickelskutterudite and ferroskutterudite have been identified in the Norilsk ore field for the first time. They are hosted in the apophyllite – anhydrite – dolomite – calcite metamorphic hydrothermal veins that occur within the proximal zone of the magmatic Co-Ni-Cu sulfide ores, which have been affected by epigenetic prehnite-pumpellyite and zeolite facies metamorphism. The Co-Ni-Fe triarsenides have overgrown the Co-Ni diarsenide segregations with which they form complex intergrowths. Both skutterudite and nickelskutterudite, and skutterudite and ferroskutterudite, from Norilsk form continuous isomorphic series. Clear negative correlation between Ni and Fe and strong positive correlation between Co and Fe and Co and S have been identified.

6 tables, 12 figures, 25 references.

A wide range of isomorphic substitutions of Fe-Co-Ni is characteristic of the iron, cobalt and nickel chalcogenides, including sulfides, sulfoarsenides, arsenides and other compounds. Frequently, there are continuous series of solid solutions including disulfides: pyrite – vaesite NiS_2 – cattierite CoS_2 , diarsenides: safflorite CoAs_2 – rammelsbergite NiAs_2 – loellingite FeAs_2 (Krutov, 1959; Shishkin, 1973; Vaughan & Craig, 1978; Vinogradova, 2002; Gritsenko & Spiridonov, 2005a). Currently, triarsenides skutterudite CoAs_3 – nickelskutterudite NiAs_3 – ferroskutterudite $(\text{Fe,Co})\text{As}_3$ are attributed to them. The continuous skutterudite-nickelskutterudite series has been described previously (Godovikov, 1959; Roseboom, 1962; Radcliffe, 1968; Petruk *et al.*, 1971; Rudashevsky *et al.*, 1975, 1976; Vaughan & Craig, 1978; Vinogradova, 2002; Fanlo *et al.*, 2004).

The skutterudite-group minerals, MeAs_3 , crystallize at low sulfur activity from hydrothermal fluids and are the As-richest arsenides of Co-Ni-Fe. Therefore, they are probably deposited in carbonate veins, whereas the As-depleted maucherite, $\text{Ni}_{11}\text{As}_8$, and niccolite, NiAs , are common in hydrothermally altered peridotite, basic rocks, and metamorphosed Cu-Ni sulfide ores.

Arsenide mineralization occurs in metamorphosed Ni-Cu sulfide ores (Schneiderhöhn, 1955; Yakovlev *et al.*, 1981; Hytönen, 1999;

Spiridonov *et al.*, 2000; Gritsenko & Spiridonov, 2005a, 2005b, 2006). The skutterudite-group minerals are characteristic of Co-Ni-Ag-Bi-U deposits and Ni-Co arsenide deposits (Schneiderhöhn, 1955; Krutov, 1959; Petruk *et al.*, 1971; Shishkin, 1973; Rudashevsky *et al.*, 1975, 1976; Fanlo *et al.*, 2004).

NORILSK ORE FIELD

The Norilsk ore field is located in the plate cover of the Pre-Rephean East Siberian Platform within the zone of marginal deformation. The Co-Ni-Cu magmatic ores of the 250 ± 5 Ma age are related to the gabbrodolerite intrusions of the Upper Permian to Lower Triassic trap assemblage (Godlevsky, 1959; Dodin *et al.*, 1971; Genkin *et al.*, 1981). Magmatic sulfides are disseminated near the base (and at some other levels) of the Norilsk, Talnakh and Taimyr plutons and form massive orebodies, veins and impregnations, mainly in the lower near-contact igneous rocks and adjacent wall rocks. The Norilsk-1 deposit is exploited by the Zapolyarny, Medvezhy Ruchei, and Ugol'ny Ruchei Mines; the Talnakh deposit, Mayak, Komsomol'sky, and Skalisty mines; Taimyr (Oktyabr'sky), Oktyabr'sky and Komsomol'sky mines.

The primary ores are composed of segregations of pyrrhotite- and chalcopyrite-group minerals, cubanite and pentlandite (which are the result of solid-state modifications of Mss and Iss crystallized from sulfide melts) and

¹ A new mineral ferroskutterudite and its name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, October 24, 2006. The type ferroskutterudite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. Registration number is 3440/1

magnetite. The composition of the primary ores ranges from pentlandite-troilite-pyrrhotite through pentlandite-pyrrhotite-cubanite and pentlandite-cubanite-talnakhite to pentlandite-chalcopyrite (Godlevsky, 1959; Kulagov, 1968; Genkin *et al.*, 1981). During post-intrusion fluid conversion, magmatic sulfides recrystallized and minerals of Pd, Pt, Au and Ag formed (Spiridonov *et al.*, 2004).

Areas of the East Siberian Platform are covered by thick sequences of basalt and tuff, and are intruded by numerous dolerite and gabbrodolerite plutons of the trap assemblage. The trap assemblage and lower sequences were affected by the 3-generation regional metamorphism. Generation-1 involved the zeolite facies (Rb/Sr age estimated from apophyllite is 232 to 212 Ma), generation-2, zeolite to prehnite-pumpellyite facies (Rb/Sr age estimated from apophyllite and metabasalt as whole rock is of 212 to 196 Ma), and generation 3, high- to low-temperature part of the zeolite facies (Rb/Sr age estimated from apophyllite is of 212 to 196 Ma) (Spiridonov *et al.*, 2000). The copper-zeolite assemblage, Iceland spar and zeolite deposits, agate and datolite mineralization, and barite, celestine, and (Zn, Pb, Cu, and Ag)-sulfide occurrences are related to this metamorphism (Fig. 1).

The Norilsk ore-bearing plutons and sulfide ores were also affected by low-grade metamorphism. Metadolerite contains prehnite, pumpellyite, epidote, albite, potassium feldspar, titanite,

chlorite and serpentine-group minerals, carbonate, hydrogarnet, actinolite, grunerite, seladonite, ilvaite, diverse zeolites, apophyllite, xonotlite, pectolite, datolite, okenite and thaumasite. The metamorphosed sulfide ores contain pyrite, Ni-pyrite, valleriite, acicular bornite, millerite, heazlewoodite, chalcocite, mackinawite, hematite, ilvaite, violarite, godlevskite, cobaltpentlandite, tochilinite, vyalsovite, and arsenides and antimonides of Ni and Co (Spiridonov *et al.*, 2000). Typical paragenetic associations of the metamorphosed ores are Ni-pyrite + magnetite + valleriite, chalcopyrite + millerite + pyrite, bornite + millerite, and chalcocite + heazlewoodite. Segregations of bornite are cut, overgrown and replaced by segregations of chalcocite.

Antimonide-arsenide mineralization

Metamorphic hydrothermal impregnated and vein mineralization is prominent in the joint zones adjacent to tectonic faults, especially in the zone of the large Norilsk-Kharaelakh fracture, as well as in sedimentary rocks enriched in anhydrite and clay minerals. Ni, Co and Fe arsenides and Ni antimonides are disseminated in metamorphosed Co-Ni-Cu sulfide ores and form pods and impregnations in hydrothermal veins (Godlevsky, 1959; Kulagov, 1968; Dodin *et al.*, 1971; Izoitko & Vyal'sov, 1973; Distler *et al.*, 1975; Genkin *et al.*,

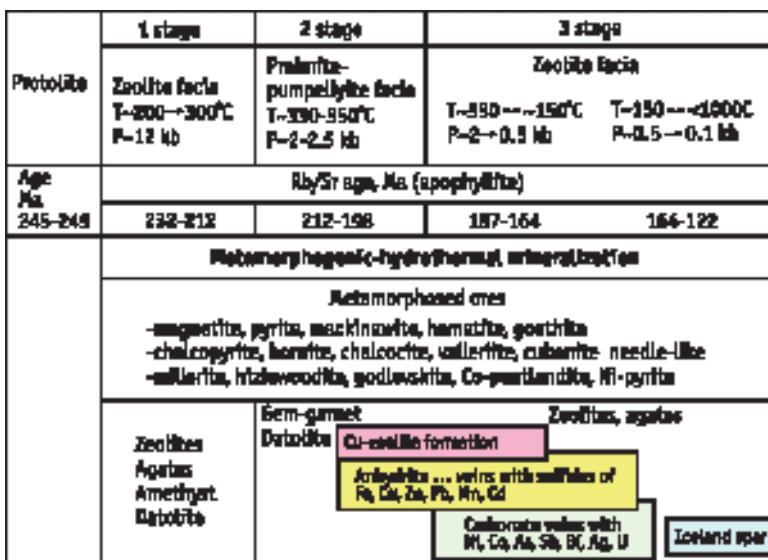


Fig. 1. Low grade metamorphic generations and their isotopic age in the Norilsk region, East Siberian Platform.

1981; Gritsenko & Spiridonov, 2005a, 2005b, 2006). The Co-Ni-Fe triarsenides were identified in the Norilsk ore field for the first time.

The chlorite-carbonate, carbonate (with prehnite and quartz), and apophyllite-anhydrite-carbonate veins with antimonides and arsenides occur at each deposit of the ore field. They are numerous at Talnakh, in the eastern part of Oktyabrsky (Komsomolsky Mine), and in the southern part of Norilsk-1 (Medvezhy Ruchei Mine). The veins of 0.3 to 150 cm thick and 0.1 to 15 m long. Calcite from the arsenide-bearing veins contains primary inclusions of NaCl-MgCl₂ fluids with high salinity ranging from 6.5 to 12.6 wt % eq NaCl. Pressure and temperature of deposition estimated from these inclusions range 0.9 to 0.1 kb and from 216 to 127°C. PT parameters of the arsenide mineralization correspond to those of zeolite-facies metamorphism. The isotopic age of apophyllite from the arsenide-bearing veins is 164 Ma, corresponding to the late generation of the burial regional metamorphism (Spiridonov *et al.*, 2002).

The calcite, calcite-dolomite and apophyllite-anhydrite-carbonate veins with the Ni-Co arsenides occur only within or adjacent to the metamorphosed deposits of Co-N-Cu ores. The calcite and anhydrite-calcite veins with native arsenic and loellingite occur both within and outside the metamorphosed deposits of sulfide ores. The metamorphosed Co-Ni-Cu sulfide ores were the source for the Co-Ni-Sb-As mineralization.

The history of the antimonide-arsenide mineralization is complex. On the basis of relations of brecciation, cross-cutting, overgrowth, and replacement, 12 mineral assemblages formed during these three generations have been recognized.

The generation-1 antimonide-arsenide mineralization is associated with bornite-bearing ore, trending from Ni monoarsenide through Ni and Co di- and triarsenide to native arsenic. Generation-1 comprises nine mineral assemblages:

- 1) cobaltite-gersdorffite-maucherite-Sb-niccolite-niccolite,
- 2) maucherite-gersdorffite-niccolite with Sb-niccolite,
- 3) breithauptite-maucherite,
- 4) loellingite-rammelsbergite-breithauptite-niccolite,
- 5) cobaltite-breithauptite-maucherite-Co-niccolite,
- 6) maucherite-breithauptite-Co-niccolite,
- 7) rammelsbergite-niccolite,
- 8) di- and triarsenide with safflorite,

9) with native arsenic and loellingite.

The generation-2 antimonide-arsenide mineralization occurs in metamorphosed ores which are frequently enriched in chalcocite; native silver and bismuth, Hg-rich silver, pyrrargyrite, clausthalite and other selenides, and uraninite are characteristic minerals. Generation-2 comprises two assemblages: niccolite-breithauptite-rammelsbergite-loellingite and Sb-niccolite-breithauptite.

The generation-3 sulfoarsenide-sulfoantimonide mineralization (latest assemblage) is associated with the pyrite- and marcasite-bearing metamorphosed ores.

The antimonide-arsenide mineralization is enriched in Ni that correlates with the composition of the Norilsk ores. Arsenides enriched in Co periodically crystallized after deposition of significant amount of Ni minerals.

Arsenides and antimonides aggregates show us so-called geometric selection patterns, indicating crystallization from normal solutions in open space.

Material and Research

More than 100 samples from carbonate veins with arsenide mineralization from all deposits of the Norilsk ore field have been studied. These samples were collected by the authors during field investigation of 1998 to 2004 and kindly placed at our disposal by geologists of the Zavenyagin Norilsk Mining and Metallurgical Company: E.A. Kulagov, S.N. Belyakov, E.V. Sereda, A.P. Glotov, and V.V. Butenko. The chemical composition of minerals was analyzed with a CAMEBAX electron microprobe, I.M. Kulikova, analyst, Institute of Geology, Geochemistry and Crystallography of Rare Elements, Russian Academy of Sciences, Moscow and with a CAMEBAX SX-50 electron microprobe, N.N. Kononkova, analyst, Division of Mineralogy, Lomonosov Moscow State University. The BSE images were made with a CAMSCAN 4DV scanning electron microscope equipped with a LINK 10000 energy-dispersion system, N.N. Korotaeva and E.V. Guseva, analysts Division of Petrology, Lomonosov Moscow State University. The X-ray diffraction patterns of skutterudite and nickelskutterudite were collected with a DRON-4.5 diffractometer, Division of Inorganic Chemistry, Lomonosov Moscow State University. Fluid inclusions in calcite from

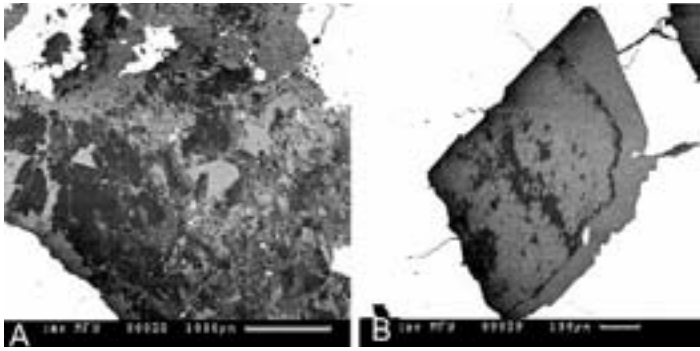


Fig. 2. BSE images of dolomite, calcite and anhydrite from the hydrothermal arsenide veins.

A) Dolomite crystals (dark grey) overgrown and partly replaced by calcite (grey). Anhedral anhydrite (light grey) fills interstices. Arsenides are white.
B) Pseudomorphs of calcite (light grey) after dolomite (dark grey). Safflorite is white.

the arsenide veins were studied in the laboratory of the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, V.Yu. Prokof'ev and Yu.D. Gritsenko, analysts.

These analysis numbers on the figures correspond to the analyzed points in the tables.

Skutterudite, nickelskutterudite and ferroskutterudite from carbonate veins

The Co-Ni-Fe triarsenides were identified only in one of the small systems of anhydrite-calcite-dolomite veins at the South-East flank of the Taimyr ore-bearing pluton (Komsomolsky Mine). In this area, there were steeply dipping carbonate veins to 7 cm thick with irregular impregnation of arsenide segregations, as well as light sphalerite, magnetite and galena within about 2 m of the thick joint zone. The arsenide segregations are microscopic to small pods up to 21 mm cross. Sulfide and magnetite grains are less than 2 mm in size. Bluish anhydrite forms tabular crystals up to 25 x 20 x 3 mm in size and aggregates of plates or isomet-

ric grains included in milky dolomite and white or pinkish calcite. Fluor-hydroxyapophyllite and anhydrite occur in separate vein domains. Dolomite, $\text{Ca}_{1.00-1.02}\text{Mg}_{0.76-0.96}\text{Fe}_{0.03-0.15}\text{Mn}_{0.00-0.07}(\text{CO}_3)_2$, forms segregations of rhombohedral crystals 0.3 to 2 mm in size. The average composition of these dolomite is $\text{Ca}_{1.01}\text{Mg}_{0.86}\text{Fe}_{0.10}\text{Mn}_{0.03}(\text{CO}_3)_2$. Dolomite is overgrown and replaced by calcite up to entire pseudomorphs (Fig. 2). The average chemical composition of this calcite is $\text{Ca}_{0.96}\text{Mn}_{0.02}\text{Fe}_{0.01}\text{Mg}_{0.01}(\text{CO}_3)$.

Calcite-dolomite veins with Co-Ni-Fe triarsenides are composed mainly of aggregates of the 8th and to some extent 7th mineral assemblages. Fragments of niccolite up to 12 mm in size from the 7th mineral assemblage locally occur in pods of di- and triarsenides. Relic niccolite is irregularly distributed. Sb-depleted or Sb-free niccolite contains up to 0.5 wt % Co (Table 1).

Arsenides of generation-1. Niccolite is strongly corroded and overgrown by rammelsbergite-1, which in turn is partly corroded and overgrown by nickelskutterudite-1 (Figs. 3-6). Rammelsbergite-1 is characterized by blocky structure (Figs. 3B, 3C). Nickelskutterudite-I

Fig. 3. Relic niccolite in rammelsbergite-1 surrounded by nickelskutterudite-1.

A) Photomicrograph of relic niccolite (pink) in rammelsbergite-1 (light) surrounded by nickelskutterudite-1 (darker). Black veinlets are composed of calcite and anhydrite. Polished section. Width of image is 0.8 mm.

B) BSE image of relic niccolite (grey, nc, analyses 01 and 02) in rammelsbergite-1 with different S content (light grey to dark grey, analyses 03 and 04) overgrown by nickelskutterudite-1 (white, analyses 10 and 11). Black veinlets are composed of calcite.

C) Fragment of Fig. 3B.

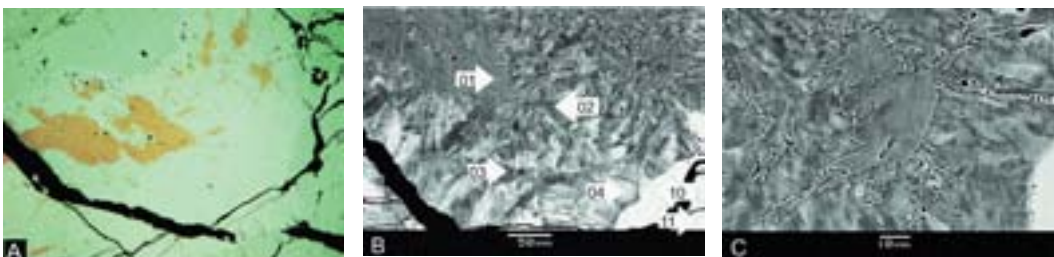


Table 1. Chemical composition of niccolite of mineral complex 7, rammelsbergite-1 and nickelskutterudite-1 of mineral complex 8 from the carbonate veins, Norilsk ore field

No anal.	Element, wt %							Formulae normalized on the basis of 2, 3, or 4 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Total
Niccolite (Fig. 3)																	
01	42.91	0.26	0.02	55.37	—	0.02	—	98.58	0.991	0.006	0.001	0.998	1.001	—	0.001	—	1.002
02	43.31	0.40	0.02	55.87	—	0.09	—	99.69	0.987	0.010	0.001	0.998	0.998	—	0.004	—	1.002
03	43.84	0.23	0.03	55.51	—	0.10	—	99.71	0.996	0.005	0.001	1.002	0.994	—	0.004	—	0.998
Rammelsbergite-1 (Fig. 3)																	
04	26.18	1.75	0.15	70.35	—	0.74	—	99.17	0.929	0.062	0.006	0.997	1.955	—	0.048	—	2.003
05	24.60	3.87	0.13	70.25	—	1.38	—	100.23	0.856	0.134	0.005	0.995	1.917	—	0.088	—	2.005
09	25.42	3.91	0.21	68.62	—	1.58	0.45	100.18	0.888	0.134	0.008	1.030	1.859	—	0.100	0.011	1.970
Rammelsbergite-2 (Fig. 6)																	
07	27.88	1.04	0.05	67.42	3.99	0.05	0.32	100.77	0.999	0.037	0.002	1.038	1.882	0.069	0.004	0.008	1.962
08	28.01	0.38	0.01	72.74	0.26	0.39	—	101.79	0.974	0.013	—	0.988	1.983	0.004	0.025	—	2.012
Nickelskutterudite-1 (Figs. 3, 9B)																	
15	19.60	0.79	0.17	78.92	—	0.03	—	99.51	0.948	0.038	0.008	0.994	2.990	—	0.016	—	3.006
13	17.76	2.60	0.27	79.48	—	0.11	—	100.22	0.854	0.124	0.014	0.992	2.998	—	0.010	—	3.008
11	17.35	3.02	0.54	79.51	—	0.39	—	100.81	0.827	0.143	0.027	0.997	2.968	—	0.035	—	3.003
12	17.20	3.60	0.54	78.70	—	0.58	—	100.62	0.818	0.171	0.026	1.015	2.934	—	0.051	—	2.985
10	16.15	3.95	0.33	78.41	—	0.32	—	99.16	0.783	0.191	0.017	0.991	2.981	—	0.028	—	3.009
14	15.58	4.20	0.71	78.09	—	0.64	—	99.22	0.752	0.202	0.036	0.990	2.953	—	0.057	—	3.010

Notes: Dash means that the element has not been detected or has been below detection limit. Numbers of analyses correspond to those in the figures.

Table 2. Chemical composition of nickelskutterudite-2, skutterudite-2, and Fe-skutterudite-2

No anal.	Element, wt %							Formulae normalized on the basis of 4 atoms									
	Ni	Co	Fe	As	Sb	S	Se	Total	Ni	Co	Fe	Total	As	Sb	S	Se	Total
Sharply zoned crystals of nickelskutterudite-2 - skutterudite-2 (Figs. 6, 7)																	
17	19.19	2.09	0.40	78.59	—	0.10	0.33	100.70	0.917	0.099	0.020	1.037	2.943	—	0.009	0.012	2.963
18	18.69	1.99	0.54	80.31	—	0.09	0.13	101.76	0.876	0.093	0.027	0.996	2.989	—	0.008	0.005	3.002
19	17.89	2.62	0.83	79.88	—	0.09	0.12	101.43	0.844	0.123	0.041	1.007	2.980	—	0.008	0.004	2.992
20	15.71	4.77	0.82	79.65	0.08	0.32	0.12	101.46	0.741	0.223	0.040	1.004	2.963	0.002	0.028	0.004	2.996
16	11.24	6.94	1.56	77.95	0.07	0.38	0.41	98.56	0.605	0.332	0.079	1.016	2.934	0.002	0.033	0.015	2.984
21	9.87	9.17	1.75	76.23	0.14	1.21	—	98.37	0.476	0.442	0.089	1.007	2.884	0.002	0.107	—	2.993
22	7.45	12.06	1.97	78.70	0.31	1.40	—	101.89	0.347	0.560	0.096	1.003	2.871	0.007	0.119	—	2.997
23	5.92	12.95	1.88	77.00	0.14	1.89	—	99.78	0.281	0.610	0.093	0.984	2.851	0.002	0.163	—	3.016
Skutterudite-2, Fe-skutterudite-2, and nickelskutterudite-2 overgrowing sharply zoned crystals																	
nickelskutterudite-2 - skutterudite-2 (Figs. 7, 9A)																	
24	14.58	5.99	0.77	79.32	—	0.66	0.11	101.43	0.681	0.279	0.038	0.998	2.937	—	0.056	0.004	2.997
25	6.99	12.44	0.86	77.23	0.09	1.58	—	99.19	0.337	0.598	0.044	0.979	2.880	0.002	0.139	—	3.021
26	7.46	11.70	2.02	78.19	0.02	1.58	—	100.97	0.349	0.546	0.100	0.995	2.869	0.001	0.135	—	3.005
27	7.25	11.97	2.84	77.64	0.20	1.44	—	101.34	0.342	0.516	0.141	0.999	2.873	0.004	0.124	—	3.001
28	6.81	11.83	2.95	77.41	0.22	1.27	0.09	100.58	0.325	0.515	0.148	0.988	2.894	0.005	0.111	0.002	3.012
29	4.73	13.22	3.39	76.67	0.38	1.62	—	100.01	0.223	0.622	0.168	1.013	2.838	0.009	0.140	—	2.987
30	7.22	13.07	0.63	76.67	0.02	1.67	0.15	99.43	0.343	0.619	0.032	0.994	2.855	0.001	0.145	0.005	3.006

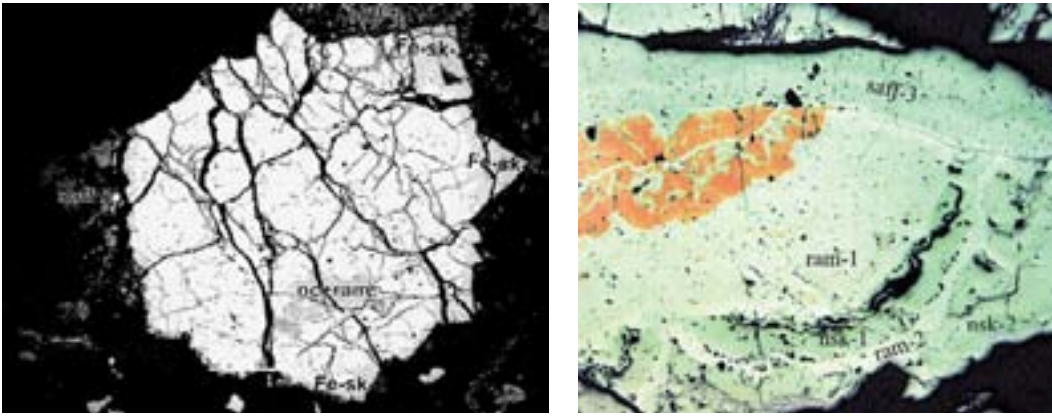


Fig. 4. BSE image of intergrowth of cubic crystals of nickelskutterudite-2 and skutterudite (white). Outer zones are Fe-skutterudite-2 (light grey, Fe-sk-2); relic niccolite in rammelsbergite (grey, nc+ram) in the intergrowth. The generation-3 assemblage of dolomite (black) and Fe-safflorite (dark grey, saff-3) surrounds the large intergrowth.

Fig. 5. Photomicrograph of relations between the three generations of rammelsbergite, nickelskutterudite and safflorite. Relic niccolite (pink) in rammelsbergite-1 (ram-1) and nickelskutterudite-1 (nsk-1). Rim of rammelsbergite-2 on nickelskutterudite-1 followed by zoned crystals of nickelskutterudite-2 (nsk-2). Segregation of rammelsbergite and nickelskutterudite of generations 1 and 2 is overgrown by safflorite-3 (saff-3) and Co-rammelsbergite-3. Polished section. Width of image is 15 mm.

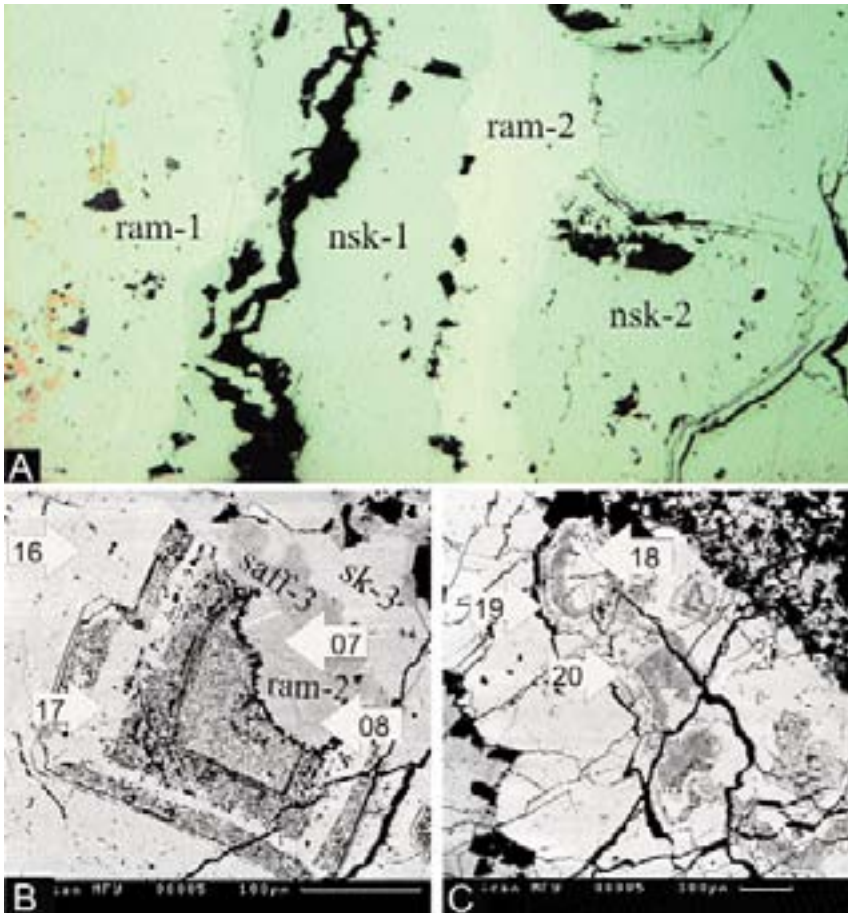


Fig. 6. Intergrowths of three generations of rammelsbergite, nickelskutterudite and safflorite.

A) Photomicrograph of rammelsbergite-1 (ram-1) with relic niccolite (pink) overgrown by nickelskutterudite-1 (nsk-1) with the rammelsbergite-2 rim (ram-2), which is substrate for zoned crystals of nickelskutterudite-2 (nsk-2). Polished section, width of image is 5 mm.

B) BSE image of zoned crystal of Co-nickel-skutterudite-2 (white, analyses 16 and 17) has overgrown split rammelsbergite-2 (ram-2, analyses 07 and 08). This is fragment of the generation-2 arsenides overgrown by the generation 3 arsenides safflorite (saff-3) and Ni-skutterudite (sk-3). C) BSE image of zoned crystals of nickelskutterudite-skutterudite-2 (grey white, analyses 18-20).

and dolomite have compromise growth surface. This is the first generation of the 8th mineral assemblage.

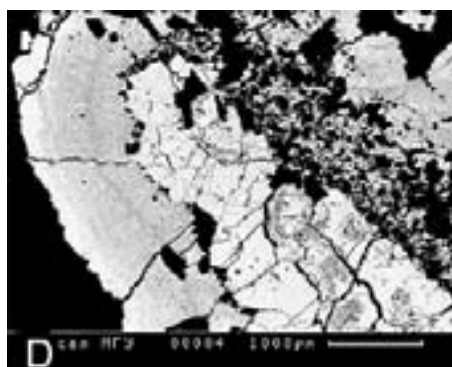
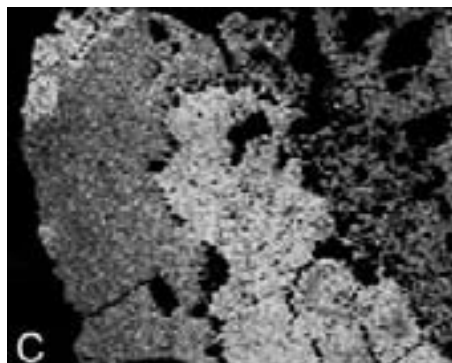
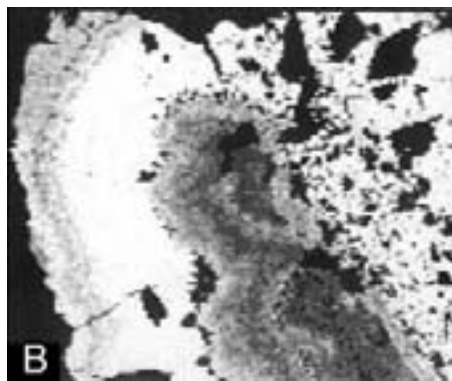
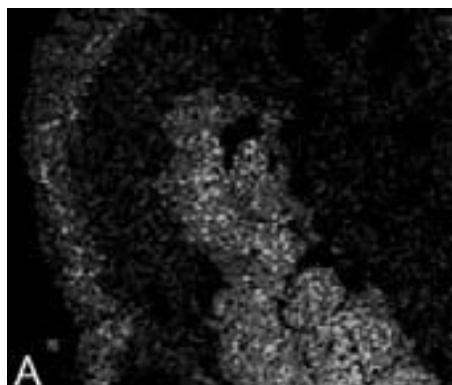
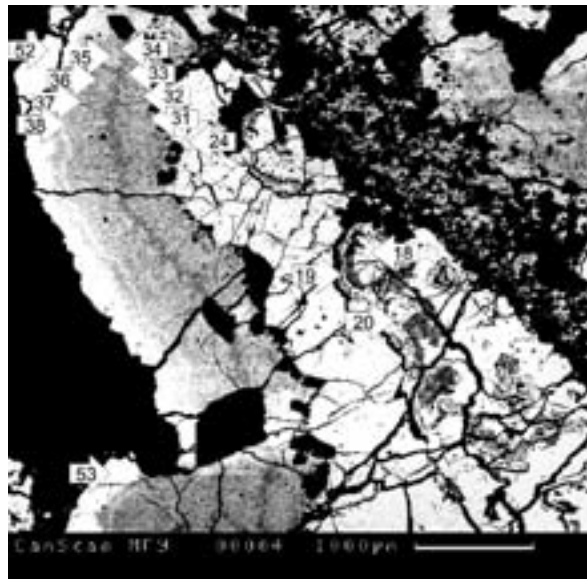
Rammelsbergite-1 is moderately low in S and Fe-free and contains up to 4 wt % Co and 0.5 wt % Se (Table 1). Nickelskutterudite-1 is low in Co and Fe (Table 1) and shows strong negative correlations between Ni and Co ($r = -0.96$) and Ni and Fe ($r = -0.80$) and strong positive correlations between Co and Fe ($r = +0.75$) and Co and S ($r = +0.70$) ($n = 14$).

Arsenides of generation-2. Generation-1 segregations are overgrown by complex zoned aggregates of generation-2 di- and triarsenides. Relic niccolite-free crystals of rammelsbergite-2 (Figs. 5, 6A, 6B) are overgrown by zoned cubic and cuboctahedral crystals of nickelskutterudite-2 with outer zones of Co-nickelskutterudite-2 and skutterudite-2 (Figs. 5–8, Table 2), which are followed by relatively homogeneous skutterudite-2 with thin zones of Fe-skutterudite-II (Fig. 9A, Table 2). Separate cuboctahedral crystals and intergrowths (up to 5 mm across) of generation-2 triarsenides are observed; Fe-skutterudite-2 is frequently dominant in the outer zones of such grains (Fig. 4).

Rammelsbergite-2 is low in S, moderately low in

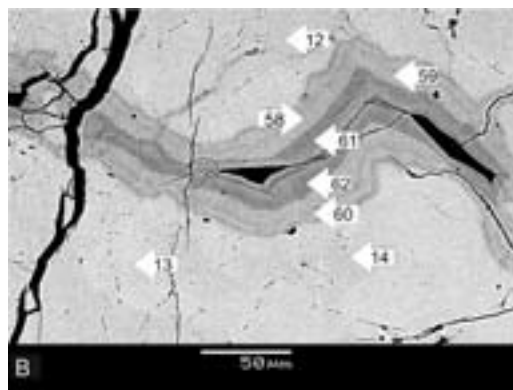
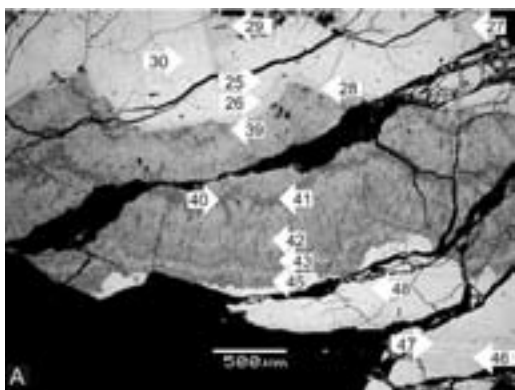
Fig. 7. BSE image of aggregation of safflorite-3 (analyses 31-36), dolomite and Co-rammelsbergite-3 (analyses 37 and 38) split crystals, which have overgrown aggregate of the nickelskutterudite – skutterudite-3 (grey-white, analyses 18–24) zoned crystals. Diarsenides are overgrown by Ni-skutterudite (white, analyses 52 and 53) and calcite (black).

Fig. 8. Aggregation of nickelskutterudite – skutterudite-3, safflorite-3, and Co-rammelsbergite-3. Maps of Ni (A), Co (B), and As (C) distribu-

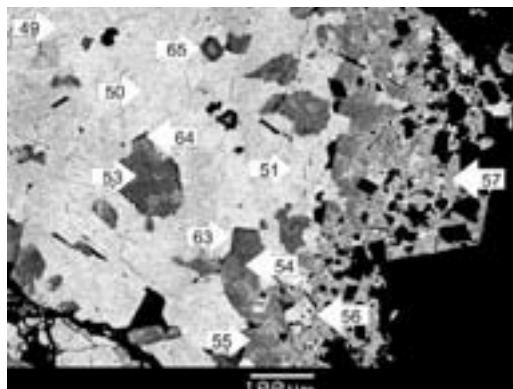


CanCam HF3 0004 1000μm

CanCam HF3 0004 1000μm



tion; D) BSE image.



Sb, and low in Co (Table 1). Zoned triarsenides of generation-2 form a continuous nickelskutterudite-skutterudite series and do not contain significant Sb or Se (trace to 0.4 wt %). The concentration of Fe and S in these minerals increases as the skutterudite component increases (Table 2). Strong negative correlations between Ni and Co ($r = -0.98$) and Ni and Fe ($r = -0.64$) and positive correlations between Co and Fe ($r = +0.51$) and Co and S ($r = +0.97$) ($n = 36$) are characteristic of these triarsenides. Later generation-2 triarsenides are skutterudite enriched in Fe and Ni, and infrequently, nickelskutterudite enriched in Co (Table 2), and contain practically no Sb and Se.

Arsenides of generation-3. Segregations of di- and triarsenides with inclusions of dolomite rhombohedra and arsenide-dolomite segregations of generation-3 overgrow individual crystals and aggregates of generation-1 and generation-2 minerals (Figs. 4-8, 9A), cementing them (Fig. 7) and forming veinlets in them (Fig. 9B). They are also present as separate grains. Segregations of strongly fractured

Fe-safflorite-3, S-rich safflorite-3, Ni-safflorite-3 and Co-rammelsbergite-3 (Figs. 7-9A) are earlier, and are overgrown by compositionally homogeneous nickelskutterudite-3 (Fig. 9A, Table 3). Occasionally, arsenide pseudomorphs after safflorite (Fig. 7) involve skutterudite enriched in Fe and Ni (Table 3, analyses 52 and 53). Numerous small sharply zoned crystals of Fe-skutterudite-3 enriched in Fe with rims of ferroskutterudite-3 (Fig. 10) are included in large areas of nickelskutterudite-3. The same Fe-Co- and Co-Fe-triarsenides form veinlets cross-cutting the generation-1 minerals (Fig. 9B) and overgrowing the latter.

Diarsenides of the generation-3 form the continuous safflorite-rammelsbergite series. As with the triarsenides of generation-2, they are depleted in Sb and Se. Safflorite-3 is enriched in Fe, more frequently in combination with S. In general, there are strong negative correlations between Ni-Co ($r = -0.96$), Ni-Fe ($r = -0.84$), and As-S ($r = -0.98$) and a positive correlation between Co-Fe ($r = 0.66$) ($n = 62$).

The triarsenides of generation-3 commonly are nickelskutterudite depleted in Co and almost

Table 3. Chemical composition of nickelskutterudite-3, Ni-skutterudite-3, and Fe-skutterudite-3

No anal	Element, wt %					Formulae normalized on the basis of 3 atoms											
	Ni	Co	Fe	As	Sb	S	Se	Total	Ni	Co	Fe	Total cat.	As	Sb	S	Se	Total anions
Nickelskutterudite-3 overgrowing safflorite-3 (analyses 46-48, Fig. 9A) and isolated grains (analyses 49-51, Fig. 10)																	
46	19.57	0.90	0.24	78.81	—	0.04	—	99.56	0.948	0.044	0.012	1.004	2.993	—	0.003	—	2.996
47	19.27	1.40	0.33	78.92	—	0.14	—	100.06	0.928	0.067	0.016	1.011	2.977	—	0.012	—	2.989
48	18.86	1.75	0.20	79.01	—	0.38	—	100.20	0.904	0.084	0.100	1.088	2.969	—	0.033	—	3.002
49	17.28	2.96	0.34	78.54	—	0.29	—	99.41	0.836	0.143	0.017	0.996	2.978	—	0.026	—	3.004
50	18.50	2.17	0.24	78.02	—	0.30	—	99.23	0.896	0.105	0.012	1.013	2.960	—	0.027	—	2.987
51	15.98	3.15	1.29	78.81	—	—	—	99.23	0.778	0.152	0.066	0.996	3.004	—	—	—	3.004
Ni-skutterudite-3 overgrowing Co-rammelsbergite-3 (Fig. 7)																	
52	8.03	11.63	1.65	76.55	0.12	1.32	0.15	99.45	0.376	0.542	0.081	1.000	2.879	0.003	0.114	0.005	3.000
53	7.21	11.39	2.37	77.84	0.34	1.48	0.15	100.77	0.336	0.529	0.116	0.981	2.880	0.008	0.126	0.005	3.019
Fe-skutterudite-3 (Figs. 9B 10)																	
54	0.98	10.94	8.36	78.82	0.07	0.33	0.05	99.55	0.047	0.525	0.423	0.995	2.972	0.002	0.029	0.002	3.005
55	0.28	11.56	8.22	78.48	0.09	0.71	—	99.34	0.018	0.552	0.415	0.985	2.951	0.002	0.062	—	3.015
56	6.05	10.13	4.43	77.12	0.41	1.34	—	99.48	0.288	0.481	0.222	0.991	2.882	0.010	0.117	—	3.009
57	2.16	13.66	5.10	76.89	0.08	0.97	0.13	98.99	0.104	0.653	0.257	1.014	2.894	0.002	0.085	0.005	2.986
58	0.59	12.89	7.84	77.70	—	1.55	—	100.57	0.028	0.601	0.386	1.015	2.852	—	0.133	—	2.985
59	0.89	14.22	6.04	77.77	—	1.44	—	100.36	0.042	0.667	0.299	1.008	2.869	—	0.124	—	2.993
60	0.29	13.49	7.54	77.23	0.20	1.23	0.20	100.18	0.014	0.635	0.374	1.023	2.860	0.004	0.106	0.007	2.977

Table 4. Chemical composition of Fe-safflorite-3 and Co-rammelsbergite-3

No anal	Element, wt %					Formulae normalized on the basis of 3 atoms											
	Ni	Co	Fe	As	Sb	S	Se	Total	Ni	Co	Fe	Total cat.	As	Sb	S	Se	Total anions
Profile from contact with the generation 2 triarsenides (Fig.7)																	
31	0.49	25.22	3.37	65.46	0.36	5.64	0.25	100.78	0.027	0.824	0.116	0.968	1.682	0.006	0.338	0.006	2.032
32	1.11	23.12	3.95	67.02	0.32	4.21	0.13	99.86	0.055	0.775	0.139	0.969	1.764	0.005	0.259	0.003	2.031
33	—	22.43	4.99	71.02	0.09	1.22	0.21	99.95	—	0.803	0.182	0.985	1.931	0.002	0.077	0.005	2.015
34	—	24.79	4.48	64.82	0.30	5.73	0.08	100.21	—	0.821	0.156	0.977	1.671	0.005	0.345	0.002	2.023
35	0.19	23.70	5.21	65.56	0.17	5.01	0.14	99.97	0.007	0.787	0.182	0.976	1.712	0.003	0.306	0.003	2.024
36	3.55	21.07	3.64	67.00	0.11	4.29	0.14	99.80	0.123	0.707	0.129	0.959	1.770	0.002	0.265	0.003	2.041
37	17.60	11.38	0.81	65.37	0.09	4.98	0.16	100.38	0.586	0.376	0.028	0.991	1.701	0.001	0.303	0.004	2.009
38	17.49	12.52	0.61	67.95	0.10	3.98	0.10	102.74	0.576	0.410	0.021	1.007	1.750	0.002	0.240	0.002	1.993
Profile from contact with the generation 2 triarsenides (Fig.9A)																	
39	0.02	22.81	5.47	69.16	—	1.48	—	98.94	0.001	0.798	0.202	1.001	1.904	—	0.095	—	1.999
40	0.06	23.22	6.48	65.17	—	4.17	—	99.10	0.002	0.782	0.230	1.014	1.728	—	0.258	—	1.986
41	0.05	27.02	4.04	61.57	—	6.87	—	99.55	0.002	0.878	0.138	1.018	1.572	—	0.410	—	1.982
42	8.73	17.16	2.56	67.55	—	3.28	—	99.28	0.293	0.573	0.157	1.023	1.776	—	0.201	—	1.977
43	15.68	12.66	1.20	65.57	—	4.93	—	100.04	0.523	0.420	0.042	0.985	1.714	—	0.301	—	2.015
44	16.64	11.71	0.61	65.32	—	4.10	—	98.38	0.566	0.397	0.038	1.001	1.743	—	0.256	—	1.999
45	18.16	9.31	0.48	68.89	—	2.43	—	99.27	0.631	0.322	0.018	0.971	1.874	—	0.155	—	2.029

Table 5. Chemical composition of ferroskutterudite

No	Element, wt %						Formulae normalized on the basis of 4 atoms						
	anal.	Ni	Co	Fe	As	S	Total	Ni	Co	Fe	Total	As	S
61	0.05	8.70	12.95	79.43	1.31	102.44	0.002	0.398	0.626	1.026	2.864	0.110	2.974
62	0.01	7.94	12.63	77.56	1.43	99.57	0.001	0.374	0.628	1.003	2.843	0.124	2.967
63	0.05	8.04	12.38	77.09	1.39	98.95	0.002	0.381	0.619	1.002	2.877	0.121	2.998
64	0.10	8.82	10.38	77.96	1.24	98.50	0.005	0.423	0.525	0.953	2.938	0.109	3.047
65	0.05	8.38	12.09	78.01	1.34	99.87	0.002	0.394	0.600	0.996	2.888	0.116	3.004

Note: See Figures 9 and 10

Fe-, Sb-, S- and Se-free (Table 3, analyses 46-50). Strong negative correlations Ni-Co ($r = -0.99$), Ni-Fe ($r = -0.83$), and As-S ($r = -0.91$) and positive correlation Co-Fe ($r = +0.76$) and Co-S ($r = +0.93$) ($n = 27$) are characteristic of nickelskutterudite-3. Sb-low skutterudite-3 moderately enriched in S and ranging from Ni-free to moderately enriched in Ni (Table 3, analyses 52–60) is less frequent. Strong negative correlations Ni-Co ($r = -0.83$), Ni-Fe ($r = -0.64$), Co-Fe ($r = -0.72$), and As-S ($r = -0.92$) and strong positive correlation Co-S ($r = +0.81$) ($n = 37$) are characteristic of Fe-rich skutterudite-III.

Ferroskutterudite from carbonate veins

The ferroskutterudite-3 grains range in size from 1 to 40 μm . Relief is high close to skutterudite and safflorite and is higher than nickelskutterudite. Values of VHN_{50} (4 indentations) range from 700 to 1050 kg/mm^2 . The mineral is highly reflective (58–54%), white and isotropic under reflected light. The reflectance spectrum close to skutterudite with the slightly higher R values was measured in air with a WTiC certified standard. Reflectance values ($R\%$) are as follows: 400 nm (57.2), 420 nm (57.6); 440 nm (58.0), 460 nm (58.2), 470 nm (58.2) (COM), 480 nm (58.2), 500 nm (58.0), 520 nm (57.6), 540 nm (57.3), 546 nm (57.2) (COM), 560 nm (56.9); 580 nm (56.4); 589 nm (56.2) (COM), 600 nm (56.0), 620 nm (55.5), 640 (55.2 nm), 650 nm (54.9) (COM), 660 nm (54.7), 680 nm (54.3), and 700 nm (53.8).

Ferroskutterudite-3 contains only traces of Ni, Sb and Se (Table 5). The average composition ($n = 5$) is $(\text{Fe}_{0.600}\text{Co}_{0.394}\text{Ni}_{0.002})_{0.996}(\text{As}_{2.888}\text{S}_{0.116})_{3.004}$, i.e., close to $(\text{Fe}_{0.6}\text{Co}_{0.4})_1\text{As}_3$.

X-ray diffraction data for the cubic triarsenides nickelskutterudite, skutterudite and ferroskutterudite are similar. The X-ray diffraction pattern of ferroskutterudite (Table 6) was

Table 6. X-ray powder diffraction data for ferroskutterudite

I_{hkl}	$d_{hkl}, \text{\AA}$	$d_{\text{obs}}, \text{\AA}$	hkl
3	5.8	5.77	110
3	4.10	4.085	200
4	3.34	3.335	211
10	2.585	2.584	310
9	2.182	2.184	321
4	1.928	1.926	411
7	1.829	1.827	420
3	1.744	1.742	332
5	1.667	1.6677	422
7	1.602	1.6023	510
6	1.402	1.4011	530
3	1.364	1.3617	600
2	1.291	1.2918	620

Note: Debye-Scherrer camera, D 57.3 mm, $\text{CuK}\alpha$.

indexed by analogy with skutterudite. The mineral is cubic, space group $Im\bar{3}m$, $a = 8.17(1) \text{\AA}$, $V = 545.34(3) \text{\AA}^3$, $Z = 8$.

Conclusions

1. Di- and triarsenide minerals of the anti-monide-arsenide mineralization in the Norilsk ore field was formed during multiple tectonic movements. Later mineral segregations in this complex overgrow and replace earlier ones and are present as veinlets and matrix breccia in the latter. Dolomite is characteristic of di- and triarsenide intergrowths, whereas calcite occurs in mono- and diarsenide intergrowths.

2. During each generation, Ni-Co diarsenides were deposited earlier than the Ni-Co-Fe triarsenides. Diarsenides form a continuous rammelsbergite-safflorite solid-solution series (Fig. 11).

3. During each generation of the di- and triarsenide mineral formation, nickelskutterudite is

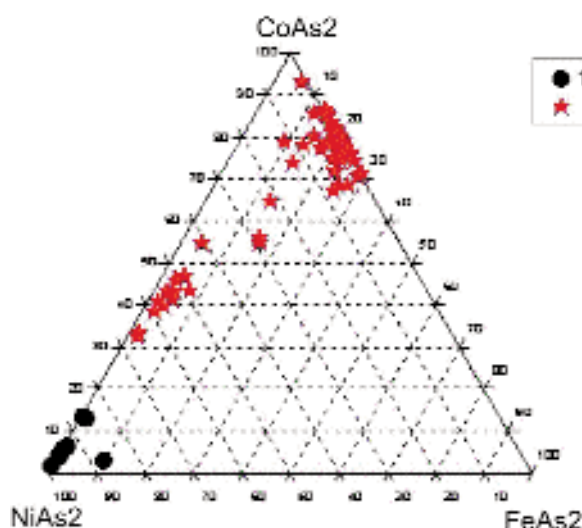


Fig. 9. BSE images of the relations between nickel-skutterudite, Fe-skutterudite, ferroskutterudite and safflorite.

A) Fe-skutterudite-2 (white-grey, analyses 26–30) is overgrown by aggregation of the generation-3 di- and triarsenides: strongly split Fe-safflorite (light grey, analyses 39–42) and Co-rammelsbergite-3 (grey, analyses 43–45) with different S content followed by nickelskutterudite-3 (white-grey, analyses 46–48). Calcite and dolomite are black.

B) Fragment of Fe-skutterudite (grey, analyses 58–60) and ferroskutterudite (dark-grey, analyses 61 and 62) veinlet in nickelskutterudite-1 (light grey, analyses 12–14). Branching calcite veinlets (black).

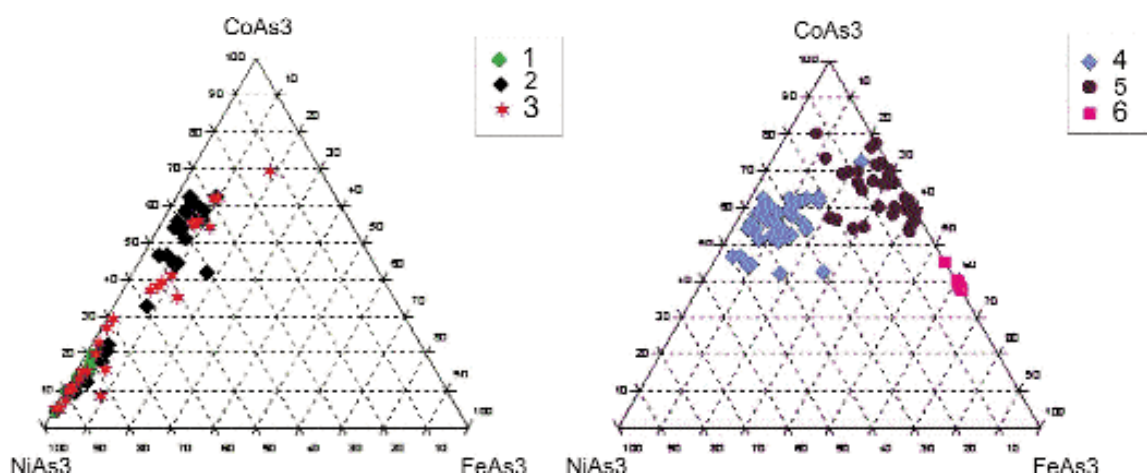


Fig. 10. BSE images of zoned crystals of ferroskutterudite-3 (dark grey, analyses 63–65) - Fe-skutterudite (grey, analyses 53–57) in nickelskutterudite-3 (white, analyses 49–51). Rhombohedra of dolomite and veinlets of calcite are black.

earlier than skutterudite and Fe-skutterudite.

4. The Norilsk triarsenides form two compositional series in: skutterudite-nickelskutterudite and skutterudite-ferroskutterudite (Fig. 12), characterized by a well-defined negative correlation between Ni and Fe and strong positive correlations between Co and Fe and Co and S.

Acknowledgment

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THE NEW FINDS OF PERTSEVITE

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A revision of samples and thin sections collections of kotoitebearing rocks by optics and Electron Micro Probe methods has permitted to find two new occurrences of pertsevite $Mg_2(B,Si)(O,F,OH)_4$. In comparison with the pertsevite holotype having a rather broad meaning of B/Si the new finds of the mineral are more homogeneous in X_{Si} 0.12–0.20 in the sample from Titovskoye deposit, East Verkhoyansk region, and 0.24–0.32 from Gonochan deposit (Djugdjur Ridge, near Okhotsk Sea Coast). The last has the predominance of hydroxile over fluorine. The compositions of accompanied minerals – kotoite, ludwigite and humite group minerals have been studied and presented as well. Pertsevite was formed after kotoite and clinohumite with their reciprocal replacement owing to their chemical interaction.

2 tables, 1 figure, 7 references

After the approving of pertsevite as a new mineral species (Schreyer et al., 2003) the discoverer of it, outstanding mineralogist and petrologist Werner Schreyer decided prolongate the investigation. We have made attempts to find pertsevite in other occurrences, localities and regions. Thin sections of samples with kotoite mineralization collected by N.N. Pertsev and V.V. Rudnev from the 1950s to the 1990s at different localities in Russia were reexamined. The revision had allowed us to separate several samples with assumed pertsevite presence. Two of them have been studied in Ruhr University Bochum where the pertsevite holotype was investigated before using the same technique and equipment (EMP – CAMECA SX 50, etalons: synthetic pyrope, andradite, spessartite, TiO_2 , Cr_2O_3 , V_2O_5 , borosilicate glass and natural topaz; accelerating voltage 15 kV, beam current 15 nA). The results approved pertsevite presence. We finished the work after W. Schreyer left us in January, 2006.

The specimen from Titovskoye deposit (East Verkhoyansk region, Tas-Khayaktakh Ridge).

It is the sample VR-10 from V.V. Rudnev's collection. This locality is in the region east of Verkhoyansk, same to that of the initial find-

ing, or type locality of pertsevite (Schreyer et al., 2003; Pertsev et al., 2004) but from a different deposit distant about 30 km to east (Dorofeyev, 1979; Lisitsin et al., 1995). Kotoitite and kotoite marble zone occupy place between spinel-forsterite skarn zone and marble in which periclase has been replaced by typical brucite pseudomorphs.

The studied part of the sample is a small chip (about 3 x 3 x 1 cm) of a dense, massive, light-grey rock containing some black patches of about 5 mm in diameter. Using a hand lens, the latter can be identified to be made up of numerous prisms and needles of what looks like opaque members of the ludwigite-vonsenite series. Except for these, the rock is transparent in thin section and consists of a regular, non-oriented fabric of interlocking mineral grains with generally medium refringence as well as medium birefringence. Average grain size is about 1 to 2 mm. In very few cases of favorable orientation, grains having a higher birefringence can be recognized as pertsevite, which is but a minor constituent of the rock. Otherwise, pertsevite is hard to distinguish from the main constituent kotoite, if it were not for BSE images, in which pertsevite is just slightly brighter than kotoite. The whole rock, best named as kotoitite, is irregularly dissected by a multitude of veins and cracks, up to half a millimeter wide, which contain extreme-

Table 1. EMP (Electron microprobe) analyses of minerals in the kotoite (sample VR-10)

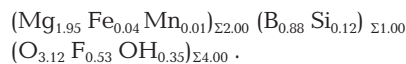
Mine	Perts.1 ¹	Perts.6	Perts.5	Koto3	Koto. id	Ludw.7	Alter.9 ¹	aib.id	ral
SiO ₂	5.41	7.81	8.82	0.31	—	0.04	0.24	—	
B ₂ O ₃ ²	22.36	21.88	20.93	36.79	36.79	15.31 ³	n.d.	41.38	
Al ₂ O ₃	0.01	0.00	0.00	0.00	—	1.01	0.00	—	
MgO	59.98	59.66	58.94	58.32	63.21	28.93	48.13	47.91	
FeO	2.18	2.38	2.05	4.22	—	47.93	1.07	—	
MnO	0.27	0.25	0.28	0.34	—	0.18	0.36	—	
CaO	0.03	0.02	0.08	0.01	—	0.04	0.08	—	
F	7.65	6.93	6.10	0.02	—	0.18	0.00	—	
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	—	n.d.	0.00	—	
Total	98.89	98.93	97.20	100.01	100.00	93.62	49.88	—	
-O=F ₂	3.22	2.92	2.57	0.01	—	0.08	0.00	—	
H ₂ O	2.43	2.38	2.53	n.d.	—	n.d.	n.d.	10.71	
Total	(wt.%)	98.10	98.39	97.16	100.00	100.00	93.54	49.88	100.00
Recalculations of ions per formula units (for details see text)									
Si	0.118	0.171	0.196	0.010	—	0.001	—	—	
Al	0.000	0.000	0.000	0.000	—	0.042	—	—	
B	0.881	0.828	0.804	2.041	2.000	1.000	—	1.000	
Sum 1	0.999	0.999	1.000	—	2.000	—	—	1.000	
Mg	1.954	1.951	1.955	2.795	3.000	1.528	—	1.000	
Fe ²⁺	0.040	0.044	0.038	0.113	—	0.464 ³	—	—	
Fe ³⁺				—	—	0.957 ³			
Mn	0.005	0.005	0.005	0.009	—	0.005	—	—	
Ca	0.001	0.001	0.002	0.000	—	0.001	—	—	
Sum 2	2.000	2.001	2.000	2.918	3.000	—	—	1.000	
F	0.529	0.481	0.429	—	—	0.020	—	—	
O ²	3.117	3.170	3.195	—	6.000	—	—	2.000	
OH ²	0.354	0.349	0.375	—	—	—	—	1.000	
Sum 3	4.000	4.000	3.999	—	—	—	—	3.000	

Note: ¹original numbers of analyses; ²calculated (see text) or as in ideal formula; ³calculated by distribution Fe²⁺ and Fe³⁺; id = ideal; Alter. = bulk of finegrained alteration products within veins; n.d. = not determined.

ly finegrained secondary alteration products and make up some 40 volume percent. No doubt, these finegrained vein materials contribute to the megascopically dense character of the rock.

Electron microprobe (EMP) analyses on sample VR-10 yield a rather restricted compositional range of pertsevit with SiO₂ varying from 5.4 to 8.2 wt%, FeO from 1.92 to 2.38 wt% and F from 6.10 to 8.20 wt%. This is well within the range found for the original pertsevit locality (Schreyer *et al.*, 2003), but clearly on the low side regarding SiO₂ and FeO.

Table 1 lists the analytical results obtained on some pertsevit crystals, one each on kotoite and ludwigite as well as one on the finegrained alteration product. For the recalculation on formula units for pertsevit, the experiences with the first occurrence (Schreyer *et al.*, 2003) were employed. These are expressed by the ideal general formula (Mg + Fe + Mn + Ca)₂(B + Si + Al)₁(O + F + OH)₄. Relative to the silicon-free pertsevit phase, Mg₂BO₃(F,OH), the substitution introducing Si is: Si + O for B + (F,OH). Thus excess-oxygen beyond 3.0 must equal Si, and OH = 1 - Si - F or OH = B - F. The formula of pertsevit No.1 in Table 1 so becomes:



Because H₂O could not be determined, it was calculated following the above equation.

The kotoite analysis of Table 1 was recalculated on the basis of 12 anion valences (six oxygens) and lies close to that of the ideal formula Mg₃(BO₃)₂. It contains more Fe than coexisting pertsevit. The main uncertainty derives from the unknown amount of B₂O₃, which was calculated by difference.

The ludwigite analysis was recalculated with a glance of high content

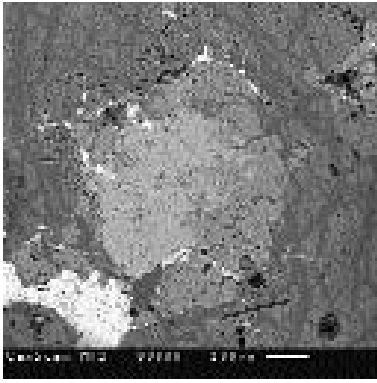


Fig. 1. BSE image of a part of the sample 900018. Pertsevitite forms the edge (grey) around the inclusion of clinohumite (light grey in the centrum) in kotoite (dark grey streaked by ssaibelyite veinlets). Relics of kotoite and clinohumite in pertsevitite are distinctly visible. White crystals and grains – ludwigite. Scale 100 μm .

of Fe^{3+} using the formulae: $\Sigma\text{Fe} + \text{Al} + \text{Sn} + \text{Ti} + \text{Mg} = 3$; $\text{B} = 1$; $\text{O} = 5$.

No recalculation was attempted for the secondary alteration material analysed from one of the veins, because neither B_2O_3 nor H_2O could be determined. However, the composition of ideal ssaibelyite, $\text{MgBO}_2(\text{OH})$, shown for comparison suggests that indeed ssaibelyite is the main mineral within the veins, possibly with a small admixture of brucite, $\text{Mg}(\text{OH})_2$.

The specimen from Gonochan deposit, Djugdjur Ridge, Russian Far East

There are several localities of magnesian skarn boron mineralization in central part of Djugdjur Ridge in 60–70 km from Okhotsk Sea coast at $\sim 56^\circ 30' \text{N}$ and $136^\circ 20' \text{E}$. Here, platform sediments of Upper Precambrian have been subjected to strong Mesozoic tectono-magmatic activation. The magnesian skarns with boron mineralization developed in contacts of Upper Riphean dolomites with Cretaceous subalkaline hypabissal bodies of granitoids (Gramenitskii, 1969, Stepanov, 1973). Sample 90018 (Fersman Mineralogical Museum) was collected by N.N. Pertsev in 1964 in the small deposit Gonochan located in the bed of the small river of the same name. The rock was recognized as a very coarse grained kotoitite in the field analogy (in position and peculiarities of weather-

ing) with kotoitites of Tas-Khayakhtakh deposits (Pertsev, 1971, p. 131–132). Carbonate rocks (mainly dolomites) of Upper Riphean were cut by stocks Upper Cretaceous granites. The magmatic

rock in a band (up to several meters thick) along the contacts with skarns is represented by rather fine grained sub-alkaline (clinopyroxene facies) granite. The thickness of kotoite-containing lenticular bodies runs up to 1 m.

The studied part of the sample was also only a small chip (originally about $2 \times 3 \times 1 \text{ cm}$) of a light grey, dense rock with only minor amounts of small black prisms (ludwigite) aligned in parallel trails. In contrast to specimen VR-10, the thin section of the present rock is dominated by a medium grained fabric of carbonate minerals (calcite) forming a sort of matrix for the roundish, anhedral grains of the remaining transparent silicate and borate minerals. These show, as a function of orientation, low to medium to high birefringence and medium refringence, often without offering any characteristic optical features for their distinction. EMP work identified them as clinohumite, pertsevitite and kotoite. Only clinohumite is safe to recognize, when it exhibits characteristic polysynthetic twinning. Ludwigite has in thin edges strong pleochroism from very dark green (across to elongation) to dark brown (along).

Typically, it is only with the aid of BSE images that the mutual space relationships between clinohumite, pertsevitite and kotoite can be characterized (Fig.1). Clinohumite occupies the central portions of the three minerals complex aggregates and shows clear signs of corrosion. For example, it occurs as a multitude of small inclusions within the more peripheral mineral pertsevitite. This is in turn surrounded by often large crystals of kotoite, which are fractured by veins containing retrograde alteration products (ssaibelyite, brucite). The intermediate textural position of pertsevitite – between clinohumite and kotoite – is also obvious when pertsevitite forms only small crystals or selvages around clinohumite. Thus, pertsevitite must have formed in the rock at a relatively late stage, probably by a reaction of kotoite with clinohumite. Such reaction was also envisaged for the original pertsevitite occurrence east of Verkhoyansk (Schreyer *et al.*, 2003). Altogether, the sample 90018 is a kotoite marble with very similar petrographic features as sample B-1048 studied previously.

EMP analyses of sample 90018, however, introduce some new mineral chemical features. In Table 2 are listed five analyses of pertsevitite, two of clinohumite and one of kotoite. SiO_2 in

Table 2. Electron microprobe analyses of minerals in the kotoite marble (sample 90018)

Mineral	Perts30 ¹	Perts45	Perts52	Perts53	Perts41	Clinoh28	Clinoh46 ⁴	Koto16
SiO ₂	13.55	13.14	12.49	11.39	10.86	35.69	36.92	0.31
B ₂ O ₃ ²	16.91	18.71	18.97	19.70	20.13	1.45	0.76	37.13 ³
Al ₂ O ₃	0.03	0.02	0.01	0.1	0.3	0.1	0.00	0.1
MgO	56.95	60.51	60.22	60.39	60.76	57.27	57.39	61.59
FeO	0.58	0.55	0.64	0.66	0.57	0.45	0.30	0.70
MnO	0.13	0.20	0.15	0.17	0.16	0.15	0.23	0.23
CaO	0.07	0.09	0.08	0.08	0.12	0.05	0.05	0.03
F	4.34	5.10	4.85	4.86	4.98	4.15	2.66	0.00
Total	92.56	98.32	97.41	97.26	97.61	99.22	98.31	100.00
-O=F ₂	1.83	2.15	2.04	2.05	2.10	1.75	1.12	–
H ₂ O ²	2.33	2.44	2.62	2.80	2.86	1.27	1.80	n.d.
Total (wt.%)	93.06	98.61	97.99	98.01	98.37	98.74	98.99	100.00
Recalculations of ions per formula unit (for details see text)								
Si	0.317	0.289	0.276	0.251	0.238	3.738	3.862	0.010
Al	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000
B	0.682	0.710	0.724	0.749	0.761	0.262	0.138	2.030
Sum 1	1.000	0.999	1.000	1.000	1.000	4.001	4.000	–
Mg	1.984	1.984	1.983	1.983	1.984	8.940	8.948	2.909
Fe	0.011	0.010	0.012	0.012	0.010	0.040	0.026	0.018
Mn	0.003	0.004	0.003	0.003	0.003	0.013	0.021	0.006
Ca	0.002	0.002	0.002	0.002	0.003	0.005	0.005	0.001
Sum 2	2.000	2.000	2.000	2.000	2.000	8.998	9.000	2.934
F	0.321	0.354	0.339	0.339	0.345	1.373	0.879	–
O ²	3.316	3.288	3.275	3.250	3.237	15.739	15.862	–
OH ²	0.364	0.357	0.386	0.412	0.418	0.887	1.258	–
Sum 3	4.001	3.999	4.000	4.001	4.000	17.999	17.999	

Notes: ¹original numbers of analyses; ²calculated as in table 1 (see text); ³calculated by difference to 100 wt%; ⁴hydroxycclinohumite (by calculated OH); n.d. = not determined

pertsevite ranges from 10.86 to 13.55 wt%, FeO from 0.36 to 0.66 wt% and F from 4.63 to 5.34 wt%. Thus, Si is much higher than in the pertsevite of sample VR-10, but also surpasses the highest Si-values measured in the type-pertsevite of Schreyer *et al.* (2003). On the other hand, FeO is much lower than in the pertsevites of the other two localities, so that the ones found here may truly be taken as the most magnesian pertsevites found thus far. Moreover, fluorine lies below all the values hitherto determined, so that these pertsevites also seem to be among the most hydrous ones ever investigated.

For the recalculations of the pertsevite analyses to formula unit, the same procedure was employed as described for sample VR-10. They indicate that pertsevite no.30 with 0.32 Si per formula unit of sample 90018 is now the most silicatian pertsevite ever analysed; its low

analytical totals cannot be explained but do not seem to influence this property. The Si-range extends down to as low as 0.24 *p.f.u.*, which is close to the upper Si limit in the pertsevites of sample B-1048. So, considering all three pertsevite occurrences known thus far, there is now a full range of solid solution from 0.10 to 0.32 Si *p.f.u.* Contrary to the situation found in sample B-1048, no correlation could be made out here between Si content and the proximity of the pertsevite to either clinohumite or kotoite. The pertsevites are much more homogeneous here than in B-1048. Despite the considerable variations of Si in sample 90018, there is surprisingly little, or even no, variation in the ferromagnesian elements. Likewise F remains rather constant, and the calculated values for OH always exceed those of F. Thus, these pertsevites are indeed the first ones with

OH/F > 1 and could deserve a new mineral name ("hydroxy-pertsevite"). We abstain from this procedure, however, because OH values are only calculated. The structural formulae of Table 2 confirm that the pertsevites from sample 90018 are indeed the most magnesian ones.

