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New Data on Minerals. Moscow: Ocean Pictures, 2003. volume 38, 172 pages, 66 color photos.

Articles of the volume are devoted to mineralogy, including descriptions of new mineral species (telyushenkoite — a new caesium mineral of the leifite group, neskevaaraite-Fe — a new mineral of the labuntsovite group) and new finds of minerals (pabstite from the moraine of the Dara-i-Pioz glacier, Tadjikistan, germanocolusite from Kipushi, Katanga, minerals of the hilairite group from Khibiny and Lovozero massifs). Results of study of mineral associations in gold-sulfide-tellyride ore of the Kairagach deposit, Uzbekistan are presented. Features of rare germanite structure are revealed. The cavitation model is proposed for the formation of mineral microspherulas. Problems of isomorphism in the stannite family minerals and additivity of optical properties in minerals of the humite series are considered. The section Mineralogical Museums and Collections includes articles devoted to the description and history of Museum collections (article of the Kolyvan grinding factory, P.A.Kochubey's collection, new acquisitions) and the geographical location of mineral type localities is discussed in this section. The section Mineralogical Notes includes the article about photographing minerals and Reminiscences of the veteran research worker of the Fersman Mineralogical Museum, Doctor in Science M.D. Dorfman about meetings with known mineralogists and geochemists — N.A. Smoltaninov, P.P. Pilipenko, Yu.A. Bilibin.

The volume is of interest for mineralogists, geochemists, geologists, and to museum curators, collectors and amateurs of minerals

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phone (7-095) 952-00-67;

fax (7-095) 952-48-50

e-mail mineral@fmm.ru

web-site: www.fmm.ru

Coean Pictures Ltd

4871 S. Dudley St., Littleton

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# TELYUSHENKOITE CsNa<sub>6</sub>[Be<sub>2</sub>(Si,A1,Zn)<sub>18</sub>O<sub>39</sub>F<sub>2</sub>] — A NEW CESIUM MINERAL OF THE LEIFITE GROUP

Atali A. Agakhanov

Fersman Mineralogical Museum Russian Academy of Sciences, Moscow, Russia

Leonid A. Pautov

Fersman Mineralogical Museum Russian Academy of Sciences, Moscow, Russia

Dmitriy I. Belakovskiy

Fersman Mineralogical Museum Russian Academy of Šciences, Moscow, Russia

Elena V. Sokolova

Department of Geological Sciences, University of Manitoba, Winnipeg, Canada

Frank C. Hawthorne

Department of Geological Sciences, University of Manitoba, Winnipeg, Canada

A new mineral, telyushenkoite, was discovered in the Dara-i-Pioz alkaline massif (Tajikistan). It occurs as white or colorless vitreous equant anhedral grains up to 2cm wide in coarse-grained boulders of reedmergnerite associated with microcline, polylithionite, shibkovite and pectolite. The mineral has distinct cleavage, Mohs hardness = 6, VHN $_{100}$  = 714(696-737) kg/mm², Dmeas. = 2.73(1), Dcalc. = 2.73g/cm³. In transmitted light, telyushenkoite is colorless and transparent. It is uniaxial positive,  $\omega$  = 1.526(2),  $\varepsilon$  = 1.531(2). Single-crystal X-ray study indicates trigonal symmetry, space group P-3m1,  $\alpha$  = 14.3770(8),  $\alpha$  = 4.8786(3) Å,  $\alpha$  = 873.2(1) ų,  $\alpha$  = 1. The strongest lines in the powder-diffraction pattern are [d(I, $\alpha$ )]: 12.47(7,010), 6.226(35,020), 4.709(21,120), 4.149(50,030), 3.456(40,130), 3.387(75,121), 3.161(100,031), 2.456 (30,231). The chemical composition (electron microprobe, BeO by colorimetry) is SiO<sub>2</sub> 64.32, Al<sub>2</sub>O<sub>3</sub> 7.26, BeO 3.53, ZnO 1.71, Na<sub>2</sub>O 13.53, K<sub>2</sub>O 0.47, Cs<sub>2</sub>O 6.76, Rb<sub>2</sub>O 6.76, F 2.84, -O = F 1.20, total 99.37 wt.%, corresponding to (Cs<sub>0.69</sub>Na<sub>0.31</sub>K<sub>0.14</sub>Rb<sub>0.02</sub>)<sub>1.16</sub>Na<sub>6.00</sub> [Be<sub>2.04</sub>(Si<sub>15.46</sub>Al<sub>2.06</sub>Zn<sub>0.30</sub>)<sub>17.82</sub>O<sub>38.84</sub>F<sub>2.16</sub>]. Telyushenkoite, ideally CsNa<sub>6</sub>[Be<sub>2</sub>(Si<sub>15</sub>Al<sub>3</sub>)<sub>18</sub>O<sub>39</sub>F<sub>2</sub>], is the Cs-dominant analogue of leifite, ideally NaNa<sub>6</sub>[Be<sub>2</sub>(Si<sub>15</sub>Al<sub>3</sub>)<sub>18</sub>O<sub>39</sub>F<sub>2</sub>].

#### Introduction

Examination of specimens collected at the Dara-i-Pioz alkaline massif has resulted in the discovery of a new mineral, the cesium analogue of leifite with the chemical formula  $CsNa_6[Be_2(Si,Al,Zn)_{18}O_{39}F_2]$ . The mineral was named telyushenkoite in honor of Tamara Matveyevna Telyushenko (1930 – 1997), a petrographer who made major contributions to our knowledge of the geology of Central Asia, and who headed the Young Geologists' School of Ashkhabad for over thirty years, educating many future geologists. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The type specimen of telyushenkoite is in the collection of the Fersman Mineralogical Museum, Moscow, Russia, catalogue number 90435.

#### Location and occurrence

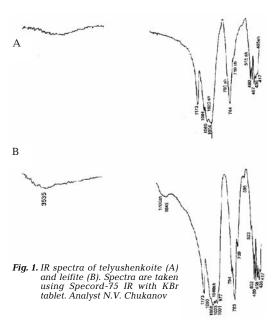
Telyushenkoite was discovered in reedmergnerite boulders found on the moraine of the Dara-i-Pioz glacier close to the mouth of the Ledovy Ravine in the Upper Dara-i-Pioz alkaline massif (Dusmatov 1970, 1971). The massif is located in the upper part of the Dara-i-Pioz valley, 45 km north-north-east of the village of Khait, Garmskiy district, at the junction of the Zeravshan, Alay and Gissar Ranges of the South Tien-Shan Mountains, Tajikistan.

Telyushenkoite occurs in a rock consisting primarily of coarse-grained reedmergnerite (85–90%) (Dusmatov *et al.*, 1967; Grew *et al.*, 1993) in which the reedmergnerite grains reach up to 15 cm in diameter. Euhedral grains of microcline (up to 5 cm) and their aggregates constitute ~10% of the rock; pectolite, hyalotekite, kentbrooksite, polylithionite and albite make up the remaining 5% of the rock.

Telyushenkoite occurs as equant grains up to 2 cm across within veinlets cutting reedmergnerite (Fig.2) and microcline, in close association with hyalotekite, shibkovite, nordite-(Ce) and leucophanite. It also occurs in interstices between grains of reedmergnerite.

#### Physical properties

Telyushenkoite is white to colorless, and vitreous with a white streak. It has distinct cleavage. Mohs hardness is 6. Vickers hardness data, obtained using a PMT-3 unit calibrated by NaCl at a loading of 100 g, is as follows:  $VHN_{100} = 714 \text{ kg/mm}^2$  (mean of 8 measurements ranging from 696 to 737 kg/mm²). The



density was measured by suspension of mineral grains in Clerici solution, giving a value of 2.73 g/cm<sup>3</sup>; the calculated density is 2.73 g/cm<sup>3</sup> for Z = 1. In transmitted light, the mineral is colorless and transparent. It is uniaxial positive, and the refractive indexes, measured using the rotating-needle method, are  $\omega =$ 1.526(2),  $\varepsilon = 1.531(2)$ . There is very dim dark-purple fluorescence under short-wave ultraviolet radiation, which allows telyushenkoite to be easily distinguished from albite and other visually similar minerals in this