Concerning the clinohumite grains analysed in the sample, the main difficulty arises from their unknown contents of B₂O₃. With the experience of the kotoite marble of sample B-1048 (Schreyer *et al.*, 2003) it seems clear that clinohumite coexisting with pertsevite must contain boron; that sample had about 1.5 wt% B₂O₃. As evidenced in B-1048, the boron is incorporated in the tetrahedra partly replacing silicon. Therefore, we used in Table 2 a similar recalculation scheme as for pertsevite, calculating B as 4.0 – Si *p.f.u.* The results for two analyses (Table 2) are very reasonable clinohumite structural formulae, that are comparable to those of the earlier study. As in pertsevite, there is very little Fe and Mn so that the clinohumite grains of sample 90018 are nearly Mg end members. Fluorine is quite variable: the two analyses nos. 28 and 46 represent the highest and the lowest F values, respectively, that were analysed. But they are quite similar to those of the clinohumite in B-1048 as well. The lower fluorine contents correspond to predomination of hydroxycclinohumite end member and appears to witness of reequilibration of clinohumite mineral during overprinting of enriched with hydroxyl pertsevite.

The kotoite analysis of Table 2 is very close to ideal composition (compare Table 1), although B₂O₃ was only calculated as difference of the measured oxides to a total of 100 wt.%. Notable is the very high Mg/Fe ratio like in all other minerals of sample 90018.

No analyses were performed on ludwigite, but from its pleochroism in thin section it is presumably quite magnesian as well.

Altogether, sample 90018 is probably among the Mg-richest, pertsevite-bearing contact skarns (kotoite marbles and kotoitites) that can be found.

In conclusion we have to point to pertsevite appears to be rather wide spread in kotoite-containing rocks where paragenesis of

kotoite with the minerals of humite group is quite usual. The modern diagnostics of pertsevite is simple enough by using BSE images. Larger pertsevite crystals seem to be found to precise the ranges of optical properties and compositions of the mineral species.

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NEW DATA ON MINERAL ASSEMBLAGES WITH BITUMINOUS MATTER IN PEGMATITES OF THE Khibiny MASSIF

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The new occurrences of solid bituminous substances (SBS) have been found in peralkaline pegmatites of the Khibiny massif, Kola Peninsula, Russia. Mineral assemblages containing rounded and drop-like segregations of SBS ranging from 1 to 10 mm in size are described. In most cases, SBS are ingrown into the grains of microporous titanium, niobium, and zirconium silicates and locally overgrow their surface. Microinclusions of Th and REE minerals frequently occur within the SBS segregations. The new findings confirm a hypothesis of catalytic role of the zeolite-like titanium, niobium, and zirconium silicates to form SBS, as well as key role of organic matters to transfer and concentrate Th and REE during hydrothermal stage of the pegmatite formation. At final stage, most thorium and part of REE incorporate into mineral phases, which saturate SBS, whereas Ca (occasionally together with part of Th and REE) remains in organic phase as carboxylate salts and/or organometallic compounds.
2 tables, 5 figures, 20 references.

Introduction

The solid bituminous substances (SBS) are repeatedly documented in the pegmatite bodies of the Khibiny-Lovozero alkaline complex, Kola Peninsula, Russia. In these bodies, SBS being endogenetic are characteristic components of the late hydrothermal assemblages and frequently form clusters reaching several cm in size (Antonov *et al.*, 1933; Labuntsov, 1937; Sokolova, 1965; Zevin & Sokolova, 1967; Loskutov & Polezhaeva, 1968; Florovskaya *et al.*, 1968; Kostyleva-Labutsova *et al.*, 1972; Pekov, 1998, 2001; Kartashov *et al.*, 2006). Commonly, organic matters are intimately associated with the microporous silicates, which contain Ti, Nb and Zr atoms in heteropolyhedral frameworks: the SBS segregations are ingrown into aggregates of these minerals and overgrow their surface. Since this relation is so stable and clear, we have set up the first hypothesis that the zeolite-like titanium, niobium, and zirconium silicates are catalysts for synthesis of bituminous matter (Chukanov *et al.*, 2005a, b; 2006) all the more so analogous synthetic zeolite titanium, niobium, and zirconium silicate compounds are sorbents of small molecules and effective catalysts for the numerous organic-assisted reactions (see

review by Chukanov *et al.* (2004)). It should be noted that peralkaline pegmatites and especially their hydrothermal assemblages are unique objects in abundance and diversity of microporous mineral phases with heteropolyhedral frameworks designed on the basis of SiO₄ tetrahedra and octahedral coordinated atoms of the transitional elements and first of all Ti, Nb, and Zr (Chukanov & Pekov, 2005; Pekov & Chukanov, 2005).

As reported in above cited papers, SBS from the Khibiny pegmatites are generally depleted in sulfur and are enriched in water and derivatives of polycyclic aromatic hydrocarbons containing hydroxyl, carbonyl, and carboxylate groups. During hydrothermal mineralization, they concentrate thorium, as well as alkaline-earth and rare-earth elements. In particular, megascopic clusters of oxidized bituminous matters from the Khibiny pegmatites are usually accompanied with thorium and/or REE mineralization. The oxidized SBS with rare high valence (Th, U, REE, Nb, Zr, Ti) and alkaline-earth elements are complex microheterogeneous systems containing mineral (the most frequent silicates of thorium and calcite), organometallic (with REE, Ca, Sr, Ba), and organic phases, which can be formed in result

of decomposition of the primary organometallic substrate at decreasing of temperature. On the other hand, thorium and *REE* minerals formed in peralkaline pegmatites during hydrothermal stage commonly contain numerous inclusions of SBS (in contrast to associated Th- and *REE*-free minerals). As a result, we set up the second hypothesis that oxidized derivatives of polynuclear arenes identified in SBS are complex-forming compounds for Th, *REE*, Ba, Sr, Ca and contribute to the transfer and concentration of these elements at low temperatures.

New findings of SBS in the Khibiny pegmatites described in this paper gave additional data to check both assumptions.

Materials

Pegmatite at Mt. Khibinpakhcorr (Khbp-1).

Aegirine-feldspar pegmatite vein hosted in khibinite at Mt. Khibinpakhcorr was found by Z.V. Shluykova in 1959. This vein was traced from West to East for 8 m with thickness ranging from 0.5 to 1.2 m. The western area of the vein is composed of microcline, arfvedsonite, aegirine, eudialite, enigmatite, and accessory loparite, whereas central and eastern parts, mainly hydrothermal minerals, including analcime, natrolite, catapleite and others. The labutsevite-group minerals are the most diverse: heterogeneous in composition (with zones sharply enriched in Ca or Sr) colorless crystals of tsepenite-Na and paratsepenite-Na overgrow (local epitactically) orange crystals of the earlier labutsevite-Mn and lemmleinite-Ba. Microheterogeneous segregations enriched in SBS are mainly hosted in the labutsevite crystals and less frequent, tsepenite and catapleite. In most cases, they occur as black spherulites up to 1 mm in diameter ingrown into the labutsevite crystals or overgrown their surface.

Pegmatite at Mt. Koashva (Koa-2) developed by quarry in the summer 2005 is subhorizontal 3 m long and 0.5 m thick lens located at the contact between urtite and nepheline-apatite orebody. Mineral assemblages of three stages are recognized in the pegmatite. Potassium feldspar, nepheline, dark grey sodalite, alkaline pyroxene and black amphibole, eudialite, lamprophyllite, and

rinkite were deposited during the first stage. Green acicular aegirine, villiamite, lomonosovite, mineral of the lovozerite group (zircinalite?), chkalovite, fluorcaphite, sphalerite, and a few galena and phlogopite were deposited during the second dry ultraagpaitic stage. Minerals, which replace the earlier phases and crystallize in cavities, are attributed to the third stage. These are natrolite (composes the main part of the pegmatite core), catapleite (occurs as complete pseudomorphs after lovozerite-like mineral), sitinakite, lemmleinite-K, vinogradovite (these three titanium silicates completely replace lomonosovite and crystallize in caverns), lilac fluorapatite (epitactically overgrows fluorcaphite and occurs as sustentative crystals in caverns), astrophyllite, fine-fibre pectolite, umbite (pseudomorphs after eudialite), sazykinaite-(Y), amichite, elpasolite, and unidentified lamellar hydrous (Cu,Fe)-sulfides. Among natrolite and in caverns, there are numerous large (up to 1 cm) segregations of black bituminous substance apparently formed during stage 3. Continuous rims and chains of spherulites of this bituminous substance frequently surround pseudomorphs of catapleite after the lovozerite-group ingrown into natrolite.

Pegmatite at Mt. Kukisvumchorr (Kuk-3).

The 10 cm thick vein body mainly composed of natrolite with subordinate aegirine and accessory mackinawite has been developed by the underground working of the Kirovsky Mine (Mt. Kukisvumchorr). This vein cut urtite close to the contact with the nepheline-apatite body and contains the small pods composed of fine-grained segregations of pyrochlore and yellow komarovite-like (Na,Ca)-niobosilicate, which are most likely pseudomorphs after the earlier alkaline niobosilicate (probably vuonnemite). Just these segregations host black bituminous substance with strong resinous to metal-like luster. Aggregates of pyrochlore and (Na,Ca)-niobosilicate are dense "stuffed" by awkward shaped segregations of this substance up to several mm in size.

The sample from **pegmatite at Mt. Kukisvumchorr (Kuk-4)** is a fragment of core from the hole drilled in underground working at level +252, Kirovsky Mine. This drill hole crosses pegmatite veinlet composed of microcline with a few black acicular aegirine; marginal parts of this veinlet are enriched in

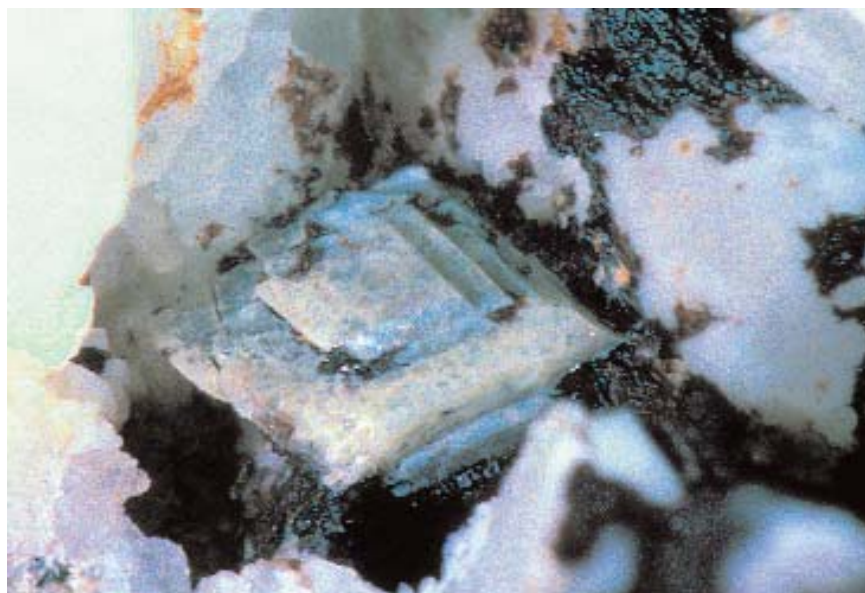


Fig. 1. Specimen from pegmatite at Mt. Kukisvumchorr (Kuk-4). Bituminous substance (dark) overgrows crystal of pyatenkoite-(Y). Photo by N.A. Pekova.

Table 1. Content of elements with atomic numbers more than 10 in organic phases, wt.%

Number of analysis	1	2	3	4	5	6	7	8	9
	Pegmatite at Mt. Khibinpakhchorr (Khbp-1)				Pegmatite at Mt. Koashva (Koa-2)		Pegmatite at Mt Kukisvumchorr (Kuk-3)		Pegmatite at Mt Kukisvumchorr (Kuk-4)
Na ₂ O	bdl	bdl	bdl	bdl	1.65	bdl	bdl	bdl	5.62
K ₂ O	bdl	bdl	bdl	bdl	0.56	bdl	0.28	1.31	0.96
CaO	3.41	3.54	3.89	3.71	0.69	0.44	bdl	bdl	1.56
SrO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.23
MgO	bdl	bdl	0.79	bdl	bdl	bdl	bdl	bdl	0.21
FeO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.44
ZnO	1.50	1.42	1.48	1.81	bdl	bdl	bdl	bdl	bdl
PbO	bdl	bdl	0.83	bdl	bdl	bdl	bdl	bdl	bdl
Al ₂ O ₃	0.85	0.90	0.67	1.39	0.51	bdl	bdl	bdl	0.27
La ₂ O ₃	6.08	6.66	6.15	6.21	bdl	bdl	bdl	bdl	bdl
Ce ₂ O ₃	0.16	0.44	0.37	0.27	bdl	bdl	bdl	bdl	bdl
Pr ₂ O ₃	1.09	0.66	0.67	0.58	bdl	bdl	bdl	bdl	bdl
Nd ₂ O ₃	2.74	2.59	2.70	2.50	bdl	bdl	bdl	bdl	bdl
Sm ₂ O ₃	0.62	0.09	0.16	bdl	bdl	bdl	bdl	bdl	bdl
ThO ₂	bdl	bdl	bdl	bdl	3.84	3.67	bdl	bdl	6.23
SiO ₂	bdl	bdl	bdl	1.15	1.88	1.50	bdl	bdl	13.07
S	0.58	0.49	0.43	0.45	1.91	0.41	1.61	2.40	0.38
Cl	bdl	bdl	bdl	bdl	0.66	0.14	bdl	bdl	0.12
-O=S	-0.29	-0.24	-0.21	-0.22	-0.95	-0.20	-0.80	-1.20	-0.19
-O=Cl ₂	—	—	—	—	-0.15	-0.03	—	—	-0.03
Total	16.74	16.55	17.93	17.85	10.60	5.93	1.09	2.51	28.86

Notes: bdl is below detection limit by electron microprobe

aegirine and contain nepheline and rinkite. The axial zone of the veinlet comprises white to colorless microcline with a few black acicular aegirine. The walls of the cavities located in the axial zone are overgrown by rhombohedral crystals of pyatenkoite-(Y) $\text{Na}_5(\text{Y}, \text{HREE})\text{TiSi}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$ up to 1.5 mm across. Relationships of *REE* in the Kukisvumchorr pyatenkoite-(Y) are interesting with the predominance of erbium (Pekov *et al.*, 2003) that is rare for minerals from peralkaline massifs. These crystals and surrounding microcline are covered by crusts of brown (to black) solid bituminous substance (Fig. 1). Rounded and drop-like segregations of this substance up to 5 mm in diameter are also occur; numerous small (< 0.1 mm) inclusions of steacyite $\text{Th}(\text{Na}, \text{Ca})_2\text{K}_{1-x}\text{Si}_8\text{O}_{20}$ have been identified in these segregations.

Electron microprobe study

Secondary and back-scattered electron images and distribution mapping of selected elements were made with a CamScan MV2300 scanning electron microscope equipped with a YAG-detector of secondary and back-scattered electrons and energy-dispersion system with a Link INCA Energy semiconductor (Si-Li) detector, A.N. Nekrasov, analyst, Institute of Experimental Mineralogy, Russian Academy of Science. During scanning, beam diameter was 0.157 μm at accumulation time of signal in each point of 0.5 ms. An accelerating potential of 20 kV and current intensity of 0.52 – 0.56 nA were used.

The bituminous substances forming inclusions in labuntsevite-Mn (pegmatite Khbp-1, Mt. Khibinpakhchorr) and segregations of SBS from pegmatite at Mts. Koashva (pegmatite Koa-2) and Kukisvumchorr (pegmatites Kuk-3 and Kuk-4) are described in this paper. Like to segregations previously documented by Chukanov *et al.* (2005, 2006), these are microheterogeneous intergrowths with two types of phases: substantially organic and mineral (Figs. 2–4). Organic phases are characterized by homogeneous BSE images, low totals of analyses (generally not higher than 20%), and constant presence of sulfur (0.4–2.4 wt.%), as well as calcium and/or potassium (Table 1). Mineral phases intergrown with SBS are diverse in chemical composition (Table 2). Si, Mn, *REE*, Th, and alkaline (Na, K), alkaline-earth (Ca, Sr, Ba) elements are the most typical components in these phases.

In contrast to the Khibiny "carbocer" and most other samples of SBS, which we previously described, the high concentration of Th and *REE* were identified not only in mineral phases, but occasionally, in organic matrix. Organic phase of SBS from pegmatite Khbp-1 concentrates *REE* and is Th-free, with La (6.1–6.7 wt.%) being

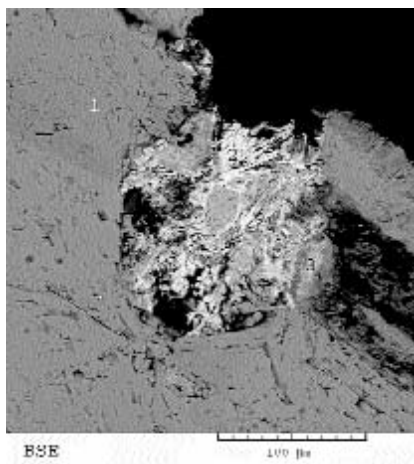


Fig. 2. Specimen from pegmatite at Mt. Khibinpakhchorr (Khbp-1). (1) Labuntsevite-Mn, (2) "Silicoxide of Mn and REE". (3) Rancieite.

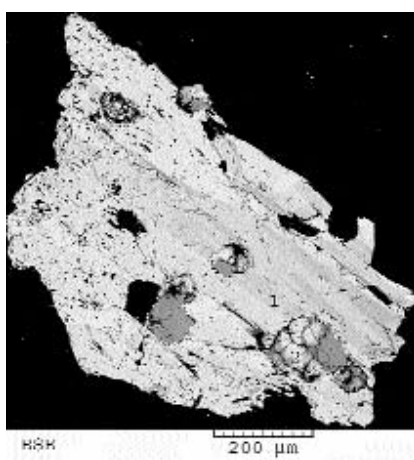


Fig. 3. Specimen from pegmatite at Mt. Khibinpakhchorr (Khbp-1). (1) Labuntsevite-Mn, (2) "Silicoxide of Mn and REE". (3) Ti,Th-silicate.

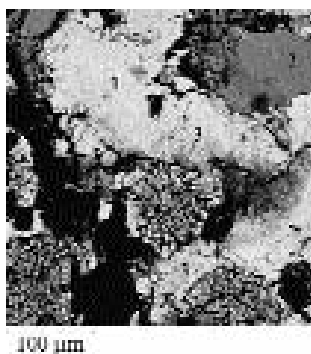


Fig. 4. Specimen from pegmatite at Mt. Koashva (Koa-2). (1) Thorium titanosilicate. (2) Lemmleinite-K. (3) Biotite. Organic matter is dark.

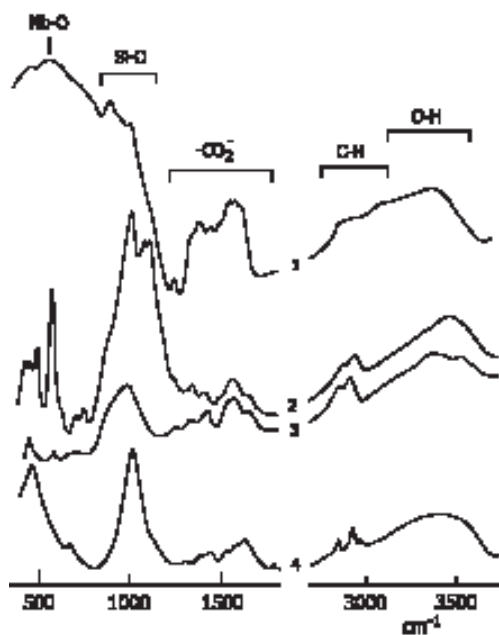


Fig. 5. IR spectra of microheterogeneous segregations with SBS from pegmatites at Mt. Kukisvumchorr (Kuk-3 (1), Kuk-4 (2)) Mt. Koashva (Koa-2 (3)), and Mt. Khibinpakchorr (Khbp-1 (4)).

dominant among *REE* and Nd (2.5–2.7 wt.%) and Pr (0.6–1.1 wt.%) being sharply predominated over Ce (0.2–0.4 wt. %). SBS from pegmatites Koa-2 and Kuk-4 are enriched in Th and are *REE*-free. Rare elements are absent in organic matter from pegmatite Kuk-3 (Table 1).

Electron microprobe data for mineral phases intimately associated with SBS are given in Table 2. Labuntsevite-Mn $\text{Na}_4\text{K}_4\text{Mn}_2\text{Ti}_8(\text{Si}_4\text{O}_{12})_4(\text{OH},\text{O})_8 \cdot 10\text{H}_2\text{O}$, lemmleinite-K $\text{Na}_4\text{K}_8(\text{Ti},\text{Nb})_8[\text{Si}_4\text{O}_{12}]_4(\text{OH},\text{O})_8 \cdot 8\text{H}_2\text{O}$, rancieite $(\text{Ca},\text{Mn}^{2+})\text{Mn}^{4+}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$, umbite or kostylevite $\text{K}_2\text{ZrSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$, and steacyite $(\text{Na},\text{Ca})_2\text{K}_{1-x}\text{ThSi}_8\text{O}_{20}$ (here and further, idealized formulae are given) were identified by composition and partially by infrared spectroscopy. These minerals as well as Nb-rich silicate $(\text{Na},\text{Ca},\text{K})_3(\text{Nb},\text{Ti})_2\text{Si}_{1-x}(\text{O},\text{OH})_x\text{F} \cdot n\text{H}_2\text{O}$, thorium titanosilicates $(\text{K},\text{Ba})_{1.5}(\text{Ca},\text{Na})(\text{Th},\text{REE}(\text{Ti},\text{Nb})_3(\text{Si},\text{Al})_8(\text{O},\text{OH})_x \cdot n\text{H}_2\text{O}$ and $\text{NaCaK}_{0.5}\text{MnTh}_4\text{REE}_{1-x}(\text{Ti},\text{Nb})_2\text{Si}_8(\text{O},\text{OH})_x \cdot n\text{H}_2\text{O}$, and silicate of zinc and thorium $(\text{Na},\text{Ca},\text{K})_2(\text{Zn},\text{Ti})_2\text{Th}_4\text{REE}(\text{Si},\text{Al})_8(\text{O},\text{OH})_x \cdot n\text{H}_2\text{O}$ are stoichiometric and their formulae are calculated with coefficients close to integral. The compositions of so called Mn and *REE* silicoxide (Table 2, analyses 4–6) probably attributed to cryptocrystalline mixtures are

variable and are characterized by low totals.

Both Th and *REE* are present in minerals of pegmatite Khbp-1. Like to content of rare earth elements in the intergrown organic phases, *REE* in minerals are characterized by the La maximum. Rare elements in the mineral phases and SBS from pegmatites Koa-2 and Kuk-4 are dominated by thorium (30.7–46.8 wt.%), but in the sample from pegmatite Koa-2, *REE* (4.6–6.9 wt.%) with the Ce maximum are present. Thorium is absent in the mineral phases from pegmatite Kuk-3, but a few *REE* (2.55–3.19 wt.%) with predominance of Ce is observed in these phases.

According to composition of organic substances and comparison with composition of intimately associated mineral phases from the same pegmatites, rare elements can be concluded to tend forming proper mineral phases. However, in contrast to carbocer and some other microheterogeneous segregations with SBS (Chukanov *et al.*, 2005a, 2005b, 2006), the clear fractionation of rare elements between different organic and mineral phases is not observable.

Infrared spectroscopy

Infrared spectra of samples in KBr disks were measured on a Specord 75 IR dual-beam spectrophotometer. Spectrum of the pure KBr disk was deducted during recording in automatic mode.

The most reliable diagnostic feature of the hydrocarbon groups is the relatively narrow bands of C-H-stretching vibrations within range 2800–3100 cm^{-1} in the infrared spectrum, with the doublet within range 2840–2980 cm^{-1} corresponding to the aliphatic groups CH_2 and CH_3 . The symmetric stretching vibrations of the methylene and methyl groups have wavenumbers 2843–2863 and 2860–2870 cm^{-1} , respectively, while asymmetric stretching vibrations, 2916–2936 and 2952–2972 cm^{-1} , respectively. The C-H bonds pertaining to unsaturated hydrocarbon groups (in alkenes and aromatic compounds) are characterized by the increased frequencies of the stretching vibrations (2990–3110 cm^{-1}). The band with the absorption maximum at 2835 cm^{-1} is characteristic of methoxygroup $\text{O}-\text{CH}_3$ linked to the aromatic ring.

Numerous absorption bands within range 1210–1740 cm^{-1} are the most reliable feature of

Table 2. Chemical composition of mineral phases intergrown with SBS

Number of analysis	1	2	3	Pegmatite at Mt. Khibinpakhchorr (Khbp-1)			
				4	5	6	7
Na ₂ O wt. %	5.64	4.73	0.88	bdl	bdl	bdl	bdl
K ₂ O	7.07	6.74	3.19	bdl	bdl	bdl	bdl
CaO	bdl	bdl	2.12	0.39	0.52	0.54	3.87
BaO	10.19	12.17	4.04	1.64	1.25	0.68	3.20
MnO	2.50	2.37	1.18	30.56	28.74	29.62	64.20
FeO	0.59	0.78	0.58	8.65	10.90	11.01	0.64
ZnO	bdl	bdl	bdl	0.87	0.71	0.84	0.60
Al ₂ O ₃	bdl	bdl	0.72	2.99	3.64	3.60	bdl
La ₂ O ₃	bdl	bdl	2.03	3.92	4.27	3.71	bdl
Ce ₂ O ₃	bdl	bdl	1.66	1.18	1.42	1.60	bdl
Pr ₂ O ₃	bdl	bdl	0.35	1.05	0.65	1.32	bdl
Nd ₂ O ₃	bdl	bdl	1.46	3.55	2.83	3.54	bdl
ThO ₂	bdl	bdl	8.49	bdl	0.56	bdl	bdl
SiO ₂	40.56	38.94	30.51	4.32	6.51	6.20	bdl
TiO ₂	26.37	23.98	11.15	0.83	0.59	0.57	bdl
Nb ₂ O ₅	1.03	3.54	5.37	bdl	bdl	bdl	bdl
Total	94.27	93.57	73.73	60.37	63.32	64.00	74.59
Na apfu	4.32	3.77	0.43	—	—	—	—
K	3.56	3.52	1.04	—	—	—	—
Ca	—	—	0.57	0.38	0.34	0.38	0.66
Ba	1.58	1.97	0.40	0.60	0.29	0.17	0.09
Mn	0.83	0.83	0.26	24.02	14.94	16.16	4.04
Fe	0.21	0.28	0.13	6.70	5.60	5.93	0.04
Zn	—	—	—	0.60	0.33	0.40	0.03
Al	—	—	0.22	3.26	2.63	2.72	—
La	—	—	0.19	1.34	0.96	0.88	—
Ce	—	—	0.15	0.40	0.31	0.38	—
Pr	—	—	0.03	0.36	0.15	0.31	—
Nd	—	—	0.13	1.18	0.62	0.81	—
Th	—	—	0.50	—	0.08	—	—
Si	16.00	16.00	7.78	4.00	4.00	4.00	—
Ti	7.83	7.41	2.14	0.58	0.28	0.28	—
Nb	0.18	0.65	0.62	—	—	—	—
Basis of calculation	Si = 16	Si = 16	Si + Al = 8	Si = 4	Si = 4	Si = 4	Total cations = 5

Notes: Labuntsevite-Mn (1, 2), Ti,Th-silicate (3), hydrous silicooxide? (4-6), rancieite (7), lemmleinite-K (8), umbite or kostylevite (9), Ti,Th-silicates (10-12), Zn,Th-silicate (13), Nb-rich silicate (14-16), and steacyite (17). These minerals are also contain SrO (7 - 1.23, 14 - 5.22, 15 - 3.49), MgO (1 - 0.23, 2 - 0.32, 7 - 0.85, 11 - 0.72), ZrO₂ (9 - 24.10), Cl (4 - 0.54, 5 - 0.94, 6 - 1.00), -O = Cl₂ (4 - 0.12, 5 - 0.21, 6 - 0.23), F (14 - 5.59, 16 - 4.57), -O = F₂ (14 - 2.35, 16 - 1.92); apfu are as follows Sr (7 - 0.05, 14 - 0.20, 15 - 0.14); Mg (1 - 0.18, 2 - 0.21, 7 - 0.09, 11 - 0.35), Zr (9 - 3.23); Cl (4 - 0.85; 5 - 0.98; 6 - 1.09); F (14 - 1.13, 16 - 1.13). bdl is below detection limit by electron microprobe.

Number of analysis	8	9	10 11 12 13 Pegmatite at Mt. Koashva (Koa-2)				14 15 16 Pegmatite at Mt Kukisvumchorr (Kuk-3)			17 Pegmatite at Mt Kukisvumchorr (Kuk-4)
	Na ₂ Owt.%	4.49	1.19	2.12	2.42	1.57	1.54	10.44	9.42	9.56
K ₂ O	14.67	19.66	1.05	2.09	1.03	0.77	1.57	1.90	1.83	3.93
CaO	bdl	bdl	1.25	1.90	2.24	1.52	10.56	10.93	11.55	5.41
BaO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	bdl	bdl	2.54	6.37	2.95	bdl	bdl	bdl	bdl	bdl
FeO	bdl	bdl	bdl	bdl	bdl	bdl	0.78	1.41	0.91	0.77
ZnO	bdl	bdl	bdl	bdl	bdl	4.83	bdl	bdl	bdl	bdl
Al ₂ O ₃	bdl	bdl	0.58	bdl	bdl	0.84	bdl	bdl	bdl	bdl
La ₂ O ₃	bdl	bdl	0.99	1.44	0.68	1.70	bdl	1.19	0.58	bdl
Ce ₂ O ₃	bdl	bdl	2.62	3.36	3.09	3.81	bdl	2.00	1.72	bdl
Pr ₂ O ₃	bdl	bdl	bdl	0.40	0.75	0.15	bdl	bdl	0.25	bdl
Nd ₂ O ₃	bdl	bdl	0.95	0.87	1.48	1.26	bdl	bdl	bdl	bdl
ThO ₂	bdl	bdl	40.46	35.06	46.83	45.02	bdl	bdl	bdl	30.69
SiO ₂	39.29	43.63	19.82	24.02	22.39	19.07	3.67	9.85	11.80	53.62
TiO ₂	16.81	3.57	3.05	8.22	5.67	1.32	5.59	6.88	6.27	bdl
Nb ₂ O ₅	17.80	2.93	1.47	4.24	2.37	bdl	59.55	54.60	46.00	bdl
Total	93.06	95.08	76.92	91.11	91.05	81.83	100.62	101.67	93.12	99.79
Na apfu	3.55	0.16	1.60	1.57	1.09	1.19	1.30	1.23	1.45	1.28
K	7.62	1.73	0.52	0.89	0.47	0.39	0.13	0.16	0.18	0.74
Ca	—	—	0.52	0.68	0.87	0.65	0.73	0.79	0.97	0.86
Ba	—	—	—	—	—	—	—	—	—	—
Mn	—	—	0.84	1.80	0.89	—	—	—	—	—
Fe	—	—	—	—	—	—	0.04	0.08	0.06	0.09
Zn	—	—	—	—	—	1.43	—	—	—	—
Al	—	—	0.27	—	—	0.39	—	—	—	—
La	—	—	0.15	0.18	0.09	0.25	—	0.03	0.02	—
Ce	—	—	0.37	0.41	0.40	0.55	—	0.05	0.05	—
Pr	—	—	—	0.05	0.09	0.03	—	—	0.01	—
Nd	—	—	0.14	0.11	0.19	0.18	—	—	—	—
Th	—	—	3.59	2.66	3.81	4.09	—	—	—	1.04
Si	16.00	3.00	7.73	8.00	8.00	7.61	0.56	0.66	0.93	8.00
Ti	5.14	0.19	0.90	2.06	1.53	0.39	0.27	0.35	0.37	—
Nb	3.27	0.09	0.26	0.64	0.39	—	1.73	1.65	1.63	—
Basis of calculation	Si = 16	Si = 3	Si + Al = 8	Si + Al = 8	Si + Al = 8	Si + Al = 8	Ti + Nb = 2	Ti + Nb = 2	Ti + Nb = 2	Si = 8

aromatic compounds with the O-bearing groups. In particular, the series of bands within range 1370–1600 cm^{-1} is attributed to the C-C-stretching vibrations in the aromatic rings. The carboxylate groups CO_2^- absorb within ranges 1550–1670 cm^{-1} (antisymmetric stretching vibrations) and 1280–1430 cm^{-1} (symmetric stretching vibrations). These groups present in most segregations of SBS from Khibiny. Bonds C=O (carbonyl and carboxylate groups including dimers of carbonic acids) have characteristic bands at 1690–1740 cm^{-1} (Smith, 1979).

According to infrared spectroscopy, all studied microheterogeneous aggregates with SBS contain both aliphatic hydrocarbons and oxidized aromatic compounds, but in different proportions (Fig. 5).

The aromatic compounds with the carboxylate groups are predominant in the sample from pegmatite Kuk-3. The amount of bonds of hydrogen atoms with the aromatic hydrocarbon ring (shoulder at 3100 cm^{-1}) is insignificant; there are side aliphatic groups (broad shoulder within range 2800–2900 cm^{-1}).

The SBS from pegmatites Khbp-1, Koa-2, and Kuk-4 are assigned to the intermediate type. The significant amount of the aliphatic hydrocarbon groups presents in them along with the oxidized unsaturated organic compounds. The position of the strongest band of the C-H-stretching vibrations (2910–1932 cm^{-1}) indicates the presence of the polymethylene chains $(\text{CH}_2)_n$ in these samples.

The bands of O-H- and Si-O-stretching vibrations (ranges 3200–3700 and 880–1200 cm^{-1} , respectively) present in each studied sample of the bituminous matter. The silicate component is the substance with the isolated SiO_4 groups (Kuk-3, band at 897 cm^{-1}), steacyite (Kuk-4), and silicates with polymerized SiO_4 tetrahedra (Koa-2 and Khbp-1, bands at 986 и 1020 cm^{-1} , respectively). The strongest broad band at 567 cm^{-1} in the sample from pegmatite Kuk-3 is characteristic of niobium and titanium silicates with $(\text{Nb} + \text{Ti}):\text{Si} > 1$ and with pyrochlore-like block (komarovite, natrokomarovite, belkovite, fersmanite, and probable mongolite) in their structures. These mineral phases may be considered as intermediate between silicates and titanoniobates. The major mineral phase with $(\text{Nb} + \text{Ti}) \gg \text{Si}$ (Table 2, analyses 14–16) from intergrowths with SBS in pegmatite Kuk-3 is most probable

attributed to this type.

Discussion

Comparison with previous data reveals common and distinct features assigned to the studied objects. The common features are:

1. Relation of SBS to microporous titanium, niobium, and zirconium silicates. In the sample from pegmatite Khbp-1, microscopic segregations of SBS occur within crystal of labuntsevite-Mn. Megascopic segregations of SBS in the sample from pegmatite Koa-2 contain microscopic umbite or kostylevite, as well as lemmleinite-K. In pegmatite Kuk-3, SBS are intimately associated with Nb-rich silicate and in pegmatite Kuk-4 overgrow titanosilicate pyatenkoite-(Y).
2. Presence of microscopic mineral phases containing *REE* and/or Th: titan-thorium and zinc-thorium silicates, Mn and *REE* silicoxide, Nb-rich silicate, and steacyite.
3. Microheterogeneous structure of the bituminous clusters (intimate intergrowths between SBS and mineral phases are observed).
4. Presence of sulfur in organics.

In most previously reported bituminous matters from peralkaline pegmatites, high valence rare elements (Ce, La, Nd, Y, Th, U, and Ti) are incorporated into inclusions of microscopic mineral phases, whereas the organic matrix mainly contains alkaline-earth elements, with the high grade of interphase partitioning of rare elements being observable (Chukanov *et al.*, 2005a, 2006). In the above described assemblages, this partitioning is not so pronounced, with presence of large amount of *REE* (pegmatite Khbp-1) or Th (pegmatites Koa-2 and Kuk-4) in organics being observed.

The term carbocer was previously noted as ineffectual in regard to hydrothermal rocks from pealkaline massifs of Kola Peninsula, because *REE* were falsely determined instead of Th (Chukanov *et al.*, 2003) in primary described material (Labuntsov, 1937). The finding of SBS containing 10 wt.% REE_2O_3 in pegmatite Khbp-1 (Table 1) allows a rehabilitation of the term carbocer. According to above data, in considered objects, both the crystal chemical mechanism and affinity of the different type

organic molecules to definite metals can be suggested to work during fractionation of elements similar in properties between phases (including separation of Th from REE and fractionation of lanthanides).

Above mentioned data confirm previous conclusion that the evolution of the carbonic matters during hydrothermal stage of the formation of peralkaline pegmatites is intimately related to Th, REE, Ti, Zr, and Nb, which are generally distinguished by the low activity and mobility at low temperatures. In this case, the conclusion by V.I. Vernadsky (1954) with regard to geochemistry of such elements is representative. Let us cite it with small brevities:

"The whole geochemistry of thorium is defined by its attractive feature differing this element from uranium... Thorium pertains to the chemical elements, which are out of geochemistry of water, rather geochemistry of aqueous solutions. It does not go into solution and does not enter aqueous equilibriums of the Earth, and it should be assumed that its concentration in the Earth environment must be poor... In this regard, it pertains to paragenetic chemical elements to which Zr, Hf, ..., elements of rare earths, Nb, and Ta are attributed. For thorium... both vadose minerals crystallized from aqueous solutions and hydrothermal ones"

It is important that along with thorium, Vernadsky distinguishes REE, Zr, Nb (Ti can be added to them) as elements "out of geochemistry of aqueous solutions". At first sight, this conclusion conflicts with the prevalence of so called "amphoterisilicates" (essentially alkaline hydrous titanium, zirconium and niobium silicates, which are zeolite-like minerals with low-dense heteropolyhedral frameworks), as well as REE and Th minerals in hydrothermal assemblages of the Khibiny-Lovozero complex. This contradiction is withdrawn if take into account that Vernadsky did not consider an opportunity of transport of low mobile elements in aqueous medium as complexes with hydrophilic ligands.

Probable mechanisms for participation of organic matters to transfer rare elements (mainly Th and REE) in hydrothermal rocks of the Khibiny-Lovozero complex can be defined subject to observed paragenetic relationships between organic and mineral phases in these objects. In particular, above described parage-

neses confirm the clear spatial relation between the segregations of condensed organic substance, amphoterosilicates, and REE and Th minerals. The SBS overgrowths of aggregates of titanium, niobium, and zirconium minerals, microscopic ingrowths of organics into thorium minerals of hydrothermal stage, and rims enriched in SBS around REE minerals testify this. By analogy with the synthetic microporous matters with heteropolyhedral frameworks, titanium, niobium, and zirconium silicates in pegmatite are suggested to be catalysts of polymerization, reforming, and selective oxidizing to form oxygen-bearing SBS from the low-molecular hydrocarbons. At the same time, the participation of organic matters to transport not only thorium and rare earth elements, but Ti, Nb, and Zr should not be excluded. Both crystallization of minerals of the elements, which are low mobile in aqueous medium and ingrowths of microscopic phases containing these elements in SBS indicate this. Thus, the new data (Tables 1, 2) confirm the hypothesis of the intimate genetic relationship of Th, REE, Ti, Nb, and Zr with the bituminous substances in the late derivatives of peralkaline plutons. At the late hydrothermal mineralizing stage of the Khibiny massif, the SBS concentrate Th, REE, Ti, Nb, and Zr. This relationship is very important for geochemistry of thorium. Relation of these elements to SBS can be explained by their ability to form the stable complex compounds with organics formed at the late hydrothermal stage. The rise of these compounds favours transport, concentration, and separation of Th, REE, Ti, Nb, and Zr at low temperature.

Acknowledgment

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FEATURES OF OCCURRENCE AND DISTRIBUTION OF NOBLE METALS IN THE ORES AND OXIDIZED ZONE OF THE ONEGA URANIUM-VANADIUM DEPOSITS, SOUTH KARELIA

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Complex uranium-vanadium ores with Mo, Cu, Bi and Pb from the Onega deposits, which contain large reserves of vanadium and probably noble metals (Pd, Au, Ag, Pt), are limited by near-surface and deep-seated bedded oxidized zones. In addition, deep joint oxidized zone and hydrothermal roscoelite – chromceladonite – dolomite veinlets occur at the deposits. The highest contents (much higher than 10 ppm) of noble metals have been identified in these veinlets. Minerals of noble metals are native gold, selenides, less frequent selenide-sulfides, tellurides, and compounds with bismuth, lead, and other elements. Redeposited native copper, auricupride, native platinum, froodite, isoferroplatinum, palladium analogue of auricupride, the new natural phase, and the phase AuO(OH) have been identified in the oxidized zones with the highest contents of noble metals. Gold segregations from the near-surface oxidized zone of low noble-metal content (lower than 10 ppm) are fine clusters up to 0.1 μm in size. In the upper part of the deep-seated oxidized zone, gold occurs as broken spindle-shaped 2-3 μm particles. Close to the intermediate part of the deep-seated oxidized zone, gold crystals are disseminated in blades of native copper that reach several tens of μm in size.

The results obtained confirm previous assumption on the probable increase in noble-metal reserves adjacent to explored uranium-vanadium deposits.

4 tables, 6 figures, 16 references.

The Onega U-V deposits with noble metals (Pd, Pt, Au, Ag), Mo, Cu and Bi are rich in vanadium reserves and these probably contain associated noble metals. Assumption of large reserves of noble metals was supported the previous studies that found significant concentrations of Pd, Pt, Au, and Ag adjacent to the U-V ores (Chernikov, 1997, 2001; Chernikov *et al.*, 2000).

The Srednyaya Padma, Tsarevskoe, and Kosmozero deposits occur at the contact with grayish red-brown (hematitized) Lower Proterozoic dolomites (Bilibina *et al.*, 1991; Laverov *et al.*, 1992; Mel'nikov *et al.*, 1992, 1993, 1995; Ledeneva & Pakul'nis, 1997) of the ancient deep-seated bedded oxidized zone (Poluektov *et al.*, 1998; Chernikov *et al.*, 2000; Chernikov, 2001) in the Onega riftogenic basin located in the southeastern Baltic Shield.

The U-V ores of the Onega deposits are different mineralogical types with distinct mineralogical and geochemical zoning. A low-temperature sodium metasomatic rock (albitite) occurs at the margins of the ore deposits at the furthest distance from the boundary with the deep-seated oxidized zone;

the U-V mineralization with Cu-Mo sulfides overprints the inner part of this metasomatic zone.

The Cu-Mo uranium-vanadium ore is followed by the V-rich chromceladonite-roscoelite zone alternating with ordinary U-V ore with the areas enriched in uranium and noble metals. The U-V ore is bounded by the hematitized dolomites. The zoning of the mineral assemblages is identified at each deposit of the district. Calcite and hematite veinlets and breaks formed as a result of deep joints in the oxidized zone and cross-cut all of the above mineral assemblages. They cut both orebodies and hematitized dolomites. Nevertheless, the hydrated uranium oxides (Fig. 1) are observed in all mineral assemblages. The boundary of the deep-seated bedded oxidized zone (Fig. 2) is the clear oxidized-reduction barrier and plays a major role in forming the complex ores. The near-surface modern oxidized zone with abundant brown and dark-brown iron and manganese oxides is the upper boundary of the U-V ore at all deposits down to 30 m (less frequent 150 m) below the surface (Fig. 2).

Dolomites near the contact with gray rocks

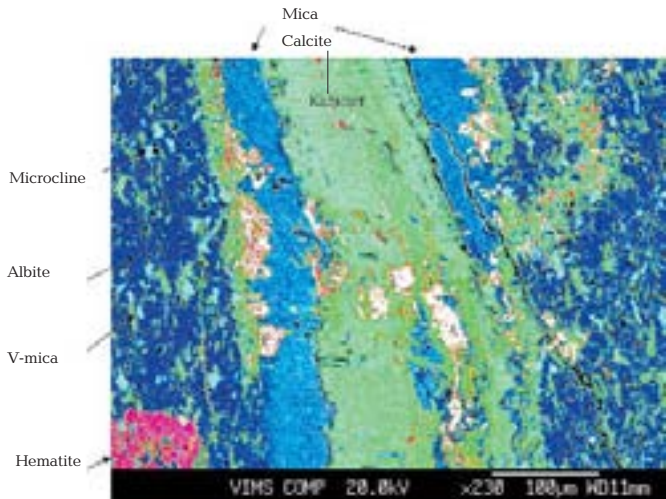
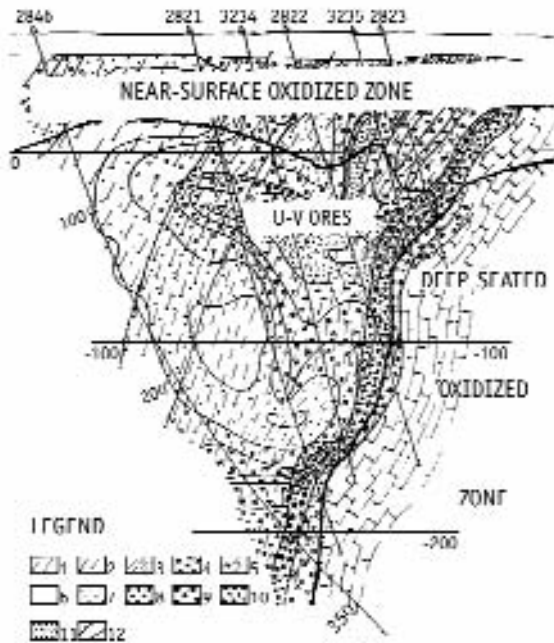


Fig. 1. Albitized rocks with superimposed U-V mineralization and calcite, micaceous, and hematite veinlets and segregations and hydrated uranium oxides (light gray on the figure).

Fig. 2. Location of the near-surface and deep-seated oxidizing zones in regard to U-V ores at the Srednyaya Padma deposit. Geology after Poluekotov et al. (1998).

(1) Variegated clay-carbonate slate. (2) Greenish grey clay-carbonate slate. (3) Chungite-bearing clay slates with interlayers of dolomite. (4) Feldspar-quartz siltstone and aleuroslate. (5) Dolomite. (6) Moraine. (7) First grade of metasomatic alteration. (8) Outer zone of metasomatic alteration. (9) Intermediate zone of metasomatic alteration. (10) Inner zone of metasomatic alteration. (11) Strongly brecciated ore. (12a) Boundaries of lithologic units. (12b) Boundaries of metasomatic zones.



and hematite veinlets are enriched in redeposited minerals of noble metals and, locally, uranium and vanadium. Conventional mineralogical methods failed to identify these minerals. Therefore, the high-resolution techniques, including scanning electron microscopy with an energy-dispersion system (SEM-EDS), transmitted-electron microscopy (TEM) with X-ray microdiffraction, and electron-microprobe analysis were used to detect ultramicroscopic concentration centers of noble metals, their chemical composition, structure and morphology.

The noble metals in the Onega ores are irregularly distributed. The maximum contents occur in the roscoelite-chromceladonite-dolomite veinlets that cut the U-V ores. According to most researchers, these veinlets are hydrothermal. Padmaite, PdBiSe, sudovikovite, PtSe₂ (Polekhovskii et al., 1991; 1997), and malyshevite, PdBiCuS₃ (Chernikov et al., 2006), the new minerals of Pd and Pt were firstly described from such veinlets at the largest Srednyaya Padma deposit. In addition to roscoelite, chromceladonite and dolomite, clausthalite, PbSe, froodite, PdBi₂, and native gold and bismuth are abundant in the veinlet, whereas moncheite, PtTe₂, sobolevskite, PdBi, insizwaite, Pt(Bi,Sb)₂, bogdanovitchite, AgBiSe₂, polarite, Pd₂PbBi, and paraganajuatite, Bi₂Se₂S, are less abundant. As is apparent, noble metals occur as selenides, and less frequently, as selenide-sulfides, tellurides and bismuthides, or are constitutive compounds with bismuth, lead and other elements. For example, in addition to froodite, intermediate members compositionally close to urvantsevite Pd(Bi,Pb)₂ were identified (Table 1).

The noble metal minerals are associated with oxides (nasturane and hydrated nasturane) and uranium silicates of the coffinite type, vanadium micas, and selenides of lead, copper, and bismuth.

Carbonate segregations with redeposited fine-grained native copper, auricupride, native platinum, froodite,

Table 1. Composition of froodite and intermediate member between froodite and urvantsevite

Com- ponent	Pd, wt%	Bi	Pb	Se	Pt	Total	Formula
1	20.6	78.9	2.4	0.2	—	102.1	Pd(Bi,Pb) ₂
2	18.0	70.8	9.3	1.6	—	101.3	Pd(Bi,Pb) ₂
3	17.6	66.8	11.8	2.8	1.5	100.5	Pd(Bi,Pb) ₂
4	21.8	78.2	—	0.2	—	100.2	PdBi ₂

Table 2. Content of noble metals in the studied samples

Depth	87.7 m	87.7 m	153 m	153 m	166.5 m
	1 an.	2 an.	1 an.	2 an.	
Pt, ppm	0.3	0.22	0.4	0.27	0.24
Pd	0.2	3.35	0.9	0.56	9.87
Au	9.3	0.28	—	0.25	0.2
Ag	0.2	0.2	—	1.0	0.49

isoperplatinum, intermetallic CuZn, iron-group intermetallides, and a novel natural phase Cu₃Pd, the palladium analogue of auricupride (Chernikov *et al.*, 2005) are observed in the near-surface and deep-seated oxidized zones at Srednyaya Padma. The size of these grains ranges from 1–5 nm to 300–500 nm.

A grain with diffuse reflections of the phase AuO(OH) was observed in hematitized dolomites. This is the second natural finding; the first one was described from weathering crusts in the South Urals (Novgorodova *et al.*, 1995). All above mineral phases were found in samples with a total noble-metal content of 10 ppm and higher. However, in most of the near-surface and deep-seated oxidized zones, the total content of noble metals ranges from 0.2 to ~10 ppm.

Modes of occurrence of noble metals in samples of the Tsarevskoe deposit collected from the near-surface oxidized zone at a depth of 87.7 m below the surface and from dolomite in the deep-seated zone at depths of 153 and 166.5 m below the surface were described for the first time by Dubinchuk *et al.* (2007). Conventional mineralogical techniques showed that the dolomite is highly silicified, limonized, and impregnated with Mn oxides. Dolomites from the deep-seated oxidized zone are hematitized and silicified, and contain native copper, apatite and rare vanadium mica. Like previous data (Dubinchuk *et al.*, 2007), the con-

tent of noble metals determined by chemical and spectral methods ranges from 0.2 to 9.87 ppm (Table 2). Segregations of noble metals have been not identified using SEM-EDS in the samples with such a content. Therefore, these samples were examined with TEM followed by extraction of phases and their identification by X-ray microdiffraction and electron-microprobe analysis.

Segregations of native gold were found in the near-surface oxidized zone at a depth of 87.7 m. They are square, irregular-shaped, and occasionally oval fine clusters (Fig. 3a). Extracted particles to replica are distinguished by both ring and discrete-point X-ray single-crystal microdiffraction patterns, which are characteristic of gold (Fig. 3b).

Numerous inclusions of apatite and sporadic grains of native copper and sphalerite were identified in quartz from dolomites collected at a depth of 153 m. With detection limits (wt.%) of 0.02 Ag, 0.06 Au, 0.06 Pd, and 0.01 Pt, the elevated contents of noble metals in the sample and in these minerals were not measured. Spindle-shaped particles of native gold, which are partly broken and leached, were found by TEM (Fig. 4a). Extracted particles are characterized by a ring X-ray microdiffraction pattern that is characteristic of metallic gold (Fig. 4b).

Different size (not less than 0.0 nm) segregations of native copper (including bladed ones), and individual crystals of gold disseminated in these blades (Fig. 5a) were observed in samples from the 166.5 m depth (closer to the middle part of the deep-seated oxidized zone). The blades are transparent to electrons and the gold crystals appear dark. Results of investigation of the bladed areas by TEM equipped with EDS are given in Table 3. Only in point 1 in native copper is Au below detection limit. However, more than 8% Ag and about 7% Co were identified in this point. At other points, more than 27% Au and 12% Ag are observed.

The polycrystalline texture of the transparent blade was established by X-ray microdiffraction (circles in Fig. 5a). In addition to the distinct reflections of native copper, weak reflections of native gold are present in the microdiffraction patterns (Fig. 5b). The gold crystals in native copper are oriented: (111)_{Au} coincides with (111)_{Cu}. Fine grains of native platinum characterized by the clear

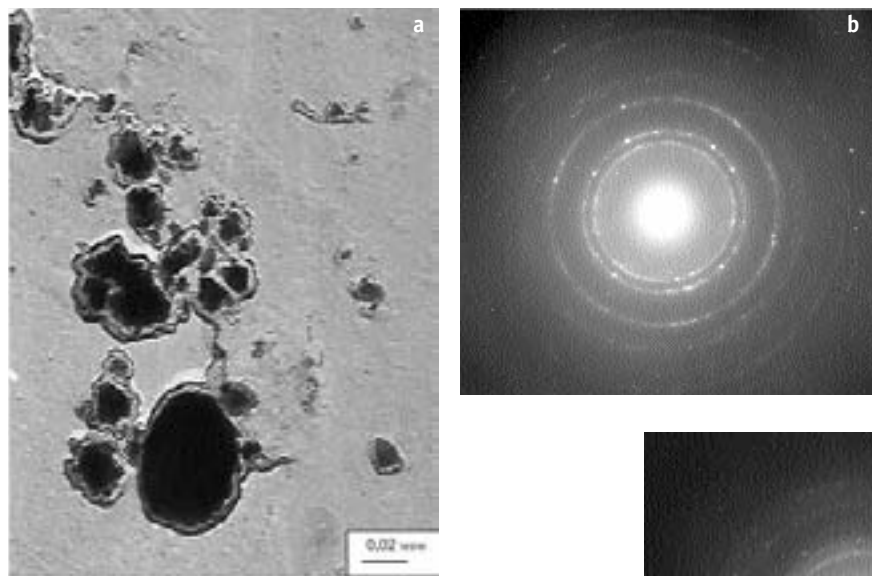


Fig. 3. Features of native gold from the near-surface oxidizing zone.

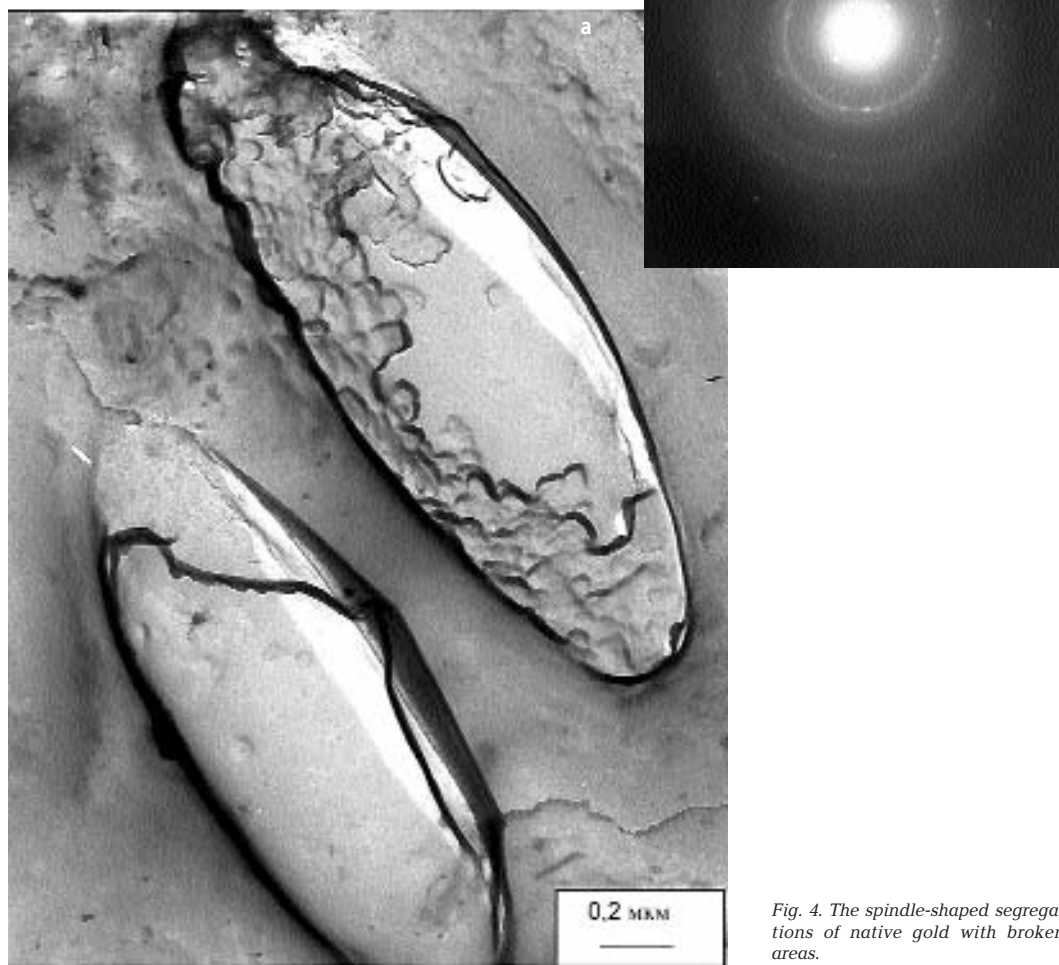


Fig. 4. The spindle-shaped segregations of native gold with broken areas.

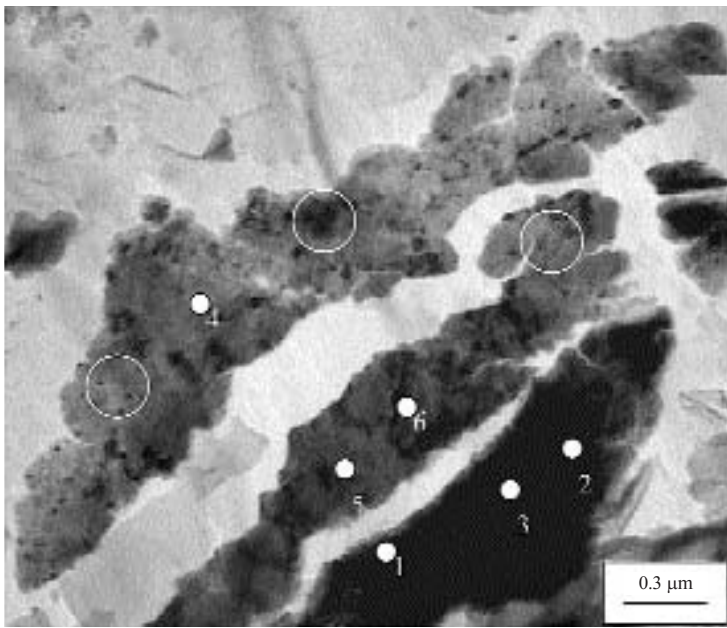


Fig. 5. Blades of Au-bearing native copper. Segregations of native gold are black in the blade transparent for electrons.

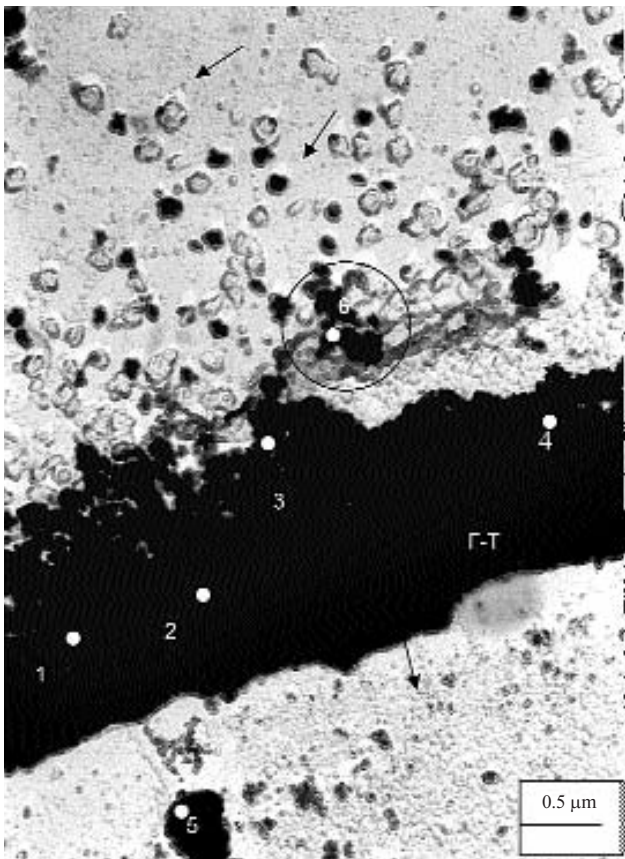
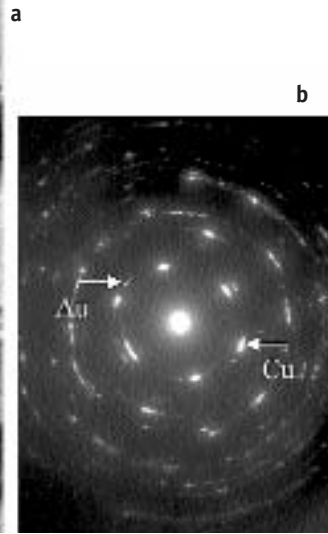


Fig. 6. Crystals of Pd-bearing native platinum close to segregations and microscopic veinlet of hydrohematite (black) containing platinum.

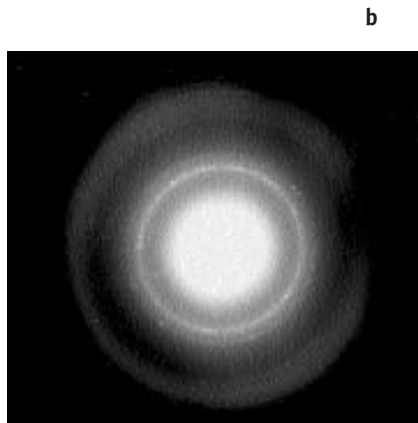


Table 3. Composition of separate areas of native copper blade (wt%)

№№	Ca	Ag	Ni	Co	Cu	Au	Total
1	0.00	8.59	0.00	7.11	84.30	0.00	100.00
2	12.48	12.36	0.48	0.00	47.28	27.41	100.01
3	12.48	12.35	0.48	0.00	47.28	27.41	100.00
4	14.17	12.52	1.07	0.00	44.87	27.37	100.00
5	13.17	12.34	0.81	0.00	46.33	27.34	99.99
6	10.51	12.17	0.01	0.00	50.05	27.26	100.00

Table 4. Composition of native platinum, wt %

№№	Si	Ca	Fe	Co	Ni	Pt	Pd	Total
1	2.89	0.11	13.72	1.19	1.22	46.58	30.21	95.92
2	1.75	0.14	10.17	1.44	1.84	54.45	24.17	93.96
3	1.11	1.45	6.18	1.55	1.97	60.74	22.81	95.81
4	1.27	2.00	1.75	1.58	0.00	58.41	16.00	81.01
5	0.22	2.15	1.26	1.21	2.17	65.48	27.70	100.19
6	0.97	2.29	0.54	1.51	1.98	65.62	27.01	99.92

X-ray microdiffraction pattern (Fig. 6b) were found, with particles located above the veinlets of hydrohematite (Fig. 6a) being larger (portions of μm) in comparison with those below the veinlet ($0.0\text{ n}\mu\text{m}$). The points shown in Fig. 6a correspond to the analyses listed in Table 4.

Pt concentration ranges from ~ 46.6 to $\sim 65.6\%$, Pd, from 16.0 to 30.2% , and Fe, from ~ 13.7 to 0.54% . Despite the absence of any positive linear correlation between platinum and iron, the largest PGE concentration is observed with the lowest Fe content (slightly higher than 0.5% at point 6).

As listed in Table 2, the noble metals are extremely unevenly distributed in the examined samples and Pd content is higher than Pt, but discrete phases of Pd were not identified. Nanocrystals of the Pd analogue of auricupride overgrown by hematite were previously described by Chernikov et al (2005). Such segregations of Pd are probable characteristic of the studied samples.

In general, modern high resolution techniques allow characterization of the mineralogical features of the hydrothermal veins and near-surface and deep-seated oxidized zones at these deposits. The noble metal minerals occur as selenides, selenide-sulfides and compounds with Bi, Te, and Pb in hydrothermal roscoelite-chromeladonite-dolomite veinlets. In contrast to these hydrothermal veinlets, grains of native copper, gold, and platinum

with palladium, nanocrystals of auricupride, phase $\text{AuO}(\text{OH})$, the new natural Pd analogue of auricupride, and CuZn intermetallic compounds, which are usually observed with carbonate material, are prevalent in the near-surface and deep-seated oxidized zones. Gold grains from the near-surface oxidized zone (above the bedded deep-seated oxidized zone) with the low content of noble metals (less than 10 ppm), are square, anhedral, or oval fine clusters up to $0.1\ \mu\text{m}$ in size. In the upper part of the deep-seated oxidized zone, gold occurs as broken spindle-shaped particles $2\text{--}3\ \mu\text{m}$ in size. Closer to the middle part of the deep-seated oxidized zone, the gold crystals are disseminated in blades of native copper up to tens of μm in size; the blades are polycrystalline and the gold crystals are oriented parallel to the copper crystals. Segregations of Pd-bearing native platinum also occur here. Thus, the results obtained indicate that leaching and redistribution of noble metals decrease with depth in the oxidized zone with total content of these metals less than 10 ppm . At the same time, the size of gold grains increases downward, suggesting larger concentrations of noble metals at depth. Together with previous data (Chernikov *et al.*, 2005), this conclusion suggests significant increase of noble-metal reserves near explored U-V deposits.

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GROSSULAR, VESUVIANITE and ACHTARANDITE MINERALOGY OF THE TALNAKH REGION

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Achтарandite, the pseudomorph after unknown mineral is a mineralogical enigma. The second locality of achтарandite described in Talnakh region, Otdel'naya mountain, by its mineral association is an analogue of the type-locality in Yakutia republic, Wiluy river valley. The comprehensive investigation was applied to the rock-forming minerals – grossular, vesuvianite and achтарandite, and also to the mineral and fluid inclusions enclosed.

The experimental modelling of Cl-containing mayenite – the achтарandite proto-mineral synthesis was carried out.

It is established that the specific mineral association containing achтарandite happened during two stages: skarn and apo-skarn. During the first stage there were formed central parts of garnet and vesuvianite crystals, fassaite which remained as inclusions in vesuvianite, and Cl-containing mayenite. During the second stage there were formed edges of garnet and vesuvianite crystals, amesite, titanite, mackinawite, and Cl-containing mayenite was replaced by achтарandite.

7 tables, 8 figures, 28 references.

The mineral composition of grossular, vesuvianite and achтарandite found at Otdel'naya Mountain (Talnakh region) located in the north-western edge part of Siberian platform is similar to that found in the Wiluy river valley. The latter was first described in 1821 by Karl Laksman (Lyakhovich, 1954; Zhabin & Lyakhovich, 1994). The unique rocks containing garnet, vesuvianite and achтарandite were discovered in 2001 not far from the 'Mayak' mine at the foot of Otdel'naya Mountain (Pletnev, Alferova *et al.*, 2001).

Geology-petrological description of the grossular, vesuvianite and achтарandite locality

The plate complex is represented by gently pitching terrigenous, carboniferous limestones, dolomites and marls, sulfate-carboniferous and other sediments of Late Cambrian and Early-Middle Paleozoic (Cambrian – Devonian) periods, with thickness up to 3 km. They are overlapped by terrigenous coal-bearing sediments of Tungussskaya series (Carboniferous-Perm), up to 3.5 km thick. Volcanic trap rocks are associated with multiple intrusions of dolerite and gabbro-dolerites, some of which are enriched with Fe-Cu-Ni-Co

sulfide ores (Godlevsky, 1959). The ore-bearing intrusives are stratified massifs; in the lower part they are represented by picrite gabbro-dolerites saturated with sulfide droplets, in the upper part – by leucocratic gabbro-dolerites with xenoliths of hornfels and schlieren enriched in olivine, chrome-spinels and sulfides. The ore-bearing intrusives are surrounded by a thick aureole of hornfels (pyroxene-hornfels and albite-epidote-hornfels facies), including calcareous-silicate hornfels (skarnoids) and various magnesium and calcareous skarns. The estimated age of the trap formation rocks is $245 \pm 3 - 5$ mln. years, which corresponds to Permian and Triassic periods boundary (Spiridonov *et al.*, 2000).

The grossular, vesuvianite and achтарandite locality is represented by blocks of vastly altered terrigenous rocks of the plate complex (C₃-D₁). These comprise sandstones with dolomitic cement, limestones and dolomites marls. The blocks are enclosed as xenoliths in the front part of the north-eastern branch of Verkhnetalnakhsky taxitic gabbro-dolerite intrusive (T_{1,2}), Leucocratic gabbro-dolerites have undergone albitization and prehnitization processes in conditions of prehnite-pumpellyite facies low-grade metamorphism. They consist of plagioclase,

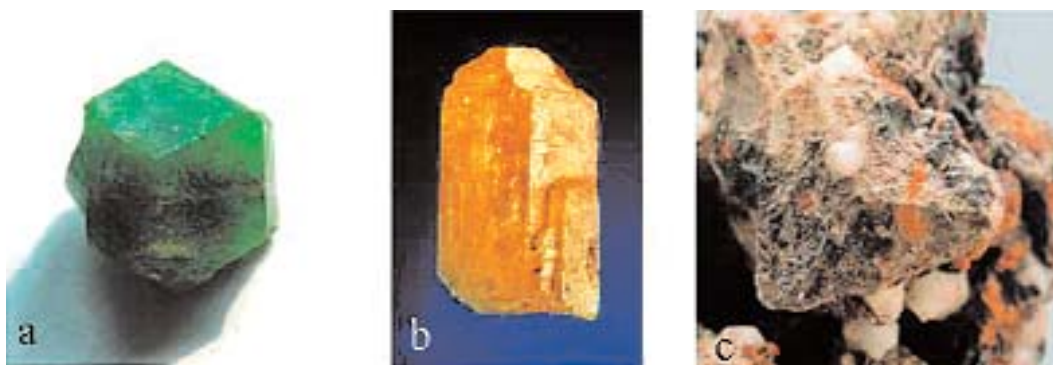


Fig. 1. Mineral association of the Talnakh locality: grossular (crystal size 5 mm), vesuvianite (crystal length 4 mm) and achtarandite (crystal size 6 mm).

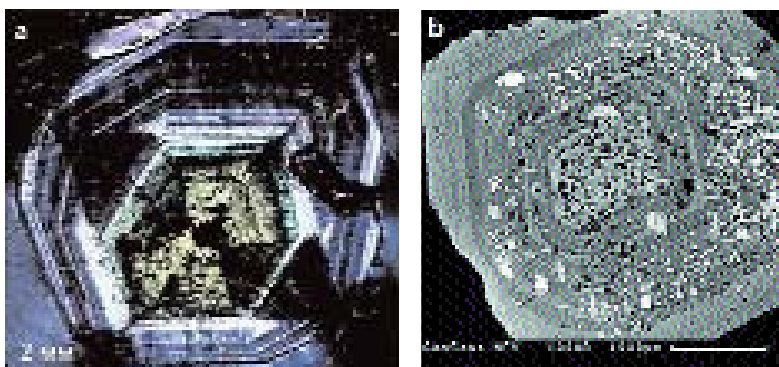


Fig. 2. Internal structure of Cr-Ti-containing grossular crystals from Otdel'naya Mt., Talnakh: a – thin section, b – BSE image

clinopyroxene, sulfides, apatite, titanite and chlorite minerals. Altered hornfels and skarns among leucogabbro are represented by non-equigranular aggregates of white and yellowish grossular, Cr-Ti-containing grossular, vesuvianite, achtarandite, chrome-spinel, calcite, chlorite group minerals, anhydrite, diopside, prehnite, serpentine in association with pyrrhotite, pyrite, sphalerite, chalcopyrite and their alteration products. The size of segregation of these minerals range from millimeter fractions up to 12 mm.

Mineralogy

The main rock-forming minerals at the aforesaid locality are grossular, vesuvianite and achtarandite. Megacrysts of these are set in the fine-grained matrix consisting of grossular, hydrogrossular, pyrite, chalcopyrite and iron oxides. The rocks are often incoherent.

Grossular – is the most common mineral at the locality. Garnet crystals and aggregates form phenocrysts, veinlets and monomineral aggregates in the altered leucogabbro. At the locality near the Otdel'naya Mountain grossu-

lar forms aggregates up to several tens of centimeters composing up to 60–80% of the rock. The mineral is represented by well-terminated crystals from 0.5–1 mm up to 8–10 mm and their aggregates. The main crystal faces are: {110}, {112}, {321} and their combinations. Garnet crystals are normally abruptly zoned; the central part is dark-green, the edge is colourless. The intermediate light-green zone as actually finely zoned with dark-green and colourless zones. In thin section they are anisotropic, sectorial and finely-zoned (Fig.2).

The garnet is chemically heterogeneous: the central dark-green part corresponds to a Cr-Ti-bearing variety of grossular whilst the colourless edge is almost a 'pure' end member (Table 1). The chemical composition of different parts of the garnets is shown in Figure 3. The distribution of the mineral-forming and accessory chemical elements in the zoned Cr-Ti-containing grossular is as follows: the central part of crystals is enriched in Cr, Ti and depleted in Si; the edge is enriched in Ca and Si. The IR spectrum of the edge zone of the garnet crystals corresponds to stoichiometric OH-free grossular.

Table 1. Chemical composition (wt.%) of garnet from Otdel'naya mountain (Talnakh) locality

Comp.	core					edge				
	1	2	3	4	5	6	7	8	9	10
SiO ₂	34.78	36.13	35.90	39.37	39.81	40.40	35.52	36.49	39.89	39.91
TiO ₂	6.47	5.70	5.30	1.38	—	0.21	6.89	5.05	—	0.11
Al ₂ O ₃	11.44	13.06	12.88	20.70	22.23	21.92	10.89	12.45	22.12	21.99
Fe ₂ O ₃	0.51	0.37	0.42	—	0.13	—	0.70	0.45	0.08	0.13
MnO	—	0.10	—	0.02	0.20	0.17	0.06	—	—	—
MgO	1.57	1.69	1.36	1.11	1.07	0.71	1.71	1.25	1.25	1.20
CaO	35.94	35.30	35.72	36.56	36.39	36.51	34.93	34.93	35.86	36.05
Cr ₂ O ₃	8.97	6.91	7.83	0.57	0.02	0.06	9.03	8.94	—	0.15
V ₂ O ₃	0.16	0.33	0.08	0.28	—	—	—	0.07	0.10	0.01
ZnO	0.01	0.25	0.11	—	—	—	0.15	0.12	0.22	0.24
Total	99.85	99.84	99.60	99.99	99.85	99.98	99.88	99.75	99.52	99.79

Notes: 1–6 analyst N.N. Korotaeva, using a CamScan electron microprobe; 7–10 analyst N.N. Kononkova using a Camebax SX-50 electron microprobe.

The central dark-green part of a garnet shows a weak peak in the 3800–3400 cm⁻¹ region indicating the presence of OH-groups in structure. According to thermal analysis of the colourless and light-green (which is a fine interchange of dark-green and colourless zones) parts of a garnet crystal, the weight loss determined were 1.1 wt.% and 1.6 wt.% for these parts respectively. The central part was not studied by this method due to difficulties with sample preparation.

The cell parameter of the edge of the garnet crystals is $a_0 = 11.849\text{\AA}$, which is after Gennady Yu. Shvedenkov's data (Shvedenkov *et al.*, 1974), corresponds to OH-free grossular.

Cr-Ti-containing grossular from the

Talnakh locality is a rare iron-free variety of grossular which, due to its bright green colour, is sometimes called 'siberian tsavolite'. At this locality colour, and hence the decorative features of the material, is due to specific geochemical conditions of high sulphur activity wherein all the Fe is combined as sulfides and not in silicates and chrome-spinel. The difference between tsavolite – V-Cr-containing grossular from Tanzania and grossular samples examined is revealed at their visible spectra. The tsavolite colour is due to Cr³⁺ and V³⁺ ions, which are seen as a double absorption band in 480–580 nm area of the visible spectra. The colour of the Cr-Ti-containing grossular

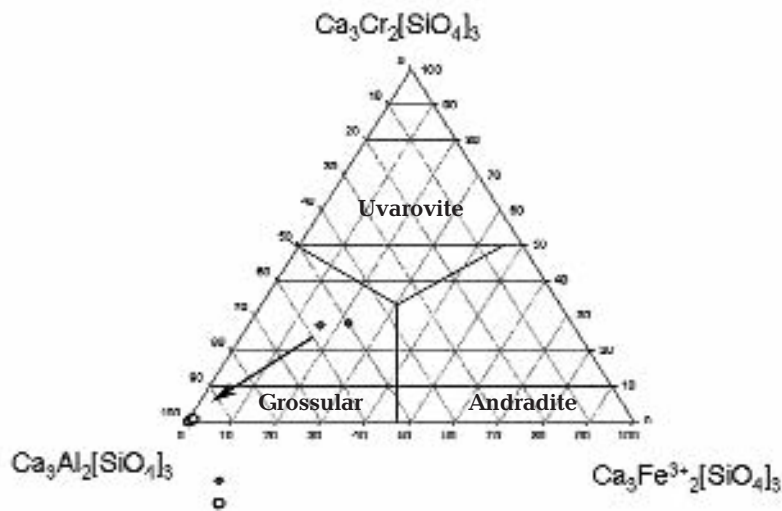


Fig. 3. Chemical composition of Cr-Ti-containing grossular from Otdel'naya Mt., Talnakh

from Talnakh is due to Cr^{3+} ions. In the visible spectra only one absorption band in 480–580 nm region is observed. This is shifted towards the shorter wavelength part of the region compared with that of tsavolite.

Cr-Ti-containing grossular from Talnakh is saturated with numerous mineral inclusions: chrome-spinel, vesuvianite, amesite, stilbite and Fe and Cu sulfides. In addition there are also fluid inclusions.

Chrome-spinel. Garnet crystals from Talnakh mostly contain numerous inclusions of chrome-spinel. Aggregates and chains of isometric brown-red translucent magnesio-chromite crystals are located within both dark-green and colourless zones (Fig. 4). Usually chrom-spinel crystals are themselves finely-zoned. Chemical composition is presented in the Table 2 and corresponds to Al-bearing magnesiochromite – an intermediate member of the $\text{MgCr}_2\text{O}_4 - \text{MgAl}_2\text{O}_4$ system (Table 2). As chrome-spinel does not contain magnetite, chromite and hercynite end members i.e. absolutely iron-free, it can be concluded that this mineral was formed at a relatively low temperatures and high sulphur activity. According to theoretic calculations (Sack & Ghiorso, 1991), there is a continuous solid solutions series in the system $\text{MgCr}_2\text{O}_4 - \text{MgAl}_2\text{O}_4$ at the temperatures above 550°C. Below this temperature chrome-spinels crystallized with chemical composition determined by the $\text{MgCr}_2\text{O}_4:\text{MgAl}_2\text{O}_4$ ratio (solvus curve). According to Viktor V. Ryabov's data this ratio in chrome-spinels in rodingite garnets from Otdel'naya Mountain can be 4:1 (magnesiochromite) or 1:4 (Al-bearing magne-

siochromite). Chemical composition of the garnets studied are of the 4:1 ratio which corresponds to a temperature of formation between 300–400°C.

Despite the high chromium content (up to 82.2%) of chrome-spinel, there is no local enrichment in Cr around grains, which is typical for many metamorphic minerals formed after chrome-spinel, such as emerald or nephrite etc. Hence, most probably, the chrome-spinel described in this paper is 'new-born', paragenetic to the garnet and has not been altered. According to experimental data (Plyusnina *et al.*, 1993), to fluid inclusions data obtained and theoretical temperatures of formation for Al-bearing magnesio-chromite, the garnet formation temperature is below 400°C. High sulphur activity is corroborated by pyrite and chalcopyrite occurrence together with chrome-spinel.

According to X-Ray tomography performed on several zoned Cr-Ti-containing garnet crystals from Otdel'naya Mountain, Talnakh, the central dark- or bright-green part enriched in Cr and Ti does not contain relics of a connate chrome-spinel, or contains it very rarely.

Troilite $\text{Fe}_{0.64}\text{Ni}_{0.36}\text{Co}_{0.01}\text{S}_{0.99}$ occurs as xenomorphic ingrowths in grossular. Troilite is a typical low-grade metamorphic mineral.

Vesuvianite and amesite. White opaque mineral inclusions with square or rhombic section occur in all of the garnet crystals zones. Sometimes these open-work segregations are spread throughout the garnet crystal making it translucent/opaque with a white tint. More frequently these inclusions are concentrated between colour zones and growth sectors (Fig. 4). The inclusions are fine aggregates of

Table 2. Chemical composition (wt. %) of chrome-spinel inclusion in garnet from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8	9	10	11
Al_2O_3	9.87	11.48	10.80	10.30	8.24	10.40	7.78	9.26	10.08	9.96	6.65
FeO	–	0.20	0.36	0.61	1.14	1.53	1.68	1.67	1.77	1.97	1.95
Fe_2O_3	0.73	0.52	–	–	–	–	0.39	–	–	–	–
MnO	0.37	0.59	0.51	0.22	0.62	0.30	0.43	0.95	0.52	0.68	0.74
MgO	21.53	21.15	21.31	20.89	20.34	19.98	20.35	19.84	20.35	19.97	19.94
Cr_2O_3	63.98	64.35	65.64	67.04	68.41	66.10	67.56	67.25	66.13	66.65	70.15
NiO	n.d.	–	–	0.02	–	–	0.24	–	–	–	–
ZnO	0.21	0.20	0.24	0.05	0.18	0.55	0.32	0.36	–	0.29	–
Total	97.56	98.49	98.86	99.13	98.93	98.86	98.75	99.33	98.85	99.52	99.43

Notes: 1 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe; 2,3,5,6,8–11 – analyst N.N. Korotaeva & 4,7 analyst E.V. Guseva, using a CamScan electrone microprobe«CamScan»

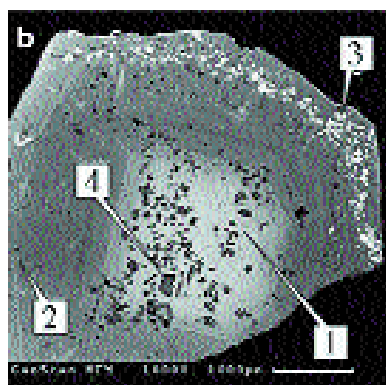
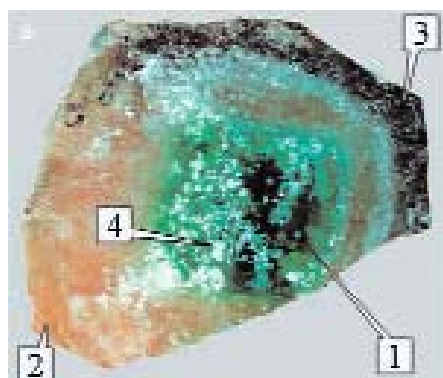


Fig. 4. Mineral inclusions in garnet crystal from Otdel'naya Mt., Talnakh:
a – reflected light,
b – BSE image.
1 – Cr-Ti-grossular,
2 – hydrogrossular,
3 – magnesio-chromite,
4 – vesuvian-amesite aggregate

vesuvianite and amesite. Chemical composition of these minerals are presented in Table 3. The theoretical formula of vesuvianite is $\text{Ca}_{19}(\text{Al}, \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+})_{13}(\text{B}, \square)_5[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4(\text{OH}, \text{O}, \text{F})_{10}$. The formula of vesuvianite derived from inclusions and calculated for 50 cations is: $\text{Ca}_{19.00}(\text{Al}_{10.28}\text{Mg}_{2.55}\text{Fe}^{2+}_{0.05}\text{Cr}_{0.05}\text{Ti}_{0.01}\text{Ni}_{0.02}\text{Zn}_{0.06})_{13.02}(\text{B}_{0.66}\square_{4.34})_5[(\text{Si}_{15.66}\text{Al}_{2.34})_{18}\text{O}_{68}](\text{Cl}_{0.68}(\text{OH})_{9.3})_{10}$. Chemical composition of amesite corresponds to the formula $(\text{Mg}_{3.68}\text{Fe}^{2+}_{0.10}\text{Mn}_{0.07}\text{Ni}_{0.02}\text{Zn}_{0.01})_{3.88}(\text{Al}_{1.92}\text{Cr}_{0.02})_{1.94}[(\text{Si}_{2.22}\text{Al}_{1.78})_{4.00}\text{O}_{10}](\text{OH})_8$.

Stilbite. Sometimes different parts of the garnet crystals contain shapeless, curved ingrowths of white opaque stilbite inclusions. Chemical composition of stilbite is represented in the Table 3 and corresponds to the formula $(\text{Ca}_{1.35}\text{Na}_{0.01}\text{Fe}_{0.01})_{1.36}[\text{Al}_{2.53}\text{Si}_{9.42}\text{O}_{24}]_9(\text{H}_2\text{O})$.

Fluid inclusions. In the vesuvianite crystals

studied multiple fluid inclusions were noted which enabled the estimation of the temperature of formation range. Fluid inclusions studied are primary, primary-secondary and secondary. The size of inclusions is up to 10 – 15 m. In those fluid inclusions where phase transfer is observed, the composition was determined as $\text{MgCl}_2 - \text{H}_2\text{O}$ with salts concentration 3.23 – 3.39 wt.% eqv. NaCl (Prokof'ev V. Yu. *et al.*, 1999). Results of the study is presented in a Table 4.

Vesuvianite occurs as crystals and crystal aggregates in the rodingite-like rocks of the Talnakh intrusive massif. Crystal sizes vary from 5 to 7 mm along the *c*-axis and from 3 to 4 mm along the *a*-axis. Colour varies from yellowish-green to pistachio-green and crystals are partially transparent. The morphology (block-like constitution, etching channels and

Table 3. Chemical composition (wt.%) of vesuvianite (1–4), amesite (5–6) and stilbite (7–9) inclusions in garnet from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8	9
SiO ₂	33.65	34.53	34.00	33.98	25.97	26.79	60.53	59.78	61.08
TiO ₂	0.02	0.08	–	–	0.16	–	0.02	0.02	0.08
Al ₂ O ₃	23.01	20.87	20.05	21.41	41.28	39.75	13.81	14.21	14.87
FeO	0.13	0.09	0.20	0.14	0.87	1.42	0.13	0.11	0.16
MnO	–	–	0.02	0.12	0.44	0.99	0.05	–	–
MgO	3.67	3.90	4.17	3.44	30.55	29.92	0.05	0.09	0.08
CaO	38.11	40.31	40.99	39.70	–	–	8.08	7.87	8.19
Cr ₂ O ₃	0.13	0.17	0.18	0.13	0.11	0.28	–	0.05	–
NiO	0.05	–	–	–	traces	0.22	n.d.	n.d.	n.d.
ZnO	0.17	–	0.39	–	–	0.14	–	–	–
Cl	0.86	n.d.	n.d.	0.86	–	–	–	–	0.01
Total	99.79	99.95	100.0	99.78	99.38	99.51	82.67	82.13	84.47

Notes: 1–6 – CamScan electrone microprobe; 1,4–6 analyst E.V. Guseva & 2,3 analyst N.N. Korotaeva; 7–9 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe. n.d. – not determined.

Table 4. Temperature conditions estimate of garnet crystals from Otdel'naya mountain (Talnakh) locality formation

Colour, (zone)	T _{hom.} , °C	Number of inclusions	T _{eut.} , °C	T _{ice melt.} , °C
green (core)	243–231	6		
colourless (edge)	206–186	7		
light-grey	215–196	8		
colourless (edge)	286	3	-32	-2.0
colourless (edge)	167–137	17	-33	-2.0–1.9

Notes: Analyst V.Yu Prokof'ev using a THMSG-600 Linkam thermocryocamera

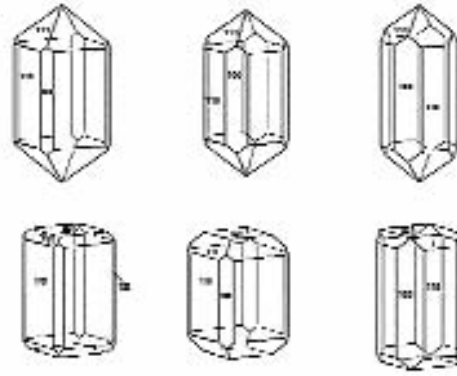


Fig. 5. Simple forms coordinations of vesuvianite crystals from Otdel'naya Mt., Talnakh

cavities) of the vesuvianite crystals are similar to that of wiluite.

Ten crystals were selected for goniometer measurements. Simple forms determined are presented in Fig. 5. Faces of prisms {110} and {100} and dipyrmaid {111} are predominant. Basal pinacoid faces {001} are subordinate or absent.

Vesuvianite crystals in thin sections are similar to the grossular crystals described above; being finely-zonal and sectorial. Sometimes they contain inclusions of bright-green zoned Cr-Ti-bearing grossular and calcite. Crystals show colour zonation across the *c*-axis: the inner zone is normally brownish-green or brownish-yellow containing many fluid and mineral inclusions. The outer zone is yellowish-green and transparent. The outline of the border between zones is normally rounded. Some crystals show splintered constitution across the *c*-axis.

According to EMPA data (Table 5), the chemical composition of the vesuvianite studied is characterized by low Fe content and relatively high Cl and F content. The formulae calculation was based on 50 cations, B and (OH)-group content were calculated according vesuvianite stoichiometry and charge balance. The presence of B was established by IR-spectroscopy.

As shown in Table 5, the Ti, Cr, B content in vesuvianite crystals decreases from the centre to the edge across the *c*-axis whilst the Cl and F content increases. This latter aspect is possi-

bly evidence of increasing Cl and F activity during the final stage of the crystal-forming process. The decrease in Ti and Cr content in vesuvianite crystals, similar to that in zonal grossular garnet, confirms their paragenesis.

The IR-spectra of the Talnakh vesuvianite are similar to the IR-spectra of wiluite (Kurazhkovskaya *et al.*, 2004); they also show [BO₃] and [BO₄] groups vibration bands. According to the EMPA data, vesuvianite from the Otdel'naya Mountain contains up to 1.5 wt.% of F, which is intermediate between the content in vesuvianite from skarns (up to 2 wt.% F) and from rodingites (up to 0.6 wt.% F) (Allen & Burnham, 1992; Armbruster & Gnos, 2000).

Vesuvianite from Talnakh contains mineral inclusions of augite, perovskite, titanite, Cr-Ti-containing grossular, hydrogrossular and iron sulfides.

Augite, perovskite, titanite, hydrogarnet (?)

Inclusions of augite occur in all the vesuvianite crystals (mostly in the central parts) studied. Under electron microscope imaging augite inclusions are seen as well-terminated crystals up to 0.1 μm in size. The typical empiric formula is Ca_{1.00}(Mg_{0.72}Al_{0.23}Ti_{0.05}Cr_{0.01})_{1.01}[Si_{1.67}Al_{0.33}]_{2.00}O₆. Perovskite grains occurring as intergrowths with augite, have the formula (Ca_{0.99}Na_{0.01})_{1.00}Ti_{0.98}O_{2.96}. The ingrowths of titanite ranging from 30–50 μm in size occur mostly in the periphery zone of the augite and perovskite grains. Titanite does not form isolated grains in vesuvianite and is possi-

Table 5. Chemical composition (wt. %) of vesuvianite from Otdel'naya mountain (Talnakh) locality

Comp.	core					edge		core					edge	
	1	2	3	4	5	6	7	8	9	10	11			
SiO ₂	37.58	36.42	37.27	37.04	37.32	37.32	36.66	36.59	35.78	36.39	37.19			
TiO ₂	1.53	1.34	1.64	0.37	0.55	0.94	1.90	1.35	1.08	1.20	0.94			
Al ₂ O ₃	15.14	14.98	15.49	17.23	17.68	17.21	14.23	15.37	16.06	16.03	17.03			
FeO	0.12	0.06	—	0.17	0.17	0.15	0.28	0.11	0.09	0.11	0.21			
MnO	0.06	—	—	traces	0.05	0.03	—	0.03	0.02	0.10	—			
MgO	5.80	6.00	5.75	5.03	4.33	4.73	5.72	5.94	5.23	5.43	5.06			
Na ₂ O	0.01	0.01	—	0.02	0.07	0.02	0.04	0.03	0.01	0.02	0.01			
CaO	35.69	36.04	36.14	36.44	36.85	36.37	36.39	36.28	36.26	36.69	36.80			
Cr ₂ O ₃	0.07	0.17	0.09	0.01	0.05	—	0.05	—	0.01	—	—			
V ₂ O ₃	0.08	0.03	0.09	0.05	0.02	0.02	0.02	0.10	0.15	0.10	0.03			
ZnO	0.16	0.25	—	—	0.11	—	0.12	0.09	—	0.03	—			
Cl	0.05	0.05	0.02	0.10	0.04	0.09	0.04	0.01	0.12	0.06	0.14			
F	0.74	0.98	0.84	0.90	0.81	1.22	0.75	0.91	1.39	1.41	1.47			
B*	1.22	1.14	1.12	1.04	1.02	0.85	1.28	1.10	0.96	0.76	0.55			
OH*	1.75	2.53	1.55	1.60	0.93	1.05	2.52	2.09	2.84	1.67	0.57			
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0			
Apfu calculated for 50 cations														
Ca	18.11	18.33	18.25	18.32	18.48	18.14	18.65	18.37	18.38	18.35	18.15			
Na	0.01	0.01	—	0.02	0.06	0.02	0.03	0.02	0.01	0.02	0.01			
Mg	4.10	4.25	4.04	3.52	3.02	3.28	4.07	4.19	3.69	3.77	3.47			
Mn	0.02	—	—	—	0.02	0.01	—	0.01	0.01	0.04	—			
Zn	0.06	0.09	—	—	0.04	—	0.04	0.03	—	0.01	—			
Fe ²⁺	0.05	0.02	—	0.07	0.07	0.06	0.11	0.04	0.04	0.04	0.08			
Al	8.45	8.38	8.61	9.53	9.75	9.44	8.02	8.56	8.95	8.82	9.24			
Cr	0.03	0.06	0.03	0.01	0.02	—	0.02	—	сл.	—	—			
Ti	0.54	0.48	0.58	0.13	0.19	0.33	0.68	0.48	0.39	0.42	0.33			
V	0.03	0.01	0.04	0.02	0.01	0.01	0.01	0.04	0.06	0.04	0.01			
B*	3.22	3.00	2.95	2.71	2.65	2.20	3.42	2.90	2.57	1.96	1.41			
Si	17.80	17.29	17.56	17.38	17.47	17.38	17.53	17.29	16.93	16.98	17.12			
(OH) ₄ *	0.74	1.07	0.64	0.66	0.77	0.44	1.07	0.87	1.18	0.69	0.24			
Cl	0.04	0.04	0.02	0.08	0.03	0.07	0.03	0.01	0.09	0.05	0.11			
F	0.78	1.04	0.88	0.94	0.85	1.26	0.79	0.96	1.46	1.46	1.50			

Notes: Analyst N.N. Kononkova using a Camebax SX-50 electron microprobe. *Calculated according to valence balance and stoichiometry.

by the alteration product of augite and perovskite. Chemical composition of titanite corresponds to the formula Ca_{1.01}(Ti_{0.75}Al_{0.23}Cr_{0.01})Si_{1.01}O_{4.85}F_{0.09} (Table 6).

Augite and perovskite inclusions (typical minerals of magnesium skarns) in the central zone of vesuvianite crystals are the probably evidence of relatively high-temperature conditions during the crystal-forming process.

Garnet inclusions occur in the periphery

zone of the vesuvianite crystals. According to the thermobarogeochemical data obtained from garnet crystals, the paragenetic late stage vesuvianite-forming process was at a temperature of nearly 250°C.

Sometimes between the two zones in vesuvianite crystals well-terminated inclusions of white opaque micrograin aggregate up to 50 μm in size occur. By chemical composition these correspond to either vesuvianite (formula

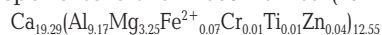


Table 6. Chemical composition (wt. %) of augite (1-2), perovskite (3-4), titanite (5) and vesuvianite-hydrogarnet aggregate (6-8) inclusions in vesuvianite from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8
SiO ₂	45.77	46.08	—	—	31.29	35.88	36.02	36.26
TiO ₂	1.85	1.62	57.79	55.01	30.85	0.14	0.03	0.02
Al ₂ O ₃	13.53	12.75	0.29	0.62	5.99	21.90	19.23	17.30
FeO*	0.08	0.05	—	—	0.09	0.58	0.55	0.17
Fe ₂ O ₃ *	—	—	0.07	0.36	—	—	—	—
MnO	0.09	0.01	—	—	0.04	0.27	0.19	0.12
MgO	13.29	13.25	0.01	0.01	ca.	3.90	3.06	4.55
CaO	25.71	25.81	40.79	39.33	29.24	32.41	36.59	37.53
Na ₂ O	0.04	0.02	0.17	ca.	—	0.03	0.01	—
Cr ₂ O ₃	0.22	0.47	0.45	0.80	0.20	0.15	0.06	0.01
V	—	—	0.26	0.13	0.12	0.05	—	0.07
ZnO	—	0.19	—	—	—	0.11	0.15	0.11
Cl	0.01	0.02	0.07	0.02	—	0.03	0.02	0.12
F	—	0.07	0.17	0.40	1.26	0.44	—	—
Total	100.59	100.34	100.07	96.68	99.08	95.89	95.89	96.25

Notes: 1–5 –CamScan electrone microprobe; 1,2,5 analyst E.V. Guseva & 3,4 analyst N.N. Korotaeva; 6–8 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe.

(B_{4.04}□_{0.96})₅ [(Si_{17.39}Al_{0.61})₁₈O₆₈](Cl_{0.09}(OH)_{9.91})₁₀ or hydrogrossular (formula (Ca_{2.54}Mg_{0.43}Mn_{0.02})_{2.99}(Al_{1.89}Fe³⁺_{0.03}Cr_{0.01}Ti_{0.01})_{1.94}[Si_{2.62}(O₄H₄)_{0.38}]_{3.00}O_{10.48}F_{0.07}). Probably the inclusions are a fine grained mixture of these minerals (Fig. 6).

Pyrite, pyrrhotite

Pyrite and pyrrhotite occur as xenomorphic segregations up to 0.5 mm in size, normally 0.2 mm. Pyrite formula – (Fe_{0.98}Ni_{0.01})_{0.99}S_{2.01}, pyrrhotite formula – (Fe_{6.83}Ni_{0.04})_{6.87}S_{8.13}. Pyrrhotite and pyrite formation indicates high S activity in the mineral system resulting in widespread occurrence of sulfides in the host rocks. Thus, Fe preferentially appears in the sulfides rather than silicates.

Achtarandite occurs as trigon-tristetrahedral crystals (Fig. 7), their twins and aggregates, normally 3–6 mm but up to 9–12 mm in size. As a rule the content of achtarandite in the rocks of Otdel'naya Mountain is approximately 5 vol. %. Achtarandite is unevenly distributed. Separate nests up to 5 cm in size are composed of 50–80 vol.% achtarandite. The achtarandite is colourless. Sometimes achtarandite is characterised by 'stuffed' crystals with multiple inclusions of zoned green

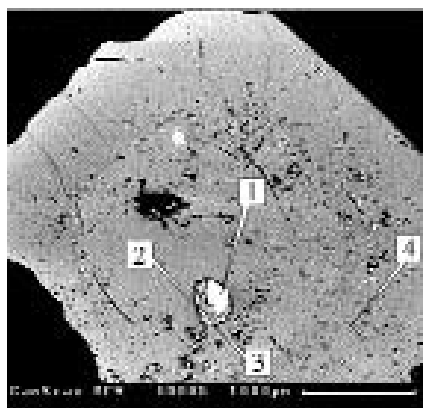


Fig. 6. Mineral inclusions in vesuvianite crystals from Otdel'naya Mt., Talnakh: (1) perovskite, (2) augite, (3) titanite, (4) hydrogrossular



Fig. 7. Achtarandite crystals from Otdel'naya Mt., Talnakh: a – terminated with direct and reverse trigontristetrahedrons, b – in association with zonal Cr-Ti-containing grossular and calcite (thin section)

Table 7. Chemical composition of achtarandite: 1 – achtarandite from Otdel'naya mountain (Talnakh) locality, 2–5 achtarandite from Wiluy river valley

Comp.	1	2	3	4	5
SiO ₂	39.52	39.25	34.70	40.10	34.72
TiO ₂	0.24	–	0.30	–	0.31
Al ₂ O ₃	14.30	11.11	11.17	12.36	13.40
Fe ₂ O ₃	6.71	17.09	7.48	n.d.	5.42
FeO	–	–	1.95	n.d.	2.15
MnO	0.65	–	0.14	–	0.12
MgO	9.77	3.60	19.46	n.o.	19.40
CaO	22.54	12.54	17.03	11.27	16.60
Na ₂ O	0.07	–	n.d.	–	n.d.
K ₂ O	0.01	–	n.d.	–	n.d.
P ₂ O ₅	0.01	–	–	–	–
Cr ₂ O ₃	0.06	–	–	–	–
S	0.12	–	–	–	–
F	0.09	–	–	–	–
Cl	0.04	–	–	–	–
H ₂ O ⁻	–	–	0.56	–	0.83
H ₂ O ⁺ (decrepitation weight loss)	5.93	10.09	7.30	12.27	7.80
CO ₂	–	–	0.54	–	n.d.
Total	100.06	93.68	100.63	76.00	100.75

Notes: 1 – analyst A.I. Yakushev using a Philips PW-2400 XRD; 2, 3 – data after Beck, Hermann (Lyachivich, 1954); 4 – (Lyakhovich, 1954); 5 – (Zhabin & Lyakhovich, 1994). N.d. – not determined

(Cr-Ti-containing) and white (Cr-Ti-free) grossular. In general, achtarandite consists of micro-grained aggregates of garnet, vesuvianite, magnesium rich chlorite and/or serpentine, sphaalerite and chalcopyrite. According to the X-Ray (diffractometer DRON-3.5, $2\theta = 5-120^\circ$) phase analysis data obtained, achtarandite pseudomorphs consist of hydrogrossular ($a_0 = 11.971(2) \text{ \AA}$) for 2/3 volume and of serpentine-7Å septechlorite (berthierine) for 1/3 with admixture of calcite, quartz and hematite. These data directly correlates with EMPA data.

Chemical composition of the Talnakh achtarandite (Table 7, analysis 1) is close to that of Wiluy achtarandite (Table 7, analyses 2–4); the latter is enriched in Mg and H₂O, the former is enriched in Ca. Therefore, achtarandite from Wiluy is enriched in minerals of the serpentine and chlorite groups, and from Talnakh – enrichment in hydro- and grossu-

lar. The microelements composition according to RFA is the following (ppm): Cr 417, Ni 73, Co 13, Cu 137, Zn 815, S 1190, F 900, Cl 351, V 22, Sr 14, Ba 36, Y 2, Sc 11, Zr 112, Nb 5, Rb 9 (Pletnev *et al.*, 2001). Relatively high concentration of Zr is due to hydrogrossular enriched in ZrO₂ up to 0.7 wt.% (Ryabov *et al.*, 1996).

Synthesis of achtarandite proto-phase

The first attempts to synthesise high-pressure garnet as a proto-mineral of achtarandite (Gorokhov *et al.*, 1971), were based on a later disproved hypothesis *r* (Pertsev, 1972). Since then scientists made theoretical investigations and speculated about a possible proto-phase (Tchesnokov *et al.*, 1993–1996; Galuskin *et al.*, 1995; Galuskina, 1998; Pavlushin, 2000).

In 1996 Boris V. Tchesnokov *et al.* discovered, in the mineral association of burnt dumps, fumarolitic oxo- and chlorine-bearing garnetoids (those compounds that have structures similar to that of true garnets (McConnell (1942)) – Cl-bearing wadalite and Cl-bearing mayenite, whose crystal shape is similar to that of achtarandite, and assumed that these minerals are the most probable achtarandite proto-phases (Tchesnokov *et al.*, 1996).

Mayenite was first described from Mayen, Eifel Mountains, Germany (Hentschel, 1964). It was found in lava vents which indicates its pneumatolytic origin. This mineral belongs to the so called garnetoids – complex oxides with garnet structure, its formula – Ca₁₂Al₁₄O₃₃, space group – *I*-43d. In natural mayenite oxygen is partially replaced by (F-, Cl-, OH-) which brings it closer to wadalite Ca₆Al₅Si₂O₁₆Cl₃ – an isostructural Cl-bearing mineral (Glasser, 1995). Wadalite and grossular are related to each other structurally (Tsukimura *et al.*, 1993) which was later proven experimentally: wadalite was formed after heat treatment of hydrogrossular (hibschite) in chlorine vapor (Fujita *et al.*, 2001).

In this study the synthesis of the probable proto-phase of achtarandite was performed on the basis of its genetic and structural similarity with grossular-hydrogrossular and the assumption about its pneumatolytic character of a process based on the literature and own analytical data. Method of the synthesis of Cl-bearing garnetoids wadalite-mayenite was based on the

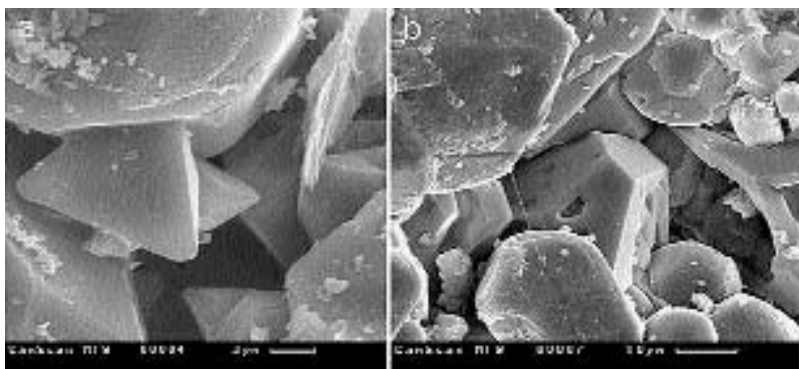
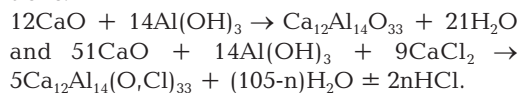


Fig. 8. BSE images of the phases synthesized: a – mayenite ($T=550^{\circ}\text{C}$, $P=1\text{ kb}$), b – Cl-containing mayenite ($T=550^{\circ}\text{C}$, $P=3\text{ kb}$)

data for hydrogrossular synthesis (Shvedenkov *et al.*, 1974). A series of experiment were undertaken in order to obtain the most probable proto-phases of achtearandite: Cl-bearing mayenite, Cl-bearing hibschite, Cl-bearing wadalite and their Cl-free analogues. Experimental conditions were held at 550°C and pressures of 1 kbar and 3 kbar, experiment duration – 14 days. The source materials are: CaO, Al_2O_3 or $\text{Al}(\text{OH})_3$, SiO_2 , CaCl_2 . Synthesis was according to the reactions:



The size of the garnet-like crystals obtained ranged from fractions of a micron up to 20 micron. Among them were trigon-tristetrahedral mayenite crystals with Cl content up to 0.59 wt.% of Cl (Fig. 8). Chemical composition of mayenite synthesized (wt.%): SiO_2 10.56–11.70, Al_2O_3 45.07–45.62, CaO 43.48–42.8 (Alferova, 2004).

The origin of mineral association with achtearandite

As it was noted above, the studied mineral associations at the Otdel'naya Mountain locality for grossular, vesuvianite and achtearandite and those at the Wiluy River deposit for grossular, vesuvianite and achtearandite are similar. They are thought to be of skarn origin (Ryabov, 1996; Lyakhovich, 1954), however mineral paragenesis, IR data, fluid inclusions data and experimental data obtained testify to a more complex process which consisted of at least two stages: a high-temperature skarn and a low-temperature apo-skarn.

During the high-temperature stage augite

and perovskite were formed which can be observed as mineral inclusions in the central parts of vesuvianite crystals, and also the central parts of vesuvianite crystals themselves.

During the low-temperature stage the paragenesis: grossular, hydrogrossular (containing over 10 wt.% of Cr_2O_3 and TiO_2 (Ishimoto *et al.*, 1983)), boron-containing vesuvianite (edge parts of the crystals), amesite, diopside, Al-bearing magnesiochromite, titanite, troilite, chlorite, serpentine were formed. These are typical minerals of the prehnite-pumpellyite facia of low-grade metamorphism.

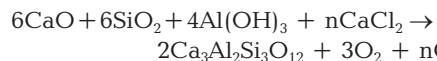
Well-terminated inclusions of aggregates of vesuvianite, amesite and hydrogrossular, occur in grossular and vesuvianite crystals, resemble pseudomorph alike achtearandite which is in the same mineral association. Starting from assumption that these inclusions are achtearandite, one could state that they were altered as well as separate crystals of achtearandite.

Possibly, the mineral forming process was as follows: at the early skarn stage the high-temperature minerals, central parts of vesuvianite crystals and proto-achtearandite (Cl-bearing mayenite) were formed. At the apo-skarn stage the low-temperature minerals were formed, partially as products of alteration of the high-temperature phases: grossular – after plagioclase, Cr-Ti-bearing grossular and Al-bearing magnesiochromite – after primary chome-spinel, low-temperature vesuvianite – after the high-temperature vesuvianite, achtearandite – after Cl-bearing mayenite, titanite – after perovskite. The whole process ended with the formation of thin veinlets of chalcopyrite, troilite and stilbite. We believe that the mineral-forming process at the Wiluy deposit was similar. At the high-temperature stage grossular, wiluite and Cl-bearing mayen-

ite were formed, and at the low-temperature stage the latter was replaced by achtarandite.

In our opinion, the mineral that was later replaced by achtarandite, was initially formed during a distinctive high-temperature skarn process with chlorine-based pneumatolytic influence. The supposed proto-mineral for achtarandite – Cl-bearing mayenite – conforms to the character of the process. The following data indicates the type of pneumatolytic process: 1 – mayenite was first discovered in a post-magmatic fluid-rich lava derivative, 2 – Cl-bearing mayenite with morphology similar to that of achtarandite was found in the burnt dumps of the Chelyabinsk coal basin. This fumarolytic process occurred as a result of human intervention, 3 – synthesis of Cl-bearing mayenite was held in a 'dry' system, after the experiment the excess of HCl was recorded, 4 – transformation of hibschite into wadalite was achieved by the effect of vaporized chlorine phases on hibschite (Fujita *et al.*, 2001).

Grossular and proto-achtarandite – mayenite are structurally and chemically related to each other, and this lead many scientists to consider grossular as a proto-mineral of achtarandite. The first relationship is confirmed by the hibschite-wadalite transformation reaction and isostructural series wadalite-mayenite; the second relationship is proved to be true by obtaining grossular during mayenite and wadalite synthesis according to the chemical reaction:



without free chlorine. Thus achtarandite occurrence is probably, an indicator of a local increased content of Ca in rocks subject to pneumatolysis.

After that the transformation mayenite – wadalite – hydrogrossular took place under the low-temperature process conditions; and the initial morphology was retained. As a result we observe achtarandite represented mainly by hydrogrossular aggregate. During this low-temperature process associated minerals containing Cr- and Ti-bearing grossular, structurally unusual vesuvianite (Otdel'naya Mountain, Talnakh), large grossular and wiluite (Wiluy River, Yakutia) crystals were formed.

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FEATURES OF TRANSFORMATION OF THE MINERAL PARAGENETIC ASSEMBLAGES FROM COPPER SULFIDE ORES OF THE KRASNOV HYDROTHERMAL FIELD (16°38' N Mid-Atlantic Ridge)

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Copper sulfide ores of the 5–80 thousands age from the Krasnov relic hydrothermal field (16°38' N, Mid-Atlantic Ridge) have been studied with optical microscope, electron microscope equipped with energy dispersion system (SEM-EDS), electron microprobe, and X-ray diffraction.

According to the mineralogy, three types of paragenetic assemblages are recognized. Type I is homogeneous isocubanite with Cu-rich sulfides (bornite and copper sulfides of the chalcocite-digenite series). Type II is exsolved isocubanite and its unique products of subsequent transformation. Type III is oxide-sulfate-sulfide, which is characterized by iron specialization and is divided into two subtypes: with predominant pyrite (IIIa) and with predominant Fe-Cu sulfates and Fe oxides (IIIb). Type III contains relics of the highly modified type II paragenesis. The age relationship of type I has not been established.

6 tables, 8 figures, 23 references.

General review of the Krasnov hydrothermal ore field

The new hydrothermal field at 16°38' N of the Mid-Atlantic Ridge (MAR) was discovered in 2004 by the Polar Marine Geosurvey Expedition and All-Russia Research Institute for Geology and Mineral Resources of the World Ocean, (St. Petersburg, Russia) during Cruise 24 of the R/V *Professor Logachev*. During a subsequent voyage in 2006, this field was extended and was named Krasnov in honor of Sergei Gelievich Krasnov (1952-1996), a marine geologist, who investigated oceanic hydrothermal mineralization for the last 15 years of his brilliant professional career. Brief information on geology, zoning and mineralogy of ores was previously reported by Bel'tenev *et al.* (2006).

The Krasnov ore field, located in the eastern margin of the rift valley at a depth of 3700–3760 m is confined to the junction zone of the axial rift rise and the slope of the rift val-

ley and is controlled by the intersection of the nearmeridian deep margin fault and the sublatitudinal fault. Approximately 60% of the bottom surface, which was studied with teleprofiling is covered by carbonate sludge up to 160 cm thick. Two sulfide ore bodies of 370 x 580 m and 110 x 130 m in size occur over the outcrops of primary basalts and occur as fine and medium blocks and relics of sulfide mounds covered by sediments and red crusts.

Sulfide bodies are composed mainly of pyrite; copper and copper massive sulfide ores are less abundant and zinc massive sulfide ores are practically absent. According to texture and morphology, massive, porous, and veinlet-impregnated ores, as well as ores of the chimney complex were defined in the ore field. In addition to massive sulfides, the ore-bearing sediments with Fe > 10% and Cu + Zn > 0.25% occurred as a band 30–150 m wide north and northeast of Orebody 1, and are found within the ore field. Pyrite, atacamite, aragonite, chalcocite, native copper, hematite, barite, and Fe

and Mn hydroxides were identified in these sediments.

The high oxidation of the ores, weak anomalies of metals content in dissolved and suspended phases in water samples, as well as the absence of hydrothermal fauna, indicate the relict nature of the ore field, of which the hydrothermal activity has actually terminated. This is confirmed by the dating of sulfide ores; the U/Pb age determined for 16 samples ranges within 5–80 kyr (Kuznetsov *et al.*, 2007). Iron specialization, continuance of formation, and the presence of sedimentary cover differentiate this field from the other hydrothermal fields within the Mid-Atlantic Ridge.

According to Bel'tenev *et al.* (2004), the ore types and major minerals were recognized as a result of the initial mineralogical and geochemical studies of the new field. The aim of this study is to provide more detailed textural, structural, and chemical investigation of ores from the chimney complex of the copper mineralization and to reveal the features of transformation of the mineral paragenetic assemblages in the hydrothermal field that is uncommon for this region.

Materials and experiments

Samples of the copper mineralization have been studied as the most interesting in terms of mineralogy and the easiest transformation due to the high mobility of copper. The samples occur as irregularly-shaped fragments containing copper minerals and are frequently covered by the black soot crust. Small pieces of these samples were fixed by epoxy to prepare polished sections (without heating).

After study under reflected light, microsamples and polished sections were investigated with a JEM-100C scanning electron microscope and a CamScan MX 2500S scanning electron microscope equipped with a Link-10000 energy dispersion system (accelerating potential 25 kV, current 0.4 nA) (SEM-EDS), Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (IGEM RAS), Moscow and a CamScan MV2300 scanning electron microscope equipped with an energy dispersion system – INCA Energy

200, Geological Institute, Russian Academy of Sciences, Moscow. In the latter case, the utilized software requires the normalization procedure to 100% of the total elements recorded in spectrum. A number of analyses was performed with a Camebax SX-50 electron microprobe, Lomonosov Moscow State University. Accelerating potential was 20 kV, current, 30 nA. The following standards were used (K α X-ray lines): FeS(Fe, S), CuS (Cu), ZnS (Zn). Most analyses were made with SEM-EDS since the low current allowed measurements of numerous points in the fine grains of minerals. Total analyses were about 500. X-ray study was performed with a Rigaku D/Max 2200 diffractometer, CuK α radiation in IGEM RAS and a RKD 57.3 camera (Fe radiation, 6 h exposure) in Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

Mineralogy of the copper ores from the Krasnov field

Sulfides common for the oceanic ores from the Mid-Atlantic Ridge were identified in the studied samples. Isocubanite, chalcopyrite, and pyrite are the major minerals; bornite and copper sulfide are minor and sphalerite and marcasite are rare. Prevalence of idaite, Cu₃FeS₄, previously described from the submarine ores of the black smokers at 21° N East Pacific Rise (Oudin, 1983) and the presence of new phases of the Cu-Fe-S system with provisional names *X*, *Y*, and *M* are noticeable. In addition to sulfides, Fe-Cu sulfate and Fe oxides are important; quartz, opal, barite, and native sulfur are also abundant.

The size of studied sulfide grains ranges from 0.3–0.5 mm (occasionally up to 1 mm), but usually ranges from 1–2 to 50 μ m. Diagnostics of the minerals have been performed by electron microprobe and SEM-EDS; in some cases, an X-ray diffraction study was applied. The representative data are given in Tables 1–6, in ternary plot Cu-Fe(Zn)-S (Fig. 1), and in photomicrographs of polished sections and microsamples (Figs. 2–8).

Isocubanite, the cubic analogue of rhombic cubanite, plays the most important role in the copper ores of Krasnov. Some explanations in regard to this mineral appear to be necessary. As a new mineral species, it was found for the first

Table 1. Chemical composition of isocubanite (polished sections and microsamples)

Anal.	Sample	Cu, wt. %	Fe	S	Total	Formula	Fig.
1**	1271-4	25.56	38.57	35.89	100.02	Cu _{1.1} Fe _{1.9} S _{3.0}	5d
2	1269-6/1	23.42	40.16	35.98	99.56	Cu _{1.00} Fe _{1.95} S _{3.05}	
3*	1269-6/1	23.09	42.27	35.29	100.65	Cu _{0.98} Fe _{2.05} S _{2.97}	
4*	1269-6/1	22.77	42.45	35.75	100.98	Cu _{0.96} Fe _{2.04} S _{3.00}	4d
5*	1269-6/2c	22.92	42.03	35.32	100.27	Cu _{0.98} Fe _{2.04} S _{2.98}	
6	1269-6/1	22.67	44.87	34.64	99.18	Cu _{0.98} Fe _{2.06} S _{2.96}	4b
7	1269-6/1	21.97	42.07	36.17	100.21	Cu _{0.93} Fe _{2.03} S _{3.04}	
8	1269-6/1	21.88	42.01	34.58	98.47	Cu _{0.95} Fe _{2.07} S _{2.98}	4b
9	1271-4	21.34	42.57	36.26	100.17	Cu _{0.91} Fe _{2.05} S _{3.04}	7b
10*	1271-4	21.29	43.46	36.39	101.14	Cu _{0.89} Fe _{2.08} S _{3.03}	8c

Notices: * is EDS-SEM analysis, without *, is electron microprobe analysis. ** is microsample. Formula coefficients for phases analyzed in polished sections are accurate within two decimal digits, in microsamples, to one

Table 2. Chemical composition of chalcopyrite and phase X (polished section and microsamples)

Anal.	Sample	Cu, wt. %	Fe	S	Total	Formula	Fig.
Chalcopyrite							
1*	1269-6/1	36.73	29.51	33.77	100.01	Cu _{1.07} Fe _{0.96} S _{1.95}	4a
2*	1269-6/1	35.21	30.69	34.09	99.99	Cu _{1.02} Fe _{1.02} S _{1.96}	
3*	1269-6/2c	34.50	31.17	34.33	100.00	Cu _{1.00} Fe _{1.03} S _{1.97}	4c
Phase X							
4	1269-6/2c	33.12	35.58	34.72	103.42	Cu _{0.93} Fe _{1.14} S _{1.93}	
5	135-6/1	32.86	29.58	37.40	99.84	Cu _{0.94} Fe _{0.96} S _{2.11}	6a
6	1269-6/2c	32.54	35.42	33.64	102.12	Cu _{0.93} (Fe _{1.15} Zn _{0.02}) _{1.17} S _{1.90}	3e
7	1269-6/2c	32.49	37.14	33.65	103.28	Cu _{0.92} Fe _{1.19} S _{1.89}	3e
8	1269-6/2c	31.41	31.76	35.41	98.58	Cu _{0.91} Fe _{1.05} S _{2.04}	
9*	1269-6/2c	31.20	32.64	34.66	98.50	Cu _{0.91} Fe _{1.08} S _{2.01}	
10*	1269-6/2c	30.98	34.18	34.37	99.53	Cu _{0.90} Fe _{1.12} S _{1.98}	
11	1269-6/2c	30.72	35.50	34.57	100.79	Cu _{0.88} Fe _{1.16} S _{1.96}	
12	135-6/1	32.41	33.10	33.96	99.99	Cu _{0.94} (Fe _{1.09} Zn _{0.02}) _{1.11} S _{1.95}	6a
13**	1269-6/1	29.21	32.14	38.65	100.00	Cu _{0.8} Fe _{1.0} S _{2.2}	

Notices: 0.62 (anal. 6) and 0.47 (anal. 12) wt. % Zn

time in the oceanic ores (Caye *et al.*, 1988) and had previously been often described from continental and oceanic ores under different names including "chalcopyrrhotite" (Ramdohr, 1980; Oudin, 1983), "cubic cubanite" (Genkin *et al.*, 1966), "high cubanite" (Vaughan & Craig, 1978; Lebedev *et al.*, 1988). Despite the stoichiometric formula CuFe₂S₃ listed in handbooks, isocubanite is attributed to the typical minerals with variable compositions and is commonly considered the natural analogue of the high-temperature intermediate solid solution (Iss) phase in the central part of the Cu-Fe-S system. In oceanic ores, exsolution textures of Iss are observed much more frequently than homogeneous crystals.

Isocubanite from the Krasnov field is not exceptional. It occurs as homogeneous grains and crystals, but usually plays the role of matrix in the exsolution textures of the higher-temperature isocubanite solid solution. The matrix comprises regular (most frequently latticed) intergrowths of lamellae of chalcopyrite and close phases and is often rimmed by diffused chalcopyrite. As shown below, these textures in Krasnov are characterized by the unique feature of subsequent strong transformations. According to analyses (Table 1), the chemical composition of isocubanite in examined samples ranges within limits (wt.%) 21.29 – 25.56 Cu, 38.57 – 44.87 Fe, and

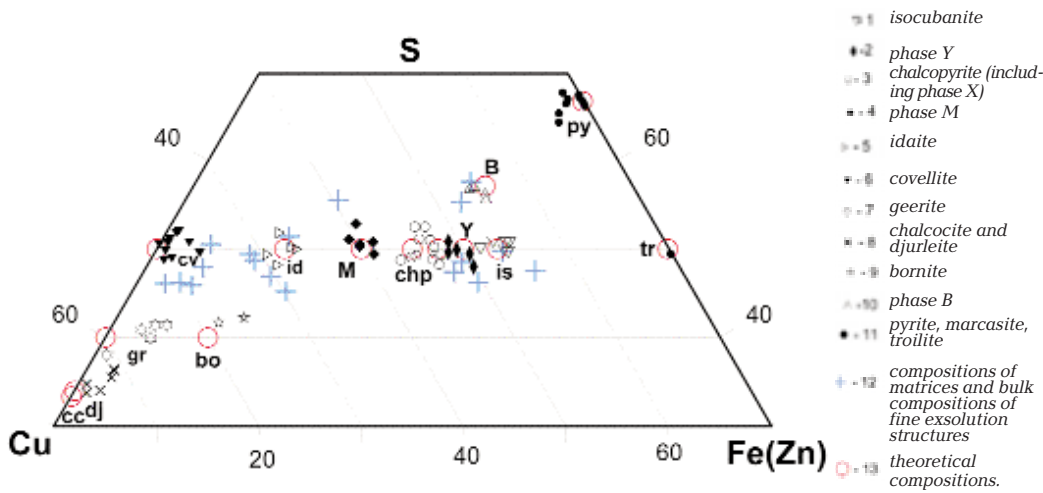


Fig. 1. The Cu-(Fe+Zn)-S ternary plot showing the distribution of chemical composition of the studied minerals (set of representative and averaged analyses is used; see Tables 1–5). Abbreviations of minerals: isocubanite (Is), - chalcocopyrite (Chp), idaite (Id), bornite (Bo), covellite (Cv), chalcocite (Cc), geerite (Gr), djurleite (Dj), pyrite (Py), marcasite (Mc), troilite (Tr); new phases (X, Y, M, B).

Table 3. Chemical composition of idaite and new phases Y, M, and B (polished sections and microsamples)

Anal.	Sample	Cu wt%	Fe	S	Total	Formula	Fig.
Idaite, $\text{Cu}_3\text{Fe}_4\text{S}_7$, calculated on the basis of 8 atoms							
1**	135-1b	53.18	13.23	33.59	100.00	$(\text{Cu}_{3.1}\text{Fe}_{0.9})_{4.0}\text{S}_{4.0}$	
2*	1269-6/1	52.35	15.06	32.57	99.08	$(\text{Cu}_{3.1}\text{Fe}_{1.0})_{4.1}\text{S}_{3.9}$	4b
3**	187-1/2	48.60	17.33	34.07	100.00	$(\text{Cu}_{2.9}\text{Fe}_{1.1})_{4.0}\text{S}_{4.0}$	
4*	1269-6/1	49.97	15.52	34.53	100.02	$(\text{Cu}_{2.94}\text{Fe}_{1.04})_{3.98}\text{S}_{4.02}$	
Phase Y $\text{Cu}_2\text{Fe}_3\text{S}_5$, calculated on the basis of 10 atoms							
1**	1269-6/1	30.63	35.72	35.44	101.79	$\text{Cu}_{2.1}\text{Fe}_{2.8}\text{S}_{5.1}$	
2	1269-6/1	30.40	34.04	35.54	99.98	$\text{Cu}_{2.18}\text{Fe}_{2.77}\text{S}_{5.05}$	
3**	1269-4/2	29.95	35.16	36.50	101.61	$\text{Cu}_{2.1}\text{Fe}_{2.8}\text{S}_{5.1}$	
4*	1269-6/2c	28.66	35.65	34.82	99.13	$\text{Cu}_{2.07}\text{Fe}_{2.94}\text{S}_{4.99}$	4c
5	1289-6/2c	28.25	39.92	33.64	101.79	$\text{Cu}_{2.10}\text{Fe}_{2.82}\text{S}_{5.08}$	
6	135-6/1	28.81	36.09	33.82	100.00	$\text{Cu}_{2.08}(\text{Fe}_{2.97}\text{Zn}_{0.08})_{3.05}\text{S}_{4.85}$	
7	1269-6/2c	27.39	37.86	34.77	100.02	$\text{Cu}_{1.96}\text{Fe}_{3.09}\text{S}_{4.95}$	
8	135-6/1	30.45	36.10	32.79	100.01	$\text{Cu}_{2.21}(\text{Fe}_{3.00}\text{Zn}_{0.05})_{3.05}\text{S}_{4.74}$	6a
9	1269-6/2c	30.68	37.93	34.28	103.65	$\text{Cu}_{2.15}(\text{Fe}_{3.03}\text{Zn}_{0.05})_{3.06}\text{S}_{4.77}$	
Phase M (Me_5S_8, $\text{Cu}_3\text{Fe}_2\text{S}_5$), calculated on the basis of 10 atoms							
1*	135-6/2a	42.27	22.16	35.56	99.99	$(\text{Cu}_{3.06}\text{Fe}_{1.83})_{4.89}\text{S}_{5.11}$	
2*	135-1/2c	40.61	22.16	37.22	99.99	$(\text{Cu}_{2.91}\text{Fe}_{1.81})_{4.72}\text{S}_{5.28}$	
3*	1269-6/1	40.31	26.28	34.62	101.21	$(\text{Cu}_{2.90}\text{Fe}_{2.16})_{5.06}\text{S}_{4.94}$	4d
4*	1269-6/1	41.26	23.81	34.91	99.98	$(\text{Cu}_{3.00}\text{Fe}_{1.97})_{4.97}\text{S}_{5.03}$	4d
5*	1269-6/1	41.14	23.76	35.12	100.02	$(\text{Cu}_{2.99}\text{Fe}_{1.96})_{4.95}\text{S}_{5.05}$	4d
Phase B (Me_3S_4, CuFe_2S_4), calculated on the basis of 7 atoms							
1*	135-6/1	22.54	33.78	40.69	97.01	$\text{Cu}_{1.11}\text{Fe}_{1.90}\text{S}_{3.99}$	6c
2*	135-6/1	22.16	34.82	41.57	98.55	$\text{Cu}_{1.08}\text{Fe}_{1.92}\text{S}_{4.00}$	6c
3*	135-6/1	22.08	33.75	41.43	97.26	$\text{Cu}_{1.08}\text{Fe}_{1.89}\text{S}_{4.03}$	
4*	135-6/1	21.15	31.17	39.87	98.45	$\text{Cu}_{1.04}(\text{Fe}_{1.75}\text{Zn}_{0.30})_{2.05}\text{S}_{3.91}$	6b
5*	135-6/1	20.95	30.90	40.51	98.61	$\text{Cu}_{1.03}(\text{Fe}_{1.73}\text{Zn}_{0.30})_{2.03}\text{S}_{3.94}$	6b

Notices. Zn (wt.%) has been detected in phase Y 1.28 (anal. 6), 0.56 (anal. 8) and 0.76 (anal. 9); in phase B, 6.26 (anal. 4) and 6.25 (anal. 5); in the idaite item analyses 1 and 3 have been made with a CamScan MV2300 electron microscope.

Table 4. Chemical composition of high Cu copper sulfides and bornite (polished sections, sample 135-1b)

Number of anal.	Cu wt. %	Fe	S	Total	Formula	Fig.	Mineral
1*	78.68	1.26	20.06	100.00	(Cu _{1.98} Fe _{0.04}) _{2.02} S	2a	Chalcocite
2*	77.44	1.38	20.54	99.36	(Cu _{1.90} Fe _{0.04}) _{1.94} S		Djurleite
3*	76.66	2.60	20.74	100.00	(Cu _{1.86} Fe _{0.07}) _{1.93} S		Djurleite
4*	74.71	2.81	22.48	100.00	(Cu _{1.68} Fe _{0.07}) _{1.75} S		Digenite
5*	74.54	2.92	22.37	99.83	(Cu _{1.68} Fe _{0.08}) _{1.76} S		Digenite
6*	74.82	3.26	21.92	100.00	(Cu _{1.72} Fe _{0.08}) _{1.80} S		Digenite
7*	75.82	2.60	21.58	100.00	(Cu _{1.77} Fe _{0.07}) _{1.84} S		Roxbyite
8*	61.57	11.50	26.94	100.01	Cu _{4.81} Fe _{1.02} S _{4.17}	2b	Bornite
9*	58.19	14.00	27.34	99.53	Cu _{4.54} Fe _{1.24} S _{4.22}	2a	Bornite

Notice: All analyses (with the exceptions of 2, 7, and 8) were made with a CamScan MV2300 scanning electron microscope.

Table 5. Chemical composition of covellite (Me/S ≈ 1) and geerite (series of low Cu copper sulfides) (polished sections and microsample)

Number of anal.	Sample	Cu, wt. %	Fe	S	Total	Formula	Fig.
Geerite							
1*	135-1b	75.11	1.19	23.70	100.00	(Cu _{1.6} Fe _{0.03}) _{1.63} S	
2*	135-1b	70.64	3.37	25.99	100.00	(Cu _{1.37} Fe _{0.07}) _{1.44} S	
3*	135-1b	69.82	4.90	25.28	100.00	(Cu _{1.39} Fe _{0.11}) _{1.5} S	
Cu-sulfide of the covellite series							
4*	135-1b	68.95	4.61	26.44	100.00	(Cu _{1.32} Fe _{0.10}) _{1.42} S	
5*	135-1b	67.63	5.90	26.47	100.00	(Cu _{1.29} Fe _{0.13}) _{1.42} S	
Covellite							
6*	1271-4/3	67.60	0.31	33.39	101.30	Cu _{1.02} S	7a
7*	135-6/2a	64.61	0.85	34.54	100.00	(Cu _{0.94} Fe _{0.01}) _{0.95} S	
8**	1269-4/2	64.08	1.64	32.16	97.88	CuS	
9*	135-6/2a	63.19	1.38	35.43	100.00	(Cu _{0.9} Fe _{0.02}) _{0.92} S	
10**	135-1b	61.42	5.23	33.35	100.00	(Cu _{0.9} Fe _{0.1}) _{1.0} S	

Notices: analyses 1–5, 7, 9, and 10 were made with a CamScan MV2300 scanning electron microscope.

34.58–36.39 S, which is close to the ranges of contents listed in the review on oceanic isocubanite (Mozgova *et al.*, 1995).

On the basis of the data given in the tables and figures, let us briefly characterize the other sulfides from our samples.

Along with lamellae and rims in exsolution textures, chalcopyrite is less frequently observed as grains and homogeneous crystals. Its chemical composition given in Table 2 ranges within the limits of (wt.%) 29.21–36.73 Cu, 29.51–35.58 Fe, and 33.64–38.65 S. These data include both compositions close to the stoichiometry and Fe-rich variety of this mineral, which was previously called phase X (Mozgova *et al.*, 2005). Diversion from stoichiometry is expressed by the approximate formula Cu_{1-x}Fe_{1+x}S₂, where x is

most frequently about 0.1. Sporadically, an impurity of 0.1% Zn was identified.

Idaite, which is occasionally observed in the oceanic ores, therein is characterized by various morphologies. These are matrices, altered areas of lamellae, colloform zones, and even euhedral crystals. The chemical composition listed in Table 3 is as follows (wt.%): 48.60–53.18 Cu, 13.23–17.33 Fe, and 32.59–34.53 S.

Close to isocubanite phase Y, Cu₂Fe₃S₅, was discovered in the oceanic ores as lamellae within the isocubanite exsolution textures (Mozgova *et al.*, 2002), then described as homogeneous grains from Rainbow (Borodaev *et al.*, 2004), and is distinguished by the larger Cu/Fe value in comparison with isocubanite. Previously, such a stoichiometric compound was observed in mete-

orites (Rambaldi *et al.*, 1986). In the Krasnov field, this phase occurs as fine grains among weakly and highly altered products of the isocubanite exsolution, as well as euhedral crystals identified for the first time. Microprobe analysis with a unfocused beam of 15 x 15 µm of some grains within the exsolution texture revealed a bulk composition which corresponded to phase *Y*, implying that the exsolution of phase *Y* is similar to isocubanite when conditions change. The chemical composition of this phase listed in Table 3 ranges within the limits (wt.%): 27.39–30.68 Cu, 34.04–39.92 Fe, and 32.79–36.50 S. Zn occurs as an impurity varying from 0.56 to 1.28 wt.%.

Phase *M*, $\text{Cu}_3\text{Fe}_2\text{S}_5$, the intermediate between chalcopyrite and idaite (Fig. 1), was identified for the first time. It most frequently originated from the transformation of chalcopyrite lamellae leading to the distortion of their morphology; but locally, it is present within the altered matrix. The range of composition is as follows (wt.%): 41.14–42.27 Cu, 22.16–26.28 Fe, and 34.62–37.22 S (Table 3).

A new phase *B* that is richer in Fe and enriched in S in comparison with isocubanite was observed as zoned and zoned-colloform bands within the transformed isocubanite exsolution textures. The chemical composition of this phase given in Table 3 ranges within the limits (wt.%): 20.95–22.54 Cu, 30.90–34.82 Fe, and 39.87–41.57 S. Impurities of Zn – up to 6.26 wt.%, are frequent and are probably the result of adjacent grains of sphalerite.

Bornite and Cu-rich sulfides of the chalcocite-digenite series frequently occur as fine two-phase or polymineralic mixtures (Table 4). Sulfides depleted of Cu occur as the geerite-covellite series (Table 5). As shown below, they are different both in composition and type of assemblages. In some cases, diagnostics of the copper sulfides is provisionally because X-ray data, which are necessary for identification of nonstoichiometric sulfides, could not be collected due to tiny grains and fine intergrowths

It should be noted that the composition of all sulfides of the system of Cu-Fe-S occurred in a matrix of the exsolution textures has the most significant deviation from the ideal formulae of corresponding minerals and phases. It is evidently caused by extremely fine mechanical admixtures. In the compositional diagram

(Fig. 1), these data are marked by blue crosses.

Pyrite, marcasite, and troilite are the examined iron sulfides. Pyrite is characterized by diverse morphologies, such as skeletal pseudomorphs after pyrrhotite crystals, single euhedral crystals, irregular-shaped grains, branchy aggregates, and rims around grains with an exsolution texture. Subordinate marcasite is included in pseudomorphs after pyrrhotite and occurs as irregular-shaped grains and fine rims around branchy pyrite. The impurity of copper (0.03–4.76 wt. %) is frequently detected in the iron disulfides, but their compositions are usually close to stoichiometry. Troilite was observed in only one polished section as small inclusions in goethite. Its composition is close to stoichiometry as follows (wt.%): 64.04 Fe, 35.96 S; formula is $\text{Fe}_{1.01}\text{S}_{0.99}$.

Sphalerite was observed as euhedral crystals and rims around grains with the exsolution texture structure of the isocubanite solid solution. The content of iron in this mineral ranges from 13.22 to 16.08 wt.% with an average value of 14.84 wt.%.

Paragenetic types of sulfides

As a result of this study, three types of paragenetic assemblages were recognized:

- **Type I** is homogeneous isocubanite and Cu-rich copper sulfides of the chalcocite-digenite series. Age relationship with other types was not revealed.
- **Type II** is exsolved isocubanite and the products of its diverse and unique transformations.
- **Type III** is an oxide-sulfate-sulfide, which in contrast to the two other types is characterized by the iron specialization and is divided into two paragenetic subtypes: with predominant pyrite (IIIa) and with predominant Fe-Cu sulfates and Fe oxides. Type III contains relics of the highly transformed type II paragenetic assemblages.