N.V. Chukanov obtained the IR spectrum of telyushenkoite (Fig.1) using a Specord 75 IR spectrophotometer. The spectrum is very similar to that of leifite, but differs in the absence of OH (vOH 3535 cm $^{-1}$ ) and H<sub>2</sub>O (vHOH 1645 cm $^{-1}$ ) bands, consistent with the structural and chemical data. There are strong IR-absorption bands at 405 417, 436, 457, 480, 500, 515, 710, 764, 790, 1004, 1020, 1060, 1094 and 1173 cm<sup>-1</sup>.

#### Chemical composition

The chemical composition of telyushenkoite was determined using a JXA-50A electron-microprobe equipped with three wavelength-dispersion spectrometers (Table 1). Five different grains (30 points) were analyzed at the following conditions: excitation voltage 20 kV; specimen current: 20 nA; beam size 3 µm. The following standards were used: microcline USNM

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

(Mean value of 7 microprobe analyses, WDS)

ent wt.%	Range
64.32	63.76 - 65.56
7.26	7.14 - 7.48
3.53	
1.71	1.54 - 1.90
13.53	12.59 - 14.32
0.47	0.35 - 0.53
6.76	5.75 - 7.49
0.15	0.11 - 1.26-
2.84	2.10 - 2.84
100.57	
-1.20	
99.37	
	64.32 7.26 3.53 1.71 13.53 0.47 6.76 0.15 2.84 100.57 -1.20

\*BeO was determined by the colorimetric method with quinalizarin. Analysts: L.A.Pautov and A.A.Agakhanov

143966 (Al, K), gahnite USNM 145883 (Zn), CsHo[PO3]<sub>4</sub> (Cs), RbSc(WO<sub>4</sub>)<sub>2</sub> (Rb), chkalovite (Si, Na), and synthetic fluorphlogopite (F). Grains of telyushenkoite are homogenous for all elements analyzed. Raw data were corrected using the PAP procedure. The beryllium content was measured by the colorimetric method with quinalizarin. The mean chemical composition of analyzed grains (Table 1) was recalculated on the basis of O + F =41 apfu (atoms per formula unit) to give the empirical formula  $(Cs_{0.69}Na_{0.31}K_{0.14}Rb_{0.02})_{\Sigma=1.16}Na_{6.00}$  $[Be_{2.04}(Si_{15.46}Al_{2.06}Zn_{0.30})_{\Sigma=17.82}O_{38.84}F_{2.16}]$ . The formula of telyushenkoite can be written generally as  $(Cs, Na, K)Na_{6}[Be_{2}(Si, Al)_{18}O_{39}F_{2}]$ end-member formula is  $CsNa_6[Be_2(Si_{15}Al_3)O_{39}F_2]$ . The Gladstone-Dale compatibility index (Mandanno, 1981) for telyushenkoite (1 - Kp/Kc) is -0.004 (superior).

# X-ray powder pattern

The X-ray powder-diffraction pattern for telyushenkoite was obtained with a DRON-2 diffractometer equipped with Fe $K\alpha$ -radiation and a graphite monochromator, and using quartz as an internal standard. The pattern (Table 2) was indexed in the space group P-3m1based on cell parameters obtained from the refined crystal-structure.