Paragenetic type I, comprising homogeneous isocubanite, bornite, and Cu-rich copper sulfides, is not abundant in the studied samples. Bornite, chalcocite, and nonstoichiometric sulfides of the chalcocite-digenite series are developed metasomatically in isocubanite along different oriented cracks and form

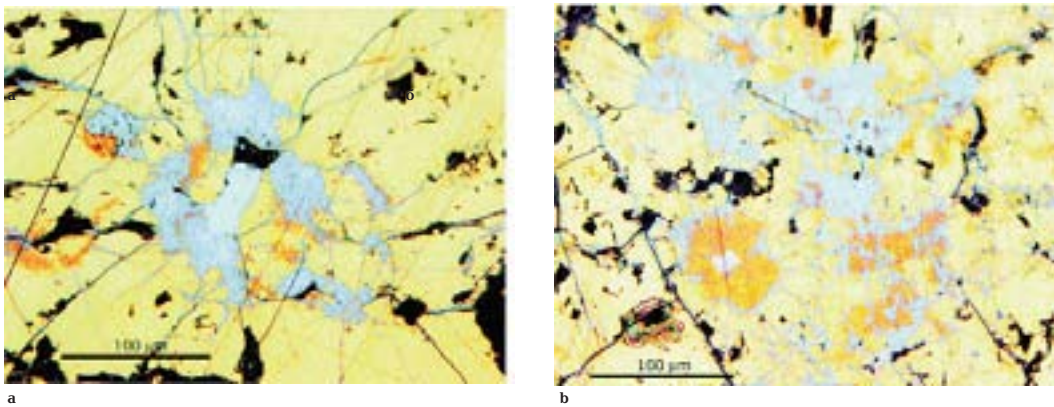


Fig. 2. Type I sulfide assemblages presented by bornite and Cu-rich copper sulfides.

Polished sections under reflected light. Sample 135-1b.

(a) Thin metasomatic veinlets and nests of bornite (orange), chalcocite (bluish gray), and a mixture of the Cu-rich sulfides of the chalcocite-digenite series (blue, heterogeneous) in homogeneous isocubanite. Chalcocite (Table 4, anal. 1) surrounded by sulfides depleted in copper occurs in the central parts of nests and veinlets; bornite (Table 4, anal. 10) originates at the contact between the Cu-poor sulfides and isocubanite. (b) The same assemblage in the neighboring areas, where in the left lower part of photomicrograph, the chalcocite core (Table 5, anal. 1) within round nest which is surrounded by bornite (Table 4, anal. 9), which in turn is surrounded by the copper sulfides (Table 4, anal. 7). In the other places, the veinlets of copper sulfide cut bornite and contain its relics.

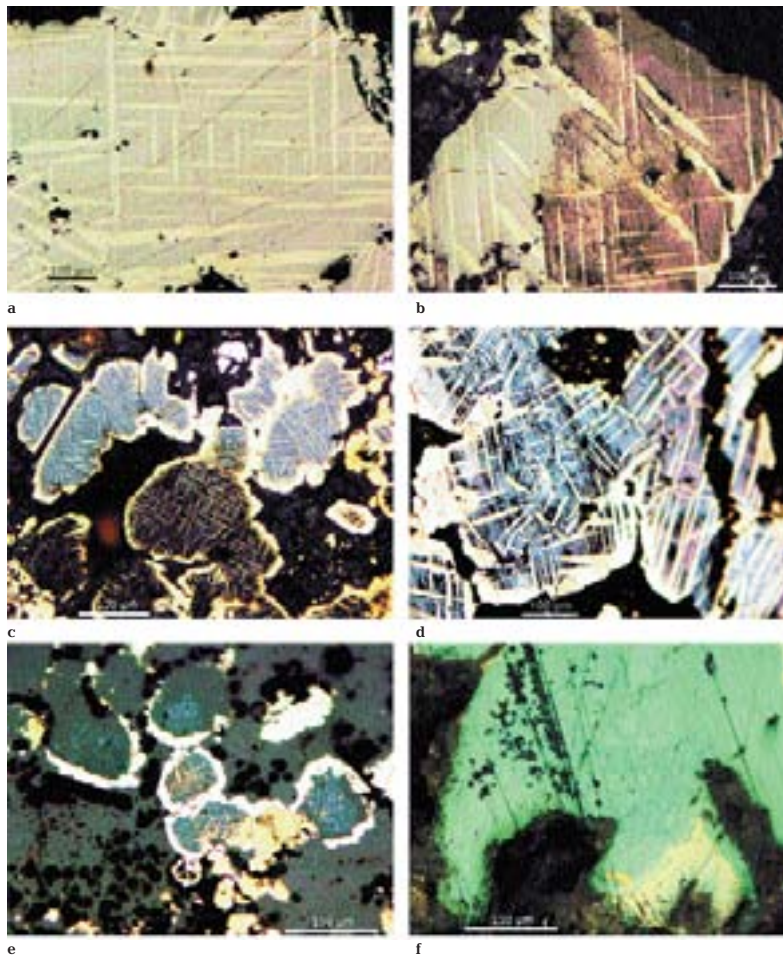


Fig. 3. Type II sulfide assemblages presented by exsolved isocubanite with different color of matrix. Polished sections under reflected light.

(a) Exsolution texture with untransformed light beige matrix and lattice of chalcopyrite lamellae. Sample 135-6/2.

(b) Grain with untransformed light beige matrix and transformed brown matrix. Sample 135-6/2.

(c) Segregation of grains with bluish gray and black matrices with lamellae and rims of chalcopyrite. Sample 1269-6/2c.

(d) Segregation of grains with blue and pinkish matrices with lamellae and rims of chalcopyrite. Sample 135-6/2.

(e) Olive matrix in exsolution texture with rims of pyrite (white) and Fe-rich chalcopyrite (light yellow) (Table 2, rim (anal. 6), lamellae (anal. 7)). Sample 1269-6/2c.

(f) Fine flake segregations of covellite (blue) after Cu-poor copper sulfides (greenish gray); covellite metasomatically replaces the isocubanite exsolution texture; light relict of untransformed texture in the lower part of photomicrograph. Sample 135-6/1.

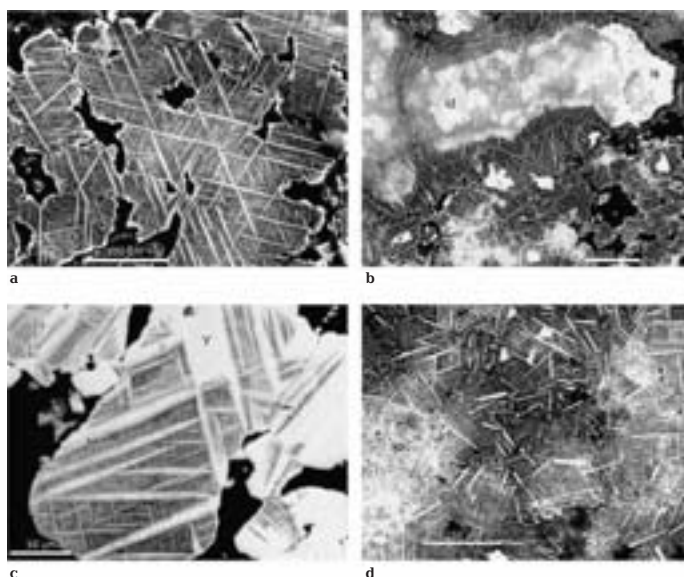


Fig. 4. BSE images of latted textures in transformed matrices of the exsolved isocubanite and the newly formed sulfides in them. Polished sections.

(a) Black covellite-bearing matrix with two systems of lamellae and rims of chalcopyrite (Table 2, anal. 1) around pores. Sample 1269-6/1.

(b) Elongate heterogeneous grain with grayish white fuzzy spots of the newly formed idaite (id) and phases close to it (Table 3, anal. 2) against the background of the latted exsolution texture with black matrix in the light "head" of the grain, which is newly formed isocubanite (is) (Table 1, analysis 6). Sample 1269-6/1.

(c) Large lamellae of chalcopyrite (Table 2, anal. 3) with traces of transformation are superimposed on the net of fine lamellae in the dark matrix. Locally, phase Y (Table 3, anal. 4) is developed after the matrix between the lamellae with partial trapping of the latter. Sample 1269-6/c

(d) Different oriented large lamellae of

phase M deviated from squared shape (Table 3, analyses 3–5) are superimposed on fine exsolution texture with black matrix; minute white grains between the large lamellae are the newly formed isocubanite (Table 1, anal. 4). Sample 1269-6/1.

branchy thin veinlets and nests in the intersections of the latter. On the basis of the Me/S ratio, among copper sulfides, chalcocite, djurleite, digenite, and roxbyite were identified. Only chalcocite and djurleite were confirmed by X-ray diffraction study.

As shown in Fig. 2a, relationships between bornite and copper sulfides are unambiguous. On the one hand, bornite (Table 4, anal. 8) directly contacting with isocubanite surrounds veinlets and pods of the copper sulfides, with the replacement of bornite by a heterogeneous mixture of Cu sulfides derived from the veinlets. Chalcocite occurs in the central parts both of veinlets and pods. On the other hand, in some pods, bornite alternates with Cu sulfides in the zoned structures. Figure 2b demonstrates that the chalcocite grain is surrounded by bornite (Table 4, anal. 8), which in turn is rimmed by copper sulfides (Table 4, analysis 7). Frequently, veinlets of copper sulfides intersect bornite and contain its relics.

Paragenetic type II occurs as exsolution textures of the high-temperature isocubanite and products of their transformations are predominant in the examined samples and are characterized by a number of specific features.

First of all, the relationships of lamellae within matrices indicate the complexity of the exsolution. In addition to the lattices consisting of the blades of one generation, the juxta-

position of two or more different oriented systems is observed; lamellae of these systems are different in morphology and size (Figs. 3a, 4a). These evidently argue multiple exsolutions and the variable dynamics of this process.

The unique features of the isocubanite exsolution texture in the Krasnov field are various marks of succeeding strong transformations. The change of the matrix color is the most demonstrative feature. In the "fresh" unmodified textures, the matrix is light beige under reflected light (Fig. 3a). However, more frequently, due to metasomatic replacement with the later minerals, the matrix is brown, gray, blue, and olive, ranging to black (Figs. 3b-g). Often, the color changes within a single grain (Fig. 3b), with lamellae remaining without modifications.

The chemical composition of the replaced matrices (Tables 1-5, Fig. 1) demonstrates that coloration is caused by replacement minerals: grayish brown matrices are close to phase Y in composition, light brown, to phase B, dark brown, to phase M, much darker brown, to idaite, blue, to Cu-poor sulfides of the covellite series; sulfates were identified in a dark gray matrix and mixtures with covellite, in a black one. The elevated contents of sulfur in comparison with the formula indicate an admixture of sulfates.

During further transformations, the newly

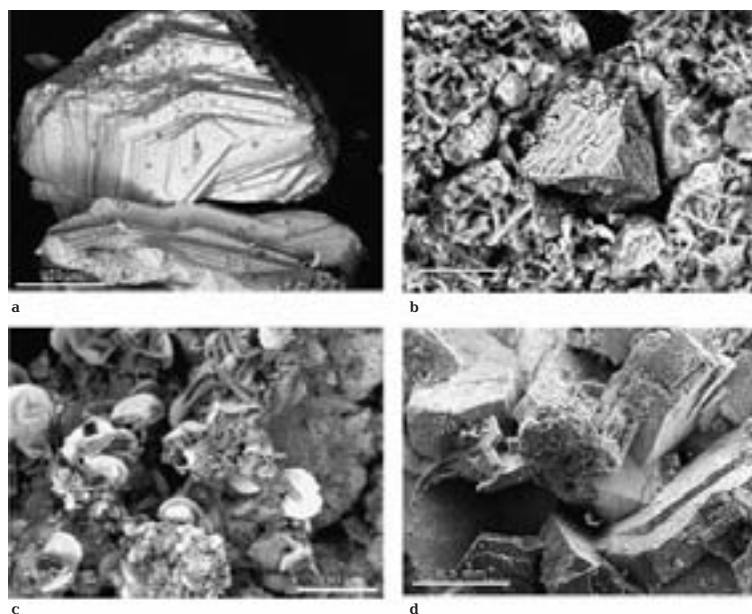


Fig. 5. BSE images of crystals of the newly formed sulfides among the secondary products. Micro-samples.

(a) Intergrowths of the lamellar isocubanite crystals (Table 1, anal. 1) with the rare fine powder of pyrite and copper sulfides on faces. Sample 1271-4.

(b) Crystal of phase Y among exsolution products of isocubanite. Sample 1269-6/1.

(c) Crystals of covellite (white, Table 4, anal. 8) partially with the crust of copper and iron sulfate among the secondary products. Sample 1269-4/2**.

(d) Crystals of marcasite with powder of copper sulfides (probably pseudomorph after pyrrhotite). Sample 187-1/2.

formed homogeneous phases appear against the background of selected replacement matrices. These phases are nearly all Cu-Fe and Cu sulfides, as well as their mixtures added by sulfates and oxides of the same metals (unfortunately, study of these mixtures failed because of their small size).

According to morphology, color and chemical composition, the following newly formed minerals and phases were identified:

1. Thin whitish (bluish under reflected light) spots with sporadic light clusters, which are spread on the transformed dark matrix and lamellae. The composition of such spots and clusters is close to idaite (Table 3, anal. 2) within elongated grains (Fig. 4b) hosted in the exsolution texture with black covellite-bearing matrix. At the same time, the denser newly formed homogeneous isocubanite (Table 1, anal. 6, 8) is observable in the host matrix. The black matrix and lamellae of the primary exsolution texture appear through the whitish spots, whereas they are not observed in the dense isocubanite grains.

2. The homogeneous light grains developed after the transformed matrix between lamellae and partially trapping the latter or "spilling" along the contact. For example, the newly formed phase Y (Fig. 4c; Table 3, anal. 4) replaces the areas of dark matrix between the large lamellae of chalcopyrite (Table 2, anal. 3). These lamellae in turn are juxtaposed on the frame of

small lamellae, which were also transformed.

3. The small newly formed generations modify the composition and distort the shape of host chalcopyrite lamellae. Such transformed lamellae correspond to phase M in composition (Fig. 4d; Table 3, anal. 3-5) and accompany the appearance of the above mentioned whitish spots.

4. Well-shaped crystals of sulfides appear among extremely transformed products of the isocubanite exsolution on the surface of microsamples (Figs. 5a-d). They occur as segregations of homogeneous isocubanite with the fine powder of copper sulfides and pyrite or as different sulfides, which are involved in the transformation of exsolution products. Presence of homogeneous isocubanite crystals among the modified exsolution products of high-temperature generations of this mineral clearly proves the neoformation of these crystals.

Further transformation of the exsolved isocubanite results in the conversion to the lattice-type structure. The juxtaposition of rounded phenocrysts of chalcopyrite (Table 2, anal. 5) on the very fine latticed exsolution texture with a bulk composition close to phase Y (Table 3, anal. 8) transforms this texture to nearly impregnated one (Fig. 6a). Fine grains with practically indistinguishable lattice are occasionally transformed into colloform and zoned structures (Figs. 6b, 6c). The new phase B occurred as thin zones (Table 3, anal. 4, 5) in the

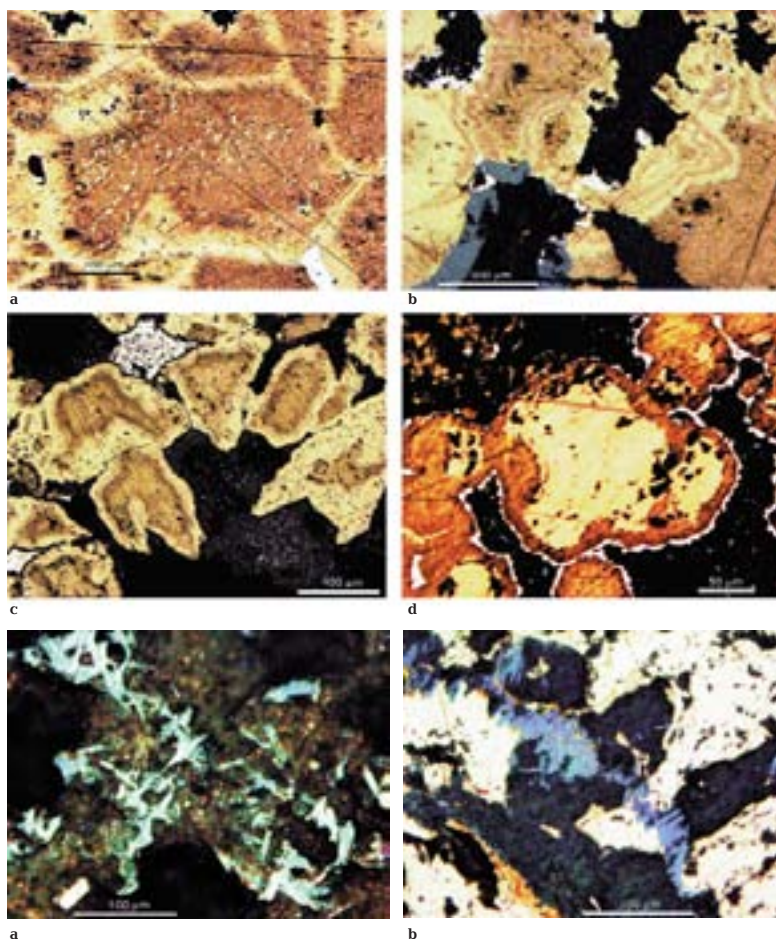


Fig. 6. Transformation of exsolution texture of isocubanite. Sample 135-6/1. Photomicrographs of polished sections under reflected light.

(a) Oriented rounded phenocrysts of chalcopyrite (Table 2, anal. 5) is superimposed on the very fine light brown exsolution texture of phase Y (Table 3, analysis 8) with the chalcopyrite rim.

(b) Colloform segregation developed after the isocubanite exsolution texture with light zones of new phase B (Table 3, anal. 4, 5); in the left lower corner, sphalerite is dark gray band and cavities are black.

(c) Zoned texture formed at transformation of isocubanite: fine heterogeneous sulfide-sulfate cores with dark rims dominated by sulfates are surrounded by the light zones of new phase B (Table 3, anal. 1, 2). Relief grain of pyrite is in the upper part of the photomicrograph.

(d) Light grain of isocubanite with dark heterogeneous sulfide-sulfate rim and outer rim of pyrite (white).

Fig. 7. Segregation of late covellite. Photomicrographs of polished sections under reflected light.

(a) Intergrowths of sheet-like covellite crystals with clearly pronounced bireflectance (from blue to bluish gray) (Table 5, anal. 6) in fine-grained sulfide-oxide mass. White grain in the left lower corner is pyrite. Sample 1271-4/3.

(b) Veinlet of blue sheet-like crystals of covellite in isocubanite (Table 1, anal. 9). Locally, crystals of covellite are outlined by thin rim of newly formed chalcopyrite. Sample 1271-4.

colloform areas and margins (Table 3, anal. 1, 2) of zoned grain and was observed solely in such structures. In the newly formed zoned textures, the heterogeneous sulfate segregations with different locations are also observable. For example, in Fig. 6c, the thin dark zone enriched in sulfate separates the sulfate-sulfide core from the light outer band of phase B, whereas in Fig 6d, sulfates occur as a broad zone along the margins of the isocubanite grain and are outlined by an outer thin rim of pyrite. In some cases, the primary texture of the isocubanite solid solution completely disappears at the zone of dense metasomatic replacement, both of lamellae and matrix by the grained Cu-poor

copper sulfides with fine-flake segregations of early covellite (see Fig. 3f). The later coarse lamellar covellite is associated with the sulfate-oxide segregations (Fig. 7a) and cut through homogeneous isocubanite (Fig. 7b).

It should be emphasized that the mineral assemblages that are exsolution products of isocubanite, subsequent to their transformation, are prevalent in the Krasnov field and are observed for the first time.

The oxide-sulfate-sulfide paragenetic type III is significantly different from the two mentioned above by its iron specialization and is divided into two subtypes: with predominant pyrite (a) and with predominant Cu-Fe sulfates and Fe

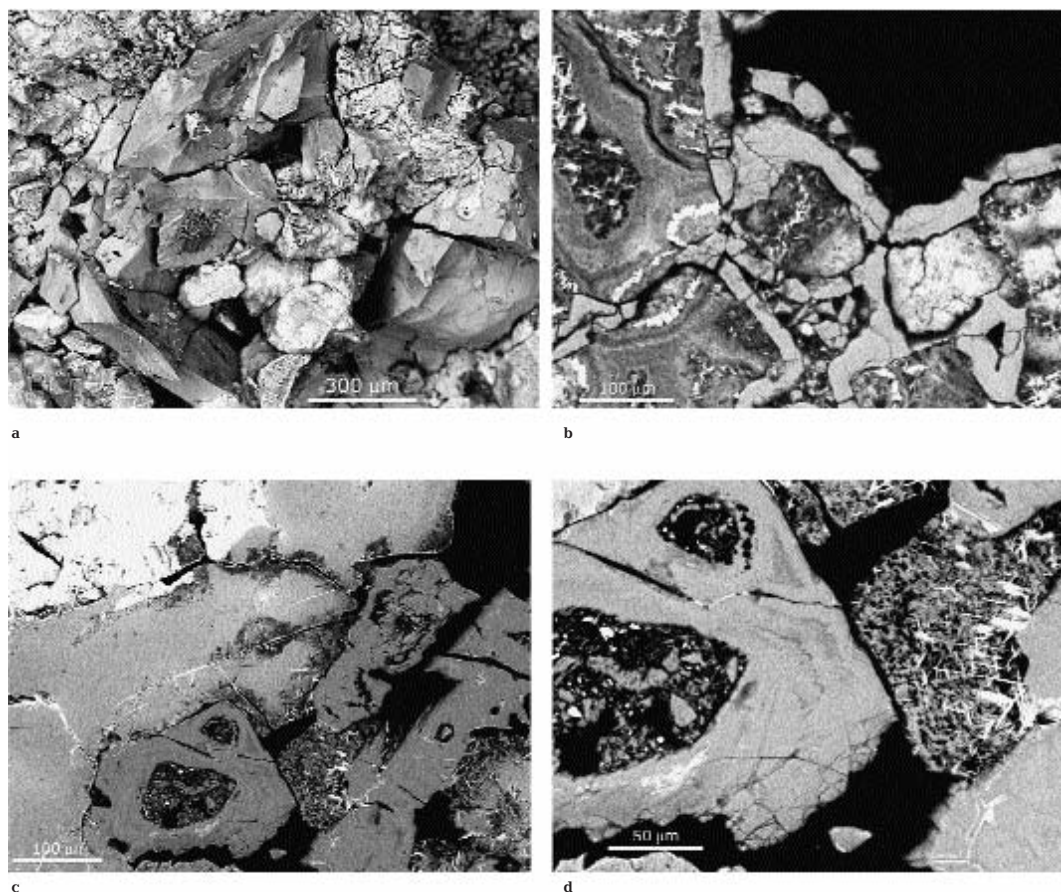


Fig. 8. Type III of paragenetic assemblages is oxide-sulfate-sulfide.

(a) BSE image of microsample. Sample 187-1/2. (b-d) Photomicrographs of polished sections under reflected light. Sample 1271-4. (a) Desintegrated area of ore on the piece surface presented by relic grains with the traces of highly transformed latticed exsolution texture surrounded by the larger fragments of pyrite.

(b) Breccia-like structure with broad rims of Cu-bearing pyrite around the highly transformed heterogeneous ore fragments. The lightest and coarse-grained zone in colloform area of fragment is a phase close to idaite. The other white grains are unidentified Cu-Fe sulfides enriched in sulfur (probably due to surrounding sulfates).

(c) Assemblage of goethite (relief isometric dark-gray grains of subtle-zoned structure) and Cu-Fe sulfate (light gray in centre) in contact with homogeneous isocubanite (white, in the left upper corner, Table 1, anal. 10); thin veinlet-like segregations in sulfates and goethite are syngenetic sulfides; the highly transformed fragment of the type II assemblage is between grains of goethite; two rounded cavities with microbreccia of dissolution (contains grains of goethite and sporadic sulfides) are in isometric goethite grain.

(d) Detail of the same photomicrograph. In the isometric goethite grain, light veinlet-like segregations concordant to zoning of goethite are composed of troilite. The other sulfides are not identified. Highly transformed fragment displays the latticed structure, where portions of lamellae were converted to the idaite-like phase.

oxides (b). In regard to type II, type III formed later, because it contains only relics of grains with extremely transformed latticed textures.

An example of paragenesis with predominant late pyrite (subtype a) is shown in Figs. 8a and 8b, where it is observed within extremely disintegrated and brecciated areas of ores, which host the most modified primary exsolution tex-

tures of isocubanite. These textures in relic fragments are frequently transformed to colloform-zoned areas (Fig. 8b), where separated thin zones are composed of the newly formed Cu-Fe sulfides close to idaite in composition. These newly formed sulfides are assumed to be formed nearly simultaneously with surrounding pyrite.

An example of oxide-sulfate paragenesis

with subordinate sulfides (subtype b) is shown in Figs. 8c and 8d. Goethite and sulfate close to natrojarosite are the predominant minerals. Goethite (α -FeOOH) occurs as gray relief grains with thin-zoned texture and deep red inner reflections. Analysis was confirmed by chemical composition (wt.%): 52.99 Fe, 4.85 Cu, 36.73 O, 1.98 S, and 0.96 Cl, total is 97.31 and X-ray diffraction pattern with the following strongest reflections (\AA): 4.195(9), 2.715 (10), 2.434 (9), 2.217 (7), and 2.718 (4).

In comparison with goethite, the sulfate grains are lighter and in lower relief. Proximity to natrojarosite is indicated by the X-ray powder pattern collected from the material extracted from the analyzed sample (Table 6). However, according to electron microprobe data, this sulfate contains (wt.%) 39.60 Fe, 19.86 Cu, 30.98 O, 10.43 S, 0.85 Cl, total is 101.87; copper occurs instead of sodium and the Fe/S atomic ratio exceeds that which is typical of jarosite (2 as opposed to 1.5) (the composition of natrojarosite is calculated from the theoretical formula $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ and is as follows (wt.%): 34.57 Fe, 4.74 Na, 46.21 O, 13.23 S, 1.25 H).

The Cu-Fe sulfate from the Krasnov field is not excluded from being a new mineral species (or variety) of the alunite group and further examination is needed. In any case, incorporation of the smaller copper ion instead of sodium probably explains the decreasing of some d-spacings in the studied sulfate in comparison to the standard values of natrojarosite. In this connection, it may be noted that the wide range of the Fe/S value even in individual minerals is given in the last review on sulfates. For example, in schwertmannite discovered in 1994 with the ideal formula $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x \cdot n\text{H}_2\text{O}$, where $1 \leq x \leq 1.75$, the Fe/S ratio ranges from 8 to 4.6 indicating intermediate composition between goethite and jarosite (Bigham & Nordstrom, 2000).

In polished sections (Figs. 8c, 8d), the sulfate segregation borders on the homogeneous isocubanite at one margin (Table 1, anal. 10) and slightly corrodes this mineral and at the other margin, on goethite, but in the latter case, their relationship is masked by very fine branchy black segregations developed after sulfate in the near-contact area. Along cut cracks, these segregations penetrate into isocubanite. They are similar in morphology to fine-acicular aggregates of schwertmannite

Table 6. Comparison of X-ray powder pattern for Cu-Fe sulfate and standard X-ray patterns of natrojarosite

Sample 1271-4		PDF # 110302		PDF # 301203	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
		40	5.94	30	5.94
		50	5.57	40	5.57
6	5.00	100	5.06	90	5.06
		20	3.67	30	3.66
7	3.46	20	3.49	20	3.49
		70	3.12	90	3.12
10	3.06	80	3.06	100	3.06
		20	2.960	20	2.960
4	2.746	20	2.780	30	2.783
4	2.536	40	2.530	30	2.527
				10	2.308
1	2.245	60	2.240	50	2.236
2	2.087	20	2.130		
3	1.928	60	1.980	50	1.979
4	1.905	5	1.910	30	1.909
5	1.856			10	1.857
		50	1.830	50	1.834
		5	1.740	20	1.743
7	1.714	5	1.720	20	1.724
				5	1.693
				5	1.657
3	1.602			20	1.623
5	1.583	20	1.570	20br	1.578
		20	1.540	20	1.560
				30	1.532
		20	1.480	10	1.484
5	1.453	40	1.479	40br	1.479
1	1.311	5	1.340		
1	1.198				
3	1.072				

reported in the above cited paper, where jarosite and goethite are described as common members of the schwertmannite assemblages.

The grains of goethite and sulfate contain thin veinlet-like segregations of simultaneous Fe sulfides concordant to the zoning of goethite. Troilite has been identified in one such veinlet. Two oval cavities with the microbreccia of dissolution are observed in the goethite grain as traces of the later effect. Fragments within these cavities mainly present the same goethite with the sporadic grains of

sulfides. The chain of fine goethite grains arranged along the wall of the smaller cavity follow its morphology (Fig. 8d).

In the polished section (Fig. 8d), an "alien" component is relict of highly transformed primary exsolution texture in the cavity between the goethite grains. The latticed structure of the relict nearly disappeared and the residual thickened lamellae were converted to the idaite-like phase.

Taking into account the relationship between type II and type III paragenetic assemblages, the latter is suggested to finalize the subordinate copper mineralizing process and signal the transition to the pyrite ores, which are predominant in the Krasnov hydrothermal field.

Discussion

The results obtained display the specific character of the mineral paragenetic assemblages of the copper ores at Krasnov.

Briefly described type I paragenetic assemblages, where isocubanite does not exsolve are similar to the mineral assemblages from the youngest active sulfide chimneys in the Rainbow hydrothermal field (36°14' N, Mid-Atlantic Ridge), which were studied in detail (Bogdanov *et al.*, 2002; Borodaev *et al.*, 2004; Mozgova *et al.*, 2005). The sulfide mineralogy in these chimneys is nearly identical to the type I paragenetic assemblages in the Krasnov field and phase Y, that is close to isocubanite preserves as homogeneous. Despite the small dimensions of cut veinlets, in most cases, the mineral distribution is similar to that in the Rainbow chimneys: bornite in contact with isocubanite alternates with the heterogeneous copper sulfides toward the center of the veinlet (or nest), where chalcocite, the Cu-richest sulfide of this assemblage, occurs. Taking into account the Mössbauer data on Cu and Fe valances in the examined sulfides (Vaughan & Craig, 1978), the major steps of the transformation are as follows: isocubanite $\text{Cu}^+\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_2 \rightarrow$ bornite $\text{Cu}^+\text{Fe}^{3+}\text{S}_4 \rightarrow$ chalcocite Cu^+S . These metasomatic conversions appear to be caused by increasing oxidation, potentially due to the effect of sea water penetrating along fissures. As a result of this, iron is oxidized and removed and minerals are enriched with the remaining copper. Some

deviations from this scheme (for example, indications of zoning) are due to the dynamic environment during the formation of this assemblage. It should be added that the increased oxidation potential does not reach the levels that were documented in the young Rainbow chimneys where chalcocite is replaced with minerals depleted in Cu. By analogy with Rainbow, this type can be assumed to have been derived from the sufficiently high-temperature short-lived source.

Similar schemes reflect some common features of the Cu-Fe-sulfide transformation. In particular, it is consistent with the documented supergene alteration of these minerals at continental deposits (Sillitoe & Clark, 1969; Constantinou, 1975; Large *et al.*, 1995).

The much more abundant type II, which is related to the exsolution texture of isocubanite, is characterized by indications of the subsequent transformations. First of all, these are multiple repetitions of exsolution that indicate the violent dynamics and high temperature of the initial stage of the copper ore formation, since the thermal stability of isocubanite is $\geq 200^\circ\text{C}$ (Vaughan & Craig, 1978).

Resulting heterogeneity of the matrix in the exsolution products can explain another feature of these paragenetic assemblages that is widespread, the unique selective replacement of the matrix. The involvement of different minerals in this process is apparently due to localized conditions, which vary depending upon the decreasing of temperatures and the increasing of the oxidation potential. As a result, replacement minerals and phases become Fe-poorer and are enriched in Cu (see compositions on the line with $\text{Me/S}=1$ in Fig. 1) and in some cases, sulfates are developed separately after the matrix.

The further transformation results in newly formed homogeneous minerals and phases of the Cu-Fe-S system incorporated in modified matrices and lamellae in the exsolution textures. The presence of non-exsolved isocubanite among the newly formed phases as grains and homogeneous crystals indicates an increase of temperature that can be caused by renewed fluid influx. The appearance of the metastable phases, which were observed neither in nature nor experiment under equilibrium is noteworthy. According to terminology suggested by F.V. Chukhrov, such phases may be defined as

"ephemer-minerals". The reason for their appearance "is the rapid chemical reactions that prevent the formation of stable phases" (Chukhrov, 1973). They are easily converted under change of conditions that contribute to the transition of the exsolution textures to other structural-textural generations change.

In this type of paragenetic assemblages, most minerals are identified as Cu-Fe and Cu sulfides, involved in all stages of the isocubanite exsolution texture transformation: from the metasomatic replacement of the matrix at an early stage, through the newly formed phases, to the formation of cut veinlets at the latest stage. It can be emphasized that the presence of Cu-poor sulfides (covellite Cu^{2+}S and related nonstoichiometric sulfides) in this paragenetic type, and Cu-rich sulfides in type I, testify to the more oxidizing conditions of transformation for type II.

In the type III assemblages, the subtype with predominant late pyrite cementing highly transformed fragments of the isocubanite exsolution textures apparently indicates an influx of new portions of hot fluids enriched in Fe.

Goethite and poorly studied Cu-Fe sulfate that is intermediate between the jarosite family and schwertmannite in the Fe/S ratio are the major minerals of the oxide-sulfate subtype. According to the recent reviews (Bigham & Nordstrom, 2000; Dutrizac & Jambor, 2000; Jambor *et al.*, 2000), goethite and Fe sulfate of the jarosite family, the most common components of oxidized zones of massive sulfide deposits, also occur in hypogene settings. Hypogene jarosite is documented in hot springs of Yellowstone National Park in the USA, crater lake of the Mendeleev volcano in the Kunashir Island, Kurily and other similar localities. A.A. Godovikov reported (1983) that hypogene jarosite is uncommon and is not abundant. As a secondary mineral, it is metasomatically developed after nearly all iron minerals due to the oxidizing of the latter (Ramdohr, 1980).

The relationships of minerals described from our samples of the oxide-sulfate paragenetic assemblages contribute to the hypogene origin of these minerals, because the features of high replacement of primary Cu-Fe sulfides with these minerals are absent and the minerals contain fine segregations of simultaneous Fe sulfides (including troilite, FeS; although, Fe-monosulfides are absent in the other paragenetic

types). Any interaction between the type III paragenetic assemblage and relics of the greatest transformed primary assemblage was not observed (see Fig. 8d).

Comparison of the data obtained allows the following conclusion. The type I paragenetic assemblages not in contact with the other types may be considered by analogy with the Cu chimneys from Rainbow as young mineralizations formed for the short period which appears to explain their weak transformation. Predominant paragenetic type II of the highest transformed assemblages is most probably related to the oldest and long-lived source. Iron assemblages of type III accomplish the deposition of Cu-Fe ores and are transitional to the major pyrite stage of mineralization in this field. The alternation of the geochemical specialization of fluids is probably the result of modifications in the ore-forming system.

Thus, the study of the transformation of the copper-bearing paragenetic assemblages (some of which are unique) from the Krasnov field show the complex nature of the mineralizing processes in this area and gives additional information on oceanic mineralization.

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CODIFICATION OF UNNAMED MINERALS*

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The Subcommittee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC, formerly CNMMN) has developed a codification system that includes the year of publication and qualitative chemical composition for unnamed minerals reported in the literature. Such minerals are divided into two categories: Those regarded as being "valid as unnamed minerals" are those that do not correspond to existing species, have not been reported previously, and whose published descriptions enable them to be recognized if found elsewhere. Unnamed minerals regarded as being "invalid as unnamed minerals" are those whose published descriptions are inadequate for their confident recognition if found elsewhere, or which correspond to existing mineral species or unnamed minerals published previously.

Introduction

References to unnamed mineral are frequently encountered in the literature, where they are described in varying degrees of detail and referred to in a haphazard manner. Furthermore, no comprehensive compilation of unnamed minerals has been published, which makes it difficult to find descriptions of unnamed minerals of a particular composition. In an effort to remedy this situation, the authors, together with the late Jiri Just (d. 1994) submitted a proposal to the IMA Commission on New Minerals and Mineral Names (CNMMN, now CNMNC) to establish a subcommittee to compile a list of unnamed minerals from the literature, and to devise a systematic method of codifying them. This proposal was approved as CNMMN Nomenclature Proposal 95-B. A final report, including a proposed coding system and compilations of unnamed minerals using the coding, was submitted to the CNMMN and was approved in 2005. The report was published by Smith & Nickel (2007). This paper is a brief summary of the report.

The Coding System

For the purposes of this work, an unnamed mineral is one that is referred to as being unnamed, has been given a designation such as

"Mineral A" or some descriptive or working name that does not correspond to the name of a valid mineral species.

In the literature, descriptions of unnamed minerals vary from detailed descriptions that would enable the mineral to be recognized and identified in a different context, to incomplete descriptions that would not enable a confident identification to be made. We have endeavoured to separate these minerals into two categories, "valid as an unnamed mineral" and "invalid as an unnamed mineral", respectively. For simplicity these categories will hereafter be referred to as "valid" and "invalid". Included among the "invalid" unnamed minerals are those that **have** been found to correspond to existing mineral species, either at the time of publication, or subsequently. In making a distinction between these two categories, there is, of course, a "grey" area that comprises minerals that could have been assigned to either category.

In an effort to make the coding as meaningful as possible, the coding includes the year of first publication and compositional information. In addition, the two categories of unnamed minerals are distinguished by differences in the coding system.

For minerals in the "Valid" category, a primary concern in devising a system was to make the codes indexable and to simplify literature and computer database searches. The designation finally adopted takes the form shown in

* The paper of the chairman and vice-chairman, Subcommittee for Unnamed Minerals, IMA Commission on new Minerals, Nomenclature and Classification, published earlier in *Canadian Mineralogist*, is reproduced here in brief version by request of the Commission in order to introduce the new and approved coding system as widely as possible.

¹ Chairman and ² vice-chairman, Subcommittee for Unnamed Minerals, IMA Commission on New Minerals, Nomenclature and Classification

the following example:
UM1959-01-BO:CaMgMn.

The use of the initial letters "UM" clearly places unnamed minerals in an alphabetical listing such as is used in most journals and books, as well as in computer databases. It also has the somewhat fortuitous advantage that the abbreviation could also stand in some other Germanic languages.

The "UM" is followed by two groups of numerals. The initial group indicates the year when the mineral was first reported. The two numerals after the first hyphen constitute a trivial "serial" number which has been assigned to give different identities to minerals described in the same year. Although it is recognized that, in time, some numbers will be eliminated when previously unnamed minerals are given names, discredited, or declared synonymous with other named or unnamed minerals, to avoid confusion, the sequential numbers will not be changed, nor will eliminated numbers be reused, now that this system of coding has been adopted by the IMA.

The numerals are followed by a further hyphen and then one or more alphabetic characters that represent a chemical code designed to indicate the chemical grouping to which the mineral has been assigned. The following chemical codes have been devised:

As arsenides (if both S and As present, S takes precedence)

AsO	arsenates or arsenites
Bi	bismuthides
BO	borates
Br	bromides
C	carbides
CH	hydrocarbons, oxalates, porphyrins, organic compounds
CO	carbonates
Cl	chlorides
CrO	chromates
E	elements and intermetallic compounds
F	fluorides
FCO	fluorcarbonates
GeO	germanates
I	iodides
IO	iodates
MoO	molybdates
N	nitrides
NO	nitrates
O	oxides
OC	oxalates
OH	hydroxides

OS	oxysulphides
P	phosphides
PO	phosphates
S	sulphides or sulphosalts
Sb	antimonies
SO	sulphates or sulphites
Se	selenides
SeO	selenates or selenites
Si	silicides
SiO	silicates
Te	tellurides
TeO	tellurates or tellurites
VO	vanadates
WO	tungstates

Thus, in the above example, BO indicates that the mineral is a borate. In cases where a mineral includes multiple anions or anionic groups of similar importance, both have been used; for example, carbonate-phosphate minerals have been represented by the coding COPO. It is possible that some further composite groups may be introduced in the future.

Following a colon are further element symbols (in mixed case and alphabetical order) for the **principal** elemental constituents, but omitting any element defined by the chemical code. Thus, oxygen can also be omitted in most cases since its presence will be implied by the chemical code. This system allows rapid computer searching/matching on the basis of observed elements and the compositional symbol for an unnamed mineral. In alphabetical listings, indices and databases, the chemical extension of the coding (-BO:CaMgMn in the above example) may, if appropriate, be omitted for the sake of brevity since the number alone makes the code unique. It was further decided that only the chemical elements **reported or implied** for an unnamed mineral would appear in its code. Thus, if an unnamed mineral was later shown to contain one or more elements that had originally been missed, such additional elements would not be included in the code.

The coding for minerals in the "invalid" category is similar to that used for those in the "valid" category, except that the second set of numerical symbols (the serial number) is replaced by a double forward stroke, as, for example, UM1997-//F:KMgNa.

Compilation of Unnamed Minerals

The authors have searched the available literature for unnamed minerals and have found ref-

ferences to about 2800 at the time of writing. Most of the data have been acquired directly from the primary literature sources, but where access to the primary literature was lacking, reliance was placed on secondary sources. The unnamed minerals were coded according to the system outlined above, and compiled into two lists, representing "valid" and "invalid" types. In the interest of saving space, these lists are not included in this paper, but have been published elsewhere (Smith & Nickel, 2007). The lists will also appear in due course on the CNMNC website <<http://www.geo.vu.nl/-ima-cnmmn/imareport.htm>> in a computer-searchable form

The data in both lists include the codings, primary and/or secondary literature references, and relevant comments, commonly including the chemical formulae, if known. During the compilation of the lists, the authors had recourse to their completely independent and very comprehensive databases "Minident" and "Mineral" (www.micronex.ca), Smith & Leibovitz, 1986; and www.materialsdata.com, respectively), and vigorously discussed contentious aspects until agreement was attained.

Future Developments

The codings for the unnamed minerals in the two lists published by Smith & Nickel (2007) represent the official IMA designations for the mineral, Additions and/or changes to the lists should be made solely by the Subcommittee for Unnamed Minerals of the CNMNC. At the present time this Subcommittee, which is expected to be a permanent subcommittee of the CNMNC, consists of the two authors of this paper, and they intend to provide periodic updates, and to make necessary changes such as transferring unnamed minerals from the "valid" to the "invalid" list as they are equated with existing species. However, it is anticipated that, over the course of time, additional members will be added to the Subcommittee, and a new executive established.

Researchers encountering what they believe to be new unnamed minerals are encouraged to submit their data to the Subcommittee on Unnamed Minerals, preferably via the CNMNC website. Pending approval of the final coding, it is recommended that they use the following scheme for interim coding. As in the example below, the code

should begin with the letters UKI, all in upper case. These letters may be thought of as standing for "unknown" and "interim" and are distinct from any IMA code that may eventually be assigned. Then, following a hyphen, four alpha/numeric characters (in lower case) take the place of the serial number in the IMA code for valid unnamed minerals. Following a further hyphen, and in parentheses, a chemical code can be indicated using the system described earlier in this paper. Note that the year of description has been deliberately omitted from this code because of uncertainties concerning publication delays.

Example: UKI-ab71-(S:CoCuFeZn)

It should be noted **that** authors who have described new minerals without names do not have any priority rights on the subsequent naming of such minerals. Any names proposed subsequently (for previously unnamed minerals) have to be approved by the CNMNC, as do the minerals for which the names are proposed.

Conclusions

The CNMNC will establish a permanent Subcommittee for Unnamed Minerals whose job it will be to:

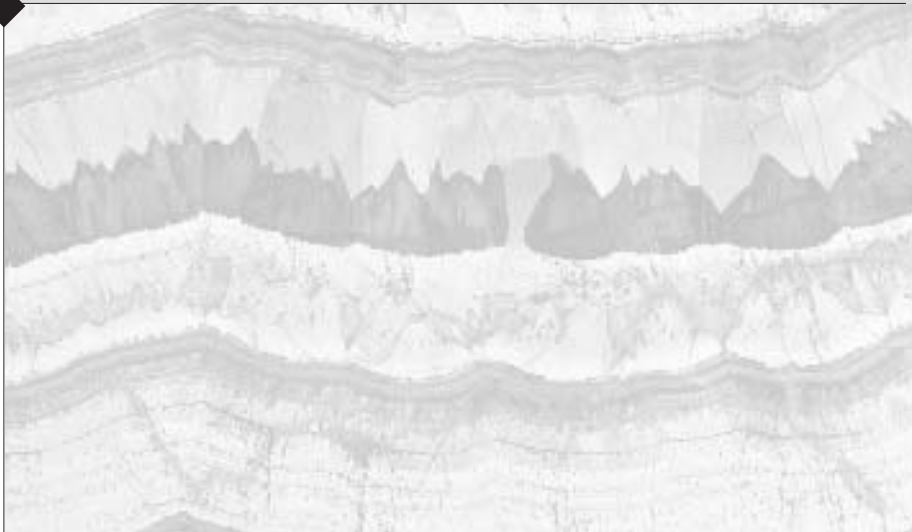
- oversee the assignment of numbers to future unnamed minerals, including those already described but which have not been identified in the initial lists.
- decide and act upon future recommendations from the mineralogical community concerning the rejection of previously "Valid" unnamed minerals.

The Subcommittee will make recommendations to the CNMNC regarding the status of unnamed minerals.

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



NEW DATA ON MEGACYCLITE

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The second and the third occurrences of megacyclite $\text{KNa}_8\text{Si}_9\text{O}_{18}(\text{OH})_9 \cdot 19\text{H}_2\text{O}$ in two alkaline massifs of Kola Peninsula, Russia are described. This mineral occurs as abundant late hydrothermal veinlets up to 1.5 mm thick and rare prismatic individual crystals up to 1.5 cm long, hosted in a large peralkaline pegmatite in association with microcline, aegirine, sodalite, lamprophyllite, lomonosovite, shcherbakovite, villiaumite, delhayelite, phosinaite-(Ce), clinophosinaite, natisite, lovozerite, tinalite, nacaphite, rasvumite, and revdite at Mt. Rasvumchorr, Khibiny massif. In the Lovozero massif, megacyclite have been found in the Palitra pegmatite at Mt. Kedykverpakhk as white and yellowish brown spherulites up to 2 mm in diameter together, with revdite and zakharovite with microcline and natrosite in cavities. The chemical composition of megacyclite from Khibiny is as follows: wt %: 3.69 K_2O , 19.85 Na_2O , 42.74 SiO_2 , 33.03 H_2O , total 99.31. The empirical formula calculated on the basis of $[\text{Si}_9(\text{O},\text{OH})_{27}]$ is as follows: $\text{K}_{0.99}\text{Na}_{8.11}\text{Si}_9\text{O}_{18.10}(\text{OH})_{8.90} \cdot 18.75\text{H}_2\text{O}$. The IR-spectrum and X-ray powder diffraction pattern are reported. The crystal structure of megacyclite has been refined to $R_{\text{int}} = 0.0339$ for 8206 unique reflections with $I > \sigma 2(I)$. The mineral is monoclinic, space group $P2_1/c$, $a = 24.8219(16)$, $b = 11.9236(8)$, $c = 14.8765(9)$ Å, $\beta = 94.486(5)^\circ$; $V = 4389.5(5)$ Å³. Structural formula is $\text{K}_2\text{Na}_{16}\text{Si}_{18}\text{O}_{34}(\text{OH})_{18}[\text{O}_{0.75}(\text{OH})_{0.25}]_2(\text{H}_2\text{O})_{36}[(\text{H}_2\text{O})_{0.75}(\text{OH})_{0.25}]_2$ ($Z = 2$). The system of the hydrogen bonds is characterized in detail.

6 tables, 5 figures, 11 references

The hydrous silicate of potassium and sodium megacyclite was found earlier only in the peralkaline pegmatoid veins (mainly composed by potassic feldspar, fenaksite and delhayelite) at Mt. Rasvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. The mineral occurs as colorless anhedral grains up to 3 mm in size and aggregates up to 5 mm in size included in large individual crystals of fenaksite, and intimate intergrowths of megacyclite and revdite, $\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_5]_2[\text{Si}_8\text{O}_{15}(\text{OH})_6](\text{OH})_{10} \cdot 28\text{H}_2\text{O}$ (Khomyakov *et al.*, 1993). The large ring radical composed of 18 Si-tetrahedra is the most interesting feature of the mineral and is reflected in the mineral name (from the Greek *mega* – large, *kyklos* – ring) According to the X-ray study of a single crystal drawn from holotype material, megacyclite is monoclinic, space group $P2_1/c$, $a = 24.91$, $b = 11.94$, $c = 14.92$ Å, $\beta = 94.47^\circ$, $V = 4426$ Å³. The chemical composition determined with an electron microprobe is as follows, wt %: Na_2O 19.75, K_2O 3.62, SiO_2 43.42,

total 66.79 mac.%. From the structure solution, the ideal formula of the mineral is $\text{Na}_8\text{KSi}_9\text{O}_{18}(\text{OH})_9 \cdot 19\text{H}_2\text{O}$, $Z = 4$ (Yamnova *et al.*, 1992; Khomyakov *et al.*, 1993).

We have discovered two more occurrences of megacyclite in the Khibiny and neighbouring Lovozero alkaline massifs. In Khibiny, the mineral was found also at Mt. Rasvumchorr, but in a slightly different environment. Megacyclite occurs in a large peralkaline pegmatite in the quarry of the Tsentral'ny Mine. This pegmatite is hosted in urtite adjacent to the contact with the nepheline-apatite rock has been traced for more than 10 m along strike with a maximum thickness not less than 1 m. Three mineral assemblages corresponding to three sequential stages of crystallization were recognized within the pegmatite. Potassic feldspar, nepheline, sodalite, alkali pyroxene (aegirine-salite) and amphibole, eudialyte, lamprophyllite, ilmenite, and fluorapatite are the earliest minerals. The anhydrous and

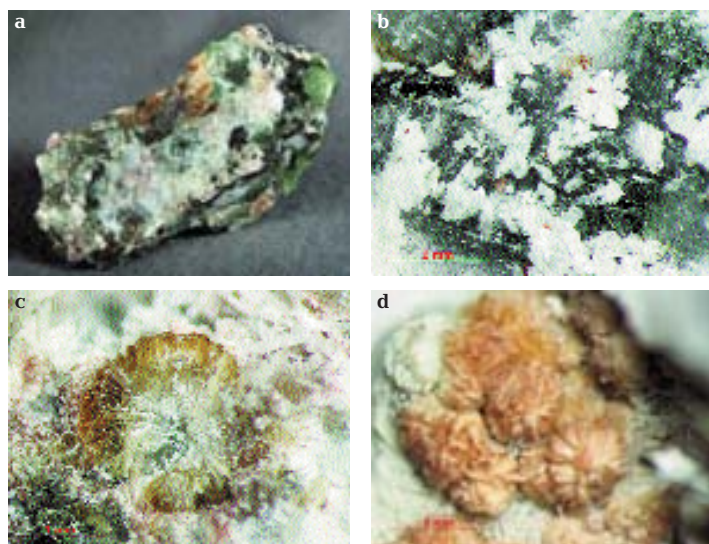


Fig. 1. Segregations of megacyclite: a,b – the Central mine, Mount Risvumchorr, Khibiny; c, d – the Palitra pegmatite, Mount Kedykverpakh, Lovozero. Fotos by S.I. Pekov (a), A.V. Kasatkin and I.V. Pekov(b–d). a – white crust of megacyclite on the walls of fissure in peralkaline pegmatite (the sample was split along veinlet of megacyclite; tisinallite is brown; lomonosovite is dark brown; aegirine is green). Size of sample is 3 x 7 cm. Collection by D.V. Lisitsyn. b – intergrowths of the megacyclite crystals encrusting the wall of crack. Collection by I.V. Pekov. c – polychromatic (colorless core and amber-brown margins) spherulite in a matrix of revdite. Collection by V.G. Grishin. d – segregation of light brown radiant intergrowths of megacyclite and revdite hosted by microcline in pocket. Collection by V.G. Grishin.

H₂O-low alkali-rich minerals green acicular aegirine (the major mineral of this assemblage), pectolite, magnesium astrophyllite, lomonosovite, shcherbakovite, barytolamprophyllite, villiaumite, fenaksite, delhayelite, phosinaite-(Ce), natisite (replaces ilmenite), zyrinalite (rims and pseudomorphs after eudialyte), kazakovite, nakaphite (after fluorapatite), sidorenkite, djerfisherite, rusvumite, sphalerite and molybdenite crystallized during stage-2, which may be defined as "dry peralkaline". According to the presence of water-rich minerals with open structures, the stage-3 minerals were deposited from hydrothermal high-alkali fluids at temperatures not higher than 200–250°C. Some of "dry" peralkaline minerals are unstable in this environment and are replaced with water-bearing phases depleted in alkali cations and water-bearing: zyrinalite with lovozerite, kazakovite with tisinallite, delhayelite with hydrodelhayelite and pectolite. Shafranovskite, ershovite, megacyclite, revdite, grumantite and poor-crystalline alkaline silicates with Mn and Ti are the other products of the hydrothermal stage, and fill small cavities and cracks.

Megacyclite is one of the latest phases and occurs as dense branching veinlets. At the type locality (Khomyakov *et al.*, 1993), this K,Na-silicate occurs in insignificant amount, whereas here, it is common: monomineralic veinlets are locally more than 10 cm long and up to 1.5 mm thick. Splitting the rock along

these veinlets provides specimens with colorless or white crusts of megacyclite (Fig. 1) up to 5 x 7 cm in size. These veinlets are composed of elongated (less frequent isometric) lammellae without pronounced faces, reaching 1–1.5 mm in maximum dimension, occasionally 2–3 mm, and usually distorted. As a rule, these veinlets comprise subparallel lamellar segregations in which individual crystals of megacyclite are oriented normal or oblique to the selvages. Two other morphological types of megacyclite have been observed: (1) euhedral crystals as rhomb-like lamellae and plates up to 0.5 mm (goniometric study was not done due to the low quality of the crystal faces) covering the walls of small fissures, and (2) rosettes occurring in fissures and composed of coarse colorless crystals up to 0.2–1.5 cm in size; these are the largest individual crystals of the mineral.

In the Lovozero massif, megacyclite has been identified in the large peralkaline Palitra pegmatite developed by the underground working at Mt. Kedykverpakh and has been recently described in detail by Pekov (2005). Megacyclite occurs in small cavities as inclusions in microcline and natrosilite. It is intimately associated with revdite, locally zakharovite, and earlier aegirine, villiaumite, serandite, nordite-(Ce), vuonnemite, potassic arfvedsonite and sphalerite. Megacyclite occurs as compact spherulites up to 1.5–2 mm in diameter, which are locally present as clusters included in a sugar-like matrix of revdite

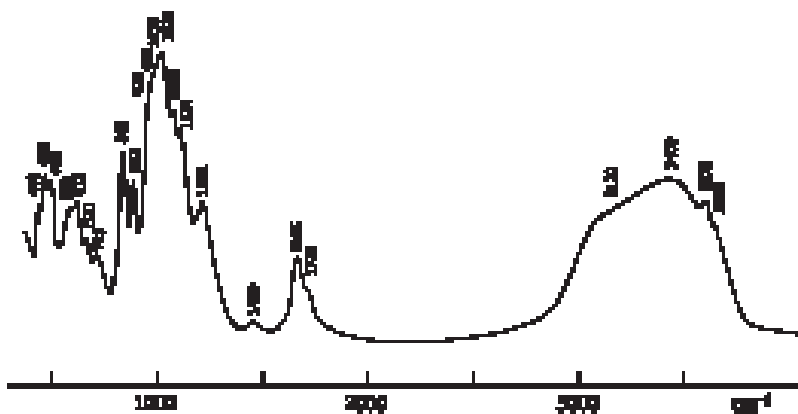


Fig. 2. IR spectrum of megacyclite.

or in crusts overgrown microcline. These spherulites are white, jonquil, or yellowish brownish on the surface and are composed of individual lamellar or columnar crystals.

According to local environment and intimate association with minerals unstable in the presence of surface water (villiaumite, natrosilite and revdite), megacyclite is endogenic rather than supergene. It seems to crystallize from residual fluid enriched in Na and K and derived from earlier peralkaline minerals during alteration. Megacyclite is one of the low-temperature phases in these pegmatites. It formed at temperatures not higher than 100–130°C, where the mobility of Ti, Zr, Fe and Al is already low, even in high-alkali media. Conditions of formation of such hydrothermal rocks are described by Lovskaya *et al.* (2002).

Individual crystals of megacyclite have mica-like cleavage and vitreous luster. In most cases, they are colorless and water clear. During extended interaction with dry air, megacyclite becomes opaque and white. However, its X-ray diffraction pattern and IR-spectrum were not modified. Optical properties of our samples are practically identical to those of the type material described by Khomyakov *et al.* (1993). Density of the Khibiny sample measured by A.E. Zadov by heavy liquids is 1.89(1) g/cm³.

The chemical composition was studied with a Camebax MBX/Link AN 10000 at an accelerating voltage 15.7 kV, current 1.5 nA, analyst A.N. Nekrasov. The low current and the defocused beam (10 x 10 μm) avoided damage of the sample during analysis. The water content

in our sample from Khibiny was determined by the Alimarin method: a ground sample was heated up to 1000°C and the released water was trapped in an adsorption tube filled with Mg(ClO₄)₂, analyst A.S. Astakhova. The average chemical composition is as follows (wt %, range of contents in parentheses, 6 analyzed points): 3.69 (3.5–4.0) K₂O, 19.85 (19.1–20.1) Na₂O, 42.74 (41.3–43.8) SiO₂, 33.03 H₂O, total 99.31. Other elements with Z > 8 are below detection limit. The empirical formula calculated on the basis of [Si₉(O,OH)₂₇] is as follows: K_{0.99}Na_{8.11}Si₉O_{18.10}(OH)_{8.90}·18.75H₂O, very close to the ideal formula KNa₈Si₉O₁₈(OH)₉·19H₂O. The ideal chemical composition calculated from this formula is (wt %): 3.74 K₂O, 19.69 Na₂O, 42.94 SiO₂, 33.63 H₂O, total 100.00. For the Lovozero specimen, the following electron microprobe data were obtained (wt %): 3.8 K₂O, 19.5 Na₂O, 43.5 SiO₂, total 66.8.

In contrast to the authors of the original description of megacyclite, we had sufficient material to allow collection of much higher quality infrared and X-ray powder diffraction data.

In Khomyakov *et al.* (1993), only the set of maximum frequencies of bands in the IR-spectrum was published, whereas the spectral curve was not given and virtually no interpretation of the spectrum was given.

The IR-spectrum of our Khibiny sample (Fig. 2) (in KBr disc, measured on a Specord 75 IR spectrophotometer) contains characteristic absorption bands of water (3300–3700 cm⁻¹ stretching vibrations, 1665 cm⁻¹ = bending vibrations). Most water molecules form hydrogen bonds and appear in the spectrum as a

Table 1. X-ray powder diffraction data of megacyclite

$I_{meas.}$	$I_{calc.}$	$d_{meas.}$	$d_{calc.}$	hkl	$I_{meas.}$	$I_{calc.}$	$d_{meas.}$	$d_{calc.}$	hkl	$I_{meas.}$	$I_{calc.}$	$d_{meas.}$	$d_{calc.}$	hkl	
3	13	24.61	24.746	100	7	7	3.168	3.177	-6 1 3						
10	31	12.41	12.373	200		3		3.177	-4 1 4	4	3	2.207	2.210	-4 5 1	
2	5	9.27	9.293	011		3		3.162	-6 2 2	5	5	2.188	2.191	4 5 1	
6	6	8.84	8.843	-1 1 1	9	11	3.142	3.148	0 2 4	2	4	2.158	2.165	6 2 5	
5	15	8.23	8.249	300	100	100	3.089	3.098	1 2 4	1	1		2.153	7 1 5	
31	35	7.394	7.415	002	33	42	3.056	3.064	-5 3 1	1	2	2.134	2.141	10 2 2	
	1		7.261	2 1 1	9	17	2.999	3.004	5 3 1	1	1		2.136	-5 5 1	
7	5	7.276	7.261	-1 0 2	2	2		3.004	2 2 4	1	3	2.114	2.116	5 5 1	
32	36	6.944	6.955	1 0 2	40	40	2.976	2.981	0 4 0	1	1		2.113	10 1 3	
	4		6.325	-3 1 1	4	4		2.979	-8 1 1	2	2		2.101	10 3 0	
7	8	6.283	6.297	0 1 2	13	12	2.949	2.956	6 1 3	2	7	2.090	2.092	-8 4 2	
1	3	6.171	6.186	4 0 0	2	2		2.948	-3 3 3	2	1		2.083	-2 1 7	
2	8	6.123	6.152	2 0 2	28	29	2.930	2.938	-8 0 2	2	1	2.079	2.078	-11 1 3	
35	33	5.957	5.962	0 2 0	21	21		2.933	5 2 3	1	5	2.067	2.072	-7 1 6	
22	19	5.786	5.796	1 2 0	4	5	2.914	2.922	0 4 1	5	8	2.054	2.060	-3 1 7	
2	3	5.749	5.742	-3 0 2		3		2.907	-1 4 1	1	1		2.056	-6 5 1	
1	2	5.535	5.532	0 2 1	9	6	2.895	2.898	2 4 0	1	2	2.027	2.034	6 5 1	
1	2	5.487	5.491	4 1 0	1	1		2.897	1 4 1	1	2	2.020	2.025	-4 4 5	
5	7	5.355	5.371	2 2 0	1	1		2.878	3 2 4	1	1		2.020	10 2 3	
	1		5.365	1 2 1	1	2	2.877	2.871	-6 0 4	1	3	2.004	2.009	-8 0 6	
1	2	5.248	5.270	-4 1 1	1	2		2.877	2.871	10	11	1.989	1.992	1 5 4	
2	8	5.030	5.037	4 1 1	1	3	2.852	2.852	-8 1 2	1	2	1.942	1.946	5 5 3	
2	4	4.951	4.944	-4 0 2	8	15	2.820	2.826	-4 3 3	1	1		1.932	-12 1 3	
1	1	4.892	4.852	3 1 2	3	8	2.796	2.803	3 4 0	3	3	1.913	1.918	7 3 5	
15	18	4.633	4.646	0 2 2	2	2		2.791	-6 1 4	1	1		1.914	12 2 1	
1	1	4.605	4.608	-1 2 2	3	7	2.776	2.782	6 3 1	2	2		1.904	10 4 0	
	2		4.577	4 0 2	3	3		2.763	2.766	0 4 2	2	2	1.900	1.904	-8 2 6
12	23	4.517	4.526	1 2 2	1	2	2.733	2.734	-8 2 1	1	1		1.901	-5 2 7	
14	35	4.452	4.460	-5 1 1	1	1	2.706	2.702	7 1 3	2	7	1.883	1883	-13 1 1	
40	69	4.275	4.282	5 1 1	6	6		2.685	4 4 0	7	8	1.876	1.879	6 5 3	
1	4	4.176	4.185	-4 2 1	23	14	2.674	2.679	9 1 0	1	1		1.864	-11 3 3	
1	1	4.130	4.136	-3 2 2	7	7		2.678	1 3 4	2	1	1.857	1.855	-2 0 8	
	1		4.124	6 0 0	2	2		2.672	-9 1 1	1	3	1.828	1.832	-3 5 5	
2	3	3.972	3.975	5 0 2	7	7	2.651	2.658	-4 4 1	2	5	1.812	1.816	-13 2 1	
	2		3.966	3 2 2	2	2		2.656	6 0 4	1	1		1.815	-4 0 8	
1	1	3.834	3.840	-6 1 1	18	26	2.641	2.646	-9 0 2	2	2		1.813	2 0 8	
31	38	3.798	3.808	-4 1 3	2	3	2.620	2.627	4 4 1	3	5	1.802	1.804	-4 5 5	
3	5	3.739	3.743	-5 2 1	1	1		2.617	2 3 4	5	5		1.781	-4 6 3	
14	8	3.714	3.728	1 2 3	1	7	2.566	2.570	5 3 3	10	8	1.776	1.778	10 3 4	
4	2	3.690	3.708	0 0 4	1	1	2.528	2.537	4 1 5	1	1		1.752	-14 1 1	
	5		3.703	6 1 1	10	17	2.495	2.500	5 4 1	3	2	1.748	1.752	-1 6 4	
	1		3.700	-2 2 3	3	4	2.464	2.472	-8 0 4	2	2		1.751	0 6 4	
5	15	3.632	3.636	5 2 1	6	5	2.434	2.441	1 0 6	3	3		1.745	-13 2 3	
	1		3.631	4 2 2	17	17	2.414	2.421	-8 1 4	10	9	1.740	1.743	1 6 4	
19	16	3.617	3.625	1 0 4	9	3		2.420	6 3 3	2	2		1.740	-12 1 5	
3	8	3.570	3.577	2 2 3	6	7	2.405	2.410	5 1 5	3	3		1.734	2 2 8	
1	2	3.536	3.540	0 1 4	9	12	2.385	2.391	1 1 6	4	4		1.719	-13 3 1	
2	3	3.504	3.503	0 3 2	2	2	2.374	2.377	0 3 5	5	5		1.716	-8 5 4	
	3		3.490	6 0 2	2	2	2.348	2.352	1 3 5	7	1	1.712	1.712	5 5 5	
10	11	3.480	3.484	-5 1 3	1	4	2.336	2.342	2 1 6	1	1		1.712	-3 4 7	
36	23	3.464	3.469	1 1 4	2	4	2.312	2.317	9 2 2	4	4		1.712	5 6 3	
1	3	3.373	3.379	3 2 3	3	3		2.307	-5 4 3	1	2	1.693	1.698	-14 2 1	
1	2	3.361	3.359	-7 1 1	9	7	2.297	2.302	1 4 4	2	2		1.697	-7 0 8	
	2		3.339	2 1 4	8	11	2.275	2.281	6 1 5	1	1		1.691	-4 4 7	
	1		3.338	2 3 2	1	1		2.275	-2 2 6	1	1	1.688	1.687	-12 2 5	
5	4	3.331	3.332	-4 2 3	3	3		2.275	5 2 5	3	3		1.680	-7 1 8	
	5		3.293	-7 0 2	1	1		2.271	-3 5 1	4	4		1.664	6 5 5	
8	8	3.285	3.292	-4 3 1	9	3	2.268	2.270	0 5 2	4	9	1.659	1.660	6 3 7	
3	4	3.243	3.252	7 1 1	2	2		2.267	-4 3 5	2	1		1.648	-8 0 8	
	1		3.241	5 1 3	5	3	2.253	2.259	1 2 6	3	3	1.646	1.641	-14 2 3	
					1	1		2.256	1 5 2	4	4	1.629	1.633	-3 6 5	
										2	2		1.625	-3 1 9	

Table 2. Crystal data and X-ray single-crystal measurement parameters for megacyclite

Formula	$K_2Na_{16}Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2(H_2O)_{36}[(H_2O)_{0.75}(OH)_{0.25}]_2$
Unit-cell parameters, Å	$a = 24.8219(16)$, $b = 11.9236(8)$, $c = 14.8765(9)$, $\beta = 94.486(5)^\circ$
Space group; Z	$P2_1/c$; 2
Unit-cell volume of unit cell V , Å ³	4389.5(5)
Calculated density ρ , g/cm ³	1.905
Extinction coefficient μ , mm ⁻¹	0.573
Formula weight	1259.21
F_{000}	2592
Crystal size, mm	0.24 x 0.45 x 0.32
Diffractometer	Xcalibur S (CCD)
Radiation; wave length, Å	MoK α $\lambda = 0.71073$
Range for data collection θ , °	3.68, 57.79
Scanning intervals	$-54 \leq h \leq 57$; $-17 \leq k \leq 17$; $-32 \leq l \leq 32$
Total reflections	130583
Number of reflections with $I > \sigma(I)$	39442
Number of inequivalent reflections with $I > \sigma(I)$	10773
Number of inequivalent reflections with $I > 2\sigma(I)$	8206
Number of refined parameters	761
$R_f [I > 2\sigma(I)]$	0.0339
$wR(F^2) [I > 2\sigma(I)]$	0.0598
GOF	0.973
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å ³	0.502/-0.388

strong broad band with a maximum at 3400 cm⁻¹. The weak narrow band at 3575 cm⁻¹ corresponds to stretching of O-H fragments of H₂O groups where the H is not involved in hydrogen bonding. The total intensity of this band is about 1% of the intensity of band at 3400 cm⁻¹, indicating an insignificant content of free OH-groups (really, taking into account a decreasing transition probability coefficient, it can be concluded that the amount of such groups rather more than 1%).

The broad shoulder at 3120 cm⁻¹ is attributed to O-H-stretching fragments of Si-OH, "weak-acid hydroxyls". The shoulder at 1720 cm⁻¹ is not characteristic of H₂O molecules. Usually, the bands in the range of 1700–1760 cm⁻¹ are assigned to oxonium ions (Yukhnevich, 1973; Wilkins *et al.*, 1974). Taking into account the acid nature of the Si-OH groups, the existence of equilibrium $Si-OH^{+\delta} + H_2O \leftrightarrow Si-O^{\delta-} + H_3O^+$ in megacyclite to form short-lived oxonium ions may be assumed. In the case of megacyclite, this equilibrium should be shifted left, because accord-

ing to the frequency of SiO-H stretching vibrations (3120 cm⁻¹), cyclic anion of megacyclite may be considered as residual of very weak acid.

The weighted average frequency of Si-O stretching vibrations $\langle \nu \rangle$ (range 840–1230 cm⁻¹) is shifted more than 30 cm⁻¹ to higher values from ~980 cm⁻¹, which is typical of silicates with simple isolated rings of Si-tetrahedra (Chukanov, 1995). According to our data, the increasing of $\langle \nu \rangle$ during protonation of the Si-O anion is characteristic of most acidic silicates, including rosenhanite, chesnokovite, afwilite and hydroxyl members of the lovozerite group.

The IR-spectrum of megacyclite from Lovozero is identical to that from Khibiny.