#### **Crystal structure**

The crystal structure of telyushenkoite was refined by Sokolova et al. (2002) using single-crystal X-ray data. Telyushenkoite is trigonal, space group P-3m1 with cell parameters a =14.3770(8)Å, c = 4.8786(3) Å, V = 873.2(1) Å<sup>3</sup>, Z =

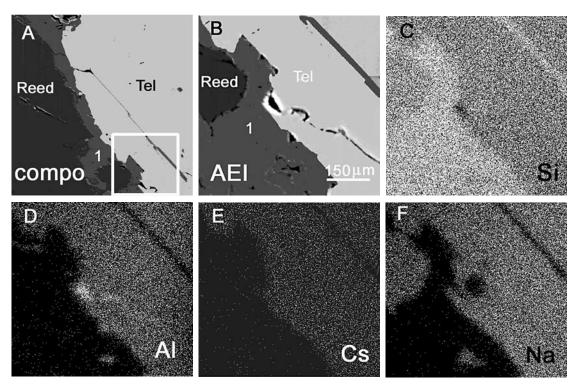


Fig. 2. Intergrowth of telyushenkoite (Tel) with reedmergnerite (Reed) and phase (1), corresponding by composition to SiO<sub>2</sub>. A – image in the COMPO mode, B – fragment of the previous image. The absorbed current (AEI) image. C, D, E, F – images in X-ray characteristic radiation of specified elements

1. The empirical formula of the mineral from the structural study is  $(Cs_{0.72}K_{0.15}Na_{0.11}Rb_{0.02})_{\Sigma=1.00}Na_{6.00}$  [Be $_{2.00}Si_{6.00}(Si_{4.89}Al_{1.11})_{\Sigma=6.00}$   $(Si_{4.5}Al_{1.20}Zn_{0.30})_{\Sigma=6.00}$   $O_{38}F_2$ ].

The main elements of the telyushenkoite structure are shown in Figure 3. Six-membered rings of vertex-sharing (Si,Al,Zn)-bearing tetrahedra are linked together by four-membered rings of (SiO<sub>4</sub>) tetrahedra. Triplets of adjacent four-membered rings are linked by (BeO<sub>3</sub>F) tetrahedra. As a result, seven-membered rings, involving all four types of tetrahedra, are formed (Fig. 3). Down the c axis, six-membered rings are connected by 4-membered rings of (SiO<sub>4</sub>) tetrahedra. six-membered rings of tetrahedra stack along [001] to form channels parallel to the c axis, and the A (Cs, Na) and B (Na) sites occur within these channels. The Na site occurs within the channels formed by the seven-membered rings. Three (NaO<sub>6</sub>F) polyhedra share edges with the (BeO<sub>3</sub>F) tetrahedron, and these [Na<sub>3</sub>(BeO<sub>4</sub>)O<sub>13</sub>F] clusters share vertices along the c direction. As a result, the F site is tetrahedrally coordinated by one B and three Na atoms; hence there can be no substitution of (OH) for F at this site, as there is no room for the H atom within the tetrahedron of cations surrounding the F site.

The main structural difference between telyushenkoite and leifite is the occupancy of the octahedrally coordinated A site; it is occupied by Cs in telyushenkoite, whereas in leifite, this site is occupied by Na and surrounded by six atoms of oxygen and two (H<sub>2</sub>O) groups. The B site in telyushenkoite is not occupied, whereas in leifite, it is partly occupied by (H<sub>2</sub>O).

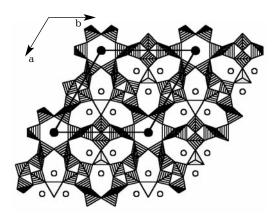


Fig. 3. The crystal structure of leifite viewed down the c-axis; (Si,Al,Zn)O4 tetrahedra are dashed-line shaded, (BeO3F) tetrahedra are unshaded, A sites (Cs) are shown as black circles, B sites are shown as highlighted circles

Table 2. X-ray powder pattern of telyushenkoite

d(meas.)\* (Å) d(calc.) (Å) 0 1 0 6.225 35 6.226 4.706  $\begin{smallmatrix}0&2&0\\1&2&0\end{smallmatrix}$ 21 4.706 030 4.149 4.150  $\begin{smallmatrix}0&2&1\\2&2&0\end{smallmatrix}$ 10 7 3.840 3.840 3.594 3.598 130 3.456 3.453 75 100 3.382 3.387 121 0.3.1 3.162 3.161 040 3.113 3.113 8 30 25 2.717 2.717 1 4 0 2.465 2.465 231 330 2.396 2.396 4 2 2.375 2.374 2.309 2.310 112 15 2.218 2.218 051 2.151 2.151 3 3 1 5 4 2.217 2.119  $\begin{smallmatrix}2&4&1\\0&3&2\end{smallmatrix}$ 2.104 2.103 8 2 2 1.910 1.910 061 1.899 1.899 160 1.816 1.815 1.797 4 4 0 3 7 1.771 1.770 161 1.744 1.743 052 1.708 1.709 332 1.695 1.694  $\begin{smallmatrix}2&4&2\\2&6&1\end{smallmatrix}$ 1.629 1.628 1.627 1.626 003 1.581 1.581 062 1.568 1.569 360

	Telyushenkoite	Leifite
Chemical formula	$CsNa_6[Be_2(Si_1Al_1Zn)_{18}O_{39}F_2]$	$NaNa_{6}[Be_{2}(Si_{7}Al_{7}Zn)_{18}O_{39}F_{2}](H_{2}O)$
Space group	P-3m1	P-3m1
a, Å	14.3770	14.352
c, Å	4.8786	4.852
Z	1	1
Strongest X-ray lines	12.47(7)	12.429(25)
d(meas.) (Å), (Ĭ)	6.226(35)	6.215(10)
	4.709(21)	4.698(40)
		4.520(25)
	4.149(50)	4.143(17)
	3.456(40)	3.588(17)
	3.387(75)	3.375(70)
	3.161(100)	3.151(100)
	2.456(30)	2.458(25)
Color	White, colorless	White, colorless
Luster	Vitreous	Vitreous
D(meas.) q/cm <sup>3</sup>	2.73	2.58
Mohs hardness	6	6
Optical properties	Uniaxial positive	Uniaxial positive
$\omega_o$	1.526	1.511 – 1.518
$\mathcal{E}_e$	1.531	1.519 - 1.522

Table 3. Comparatison of the properties telyushenkoite and leifite

Note: Diffractometr DRON-2, (FeKα–radiation, graphite monochromator, internal standard: quartz)

#### The leifite group

The properties of telyushenkoite are similar to those of leifite (Table 3), and there is probably an isomorphous series between these minerals. Petersen et~al.~(1994) reported Cs-bearing leifite from Greenland with a Cs<sub>2</sub>O content ranging between 0.23 and 1.38 wt.%. The presence of 1.52B2.55 wt.%  $K_2O$  in the Greenland lefite indicates existence of a new K member of this group. Three of four analyses of leifite from Greenland shows K in excess of 0.50 apfu. If K occupies the A site, as Cs does in telyushenkoite, there will be a new mineral with the chemical formula KNa<sub>6</sub> [Be<sub>2</sub>(Si<sub>15</sub>Al<sub>3</sub>)<sub>18</sub>O<sub>39</sub>F<sub>2</sub>] (Sokolova et.~al.,~2002).

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UDC 549.657 + 548.6

# NESKEVAARITE-Fe, - NaK<sub>3</sub>Fe(Ti, Nb)<sub>4</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>(O,OH)<sub>4</sub>·6H<sub>2</sub>O, - A NEW LABUNTSOVITE GROUP MINERAL<sup>1</sup>.

Nikita V. Chukanov

Institute of Problems of Chemical Physics, RAS, Chernogolovka, Moscow oblast. E-mail: chukanov@icp.ac.ru

Viktor.V. Subbotin

 $Geological\ Institute,\ Kola\ Scientific\ Centrum,\ RAS,\ Apatity.\ E-mail: sub@geoksc.apatity.ru$ 

Igor V. Pekov

Lomonosov Moscow State University, Moscow, e-mail: igorpekov@mtu-net.ru

Aleksandr E. Zadov

R&D Association «Regenerator», Moscow

Anatoliy I. Tsepin

Institute of ore geology, petrography, mineralogy and geochemistry, RAS, Moscow. e-mail: vak@igem.ru