X-ray powder diffraction pattern of our sample of megacyclite from Khibiny was recorded with a STOE - STADI MP powder diffractometer using a Ge(111) curved monochromator, linear position-sensitive detector, and CuK α radiation. Calculation of the theoretical XRD powder pattern (software package WinXPOW, 2005) in accord with experiments (Table 1).

Table 3. Atom coordinates, equivalent atom displacements, and site occupancy in the structure of megacyclite

Atom	x	y	z	U_{eq}/U_{iso}^*	Atom	x	y	z	U_{eq}/U_{iso}^*
K	0.91382(2)	0.14525(5)	0.72291(3)	0.03881(13)	O(25)	0.09694(5)	0.16394(11)	0.70337(8)	0.0215(3)
Na(1)	0.34232(3)	0.12237(7)	0.34597(5)	0.02689(19)	O(26)	0.52769(7)	0.18390(14)	0.76158(13)	0.0272(4)
Na(2)	0.44824(3)	0.13180(7)	0.82325(5)	0.0289(2)	H(26a)	0.5282(11)	0.164(2)	0.7162(18)	0.054(10)*
Na(3)	0.55939(3)	0.12869(7)	0.28837(6)	0.0324(2)	H(26b)	0.5536(10)	0.1526(19)	0.7832(15)	0.033(8)*
Na(4)	0.22742(3)	0.13972(6)	0.86258(5)	0.02652(19)	O(27)	0.63890(7)	0.18017(14)	0.23162(12)	0.0264(4)
Na(5)	0.78914(3)	0.12064(7)	0.25418(5)	0.02935(19)	H(27a)	0.6627(9)	0.1479(19)	0.2508(15)	0.027(8)*
Na(6)	0.67336(3)	0.13710(7)	0.76626(6)	0.0324(2)	H(27b)	0.6405(9)	0.166(2)	0.1835(16)	0.036(8)*
Na(7)	0.11812(3)	0.11694(7)	0.40322(6)	0.0354(2)	O(28)	0.19670(6)	0.16976(14)	0.33956(13)	0.0266(4)
Na(8)	0.01282(4)	0.05626(9)	0.11570(6)	0.0446(3)	H(28a)	0.2213(9)	0.1435(18)	0.3683(15)	0.028(7)*
Si(1)	0.297439(19)	0.17493(4)	0.54092(3)	0.01369(11)	H(28b)	0.2008(11)	0.157(2)	0.2943(18)	0.052(10)*
Si(2)	0.71951(2)	0.17838(4)	0.44664(3)	0.01423(11)	O(29)	0.30838(6)	0.19508(14)	0.80967(12)	0.0255(4)
Si(3)	0.400360(19)	0.17567(4)	0.01732(3)	0.01369(11)	H(29a)	0.3297(9)	0.1563(19)	0.8418(15)	0.034(7)*
Si(4)	0.61727(2)	0.18088(4)	0.97530(3)	0.01496(11)	H(29b)	0.3114(11)	0.181(2)	0.7653(19)	0.063(11)*
Si(5)	0.50792(2)	0.18194(4)	0.49761(3)	0.01547(11)	O(30)	0.94346(5)	0.14092(11)	0.48509(9)	0.0243(3)
Si(6)	0.19635(2)	0.18284(4)	0.06553(3)	0.01437(11)	O(31)	0.45601(5)	0.23503(11)	0.99030(9)	0.0271(3)
Si(7)	0.81558(2)	0.17287(4)	0.92411(3)	0.01483(11)	O(32)	0.12566(6)	0.00013(11)	0.59820(9)	0.0285(3)
Si(8)	0.14334(2)	0.11673(4)	0.64686(3)	0.01471(11)	O(33)	0.41257(8)	0.06048(14)	0.68015(11)	0.0318(4)
Si(9)	0.88173(2)	0.11110(4)	0.46350(3)	0.01564(11)	H(33a)	0.4321(11)	0.085(2)	0.6483(18)	0.055(10)*
O(1)	0.71992(5)	0.10119(12)	0.35537(9)	0.0191(3)	H(33b)	0.3768(12)	0.077(2)	0.6651(18)	0.067(9)*
H(1)	0.7150(9)	0.0333(18)	0.3548(14)	0.028(7)*	O(34)	0.75341(7)	0.19701(15)	0.70393(12)	0.0290(4)
O(2)	0.27993(5)	0.09279(12)	0.45507(9)	0.0200(3)	H(34a)	0.7550(10)	0.182(2)	0.6552(17)	0.043(9)*
H(2)	0.2728(11)	0.026(2)	0.4583(18)	0.066(10)*	H(34b)	0.7731(9)	0.1575(18)	0.7254(15)	0.021(7)*
O(3)	0.16938(5)	0.10964(12)	0.98044(9)	0.0192(3)	O(35)	0.62623(8)	0.06541(14)	0.62515(12)	0.0348(4)
H(3)	0.1672(10)	0.039(2)	0.9860(17)	0.059(9)*	H(35a)	0.5896(11)	0.082(2)	0.6129(16)	0.052(8)*
O(4)	0.29887(5)	0.11160(11)	0.63522(8)	0.0203(3)	H(35b)	0.6392(13)	0.093(3)	0.590(2)	0.077(13)*
O(5)	0.61265(6)	0.10717(13)	0.88171(9)	0.0217(3)	O(36)	0.55876(5)	0.23442(12)	0.98791(10)	0.0351(4)
H(5)	0.6071(11)	0.043(2)	0.8851(18)	0.060(10)*	O(37)	0.74524(7)	0.05079(13)	0.11455(10)	0.0286(4)
O(6)	0.38321(6)	0.09797(12)	0.92889(9)	0.0215(3)	H(37a)	0.7666(11)	0.075(2)	0.0840(17)	0.053(9)*
H(6)	0.3776(11)	0.031(2)	0.9326(18)	0.061(9)*	H(37b)	0.7074(11)	0.074(2)	0.0944(16)	0.060(8)*
O(7)	0.75123(5)	0.20640(10)	0.92225(9)	0.0205(3)	O(38)	0.30555(8)	0.05356(14)	0.20507(11)	0.0300(4)
O(8)	0.51367(6)	0.10963(11)	0.58735(8)	0.0275(3)	H(38a)	0.3247(11)	0.078(2)	0.1746(17)	0.051(10)*
O(9)	0.19976(5)	0.11501(10)	0.15772(8)	0.0194(3)	H(38b)	0.2697(12)	0.075(2)	0.1889(17)	0.066(9)*
O(10)	0.40724(5)	0.10633(11)	0.10854(8)	0.0233(3)	O(39)	-0.00211(8)	0.24854(15)	0.62662(13)	0.0426(5)
O(11)	0.82367(5)	0.09931(12)	0.83298(9)	0.0198(3)	H(39a)	0.9833(13)	0.215(3)	0.581(2)	0.104(14)*
H(11)	0.8171(9)	0.0367(18)	0.8338(15)	0.032(7)*	H(39b)	0.0262(14)	0.215(3)	0.639(2)	0.108(15)*
O(12)	0.35638(5)	0.22273(11)	0.51836(9)	0.0235(3)	O(40)	0.08499(7)	0.20186(14)	0.87558(12)	0.0295(4)
O(13)	0.50322(6)	0.10376(13)	0.40678(9)	0.0278(4)	H(40a)	0.0913(10)	0.185(2)	0.8190(19)	0.060(9)*
H(13)	0.4965(11)	0.041(2)	0.4101(18)	0.061(10)*	H(40b)	0.1067(11)	0.172(2)	0.9051(18)	0.059(10)*
O(14)	0.74530(5)	0.11403(11)	0.53314(8)	0.0216(3)	O(41)	0.03014(7)	0.04650(16)	0.41017(11)	0.0303(4)
O(15)	0.83506(5)	0.10594(11)	0.01271(8)	0.0222(3)	H(41a)	0.0334(9)	-0.0070(19)	0.4371(15)	0.029(8)*
O(16)	0.84737(5)	0.20972(10)	0.40773(8)	0.0205(3)	H(41b)	0.0046(10)	0.082(2)	0.4368(16)	0.051(8)*
O(17)	0.65669(5)	0.21333(11)	0.45761(9)	0.0246(3)	O(42)	0.87103(8)	0.14303(16)	0.18903(13)	0.0352(4)
O(18)	0.25601(5)	0.21879(10)	0.03407(9)	0.0210(3)	H(42a)	0.8969(11)	0.113(2)	0.1981(17)	0.050(10)*
O(19)	0.16028(5)	0.20192(10)	0.56640(8)	0.0188(3)	H(42b)	0.8651(9)	0.134(2)	0.1413(16)	0.035(8)*
O(20)	0.41959(7)	0.18052(14)	0.28331(13)	0.0273(4)	O(43)	0.96867(8)	0.00773(16)	0.24304(12)	0.0379(4)
H(20a)	0.4443(10)	0.145(2)	0.3088(16)	0.039(8)*	H(43a)	0.9485(9)	-0.041(2)	0.2583(15)	0.038(8)*
H(20b)	0.4181(11)	0.163(2)	0.2375(18)	0.050(10)*	H(43b)	0.9844(10)	0.021(2)	0.2860(11)	0.051(10)*
O(21)	0.19890(6)	0.09026(12)	0.71178(9)	0.0231(3)	O(44)	0.51857(8)	0.05720(14)	0.14594(12)	0.0343(4)
H(21)	0.2250(9)	0.0995(19)	0.6896(14)	0.030(7)*	H(44a)	0.5338(13)	0.083(3)	0.111(2)	0.083(13)*
O(22)	0.63775(6)	0.10804(11)	0.06030(9)	0.0288(3)	H(44b)	0.4816(11)	0.073(2)	0.1367(16)	0.056(8)*
O(23)	0.09260(7)	0.09683(14)	0.21876(11)	0.0309(4)	O(45)	0.97420(8)	0.18565(17)	0.87773(13)	0.0448(5)
H(23a)	0.1210(11)	0.094(2)	0.1956(17)	0.058(9)*	H(45a)	0.9658(12)	0.235(3)	0.912(2)	0.093(13)*
H(23b)	0.0898(12)	0.176(3)	0.215(2)	0.089(11)*	H(45b)	0.0075(12)	0.192(2)	0.8738(17)	0.059(9)*
O(24)	0.85386(6)	0.08407(12)	0.55810(9)	0.0253(3)	O(46)	0.94217(7)	0.02574(19)	0.00379(15)	0.0680(6)
H(24)	0.8199(9)	0.0927(18)	0.5588(14)	0.032(7)*	H(46a)	0.9136(5)	0.0501(19)	0.0070(16)	0.043(8)*

Notice: Positions of H atoms are given as coordinates of the electron density maximums resulted from these atoms

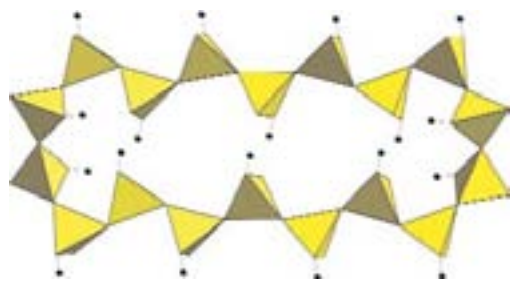


Fig. 3. Silicate ring in the structure of megacyclite (H atoms of OH groups on the apices of Si tetrahedra are shown as circles).

The crystal structure of megacyclite was refined using a single crystal selected from the new Khibiny material. Three-dimensional set of reflections was collected with a Xcalibur S CCD single-crystal diffractometer at room temperature. The crystal data are given in Table 2.

The crystal structure was determined by direct methods in the $P2_1/c$ using the SHELX-97 software package (Sheldrick, 1997). The final R_{hkl} is 0.0339 for 8206 unique reflections with $I > 2\sigma(I)$ in comparison with the refinement of the mineral structure to $R = 0.048$ for 2860 unique reflections with $I > 1.96\sigma(I)$ published by Yamnova *et al.* (1992). The final atom coordinates and parameters of equivalent atom displacements are listed in Table 3, interatomic distances, in Table 4, and characteristic of H-bonds, in Table 5.

As a result, the structural formula $K_2Na_{16}Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2(H_2O)_{36}[(H_2O)_{0.75}(OH)_{0.25}]_2$ has been refined and it is close both to the empirical formula of megacyclite calculated from the electron microprobe data and the formula given by Yamnova *et al.* (1992). Calculation of the bond valences for anions in the structure (Brese & O'Keefe, 1991) is given in Table 6.

As previously shown by Yamnova *et al.* (1992), Si-O rings consist of 18 tetrahedra and of composition $[Si_{18}O_{34}(OH)_{18}[O_{0.75}(OH)_{0.25}]_2]^{17.5-}$ are present in the structure of megacyclite (Fig. 3). The partial replacement of one oxygen atom [O(30)] by an OH-group is the only difference of our data from that previously reported (Yamnova *et al.*, 1992). This replacement is confirmed by calculated local valency balance (Table 6). Sum of the bond valences for O(30) is 1.72 vu, allowing the presence of both O and OH at this position.

The deficiency of negative charge resulted from this replacement is compensated by the partial substitution of one of water molecule [O(46)] by an OH-group, that is also confirmed by the calculation of valency balance the sum of which for this position is 0.27. In addition, only one hydrogen atom H(46a) is allocated near to the position of oxygen atom O(46), rather than two. In our case, the position corresponding to the second hydrogen atom for O(46) reported by Yamnova *et al.* (1992) is present in the difference synthesis as an extremely weak maximum ($0.31 e/\text{\AA}^3$) and its introduction into the structure model. Taking into account allocation of the other 46 hydrogen atoms, the above data suggest the following replacement $[(H_2O)_{0.75}(OH)_{0.25}]$.

Polyhedra of eight non-equivalent Na atoms and one K atom in the structure of megacyclite form a framework (Fig. 4). In contrast to Yamnova *et al.* (1992), we have assigned larger coordination numbers to most cations: six Na atoms are [6]-coordinated, two are [5]-coordinated and K is [7]-coordinated. An overview of the crystal structure of megacyclite is shown in Figure 5.

The major differences of our results from data reported by Yamnova *et al.* (1992) are related to the allocation of several hydrogen atoms and description of the hydrogen bond system in the structure. The position of H(3) reported by Yamnova *et al.* (1992) that should correspond to atom H(39b) according to our data does not result in an O(39) – H(3) distance of 2.541\AA (Yamnova *et al.*, 1992). The atom coordinates of H(45) and H(46) given in the first description of the megacyclite structure are entirely consistent with the position of the Si(1) atom (Yamnova *et al.*, 1992). These discrepancies are probably related to the errata in the referred article. In our case, these hydrogen atoms (H(13) and H(40a), respectively) are allocated with different coordinates and are characterized by the following distances to the corresponding oxygen atoms O(13) – H(13) = $0.77(3)$ and O(40) – H(40a) = $0.89(3)\text{\AA}$. The H(1) atom coincides with H(44) (Yamnova *et al.*, 1992). However, in our case, this atom is slightly displaced and the O(44) – H(1)[H(44a)] ... O(22) hydrogen bond is not observed. The presence of such a "free" hydrogen atom is confirmed by IR-spectroscopy (see above). The O(5) – H(5)

Table 4. Interatomic distances (Å) in the structure of megacyclite

K seven-vertex polyhedron		Na(1) six-vertex polyhedron		Na(2) six-vertex polyhedron		Na(3) six-vertex polyhedron	
K - O(45)	2.6913(19)	Na(1) - O(20)	2.3039(18)	Na(2) - O(26)	2.3239(17)	Na(3) - O(27)	2.2902(18)
- O(42)a	2.770(2)	- O(2)	2.3560(15)	- O(6)	2.3737(16)	- O(13)	2.3495(17)
- O(24)	2.8613(15)	- O(38)	2.3665(18)	- O(33)	2.3966(18)	- O(26)d	2.3921(19)
- O(39)b	2.897(2)	- O(29)d	2.3808(18)	- O(20)a	2.4084(19)	- O(33)c	2.3958(18)
- O(11)	2.9260(15)	- O(35)c	2.3989(19)	- O(44)c	2.4307(19)	- O(44)	2.4305(19)
- O(23)c	3.0220(18)	- O(12)	2.8267(16)	- O(31)	2.7665(16)		
- O(41)c	3.3932(19)						
<K - O>	2.937	<Na(1) - O>	2.439	<Na(2) - O>	2.450	<Na(3) - O>	2.372
Na(4) six-vertex polyhedron		Na(5) six-vertex polyhedron		Na(6) five-vertex polyhedron		Na(7) six-vertex polyhedron	
Na(4) - O(29)	2.3111(18)	Na(5) - O(42)	2.3347(19)	Na(6) - O(38)c	2.3641(18)	Na(7) - O(28)	2.3209(18)
- O(21)	2.3734(16)	- O(1)	2.3825(15)	- O(34)	2.3678(19)	- O(40)d	2.3367(18)
- O(3)	2.3819(15)	- O(37)	2.4171(18)	- O(27)a	2.3823(18)	- O(41)	2.3496(18)
- O(37)c	2.3875(17)	- O(34)d	2.4431(19)	- O(5)	2.3985(16)	- O(24)c	2.5488(16)
- O(28)a	2.4121(18)	- O(21)c	2.5777(16)	- O(35)	2.474(2)	- O(19)	2.7599(15)
- O(18)e	2.7600(15)	- O(16)	2.8140(15)			- O(23)	2.7780(18)
<Na(4) - O>	2.438	<Na(5) - O>	2.495	<Na(6) - O>	2.397	<Na(7) - O>	2.516
Na(8) six-vertex polyhedron		Si(1)-tetrahedron		Si(2)-tetrahedron		Si(3)-tetrahedron	
Na(8) - O(43)f	2.334(2)	Si(1) - O(4)	1.5910(13)	Si(2) - O(14)	1.5892(13)	Si(3) - O(10)	1.5869(13)
- O(46)f	2.350(2)	- O(12)	1.6295(13)	- O(17)	1.6346(13)	- O(31)h	1.6301(13)
- O(39)d	2.364(2)	- O(18)a	1.6302(13)	- O(7)d	1.6381(13)	- O(12)d	1.6315(13)
- O(46)g	2.382(2)	- O(2)	1.6408(15)	- O(1)	1.6411(14)	- O(6)h	1.6378(14)
- O(23)	2.4558(18)						
- O(45)c	2.903(2)						
<Na(8) - O>	2.465	<Si(1) - O>	1.623	<Si(2) - O>	1.626	<Si(3) - O>	1.622
Si(4)-tetrahedron		Si(5)-tetrahedron		Si(6)-tetrahedron		Si(7)-tetrahedron	
Si(4) - O(22)e	1.5847(14)	Si(5) - O(8)	1.5863(14)	Si(6) - O(9)	1.5887(13)	Si(7) - O(15)e	1.5837(13)
- O(36)	1.6108(14)	- O(31)d	1.6218(13)	- O(3)h	1.6370(14)	- O(16)a	1.6346(13)
- O(17)a	1.6303(13)	- O(36)d	1.6238(14)	- O(19)d	1.6406(13)	- O(11)	1.6401(14)
- O(5)	1.6430(15)	- O(13)	1.6381(16)	- O(18)	1.6445(13)	- O(7)	1.6448(13)
<Si(4) - O>	1.617	<Si(5) - O>	1.617	<Si(6) - O>	1.628	<Si(7) - O>	1.626
Si(8)-tetrahedron		Si(9)-tetrahedron					
Si(8) - O(25)	1.5816(13)	Si(9) - O(30)	1.5813(13)				
- O(32)	1.6123(14)	- O(32)c	1.6152(14)				
- O(19)	1.6492(13)	- O(16)	1.6394(13)				
- O(21)	1.6511(15)	- O(24)	1.6479(14)				
<Si(8) - O>	1.624	<Si(9) - O>	1.621				

Notice: a: x, -y + 1/2, z + 1/2; b: x + 1, y, z; c: -x + 1, -y, -z + 1; d: x, -y + 1/2, z - 1/2; e: x, y, z + 1; f: x - 1, y, z; g: -x + 1, -y, -z; h: x, y, z - 1

Table 5. Hydrogen bonds in the structure of megacyclite

D-H	d(D-H), Å	D-H...A	d(D-A), Å	$\angle(\text{D-H}\cdots\text{A})^\circ$	H-D-H	$\angle(\text{H-D-H})^\circ$
O(1)-H(1)	0.82(2)	O(1)-H(1)···O(4)a	2.5855(19)	173.75		
O(2)-H(2)	0.82(3)	O(2)-H(2)···O(14)a	2.5537(19)	177.13		
O(3)-H(3)	0.84(3)	O(3)-H(3)···O(15)a	2.5752(19)	174.55		
O(5)-H(5)	0.78(3)	O(5)-H(5)···O(10)a	2.599(2)	178.58		
O(6)-H(6)	0.81(3)	O(6)-H(6)···O(22)a	2.5187(19)	176.87		
O(11)-H(11)	0.76(2)	O(11)-H(11)···O(9)a	2.6268(19)	176.86		
O(13)-H(13)	0.77(3)	O(13)-H(13)···O(8)a	2.581(2)	174.73		
O(20)-H(20a)	0.81(2)	O(20)-H(20a)···O(13)	2.815(2)	158.42	H(20a)-O(20)-H(20b)	106(3)
O(20)-H(20b)	0.71(3)	O(20)-H(20b)···O(10)	2.741(2)	174.74		
O(21)-H(21)	0.76(2)	O(21)-H(21)···O(4)	2.8217(19)	174.78		
O(23)-H(23a)	0.81(3)	O(23)-H(23a)···O(9)	2.885(2)	167.04	H(23a)-O(23)-H(23b)	94(2)
O(23)-H(23b)	0.94(3)	O(23)-H(23b)···O(25)b	2.864(2)	170.30		
O(24)-H(24)	0.85(2)	O(24)-H(24)···O(14)	2.7148(19)	167.60		
O(26)-H(26a)	0.72(3)	O(26)-H(26a)···O(8)	2.735(2)	168.80	H(26a)-O(26)-H(26b)	99(3)
O(26)-H(26b)	0.79(2)	O(26)-H(26b)···O(5)	2.809(2)	157.50		
O(27)-H(27a)	0.74(2)	O(27)-H(27a)···O(1)	2.782(2)	153.36	H(27a)-O(27)-H(27b)	99(2)
O(27)-H(27b)	0.74(2)	O(27)-H(27b)···O(22)	2.688(2)	171.48		
O(28)-H(28a)	0.78(2)	O(28)-H(28a)···O(2)	2.740(2)	171.30	H(28a)-O(28)-H(28b)	106(3)
O(28)-H(28b)	0.71(3)	O(28)-H(28b)···O(9)	2.790(2)	170.96		
O(29)-H(29a)	0.83(2)	O(29)-H(29a)···O(6)	2.724(2)	167.12	H(29a)-O(29)-H(29b)	108(3)
O(29)-H(29b)	0.69(3)	O(29)-H(29b)···O(4)	2.772(2)	162.58		
O(33)-H(33a)	0.76(3)	O(33)-H(33a)···O(8)	3.015(2)	156.55	H(33a)-O(33)-H(33b)	115(3)
O(33)-H(33b)	0.92(3)	O(33)-H(33b)···O(4)	2.914(2)	178.65		
O(34)-H(34a)	0.75(2)	O(34)-H(34a)···O(14)	2.719(2)	165.70	H(34a)-O(34)-H(34b)	101(2)
O(34)-H(34b)	0.73(2)	O(34)-H(34b)···O(11)	2.750(2)	153.27		
O(35)-H(35a)	0.94(3)	O(35)-H(35a)···O(8)	2.856(2)	177.70	H(35a)-O(35)-H(35b)	104(3)
O(35)-H(35b)	0.72(3)	O(35)-H(35b)···O(17)	3.192(2)	162.75		
O(37)-H(37a)	0.78(3)	O(37)-H(37a)···O(15)	2.868(2)	166.36	H(37a)-O(37)-H(37b)	113(2)
O(37)-H(37b)	1.00(3)	O(37)-H(37b)···O(22)	2.811(2)	176.53		
O(38)-H(38a)	0.74(3)	O(38)-H(38a)···O(10)	3.065(2)	158.07	H(38a)-O(38)-H(38b)	112(3)
O(38)-H(38b)	0.94(3)	O(38)-H(38b)···O(9)	2.764(2)	179.55		
O(39)-H(39a)	0.84(4)	O(39)-H(39a)···O(30)	2.731(2)	173.78	H(39a)-O(39)-H(39b)	105(3)
O(39)-H(39b)	0.81(3)	O(39)-H(39b)···O(25)	2.815(2)	161.88		
O(40)-H(40a)	0.89(3)	O(40)-H(40a)···O(25)	2.641(2)	172.52	H(40a)-O(40)-H(40b)	106(3)
O(40)-H(40b)	0.76(3)	O(40)-H(40b)···O(3)	2.742(2)	173.07		
O(41)-H(41a)	0.75(2)	O(41)-H(41a)···O(30)a	2.773(2)	169.25	H(41a)-O(41)-H(41b)	103(2)
O(41)-H(41b)	0.88(3)	O(41)-H(41b)···O(30)c	2.741(2)	171.42		
O(42)-H(42a)	0.74(3)	O(42)-H(42a)···O(43)	2.969(3)	171.06	H(42a)-O(42)-H(42b)	102(3)
O(42)-H(42b)	0.72(2)	O(42)-H(42b)···O(15)	2.740(2)	170.18		
O(43)-H(43a)	0.81(2)	O(43)-H(43a)···O(25)a	2.771(2)	176.68	H(43a)-O(43)-H(43b)	102(3)
O(43)-H(43b)	0.739(10)	O(43)-H(43b)···O(41)d	2.851(2)	176.32		
O(44)-H(44a)	0.73(3)				H(44a)-O(44)-H(44b)	112(3)
O(44)-H(44b)	0.93(3)	O(44)-H(44b)···O(10)	2.837(2)	175.58		
O(45)-H(45a)	0.81(3)	O(45)-H(45a)···O(30)e	2.757(2)	175.99	H(45a)-O(45)-H(45b)	107(3)
O(45)-H(45b)	0.84(3)	O(45)-H(45b)···O(40)	2.760(3)	175.07		
O(46)-H(46a)	0.771(9)	O(46)-H(46a)···O(15)	2.838(2)	176.49		

Notice: D – donor, A – acceptor **a**: -x + 1, -y, -z + 1; **b**: x, -y + 1/2, z - 1/2; **c**: x - 1, y, z; **d**: x + 1, y, z; **e**: x, -y + 1/2, z + 1/2

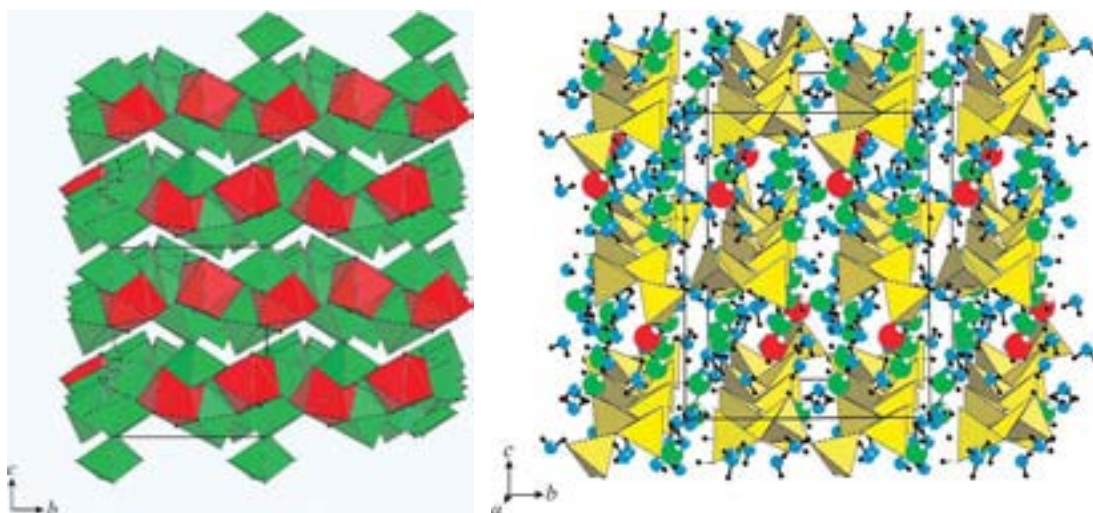


Fig. 4. The quasi-framework formed by Na-polyhedra (green) and K-polyhedra (red) in the structure of megacyclite; small black circles are H atoms.

Fig. 5. The crystal structure of megacyclite. SiO_4 tetrahedra are yellow, K atoms are shown as red circles, Na as green circles, O atoms of water molecules are blue, H atoms are small black circles.

... O(10) hydrogen bond recorded in our case is absent in the description of the megacyclite structure reported by Yamnova *et al.* (1992), and despite practically entire coincidence of hydrogen atomic coordinates (H(5) atom in our case corresponds to H(2) in referred article), the O(5) – H(2)[H(5)] ... O(28) hydrogen bond with the O(5)–O(28) distance of 2.602(8) Å given in the first description of the structure does not correspond to the distance O(5)–O(28) that is more than 6.8 Å. Furthermore, in our case, the bifurcated hydrogen bonds are not observable.

Since discovery of megacyclite, the 18-membered elliptic rings of ~19 Å in diameter containing in its structure are still the largest among the ring silicates. However, they are less than the ring components of tetrahedral frameworks of zeolites of different composition. Practically simultaneously with the discovery of megacyclite, a synthetic gallophosphate named cloverite (due to similarity of the zeolite cavity outlines to the leaves of clover). In its structure, 20-membered rings with a diagonal of 29–30 Å (Estermann *et al.*, 1991) that exceeds the usual sizes of pores in microporous compounds (2.5–20 Å). A framework containing 20-membered elliptical rings was identified in the structure of aluminophosphate zeolite JDF-20 with the following composition:

$[\text{Al}_5\text{P}_6\text{O}_{24}\text{H}]^{2-} 2[\text{N}(\text{C}_2\text{H}_5)_3\text{H}]^+ 2\text{H}_2\text{O}$ (Jones *et al.*, 1993). The gallophosphate zeolite NTHU-1, in the framework of which channels are formed by 24-membered rings, has been synthesized by Lin *et al.* (2006). These wide channels can comprise atoms of five transition metals that define peculiar fluorescent and magnetic properties of this compound. Against the background, silicogermanate zeolite ITQ-33 (abbreviation of Spanish name of Institute of Chemical Technology, Valencia, Spain) with pores outlined by 18- and 10-member rings does not appeared so effective, although the inner surface of its tetrahedral framework and its catalytic properties are great (Corma *et al.*, 2006). The above examples indicate extensive opportunities to synthesize novel materials with large tetrahedral structure components, which define their catalytic, ion-exchange, and sorption properties.

Acknowledgments

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Table 6. Calculation of bond valences for megacyclite

	K	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Na(7)	Na(8)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Si(7)	Si(8)	Si(9)	Σ^*	Contribution of hydrogen bonds**	Σ
O(1)[OH]							0.21			0.95									1.16	-0.30(O4) 0.19(O27)	1.05
O(2)[OH]		0.22							0.95										1.17	-0.32(O14) 0.21(O28)	1.06
O(3)[OH]					0.21									0.96					1.17	-0.31(O15) 0.21(O40)	1.07
O(4)							0.20		1.09				0.95						1.09	0.30(O1) 0.18(O21) 0.19(O29) 0.15(O33)	1.91
O(5)[OH]											0.96								1.15	-0.29(O10) 0.18(O26)	1.04
O(6)[OH]			0.21							0.96						0.94			1.17	-0.35(O22) 0.21(O29)	1.03
O(7)																			1.90		1.90
O(8)														1.10					1.10	0.30(O13) 0.21(O26) 0.13(O33) 0.16(O35)	1.90
O(9)																			1.10	0.27(O11) 0.16(O23) 0.19(O28) 0.20(O9)	1.92
O(10)																			1.10	0.29(O5) 0.21(O20) 0.12(O38) 0.17(O44)	1.89
O(11)[OH]		0.12							0.99										1.08	-0.27(O9) 0.20(O34)	1.01
O(12)																			2.03		2.03
O(13)[OH]			0.23							1.10				0.96					1.19	-0.30(O8) 0.18(O20)	1.07
O(14)																			1.10	0.32(O2) 0.22(O24) 0.22(O34)	1.86
O(15)													1.11						1.11	0.31(O3) 0.16(O37) 0.21(O42) 0.17(O46)	1.96
O(16)					0.06					0.97			0.97						1.99	0.10(O35)	1.99
O(17)									0.98					0.95					2.00		2.00
O(18)					0.07			0.07						0.95					1.95		2.05
O(19)																			1.95		2.00
O(20)[H ₂ O]		0.26	0.19		0.21	0.12													1.95	-0.18(O13) -0.21(O10)	0.06
O(21)[OH]																			0.45	-0.18(O4)	1.08
O(22)																			1.26		1.08
O(23)[H ₂ O]		0.09						0.07	0.17				1.11						1.11	0.35(O6) 0.23(O27) 0.18(O37)	1.87
O(24)[OH]		0.14						0.13											0.33	-0.16(O9) -0.16(O25)	0.01
O(25)																			1.21	-0.22(O14)	0.99
O(26)[H ₂ O]			0.24	0.20													1.12		1.12	0.16(O23) 0.18(O39) 0.26(O40) 0.19(O43)	1.91
O(27)[H ₂ O]			0.27		0.19		0.21												0.44	-0.21(O8) -0.18(O5)	0.05
O(28)[H ₂ O]					0.25			0.24											0.48	-0.19(O1) -0.23(O22)	0.06
O(29)[H ₂ O]																			0.43	-0.21(O2) -0.19(O9)	0.03
O(30)[O ₂ H]		0.21			0.21														0.46	-0.21(O6) -0.19(O4)	0.06
O(31)			0.07																1.12	0.21(O38) 0.19(O41) 0.21(O41) 0.20(O45)	1.72
O(32)												0.98							2.05		2.05
O(33)[H ₂ O]			0.20		0.20									1.00					2.05		2.05
O(34)[H ₂ O]						0.18	0.21												0.40	-0.13(O8) -0.15(O4)	0.12
O(35)[H ₂ O]					0.20		0.16												0.39	-0.22(O14) -0.20(O11)	0.12
O(36)													1.04						0.36	-0.16(O8) -0.10(O17)	-0.03
O(37)[H ₂ O]					0.20	0.19	0.22												2.04		2.04
O(38)[H ₂ O]																			0.39	-0.16(O15) -0.18(O22)	0.05
O(39)[H ₂ O]																			0.44	-0.12(O10) -0.20(O9)	0.12
O(40)[H ₂ O]		0.13																	0.35	-0.21(O30) -0.18(O25)	0.12
O(41)[H ₂ O]		0.03						0.23											0.23	-0.26(O25) -0.21(O3) 0.20(O45)	-0.04
O(42)[H ₂ O]		0.18						0.23											0.26	-0.19(O30) -0.21(O30) 0.17(O43)	0.03
O(43)[H ₂ O]						0.23													0.41	-0.14(O43) -0.21(O15)	0.06
O(44)[H ₂ O]			0.18	0.18				0.24											0.24	0.14(O42) -0.19(O25) -0.17(O41)	0.02
O(45)[H ₂ O]									0.05										0.36	-0.17(O10)	0.19
O(46)[H ₂ O]									0.21										0.27	-0.20(O30) -0.20(O40)	0.13
OH										0.23									0.44	-0.17(O15)	0.27
Σ			0.91	1.17	1.09	1.08	1.13	0.99	1.00	0.97	1.12	4.01	3.98	4.02	4.08	4.06	3.96	3.98	4.01	4.04	

Notice: * Sum excepting hydrogen bonds.

** Oxygen atoms, which are donors (negative values) and/or acceptor (positive values) are in parentheses; values of valence contributions of oxygen and water molecules located at the longest distances in the Na and K polyhedra are in italic

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ON THE COMPOSITION AND NOMENCLATURE OF THE LOELLINGITE-GROUP DIARSENIDE MINERALS

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The composition of loellingite-group diarsenide minerals with wide range of Fe, Co, and Ni content is discussed. A nomenclature distinguishing mineral species loellingite, safflorite and rammelsbergite, and Co-bearing loellingite, Ni-bearing loellingite, Fe-bearing safflorite, Co-bearing rammelsbergite, and Fe-bearing rammelsbergite is suggested. Chemical composition fields and Fe, Co, Ni concentration (at %) range in minerals and varieties are presented. This nomenclature allows to recognize features of individual compositions of the loellingite-group diarsenides that corresponds to their names.

1 table, 1 figure, 12 reference

Rhombic diarsenides of the loellingite group including loellingite FeAs_2 , safflorite CoAs_2 , and rammelsbergite NiAs_2 with structures similar to marcasite (Borishanskaya *et al.*, 1981; Vinogradova & Bochek, 1980). Rhombic parammelsbergite NiAs_2 , cubic krutovite NiAs_2 , and monoclinic clinosafflorite CoAs_2 are less abundant and are different from the loellingite-group minerals in structure. However, the structure of clinosafflorite is very similar to the structure of loellingite/safflorite.

Diarsenides of the loellingite group (Borishanskaya *et al.*, 1981) are characteristic of Co-Ni-Ag-Bi-U deposits and similar Ni-Co arsenide deposits. In addition, they occur in Cu-Ni sulfide deposits and in niccolite-chromite veins. Loellingite and safflorite have been described from iron-bearing skarns, alkaline and granitic pegmatites. Furthermore, loellingite has been identified in greisen, sulfide-cassiterite, and arsenopyrite deposits.

Compositional data on the natural diarsenides of the loellingite group are reviewed by Borishanskaya *et al.* (1981), Vinogradova & Bochek (1980) and Gritsenko *et al.* (2004). All three metals of the iron group form these diarsenides with one or two of them predominating. Natural solid-solutions of the continuous loellingite-safflorite series are common, whereas the solid solutions of the continuous safflorite-rammelsbergite series are less abundant. Recently, solid solutions of the continuous safflorite-rammelsbergite series were discovered (Gritsenko *et al.*, 2004). Due to the latter discovery, the previously recorded field of ternary solid-solution (Vinogradova & Bochek, 1980) in the loellingite group indicates

the practically complete isomorphic substitution between Fe, Co, and Ni in the loellingite-group diarsenides and wide range of concentrations of these elements (Fig. 1a).

Previously, some scientists have tried to define limits of the loellingite-group minerals on the basis of chemical composition, but such limits are not universally agreed upon (Vinogradova & Bochek, 1980). Current available compositional data for the loellingite-group diarsenides and suggested nomenclature of minerals in ternary systems (Nickel, 1992) allow development of a comprehensive nomenclature of the loellingite-group diarsenides. According to Nickel (1992), loellingite $(\text{Fe,Co,Ni})\text{As}_2$, safflorite $(\text{Co,Fe,Ni})\text{As}_2$, rammelsbergite $(\text{Ni,Co,Fe})\text{As}_2$, and corresponding composition fields should be defined on the basis of the predominant iron-group metal (Fig. 1b). However, compositional features of individual representatives of the loellingite group are lost in this approach due to the wide range of composition of each mineral. Therefore, modification of the nomenclature is advisable, and proper minerals (loellingite, safflorite, and rammelsbergite) and their varieties should be defined. The 80 at.% content of the major metal is taken as the limit between a mineral species and a variety. This is justified by the observation that diarsenides with 80 and more at.% of the major metal are not zoned under reflected light, whereas diarsenides with more complex composition are characterized by zoning. It should be noted that the rhombic symmetry of safflorite is modified to monoclinic (clinosafflorite) at a Co content of 80 at.% (Radcliffe & Berry, 1968; 1971)

and there is dimorphism of CoAs_2 at higher Co contents. Furthermore, it should be taken into account that simple formulae MeAs_2 , corresponding to the compositions of type minerals with dominant content of Fe, Co, or Ni, are given in textbooks and handbooks on mineralogy. Previously reported Co-rich rammelsbergite (Vinogradova *et al.*, 1972), Ni-rich loellingite (Oen *et al.*, 1971; Bukovshin & Chernyshov, 1985; Cervilla & Ronsbo, 1992; Gamyarin & Lykhina, 2000), Ni- and Co-rich loellingite (Distler *et al.*, 1975), and Ni-rich safflorite (Radcliffe, Berry, 1968) correspond to varieties of corresponding minerals named according to their chemical features.

Taking into account the above arguments, the nomenclature of the rhombic diarsenides of the loellingite group can be presented as follows. In the composition fields of loellingite, safflorite and rammelsbergite (Fig. 1b), mineral species (end members) are defined as follows: loellingite, safflorite and rammelsbergite with a content of the major metal of 80 and more at.%. Varieties (intermediate members) are as having a content of major metal of less than 80 at.%

Table. Nomenclature and chemical composition of the loellingite-group diarsenides (MeAs_2) based on relationship of Fe, Co, and Ni

Mineral species (end-members of isomorphic series)	Variety (intermediate members of isomorphic series)
Content of major Me > 80 at.%	Content of major Me < 80 at.%
1. Loellingite	1a. Co-bearing loellingite
$\text{Fe} \gg (\text{Co} + \text{Ni})$	$\text{Fe} > \text{Co} > \text{Ni}$
$\text{Fe}_{80-100}^* (\text{Co} + \text{Ni})_{20-0}$	$\text{Fe}_{80-33.3} \text{Co}_{10-50} \text{Ni}_{0-33.3}$
	1b. Ni-bearing loellingite
	$\text{Fe} > \text{Ni} > \text{Co}$
	$\text{Fe}_{80-33.3} \text{Ni}_{10-50} \text{Co}_{0-33.3}$
2. Safflorite	2a. Fe-bearing safflorite
$\text{Co} \gg (\text{Fe} + \text{Ni})$	$\text{Co} > \text{Fe} > \text{Ni}$
$\text{Co}_{80-100} (\text{Fe} + \text{Ni})_{20-0}$	$\text{Co}_{80-33.3} \text{Fe}_{10-50} \text{Ni}_{0-33.3}$
	2b. Ni-bearing safflorite
	$\text{Co} > \text{Ni} > \text{Fe}$
	$\text{Co}_{80-33.3} \text{Ni}_{10-50} \text{Fe}_{0-33.3}$
3. Rammelsbergite	3a. Co-bearing rammelsbergite
$\text{Ni} \gg (\text{Co} + \text{Fe})$	$\text{Ni} > \text{Co} > \text{Fe}$
$\text{Ni}_{80-100} (\text{Co} + \text{Fe})_{20-0}$	$\text{Ni}_{80-33.3} \text{Co}_{10-50} \text{Fe}_{0-33.3}$
	3b. Fe-bearing rammelsbergite
	$\text{Ni} > \text{Fe} > \text{Co}$
	$\text{Ni}_{80-33.3} \text{Fe}_{10-50} \text{Co}_{0-33.3}$

Notes: * is range of concentration of the iron-group metals (at.%). The composition fields of mineral species and varieties listed in this table are shown in Figure 1c.

and a predominance of one of two other metals: Co- and Ni-bearing loellingite, Fe- and Ni-bearing safflorite, and Co- and Fe-bearing rammelsbergite (Fig. 1c, Table).

The nomenclature suggested here is more exact and the individual compositions of diarsenide minerals are represented in the corresponding name.

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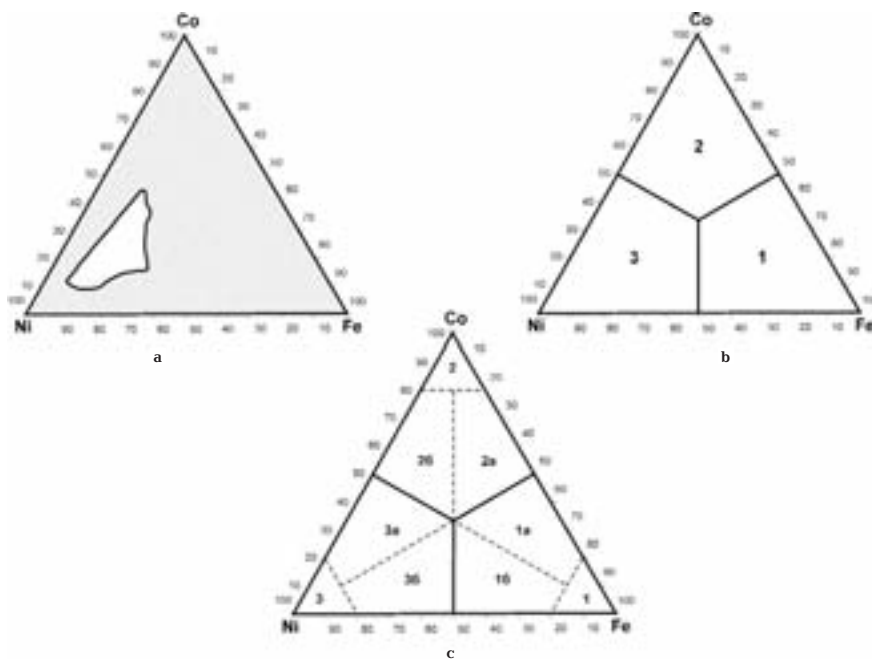


Fig. 1. Chemical composition and nomenclature of the loellingite-group diarsenide minerals on the basis of the proportion of Fe, Co u Ni (at. %).

(a) data on chemical composition (Vinogradova & Boček, 1980; Gritsenko et al., 2004); not identified natural compositions are white field.

(b) nomenclature and composition fields according to (Nickel, 1992): loellingite (1), safflorite (2), and rammelsbergite (3).

(c) suggested nomenclature and composition fields: loellingite (1), Co-bearing loellingite (1a), Ni-bearing loellingite (1b), safflorite (2), Fe-bearing safflorite (2a), Ni-bearing safflorite (2b), rammelsbergite (3), Co-bearing rammelsbergite (3a), and Fe-bearing rammelsbergite (3b). Crosspoint of lines in the center of ternary plot corresponds to equal contents of three metals (by 33.3 at. %)

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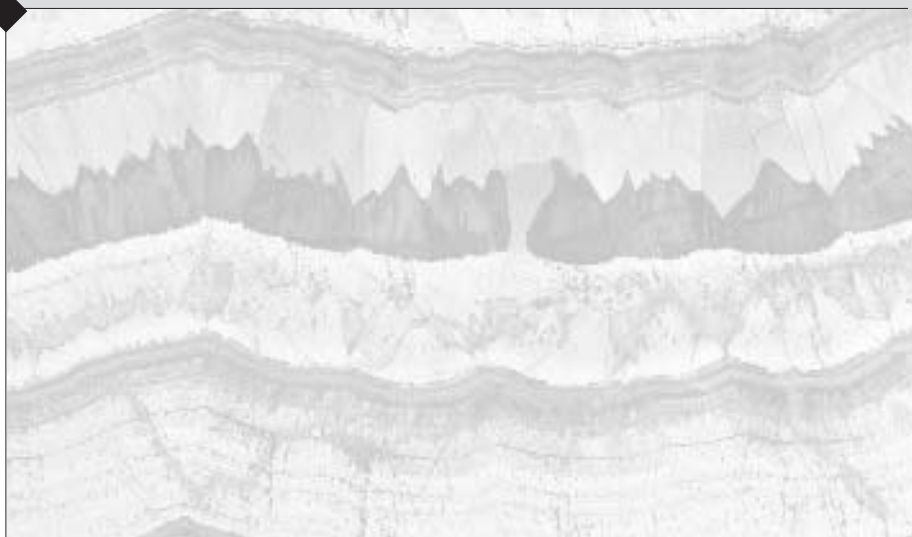
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Mineralogical Museums and Collections



STONE CUTTING IN THE URALS. ARTICLES OF MASTERS FROM EKATERINBURG IN THE FERSMAN MINERALOGICAL MUSEUM

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A brief history of the Ekaterinburg cutting factory and manufactures of this factory, private works, and artisans from the Urals are described.

20 photos, 20 references

The Urals Stone Belt of Russia, extending for thousands kilometers, was the first that opened its subsoil resources for people in our large country. The Russian stone-cutting art originated from this region nearly 300 years ago.

Everyone who is interested in the art of stone-cutting is familiar with the work of the skilled artisans of the Urals. The modern jewelry products of Russian gem factories are attractive for stone-cutting connoisseurs; appealing and inexpensive sculptures from the Kungur gypsum-selenite and anhydrite deposits gladden the eye of not too wealthy judge; and collectors search antique shops for goods produced by the workshops of A.K. Denisov-Ural'sky and I.N. Lagutyaev. Numerous magnificent articles of the Ekaterinburg stone-cutting factory, which was the pride of Russia's stone-cutting art in the 19th century, are the summit of the stone-cutting art in the Urals and are highly valued within the country and abroad. Undoubtedly, the products of this factory are the finest representatives of the Urals handicrafts, many of which reside in the Fersman Mineralogical Museum.

The Ekaterinburg cutting factory was founded by decree of the Senate on July 24, 1805. However, this was only the formal ratification of its existence. In reality, by this period, the factory had already successfully operated with fine local ornamental stone for many years. The first data on this stone appeared in the middle of the 17th century. In 1668, native Mikhail Tumashev found tourmaline, amethyst, and so called "*tumpasy*" (rock crystal after Mostovenko (1919) or rock crystal and morion after Bobylev (2005)) in the outskirts of the stockade town of Murzinka. Around the same time, Dmitry Tumashev announced about the finding of colored stones near village Murzinka. These stones were white rock crystals, cherry "*fatisy*" (amethyst after Bobylev

(2005) and/or hyacinth after Danilevsky (1948)), green "*yugi*" (chrysolites after Danilevsky (1948)) and yellow tumpasy and two emeralds, three stones with bright-red sparkles and three tumpasy upstream of the Neiva river in a mountain (Semenov, 2001).

The early 18th century, Russia was affirmed as a mighty empire that demanded the corresponding external appearances. Foundation of a new and distinctly well-planned majestic capital built of stone, which was extremely different from the other Russia's towns, had been one its the grandiose goals. This resulted in a necessity for of numerous building and ornamental materials that were practically unknown in Russia at the beginning of the century. The Revel' granite quarries were mined, but they did not play a key role. A special agency responsible for the development of a mining industry had to be created. In 1719, Peter the First established Berg College that had to provide regular exploration and mining of diverse domestic deposits including colored and building stone. At the same time, the state monopoly on mining was constituted (Semenov & Timofeev, 2001).

The Urals was the closest and most encouraging region, where iron and copper ores had been already mined and silver, gold, tin deposits, and gems as byproducts had been prospected. In 1722, the regular mining of malachite in Gumeski was commenced but only for copper (Semenov, 1987); in 1720, diamonds were identified; in 1723, the first marble deposits were found. There were the first attempts to manufacture gems; handicraftsmen had already "touched-up" stones of rock crystals (Shakinko, 1976).

Toward the end of the reign of Peter the First, interest in gems and their processing had become permanent. A project to establish a cutting-stone centre in Tobolsk was initiated but not realized.

In 1721, V.N. Tatishchev, mining chief of the Urals and Siberian works, proposed to build a new plant in the Urals on the Iset' river. According to his intention, therein, not only iron and copper had to be smelted but the finished commodity had to be produced; in the future, stone-cutting and lapidary production were planned at this plant. In 1723, because of the building of this factory, the foundations of Ekaterinburg were laid. In 1726, the small special stone-cutting government workshop was opened. As above mentioned, there were predecessors to this establishment. In 1723, Tatishchev wrote to the Siberian governor: "[I] amuse myself with books and lathe machine. And next summer, I shall cut the local diamonds..." (Semenov & Timofeev, 2001).

To the early 1730s, marble, rock crystal, amethyst, smoky quartz, aquamarine, beryl, tourmaline, and topaz were known in Russia, mostly in the Urals. In Dauria on the Argun' river, jasper was found. In 1735, to process available material, Tatishchev established the first separate lapidary works in the Isetsy plant.

The Swiss craftsmen Ya. Reiner had been invited to teach local workers. However, he had known only techniques of working by hand. Used these methods, the amount of material supplied to the capital was insufficient. In 1747, at the urgently built factory, Russian artificer N. Bakhorev installed a "machine operated by water" to cut marble. The processing of the first large marble block indicated that in cutting by hand, three men had to work for six days (Shakinko, 1976), whereas use of the machine allowed it to be done in 14 hours. Industrial processing of stone had started in Russia.

In 1751, an additional factory to cut hard stones such as agate, jasper and others was established in the Ekaterinburg works. In 1752, there were already three factories and one of them was used for faceting and polishing of stones. In addition, one more similar factory was built in the Siversky works near Ekaterinburg. Thus, an industrial complex for the all-purpose stone processing was established in the Urals. Unique engineering applications were developed. However, the increasing need for decoration of palatial rooms with various stones was still not satisfied due to lack of raw materials.

In 1765, Ekaterina II (Catherine the Great) issued an edict "*On establishment of the Expedition for prospecting of diverse color stones*" to improve the situation. The Expedition was under the leadership of Major General Ya.I. Danneberg, who had played a great role in development of the Urals industry. Numerous deposits, including ornamental stones, were explored during this period. At this time, marble, jasper-tuffite, jasper, chalcidony, perelivt (agate), quartzite, and porphyry were mined in the Urals. For the first time, to classify and estimate materials, rock collections were created that resulted in a necessity to polish hard rocks. Danneberg assured an affiliation of stone-cutting factory to the Expedition for better administration. Thereafter, the Expedition became subordinate to the Chancellery for buildings of Her Majesty of houses and gardens. The Empress became the exclusive owner of gems in Russia and enhanced attention was given to the factory.

Mapping of the colored stone deposits was the remarkable innovation for that time. The first map composed in 1766 was presented together with polished samples to the Empress, for her selection of material.

The 1770s were marked by the appearance of the first goods from hard stone. Initially, there were only pharmaceutical mortars, snuff-boxes, tabletops, and salvers. In 1782, the first bowls from agate and jasper were ordered.

The time of Ekaterina II is notable by the numerous events in cultural life of the capital. The passion for mineralogy was one of them. Mineralogical collection of Cabinet of curiosities was replenished; private collections arose. In 1780–1790, this passion was expressed in terms of the creation at the Ekaterinburg factory of a number of collections as distinctive embellishments of room *dé cor* including pyramids, grottos, and frames of mirrors. These were made from different stones and were accompanied with explanations. Against the background of this interest, the popularity of stone articles, including large ones, was increased. The orders came from the Cabinet of Her Majesty* and private individuals.

In 1784, I.K. Patrushev, manager of the Expedition, reorganized fabrication that had been a step forward for the development of

* The Cabinet of His Imperial Majesty (Cabinet) was established by Peter the Great as his chancellery. In 1832, the Ekaterinburg factory was under the jurisdiction of the Cabinet.

stone-cutting business in Ekaterinburg. In his time, the factory was technically reequipped; novel machines were installed; and the strict stocktaking and sorting of raw material were initiated. The term "rating" of masters and division of labor appeared for the first time. The children of artisans were become getting involved in stone cutting. This resulted in the appearance of many dynasties of the Urals stone-cutters. All these innovations allowed increasing production and the making of large manufactures.

In 1797, by the edict of Pavel I, the Expedition of stone breaking (the name appeared in 1782) was subordinated to the Academy of Arts. This was favorable for a rise in the level of prospecting and stone cutting. In 1880, the President of the Academy of Arts, Count A.S. Stroganov, who made an important contribution to development of Russian art stone cutting, headed the factory. In his time, by diverse innovations, the Expedition turned from industrial stone cutting into the Academy artistic shop of monument-decoration and sculpture art. The highly artistic products were made by individual orders. Designs, but not drawings, created for such projects and alabaster or wood models performed by the famous artist-architects A.N. Voronikhin and K.I. Rossi, made for the most complicated goods. The project development was so careful that even the number of stones recommended by the author was displayed in the design. This led to cost increases, and the funds assignable by the state treasury were insufficient. To increase finances, Stroganov permitted to manufacture small articles, including "...*snuffboxes round, oval salt-cellars, various inkstands, earrings, signets and others, using different kinds of decorative stone*" (Mavrodina, 2000). However, due to lack of money, in addition to public funds of 15,000 rubles, the count paid the remaining needed 5,000 rubles out of his own funds (Semenov & Timofeev, 2001).

The requirement for further development resulted in the opening of the "class for cutting of antiques" attached to the Expedition, where local boys received training in stone cutting. The most gifted children were sent to the Academy of Arts in St. Petersburg. Many of them became top quality masters.

After death of Stroganov, the factory lost its financial support. Strict economy was initiated;

the execution of private orders was forbidden; training in stone cutting was discontinued; despite the fact that most goods were made from hard stone, its mining was nearly curtailed. Curiously enough, these strict measures resulted in much more careful use of colored stone.

The burst of patriotic consciousness in Russia followed the victory over Napoleon was reflected in various arts, including architecture and interior design. Practically all stone-cutting products of this period have a mark of heroism and solemnity.

In the early 19th century, the Kolyvan' factory opened in Altay in 1802 became a serious rival for the Ekaterinburg factory. Therein, the production was based exclusively on the local raw material (jasper, quartzite, and porphyry) mined as giant monoliths. Those were used as a lapidary material for monumental pieces of art. The Urals with its diversity of ornamental stone and the highest professionalism of its masters, were crowded.

The Ekaterinburg factory had to defend its importance by the improvement and reduction in price of articles and perfecting of masters' skills using novel processing techniques. During this period, V.E. Kokovin, the famous Urals master, designed new facilities for stone processing. Shortly, Ya.V. Kokovin, his son, who become the master-in-chief of the factory after death of his father in 1818, had invented the famous machine that facilitated the processing of large products. Soon, this machine was used in Kolyvan' and Peterhof. In 1823, the Cabinet gave an award to Kokovin for this device (Semenov & Timofeev, 2001).

Due to different improvements, the factory began producing large lapidary goods, which were perfect by shape and high-level of master performance. In addition to usual stone cutting, the glyptic and methods of malachite mosaic were applied. Despite the regime of economy, the Cabinet planned radical technical reconstruction of the factory and the erection of new buildings. All predicted prosperity of stone-cutting production in Ekaterinburg, but it had not happened.

In 1830, the event that amazed the world of stone-cutting art in Russia took place and had a regrettable effect on the factory. Maxim Kozhevnikov, a tar extractor, found a few emerald crystals among the roots of a fallen tree and in January, 1831 Ya.V. Kokovin located the

emerald vein. One faceted stone accompanied with the message about the discovery was immediately sent to St. Petersburg. The "emerald rush" began. The Cabinet immediately monopolized mining of this precious stone and entrusted it to the Ekaterinburg factory. As a result, the stone-cutting production was nearly completely turned into mining, and skilful masters for the ornamental stone processing turned into miners.

At the same 1830s, the factory went through one more shock. The abuses permitted by Kokovin, the chief of the factory, who was fine artist, stone-cutter, connoisseur and lover of stone and a graduate of the Academy of Arts in St. Petersburg, had been revealed. The period of his leadership is considered as one of prosperity of stone-cutting art in the Urals. However, the submitted incriminations appeared to be so serious that he was suspended from leadership. The confidential relationship of the Cabinet to the administration of the factory was revised, and the factory was divested of self-dependence and was placed under the direct and absolute authority of the Cabinet. The special "Regulations" ordering the management of production were published to prevent such breaches in the future. A more accurate system of assessment was instituted; carving of the name of the master who had made an article became compulsory; the quality requirements were enhanced. Large pieces were produced only according to projects designed by metropolitan architects, who were outstanding art workers; only small articles were permitted by drawings of local masters. A.I. Lyutin, who had been an assistant of the factory leader since 1839, prepared the numerous drawings of such goods; in 1839, he became a director of the factory.

During this time, a new trend in stone-cutting art was originated at the factory due to effort of Lyutin. Mosaic goods began to be produced and the new techniques for creation of three-dimensional mosaic were assimilated. This original Ekaterinburg art was developed on the basis of Italian Florentine mosaic but instead of plane images, the masters created three-dimensional still lifes from berries, flowers, and leaves and sometimes, humorous subjects with figurines of animals. Mainly, there were "covers on paper" (paperweights). Bowls with fruits appeared to the end of the century. These products became popular and

since 1841, few articles had been produced each year (Semenov & Trofimov, 2003). The special creative period at the Ekaterinburg factory when the stone-cutting art acquired original features and developed simultaneously with the formal traditions was related to Lyutin.

In 1820 – 1840s, the art of malachite mosaic also thrived at the Ekaterinburg factory. During this period, unique goods were manufactured from this material. However, production of expensive large articles gradually declined. This was especially the case after the abolition of serfdom in 1861 when the increasing of remuneration of labor of civilian workers resulted in a significant rise in the cost of goods. The Court began to decline large articles in preference to small cabinet goods. Previously, in 1858, the production of high-priced malachite articles commercially purveyed for the Court was abrogated. After 1873, the factory did not operate with malachite at all (Semenov, 1987).

Fortunately, in the 1860s, the outstanding products of the Ekaterinburg factory were known throughout Europe. In 1851 and 1862, the stone-cutting goods were displayed at the World Fairs in London and in 1867, in Paris. Later, the invitation for the similar fair held in 1873 in Vienna was received. The Cabinet became interested again in large goods, which could amaze Europe. It was planned to produce the bowl from Kalkan jasper for the Vienna Fair. Architect A.I. Krakau developed the project. The work was continued for five years (1868 – 1873) under direct supervision of academician Lyutin.

In Vienna, the bowl made a great impression and was appreciated as the best of Russia's goods, and saved the factory from closing or handing over to private ownership.

The following years, the products of the Ekaterinburg factory were demonstrated at the World Fairs in Chicago (1893), Stockholm (1897), and again in Paris (1900).

In Russia, the products from Ekaterinburg were exhibited in St. Petersburg (1861), Moscow (1865, 1870, and 1882), and Nizhniy Novgorod (1896).

Despite the great success of goods from Ekaterinburg, the end of the 19th century was very stressful and troubled for the factory. Mining and faceting of gems were curtailed; articles from marble, malachite, porphyry, and

jasper were not produced. The Cabinet ordered the large goods mainly from rhodonite and the Kalkan jasper. Most orders were small art things, whereas the large things mainly repeat previous classic forms and ornament that is more complicated. Occasionally, this various ornament with some additions attracted more attention than the stone itself. However, during these years, the unique large articles in which the beauty of stone had been emphasized were produced according to the designs of famous architects, but such sporadic goods shortly disappeared from specification. This was mainly caused by the grandiose and honorable order in 1883 to produce stone ornamentation of two choir icon-cases, the ciborium, and tabernacle in Temple of Ascension that was built at the place of death of Alexander II. The order for the tabernacle in the Cathedral of the Redeemer at the Borki railway station, where the tsarist train crash took place in 1888, was also received. In contrast to the other products of the factory, the various colored stones of the Urals were used for decoration of this temple: various types of jasper, rhodonite, marble, and quartz. The production for the temple was continued till 1916.

During the period from 1885 to 1911, V.V. Mostovenko was the leader of the factory. According to his memoirs (Skurlov, 2001), he received the factory in a state of nearly complete devastation. Due to his energy and resourcefulness, the factory was again put into condition for production. Some new techniques for stone processing, which simplified the production of goods and notably improved working conditions, were initiated. The school for learning in reading and writing, drawing, and modeling was opened again. Methods of stone faceting, etching of stamps, and composition of glues were investigated in the newly established laboratory.

As in the past, the drawings for large goods came from the Cabinet. Occasionally, they were so poor that Mostovenko was permitted to correct them. The models for the numerous small things (cabinet, suite, fancies, and jewels) were elaborated at the factory. These items were supplied in St. Petersburg in abundance.

Despite still being occupied with the order for the temple, the factory was not released from other very important and prestigious orders for exhibitions in Russia and abroad. So,

in 1900, a unique mosaic map of France of 1 x 1 m in size was manufactured for the World's Fair in Paris. Mostovenko suggested the creation of this map and selected the material for its different portions. Diverse semi-precious and precious stones, gold, and platinum were applied. This map had great success, and the Ekaterinburg factory received the highest prize. The map was placed in the Louvre after the Fair and Mostovenko was decorated with the Knight Commander Cross of the Legion of Honour (Skurlov, 2001).

As above mentioned, at this time, the Court ordered mainly small articles. Numerous variegated Easter eggs to be presented to a wide circle of relatives and retainers were needed. According to reminiscences by Mostovenko, it had been the most monotonous work, during which the best color jasper was used up (Skurlov, 2001). At the same time, the Ekaterinburg factory purveyed fine numerous Urals semi-precious and precious stones to the other famous factories and workshops, including the Peterhof Lapidary and company of Faberge.

In 1917, the Ekaterinburg factory was nationalized. At the same time, different plans concerned rearrangement of stone cutting, organization of production of scientific equipment for laboratories and schools to study minerals and rocks, and training of stonecutters and lapidaries. These plans were not realized. A Russian Gems trust was established and the Ekaterinburg factory became one of its departments. The mining and faceting of emeralds was the main target of the factory.

The work at articles with the Soviet symbols had commenced in 1924. The unique mosaic map more than 25 m² in area of the Soviet Union was the greatest product and can never be forgotten. Diverse colored and precious stones including marble, rhodonite, jasper, amazonite, ophite, tuff, quartz, cacholong, opal and lazurite were employed. Meridians were marked with platinum, and Moscow with a ruby star. Emerald, aquamarine, topaz, phenakite, smoky quartz, citrine, almandine, alexandrite, chrysolite, and others (Semanov & Timofeev, 2001) marked the other cities. The map was exhibited at the World Fair in 1937 in Paris, where it received the grand prize and in New York in 1939. For a long time, the map was displayed in the State Hermitage and currently, in Chernyshov Central Research Exploration Museum in St. Petersburg.

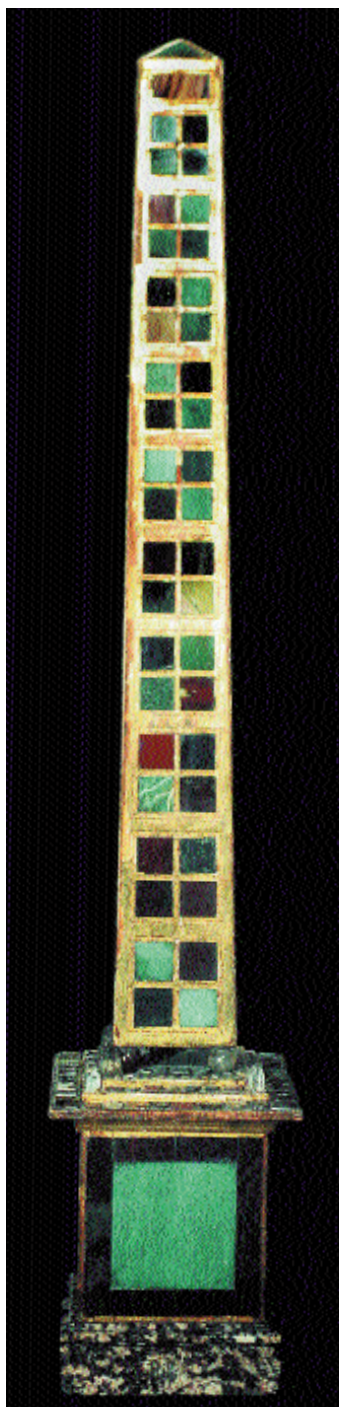


Fig.1. Set of Urals colored stones as a pyramid. Jaspers, chalcedony, quartz. Ekaterinburg cutting factory, 1794–1799. Height is 125 cm. Source and date of receipt are unknown. FMM No PDK-846

Photos to this article are made by Michael Leybov

In the Fersman Mineralogical Museum, Russian Academy of Sciences, goods made at the Ekaterinburg cutting factory had been received from the different state organizations during the 1920s. The activity of the factory during the Soviet period is not described in this paper because the articles manufactured for this time are absent from the Museum collection. Readers, who are interested in the later events related to the factory and its goods, can find information in Semenov & Timofeev (2001).

The small and casual sets of goods produced at the Ekaterinburg factory and stored in the Mineralogical Museum only partially reflect the diversity and magnificence of its articles and the skill of the Urals stonecutters. Nevertheless, there are unique articles in terms of history and art among few museum pieces. In spite of the limited amount of exhibits, the period of their production ranges from the end of 18th to the end of 19th century. Obelisks, bowls, small vases, pencil holders, paperweights, the Easter eggs, and others are among the exhibits. Some of articles are not dated and only by indirect features can they be attributed to any period.

The set of the Urals jaspers as an obelisk-pyramid (Fig. 1) is the earliest article of the Ekaterinburg factory in the Museum. The tetrahedral pyramid slightly convergent upward is based on chalcedony balls mounted on the broader square base. The article is completely faced with polished plates of the various Urals jaspers. On the pyramid, gilded bands separate square plates with scratched numbers corresponding to specific deposits of colored stones of the Urals in "General Description of Deposits" for 1792 – 1796 (Semenov & Timofeev, 2001).

This exhibit has been registered in the Collection of Ornamental and Precious Stones with no. 846 without date and source, but with notice that this article was from the time of Peter the Great. According to this notice, the set was believed to be manufactured at the Peterhof Lapidary that had been opened shortly before the death of Peter the Great. However, at this time, the deposits of jaspers by which the obelisk was faced had been not discovered in the Urals and only glasses were polished in Peterhof. According to research by Semenov and Timofeev, the first sets of the Urals colored stones were made for Ekaterina II in the 1780s, with such sets already including pyramids in 1786. According to these researchers, the pyramid stored in the Mineralogical Museum dates to 1794 – 1799, because numbers of deposits on it correspond to the inventory of 1792 – 1796.

The large obelisk, 195 cm high, from the Fomin marble (grayish yellow with brownish veinlets) produced at the Ekaterinburg factory is stored in the Museum. This obelisk was donated by the Department of non-metal mineral resources of the Commission for study of natural productive forces (CNPF) in 1925.

Since obelisks have been used extensively as park embellishments within the period of the 18th to 20th centuries, there is no basis for any assumptions about the dates of the obelisk production.

The small vase of Kalkan jasper (Fig. 2) is one of the best articles stored in the Museum. It is a square vase with deflected side,

profiled body, and a round bottom decorated with salient stems, and on the expanded downward leg has incurved sides, which is based on the square plinth. In the interior, the vase is also decorated with round rosette carvings on the incurved stems (Fig. 2). "In Ekaterinburg Mast. Kokovin 1828" is engraved on the plinth. A wonderful feature of the vase is its fine metal-like ringing tone during a gentle stroke. The vase was received by the Museum in 1927 from the State Museum Fund.