Kseniya A. Rozenberg

Lomonosov Moscow State University, Moscow

Ramiza K. Rastsvetaeva

Institute of Crystallography, RAS, Moscow. E-mail: rast@ns.crys.ras.ru

Giovanni Ferraris

Dpt. Scienze Mineralogiche e Petrologiche, Univ. Torino, Italy. E-mail: giovanni.ferraris@unito.it

Neskevaaraite-Fe, a new labuntsovite-group mineral, was found in the Vuoriyarvi alkaline-ultramafic pluton, Northern Karelia, within a hydrothermally altered carbonatite body. The mineral occurs as rough brown translucent prismatic crystals up to 6 mm long. Associated minerals are dolomite, calcite, phlogopite, fluorapatite, pyrite, pyrrhotite, chalcopyrite, serpentine, and nenadkevichite. Another occurrence is a field-spare-calcite vein located in the Kukisvumchorr Mt., Khibiny, Kola Peninsula, where the new mineral is closely associated with labuntsovite-Fe.

3 tables, 3 figures, 12 references

The labuntsovite group takes a special position among a wide variety of aqueous alkaline Ti- and Nb-silicates («amphoterosilicates») due to a unique structural pattern inherent in these minerals. The basis of their structure is a framework consisting of chains (Ti,Nb)O-octahedra (M) that are linked by four-membered rings of Si,O-tetrahedra (T). Large low-valent cations («extra-framework cations» hereafter) and H<sub>2</sub>O are situated in open cavities of this zeolite-like framework. In monoclinic members of the group, chains of (Ti,Nb)O-octahedra (M) can be linked also by additional D,O-octahedra, where D = Mq, Mn, Fe, and Zn (Chukanov et al., 1999, 2002).

If present, the labuntsovite group minerals delimit the boundaries of very special conditions of mineral formation. Hypothetically, the labuntsovite parageneses were formed in alkalic hydrothermalites under a combination of high activities of water, K and/or Na, Ti and/or Nb, and Si at a relatively low P-T level.

While resembling each other in their structural pattern, the labuntsovite group minerals exhibit a considerable variability in their symmetry, topological features of frameworks, and, especially, chemical compositions. Recent

studies indicate that these minerals respond to minor changes in the geochemical environment during the course of crystallization, as well as in subsequent cation-exchange processes. Wide-ranged isomorphous substitutions are common for the extra-framework cations Na, K, Ca, Sr, and Ba (which is also typical of common aluminosilicate zeolites) along with octahedral framework cations. These controls are responsible for the variations within this group of minerals. It provides an effective tool for estimation of large-scale and local activities of mineral forming components. On the other hand, ion-exchange properties inheent in the labuntsovite-like minerals (Pekov et al., 2002a) and their synthetic analogues (Dyer et al., 1999) are of practical interest. The new mineral of the labuntsovite group described here has been found in a drillcore from the Neskevaara Hill, central part of the alkaline-ultrabasic massif Vuoriyarvi, Northern Karelia, Russia (holotype) and in the Khibiny peralkaline massif, Kola Peninsula, Russia. It was named neskevaaraite-Fe after the discovery locality at the Neskevaara Hill. The suffix -Fe shows Fe prevailing in the D site of the structure, in accodance with accepted rules of

Approved by the Commission on New minerals and Mineral Names of the International Mineralogical Association, May 02, 2002

Table 1. Chemical composition of neskevaaraite-Fe (columns 1 and 2) and labuntsovite-Fe (from the intergrowth with the former)