In 1920s, the Mineralogical Museum was known to make requests to different organizations in Leningrad (the Museum collections were transported to Moscow only in 1934) to deposit stone articles in its collection. Permission was received (December 7, 1926) from the Department of Museums of the Head Commission on Sciences of the National Commissariat of Public Education to issue to the Mineralogical Museum the goods from ornamental stone collected by the Leningrad fund in storerooms of the Gatchina Palace and Stroganov Museum (State Hermitage. File 192, no. 65). According to this permission, the articles listed in two acts by December 13, 1926 and January 8, 1927 were passed to the Museum (State Hermitage. File 192, no. 66).

According to archival documents (Mavrodina, 2000), square vases made according to the drawings of architect I.I. Gal'berg from December 13, 1826 were produced in Ekaterinburg many times from diverse materials and many are displayed in the State Hermitage. The vase stored in the Mineralogical Museum appears to be one of the earliest articles of this variety. According to Semenov and Timofeev (2003), fabrication of it commenced in 1826 and the cost was 1644.63 rubles.

In the Museum, there are excellent vases made from malachite, with the largest one being 75 cm high. If these articles were made at the Ekaterinburg factory, they can be assigned with care to 1830s–1840s. However, the Peterhof Lapidary also produced mosaic malachite articles for a long period. Unfortunately, there are no features which can help to distinguish the products of these two factories. Therefore, it should be confined to the statement of the presence in the Museum of these goods produced from malachite that most visitors associate with the Urals.

The later articles with ascertained dates of manufacturing are assigned to the 1890s. The first of them is the unique rhodonite vase 100 cm high (Fig. 3) cut out from a single block in 1878 at the direction of architect A.I. Valbergh. Round-profiled legs support a high egg-shaped body with two scroll-shaped handles passing into a top terminated by a dome. According to Mavrodina (2000), two pairs of such vases with bases



Fig. 2. Vase from the Kalkan (district of the Kalkan lake, Middle Urals) jasper. Ekaterinburg cutting factory, 1828. Height is 30 cm. FMM No PDK-1610

Fig. 3. Vase. Rhodonite. Ekaterinburg cutting factory; 1893. Received in 1919 from Leningrad City Museum. Height is 100 cm. FMM No PDK-1719





Fig. 4. Pencil holder as stub. Jasper from different deposits in the Urals. Ekaterinburg cutting factory, 1892. Size is 10 x 9.5 x 8 cm. Received from the Gatchina Palace in 1926. FMM No PDK-1782



Fig. 5. Vase. Rhodonite, jasper. Ekaterinburg cutting factory, the end of 19th century (?). Height is 19 cm. Received from V.G. Druzhinin in 1930. FMM No PDK-4146.

of Kalkan jasper were produced at the factory. The first pair was created from 1879 to 1885 (its cost was 28550 rubles, a huge amount at that time). In 1893, the pair was presented to Pope Leo XIII and an additional two identical vases on the bases were then ordered. The work commenced on April 5, 1893. The date of completion is unknown. Currently, one of these vases is exhibited in the George Hall of the State Hermitage (Mavrodina, 2000). The second vase was received by the Mineralogical Museum from the Leningrad City Museum in 1923.

The second exhibit of the 1890s is the amusing article of small plastic art as a hollow stub surrounded by mushrooms and a lizard (Fig. 4). Therein, the variegated Urals jaspers were employed. On its lower part, there are engraved inscriptions in Russian and English: "1892, Russia. The Imperial Ekaterinburg Cutting Factory. Leader V. Mostovenko, 1892". This product was received by the Museum from the Gatchina Palace in 1927. Apparently, this is one of the small articles manufactured in quantity for the Court at the end of the 19th century.

As mentioned above, at the end of the 19th century, rhodonite and Kalkan jasper were the colored stones most frequently used at the Ekaterinburg factory (Semenov & Timofeev, 2001). The combination of these two materials was very popular. Numerous "carved small cups from orlets (rhodonite rock) on the small bases from the Kalkan jasper" appear on the list of articles from 1860s to the early 1890s (Semenov & Timofeev, 2003). The bases of the above-mentioned large rhodonite vases made from Kalkan jasper also indicate this. Based on this, the small rhodonite flat round vase mounted on the octahedral plinth of Kalkan jasper (Fig. 5) is assigned to the products of the Ekaterinburg factory for the last third of the 19th century.

However, there is a description of similar small vases from the State Russian Museum assigned to 1840 (Golomzik, 1983), but the reasons for such dating were not given. In our Museum, the vase was received from a private person in 1930.

In 1926, the State Hermitage transferred to Mineralogical Museum two nephrite vases with bronze handles and two rhodonite plinths. Nephrite and rhodonite articles were registered separately, but with notice that the plinths were appropriated for these vases. The garish color combination did not appear to be appropriate to the Museum workers and the nephrite vases on the rhodonite plinths were never exhibited (Fig. 6).

Publications for the last years stated that nephrite had been combined with rhodonite in the things of the Ekaterinburg factory. So, in 1859, Empress Mariya Alexandrovna received a present the "plinth from orlets..." as additional to her "nephrite cup" (Semenov & Timofeev, 2003). We suppose that Museum stone-cutting exhibits were made at the Ekaterinburg factory. That was in 19th century, but we can't point the dates more exactly.

Two "covers on paper" (blotting paper pads) with berries from colored stones appeared also to be made in Ekaterinburg (Figs. 7, 8). A.I. Golomzik (1983) reported in his book "Rhodonite" two similar products (one of them stored in the Museum of St. Petersburg State Institute, another is private) and dated them to the early 19th century considering them to be articles of the Ekaterinburg artisans. However, as above mentioned, similar covers were typical products of the Ekaterinburg factory over a long period of time and numerous drawings for them were made by Luytin, the outstanding worker of stone-cutting art (Pavlovsky, 1976; Semenov & Timofeev, 2003).

Similar blotting paper pads should be noted also to have been produced at



Fig. 6. Vase (nephrite, Sayan) on plinth (rhodonite, Urals). Late 19th century. Ekaterinburg cutting factory. Total height is 38.5 cm. Transferred by Hermitage in 1926. FMM No PDK-1649, PDK-1650

the Peterhof Lapidary. The described blotting paper pads are attributed to the goods of the Ekaterinburg cutting factory on the basis of practically complete coincidence both of subject and style of performance of the articles stored in the Fersman Mineralogical Museum and reported by Golomzik and identical location of the parts of the general composition with those described by Pavlovsky according to

the drawings by Luytin (colored berries on the black background).

In our case, the still life from berries (Fig. 7) is also on the black marble background and this cover is mounted on the heavy base made from Kalkan jasper. On the other blotting paper pad (Fig. 8), a bunch of grapes from amethyst is also on the base of black marble. One more reason according to which these articles should be



Fig. 7. Paperweight. Jasper, serpentine, rock crystal, cornelian, rhodonite, gypsum-selenite, and marble. Ekaterinburg cutting factory, before 1860. Size is 17 x 11 cm. Gift by A.N. Kupriyanov, 1959. FMM No PDK-4816

Fig. 8. Paperweight. Amethyst, serpentine, ophicalcite, marble. Ekaterinburg cutting factory (?). Size is 6,5 x 10,5 cm. Received from the Stroganov heritage in 1919. FMM No PDK-1138

Fig. 9. Paperweight. Amethyst, nephrite, Korgon porphyry. Ekaterinburg cutting factory (?). Size is 19 x 12 cm. Received from the Stroganov heritage in 1919. FMM No PDK-1062



assigned to the Ekaterinburg factory is the mounting of berries and leaves to the base with mastic rather than metal fids as was done in Peterhof and as later there was ordered to do in the Urals (Pavlovsky, 1976).

The blotting paper pad with berries was presented to the Museum in 1959 by A.I. Kupriyanov, resident of Moscow. According to him, in 1860s, the Siberian manufacturer Mikhailo Petrov gave this article to his grandfather. The second pad with the amethyst bunch of grapes was received from the heritage of Stroganov in 1919.

One more similar pad (Fig. 9) also pertained to Stroganov's family. In this case, the vine from the green Urals jasper with foliage from nephrite and bunch of berries from amethyst are mounted on an octahedral plinth of Korgon (Altai) porphyry. According to the registration book, the "paperweight was manufactured at the Peterhof Lapidary in 1898 for 140 rubles". Since such paperweights have also been produced in Peterhof this note did not give rise to doubt. Information about this article was taken from documents of the Stroganov Palace. At the same time, the vine is mounted on the paperweight with mastic that according to Pavlovsky had been not made in Peterhof. We do not know to what extent this statement is true. Therefore, the problem of the article's origin is not resolved.

It should be noted that similar goods with high-relief mosaic produced by the Peterhof Lapidary were shown at the international exhibition in London in 1851. According to Muntyan (2000), they were considered to be one the wonders of the Crystal Palace and were distinguished by the exact reproduction of reality. The Prince of Wales jokingly wished to eat up the amethyst stick of juicy grapes produced by master Ya. Kokovin.

One more paperweight from the Stroganov heritage is stored in the Museum. This is a specific set of the most abundant and spectacular hard Urals ornamental stones (Fig. 10). The octagonal star composed of diamond-shaped insets made from grayish-green Kalkan jasper is in an octagonal frame from bright pink rhodonite. The rest of the field is filled with rectangular insets from different jasper, agathes, aventurine, and quartz. This variegated composition is in a malachite frame (therein, just one soft stone of the Urals).



Fig. 10. Paperweight. Jasper, rhodonite, quartz, agate, porphyry, malachite and others. Ekaterinburg (?). Size is 16.5 x 11.5 cm. Received from the Stroganov heritage in 1919. FMM No PDK-1112.

This article was received by the Museum in 1919, included in the large collection from the Stroganov Palace. We have no information at all about the workshop wherein this mosaic was produced. Only the selection of Urals stones exclusively, as well as continuous relation of the Stroganov's family with the Urals indicate the probable manufacture of this article in Ekaterinburg (the Imperial factory or artisan workshop).

It should be noted, if the dating of the first of the above-mentioned paperweights (not later than 1860s) is based on the information received from its owner, three others could have been produced at the end of the 19th century both at the factory and by artisans. For example, such articles were displayed at the fairs in Nizhniy Novgorod, Irbit, and other cities in 1879–1880. The cabinet accessories including candelabrum, desk sets, personalized stamps, and other articles were offered to businessmen. The paperweights decorated with filigree sticks of berries were a special appeal of the sets (Dmitriev, 2005). Fersman described in detail the similar artisanal articles from the end of 19th to the early 20th centuries. According to his publications, despite the technical perfection of the artisans, the art importance of these goods was low. Nevertheless, "the cost of the best paperweights with fruits from hard stone reached 500 rubles in 1910", which was a quite high price for that time (Fersman, 1961).

In addition, in the Museum, a few articles received from different sources present the



Fig. 11. Small articles of the Ekaterinburg cutting factory. (a) Vase. Marble. Height is 16 cm. Received from Gatchina Palace in 1926. FMM No PDK-1810. (b) Faceted glass. Rhodonite. Height is 5.5 cm. Received from V.G. Druzhinin in 1930. FMM No PDK-4160. (c) Egg. Malachite. Length is 5 cm. Purchased from V.V. Mostovenko in 1919. FMM No PDK-502. (d) Polished column. Rhodonite. Height is 9.5 cm. Purchased from V.V. Mostovenko in 1919. FMM No PDK-539

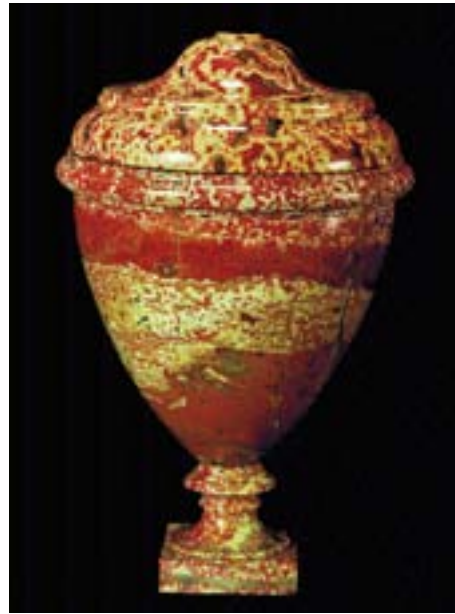


Fig. 12. Vase. Tungotarov jasper (South Urals). Height is 10.5 cm. Received from the Stroganov heritage in 1919. FMM No PDK-1184

Fig. 13. Vase. Amazonite. Ekaterinburg cutting factory. Height is 26.5 cm. Received from the State Hermitage in 1926. FMM No PDK-1633



work of the Ekaterinburg factory. These are a small vase from white marble received from Gatchina, the malachite egg and rhodonite column purchased in 1919 from Mostovenko, and a faceted rhodonite glass received from Druzhinin in 1930 (Fig. 11). Such small articles in quantity were delivered from the Urals.

The small vase of Tungatar jasper (South Urals) displayed in the Museum is included among the similar cabinet articles. A semi-egg-shaped body covered with a broad profiled cap is on the short round stem that is mounted on the square plinth (Fig. 12). It was received from the Stroganov heritage in 1919.

Two hollow amazonite vases with oval bodies (Fig. 13) were received from the Hermitage in 1929. At this time and previously, in Russia, amazonite was known only in the Urals. Therefore, Ekaterinburg is the most probable locality of their production. Goods made from amazonite at the Ekaterinburg factory are known to have been produced since the 1820s. Ekaterinburg is famous for not only the stone-cutting

articles of its cutting factory. Many generations of artisanal stonecutters worked with the varied Urals materials. After the abolition of serfdom, many masters left the Imperial factory. Among them, there were eminent persons. Some of them started as artisans and set up their own workshops, and their shops and were well-known not only in the Urals, but in St. Petersburg. Denisov-Ural'sky, an outstanding artist and stonecutter, was very popular among them. As a gorshchik (this local term means prospector) and artisan by birth, he had an excellent knowledge of the Urals stone, could mine it, and he used it both in natural and processed form, composing usual and decorative collections and creating poured pictures, relief icons, and stone-cutting figurines.

One of the few extant collections as a stone grotto is shown in the Mineralogical Museum (Fig. 14). As above mentioned, collections as rockeries, grottos, and fountains have been produced in the Urals since the times of Ekaterina II.

The grotto by Denisov-Ural'sky was manufactured as an arch, in which is mounted a translucent plate of gypsum-selenite probably simulating an underground waterfall. The grotto is pasted over with crystals and polished pieces of various Urals minerals. Sometimes all minerals of the grotto were with small numbered labels and a list of mineral names with these numbers was supplemented. The grotto is mounted on a malachite base with a label on the lower side indicating that Denisov received a honorary reference from Moscow in 1882 and in 1887 he was decorated with the Greater Silver Medal for pictures, icons, and grottos. In the lower left corner of the label, there is inscription "СПБ" (it means St. Petersburg). Denisov-Ural'sky was known to have a shop at Bol'shaya Morskaya Street in St. Petersburg.

This attractive collection was received from the Gatchina Palace in 1926. Probably, it was used as a visual aid for the tsar's children. As is known, they learned diverse sciences including mineralogy. The catalogue of the miner-

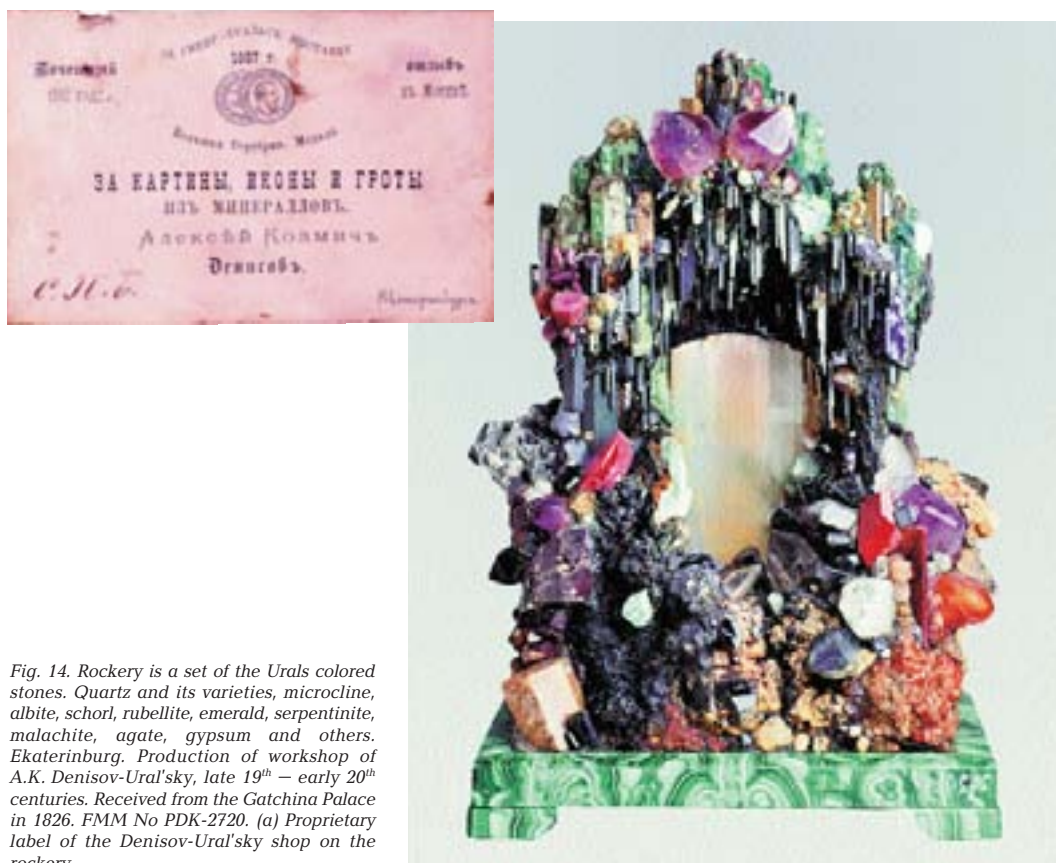


Fig. 14. Rockery is a set of the Urals colored stones. Quartz and its varieties, microcline, albite, schorl, rubellite, emerald, serpentinite, malachite, agate, gypsum and others. Ekaterinburg. Production of workshop of A.K. Denisov-Ural'sky, late 19th – early 20th centuries. Received from the Gatchina Palace in 1826. FMM No PDK-2720. (a) Proprietary label of the Denisov-Ural'sky shop on the rockery



Fig. 15. Donative dish. Jasper, emeralds, rubies, sapphires, beryls, amethysts, alexandrites, demantoids, hessonites and others. Diameter is 32.5 cm. Ekaterinburg. Shop of I.N. Lagutyaev, 1891. Came from Museum of Palace of Arts in 1922. FMM No PDK-2622. (a) Stamp on the proprietary box of the Lagutyaev workshop.

alogical collection of Cesarevitch Nikolay was stored in the Museum and part of the samples from this collection were acquired under supervision of V.V. Nefed'ev, professor of St. Petersburg Mining Institute, the author of the first catalogue of the Mining Museum.

One more interesting article made at the private workshop in Ekaterinburg is a paten on which bread-and-salt was presented to Cesarevitch Nikolay in Orsk when he had returned to St. Petersburg from Japan (Fig. 15). A round dish from the parti-colored Orsk jasper is ornamented with gold with covers from precious stones, which bear the image the crown and monogram of Cesarevitch and the arrival date to Orsk 15.VII.1891. Cesarevitch was late and the solemnity of the presentation took place only on July 24. Prince E.E. Uspensky who accompanied Nikolay wrote: "...the guard of honor was formed up...; therein...the deputation of Cossacks from Novocheerkassk stanitsa with bread-and-salt on the silver paten was placed, then deputies from factorial peasants and Bashkirs also with bread-and-salt: the peasants have presented bread-and-salt on the silver dish, whereas

Bashkirs, on very fine marble paten with inscription, crown, and ornaments being composed of many-colored stones. This paten can be considered as the most elegant" (Uspensky, 1897). Stones from both the Urals and abroad (ruby and sapphire) were applied in the article. The large demantoids, bright colored emeralds, and small alexandrites, which compose the letter "A" in the monogram stand out against the other stones.

The dish was received in 1922 from the Museum of Art Palace in the original red velvet box which bore the manufacturer's mark of the owner of the producing workshop: "Production from the Urals stones by Lagutyaev in Ekaterinburg". The image of two sides of the medal "For diligence and art. 1898" is on the sides of the mark.

Information about workshop of Lagutyaev is very poor. It was established in 1843 (Semenov, 1987) and its goods had appeared to be popular because they were displayed at the exhibitions in Nizhniy Novgorod, Irbit, and St. Petersburg (Semenov, 1987; Dmitriev, 2005). P.P. Bazhov (1976) reported that "sweat for Nurov, Lagutyaev, and Lipin meant faceting of

gems and small articles from colored stone". According to Dmitriev (2005), two Ivans, Stebakov and Lagutyaev, dominated at the stone market in the late 19th century. Many people visited their shops during a fair. Therein, "...specimens and faceted rarities were offered to collectors. Beads, finger-rings, earrings, bracelets, studs, fine caskets, boxes, and poured pictures were offered to devotees of adornments and souvenirs. The "cabinet" accessories..., candelabrum, desk sets, nameplates... were offered to businessmen". In contrast to many other owners of the Urals workshops, Lagutyaev did not own mines but had purchased raw materials. Ten wage laborers worked in his workshop in the early 20th century. In addition, 20–30 artisan-outworkers worked for him (Fersman, 1961).

Currently, we do not know of any other products of the Lagutyaev workshop.

In addition to the already described two articles of the big private workshops in Ekaterinburg, in the Museum, there are products of artisans whose names we have not been able to learn. The artisan production in the Urals was known to be very diverse. Fersman (1961) reported nine specific specialties of artisans in Ekaterinburg among which there had been "signeters" i.e. manufacturers of signets.

A quite large collection of signets received from different sources is stored in the Museum. Part of them was purchased from O.A. Shikhova in 1936 (Fig. 16–18). The correspondence between the Museum and A.S. and O.A. Shikhovs about purchasing and sale of the

stone material was preceding (Shikhovs lived in Ekaterinburg (then Sverdlovsk) that time) (St. Petersburg Branch of Archives, Russian Academy of Sciences). Since the material had been received from dwellers of Ekaterinburg, the signets could be assumed to cut by local masters. Most of them were made from local material including rock crystal, jasper, and rhodonite. Aquamarine from Sherlova Gora in Transbaikalia was applied for one of them (Fig. 16), porphyry from the Kolgon river, Altai, for another (Fig. 17). In Altai, there was lapidary work, which had produced diverse stone articles from huge to the smallest. Therefore, the porphyry signet could have been manufactured far from the Urals. The aquamarine signet can be considered to be from the Urals, because such goods of the Transbaikalia workers are unknown. Aquamarine from Sherlova Gora was delivered for many jewelry and stone-cutting workshops of Russia, including the Urals ones.

One more signet of the Urals masters from rock crystal was received in 1925 from the Commission on Investigation of Natural Productive Forces. It is the article with fourteen facets with zodiacal signs and names of months carved on twelve facets (Fig. 18). Pavlovsky (1976) reported the special subtlety of engraving and accuracy of drawing of such signets.

At the end of 19th to the early 20th centuries, the artisans continued to produce covers of carved berries and fruits on the articles, made from colored stones. Mostovenko, the former director of the Ekaterinburg cutting factory,

Fig. 16. Signets from rock crystal (FMM No PDK-681, FMM No PDK-4249), amethyst (FMM No PDK-4260), aquamarine (FMM No PDK-4263), and heliodor (FMM No PDK-4262). Artisan production, Ekaterinburg (?), late 19th–early 20th century. Purchased from O.A. Shakhova in 1936.

Fig. 17. Signet from the Korgon (Altai) porphyry. Size is 5.5 3.5 cm. Handicraft ware from Ekaterinburg (?). Purchased from O.A. Shakhova in 1936. FMM No PDK-4261



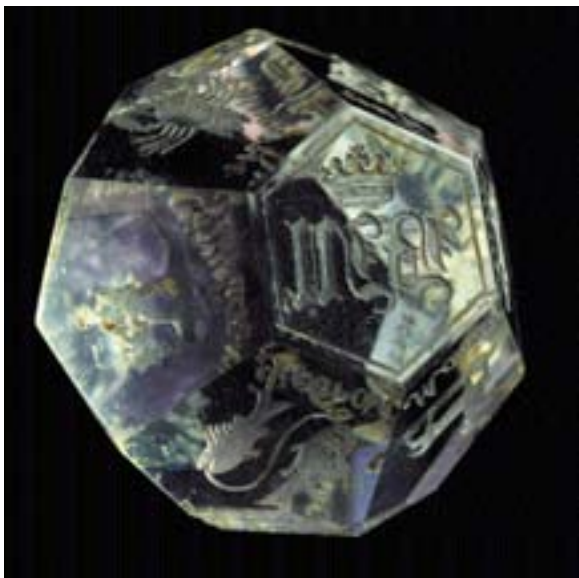


Fig. 18. Signet with zodiacal symbols from rock crystal. Size is 2.5 x 2.4 cm. The product is of the Urals artisans (?). Received from CNPF in 1925. FMM No PDK-2541



Fig. 19. Paperweight (fragments). Microcline, albite, quartz, schorl, cornelian, and serpentinite, Size is 16 x 8.5 cm. The product is of the Urals artisans. Received from V.G. Druzhinin in 1919. FMM No PDK-2621

reported that everything was performed naturally, but general composition had been overloaded. These products were expensive because a lot of work was required to make them. "I have advised for a long time to produce the simplest covers: take a piece of albite and any other fine rocks and drop on it only one branch of raspberry, currants, or others. This will be inexpensive, simple, and nice. Finally, the artisans had followed this advice and these paperweights sold briskly" (Skurlov, 2001).

The similar article of an unknown Urals artisan is stored in the Museum (Fig. 19). The branch of red currants from bright cornelian and small leaf from serpentinite are on a druse of albite and microcline with a few crystals of smoky quartz, schorl, and mica. Here and there, traces of glue are seen on the crystals, but details of the article fell apart before the receipt of this cover by the Museum. The peeled off berries and leaves are attached to the exhibit. However, it is unknown whether they can be attributed to this article. Despite bad preservation, the exhibit provides insight into the nature of such products.

The stone cutting in the Urals also developed in the Soviet Union. A Russian Gems trust was established on the basis of the Ekaterinburg cutting factory; and in 1941, the Urals Jeweller Plant was founded; then, the other stone-cutting and jewelry enterprises supplying and developing stone-cutting and jeweler arts in the Urals were established. New excellent masters known both in Russia and abroad have appeared (Skurlov, 2001; Semenov & Timofeev, 2001). Recently, the artisanal art using both new trends and traditions of the 19th century including tendencies related to Denisov-Ural'sky has been revived. The stone-cutting art based on utilization of the wonderful Urals gypsum-selenite and associated anhydrite is well known.

Unfortunately, the Mineralogical Museum has no articles of the Urals masters from the last 80 years with the exception of selenite and anhydrite figurines deposited in the period from the late 1980s



Fig. 20. Statuettes from gypsum-selenite, Kungur, Perm Region. Sizes are 6.5 cm, 6.1 cm, and 9.8 cm. Products of a Urals stone cutter enterprise, Krasny Yasyl, Perm Region. Purchased by Museum in 1990–1991. FMM, NoNo PDK-7511, PDK-7586, and PDK-7635

to the early 1990s. Generally, these are small figurines of birds and animals (Fig. 20), which are very expressive despite laconic workup. The polished surface of the products without carved details which emphasize the warm golden and cold white luster of silky gypsum. This small collection does not compensate for the absence of goods of the other stone-cutting branches of the Urals, which have not been received for a long time.

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THE MINERALOGICAL COLLECTION OF THE GEOMUSEUM, COLOGNE UNIVERSITY, GERMANY

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Mineralogical exhibits of the GeoMuseum, Cologne University, and the history of this collection are described. 17 figures, 3 references.

The history of this small museum is fairly old and not nearly simple, as it often happens with old collections. It begins upon a private collection, a mineral cabinet of the second half of the eighteenth century. Unfortunately, it was destroyed and broken almost entirely during the World War II; the registration books were burnt after the bombing in 1944, so it is impossible now to determine, which specimens have come from that historical collection and which ones appeared later. The only authentically known historical exhibit, the calcite (or aragonite) pseudomorph after the bird's nest, belonged to Ferdinand Franz Wallraf (1748 – 1824) who was the first Cologne honorary inhabitant. Another remarkable museum of the city is bound with his name too. F.F. Wallraf, the son of a Cologne tailor, pulled himself up thanks to his own labor, graduated several faculties at the Cologne University – medical, theological, became canonic, Doctor of medicine and Doctor of philosophy and, later, Professor of history and fine sciences. In 1793, he was elected the University Rector. Yet collecting was his favorite occupation. He collected whatever pertaining to the history of Cologne.

Besides the natural-historical collection, the Wallraf's assemblage contained archeological finds dated by the Roman Empire as well as paintings, sculptures, religious relics and works of art, and historical weapons. At the Napoleon times, when the French bossed in the town and the University has been closed (it was only opened more than one hundred years later, in 1919), he was protecting, as far as was possible, church valuable exhibits from plunder and spoiling. After Wallraf's death and with the assistance of Johann Heinrich Richartz, a Cologne merchant, a museum was established on the base of his collection. The Museum was opened for visi-

tors on 1 July 1861 and was named, in honor of these two prominent persons, the Wallraf-Richartz Museum. Today, this is one of the greatest classic pictorial art galleries in Germany.

As was noted, there was a great natural-historical collection in the assemblage of F.F. Wallraf, a naturalist and a teacher, and some part of the GeoMuseum's specimens was apparently linked with this first university collection. Having been saved at the turn of the eighteenth and nineteenth centuries, it unfortunately met with a grievous loss in the twentieth century, and the lost attribution cannot be restored.

The mentioned historical specimen, calcite (or aragonite) pseudomorph after a bird's nest, was more lucky: it is excellently preserved (Fig 1). It was demonstrated not only at the GeoMuseum itself but at various temporal exhibitions, including the joint exhibition of Cologne museums, 1995 – 96. In this exhibition catalogue (Kier, Zehnder, 1995) it is registered under No 397 as the exhibit from the Wallraf's collection where it is registered as "Inlay". It should be emphasized that in the Western literature the sense of the latter term is somewhat wider than what is accepted in Russia and means, particularly, some crust or mineral cover on some alien matter, e.g., a rock (Tolkovyi slovar' angliiskikh geologicheskikh terminov, 1978).

As to the GeoMuseum collection in a whole, it consists nowadays of two large and formerly independent parts: from the 1960-ies, the Mineralogical Museum and the Museum of the Geological Institute of Cologne University were existing parallel; however, after establishing in 1999 the united Library of geology, mineralogy, crystallography, and geophysics, which needed special premises, they were united into a single museum that retained former dividing into mi-



Fig 1. Calcite (or aragonite) pseudomorph after a bird's nest, 10 cm high, 13 cm across, cavity diameter 5 cm. No 129e. Photo: E.A. Borisova.

Fig 2. The Cologne GeoMuseum exhibition hall. Photo: R. Hollerbach.

neralological and geological (or geological-paleontological) collections.

The geological collection also has its own history. Not entering into details, we have only to note that its most part was formerly staminal for the Cologne Natural-Historical Museum, the so-called Stapelhaus Sammlung. The unique exhibits like skeletons of ichthyosaurus – *Stenopterygius quadriscissus* and saltwater crocodile – *Steneosaurus bollensis*, both more than 2.5 meter long, found in the Lower Jurassic near Holzmaden (Württemberg vicinities, Germany), as well as the skeleton of a cave bear, are the honor of this collection. Dr. Michael Grigo is now the curator of this part of collection.

The mineralogical collection is fairly diverse and counts more than 50 thousand showpieces. Some part of them, about one thousand of most interesting and attractive specimens, is exhibited in the museum hall directly (Fig 2). About 30 thousand specimens make up a systematic collection and are the museum funds off limits to public and only accessible for specialists and workers of the two institutes of the Cologne University, Institute for Crystallography and Institute for Geology and Mineralogy that are located within the same building. The systematic collection includes about 1500 mineral species.

Another small part, about two thousand specimens, is a petrographic collection. It is stored also separately in the Museum funds being used mainly for training. For the same aim, the special demonstration hall with the specimens of wide-spread minerals and ores is always open for students adjacently to the exhibition hall. As a rule, these specimens are of standard size and shape and arranged by one or another preferential principle. For example, some cases show

physical properties of minerals such as hardness, color, luster etc. Some cases show aggregate shapes, mineral varieties and diversity of natural occurrences. The entire tutorial collection with its funds numbers about 20 thousand specimens. Of course, the advantage of such a training separate collection is its accessibility. While the main exposition hall is open for public only one day in a week (Wednesday) and one Sunday in a month, the students can visit the training hall, as mentioned above, practically at any day and at any time, it is always open if the Institute for Geology and Mineralogy in whose area it is situated is in operation. Besides, the mineral collections gathered by students at field trips can be demonstrated in special cases in the Institute hall, which is, too, very much useful for the educational process and forwards to engage the young people in the work with stone material.

Let us now contemplate the mineralogical expositions of the main exhibition hall in detail. They are divided into 8 topical exhibitions: Meteorites and Tektites, Gems and Precious Stones, some mineral groups (quartz varieties, agates, calcites, zeolites), Minerals from Cologne Vicinities, Russian Minerals, Mineral Prominent Finds from All-Over the World, Synthetic Crystals, New Aquisitions. Besides, two more cases are in the vestibule before the entrance to the exhibition hall: The Biogenic Mineral Formations and The Matter Crystalline and Non-Crystalline States. In the first one, you can enjoy corals, echinoid skeletons, shells; in the second one, quartz crystals, quartzite and quartz sand are placed at one side and, for comparison, amorphous natural (obsidian, tektites) and technical glasses – at the other side.

In the main hall the most interesting and various exhibits are presented in the exposition the



Fig 3. Rhodochrosite. Kalahari, South Africa. 9 by 17 cm. No number. From P. Ney collection. Photo: E.A. Borisova.

Fig 4. Rhodochrosite. Mina Capillitas, Argentina. Polished section 10 by 14 cm. No M5426/96. Photo: R. Hollerbach.

Fig 5. Stibnite, barite. Baia Sprie, Romania. 15 cm. No M3800/70. Photo: R. Hollerbach.

Most Valuable Mineral Findings from All-Over the World, as one can see from its title. One of the best specimens here is rhodochrosite from the Kalahari Desert (South Africa), which was collected personally by the former curator of mineralogical collection and Museum coordinator Prof. Paul Ney (beginning from 1988, Dr. Rolf Hollerbach is curator of mineralogical collection and coordinator of GeoMuseum). A dramatic story is tied with this rhodochrosite. Yet in Kalahari, after Ney has packed the specimen in his knapsack, several robbers attacked him to rob the valuable load; however, Ney did not lose courage and, using the knapsack like a sling, could struggle the assailants and escape. Unfortunately, the specimen was harmed, several crystals were damaged or broken. Nevertheless, the big, to 3 cm long, brownish-red, transparent rhodochrosite crystals are certainly the exhibition ornament (Fig 3). Another rhodochrosite specimen (from Capillitas, Argentina) is pink radial aggregates (Fig 4), which attracts visitors' attention too.

The luxurious stibnite specimens from Baia-Sprie, Romania (Fig 5) as well as large, up to 4 cm across, native sulfur crystals on calcite from Racalmuto, Sicily, Italy are the GeoMuseum visiting cards. The big epidote crystal (20 cm long) from Knappenwand, Untersulzbachtal, Salzburg, Austria; orange-olivaceous crystals to 1 cm upon the brush of minor yellow-greenish-pink masses of the same famous pyromorphite from Bunker Hill, Kellogg, Idaho, USA; blue crystals of linarite (up to 6 or 7 mm) from Blancher Mine, New Mexico, USA; wulfenite tabular crystals (up to 1.5 cm across) on galena from Schwarzenbach, Slovenia; as well as grossular white crystal (11 cm

across) from Lago Jaco, Chihuahua, Mexico deserve to be marked. Very much spectacular are the tourmaline specimens, the zonar one from Anjanabonoina, Madagascar, and the pink transparent rubellite from Paprok, Nuristan, Afghanistan; apatite transparent and zonar crystals to 3 cm long from Panasqueira, Portugal; azurite wonderful rose, 10 cm in diameter, from China (Silu, Guangdong Province); azurite crystal group (with crystals to 4 cm) from Tsumeb, Namibia, as well as cavansite radial aggregates on stilbite from Poona, India (Fig 6).

The native copper specimen from Lake Superior, Michigan, USA is impressive. The intergrowth of the two large translucent crystals of calcite and fluorite from Elmwood Mine, Tennessee, USA (Fig 7) is amazingly beautiful.

The pale pink rhodochrosite from Capnic, Romania; the two tourmaline splendid specimens – zonar crystal (30 by 10 cm across) in quartz (Caribib, Namibia) and the partly fibrous pink elbaite with lepidolite and quartz (Pederneira Mine, Minas Gerais, Brazil) as well as luxurious intergrowths of gypsum twins from Santa Eulalia, Chihuahua, Mexico should be marked amidst the major pieces.

The polished specimens of pale clay shales (or aleurolites) with bright brown stripes and patches due to iron oxide or hydroxide admixtures – the so called Zebra-Rocks from Kimberley, Australia (Fig 8) are the extraordinary in this exposition.

Minerals from Cologne vicinities (Siegerland) are presented at the exposition of the same name mainly with carbonates (rhodochrosite, siderite, calcite, dolomite), iron and manganese oxides and hydroxides (pyro-

* Geographic names are given according A.A. Evseev (Evseev, 2000).

lusite, limonite), sulfides and sulfosalts (pyrite, galena, chalcopyrite, fahlore, bournonite) and native copper with malachite.

At the **Special Groups of Minerals exposition** the agates should be particularly marked. Their delicate patterns are well visible even from afar as the big agate plates are located at special mounts provided with booster-lights whereas the minor ones are opposite the windows. The large bluish grey agate from Brazil can be marked too.

The amethyst crystal, 12 cm long (Guanajuato, Mexico), and the split yellowish quartz crystal (9 cm long) from Tsumeb, Namibia, seem most attractive aesthetically in the Quartz Case while in the Calcite Case – pinkish-brown split crystal from the mining near Marl Huels, Ruhr Area, Germany (Fig 9). In the Zeolite Case, the creamy pink stilbite and natrolite from Poona, India (Fig 10) as well as the wonderful specimen of snow-white scolecite with

laumontite from the same locality (Fig 11) seem to attract more than the other.

Besides Australian and African diamonds, polychrome tourmalines, rubies, sapphires, and various jewelry from these and other minerals, which are customary here, the excellent transparent twins and trillings of chrysoberyl from Sri Lanka (Fig 12) and the bluish faceted crystal (4 or 5 mm in size) from the Urals (Tokovaya River) are the rare decoration of the **Gems and Precious Stones exposition**.

In the **New Aquisitions** case, the beryl varieties should be emphasized: emerald crystals (4 cm long) from the Coscuez Mine, Boyacá, Columbia, and aquamarine from Erongo, Namibia (Fig 13). The big honey yellow scheelite crystal (6 cm) from China (Fig 14), purple-blue carletonite (Saint Hilaire Mountain, Quebec, Canada), and brownish-red corundum (7.5 by 4 cm) from Mysore, India (Fig 15). The combination of the orange-red vanadinite crys-

Fig 6. Cavansite aggregates (1 cm across) on stilbite. Poona, India. Fragment. Specimen 14 by 18 cm. No M5559/02.

Fig 7. Calcite, 17 cm, with fluorite, 14 cm. Elmwood Mine, Tennessee, USA.

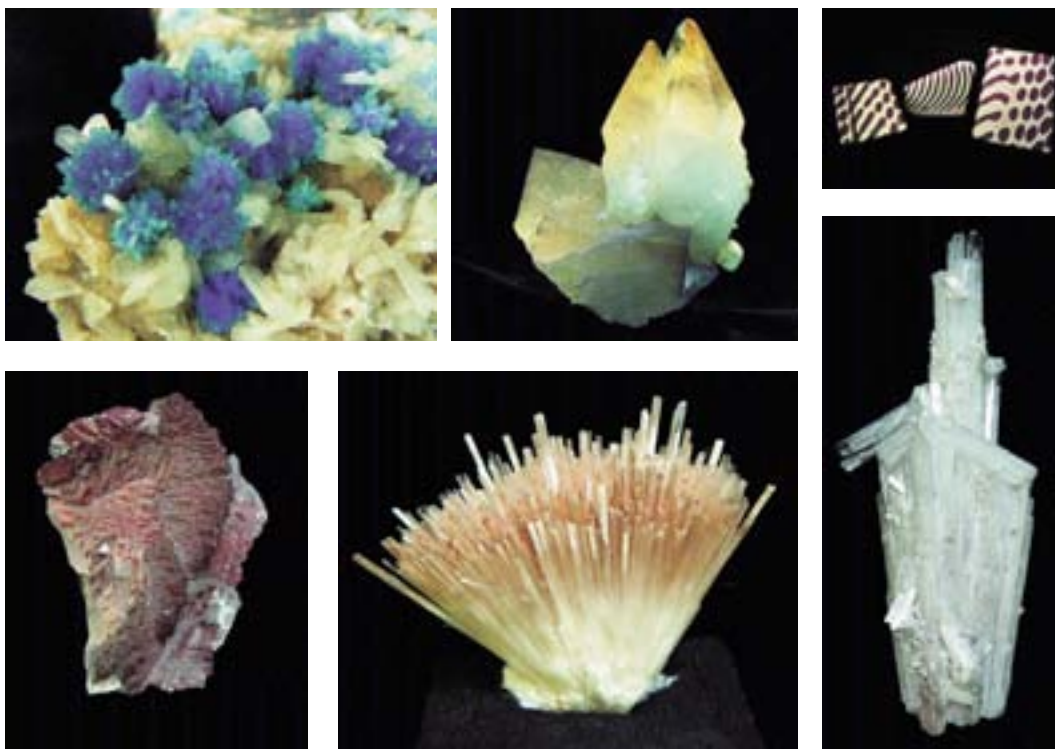
Fig 8. "Zebra rocks". Kimberley, Western Australia. Specimens up to 10 by 7 cm. No number.

Fig 9. Calcite. Marl Huels, Ruhr Area, BRD. 7.5 cm. No number.

Fig 10. Natrolite. Poona, India. 7 cm. No M4167/73.

Fig 11. Scolecite with laumontite. 15.5 cm long. Poona, India. No M4303/80.

Photo: E.A. Borisova.



tals and black iron oxides from Mibladen, Morocco, looks somewhat unusual. The white, with a slight pink tint, microcline Manebach and Baveno twins from Morro Redondo, Minas Gerais, Brazil (Fig 16) as well as aragonite with native silver from Santa Eulalia, Chihuahua, Mexico (Fig 17) are very nice.

The topical exhibition **Russian Minerals** appeared in the GeoMuseum recently. Its origin depended on the wide stream of Russian mineral material that rushed in the Western markets in early 90-ies of the past century. Pieces from Siberia, Urals, and Kola Peninsula prevail here. The Ural minerals are most diverse: quartz phantom crystals, amethyst, citrine from the Nether-Polar Urals, Sarany uvarovite, Ilmen dark grey corundum (5 to 6 cm), Beryozovskii crocoite, pyrochlore from Vyshnevye Gory, malachite and native platinum from Nizhnii Taghil. The apatite blue transparent crystals (2 or 3 mm in size) on calcite, analcime (3 cm crystal) from the Nizhnaya Tunguska River, and sperrylite from Talnakh may be emphasized amongst Siberian miner-

als. Khibiny minerals are presented by eudialyte and astrophyllite. There are about 30 specimens available at the exposition.

Twenty various meteorites and tektites of six types make up the **Meteorites and Tektites** exposition. Among the first, the two findings dated eighteenth century should be mentioned in the first line. They were identified as meteorites later, though. The iron meteorite Toluca, Mexico, was found in 1776 but described as a meteorite only 80 years later, in 1856. The meteorite Rittersgruen, Steinbach, the iron one with silicate small inclusions, was found in 1724 in the Erzgebirge, Germany, and was not, too, immediately referred to cosmic objects. The palasite Brenham, Kansas, USA (1882) and octahedrite Canyon Diablo, Arizona, USA (1891) were found in the nineteenth century.

The falls of the nineteenth century are presented by the Ca-enriched achondrite Stannern, Iglau, Czechia (22.05.1808), olivine-hypersthene chondrites Zavid, Bosnia-Herzegovina (1897), and Mocs,

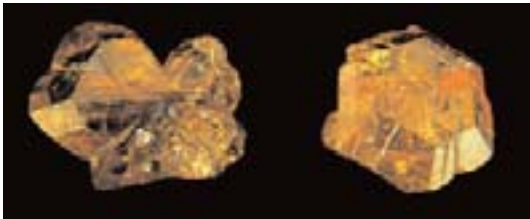


Fig 12. Chrysoberyl, 9 x 10 mm and 8 x 9 mm. Sri Lanka. No M5270/94.

Fig 13. Aquamarine, 4 cm long, with tourmaline and smoky quartz. Erongo, Namibia. No M5553/01.

Fig 14. Scheelite (6 cm) with muscovite. 6 by 10 cm. China. No M5445/97.

Fig 15. Corundum, 7.5 x 4 cm. Mysore, India. No M5278/94.

Photo: E.A. Borisova.

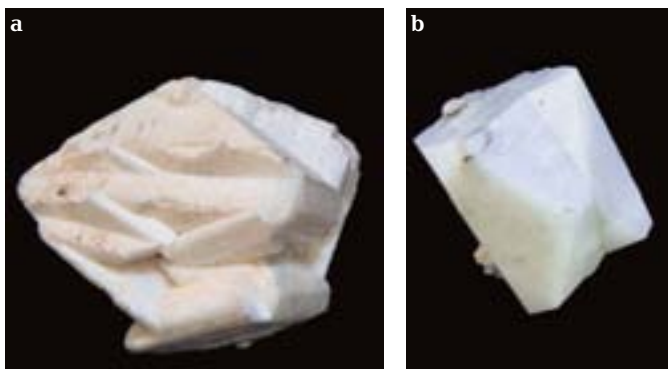


Fig 16. Microcline. Morro Redondo, Minas Gerais, Brazil. No number.
a – Manebach twinning, 7 by 8 by 6 cm.

b – Baveno twinning, 4 by 4 by 3.5 cm.

Fig 17. Aragonite with native silver and gypsum. 17 cm high. No M5446/97.

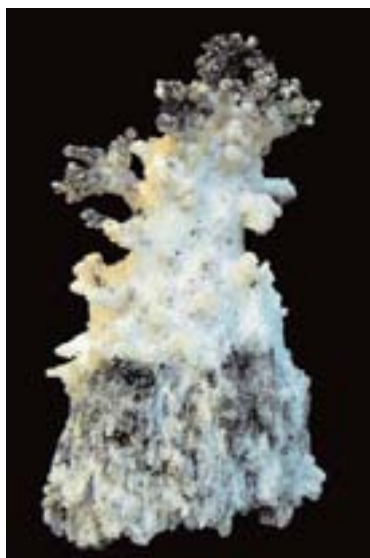


Photo: E.A. Borisova.

Romania (3.02.1882), olivine-bronzite chondrites from meteor showers Cronstad, RSA (19.11.1877), and Pultusk, Poland (30.01.1868). The rare specimen of carbonaceous chondrite is a part of the meteor shower Murchison, Victoria, Australia that has fallen on 28 September 1969. The entire mass of the fallen matter is estimated as nearly 100 kg, the Museum specimen weight is 143 g.

Tektites are presented by moldavites (Czechia), philippinites (Mindanao, the Philippines), indochinites (Thailand), bellitonites (Indonesia), australites (New South Wales), and specimens found in the Quarternary fluvial deposits of the Guangdong Province, China.

And, lastly, the **Synthetic Crystals** exposition exhibits the results of the works of the Institute for Crystallography, Cologne University, in the growth of various phases including both organic compositions (citric acid, dibensole, formates and oxalates of sodium, calcium and strontium) and inorganic ones (sulfates, phosphates, nitrates and iodates).

Therefore, the mineralogical collection of GeoMuseum, Cologne University, is tradition-

al and well adapted to the needs of educational process, and is notable, at the same time, for wide diversity of aesthetically important pieces, large and rare crystals well presented in the exhibition hall open for public, which surely awakes echo in the hearts of stone connoisseurs and amateurs and attracts childish and young audience.

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GENERAL AND HIS COLLECTION

THE MINERAL COLLECTION OF G.P. CHERNIK AT THE FERSMAN MINERALOGICAL MUSEUM OF RAS

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This article tells about a Russian Army Major-General, Georgiy Prokofievich Chernik, who donated more than 300 mineral specimens to the Fersman Mineralogical Museum and describes the present-day condition of this collection.

9 photos, 8 references.

The village of Yasenskaya, Krasnodar region, has a unique local history museum. Its main exhibition is comprised of the materials donated by the village residents, and the museum keepers treat these people with great appreciation. Their portraits are displayed in the museum halls, and the book with a list of the contributors is kept at the central location. The slogan at the museum entrance says: "Museum is a memory book of humankind". It gets us thinking that even natural science museums are not only collections of natural "memorials", but also preserve the memory of the people who found and saved these memorials for future generations.

The Fersman Mineralogical Museum of Russian Academy of Sciences is not an exception. The list of the authors donated specimens to the museum includes more than 3000 names. Among them are famous Russian and foreign scientists, museum workers, college and school students, amateurs and professionals, collectors, and patrons.

Biographic review

This article presents a story about a Russian Army Major-General, Georgiy Prokofievich Chernik. His life picturesquely reflects the fate of many people who lived during the breaking era at the junction of the 19th and 20th centuries. Chernik himself is an example of dedicated and broadly educated person, who found a way to combine his service and professional scientific work.

The search of materials about G.P. Chernik was like a detective story. Laconic records "Colonel Chernik" in the collection acquisition books did not provide any clues other than his military affiliation. Thus, our imagination drew a

headquarters office having some "special assignments" at Borneo, Sumatra, Ceylon; many of his donated specimens were from those places. Data on military officers, especially colonels, had to be kept in military archives. Indeed, the Russian State Military Historic Archive (RSMHA) had a service list of Georgiy Prokofievich Chernik. Information from that document immediately changed all our perceptions of this person. Instead of a "headquarters colonel" we discovered an army General. You can see it for yourself from the key excerpts from the archive paper (RSMHA, 1916). Comments in parenthesis are given by the authors.

Service list of the Engineer Commander of the XI Army, Military Engineer, Major-General, Chernik Georgiy Prokofievich

December 26th, 1916

Major-General Georgiy Prokofievich Chernik

Engineer Commander of the XI Army

Orders: St. Stanislav I, II, and III Degree; St. Anna II and III degree, St. Vladimir III degree with swords and IV degree with swords and bow.

Born January 6th, 1864

Origin – upper class of the Black Sea Cossack army, listed in Kuban army, Chelbaskaya Stanitsa.

(Stanitsa Chelbaskaya, Eisk district of the Kuban region in steppe zone, Middle Chaglas River, 46 verst from the Leushkovskaya Station, Vladikavkaz rail road).

Orthodox Christian

School: Petrovsko-Poltavskaya Military Gymnasium (i.e. Petrovskii Poltavskii cadet corps, which was opened in 1840, then transformed into a military gymnasium in 1965, and in 1886 again became a cadet corps).

Nikolaev Military College (Nikolaev Military Engineering College historically originated from an engineering school that was founded in 1804.

The college was established in 1819 and was named the Main Engineering College. Since 1855, it was called Nikolaev Engineering College in memory of Emperor Nikolai I. The College was located in the Mikhailovskii Engineering Palace in St. Petersburg. Among the alumni of this college were many famous people who made an impact in Russian culture and science – F.M. Dostoyevskii, Ts.A. Kyui, D.V. Grigorovich, P.N. Yablochkov, and E.I. Totleben, and others).

Nikolaev Engineering Academy (The Academy was founded in 1855 as a part of the Emperor's Military Academy for officer classes of the Main Engineering College. Since 1863, it became an independent institution. Among the alumni of the Academy were General D.M. Karbyshev, artist A.S. Vereschagin, architect B.A. Malinovskii, and military historian A.M. Zaionchkovskii. In 1932, the Academy was transferred to Moscow and then disbanded).

Service List

March 15th, 1882. After graduating from gymnasium, entered the Nikolaev Military College, CADET.

October 4th, 1882. UNDER-OFFICER

August 14th, 1884. SUB-LIEUTENANT. 2nd Caucasus field engineering battalion – military service, participation in field engineering works for shore defense in Batumi.

September 1st, 1886. Trip to Petrograd for taking exams to enter the Nikolaev Engineering Academy.

STAFF-CAPTAIN

December 4th, 1888. After completing studies in the Academy, assigned to serve in the Engineering Corps under the order of the Main Engineering Commandment.

November 16th, 1889. Assigned to the Ivangorod Fort, where he served until 1901 and received the title of lieutenant-colonel.

April 13th, 1893. Permanent Member of the Russian Physicochemical Society at the Petersburg University.

March 13th, 1898. According to the presented diploma of the Emperor's Petrograd Mineralogical Society of January 29th, 1889, signed by most august President of the Society, Princess Eugenia Maksimilianovna Oldenburgskaya, ... for his contributions to science, (Chernik) was elected a permanent member of the Emperor's Petersburg Mineralogical Society.

November, 26th, 1901. Sent from Ivangorod to serve under order of the Main Engineering Commandment.

January 17th, 1902. Accepted to Petrograd Fort Engineering Commandment

January 28th, 1904. COLONEL

November, 15th, 1904. Assigned to the Inspector's office of the 3rd Manchur Army and departed to the Army unit.

December 2nd, 1904. Arrived to Mukden

Notes on combat participation:

Participated in combat against Japan in 1904–1905 while serving in the 3rd Manchur Army. (The document further provides details of daily reconnaissance work of Colonel Chernik to determine the location of artillery units constantly being under hostile fire).

February 25th, 1905. Being among the personnel retreating (from Mukden) in the rearguard along with the Army Commander (Aleksander Aleksandrovich Bilderling), (Chernik) directly participated in rearguard combat under intense artillery cross-fire, attempted to stop and organize the retreating units of different armies, forming teams out of separated soldiers. This day (Chernik) was shell-shocked and received head trauma (losing hearing of his left ear, injuring an eye and left side of his face), but did not leave the ranks. He entered the zone of combat at 8 am and left it at 5 pm. (From both sides, eight armies (about 600 thousands people and 2300 artillery cannons) participated in the Mukden battle. The combat zone ranged up to more than 150 km on the front line and 50 km deep. The battle lasted 19 days. During this battle, the Russian army lost 89 thousands people in casualties, and Japanese army lost 71 thousands).

February, 27th, 1905. Joined Army Headquarters and carried out various tasks.

November 28th, 1905. Assigned to the Main Engineering Commandment.

July, 19th, 1906. Assigned a Headquarter Officer.

January 28th, 1909. Elected a life-time member of the Russian Geographic Society.

September 13rd, 1914. Joined war combat.

October 5th, 1914. Assigned to serve under the order of the Head of the engineering unit of the 8th Army.

June 7th, 1915. Corps Engineer of the 17th Army.

Notes on combat participation:

On April 30th, 1915, ... passages across rivers San and Barich (at that time region of the

Russia-Poland border) were restored and several bridges and drives to them were repaired in the burning village of Kalnikovo under the hurricane hostile artillery fire, before its occupation by Austrians.

Further, repeated notes are given, such as: "inspected the trenches at the front line of the 35th infantry division.." or "trenches were under artillery fire". In these notes, only numbers of the military units change and definitions "gun fire" or "hand fighting" are occasionally added.

Notes "on combat participation" end with the record: "further information on the participation of the corps units in combat until April 10, 1916, were lost with the baggage during the railroad travel from the front headquarters to the new service location and cannot be restored with absolute assurance."

March 31st, 1916–August 14th, 1916. Stewart of the 1st Construction Crew of the rear region of the Southwestern Front.

April 10th, 1916 – MAJOR-GENERAL

October 15th, 1916 – Commander of the engineers of the XI Army

October 6th, 1916 – Arrived to the army headquarters

April 24th, 1917 – Departed from the XI Army to a new service location as the Main Commander of the engineering work in the rear region of the Southwestern Front

July 6th, 1917 – Appointed the Head of the Committee for Inventory and Distribution) of technical resources of the Southwestern Front.

October 12th, 1917 – Departed from the active army to Petrograd to participate in the work of the Committee for State Defense.

October 26, 1917 – Return from Petrograd to the active army

Life off-service:

Married (first marriage) to Elena Alekseevna Kochina, has daughter Ekaterina (October 1st, 1884), son Rostislav (September 21st, 1910), and daughter Lyudmila (October 20th, 1916).

Here, the list is interrupted, but includes 2 later inserts:

May 1st, 1922 – pledged allegiance to Red Army

April 15th, 1924 – demobilized from service on grounds of redundancy

Further we continued our search at the Russian State Military Archive (RSMA), which hold documents since 1917. There is no search by name, so we had to meticulously browse

through all the documents of the Main Engineering Department, where Georgiy Prokofievich could supposedly be on service. Indeed, it was found that since September 1918, he was a Permanent Member of the Engineering Committee of the Main Military-Engineering Department (EC MMED) – the supreme organ dealing with military engineering and technical areas. The reviewed files did not contain any information shedding light on biographic milestones of Georgiy Chernik, however some minor details we found can be of interest. We sorted some of the curious facts from G.P. Chernik's biography, which seem most important and best representing that period, and are presenting them here in chronological order.

September 25th, 1918 – Chernik is listed among the candidates "to fill the staff of the re-organized EC MMED"

January 27th, 1920 – The MMED list of family members residing in the same household includes: "permanent member of the Committee Chernik Georgiy Prokofievich, wife – Elena Alekseyevna, sons – Rostislav (10 y.o.), Oleg (2 y.o.), daughter Lyudmila (3 y.o.), and wife's parents Kochin's Aleksey Petrovich and Pavla Vasilievna"

The same document indicates the address in Moscow where the family lived: 30 Trubnikovskii per.

February, 1920 – Name Chernik is listed among the employees of MMED and subordinate institutions "from whom 3-day salary is withheld to benefit the foundation of the "front week" – 435 rubles"

Further Chernik's name repeatedly appears on the lists for receiving the norms of potato, flour, cabbage, firewood..."

May 7th, 1920 – Chernik is on the list of permanent members of EC as a participant of the fortification section. The column "Personal expertise" says "chemistry and explosives"

December, 1920 – correspondence regarding establishing a personal salary for G.P. Chernik and personal application from Georgiy Prokofievich, in which he indicates that he has more than 40 publications and is "one of very few experts in explosive substances"

June 10th, 1920 – "Military Engineer Chernik, G.P., is appointed the permanent representative of MMED in the Special Group of

Extraordinary Komissar for fire arms and explosive substances"

The personal file of G.P. Chernik was held in 1921 archives (RSMA, 1921), which continues the service list:

The most recent title in old army – Major-General

Service in RKKA from – September 1918

Service in White Army – dash

War participation – 1904–1905, 1914–1918

Wounds, contusions – wounded, shell-shocked

Military awards RKKA – dash

Marital status – married

Children and other family members – 4 sons: 33, 28, 12, and 5 years old, 2 daughters: 38 and 6 years old, grandson: 6 years old, 2 granddaughters: 12 and 11 years old.

We should note that the documents in the files for 1917–1923 are quite interesting not only by their contents, but also their appearance. The records are often written or typed on back sides of old forms, torn pieces of paper; many typed copies are almost unreadable. Thus, the most interesting document among the found archive papers was written on the rear side of the August-21 page of a tear-off daily calendar for 1922:

Record ind. №1101

Engineering Committee

July 11, 1923

№141704

To: Director of the 1-st Main Military Economic Storehouse

Based on the information from the Main Military Economic Administration, according to GNS (?) order, permission slip of June 27, № 20578, was issued for dispensing 1 pair of warm stockings, 1 pair of warm foot wrappers, 1 wool fufaika (man's jersey), 1 waterproof tarpauline raincoat, 1 pair of valenki (felt boots), 1 pair of leather mittens, 1 fur hat, 1 waist belt, and 4 arshins of tarpaulin cloth to the Permanent Member of EC MMED G.P. Chernik, who is assigned to travel within a scientific exploratory crew for studying the Khibiny Massif on the Kola Peninsula. Since G.P. Chernik has already left for the trip, the Engineering Committee is asking for a permission to send these items to the director of the technical library of the Committee P.M. Volkov, according to the presented proxy letter, for further shipment the items to the present location of G.P. Chernik.

This was the last document found in the military archives.

After demobilization from the army in April 1924, Georgiy Prokofievich apparently devoted his time to mineralogy and chemistry, i.e. continued the work that had been his life-time interest. Information about this side of G.P. Chernik's life is not systematic and was gathered bit by bit from different sources. Here we present it in the chronological order.

G.P. Chernik's involvement in mineralogy was first mentioned in a document from a military archive, when he became a member of the Mineralogical Society on March 13th, 1898. In 1902, the first publication by G.P. Chernik appeared in the catalog of the Russian State Library – "A few words about the composition of two rare associated minerals found in the Batumi area", in Annual Almanac on Geology and Mineralogy of Russia, Warsaw, 1902. The list includes 22 articles published in different editions; almost all of them present studies of chemical composition of minerals.

Archives of Russian Academy of Sciences preserved the letters written by G.P. Chernik to Vladimir Ivanovich Vernadsky. One of them contains the data of chemical analysis of parisite from Manchuria:

Letter of G.P. Chernik to V.I. Vernadsky (page 1)



	A	B	C		A	B	C		A	B	C
1.1	100	100	100	100	100	100	100	100	100	100	100
1.2	100	100	100	100	100	100	100	100	100	100	100
1.3	100	100	100	100	100	100	100	100	100	100	100
1.4	100	100	100	100	100	100	100	100	100	100	100
1.5	100	100	100	100	100	100	100	100	100	100	100
1.6	100	100	100	100	100	100	100	100	100	100	100
1.7	100	100	100	100	100	100	100	100	100	100	100
1.8	100	100	100	100	100	100	100	100	100	100	100
1.9	100	100	100	100	100	100	100	100	100	100	100
1.10	100	100	100	100	100	100	100	100	100	100	100
1.11	100	100	100	100	100	100	100	100	100	100	100
1.12	100	100	100	100	100	100	100	100	100	100	100
1.13	100	100	100	100	100	100	100	100	100	100	100
1.14	100	100	100	100	100	100	100	100	100	100	100
1.15	100	100	100	100	100	100	100	100	100	100	100

Letter of G.P. Chernik to V.I. Vernadsky (page 2)

October 30, 1906

Dear Sir Vladimir Ivanovich!

At the present time, I finished the quantitative analyses of those rare-earth minerals that I was lucky to find in Manchuria and some of which You picked for crystallographic (measurements). As was suggested before, the mineral proved to be parisite (presumed museum number 16340). In this material, I distinguished three categories: the first is represented by the small most transparent crystals of honey-brown color; another group is represented by medium-size relatively transparent pieces of a similar color, which constitute the core parts of some crystals. These are the most abundant (among which You selected the examples for the measurements).

In spite of the small amount of the rare mineral material, I was able to complete the analyses (maybe even satisfactorily). Hence I prepared a short notice, which I handed to A.P. Karpinsky for publishing in Transactions of Min. Soc. Also there I included the analyses of the grains that were found together with parisite and proved to be malacon.

Regarding Your contribution, I only mentioned that the crystallographic analysis was performed by you, and a similarity was found with the parisite from Montana. I could not address this matter in more detail since I did not feel I had

a full right to do so and did not know your further intentions.

If you wish, A.P. said the article can be supplemented with Your data or ... (illegible) ... Just in case if you are interested in the results, I am enclosing them here.

If you would like to know more details, my article is now in A.P. Karpinsky's hands, and he probably would not mind giving it to You for reading, since there is hardly a hope for its publication in the near future.

I ask You, Dear Sir, to be assured of my absolute respect and always being at Your service....

It should be noted here that the museum collection keeps 4 specimens from Manchuria, which were probably collected during the Russian-Japanese war, although they were donated to the Museum in 1906 – 1907.

The second letter is more personal:

March 26th, 1917

Dear Vladimir Ivanovich!

Congratulations to You on the up-coming holidays of Pascha and my best wishes.

How did the recent events affect you? Browsing through "Kiev Mysl" and "Russkoe Slovo", I did not see Your name mentioned, although I believe the wave of events that passed over Petrograd could hardly leave you aside. The internal disorder has a really bad influence on us here: with the freedom of printed word, statements of extreme character issued by the Soviet of Working Deputies reach the army and undermine the discipline (in its roots). Certainly, some severe measures have to be taken sometimes – i.e. trials, when words and speeches do not work anymore. That was a big mistake to allow army to participate in politics. This is totally incompatible with the hard reality of the war situation.

The army pledged allegiance to the Temporary Government, unanimously and sincerely, after it became known that the Emperor abdicated the throne, and I believe that if there were attempts of counter-revolution, they would not find any support among the military. Of course, I am talking about our XI Army.

The one thing that I wish is that the Temporary Government fully used the strength of its power and did not allow any interference in its decisions...

At this point, the text is interrupted. Obviously, the rest of the letter was not saved.

It is known from the literature that in 1921 G.P. Chernik separated and analyzed fergusonite-(Y) from intergrowths with samarskite and other minerals in specimens from the Blumovskaya Mine collected in 1914 (Popov and Popova, 2006).

In 1923, Georgiy Prokofievich traveled to Khibiny with A.E. Fersman's crew. As a result of this expedition, six papers were published on the chemical studies of Khibiny minerals (calcium ancyllite, velerite, and eudialyte).

In 1927 (according to an unverified source), Georgiy Prokofievich traveled to Baikal Region by Fersman's assignment, where he studied minerals of Slyudyanka.

The last known works by G.P. Chernik were on the mineralogy of the Khibiny and Slyudyanka: "Results of the analysis of some minerals from the Khibiny laccolith of Kola Peninsula", *Gornyi Zhurnal*, 1927; and "On Mineralogy of Slyudyanka", *Proceedings of the Mineralogical Museum, Academy of Sciences of the USSR*, 1927, Issue 3.

Twenty one specimens of those collected by G.P. Chernik in Khibiny are held at the State Geological Museum and 97 specimens from Slyudyanka are held in our museum.

The name of G.P. Chernik is mentioned in published V.I. Vernadsky's dairies (2006). The record of December 28, 1938, says: "It turned out that the Samoilov's article on the Kashinskii meteorite was already prepared in 1921, and then apparently some doubts were raised about Chernik's analyses..." There is a comment to this record made by the editor, Doctor of Geological and Mineralogical Sciences, V.P. Volkov: "Chernik Georgiy Prokofievich (1864–?) – mineralogist, chemist, in the early 1930s – engineer at the Institute of Mechanical Processing of Mineral Deposits ('Mechanobra'); author of many publications on chemical mineralogy".

There is a later mentioning of G.P. Chernik's name; however this information would need a careful verification, which is now hardly possible. The inventory book of the Mineralogical Museum of the Russian Academy of Sciences lists two smithsonite specimens (№34307 и №34308), which were delivered to the museum in 1933, but there is a remark in the book: "collected 1932".

Finally, the last published material about Georgiy Prokofievich Chernik was the book "Scientists of Leningrad" issued by the Academy

of Sciences of the USSR in 1934. This book contains data "about each scientist and his or her scientific expertise – the information typically supplied by the scientists themselves and therefore supposedly accurate". Here we have the following information: "Chernik Georgiy Prokofievich, born 1864, engineering construction, construction mechanics, analytical and mineralogical chemistry, analysis of rare-earth minerals. 63 Proletarskooi Pobedy St., apt. 16. Scientist, Academy of Sciences of the USSR, Engineer at Mechanobra. Member of the Section of science employees". This information means that in 1934, Georgiy Prokofievich Chernik lived in Leningrad and worked as an engineer at the institute "Mechanobra".

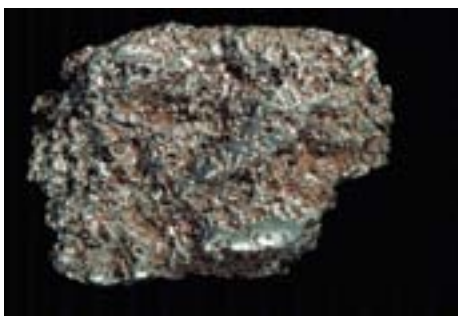
At first it seemed impossible to establish the date of death of Georgiy Prokofievich. Search of archives did not give us any results. Then help came from the employees of the Vasileostrovskii ZAGS. On our request, they found a death certificate which said "Citizen Chernik Georgiy Prokofievich died January 12th, 1942, at the age of 77, of which a record is made in the registry of death acts, № 2710 of January 17th, 1942. Place of death – Leningrad; cause of death – dystrophy." Comments to such a record are hardly necessary.

G.P. Chernik's specimens at the Fersman Mineralogical Museum RAS

Georgiy Prokofievich donated a total of 399 specimens to the museum. Those include 135 names, which represent 105 presently acknowledged mineral species. By location, the specimens represent 82 deposits outside Russia and 2 Russian deposits (Ilmeny and Slyudyanka).

In this collection, there are a number of rare mineral species and varieties. Also, the geographic reference of many of the specimens is quite unique. Only Chernik's collection has native platinum from Borneo Island, gorceixite from Brazil, uraninite from Ceylon, euxenite from Volyn, graphite from Burma, the cassiterite from Malacca Peninsula in Malaysia. 52 out of 99 museum specimens from the Borneo (Kalimantan) Island and 18 out of 19 specimens from Sumatra were donated by Chernik.

It should be noted that G.P. Chernik donated not the whole collection at once (like many our authors did), but supplied separate specimens during 30 years, from 1903 to 1933. Some of the specimens can be seen in this article. We



Native platinum, 2.5 x 1.5 cm. Choco, Columbia.
FMM No 5195.
Tourmaline (max 3 cm). Kuruwiti, Ratnapura, Sri Lanka. FMM No 11256



tried to restore the order in which the specimens were acquired. We certainly cannot claim that all details of this investigation are perfectly accurate.

Thus, in 1884, sub-lieutenant G.P. Chernik served in Batumi and participated in field engineering works. Probably the specimens from the Caucasus were collected during that time. These include unique natural alloys of noble metals – rhodite (rhodium gold) and porpezite (palladium-gold). At a much later time, microprobe analyses of Chernik's porpezite showed that in addition to the phases dominated by gold (AuPd-Au₂Pd series), there are also phases in the intergrowths in which palladium is notably dominant. Palladium content at certain points is as high as 94.4 wt. %, i.e. the exceptionally rare mineral – native palladium – was additionally found in the specimens. Chernik's interest in noble metal chemistry is also confirmed by the only synthetic specimen provided by him – acicular crystals of gold amalgam, which was synthesized, according to the records, by chemist Fedor Vasilievich Vilm (1845–1893). Obviously, the collaboration of Chernik with Vilm, an expert in chemistry of platinum group metals, is related to the finds of such rare minerals.

November 20th, 1895–December 20th, 1896. Sub-Colonel Chernik went to a two-month trip abroad for a vacation (RSMHA = PГBИYА, 1900). Based on the time, it was a trip to Europe. A collection of 51 specimens, most of which were from Germany and Norway, was handed to the Museum. Apparently, some of the specimens were bought or given to Chernik by scientists whom he met in Europe. The book of records contains remarks to specimens № 5237 (xenotime) and № 12126 (dysanalyte): "from Prof. Mayer" and "from Prof. Gussak". It is also assumed that the platinum nugget from Columbia, 38.25 g in weight, which was brought to the Museum along with other European specimens, was also purchased in Europe.

November 15th, 1904–November 28th, 1905. Colonel Chernik was at army service in Manchuria. Probably, the coal specimens and an interesting piece of amber from the Suchang coal mines were collected at that time.

The most intriguing voyage of Chernik was to the Eastern countries. Judging by brought specimens and published works, he visited Borneo, Sumatra, Sri Lanka, Madagascar, India, Pakistan, and Thailand. Maybe the geographic span of this trip was somewhat narrower, and some of these specimens were just purchased from "The Borneo company's Mines" (about which there is a note in the data base) or from other collectors.

There is no documentary evidence about the dates of this trip. We can assume that it occurred between 1906, when G.P. Chernik was "appointed a headquarter officer" and 1909, when he was elected "life-time member of the Russian Geographic Society". The service list does not have any other records between these two events. There is a record in the incoming specimens book for 1909 – "some specimens were collected personally", i.e. there is almost no doubts that this trip in fact took place.

The specimens from the Kola Peninsula were collected during the Khibiny expedition of 1923. As was mentioned before, in 1927 Chernik worked at Slyudyanka. However, on closer examination of the Chernik's specimens, one can notice that the principle of selection was quite different from the tradition of that time. There are almost no "exhibition" specimens, well-shaped crystals, or aesthetically attractive pieces, even from the regions famous by collection material, such as state of Minas-Jerais (Brazil), Sri Lanka, Kashmir (India), deposits of jewel-quality corundum in Southeastern Asia. Instead, one can see a wide selection of typical specimens from parent ores and placers, which are sources of many chemical elements – Mn, Ni, Cr, Zr, Zn, Sn, radioactive elements (U, Th), rare elements (Ta,

Nb), rare-earth elements (Y and lanthanides), and noble metals (Au, Pt-group). The specimens of gold and platinum from Borneo are enriched schlichts 0.5 to 1.2 g and small individual grains of iron-platinum and osmium-iridium minerals, hundredths of gram in weight.

It seems that minerals were interesting to Chernik above all as a natural material for studying chemical elements in the earth crust. Further, this task was taken over by the new area in geosciences – geochemistry, which originated somewhere at the threshold between the 19th and 20th centuries.

During this period, the last empty cells in the Mendeleev periodic table were filled (at least with the stable elements). Most of discoveries during that time were related to the group of lanthanides. Looking through the list of specimens donated to the Mineralogical Museum, one can notice Chernik's particular interest in the minerals of rare-earth elements. Even at Mukden "under unceasing fire of hostile artillery", Chernik managed to collect small (up to 3 mm in size) crystals of the calcium-rare-earth fluoride-carbonate, parisite.

It is likely that besides chemist's and explorer's curiosity, Chernik also had a task of finding promising strategic resources. Such metals as Mn, Ni, Cr had been long known to be used as alloying additives to steel. Probably, his interest in minerals of zirconium and rare elements is also related to military metallurgy. Chernik's specimens are usually quite small (some of them do not exceed hundredths of a gram in weight); however total of 8 listed specimens of zirconium ore (zircite from Brazil) have mass of several kilograms. This amount would provide a starting material for pilot-scale experiments. It is known that addition of just 0.1% Zr results in significant increase in the hardness and viscosity of steel, which is necessary for manufacturing armored

protective plates and shields. Quite a large number of specimens in the collection represent columbite. It is known that niobium is used as an alloying additive and nitrogen scavenger for the heat resistant steels for artillery cannons.

The strategic interest in Sn deposits in Southeastern Asia is also understandable: before 1930s, Russia had no significant resources of this metal.

Obviously, Chernik's interest in coal (specimens from Sumatra and Borneo were listed in the museum collection) and oil (as indicated in inventory books: 10 jars from different wells on Borneo and 98 (!) jars from wells on Sumatra) can be explained by the search of the energy resources for Russian Navy. The oil specimens were later (in 1929) handed over to the Institute of Oil.

Possibly, Chernik's interest in minerals of rare-earth and radioactive elements was not pure exploratory. Only 20 years passed between the discovery of the radiogenic helium in minerals by Ramzai and bombings of London by German dirigibles filled with the helium recovered from the monazite sands very similar to those handed by Chernik to the museum collection.

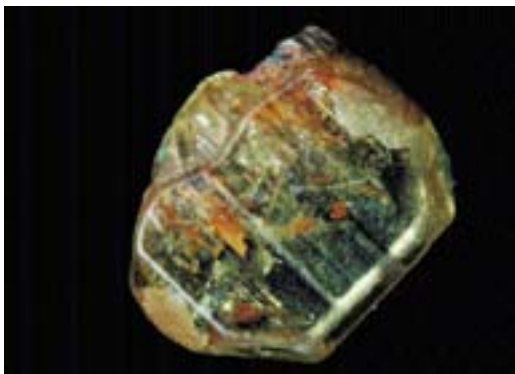
Some information about personal connections of Chernik in 1912 is given by the record for one of his donated calcite specimens from the Alupka area: "garden of the Grand Duke Georgiy Mikhailovich (Ai-Petri terrace)". No wonder, the engineer-colonel, member of the Russian Geographic Society could certainly visit the mansion of the Grand Duke. Grandson of Nikolai I – Georgiy Mikhailovich Romanov – was almost the same age as Chernik and, as a Life-Guard officer of the Cavalry and Artillery Brigade, could know Chernik from army service. Georgiy Mikhailovich was also a curator of the Russian Museum of the Emperor Aleksander III since its founding. Chernik knew and collaborat-

Monazite (max 2 cm). Balangoda, Ratnapura, Sabaragamuva province, Sri Lanka. FMM No 11261



Corundum (11 x 8 cm). Sapfir Mine, Kashmir, India. FMM No 19057





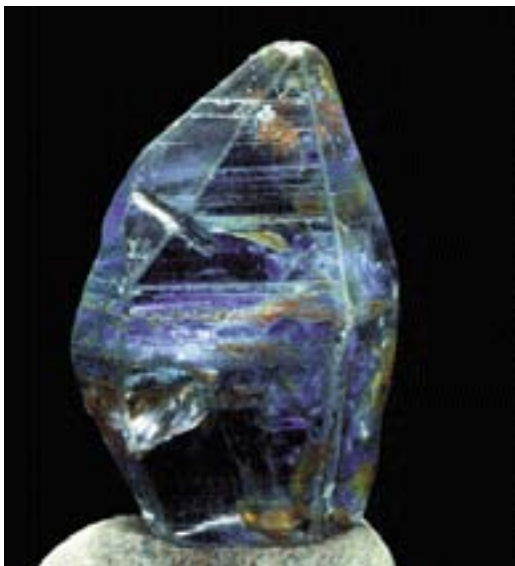
Chrysoberyl (1 x 0.7 cm). Matara district, Sri Lanka.
FMM No 11266

Cassiterite, 3 x 2 cm. Perak, Malacca peninsula, Malaysia.
FMM No 19027

Photo: Michael B. Leybov

ed (at least since 1906) with V.I. Vernadsky, who at that time was a curator of the mineralogical division of another museum in Petersburg — Geological Museum of Academy. In 1912, after moving from Moscow to St. Petersburg, Vernadsky started his work at the museum, which was later re-named "Peter the Great Geological and Mineralogical Museum". In the same year, a number of Vernadsky's specimens collected in Crimea were enlisted in the museum, including some pieces from the Alupka area. Thus, there is enough ground to suppose that Chernik knew and met Vernadsky and the Grand Duke personally. After 1919, when Grand Duke Georgiy

Corundum (0.8 x 0.5 cm). Ratnapura district, Sri Lanka.
FMM No 11301



Mikhailovich, along with other grand dukes, was executed in the yard of the Petropavlovsk Fort, it is hard to believe that any evidence would be preserved about the relations of G.P. Chernik and employees of the Mineralogical Museum with members of tsar dynasty.

Probably, collaboration between another employee of the Peter the Great Geological and Mineralogical Museum, A.E. Fersman, and G.P. Chernik gave Fersman substantial information on the strategic role of the mineral resources. Later Fersman emphasized this role during his service on the Committee on Natural Productive Resources of Russia and in his published works "Geology and War", "War and Strategic Resources", and "Atoms at War".

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A MONOGRAM ON BASALT. A HISTORY OF ONE MUSEUM SPECIMEN

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The article describes a legendary place of formation of one specimen from the Fersman Mineralogical Museum, a history of its appearance in Russia and Great Prince Konstantin Nikolaevich, his first owner.

3 figures, 6 references.

Among numerous specimens, delivered from various sources to the Fersman Mineralogical Museum in the 1920s, are such specimens, which bear evidence on previous owners, sometimes even a history of how they were initially received. These are monograms, other inscriptions, and personal labels. Unfortunately, they do not always help, because the museum specimen might have had more than one owner before it came to the museum, and the monogram will not tell who the first owner was. We managed to recognize first owners only for several specimens in the collection of decorative and precious stones.

One of these specimens is the small piece of black basalt, polished on both sides. One of its sides has a flat golden monogram consisting of united Russian letters of "K"(K), "H"(N) and "P"(R). The other side has inscription "Fingal's Cave" and a date of "July 6/18 1847" (Fig. 1).

The specimen arrived to the museum in 1926 with other objects from Gatchina and Stroganov Palaces (State Hermitage). Russian letter "P"(R) helps to suggest that the item could belong to a member of *Romanovs* (the Royal family). Initial letters and date (1847) pointed to the Great Prince Konstantin Nikolaevich Romanov (1827–1892). However, such a good coincidence was not very convincing to confirm that this fragment of basalt belonged to him. It was therefore necessary to remember a biography of Great Prince.

Konstantin Nikolaevich, youngest and favourite brother of the Emperor Alexander II, was devoted to the navy service since childhood. F.P. Litke, famous Arctic explorer, was his teacher. In addition to compulsory subjects, necessary for the future activity, the boy studied history, literature, philosophy, European languages, and music. He was one of the most educated people in Russia of the

time. His large library was filled not only with books about ship building and exact sciences, but also on history, geography, and various arts. He knew modern literature very well. He was a collector of paintings and very well played a violin.

Since 1850, Konstantin Nikolaevich began to serve in the Navy Department. He was a liberal and a supporter of many innovations. The Great Prince was a dedicated enemy of peasant's serfdom and provided much effort on its reformation and abolishment in 1861. Earlier, due to his efforts and persistence, the Admiralty liberated peasants, who belonged to the Admiralty (1858). Since 1861 to 1881, Konstantin Nikolaevich was a head of the General Committee on Agriculture. Since 1862 to 1863, he was a governor of Poland. Since 1865, he was a chairman of the State Council. In 1870, he participated in the military reform. He paid attention to art, and in 1873 he was a head of the Imperial Musical Society. This is incomplete characteristics of the interesting personality of the Great Prince. He lived a bright life, full of turbulent state activity and complex personal life experience (Barkovets, 2002), but we are interested only in a very brief period of his life during summer 1847 (6 to 18 July, if to be very precise), in relation to the history of our museum specimen.

As it was already mentioned, the Great Prince was preparing himself for the navy activity. When 8 years old, he was a nominal commander of the navy brig "Hercules"; when 17 years old, he became a true commander of brig "Ullis"; and at the age of 20, he was a first rank captain during the navy expedition around Europe on large frigate "Pallada". It was in 1847, mentioned on our specimen together with the Fingal's Cave, a cave well known in Europe and Russia, whose origin was related to the feat of ancient Celtic heroes. As follows



Figure 1. Basalt from the Fingal's cave, Isle of Staffa, Inner Hebrides, Scotland, with a monogram "KHP" (KNR) and engraved inscription. Length 9.5 cm. FMM No PDK-1609

from the diary of Konstantin Nikolaevich, he went to England after engagement with Princess of Sachsen-Altenberg in May 1847. During relatively long trip to this country, he visited various attractions, such as castles, waterfalls, zoo parks, plants, factories, museums, picture galleries, and many other locations, including Fingal's Cave (A diary of the Great Prince, 1847).

The names of Fingal and his son Ossian emerged in the collection of ancient Scottish stories of the "Poems of Ossian" by James Macpherson published in London in 1762. The author stated that during his staying in Scotland he found ancient manuscripts, containing the legends of the 3rd century, written in Gaelic, which he translated to English. These were lyric-epic stories about Fingal, a king of the legendary Morwen State on the western coast of Scotland. The ancient writer was a warrior and bard Ossian, an elder son of Fingal (Macpherson, 1762). The originality of these manuscripts was soon strongly questioned. Macpherson promised to show original manuscripts, but he never fulfilled these promises. The debates continued for decades, but regardless to the trust in originality of these poems, they had a great success in Europe and stimulated many imitations.

The "Poems of Ossian" described pictures of great nature, with detailed descriptions of battles, victories and defeats of ancient heroes, their love passions, with mourning about the relatives and passed heroic times. The poem hugely influenced development of romanticism and sentimentalism in practically all aspects of art, with dramas and operas on Ossianic subjects. Mentioning of Ossian and motifs of his poems can be traced in the writings of Scott, Goethe, and Byron. At the order of Napoleon, the Gerard, Girodet, and Ingres produced romantic land-

scape paintings with Ossianic heroes for the Malmaison Palace (Fig. 2).

By the 1830–40s, romanticism emerged brightly in music. In 1829, Mendelssohn visited the cave on the Isle of Staffa, related to the Ossian legends. It greatly impressed him. Being impressed by the great creature of nature and heroic-poetic spirit of the "Ossian" poem, he composed a concerto ouverture "The Hebrides", or "Fingal's Cave" (1830–1832). After release of the ouverture, the place became officially called Fingal's Cave.

It is important to say that in the end of the 18th century Ossian also penetrated into Russian literature together with romanticism and sentimentalism (Levin, 1980). First data about Ossian and his songs appeared in Russian press in 1781, in the translated Goethe's novel "The Sorrows of young Werther", and in 1792, a complete edition of the poems was published. Practically all the writing and reading public of Russia of the time was fascinated by the songs of ancient bard. He became a favorite poet of the youngsters, and old masters were influenced as well. It appeared in the Derzhavin's odes, Karamzin's creative works, and later in the verses of Pushkin, Lermontov, Gnedich, and others. There were publications entitled "The Ossian's Shadow", "Imitating Ossian" and alike. In 1805, tragedy "Fingal" by Ozerov was staged on one of the scenes of St. Petersburg, which survived for half a century.

Poetry of Ossian was perceived as popular and heroic. It became especially sensitive when "The Word about Igor's Regiment", the most ancient product of the Russian literature, was published in 1800. Both epics were perceived as analogous examples of the ancient military poetry.

During Patriotic wars with Napoleon, the heroic motifs of the "Ossian" poem were in har-



Fig. 2.
The painting
"Ossian" by
Gerard. 1801

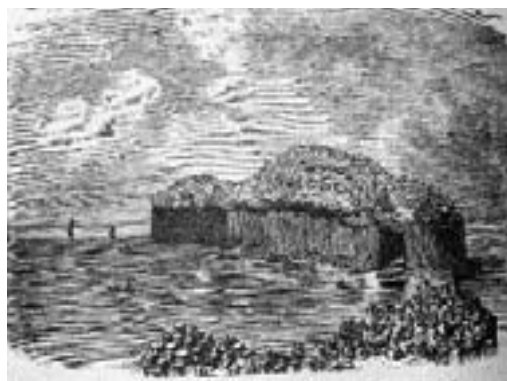


Fig. 3. The
Fingal's Cave
(illustration
from the book
by I.V. Mush-
ketov, 1924)

mony with Russian patriotic motifs. This appeared in the poetry of famous Russian poets Vasiliy Zhukovskiy, Konstantin Batyushkov, Kondratiy Ryleev and others.

In essence, by the time of our interest (1847), the Ossian songs about feats of his father Fingal and places, where they took place, were very well known to the educated Russian public. The Royal court could not be an exception. Naturally, young Great Prince Konstantin Nikolaevich was well informed about both existence of the famous cave and related legends. Therefore, the famous cave became a 'must to visit' sightseeing place during the cruise around Europe on the frigate "Pallada".

Even without legends, the Fingal's Cave deserved attention. As it was mentioned above, it is located on the Isle of Staffa near the western coast of Scotland (Inner Hebrides). It is part of the National Natural Park of Scotland and is a National Heritage.

This huge cave was washed by marine surf in the steep rock of the volcanic island, between the two rows of basaltic columns (Fig. 3). According to different data, its length is 70 to 85 m, and the height is 20 to 30 m. With its size and regularly shaped columns along the walls, it reminds a great and mysterious cathedral. Its floor is covered by water so that during the high tide the waves produce a strange and strong sound, which can be heard at long distance. This sound gives a mystic impression and reminds a heroic past of this place, when Ossian built this cave for his father Ossian. Walter Scott visited this place and wrote that it is most unusual place he ever seen and believed that none description would be able to reflect impression it produces.

The Great Prince was also impressed by the cave. On the 6th of July 1847, he wrote in his diary, "we lifted an anchor and moved to the northern side of the Isle of Mull. At about 9 o'clock in the morning, we approached the Isle of Staffa. Its basalt sides are extremely strange. Fortunately, the sea was absolutely quiet so that we could enter the famous Fingal's Cave. This is an absolutely beautiful view" (A diary of the Great Prince, 1847). The effect was so impressive that Konstantin Nikolaevich not only collected and preserved a piece of basalt from the cave, but he also ordered to rework it as a souvenir with his initials and a date of visit.

It's unknown when and how this specimen appeared in Gatchina. However, its affiliation to the Great Prince Konstantin Nikolaevich is out of doubts.

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IS THIS A REGAL ENGAGEMENT? On the mineral collection of *The Throne Crown Prince*

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The collection which was transferred in 1923 from the Museum of the City (St. Petersburg) to the Fersman Mineralogical Museum was collected in the 1870s, during the reign of Alexander II. Initially, it was created for Alexander Alexandrovich, the Crown Prince (future Tsar Alexander III), then was enlarged and completed for Nikolai Alexandrovich (future Tsar Nikolai II) and likely used in his education.

The contents of the collection, the geographical distribution of its samples, and principles of their systematization enable us to reconstruct the state of mining and the level of Russian mineralogy in the middle of the nineteenth century.

6 photos.

The course of Russian history resulted in the mineral and rock specimens that formerly belonged to the Royal family to land in the ample collection of the Fersman Mineralogical Museum. The handwritten catalogue that was accessioned together with them added substantially to their value; it was titled "*A Catalogue of the Mineral Collection Belonging to the Throne Crown Prince*".

The transfer of these materials to the Mineralogical Museum in 1923 from the Museum of the City was recorded thus by entry No 1682: "*The Museum of the City, former Anichkov Palace. Collected in 1890 by Nefed'ev, mining engineer, in the Mining Institute for Nikolai II, former Crown Prince*".

What was the Museum of the City? It was established on 4 October 1918 by a decree of the People's Commissariat of Education signed by A.V. Lunacharskii, and was based upon the exhibits of the City Board Museum, subsequently incorporating Old Petersburg's Museum as well. The Anichkov Palace's historical interiors, where the main part of exhibition was placed, were of their own special value. The Royal Apartments of Alexander III and Maria Feodorovna were here; they lived in the Anichkov Palace from 1866. Nikolai II spent his childhood and juvenile years here too.

The Museum of the City was an outstanding scientific and educational center devoted not only to the city upon the Neva River but to the way of life and architecture of a "city in general" and its urban culture. The Museum of the City was a place for personal contacts between architects, artists, and scientists. A.M. Gor'kii, A.F.

Koni, A.A. Blok, A.V. Lunacharskii delivered lectures here and attended them. The Museum was lead by L.A. Il'in, the Leningrad Chief Architect.

In 1928, the Museum of the City began to be dismembered. The historical interiors of the Royal Apartments were removed. The libraries of Nikolai II and widowed empress were moved to Moscow to the *Lenin Library*. An important part of the collection was sold abroad, including a number of unique exhibits. Eventually, the Museum was closed in 1935 to be replaced by the Leningrad Palace of Pioneers. Some of its exhibits were preserved in the collection of the State Museum of St. Petersburg History.

But who was that mining engineer, Nefed'ev? There is a signature at the end of the Catalogue made by the same hand as the text (likely by the hand of a clerk): "*Full Counselor of State*" and the personal signature "*V. Nefed'ev*". The mention of the Mining Institute in the Entries Book indicates that this would have been Vasilii Vasilievich Nefed'ev.

V.V. Nefed'ev was born in 1796 as elder son of an artisan of the St. Petersburg Mint. He began work at the same mint in 1811 as an assaying apprentice and a year later was shifted to The Mining Cadet Corps (now the St. Petersburg State Mining Institute). Here, he was learning and then teaching mineralogy and petrography. From 1825 to 1849 he was inspector of the museum of the Mining Cadet Corps and Institute of Mining Engineers' Corps (the names of the Mining Institute in 1834–1866).

In 1871, The Concise Catalogue of the Mineralogical Collection of the Mining Institute



Collection handwritten catalogue and some of specimens registered in it.

Museum was published in St. Petersburg; it was compiled by Colonel Nefed'ev. "Colonel" is not astonishing as the Mining Institute is notable for its militarization from 1834 up to this time; the entire mining corps was a paramilitary organization in Russia, and colonelcy (Berghauptman in mining) corresponded to VI Class of the *Table of Ranks* – the title of collegiate councilor. In 1875, Vasilii Vasilievich Nefed'ev (already Professor) became an honorary member of the Imperial Mineralogical Society.

However, he could not, regardless, have made up a collection for Nikolai the Crown Prince in 1890 (as recorded in the book of entries in the Mineralogical Museum). Vasilii Vasilievich past away in 1879, at a declining age of 83.

It is obvious that Nefed'ev has reached the highest class rank of full Councilor of State (Major General in military hierarchy) to the late 70s. It was the highest rank of an official. These officials had to be confirmed by the Emperor personally and occupied important appointments in the State. There was no trace of any other State councilor V. Nefed'ev who could have assembled a collection in 1890.

To determine time of formation of the collection let us scrutinize the structure and contents of the catalogue.

In the Table of Contents, the following sections are mentioned:

"Alphabetical index of minerals",
"Catalogue of mineralogical collection",
"----- crystalline minerals",
"----- rocks",
"the scale to determine mineral hardness",
"the list of minerals for replenishing collection",
(with other handwriting) "*and ores presented to Nikolai Alexandrovich, the Crown Prince and Grand Duke*".

In the Catalogue text, the headline of the sixth section appears as "*The list of minerals for replenishing the collection of His Highness the Crown Prince and Grand Duke Alexander Alexandrovich*".

Therefore, the collection was designated not for Nikolai the Crown Prince at all but for the future Emperor Alexander III at that time when he was the Crown Prince, the heir to the throne (1865–1881). Evidently, this collection was also used during the education of his son Nikolai Alexandrovich, future Emperor Nikolai II. The initial eight years of his education were dedicated to the gymnasium courses where the traditional, for gymnasium, ancient languages were replaced with the basics of natural sciences including mineralogy. The collection was surely appropriate, too, in the "*course of higher sciences*" when Academician N.N. Beketov lectured in 1887–1889 as a Chemistry course for the Crown Prince.

So the collection began not in the 90s but in the second half of the 1870s. The mineralogical collection was evidently made up not earlier than in 1872, which can be concluded from the presence of nefed'evite in the list. This earthy silicate of pinkish color was described in 1872 by P.A. Puzyrevskii, Prof. of Mineralogy at St. Petersburg University, in the paper "*Nefed'evite, a new mineral from Nerchinskii Krai*" ("Proceedings of the Imperial Mineralogical Society"). It was named in honor of V.V. Nefed'ev. Nefed'evite was later identified as a montmorillonite variety and discredited as a distinct mineral species.

Now let us observe the composition of the collection as reflected in its catalogue. In the mineralogical section, 593 specimens have been recorded divided into 136 "mineral species". Here is the list of these "species" in accordance with modern terminology:

graphite, native sulfur, rock salt, heavy spar (barite), celestine, witherite, strontianite, gypsum, limespar (calcite), aragonite, dolomite,



Nefed'evit (montmorillonite). Jar's diameter 7 cm. Transbaikalia. FMM No 14087. Photo: Michael Leybov

apatite, talc-apatite (chlorapatite), fluorspar, boracite, corundum, diaspore, gypsum (hydrargillite), alum, lazulite (blue spar), turquoise (callaite), wavellite, cryolite, monazite, rock crystal, amethyst, chalcedony, carnelian, agate, jasper, opal, apophyllite, talc, soapstone, serpentine, schillerspar (diallage), chlorite (ripidolite), wollastonite, xanthophyllite, pyrophyllite, thermophyllite (antigorite), amphibole (hornblende), nephrite, glinkite (olivine), porcelain clay, stilbite, staurolite, feldspar, Labradorite, perlite, wernerite (scapolite), glaucolite (var. of scapolite), obsidian (volcanic glass), steingelite, garnet (venisa) idocrase, orthite (allanite), mica, tourmaline (schorl), axinite, topaz, sodalite, lazurite, cancrinite, emerald, aquamarine, phenacite, chrysoberyl, zircon, gadolinite, rutile, sphene, perovskite, tantalite, mengite (monazite or columbite), samarskite, aeschynite, pyrochlore, scheelite, wolfram, molybdenite, volkonscoite, grey antimony ore, native arsenic, magnetic ironstone, iron glance, ilmenite, chrome ironstone, brown ironstone, spar ironstone, vivianite, sulfurkies (pyrite), arsenkies (arsenopyrite), pyrolusite, manganese, rhodonite (orlets), zinc spar, galmei (smithsonite), zinc blende, acicular ore, cobalt, bismuth, nickel, tinstone, red lead, white lead ore, lead vitriol, pyromorphite, red lead ore, lead glance, tellurous lead, native copper, red copper ore, malachite, chessilite, brochantite, libethenite, knufite (volborthite), fisherite, aurichalcite, diopside, copperkies, peacock ore, cinnabar, silver, glass silver ore, hornsilver (silver chloride), altaite, gold, platinum, mellite, anthracite, coal, asphalt, amber.

One can discern in this list some signs of mineral systematization by the main groups of chem-

ical elements in the tradition of the Cronstedt's systematics published in 1758. This form of systematics was applied, in particular, to the "Mineralogy Manual" (1832) by D.I. Sokolov, Prof. of St. Petersburg University and Mining Institute.

At the moment of formation of the collection, this systematization was already outdated after the classification of minerals by the type of anion complexes by J. Berzelius (1816), its improvement by K. Rammelsberg in 1841 – 1847, and taking the latter as a basis, in "The System of Mineralogy" by J. Dana in 1850. Some relics and earlier classifications that had existed until the middle of the eighteenth century being based upon physical properties of minerals can be recognized at places in the register. For example, the minerals of laminar structure (which is reflected in their names) are united: xanthophyllite (brittle mica clintonite), pyrophyllite, and thermophyllite (antigorite).

The minerals are often grouped in the catalogue in the same way as in Sokolov's "Manual"; however, some groups were replaced, which is probably due to the discovery of the Periodic Law by D.I. Mendeleev (late 1868- early 1869). For instance, one can discern the group of minerals of the alkaline earth subgroup of the second main group of the Periodic System (barite, celestine, witherite, strontianite, gypsum, calcite, aragonite, dolomite, apatite...), then the minerals of aluminum (third group), silica, titanium, zirconium (fourth group), niobium and tantalum (fifth group), chrome (volkonscoite), molybdenum and tungsten (sixth group). Having taken this into account, one can identify those minerals that are under outdated names. For example, mengite, as being in one company with tantalite, samarskite, aeschynite and pyrochlore, is evidently a variety of columbite, though the name "mengite" could have referred to monazite too.

The diversity of ore minerals of iron, manganese, lead, zinc, copper, and silver, particularly from Russian deposits, emphasizes the practical selectivity of the entire set. The group of organic substances described as minerals is listed together. Mellite, a salt of an organic acid, is juxtaposed with them. It is clear that solid combustible minerals were at that time an important natural resources of Russia.

It is interesting that about ten specimens of gold were in the collection whereas a single one

of platinum (from Brazil) was available, though Russia was a leader in platinum mining in the nineteenth century.

In the catalogue section "The list of minerals for replenishing collection of His Highness the Crown Prince and Grand Duke Alexander Alexandrovich", 80 specimens are recorded. Their sequence resembles the "species" order in the "Catalogue of the mineralogical collection" (graphite, then Ca and Ba minerals, Al (corundum), Si (quartz and silicates), then ores of iron, manganese, lead, copper, silver, and, nearer to the end, mellite and coals. This confirms the existence of a unified systematics utilized to make up the collection. It is notable that this part of the catalogue was signed not by Nefed'ev but "Vice Director of the Office" Major General Vasil'kovskii. This set was possibly made up after 1879.

It is interesting to trace the relations between "species" and "varieties" in the catalogue. On one side, rock crystal, amethyst, chalcedony, carnelian and agate, identical in composition, as well as emerald and aquamarine, are "species". On the other hand, quite different minerals are often written as one "species". For example, the species "stilbite" included, together with various zeolites (stilbite, laumontite, chabazite, harmotome, heulandite, natrolite etc.), also prehnite, kyanite, and its variety recitite. "Dioptase" included also atacamite, "slaggy copper green", "vitreous copper ore", "copper black", and even planerite.

Some boundary fuzziness between mineral and rocks is seen. Such names as "jasper", "serpentine", "rock salt", "limestone", "opal", "anthracite" etc. are present both in the catalogue of minerals and the catalogue of rocks.

The specimen geography of the "Catalogue of mineralogical collection" is also revealing. Of course, most specimens represent traditional mining regions of Russia — Karelia, the Urals, Altai, Transbaikalia. Some specimens from Kamchatka and Yakutia are found in the collection.

The European localities are widely represented. According to today's political geography, the list of European states represented in the collection appears as Austria, Finland, Great Britain, Hungary, Germany, Italy, Latvia, Norway, Poland, Romania, Ukraine, France, Czech Republic, Switzerland, and Sweden.

As to Asia, it is represented with Iran (Persia). There are specimens from Azerbaijan, Kazakh-

stan, and Turkmenia.

The American continents are only represented with specimens from South America (Brazil, Peru, Chile).

One specimen, topazes from "New Holland", evidently came from Australia, it having born this name on the maps before 1824.

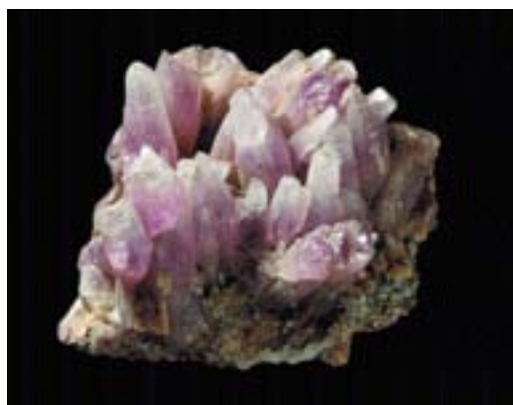
In the collection of the Fersman Mineralogical museum, authors determined 190 specimens from the "*Catalogue of mineralogical collection*". The main part of this collection has been registered in 1925–1934. These years were very difficult in Russian History. During more than forty years between the time of its assembly and the time of its transfer to the Fersman Mineralogical Museum the number of specimens probably diminished appreciably. Besides, several similar specimens from the Crown Prince's collection were often recorded under the same museum number.

The mineralogical specimens (those that are in the Mineralogical Museum collection) are, as a rule, of small sizes, from 5 to 12 cm. Only few of the display specimens exceed 20 cm. Friable minerals are placed into uniform glass jars shut with stiff paper bearing a label written on it. Some substances are stored in small glass test tubes.

In the catalogue of rocks, 200 specimens have been recorded; however, their localities were indicated in some individual cases only.

Locality references are not indicated at all in the section "The catalogue of crystalline minerals" where 134 specimens are recorded. Mostly the same names are present here as in "The catalogue of mineralogical collection". Only "brown

Amethyst with pyrite, 14 cm. Bohemia (Czechia). FMM No 27181. Photo: Michael Leybov





Baryte, 12 cm. England. FMM No 33859. Photo: Michael Leybov

iron ore" looks strange in the list; however, its proximity to "sulfur kies" inspires the supposition that this was a pseudomorph of iron hydroxides after pyrite crystals. In the collection of crystals of the Fersman Mineralogical Museum, 27 specimens were recorded that came from the Museum of the City. Some of them retained sticker numbers that correspond to the numbers of the "Catalogue of crystalline minerals". These stickers are not handwritten unlike the ones of the mineralogical set but made typographically. This set was obviously created independently from the "mineralogical collection". The specimens from the crystal set that are available in the Mineralogical Museum funds are small, some of them less than 5 mm; however, they are often quite regular crystals, such as those of pyrite or galena.

"The scale for determining hardness", the indispensable tool for mineralogical work, corresponds to the scale developed by F. Mohs in 1824. In the sample list for hardness 2, rock salt together with gypsum looks unusual.

At the end of the list of "minerals for replenishing collection...", a postscript was made by a different hand: "Specimens of copper ore taken by Nikolai Serebryakov, the retired sergeant of Siberian Cossack Troops, Omskaya Cossack village, and presented by him on 19 September 1891 to His Imperial Highness the Throne Crown Prince and Grand Duke Nikolai Alexandrovich". Further, the two specimens of copper ore and one of the "silverfish-copper" are specified. The erroneous conclusion as to the formation time and initial owner of collection was made, obviously, from this postscript.

As to the collection of rocks, scale of hardness, and specimens from additional lists, they

1 zolotnik = 4.26 gramm; 1 funt = 409.5 gramm;
1 pud = 16.38 kg;
1 versta = 1.06 km

either did not enter into the Mineralogical Museum or were not recorded for reasons of having no value for the Museum collection.

A sheet of paper is inserted in the catalogue with a detailed description of pieces delivered to the Crown Prince Nikolai. Particularly, there is mentioned: "*By the certification of Managing Director of the, Altaiskii Mining District, 21 May 1891, No. 452, the mentioned three pieces, after testing at the Zmeyerovskii plant assay lab, showed metal content:*

No. 1, found near the land of Siberian Cossack Troops between the Shul'binskii and P'anoyarskii outposts, in 3 versts from the first and 12 versts from the second, in 1 pud ore – 5 funt copper.

No. 2, found near Altaiskii Mining District of administration of His Imperial Majesty Cabinet, in 3 versts to the South from the Verkh-Ubinskii outpost – 3¹/₂ funt copper in a pud of ore.

No. 3, found in the same area, in 3 verst to the South from the Verkh-Fleiskii outpost, in a pud of ore ³/₄ zolotnik silver and 3¹/₂ funt copper".

These materials are obviously connected with the Crown Prince Nikolai's journey in 1890–1891. On his way back to Petersburg, he stayed on 14 to 16 July 1891 at Omsk, where he probably took interest in the new findings of ores in Altai. Without such an interest, the discoverer of new occurrences could hardly go to the Capital to hand the pieces to the Crown Prince.

However, there is no doubt of Nikolai's interest for minerals during this journey. A specimen is preserved in the Mineralogical Museum, which he brought from Japan where he was from 15 April to 11 May 1891. This is a piece of brownish chalcedony with a label applied with the stone name, likely local one,

Crocoite, 6 cm. Urals. FMM No 37313. Photo: Michael Leybov





Diopside (biggest crystal 5 cm). Specimen from the collection of crystals. FMM No 1680. Photo: Michael Leybov

"petrified whale flesh", and a Latin transliteration of this Japan name.

The Crown Prince also brought from the same journey "mineralogical gifts" that later entered into the Mineralogical Museum collection. In Transbaikalia, he was presented with a silver casket with engraved on its cover a map of Nerchinsk District, and twelve flasks with placer gold from various mines of the district. All this happened in Nerchinsk where the Crown Prince was on 14 July 1891.

In the Urals, Nikolai was presented with a jasper dish decorated with gems and precious stones and the inscription "from the Bashkirs of the Orsk District, 15 July 1891". It is known that the throne heir was in Orsk on 24 July 1891 where this presentation took place. Probably inaccurate information of the Prince's journey passed into the Latgulyaev works in Yekaterinburg where this dish had been made.

The interest in minerals and ores resided in many members of the tsar dynasty. A case is known when the great-grandfather of Nikolai II, Emperor Alexander I, worked during his South Urals journey as a gold digger at the Tsarevo-Aleksandrovskaia Mine (named in his honor) and even dug up a nugget of more than 3 kg; the latter had evidently been planted in advance. Nikolai I who succeeded him on the throne took much care in the development of the Mining Institute, visited it often, and attended its lectures.

The lapidary works that passed into the Mineralogical Museum from the Museum of the City – fireplaces, vases, pedestals – show the enthrallment of Alexander II family with stone. Dates preserved on the orders for some of these works made at the Kolyvan' plant show the regularity of such orders during the Alexander II reign. The two fireplaces (PDK-1704 and PDK-1705) were ordered by the His Imperial Cabinet in 1856 and manufactured in the 1860s. The porphyry vase and pedestal (PDK-1715, PDK-1716) were ordered in 1871 and made in 1872. The porphyry trumeau (PDK-1721) was ordered in 1871 and completed in 1874. The vase of Revnev jasper (PDK-1701) was manufactured in the 70s. There is a series of specimens recorded from the Museum of the City that may be considered a collection of decorative stones. These are mostly jaspers from the Urals, Altai, and Transbaikalia. They were not recorded in the Crown Prince collection and, possibly, were connected with the interests of Alexander II. Some of these specimens are large pieces surely used for interior decoration.

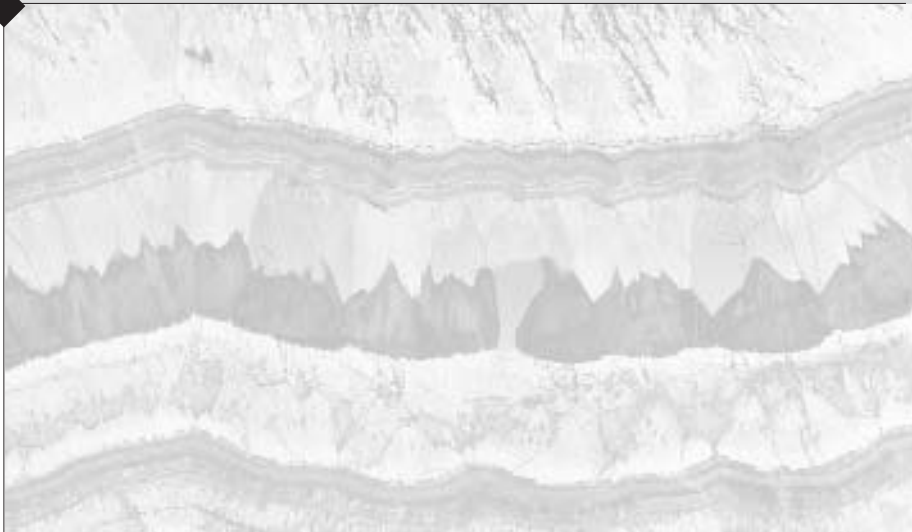
Since 1863, separate departments of geology and paleontology were established in all Russian universities which gave a strong impulse for development of the Earth sciences in Russia.

The interest of Alexander III, the next Russian monarch, in gems and precious stones is highlighted by the tradition initiated by him of Easter presents, which generated a series of masterpieces by Faberge; the last of them, the uncompleted Easter egg of 1917, is now also stored in the funds of Mineralogical Museum.

We consider that the members of Imperial family were interested for minerals collecting that Mineralogical Museum exhibits show.

History evidences that not all actions by Russian monarchs of the nineteenth and twentieth centuries fitted the needs and realities of Russia. However, their interest in mineralogy and ores of Russia, and their aspiration for knowledge in natural sciences is the example, which applies in truth now, as well, for present Russian leaders, especially in the times when Russia's prosperity and its place in the world depend in major ways on the mining of its natural resources.

Personalities



2006–2007: Jubilees and Their Heroes

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Description of a jubilee exhibition in the Fersman Mineralogical Museum RAS.
14 illustrations, 9 references

In 2006, 290 years elapsed from the purchase, by the order of Peter the Great, of a large, for those times, collection of minerals from Gottwald, Doctor of Medicine in Danzig. This was the beginning of the Mineral Cabinet which is now one of world's largest mineralogical museums, the Fersman Mineralogical Museum of the Russian Academy of Sciences.

So it happened that a series of anniversaries relating to the Museum itself, to the names of its curators and directors, and its collections and scientific publications fell both in 2006 and 2007. It is possible to retrace, not in detail, by these anniversary dates, the Museum's glorious path through 290 years of its existence. This idea has been the underlying concept behind the exhibition "*Jubilees in 2006–2007 and Their Heroes*" in the Fersman Mineralogical Museum.

In the showcase that initializes the exhibition, besides the general introduction and one of the most ancient specimen, limonite pseudomorph after pyrite (Fig. 1), the materials were presented referring to the 200th Jubilee of the Museum's present building. It is a monument of early 1800s architecture; the architect is unknown. The building was constructed as a riding hall for Count Aleksei Orlov-Chesmenskii who was a fanatic and connoisseur of horses. To that moment, this was the biggest riding hall in the Moscow area. Interestingly, the Count himself celebrated then his 70th jubilee: he was born in 1737.

Another jubilee related to the Mineralogical Museum's movement into this historical building. In 1936, 70 years ago, after the movement of the Academy of Sciences from Leningrad to Moscow and accommodation of its Presidium within the main building of the palace manor, "Aleksandrinskii Dvoretz" (after the Orlovs, the manor belonged to the tsar family having been bought by Nikolai I for his wife Aleksandra Feodorovna), the former Orlov's riding hall as a part of the Palace Ensemble was allocated for the Museum. Curiously, the main building itself, where the RAS Presidium maintains its position

up to now, also celebrated its jubilee in 2006: it was built by architect Mest 250 years ago in 1756 as a country house for the wife of Prokofii Akinfovich Demidov, a representative of the famous dynasty of Ural mining heads.

Seventy years ago, in 1936–1937, the first Museum expositions were opened in Moscow. One of them was the exhibition devoted to the geochemistry and minerals of Middle Asia. Photographs of this exhibition (Fig. 2) together with pictures of those times of the Museum building and exhibition hall can be seen in the exhibit described.

Originated in the *Kunstkammer* of Peter the Great and remained in the Academy of Sciences structure since its establishment by Peter, the Mineralogical Museum received 170 years ago in 1836 for the first time the status of a special museum. Afterwards, the Museum suffered difficult times and for several years was barely a section of the Lomonosovskii Institute; just a year ago, in spite of attempts to deprive it of its autonomy, it managed to assert its right for independence owing to the efforts of Margarita Ivanovna Novgorodova, Director, and the entire scientific team, which is also marked in the exposition.

Forty years ago the Museum celebrated its 250th Anniversary. A festive session by this date took place on 5 June 1967. There were many congratulations, a jubilee medal was made with the dates 1716–1966 and images of the Museum interiors and the unique alexandrite druse on it. The druse is a historical specimen placed now in one of permanent exhibits. Some of these rarities, including verses dedicated to the Museum and composed by Tatyana Borisovna Zdorik, were presented in a special case.

Five showcases narrated of the jubilees of Museum heads and reflected their contribution to enlarging and preserving the museum collection. For instance, Peter Simon Pallas (1741–1811), the German scientist, became the head of *Naturkammer* 240 years ago, in 1767. The Mineral Cabinet was then a part of this



Fig. 1. Limonite (after pyrite) with the old label, 3.5 cm in diameter. Czechia. FMM No. 197 OP. Collection: I.F. Henkel (No. 58, 1743).

Fig. 2. Exhibition of the geochemistry and minerals of Middle Asia in the Mineralogical Museum. 1936–1937.

Fig. 3. Halite, 7 x 6.5 x 4 cm. Astrakhan' Prov., Chapchachi. FMM No 5630. Collection: P.S. Pallas (No. 4 in I.G. Georgi's catalogue). Photo: Elena A. Borisova

Naturkammer. Pallas was invited by Catherine II; he was only 26 and already had the Doctorate degree, professorship and European acknowledgement. By the orders of the Empress, he immediately began to organize the grand Russian natural scientific expeditions. As a result, many rocks and other materials entered the Naturkammer. Particularly, the famous meteorite "Pallas's Iron", the first natural object that was acknowledged by the scientific community to be of extraterrestrial matter, was delivered from Krasnoyarsk 230 years ago in 1777. One can admire it now, too, in the Museum at the exhibition of meteorites. In the mentioned jubilee exhibition, visitors' attention was also attracted to the halite from Astrakhan' Province, the only specimen from the P.S. Pallas collection preserved to the present (Fig. 3).

Academician Vasilii Mikhailovich Severgin (1765–1826) was another remarkable director of the Museum. He was the first Russian mineralogist. Exactly 200 years ago, in 1807, he became director of the Mineral Cabinet and held this post all his remaining life long, i.e. almost for 20 years. In 2006, 180 years had elapsed since the day of his death. Another jubilee is concerned with publishing, 190 years ago, the first Russian book for identifying minerals: "*The New System of Minerals Based on External Distinctive Features*" (Severgin, 1816). The first Museum guidebook was written during Severgin's direc-

torship. And what is more, we should like to mention the special display case with guidebooks published in the Museum during the past hundred years (Fig. 4). Besides the title copies of Severgin's works, the two chalcedonies from his collection (from Kamchatka and Finland, Vuoxa River) were displayed in the exposition.

Adolf Germanovich (Fedorovich) Gebel (1826–1895) was born 180 years ago. In 1857, 150 years ago, he became custodian and, in fact, director of the Mineralogical Museum. Having been educated as a chemist (Nazarov, 1999), he was mainly engaged in meteorites and tried his best to expand the Museum collection of meteorites. In 1846, it contained 19 specimens whereas there were more than 60 by the end of the nineteenth century. Gebel's ideas of social factors playing the leading role in finding meteorites, or, formerly named, aerolites, and in their transferring to museum collections (*Gebel A.F., On the Aerolites in Russia, St. Petersburg: 1868. – In Russian*) continue to be relevant now. In the exposition, the gypsum (Azerbaijan, Menan) was exhibited; the specimen was donated to the Museum by Gebel in 1858.

In 1866, 140 years ago, Nikolai Ivanovich Koksharov (1818–1892), the prominent Russian mineralogist, was elected ordinary academician and designated to the post of Director of the Mineralogical Museum. The wollastonite from his collection found in Semipalatinsk Oblast'



Fig. 4. The guidebooks published in the Mineralogical Museum for the past hundred years.

Fig. 5. The medal of the Imperial Mineralogical Society awarded to N.I. Koksharov as the author of "Materials for Mineralogy of Russia" in connection with 50 years of the scientific activities. 5.5 cm in diameter.

Photo: Elena A. Borisova

that came into the Museum 100 years ago, in 1907, could be seen in the exposition. One of the volumes of the widely known work by this scientist, "The Materials for Mineralogy of Russia", as well as the Medal of the Imperial Mineralogical Society (Fig. 5), with which the author was awarded 120 years ago in 1887, were presented at the exposition "The History of the Museum" in the main exhibition hall. The referred-to work was being published as separate parts since 1852 – 1855 in Russian and German (Кокшаров, 1852 – 1855; 1856, 1858, 1862; 1870; Kokscharow, 1858; 1862 etc.).

Academician Feodosii Nikolaevich Chernyshev (1856 – 1914), the well-known geologist and paleontologist, Director of the Museum in 1900 – 1914, and the disciple of Academician Alexander Petrovich Karpinskii, was born 150 years ago. The 160th anniversary of A.P. Karpinskii (1847 – 1936), the first elective president of the Academy of Sciences and president of the Mineralogical Society, was at the boundary of 2006 – 2007 too (he was born on 7 January 1847). Thanks to the efforts of these two scientists, the reorganization began of the Museum that had been called since 1898 The Peter the Great Geological Museum, and it started losing its mineralogical specialization. One hundred

years ago, in 1906, an independent mineralogical department was established again; the mineral collection managed to be preserved. In commemoration of this and other merits of Academician Alexander Petrovich Karpinskii, 70 years ago the newly united Geological and Mineralogical Museum of the Academy of Sciences of the USSR was named after him. From 1937 until 1948 it was called A.P. Karpinskii Geological Museum. The diopside crystal from Congo from Karpinskii's collection (Fig. 6) and the splendid amethyst geode found by F.N. Chernyshev (Fig. 7) were displayed in the exposition.

One hundred years ago, in 1906, the Mineralogical department was headed by Vladimir Ivanovich Vernadsky (1863 – 1945), famous Russian scientist, naturalist, thinker, and public figure, who became in the same year an adjunct of the Academy of Sciences. Reactivation of scientific work in the Museum, renovation of expositions, new systematization and inventory of Museum funds were highlights of his coming to the Museum. The entire assemblage has been divided into 5 collections, which exist up to now: the Systematic collection, Collections: Ore Deposit Samples, Crystals, Pseudomorphs, and Gem and Precious Stones. They began to be registered in



Fig. 6. Diopside, 2 x 1.5 x 1.3 cm. Congo. FMM No. 29253. From collection of A.P. Karpinskii (No. 2128, 1926).

Fig. 7. Amethyst, 12 x 10 x 5.5 cm. Arkhangel'sk oblast', Chernaya River, Timan. FMM No. 21383. From collection of F.N. Chernyshev (No. 891, 1889).

Photo: Elena A. Borisova

the big inventory books separately for each collection, which continues now.

V.I. Vernadsky was the organizer of the widely known radium expedition (1906–1914). The 100-year jubilee of its start was marked in the exposition with one of many specimens from field collecting that came into museum funds, the snow-white calcite from Tuya-Muyun, Fergana Oblast' (Fig. 8).

This period of animated scientific work at the Museum united with the publication of its own scientific journal. The bottom parts of all show-cases were dedicated to the centenary of this periodical, a copy of which the reader is holding in his hands at the moment.

Both the very first thin, black-and-white issues of "*Trudy Geologicheskogo muzeya imeni Petra Velikogo Imperatorskoi Akademii nauk*", 1907, and the recent multicolored publications, in Russian and English since 2003, were placed there. It is curious that the contemporary title, "*New Data on Minerals*", celebrated, too, its 25th anniversary.

Ninety-five years elapsed from the moment when Alexander Evgen'evich Fersman, V.I. Vernadsky's faithful disciple and companion, academician, director of the Mineralogical department (since 1919) and then, since 1925, Mineralogical Museum of the Academy of Sciences, came to the Museum as a senior scientist. The Museum was named after him in 1955. The chalcopyrite specimen from Zmeinogorskii Mine, Altai, from the collection of these two scientists, that was entered into the Museum collection in 1916, and uvarovite from Sarany collected by A.E. Fersman in 1914 (Fig. 9) were displayed in the exposition. In 2006, the jubilees

took place of A.E. Fersman's important works: 85 years elapsed since the first publication of his monograph "*Samotsvety Rossii*" (Gemstones of Russia, 1921), 75 years – "*Pegmatity*" (1931), 65 years – "*Poleznye iskopaemye Kol'skogo poluostrova*" (The Minerals of the Kola Peninsula, 1941). This event was marked too: the two latter publications were displayed. Fifty-five years ago, in 1952, A.E. Fersman's "*Selected Works*" were published for the first time.

The Museum two prominent workers, Viktor Ivanovich Vorob'ev (1875–1906) and Vladimir Il'ich Kryzhanovskii (1881–1947) were contemporaries and companions of Fersman and Vernadsky. Since 1900, V.I. Vorob'ev was custodian of Mineralogical department of the Peter the Great Geological Museum; he perished tragically 100 years ago in a glacier crack in Caucasus, having left all his money (20000 rubles) and library to the Museum. On his initiative, the large collection of the Mineralogical Society was passed to the Museum. The malachite (Fig. 10), pink topaz crystals and the topaz upon quartz crystal from the Urals, all from V.I. Vorob'ev's field works were displayed in the exposition.

Several jubilee dates are concerned with V.I. Kryzhanovskii. In 2006, he would be 125. In 2007, 100 years elapsed since the moment when he became custodian for the first time, 5 years later, 95 years ago, he was elected the major scientific curator of the entire Museum collection, and 60 years elapsed from his death day on the director post (1945–1947) of the Mineralogical department of the A.P. Karpinskii Geological Museum, where he worked all his life long having had contributed much to

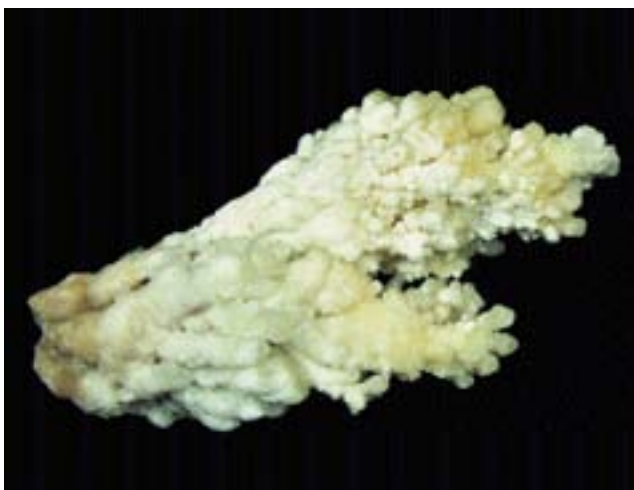


Fig. 8. Calcite, 13 x 7.5 x 4.5 cm. Fergana oblast', Margelan district, Tuya-Muyun. FMM No. 21953. From collection of Radium expedition (No. 758, 1911).

Fig. 9. Uvarovite with original label, 5 x 4.5 x 3.5 cm. Perm' prov., Perm' district, Biserskii Zavod, Saranovskii Mine. FMM No. 9677. From A.E. Fersman's collection (No. 1170, 1914).

Photo: Elena A. Borisova



Fig. 10. Malachite with original label, 6 by 3.5 by 2 cm. Urals, Perm' prov., Iron Mine of Polevskoi Zavod, FMM No. 5835.

From V.I. Vorob'ev collection (No. 391/295, 1905).

Fig. 11. The genetic collection of minerals for young mineralogists composed by V.I. Kryzhanovskii. 1941. 35 by 29 by 3 cm.

Minerals of magmatic process: 1 – chromite, 2 – magnetite, 3 – labrador, 4 – apatite, 5 – nepheline. Minerals of pegmatite veins: 6 – quartz, 7 – feldspar (orthoclase or microcline), 8 – amazonite, 9 – muscovite, 10 – topaz, 11 – beryl, 12 – hornblende, 13 – corundum, 14 – ilmenite, 15 – wolframite, 16 – lazurite. Minerals of hydrothermal process: 17 – chalcopyrite, 18 – pyrite, 19 – sphalerite, 20 – galena, 21 – orpiment, 22 – calcite, 23 – fluorite, 24 – barite, 25 – asbestos, 26 – amethyst, 27 – chalcedony. Minerals of supergene process: 28 – limonite, 29 – bauxite, 30 – magnesite, 31 – malachite, 32 – crocoite, 33 – native copper, 34 – gypsum, 35 – halite, 36 – sylvite, 37 – pyrolusite, 38 – jasper, 39 – sulfur. Minerals of metamorphic processes: 40 – hematite, 41 – talc, 42 – garnet. Rocks: 43 – dunite, 44 – gabbro, 45 – syenite, 46 – nepheline syenite, 47 – granite, 48 – pegmatite, 49 – obsidian, 50 – marble.

Fig. 12. Aragonite, 6,0 by 5,0 by 4,5 cm. Georgia, Akhaltsige district, Kisatiba. FMM No. 35624. D.S. Belyankin's collection (No.2588, 1935).

Photo: Elena A. Borisova



the systematization and enlargement of the Museum funds. The described exposition was decorated with a special wooden box with sections, the so called genetic collection of minerals for young mineralogists made up 65 years ago, in 1941, by Prof. V.I. Kryzhanovskii on the base of A.E. Fersman's ideas of mineralization processes (Fig. 11).

Academician Dmitrii Stepanovich Belyankin (1876–1953) was born 130 years ago. He became 60 years ago, after Kryzhanovskii's death, Director of the Mineralogical department, which was transformed in 1948 into the separate Mineralogical Museum of the Academy of Sciences. Thanks to his efforts, the museum journal resumed its publication after the end of world war II. Two specimens from Belyankin's collection could be seen at the exposition: radiaxial pink aragonites from Georgia (Fig. 12).

The 2007 December is the 100th jubilee of the birth of the Museum's next director, Prof. Georgii Pavlovich Barsanov (1907–1991). G.P. Barsanov led the Museum for nearly a quarter of a century, the last 15 years on a voluntary basis. On his initiative, new exhibits were created: "Pseudomorphs", "Natural Mineral Forms",

"Mineral Coloring", and "Synthetic Minerals"; some others were essentially changed. He gave great attention to the history of mineralogy and of the Museum; as a result, new expositions appeared as well as articles in the Museum journal (Barsanov, 1950, 1959a, 1959b, 1968 etc.), the chief editor of which he remained for 30 years down to 1984, even after he retired as the Museum director. Besides, Georgii Pavlovich was an excellent lecturer, and he was in charge of the chair of mineralogy in Moscow University.

In the jubilee exhibition, together with the calcite specimen (Dekanie-Tskhali, Southern Osetia) from his collection, there was the portrait of G.P. Barsanov made as a friendly cartoon (Fig. 13) by Nikolai Nikolaevich Shatagin, the leading research worker, then student at Moscow University, who sketched 45 years ago, in the autumn 1962 and the springtime 1963, at one of Georgii Pavlovich's lectures. As eyewitnesses recollect, Barsanov liked the portrait very much, and it has been hanging in his university study since that time.

Yurii Leonidovich Orlov (1926–1980) was born 80 years ago. An authority in the diamond mineralogy, he succeeded G.P. Barsanov as



Fig. 13. G.P. Barsanov. The friendly cartoon by N.N. Shatagin. 1962–1963. Photo: Elena A. Borisova

Director of the Museum 30 years ago, in 1976. The two specimens of Pamir tourmaline from his fieldwork of 1959 (Fig. 14) were presented in the exposition.

One more jubilee falls in 2007: 80 years since the birthday of Prof. Alexander Alexandrovich Godovikov (1927–1995) who succeeded as Director of the Museum in 1983. He donated his own large collection of minerals to the Museum. Thanks his efforts the large and important mineralogical collection of V.I. Stepanov was donated to the Museum. The A.A. Godovikov's ideas of mineral systematics are embodied in the Museum's main exposition. At the jubilee exhibition, one could admire the whole set of marvelous Mongolian agates that he had brought from his journey to that country. On the whole, agates were one of his favorite stones. He devoted a whole monograph to them (Godovikov, Ripinen, Motorin, 1987) and three special showcases in the continual exposition within the bounds of the exhibition "The Types of Mineral Associations in the Earth's Crust".

The two more jubilees are concerned with persons who are now in good health. In 2007, Mal'va Aleksandrovna Smirnova celebrated her 80th birthday. She was the chief custodian of Museum funds for more than 20 years (1979–2000). With her participation, numerous current expositions were created, for example, the exhibition "Natural Mineral Forms" whose principles were developed by A.A. Godovikov and V.I. Stepanov. She collected sample materials in her field work in Transbaikalia, Middle Asia, and Kazakhstan. The fire opal (Kara-Agach) from her field collecting in 1963 was displayed in the jubilee exposition.

Lastly, 10 years elapsed in 2006 from the Professor Margarita Ivanovna Novgorodova's inauguration as the Museum director. Under

her leadership, the complete revision of the exhibit hall was done, electronic databases, the museum site, new exhibits, and a modern analytical laboratory were created, and publishing of the "New Data on Minerals" scientific yearly with its modern appearance was resumed after the long pause.

Margarita I. Novgorodova donated about 30 specimens to the Museum collection. Mostly they are rare native elements (Al, Cd, Pb, Mg), intermetallides (jedwabite, chromferide, ferchromide), iron silicide – suessite, carbides – khamrabaevite and niobocarbide as well as the specimens from the Republic of South Africa – pyrite and auriferous conglomerates from the Witwatersrand, and the decorative stone "tiger eye". Many of the specimens are holotypes of new mineral species described by her: aluminium, cadmium, khamrabaevite, niobocarbide, chromferide, ferchromide. These minerals can be seen in the Museum permanent expositions: "Structural-Chemical Systematics of Minerals", "Mineralogy of Chemical Elements", and "Gems and Precious Stones". In 2007, M.I. Novgorodova was awarded the medal of the Order "For merits for Motherland of II degree" for her great contributions to the Museum and to mineralogical science.

One may also consider the jubilees of the dates of entering some collections into the Museum. The Shenshin, de Bournon, Wagner, and Razderishin private collections commemorated their 200 years in Museum. An especially interesting collection is that of Alexander Vasil'evich Razderishin (1754–1812), a state councilor and a member of the Berg-Collegia, discoverer of many occurrences of gems and precious stones, director of gold and silver mines, supplier of the Imperial Court at Catherine II, the author of training collections for numerous public schools, the Artillery Corps, Moscow University, and St. Petersburg



Fig. 14. Tourmaline, 12.5 x 7.5 x 6 cm. Southwestern Pamirs, Kuh-i-Lal. FMM No. 61088. From Yu.L. Orlov's collection (No. 3752, 1959). Photo: Elena A. Borisova

Teacher Seminary. The collection is accompanied with a detailed catalogue preserved in the Museum Archive. In the jubilee exposition, there was the gypsum from the Kama River banks registered in this catalogue under number 14 (Perm' Province, Osinskii District, Kama River opposite Osy town).

Some other collections connected with the jubilees of the transferring dates are collections of the Stroganovs and A.F. Volbort (130 years ago they were received by the Museum), V.A. Iossa's collection (90 years), E.N. Barbot-Marni's collection (80 years)*. Some specimens from these collections were demonstrated: moonstone (Ceylon) and serpentine, topaz (Transbaikalia, Nerchinskii District), malachite (Perm' Province, Verkhoturkskii District, Mednorudnyanskii Mine), and epidote (Ufa Province, Zlatoust District, Zelentsovskaya Kop').

In conclusion, the exhibition authors congratulated many of their colleagues (16 persons out of 50 Museum workers) who continue now the affairs of their precedents and work actively in the field of enlarging and preserving the very rich museum assemblage of minerals and whose jubilees, thanks to the lucky conjuncture, were in 2006–2007 too. Their jubilees marked Dr. Evgenii Ivanovich Semenov, Dr. Andrei Andreevich Chernikov, Dr. Ludmila Andreevna Matveeva, Dr. Elena Alekseevna Borisova, Dr. Elena Nikolaevna Matvienko, Dr. Alexander Dmitrievich Esikov, Elena Anatol'evna Kuvarzina, Nina Alekseevna Mokhova, Galina Alekseevna Osolodkina, Dmitrii Il'ich Belakovskii, Raisa Ivanovna Solov'eva, Vyacheslav Vladimirovich Gusakov; 50 years worked in the Museum Dr. Marianna Borisovna Chistyakova and Galina Alekseevna Osolodkina, 40 years – Tatyana Mikhailovna Pavlova, 30 years – Dr. Oksana Leonidovna Sveshnikova; 25 years ago Elena Leonidovna Sokolova began to work in the Museum.

Thus, the exhibition "*The Jubilees in 2006–2007 and Their Heroes*" showed once more the complicated and long way of the Museum development and reflected a succession of generations of scientists who headed the Museum and supervised its collection.

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* The dates are given according Barsanov, Kometova, 1989; Godovikov, 1989

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ALEXANDER ALEXANDROVICH GODOVIKOV. LIFE AND ACTIVITY

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Scientific and administrative activity of well known scientist, doctor of geological and mineralogical sciences, professor A.A. Godovikov who was the director of Fersman Mineralogical Museum of RAS from 1984 to 1995 is described. Author recalls 32 years of collaboration with Godovikov.

1 table, 2 photos, 19 references

Alexander Alexandrovich Godovikov was an outstanding scientist in theoretical, descriptive, experimental and genetic mineralogy. His scientific interests were connected to research and development of techniques to investigate natural and synthetic compounds and study of mineral deposits. There are total 200 scientific works of Alexander Alexandrovich Godovikov which include 17 monographs in 14 of which he is the only author. He received 17 certificates of authorship and trained more than 20 Ph.D. candidates in geosciences.

Godovikov's maternal family tree roots into early 18 century. Ancestors of Alexander Alexandrovich put themselves on record of Russian history. They are family members of baron Johan-Albrecht Korf, Bogdan Kreiter, Russian Bashkirovs family. Among members of the mentioned families were Russian envoys to European countries, prominent scientists of their time, remarkable professors (see table).

A.A. Godovikov was keen on mineralogy since his childhood. Being a school boy he visited Moscow construction sites accompanied with his mother, Elena Alexandrovna, looking for nice rocks samples. Later being Moscow Chemistry polytechnic college student he worked as an assistant in *Karpinskiy Geological museum of USSR AS* (now it is *Fersman Mineralogical museum of RAS*) looking through and washing samples. He participated in geological expedition of the team of well-known mineralogist A.N. Labuntsov to Khibiny Mountains as an assistant. He remembered him with sympathy and characterized him as a very intelligent, intellectual man, conversationalist and a mind of wide scope. He regarded Labuntsov as his own teacher. Godovikov continued his education at the chair of mineralogy of geological department after successful graduation from technical college.

At his student years he was occupied with studying of minerals of Moscow region investigating limestone and dolomite quarries and many natural outcrops of sedimentary rocks and their weathered crusts. He published two papers on these studies of carbonates and phosphates of Moscow region (Godovikov, 1961; Godovikov *et al.*, 1961). He lead scientific geological and mineralogical clubs over a period of years and worked in expeditions headed by mineralogists from Moscow state University and Mineralogical museum of USSR AS.

His postgraduate studies concerned cobalt and nickel arsenides from Khovu-Aksi deposit. He defended his thesis on this topic considering isomorphic peculiarities, oxidation conditions and identification techniques for this complex group of minerals. He investigated relations between arsenides while simultaneous deposition in ore bearing hydrothermal veins and a role of colloidal solutions in their formation.

A.A. Godovikov entered Institute of mineralogy, geochemistry and crystal chemistry of rare elements (IMGRE) of USSR AS as a junior research assistant after defending his thesis and started organizing laboratory of experimental mineralogy. He successfully fulfilled this task which enabled him to investigate a nature of admixtures in galena in a laboratory environment. Consequently he wrote his first monograph "Minerals of bismuthite-galena series" as a result of the work (Godovikov, 1965).

A.A. Godovikov started working in the Institute of geology and geophysics of Novosibirsk scientific centre in 1959. He was assigned to organize a laboratory of experimental mineralogy there. It was called laboratory of solution-melt crystallization from the



Alexander Alexandrovich Godovikov, 1990

beginning and there were 5 staff members including the manager. It grew later into a department of experimental mineralogy that comprised of three laboratories. Some 200 staff members worked in the department including 3 Doctors of science and more than 30 doctorate candidates. This experimental division is well-known worldwide with its scientific research. Many of its developments and achievements were applied into the practice. A.A. Godovikov becomes a deputy director of the Institute of geology and geophysics of Siberian Branch of USSR Academy of Science in 1974. The achievements in crystal synthesis gained under his leadership lead to creation of a special crystal growth technological design-engineering bureau in Siberian department of USSR Academy of Science in 1978. He was the organizer and the first head of the bureau and made a lot of efforts to develop it.

Research of the department of experimental mineralogy included following themes: 1) sulfide and chalcogenide systems with pyrosynthesis (construction of system diagrams, new compounds synthesis, investigation of growth conditions of mono crystals in dry systems) under atmospheric conditions and also in ones of high and ultra high pressure and temperature; 2) physical chemical properties of synthetic material and their natural analogues; 3) areas of stability of ore minerals, solubility of sulfides, transfer mode and forms of ore-forming elements by hydrothermal fluids depending on thermodynamic conditions; 4) physical chemical conditions of equilibrium of sulfides with oxides, native elements, wolframates and other compounds and also monocrystal growth in

hydrothermal fluids; 5) phase equilibrium in silicate systems, hydrothermal solutions, kinetics of hydrothermal reactions of silicate formation.