Component 1 2 3										
wt.%										
$Na_2O$	3.10(2.21 - 3.38)	3.45	5.09							
$K_2O$	8.83(8.18-9.37)	9.11	7.74							
CaO	0.00	0.03	0.00							
SrO	0.00	0.07	0.00							
BaO	3.37(2.05-4.69)	5.07	8.28							
MgO	0.75 (0.57 - 1.06)	0.05	0.98							
MnO	0.50 (0.38 - 0.59)	1.03	0.11							
FeO	1.82(1.62-2.14)	1.98	1.75							
ZnO	0.00	0.11	0.11							
$SiO_2$	39.29 (38.25 - 40.12)	37.95	39.62							
$TiO_2$	15.08 (13.30 - 15.94)	14.80	25.13							
$ZrO_2$	0.00	0.08	0.08							
$Nb_2O_5$	17.96 (17.21 - 19.04)	18.21	2.09							
$H_2O$	9.26	n.d.	n.d.							
Total	99.97	91.94	90.98							
	Coefficients in formulas,									

as calculated per eight Si atoms 1.22 1.41 1.99 2.29 2.45 1.99 0.01 Ca 0.01 Sr Ba 0.26 0.420.66 0.23 0.02 0.29 Mq Mn 0.09 0.18 0.02 Fe 0.31 0.35 0.30 0.02 7n8 Si 8 8 Ti 2.31 2.35 3.82 Zr 0.01 0.19 1.65 Nb 1.74

**Note:** Neskevaara, Vuoriyarvi (holotype, an average of 7 analyses; the range values bracketed) 2-3 Kukisvumchorr, Khibiny (a neskevaaraite-Fe – labuntsovite-Fe intergrowing)

nomenclature for labuntsovite-group minerals (Chukanov *et al.*, 2002)

The Vuoriyarvi pluton is a typical representative of the central type intrusions composed of alkaline-ultramafic rocks and carbonatites (Kukharenko et al., 1965). The labuntsovite-group minerals are rather common here. These are vuoriyarvite-K (Subbotin et al., 1998), nenadkevichite, labuntsovite-Mg, labuntsovite-Fe, and korobitsynite. These minerals are especially abundant in the Neskevaara area where they occur in hydrothermally altered pyrochlore-bearing carbonatite and phoscorite. All labuntsovite-like minerals have been found there in drillcore samples collected from carbonatite veins at depths of 30 to 780 m from the ground surface. The veins are up to 1 km long and up to 100 m thick, the bulges being even thicker. The pyrochlore-group minerals and zirconolite are considered as sources of Nb and Ti for forming labuntsovite-like phases, which were observed

only within the zones of low-temperature hydrothermal alterations in carbonatite and phoscorite. These hydrothermally altered rocks are cavernous, and consist of dolomite (60-90%), calcite, siderite, magnesite, chlorite, serpentine, and carbonate-fluorapatite; minor components are barite, sulfides, Ba-, Sr-, and REE-carbonates, as well as quartz and feldspar. Neskevaaraite-Fe was found here in the only holotype drillcore sample as imperfect translucent prismatic brownish crystals up to 6 mm long in hydrothermally altered carbonatite in association with dolomite, calcite, phlogopite, fluorapatite, pyrite, pyrrhotite, chalcopyrite, serpentine, and nenadkevichite. Relicts of pyrochlore occur in the slightly altered host carbonate rock containing calcite, phlogopite, pyroxene, and pyrite as major components.

In Khibiny neskevaaraite-Fe was found in only one sample in the Kirovskii apatite mine at the southern part of the Kukisvumchorr Mt., Khibiny alkaline massif, Kola peninsula, Russia. A.S. Podlesny, a well-known collector, kindly presented this sample to the authors for studies. In this mine the new mineral occurs in cavities within a vain composed of approximately equal parts of medium-grained white calcite and yellowish K-feldspar. Neskevaaraite-Fe forms almost opaque yellowish-brown flattened prismatic crystals up to 1.8 cm long and 1 mm thick in calcite or in open cavities. It forms close intergrowths with labuntsovite-Fe. The latest members of this assemblage are small crystals of donneyite-Y and thin brownish-black solid bitumen coatings. Crystals of neskevaaraite-Fe from Khibiny are usually coarse, plate-shaped and elongated along [010]. However, some vugs carry well-developed crystals with clearly shaped vertices (Fig. 1). The major habit form is the prism formed by longitudinally striated faces  $\{-201\}$ . The additional forms are  $\{100\}$ ,  $\{-101\}$ , and less frequently {001}, {021}. Parallel, probably syntaxial neskevaaraite-Fe - labuntsovite-Fe intergrowths were observed. Labuntsovite-Fe occurs as well-shaped transparent crystals (up to 5 mm long) with glossy faces of bright blood-red color; these are in sharp contrast to the murky yellow-brown striated and flattened crystals of neskevaaraite-Fe. All these intergrowths observed in several vugs are identical and consisting of only two crystals: a face {100} of labuntsovote-Fe crystal is contacted with probably a face {100} of coarse neskevaaraite-Fe crystal.