One can see from the department's topics of study that Godovikov had broad scientific interests. He participated not only in the statement of the problems which is a half of the successful problem solution but also saw into the details of difficulties encountered during experiments and interpretation of their results. These investigations were aimed to the main goal that Alexander Alexandrovich put against himself and the team he headed. He wanted to bring mineralogy to the point when it becomes a quantitative but not a descriptive science. He worked on theoretical problems of mineralogy in connection with this aim trying to create a unified mineral classification based on chemical, structural and genetic peculiarities of species. He paid particular attention to connection of properties of minerals with their chemistry and structure, development of study on chemical bonding in minerals, determination of common types of compounds by predominant type of their bonding. He proposed new techniques of assessment of donor-acceptor properties of elements, new arrangement of periodic system of elements of D.I. Mendeleev, geochemical classification of elements and cations. Results on the theoretical investigations of Godovikov are published in 7 monographs (Godovikov, 1972a, 1977a, b, 1979a, 1981, 1997 a, b) and they are the basis of natural structural-chemical systematic of minerals which represent a quintessence of his scientific life. Predominant type of chemical bond is taken as a leading attribute which determines the first higher rank of taxonomic units. There are five types of the higher rank which are common for all minerals:

1 Type: minerals predominantly with metallic and metal-covalent bond – native metals and semi-metals, intermetallic compounds and semi-metallic compounds;

2 Type: minerals with metal-covalent and ion-covalent bond rarely with residual bond – chalcogenides and native nonmetals from VI a group.

3 Type: minerals predominantly with ion-covalent bond and covalent-ion bond type – nonmetals of light (typical, centrosymmetrical) element of VIa group (O) – oxygen compounds;

4 Type: minerals with predominant covalent-ion and ion bond type – halogenide compounds;

5 Type: carbon and its compounds (excluding carbonates) and related to them compounds.

Lower taxons are determined on the base of the following: a) belonging of a mineral whether to isodesmic or anisodesmic compounds; b) type of anion, cation; c) coordinate number of main anion; d) value of force characteristic. The force characteristic was introduced by Godovikov and defines donor-acceptor (acidic-alkaline) properties of elements. The force characteristics (FC) can be calculated as the ratio of affinity to electron (in case of neutral atoms) or n -th potential of ionization (in case of cations) to orbital radius of atom or an ion; e) structural type (so structure is a secondary feature). The lowest taxon, a mineral specie is *"an individual chemical compound, an ultimate member of solid solutions; intermediate member of series of solid solutions with conventional limits of the composition"* (Godovikov, 1997a).

Godovikov tested his classification on a broad and very important for mineralogists exposition of minerals *"Structural chemical mineral systematic"* in the Mineralogical museum. He selected the most interesting samples for the exhibition in early 1990s with the help of museum's stuff. Then it contained 1895 mineral species. Collection replenishes since then with new minerals that the museum have not had yet and with new species that fit into the classification. There are 2917 mineral species in the exhibition by now.

Monograph *"Structural chemical systematic of minerals"* was published only after Alexander Alexandrovich passed away in 1997. It's second revised and corrected edition is just printed (Godovikov, Nenasheva, 2007a; Godovikov, Nenasheva, 2007b).

Special attention was paid to the pressure of a gas phase and water vapor during studying of sulfide systems under supervision of Godovikov. It enabled to determine a range of important regularities which are to be considered at mineral synthesis and applying experimental data to understand natural processes. They also were essential at growing mono crystals of semiconductors and active optical material. Methods of chalcogenic glasses produc-

tion with composition As_2S_3 , As_2S_5 , $As_{20}S_{80}$, and monocrystals of α -arsenic sulfide (orpiment) were developed. The glasses possessed optical quality and lack gas, solid inclusions and structural thermal tension. They are widely used in semiconductor industry, infrared optics, acoustic optics; arsenic crystals that are used in optical information recording devices (holograms etc.).

Studies of sulfide minerals were in the basis for original conclusions made on origin of many sulfides and sulfosalts, developing their systematic and prognosis of their synthesis conditions. The techniques of growing proustite, pyrargyrite, silver thiogallate, bromellite, chrysoberyl (alexandrite) and paratellurite crystals were developed under supervision of Godovikov. They were the first to visualize infrared image on proustite monocrystals in our country. Paratellurite crystals can be light-sound conductors and are used in production of single-channel and multiplex modulators, beam splitters, deflectors, radio frequency spectrum analyzers and other elements in optoelectronics.

The work on emerald growing from melt solution and on its hydrothermal growth on crystal seed were carried out successfully. Not only large crystals of emerald of any shades of color were grown but also other varieties: bluish aquamarine, yellow heliodor, and crimson morganite.

Techniques and hardware for quality control of crystals during their growth were developed. They allow determining photo-goniometric orientation of crystals, evaluating their resolution power, visualizing micro block structure and mechanical tensions not detectible with light microscopy, measuring block size and grain-boundary angles. These methods allowed assessing quality of grown crystals and swiftly considering these data to develop conditions of the growth of monocrystals of high perfection and select the best ones for quantum electronics investigations.

Handling of this work would be impossible without connection with theoretical studies on thermodynamics, kinetics and mechanisms of reactions in the relevant systems. They enabled the switching to common theoretical works that brought to light questions on conditions under which some elements form compounds with certain crystal structure and properties.

Consequently it led to basics of scientific prognosis and design of compounds with predetermined properties. Results of the work were published in three monographs (Godovikov, 1979b, 1989; Belov, Godovikov, Bakakin, 1982).

Tasks on high pressure petrology and development of instruments for investigations in conditions of 200–300 thousand atmospheres, cubic multi hob press instrument with maximum pressure up to 1 million atmospheres are very important even now. This gave an opportunity to study phase transition in conditions of ultrahigh pressures. Conductor-insulator transition was obtained in iron oxide under 650 thousand atm., in diamond under 700 thousand atm., in pyrophyllite under 750 thousand atm. This gave possibility to answer major questions in petrology and geophysics of high pressures and depths, modeling of new super hard materials and products and big diamond crystals.

Alexander Alexandrovich was talented professor and gave lectures on a whole mineralogical course and after *"Introductory mineralogy"*, *"Crystal chemistry"*, *"Genetic mineralogy"* at geological-, geophysical department of Novosibirsk state University from 1963. For the students and wide audience he published books *"Introduction in mineralogy"* (Godovikov, 1976b), *"Mineralogy"* (Godovikov, 1975), and later revised and edited edition of the last one (Godovikov, 1983). He trained experimental mineralogists developing original independent investigations, organizing and heading students' academic and field practices, in different expeditions to Urals, Khibiny, Khakassia, Altai putting a lot of effort and initiative to pedagogical work.

A.A. Godovikov contributed a large mineral collection counted of more than 4000 samples to Fersman Mineralogical museum. He gathered the collection in numerous expeditions at various regions of the USSR and trips abroad: USA, Czechoslovakia, Bulgaria, Rumania, Mongolia, England and Japan. Many samples from the collection are shown on different expositions. Representative agate collection including specimens from its various genetic types: from basic effusives (basalts and andesites), from acidic effusives (rhyolites), in cavities formed from burned out vegetation remnants, in solution cavities of sedimentary

rocks. Agate studies concerned many questions of their formation: cause and mechanics of cavity formation in basic volcanic rock, what part of lava flow confined cavities, coalescence of gas bubbles, their shape, gas composition in gas cavities, composition of minerals that formed agates, compositions of lava icicles and build-ups in gas bubbles, mechanics of cavity formation in rhyolite lithophysa and so on. These investigations were published in monograph *"Agates"* with O.I. Ripinen and S.G. Motorin as coauthors and are displayed in the exhibition *"Agates"* in the Mineralogical museum (A.A. Godovikov, M.B. Chistyakova).

The period of cooperation with Mineralogical museum was the years of productive and hard work in his life as well as in the museums history. His "outstanding" (by the words of academician A.A. Trofimuk) organizing abilities appeared then. The reconstruction and renovation of the museum which were gone for 8 years were finished under his leadership in a short time. Old expositions were restored and new ones created. New exhibition floor space was acquired in joined building which used to belong to Paleontology museum. This allowed to increase the number of expositions with vacating floor space from cases with funds of mineral deposit collection which were moved to the fund storage arranged in former exposition hall of Paleontology museum. New electric geological map instead of old cumbersome one was created by N.I. Zardiashvili. This made possible to widen the exposition and lighten the museum better. Alexander Alexandrovich engaged unusual mineralogist V.I. Stepanov and young enthusiastic mineralogists D.A. Romanov, D.V. Abramov and A.B. Nikiforov to the restoration of the museum. M.A. Smirnova who was a chief museum custodian then admitted that the job was a *"big challenge not only for the entire museum's stuff but also the mineralogists from the other institutes in Moscow, Novosibirsk, Kiev, amateur mineralogists, and the museum's stuff family members and their friends who were inspired with enthusiasm of A.A. Godovikov and his example"*. The restorations were finished and the museum was opened by 27th Session of international geological congress which took place in Moscow in August of 1984.

New expositions were created and old ones were remodeled during the years of work in the museum under supervision and often with personal participation of A.A. Godovikov. New



Alexander A. Godovikov with colleagues in the expedition to Mongolia, 1988.

original exposition "*Forms of occurrence of minerals in nature*" was created by A.A. Godovikov, V.I. Stepanov and M.A. Smirnova. The book "*Natural Mineral Forms*" was published with A.A. Godovikov's and V.I. Stepanov's text on the material of the exposition in 2003. The book is exceptionally illustrated with photos of samples selected by looking through the entire museum collection. It shows gradual evolution in perfection of crystal shape from almost ideal to such a defective that they can be called whether individual crystals or aggregates depending on forming conditions.

The original exhibitions "*Mineral Systematic*" (by A.A. Godovikov, M.A. Smirnova), "*Karst caves*" which is a part of "*Forms of occurrence of minerals in nature*" exposition (by A.A. Godovikov, V.I. Stepanov and M.A. Smirnova), "*Minerals of Moscow region*" (by V.I. Stepanov) were created in the same period of museum's reconstruction. The exhibitions "*Precious and ornamental stones*" (by M.B. Chistyakova, L.V. Bulgak and M.A. Smirnova), "*Skarns*" (by O.L. Sveshnikova), "*Sources of mineral coloration*" (by A.N. Platonov, T.M. Pavlova, L.A. Kudinova) were renovated. Work on new exposition "*Diversity of mineral species*" also started then and continued by the

staff members of the museum even after A.A. Godovikov has been passed away.

As we noted above A.A. Godovikov, V.I. Stepanov, M.A. Smirnova and other staff members of the museum looked through entire collection of the museum during preparation for the museums reopening. The idea of sorting the samples by quality, their genetic exemplary significance into three collections appeared during the work. Collection "A" was supposed to have unique specimens which have to stay untouched. Collection "B" was considered to contain samples which can provide matter for investigations. Samples from collection "C" should be packed and put away to give space to newly acquired samples. The idea was endorsed by A.A. Godovikov and being materialized by efforts of B.B. Shkurskiy, D.V. Abramov, T.I. Matrosova who looked through tourmaline, zeolite, beryl, pyrite, marcasite samples.

Alexander Alexandrovich invited mineralogist D.I. Belakovskiy eveate the creating computer database of the collection. Fersman Mineralogical museum of the RAS was the first museum in Russia to have a computer database on exhibits.

Godovikov started showing the museums exhibitions abroad in 1986. The first temporary

thematic exhibition took place in Hungary. After that the exhibitions took place in Czechoslovakia (Prague), France (in Paris), Finland (Helsinki), Germany (Munich), USA (Houston) and Japan (Tokyo). These expositions followed it with a great success and had lots of visitors. It was on those trips with exhibitions abroad when Alexander Alexandrovich took chances to get acquainted with mineralogical collections of different museums in those countries. He photographed unique, showing most illustratively their genetic peculiarities or beautiful samples to acquaint scientists of the museum and also the wide mineralogical public with the well-known mineralogical collections on returning from the trips. He also popularized mineralogy and the Fersman Mineralogical museum itself by giving lectures on its collections and history, showing color slides of the most interesting museums specimens.

Alexander Alexandrovich worked a lot on classification of minerals and on wrote the chapter of new book "*Mineralogy*" in his after period of life. The book was intended to contain description of all known mineral species by that time and to characterize their formation conditions. That monograph had to be the most comprehensive contemporary book on mineralogy. Godovikov had wonderful efficiency. He never had rested on weekends nor had vacations. He usually worked on a next coming book or an article during his vacations implementing his plans. He did plan a lot of things to do. For instance he wanted to write a monograph on inorganic chemistry which would contain all known inorganic compounds and he collected materials for this book and monitored new discoveries in natural sciences: chemistry, physics and biology. Also he planned to write the book on mineralogical collections from various museums of the world. He took color slides of samples from different museums gathering illustrations for this book.

One can imagine from written above that Alexander Alexandrovich devoted all his life to work. He actually possessed real humanness. He loved a lot his mother Elena Alexandrovna, his children and grand children. He helped his elder children to adjust to the new realities of life in 1990s and spent a lot of time educating the youngest son. Alexander Alexandrovich liked to spend his time in the bosom of his family in rare two or three weeks when he was out

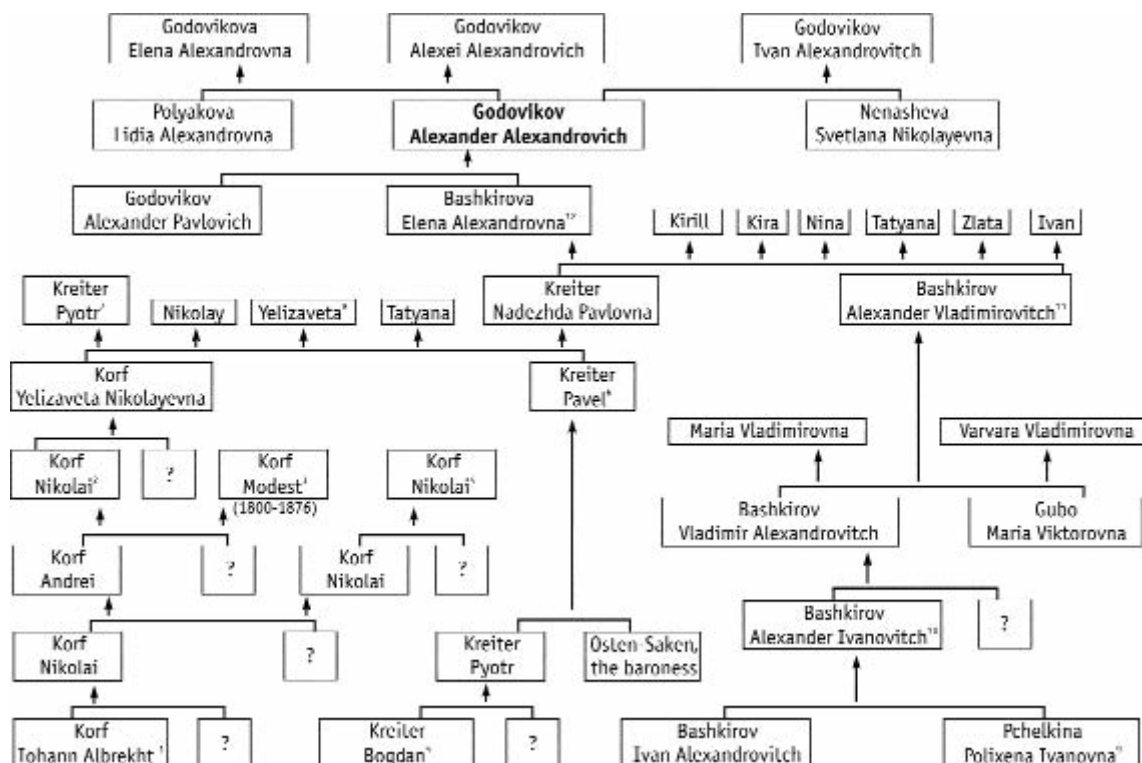
of Moscow on vacation. It means only time after 2 pm because he always worked in the mornings. He liked picking up mushrooms; sprawling out in the sun on a beach, swimming, simply walking in a forest, watching birds, butterflies and insects. He was a man of action and could not spend a minute doing nothing. He always found something to make good for surrounding people: to repair something, to fix, to go buy food. In spite of his very full employment, he had time to do renovation of his apartment by himself and even used to make decent furniture by himself. He was skilful and accurate in doing everything and did everything with gusto. He told his children that it is necessary to do with pleasure. In this case result will well and you yourself will receive pleasure from this result.

A.A. Godovikov was a very exacting person, did not suffer laxity, an indiscipline, and the negligent attitude to work. With the scientists unfairly concerning work, Alexander Alexandrovich did not wish to have anything general and they, accordingly considered him with hostility. But he considered accurate diligent members of collective with respect and warm. He always came with aid to the friends in any complex situations. He helped if he could: advice, the petitions in public organizations in different occasions, the organization of the rest, treatment.

Alexander Alexandrovich believed, that each researcher has the right to the point of view on any question and consequently very attentively listened to other treatment of each fact, other hypotheses opposed with the reasons, easy tried to convince the correctness and if it was not possible, concerned it with understanding, thought of, whether he was mistaken. Never tried to press, somehow to pursue the person for other ideas, was not vindictive, very quickly forgot the offences and if he saw, that the person can benefit business, he employed him, despite disagreements in any questions.

Last years A.A. Godovikov considered above ways of development of mineralogy as science. The monograph "The brief sketch on history of mineralogy" was written, but the publication also could not be seen by the author. Much from conceived Alexander Alexandrovich had not time to make, many materials collected by him remained not used. This stresses that he was not ordinary person, the person with a big potential,

The genealogy of Alexander Alexandrovich Godovikov by the Maternal Line



Korf family

1 Johan Albrecht Korf came to Russia in 1730 in the encirclement of Tsarina Anna Ioanovna. A baron, a Kurland knight. Had a brilliant education. An atheist, a bibliophile and an alchemist. Was the President of the Academy of Sciences. Organized the "Russian Assembly" attached to the Academy where Russian philologists were studying themselves the Russian language and consequently they composed the "Explanatory Dictionary of Russian Language". The task of J.A. Korf's activity was to educate young Russian scientists. So talented young people were sent to foreign Universities for their education; among them — M.V. Lomonosov, D.I. Vinogradov, G.V. Rikhman. Korf supported V.K. Trediakovsky (a bashful, but talented poet). After the duel Johan Albrecht became an ambassador. There is written about him in V. Pikul's book "Word and dead" from Anna Ioanovna's time.

2 Nikolay Andreyevich Korf (1834–1883) — a notable Russian teacher and methodologist, a progress-minded worker of public education. There is an article about him in BSE.

3 Modest Andreyevich Korf (1800–1876) — a historian. In Brokgauz and Efron's Dictionary is written that a work about Decembrists' revolt belongs to his pen. In 1834 — State Secretary. In 1864–1872 — chairman of the department of law of the State Council. There is an article about him in BSE.

4 Nikolay Nikolayevich Korf (organizer of schools in the countryside of Russia).

Kreiter family

5 Bogdan Kreiter came to Russia in 1730 in the encirclement of Tsarina Anna Ioanovna.

6 Pavel Petrovich Kreiter — an ambassador in Italy, then in France.

7 Pyotr Pavlovich Kreiter was married Tatyana Mikhaylovna Puschina, daughter of colonel Mikhail Nikolayevich Puschin (1846–1877) who was killed in the war. His father Nikolay Nikolayevich was the cousin of Ivan Ivanovich Puschin, a Decembrist. They were both grandsons of admiral Pyotr Ivanovich Puschin.

8 Yelizaveta Pavlovna Kreiter was married doctor Yevgeniy Mikhaylovich Ivanov.

Bashkirov family

9 Polyxena Ivanovna Pchelkina, maid of honour in the Tsarina Yelizaveta's encirclement. Voluntary governess of Ioann Antonovich (son of Tsarina Anna Leopoldovna, granddaughter of Tsar Ivan V, brother of Emperor Peter the Great). There is written about Pchelkina in V. Danilevsky's novel "Mirovich".

10 Alexander Ivanovich Bashkirov — marshal of nobility of Tulskeya province. His photo is exhibited in the Orel Museum of Regional Studies. Was married Varvara Alexandrovna Yevreinova. Had got 16 children.

11 Alexander Vladimirovich Bashkirov — a translator from French. Translated a book about the Inquisition.

12 Elena Alexandrovna Bashkirova was married Alexander Pavlovich Godovikov, a worker of the higher level of skill — a gauger.

BSE — Bol'shaya Sovetskaya Entsiklopediya (Grand Soviet Encyclopaedia). M.: Sovetskaya Entsiklopediya, 1969–1978.

profound knowledge, inquisitive mind and the person of huge working capacity.

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PROFESSOR GEORGII PAVLOVICH BARSANOV and V.I. Vernadsky and A.E. Fersman Mineralogical-Geochemical School

One hundred years elapsed from the birthday of Georgii Pavlovich Barsanov, Professor, Doctor of natural science, a worthy inheritor and successor of the V.I. Vernadsky and A.E. Fersman mineralogical-geochemical scientific school who was for a quarter of century at the head of the A.E. Fersman Mineralogical Museum and, for more than 30 years, of the Chair of mineralogy at the Moscow University.

The Georgii Pavlovich's entire life was bound with the scientific, teaching and educating work in mineralogy. Since the beginning of 1930-ies, he has been working, under the A.E. Fersman leadership, in the Lomonosov Institute and Mineralogical Museum in Leningrad, involved also in regional mineralogical and geochemical researches in Azerbaijan, Georgia, Southern and Northern Osetia and Kabardino-Balkaria. After these institutions were moved to Moscow, Georgii Pavlovich, keeping on working in the Mineralogical Museum, began, since 1937, his teaching work in the Moscow Institute for Nonferrous Metals and Gold. In 1948, G.P. Barsanov picked up these activities and created an original course of mineralogy basing himself upon the ideas by V.I. Vernadsky and A.E. Fersman. In the pre-war years, he was engaged in detailed mineralogical researches in the Ilmeny Mountains, Middle Urals. He returned to them after the pause due to his contusion that he got in the autumn of 1941 at the Northwestern Front participating in slugging as a battalion chief. He has been then evacuated in Miass, Urals, and was invalided for 7 years up to 1948. In spite of this, Georgii Pavlovich proceeded his researches yet in 1942. His unique results in the rare-earth tantaloniobates and metamictness became hereafter the bases of his Candidate and Doctoral Theses presented by him in 1943 and 1948. The latter was awarded the Academy of Sciences Prize.

In the early 1950-ies, Georgii Pavlovich was universally acknowledged as an authority in

theoretical mineralogy and a prominent connoisseur of minerals as well as extraordinary teacher and crisp lecturer.

In 1953, Georgii Pavlovich became Director of the Mineralogical Museum of AS USSR. In the same year, he was elected the holder of the Chair of mineralogy at the geological faculty of Lomonosov Moscow State University at the newly built edifice in Leninskie (Vorobyevy) Gory. Here, the traditional and new, fundamental and applied researches successfully developed under his leadership during his entire activity and hereafter.

Georgii Pavlovich Barsanov is one of remarkable inheritors to the mineralogical and geochemical school of V.I. Vernadsky and A.E. Fersman. Certainly, A.E. Fersman mostly influenced upon the formation of Georgii Pavlovich's scientific interests; he worked under Fersman's leadership at the Mineralogical Museum since 1931, after he graduated the Leningrad University. Having had headed the Mineralogical Museum and developing his teacher's ideas, Georgii Pavlovich suggested the new principle to organize museum expositions: instead of show-cases devoted to particular deposits, a series of scientifically topical exhibitions appeared. On the base of his structural-chemical classification, the exhibition "*Systematic of Mineral Species*" was created. The same classification was accepted for the widely known multivolume academic reference book "*Minerals*", which was published since 1960 by the mineralogists of some academic institutes (including the Mineralogical Museum) and the Lomonosov Moscow State University.

As the result of G.P. Barsanov's interest in history of the Museum and Russian mineralogy, the "*Historical Exhibition*" appeared. The expositions "*Mineral Coloration Causes*", "*Pseudomorphs*", "*Processes of Mineral Origin*", "*Mineral Forms*" were also created, the

exhibition "Geochemistry of Elements in Mineral Formation" was made over essentially.

Under the guidance of Georgii Pavlovich Barsanov, the Mineralogical Museum that already was named after Academician A.E. Fersman became a large world assemblage of minerals and one of main centers of scientific mineralogical researches with its own laboratories. The annual issues of "Trudy Mineralogicheskogo muzeya" (*Proceedings of the Mineralogical Museum*) that was yet established by V.I. Vernadsky appeared under the editorship of G.P. Barsanov. The Georgii Pavlovich's own works devoted to the methods of mineral investigation, history of mineralogy in 18th – 19th centuries, Academician A.E. Fersman's creative work as well as results of the researches in the mineral luminescence and coloration made on the base of the Museum vast collections were published too. They had a positive influence on formation and development of the native school of mineral physics.

Holding a chair of mineralogy at the Moscow University, G.P. Barsanov revealed his talent for organizing educational process and scientific work.

His excellent lectures of the mineralogy complete course always gathered full audience of students. They were notable for their bright and vivid form and, at the same time, exact statement of mineralogy crystallochemical, physicochemical, and genetic fundamentals. Georgii Pavlovich had a well-trained voice and impressive mimicry, which always attracted his listeners. His curriculum that included special training in traditional and up-to-date instrumental methods of mineralogical researches and theoretical seminars guaranteed the students to become specialists of highest qualification in mineralogy.

Thanks to Georgii Pavlovich's effective support the scientific and educational laboratories were outfitted with most up-to-date equipment for studying chemical composition, physical and physicochemical properties of minerals and experimental researches. Many of known specialists as well as graduated and postgraduated students were recruited for researching.

In addition to and, thereafter, instead of the classical diagnostics by external features and the blowpipe method, by optical constants and density, qualitative and complete chemical analysis,



Fig. 1. Georgii Pavlovich Barsanov

the new methods of spectral, thermal, and luminescent analyses were developed. Hereafter, laboratories of electronic microscopy and microprobe analysis were organized; the laboratory of spectral analysis with laser microprobe and the laboratory of thermal analysis with derivatograph were equipped. The researches were undertaken in mineral thermo-chemistry including specification of thermodynamic constants by the microcalorimetry method. The experiments in electrochemistry of minerals were being conducted successfully. The stability of minerals was studied under conditions that simulate the hypergenesis with participation of microorganisms. The works in mineral physics, luminescent and optical spectroscopy, electronic paramagnetic resonance, spectroscopy of Raman Effect got quite new contents.

The researches of mineral composition of cobalt, iron, and molybdenum-tungsten scarce deposits, rare metal pegmatites, and hydrothermal gold deposits were being developed in the department to solve some genetic, searching, and technologic problems.

Under G.P. Barsanov's supervision, a lot of graduation works was successfully presented as well as dozens of candidate and doctoral dissertations. There was a great deal of his direct educates and the Chair graduates who are known today as scientists, teachers and mineralogy specialists working in academic and branch institutes, in high schools and industry in Moscow and other Russian cities as well as abroad.

G.P. Barsanov published more than 130 scientific works and a series of monographs apart from numerous articles for the first and second editions of the Great Soviet Encyclopedia.



Fig. 2. Professor G.P. Barsanov with the his mineralogy chair colleagues: A.G. Teremetskaya, assistant professor (in the center), G.I. Bocharova, assistant professor (to the right). 1960-ies.

Besides, G.P. Barsanov led a very intensive scientific, organizational and public works as the Dean of Geological Faculty of Moscow University (1957–1961), member of senates, scientific editor and consultant of the Great Soviet Encyclopedia first and second editions, executive editor and editorial staff member in various periodicals, proceedings, collections, books and journals, consultant in industry and branch institutes, an active member of committees, Vice President of the International Mineralogical Association in 1960–1964. His merits were awarded with government decoration: *The Red Banner of Labor Order*, three *The Badge of Honor Orders* as well as numerous medals including "For Gallantry", "For the Victory over Germany", and "20th Anniversary of the Victory over Germany", diplomas and prizes. G.P. Barsanov was the "Honored Worker of science of the R.S.F.S.R."

Georgii Pavlovich is present to the mind of the Chair workers and graduates as exclusively bright and talented personality, prominent scientist, organizer and leader of scientific direc-

tions of wide topics range in fundamental and applied mineralogical researches. He was notable for his developed sense of responsibility and perfectionism, variety of his interests and views, permanent benevolence, optimism, and humor.

Besides his love for his profession, G.P. Barsanov was also engaged in photography. The Nature was usually his photographic object. He has created several splendid photo albums. His photo exhibitions in the library of the Geological Faculty are unforgettable.

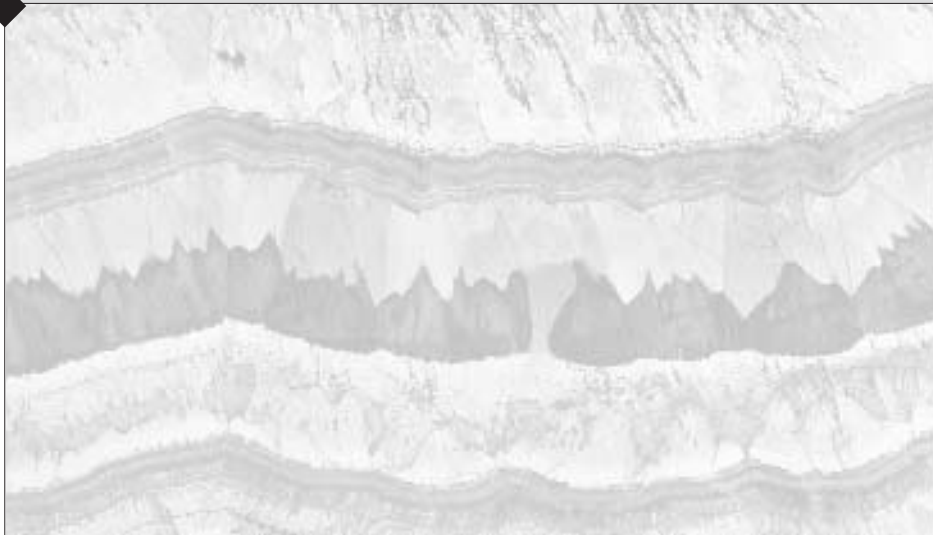
G.P. Barsanov knew well and understood classic music, he was a Conservatory regular. These interests were in harmony with character and inner contents of Georgii Pavlovich, very interesting and talented person.

However, all this can not express his special fascination. Let us remember him together with his friends and collectives that he established and worked with. In the Soviet mineralogy and petrography, there were the three famous "musketees": Valerii Petrovich Petrov, Evgenii Konstantinovich Ustiev and Georgii Pavlovich Barsanov. There were many things to connect them. Their juvenilities passed in old Tbilissi, the town of Pirosmeni and Gudiashvili. They have soaked the old Georgian culture spirit. Then they moved to Leningrad and became familiar with the particular culture of this city that brought up a lot of prominent geologists, physicists and other scientists.

The collectives of the Chair of mineralogy of Moscow State University and Fersman Mineralogical Museum remember and love Georgii Pavlovich and are proud to have worked, learned or simply kept company with this remarkable person.

*Collaborators of the Chair of mineralogy,
Lomonosov Moscow State University*

Mineralogical Notes



Ca-BEARING STRONTIANITE, BARITE, DOLOMITE, and CALCITE FROM METAKIMBERLITE, ZARNITSA PIPE, YAKUTIA

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Strontianite from metakimberlite of the Zarnitsa pipe has been studied. According to mineral assemblages and carbon and oxygen isotopic composition, strontianite and associated minerals are hydrothermal metamorphic and have been formed at the post-trap zeolite facies low-grade metamorphism of submergence.

3 tables, 6 figures, 23 references

Kimberlite pipes in the central part of the Eastern Siberian Platform cut through Paleozoic sequences of the plate cover and are of pre-trap age. Compositionally, kimberlite corresponds to ultrabasic alkaline lamprophyre with a significant amount (up to 30–50% by vol.) of magmatic lamellar calcite containing up to 3% by weight of Sr and 0.5% by weight of Ba (Nikishov, 1984; Mitchell, 1986). Early and Middle Paleozoic sequences comprise numerous evaporates, which are frequently saturated by brines; evaporates and brines are enriched with Sr; anhydrite and dolomite contain disseminated celestite (Geology..., 1966).

Significant part of the Eastern Siberian Platform is covered with thick sequences of plateau basalt and/or basaltic tuff, which are saturated by dykes, sills, and intrusions of gabbro-dolerite of the trap assemblage with an isotopic age of 251 Ma (Kamo *et al.*, 2003) corresponding to the Permian-Triassic boundary. The trap assemblage and underlying sequences with the pre-trap kimberlite bodies were submerged (similar to the submergence of Antarctica, Greenland, and the Baltic Shield under an ice load). All these rocks are affected zeolite and prehnite-pumpellyite facies regional metamorphism of submergence; the Rb/Sr age of low-grade metamorphism of the plate cover at the Eastern Siberian Platform ranges from 232 to 122 Ma, with the latter dating the formation of Iceland spar deposits (Spiridonov *et al.*, 2000, 2006).

The low-grade metamorphism is characterized by the following features. 1) Extreme heterogeneity in appearance; the number of the newly formed metamorphic assemblages

ranges from traces to 100% for short distance with the maximum being close to the feeders (fracture zones). 2) Fluid-dominated nature; therefore, metarocks in general are massive and not foliated and contain cracks of hydrofracturing filled with the metamorphic hydrothermal Alpine veins. 3) The potential for elevated oxidation of metamorphic fluids (Thompson, 1971; Fyfe *et al.*, 1981; Low Grade..., 1999). The Alpine veins are composed of zeolites, serpentine, silica minerals, Ca-Mg-Fe-Mn-Sr carbonates, Fe hydroxides, and Ca-Sr-Ba sulfates.

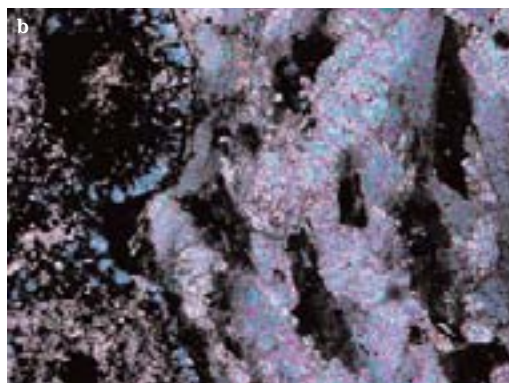
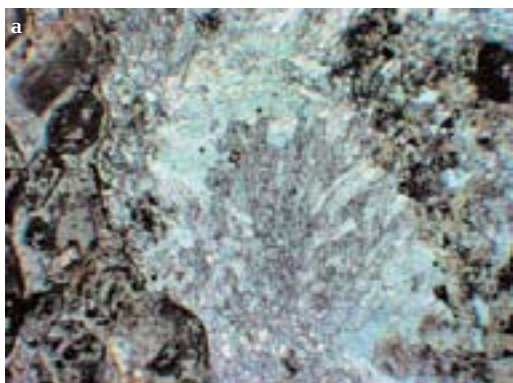
The altered kimberlite with abundant impregnation, pods, and veins of serpentine, calcite, dolomite, magnetite, pyrite, celestite, brucite-amakinite, hydrotalcite-pyroaurite, silica minerals (including pods of agate), and other low-temperature minerals, which are not modified by depth (down to 1200–1500 m), is considered to be the ancient weathering profile or as post-magmatic (Bobrievich *et al.*, 1959; Lebedev, 1963; Milashev, 1963; Francesson, 1968; Marshintsev *et al.*, 1980; Kornilova *et al.*, 1981; Podvysotsky, 1985). This conflicts with the formation temperature of carbonates, serpentine, magnetite, and celestite, which range from 80–130 to 210–250°C (Kuznetsov *et al.*, 1995; Sokolova & Spiridonov, 2006) and oxygen isotopic data (Ukhanov *et al.*, 1982, 1986). I.P. Ilupin (1961) seriously doubted the post-magmatic origin of hydrothermal Sr mineralization in serpentinized kimberlite.

The mineral assemblages of metakimberlite at the Eastern Siberian Platform correspond to the zeolite facies metamorphism (Spiridonov *et al.*, 2000): serpentine mineral is lizardite; typical



Fig. 1. Pods and veinlets of strontianite in metakimberlite: (a) sample 60063 is 10 cm in size. (b) sample M-28392 is 9.5 cm in size.

Fig. 2. (a) Photomicrograph of veinlet of Ca-bearing strontianite in metakimberlite with green lizardite. Normal light. Width of image is 4 mm. (b) Detail of (a). Metakimberlite is as fine-grained aggregates of dolomite, ankerite, calcite, and lizardite (left) and intergrowths of slightly split prismatic crystals of Ca-bearing strontianite (right). Crossed nicols. Width of image is 0.8 mm. Sample 60063.

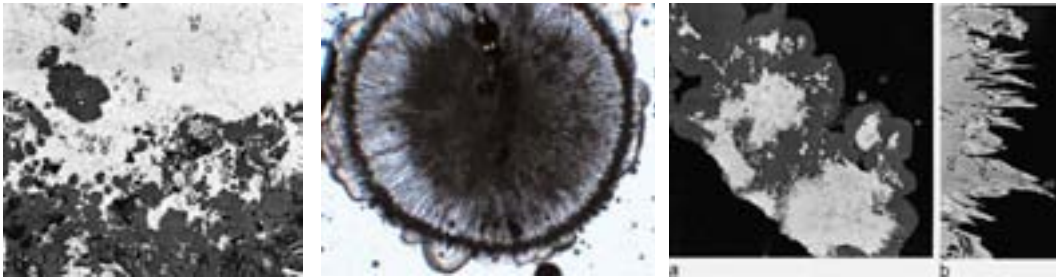


paragenetic assemblages are as follows; lizardite + calcite, lizardite + dolomite, and lizardite + goethite (Kornilova *et al.*, 1981; Nikishov, 1984; Sokolova & Spiridonov, 2006).

Strontium minerals, celestite and strontianite, are widespread in metakimberlite of the Mir, Udachnaya-East, Yakutskaya, Zapolyrnaya pipes, and especially in the Zarnitsa pipe (Bobrievich *et al.*, 1959; Ilupin, 1961). In metakimberlite of the Zarnitsa pipe, pods of celestite of 25 cm across and celestite veinlets are hosted in the lizardite clusters. Celestite replaces lizardite and is colorless, white, blue, reddish pink (with inclusions of tiny lamellae of lepidocrocite), and brown (with inclusions of bitumen and oil up to 0.5 mm in size). In the fracture zones, celestite is partially or completely replaced with strontianite due to the increased presence of $f\text{CO}_2$ in the metamorphic fluid that usually takes place as the temperature decreases (Thompson, 1971).

We have examined aggregates of porcelainous (sample 60063) and spherulitic (sample M-28392) strontianite. The chemical composition has been studied with a JXA-50A electron microprobe, L.A. Pautov, analyst, Fersman Mineralogical Museum, Russian Academy of Sciences. The following standards have been used: SrSO_4 for Sr, BaSO_4 for Ba and S, diopside USNM 117733 for Ca, Mg, Mn, and Fe. BSE images have been made at the same museum. Strontium, oxygen, and carbon isotopic compositions in strontianite have been measured in the Laboratory of Isotopic Research, Geological Institute, Russian Academy of Sciences, B.G. Pokrovsky, analyst.

Sample 60063 is brecciated metakimberlite with crusts, pods and veinlets of strontianite (Figs. 1a, 2). The thickness of the veinlets is up to 4 cm. The dense cluster of strontianite is seen microscopically as a segregation of split long prismatic crystals (Fig. 2). Chemical composition corresponds to Ca-bearing strontianite with the for-

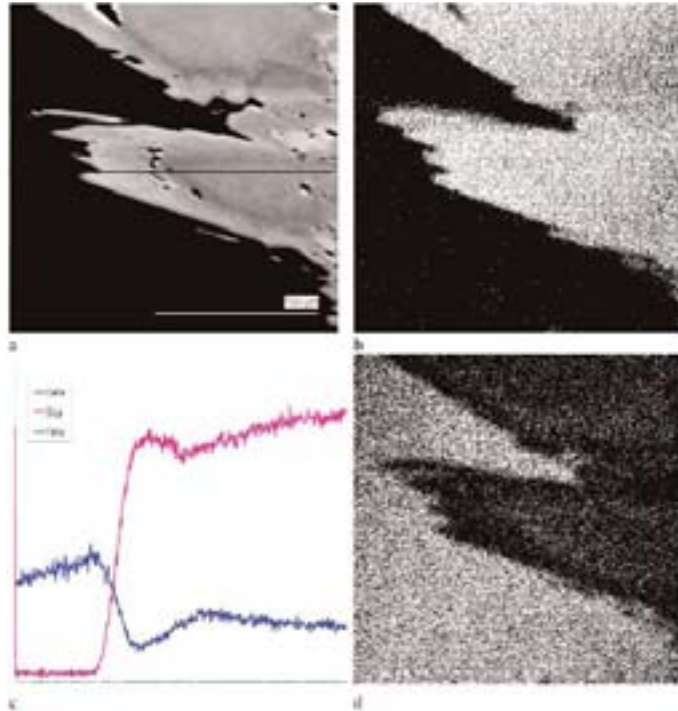


↑ Fig. 3. BSE image of segregations of Ca-bearing strontianite (light) (anal. s1-s4) with numerous crystals of calcite (grey) (analysis c1), less frequent barite (anal. b1, b2), and relic lizardite (black) onto metakimberlite. Sample 60063. Width of image is 1.9 mm.

↗ Fig. 4. Photomicrograph of spherulite of strontianite of 2 mm in size with minute crystals of dolomite. Sample M-28392. Normal light.

↗↗ Fig. 5. BSE images of intergrowths of strontianite and dolomite, sample M-28392. (a) Crusts of spherulites of dolomite (grey) (anal. d1-d3) with minute inclusions of crystals of barite (anal. b3-b5) onto aggregate of prismatic crystals of Ca-bearing strontianite (white); width of image is 2.9 mm. (b) Detail of (a), druse of zoned crystals of Ca-bearing strontianite (anal. s5-s8), width of image is 0.3 mm.

→ Fig. 6. Zoned crystals of Ca-bearing strontianite overgrown by dolomite: (a) BSE image, (b) X-ray map, SrLa, (c) concentration patterns of Sr, Ca, and Fe along line shown in a, (d) X-ray map, CaKa. Sample M-28392.



mula $\text{Sr}_{0.792-0.814}\text{Ca}_{0.181-0.203}\text{Fe}_{0.002-0.005}\text{Ba}_{0-0.001}[\text{CO}_3]$ (Table 1, anal. s1 – s4). Calcite with its' composition corresponding to the formula $\text{Ca}_{0.990}\text{Sr}_{0.007}\text{Fe}_{0.002}\text{Ba}_{0.001}[\text{CO}_3]$ (Table 1, anal. c1) is abundant in aggregates of Ca-bearing strontianite near metakimberlite. Rare grains of barite up to 20 μm in size with composition corresponding to the formula $\text{Ba}_{0.970-0.973}\text{Sr}_{0.009-0.023}\text{Ca}_{0-0.009}\text{Fe}_{0.004-0.012}[\text{SO}_4]$ (Table 2, analyses b1 and b2) also occur in the cluster of strontianite.

Sample M-28392 is metakimberlite with a large pod consisting of strontianite spherulites up to 4 mm in size (Figs. 1b, 4). These spherulites are composed of Ca-bearing strontianite of relatively homogeneous composition. Minute zoned crystals of dolomite (Fig. 4) and their aggregates or compositionally zoned prismatic crystals of Ca-bearing strontianite up to 1 mm long (Figs. 5,

6) have overgrown the spherulites. Prismatic crystals of Ca-bearing strontianite, which are diamond-shaped in cross-section, are partially hollow. The inner zones of these crystals are enriched in Ca and correspond compositionally to the formula $\text{Sr}_{0.720-0.726}\text{Ca}_{0.271-0.276}\text{Fe}_{0.003}[\text{CO}_3]$ (Table 1, anal. s7, s8), whereas the outer zones are enriched with Sr and correspond to the formula $\text{Sr}_{0.831-0.851}\text{Ca}_{0.148-0.162}\text{Fe}_{0-0.003}\text{Ba}_{0.001-0.002}[\text{CO}_3]$ (Table 1, anal. s5, s6). The spherulites of Ca-bearing strontianite are overgrown with solid spherulitic crusts of dolomite up to 0.5 mm thick (Figs. 5, 6), which cause brown coloration of the dolomite. The composition of dolomite corresponds to the formula $\text{Ca}_{1.007-1.030}\text{Mg}_{0.950-0.967}\text{Sr}_{0.016-0.026}[\text{CO}_3]_2$ (Table 3, anal. d1 – d3). Ca-bearing strontianite is associated with minor barite. Crystals of barite are included in the

Table 1. Chemical composition of Ca-bearing strontianite (s1-s8) and calcite (c1) from pods in metakimberlite, the Zarnitsa pipe, Yakutia

Component, wt%	s1	s2	s3	s4	s5	s6	s7	s8	c1
SrO	60.36	59.51	61.29	59.94	61.42	63.89	55.96	56.23	0.67
CaO	7.28	8.24	7.94	7.88	6.45	6.02	11.67	11.35	55.09
FeO	0.19	0.28	0.13	0.20	0.28	0.03	0.17	0.18	0.17
BaO	0.06	—	—	0.08	0.21	0.07	—	—	0.10
CO ₂ *	31.51	31.84	32.32	31.80	31.40	31.92	33.05	32.33	43.68
Total	99.40	99.87	101.71	99.90	99.77	101.93	100.85	100.09	99.71
Atoms per formula unit									
Sr	0.814	0.792	0.805	0.801	0.831	0.851	0.720	0.726	0.007
Ca	0.181	0.203	0.193	0.195	0.162	0.148	0.277	0.271	0.990
Fe	0.004	0.005	0.002	0.004	0.005	0.000	0.003	0.003	0.002
Ba	0.001	—	—	0.001	0.002	0.001	—	—	0.001
Total	1	1	1	1	1	1	1	1	1

Note: Bdl is below detection limit by electron microprobe. Mn is not detected. CO₂ is calculated by stoichiometry.

Table 2. Chemical composition of barite associated with strontianite from pods in metakimberlite, Zarnitsa pipe, Yakutia

Components, wt. %	b1	b2	b3	b4	b5
BaO	63.14	64.11	61.97	61.42	63.89
SrO	1.03	0.42	2.20	2.15	1.79
CaO	0.01	0.23	0.44	0.21	0.45
FeO	0.12	0.38	na	na	0.24
SO ₃	33.90	34.58	34.46	34.09	35.51
Total	98.20	99.71	99.07	99.06	101.88
Atoms per formula unit					
Ba	0.973	0.970	0.936	0.941	0.938
Sr	0.023	0.009	0.049	0.049	0.039
Ca	0.000	0.009	0.018	0.009	0.018
Fe	0.004	0.012	-	-	0.007
SO ₄	1.000	1.000	0.997	1.001	0.998
Total	2	2	2	2	2

Note: na is not analyzed

spherulites of strontianite or are located adjacent to them in surrounding dolomite. Barite contains up to 2.2 wt.% SrO; its chemical composition corresponds to the formula Ba_{0.936-0.941}Sr_{0.039-0.049}Ca_{0.009-0.018}Fe_{0-0.007}[SO₄] (Table 2, anal. b3-b5).

Strontium isotopic composition in the examined strontianite samples is uniform with the ⁸⁷Sr/⁸⁶Sr ratio of 0.7080 (sample 60063) and 0.7084 (sample M-28392). The δO¹⁸ (SMOW) values of the examined samples are different and are +11.7 (sample 60063) and +14.8 (sample

Table 3. Chemical composition of dolomite associated with strontianite from pods in metakimberlite, Zarnitsa pipe, Yakutia

Components, wt. %	d1	d2	d3
CaO	30.86	31.38	30.74
MgO	21.30	21.21	20.39
SrO	1.46	0.91	1.12
CO ₂ *	48.11	48.18	46.88
Total	101.73	101.68	99.13
Atoms per formula unit			
Ca	1.007	1.022	1.030
Mg	0.967	0.962	0.950
Sr	0.026	0.016	0.020
Total	2	2	2

Note: Fe, Mn and Ba are not detected. CO₂ is calculated by stoichiometry.

M-28392). The δC¹³ (PDB) values of the examined samples are strongly variable and equal -0.7 (sample 60063) and -9.9 (sample M-28392). Our data on strontium isotopic composition are close to the data reported in (Kostrovitsky *et al.*, 1983; Exley & Jones, 1983). Magmatic calcite from kimberlite or host evaporite sequences are both probable sources for Sr in metamorphic hydrothermal strontianite. Oxygen and carbon isotopic compositions in strontianite correspond to hydrothermal carbonates (Ferrini *et al.*, 2003).

Thus, Ca-bearing strontianite, barite, calcite,

and dolomite from metakimberlite of the Zarnitsa pipe are metamorphic hydrothermal; this assemblage have arisen under low temperature zeolite facies conditions.

Acknowledgments

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TWISTED FILIFORM MAGNESIAN CALCITE FROM CARBONATE ROCKS OF THE RUSSIAN PLATFORM

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Twisted whiskers of magnesian calcite occur in strongly dolomitized Kasimovian limestone in the Archangelsk Region and in the Podolian rocks of the Moscow area, in low magnesian Moscovian limestone in the Moscow area, and fragments of dolomitized limestone from the Don moraine at the outskirt of Moscow. Whiskers of calcite are epigenetic and result from water related to Quaternary glaciation of the Russian Platform. 5 figures 6 references.

Whiskers are a comparatively rare morphology for many mineral species, but are especially characteristic of gypsum, anhydrite, chrysotile and amphibole asbestos, tourmaline, zeolites, chalcedony, millerite, boulangerite and other acicular sulfides, malachite, supergene Fe, Cu, Mg, and Ni sulfates, ice, and rock salt (Maleev, 1971, Krasnova & Petrov, 1997). Fine linear whiskers of calcite were described from limestone caves in Bulgaria (Maleev & Filipov, 1974). So called rock milk (rock sour cream), "mondmilch (montmilch, bergmilch)" formed by noncemented aggregates of calcite whiskers about 0.0001 mm thick and up to 0.1–0.2 mm long were documented from limestone caves near Luzerne, Switzerland (Seemann, 1979; Fischer, 1988).

T.T. Abramova and L.L. Panas'yan have described filiform calcite from carbonate rocks of the Moscow area, L.L. Panas'yan, from carbonate rocks of Archangelsk Region, and M.S. Chernov, from fragments of carbonate rocks in moraine at the outskirts of Moscow. Backscattered electron images of chips and determination of chemical composition of carbonates in these rocks were made with a LEO-1450-VP scanning electron microscope equipped with an INCA-300 energy-dispersion system (SEM-EDS), V.N. Sokolov and M.S. Chernov, analysts, Laboratory of Electron

Microscopy, Division of Engineering and Environmental Geology, Geology Department, Lomonosov Moscow State University. BSE images were obtained with a Jeol JSM-6480LV scanning electron microscope equipped with an Inca Energy-350 energy-dispersion system, E.V. Guseva, analyst, Laboratory of Local Analytical Techniques, Division of Petrology, Geology Department, Lomonosov Moscow State University.

Filiform calcite from the central Russian Platform

Filiform calcite occurs in Mg-poor pelitomorphic organogenic limestone of the Myachkovo Unit of Late Carboniferous age in the Moscow area (Fig. 1). This white (milky) limestone were mined in the Middle Ages from open pits on the banks of the Moscow river (within the ancient valley of the Moscow river), where Cretaceous and Jurassic deposits enriched in Fe-rich minerals had been removed from Carboniferous carbonate rocks during the pre-glaciation period. In the ancient valley, Carboniferous limestone was affected by Quaternary glaciers and eroded by glacial waters, imparting a milky coloration. Numerous houses in white-stone Moscow were

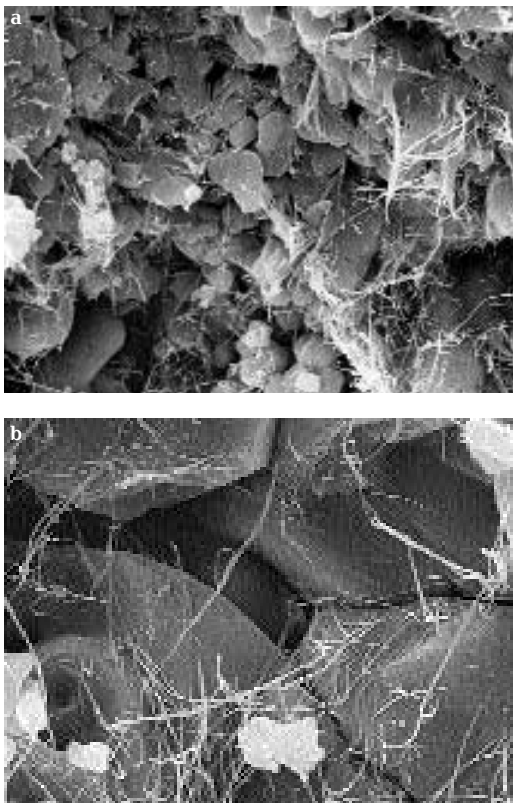


Fig. 1. Myachkovo limestone from the Moscow river valley. BSE images: (a) twisted whiskers of calcite-2 and their segregations in cavities between grains of calcite-1; (b) whiskers of calcite-2 on grains of calcite-1 and in their interstices. A thin film of hydromica covers the grains of calcite-1. Locally, minute rhombohedra of calcite-3 overgrow whiskers of calcite-2.

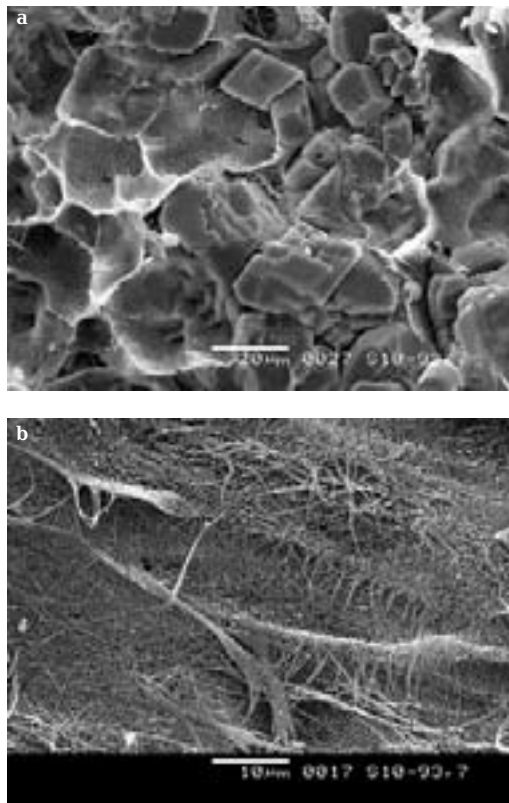


Fig. 2. BSE images of highly dolomitized Podolian limestone from the Moscow river valley. (a) Segregations of fibers of magnesian calcite and palygorskite between dolomite crystals. (b) Segregations of twisted fibers of magnesian calcite and palygorskite.

built with blocks of this limestone, for example, the historical monument in the Museum "The Chambers of the Romanov Boyars of 15th–17th centuries" (Zaryad'e, near the Moscow Kremlin). Samples of limestone were collected 10 cm below the surface of the stone masonry of the building. Pelitomorphic limestone consists of small grains of three generations of calcite with minor dolomite and clay minerals. Substantially dissolved oval grains of calcite-1 ranging from 0.001 to 0.02 mm in size (Fig. 1a) constitute the main part of limestone. Rounded and variable shaped etching pits are abundant on the surface of the calcite-1 grains (Fig. 1b).

Usually curved and twisted whiskers of calcite-2 and their aggregates overgrow calcite-1. Numerous fibers appear to grow from the partly dissolved grains of calcite-1 (Fig. 1b). The thickness of the calcite fibers is less than 0.0002 mm; the length is up to 0.02–0.06 mm

and more. In cross-section, the fibers are rounded; flat faces are absent on sides of the fibers. The fibers are occasionally twisted into complex loops and rings. The calcite fibers can interweave, forming a mat 1–5 fibers thick. Felted segregations of filiform calcite are local.

Rare regular-shaped rhombohedra of calcite-3 up to 0.002 mm in size and their small segregations overgrow filiform calcite-2.

Similar generations of calcite were found in Middle Carboniferous Podolian dolomitized limestone from drill core in the area of the Krasnaya Presnya embankment of the Moscow river (Figs. 2, 3). Here, dolomite crystals range from 0.005 to 0.2 mm in size (usually, from 0.02 to 0.07 mm) and subordinate calcite-1, is smaller than 0.005 mm. Twisted fibers of magnesian calcite-2 and their segregations fill interstices between grains of dolomite and calcite (Fig. 3) or coat dolomite crystals (Fig. 2). Tiny segrega-

tions of leather-stone, palygorskite (light grey, centre of Fig. 3c), are frequently associated with magnesian calcite.

Filiform magnesian calcite of the northern Russian Platform

Whiskers of calcite were identified in milky carbonate rock in the Archangelsk Region (northwestern Russian Platform). This rock is the clay-poor highly dolomitized Kasimovian limestone that is underlain by bauxite of the Plisetsk deposit. Fine porous microcrystalline rock was sampled from drill core at a depth of 50–90 m. The rock is composed of rhombohedra of dolomite and clusters of smaller calcite crystals covered with thin films of clay minerals. According to X-ray powder diffraction data, dolomite is approximately 90%, calcite, 5% of the rock. The insoluble residue consists of quartz, less abundant potassium feldspar and clay minerals, and does not exceed 3% of the rock (by volume). According to X-ray powder diffraction data, the clay minerals are hydromica (illite) and minor illite-smectite and palygorskite.

The size of the dolomite rhombohedra ranges from 0.02 to 0.1 mm (Fig. 4a). The chemical composition of the dolomite corresponds to $\text{Ca}_{0.99-1.04}\text{Mg}_{1.01-0.96}[\text{CO}_3]_2$; the average composition (on the basis of 3 analyzed points) is $\text{Ca}_{1.009}\text{Mg}_{0.991}[\text{CO}_3]_2$; Fe, Mn, and Sr are below their detection limit. The central part of the dolomite crystals is usually leached and/or replaced by calcite.

Calcite occurs as three generations of different individual crystals. Most of them pertain to calcite-1. Crystals of calcite-1 are nearly equant or slightly elongated, usually oval, occurring infrequently as regular scalenohedra; the crystal size ranges from 0.002 to 0.01 mm (Fig. 4). The surface of calcite-1 crystals are frequently covered by etch figures, including channels, benches and other forms (Fig. 4c). The chemical composition of calcite-1 corresponds to $(\text{Ca}_{0.96}\text{Mg}_{0.04})[\text{CO}_3]$.

The twisted whiskers of calcite-2 are of particular interest. In cross-section, the whiskers are rounded and their thickness ranges from 0.00004 to 0.00008 mm (usually, about 0.00005 mm) (Fig. 4c). Flat faces are absent on the sides of the calcite fibers. The fibers of calcite are of 0.02–0.1 mm long, are frequently curved, and adhere to form thicker fibers or mats. Fibers of calcite like to grow from the surface of dissolved calcite-1 grains (Fig. 4c). Aggregates of the calcite fibers frequently cover dolomite rhombohe-

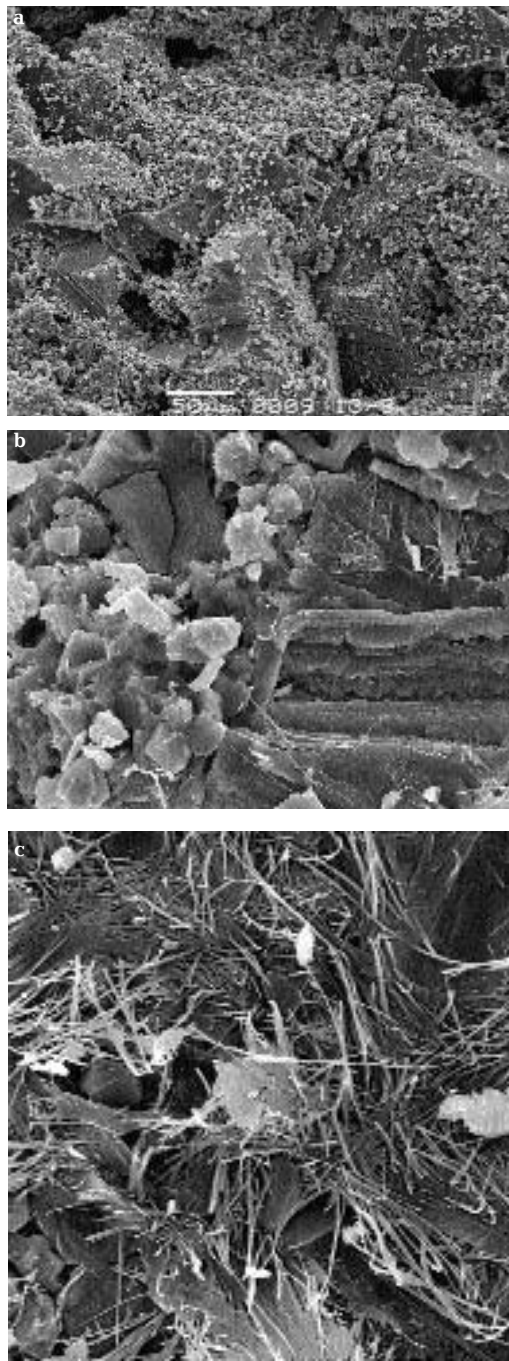


Fig. 3. Podoloian dolomitized limestone from the Moscow river valley. (a) BSE images of rock composed of rhombohedra of dolomite and minute crystals of calcite-1; dolomite crystals are significantly leached. (b) BSE image of whiskers of magnesian calcite-2 between grains of dolomite and calcite-1. (c) BSE image of separate twisted whiskers and their segregations of magnesian calcite-2. Rare crystals of calcite-3 (white) adhere to these whiskers.

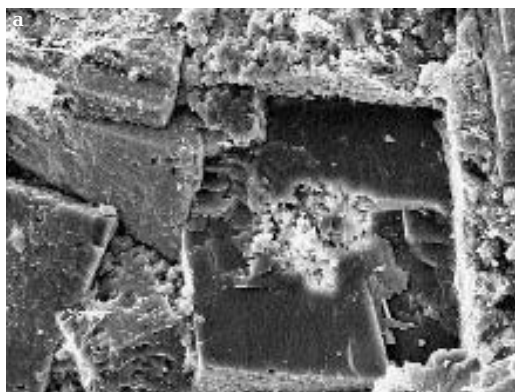


Fig. 4. BSE images of highly dolomitized Kasomovian limestone from the Archangelsk Region. (a) Rocks consist of dolomite rhombohedra and grains of calcite-1. The centres of dolomite rhombohedra are partly leached and partly replaced by calcite (white). Filiform magnesian calcite-2 fills the interstices between grains of dolomite and calcite-1. (b) Twisted fibers of magnesian calcite and their segregations fill interstices between grains of dolomite and calcite-1. (c) Twisted fibers of magnesian calcite-2 have overgrown the dissolved surfaces of calcite-1 grains with a thin film of hydromica.

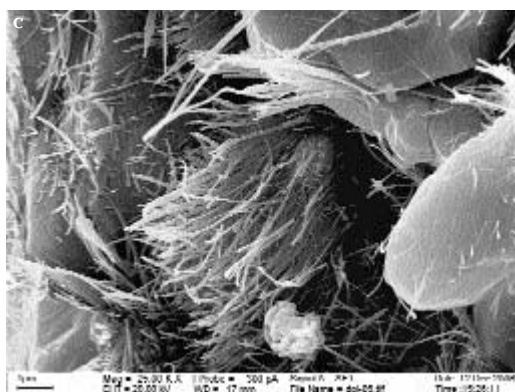
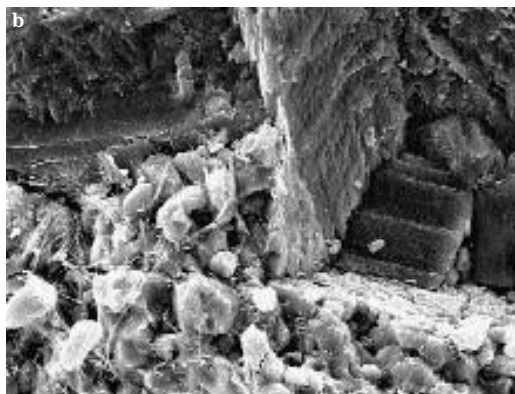
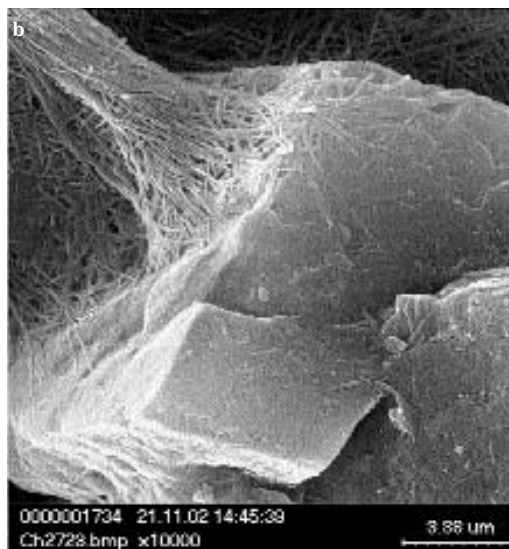


Fig. 5. BSE images of a 0.8 mm fragment of dolomitized limestone from clays of the Don moraine from southwest Moscow. (a) General view. (b) Detail of this fragment: segregations of twisted fibers of magnesian calcite around dolomite crystals.



dra. In isolated areas, filiform calcite is slightly twisted and its segregations are similar to rock milk (rock cream). The chemical composition of the Archangelsk filiform calcite corresponds to $(Ca_{0.877}Mg_{0.123})[CO_3]$, Mg-rich calcite. The presence of magnesian calcite was confirmed by X-ray diffraction.

Calcite-3 is much rarer. It occurs as tiny isolated rhombohedra and aggregates of rhombohedra, and overgrows dolomite and fibers of calcite-2. Size of the calcite-3 grains ranges from 0.0001 to 0.001 mm. They are pure calcite in composition.

Filiform calcite on the surface of small fragments of carbonate rocks from Quaternary moraine in the central part of the Russian Platform

Twisted filiform magnesian calcite that is similar to that described above occurs on the surface of fragments of dolomitized limestone from moraine clays at the outskirts of Moscow (Fig. 5). Clay samples of the Don moraine were collected from a drill hole at a depth of 12 m. Filiform calcite grew on the surface of small fragments of limestone in the moraine subsequent to deposition of the latter during thawing of the Quaternary glacier.

Probable mechanism of formation of filiform calcite on the Russian Platform

Commonly, natural whiskers grow onto a microporous substrate, and the size of the whiskers is defined by the size of the pores, i.e. the interstices between the crystals of the substrate (Maleev, 1971). The whiskers of calcite in Carboniferous carbonate rocks of the northern and central Russian Platform have probably grown on crystals of dissolved calcite covered by an extremely thin film of hydromica from

solutions enriched in Ca and Mg. The late epigenetic generations and aggregates of filiform calcite significantly altered the texture of the carbonate rocks and affected their properties.

Whiskers of relatively soluble compounds such as calcite are the latest and are only moderately stable in general. The filiform calcite and milky coloration of the host carbonate rocks result from waters related to the Quaternary glaciation of the Russian Platform (Spiridonov *et al.*, 2007).

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'Fersmaniada-2008'

Competition for the best scientific work by the young geologists and mineralogists, within the International conference 'Fersmanovskie chteniya' dedicated to the 125th anniversary of academician Alexander E. Fersman

On the 10–12th November 2008 Fersman Mineralogical Museum RAS will organize the International Scientific Conference 'Fersmanovskie chteniya'. The conference will emphasise modern state-of-the-art scientific ideas by Alexander E. Fersman, their development and also topics regarding historical aspects of the life and work of the academician. The museum invites Russian and foreign scientists to give talks on related topics. The preliminary programme is available at the museum's Internet-site www.fmm.ru.

In collaboration with the Russian Geological Society (www.georos.ru) the youth session 'Fesmaniada' is being planned within the conference. At this session the best works of young naturalists, geologists and mineralogists will be presented. The works will be selected through a two-stage competition, and the best will be presented as talks and presentations in the museum.

The general aims of the competition are to promote national heritage, to develop scientific and art skills and to give the opportunity to experience and participate in scientific events.

General guidelines

The competition will be held in two tours: correspondence and on-site.

Schoolchildren from Russia and abroad can take part in the competition, regardless of age. The works presented can be individual or collective.

Correspondence tour. The works devoted to the Alexander E. Fersman's activity should be sent to the Organizing Committee before 10th October 2008. The topics are the following:

1. Mineralogy of pegmatites
2. Mineralogy of alkaline rocks
3. Mineral deposits investigated by Alexander E. Fersman: past – present – future
4. Alexander E. Fersman and geological museums
5. Field-trips 'By Fersman's steps'
6. Alexander E. Fersman and youth geological organisations
7. Alexander E. Fersman – the legendary person

The works can be submitted as a referative description, photo gallery, video or mineral and rock collection. The materials regarding the work should be made according to the Full General Guidelines available at www.fersman.ru. Abstracts will be published in the abstract book of the conference. The winners of the correspondence tour will take part in the on-site tour in Moscow.

The on-site tour will be held in Moscow, at the Fersman Mineralogical Museum RAS within the International scientific conference 'Fersmanovskie chteniya'. The works are to be presented at a talk or video-show, or presentation of photo-gallery or mineral&rock collection. The best works will be temporarily exhibited in the museum. The full guidelines for scientific works, photo and video-galleries, collections and abstracts are available at www.fersman.ru.

Preliminary Programme:

15 April – 10 October

Works submission (correspondence tour)

11 – 12 November

Talks, photo and video-presentations, collections show (on-site tour)

The working team addresses:

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