The new mineral has a white streak and vitreous luster; the Mohs' hardness is about 5. The mineral is brittle, has an uneven fracture and

exhibits no cleavage. The density as measured by the heavy liquid method is 2.88(3) g/cm³; and the value calculated from the X-ray data is 2.90 g/cm³. The mineral is optically biaxial, positive,  $\alpha$  1.677(1),  $\beta$  1.684(2),  $\gamma$  1.790(5),  $2V=25(10)^\circ$ , practically non-pleochroic; optical orientation: Y=b.

The cation composition was studied using electron microprobe analysis (Table 1). The water content was determined by the TGA in vacuum; maximum temperature was 950°C, and the heating rate 40°C/min. The empirical formula of the holotype based on  $[Si_4O_{12}]_2$  (O, OH)<sub>4</sub> at Z=2 is:

 $\begin{array}{l} Na_{1.22}K_{2.29}Ba_{26}(Fe_{.31}Mg_{.23}Mn_{.09})_{\Sigma 0.63}(Ti_{2.31}Nb_{1.65})_{\Sigma 3.96} \\ (Si_{8.00}O_{24})[O_{2.78}(OH)_{1.22}]_{\Sigma 4}\cdot 5.68H_2O. \end{array}$ 

The simplified formula of neskevaaraite-Fe is  $NaK_3Fe(Ti, Nb)_4(Si_4O_{12})_2(O,OH)_4\cdot 6H_2O$ .

Correctness of chemical and optical determinations carried out for neskevaaraite-Fe was confirmed by the Gladstone-Dale criterium values (Mandarino, 1981): 1- $\rm K_p/\rm K_c=0.021$  for  $\rm D_{obs}$ ; 1- $\rm K_p/\rm K_c=0.028$  for  $\rm D_{calc}$ . In the Table 2 the X-ray powder diffraction data for neskevaaraite-Fe are given (the RKG-86 device, the FeK $\alpha$ -radiation). The hkl indices were assigned taking into account  $\rm I_{calc}$  obtained from the structural data.

The crystalline structure of neskevaaraite-Fe was studied for a single crystal from Vuoriyarvi using a 4-circle ENRAF NON-IUS diffractometer. In the course of crystal structure refinement, microtwinning on (001) a n d (-401) was taken into consideration. The observed doubled c parameter of the orthorhombic pseudo-cell indicated the lemmleinite-type twinning with the following matrix of transition to a true monocline cell:  $[100/010/000.5] + \{100/-0.50-0.5]$ . Estimated values of mass coefficients for the two twin components are 0.53 and 0.47.  $R_{\rm aniso} = 0.066$ .

Neskevaaraite-Fe is monoclinic, the space group  $\mathit{Cm}$ . The unit cell parameters are

Table 2. Neskevaarite-Fe from Vuoriyarvi: X-ray powder diffraction data

$I_{obs}$	D <sub>obs'</sub> E	$I_{calc}$	D <sub>calc</sub> , E	hkl
100	6.93	32	6.95	020
		100	6.93	001
20	6.45	28	6.39	200
		36	6.39	20-1
80	4.93	32	4.91	021
	3.52	3	3.60	40-1
10		3 7	3.48	040
10	3.42	7	3.40	221
		3	3.39	22-2
400	0.04	17	3.20	400
100	3.21	64	3.20	42-1
00	2.11	22	3.19	40-2
90	3.11	41 51	3.11 3.10	$041 \\ 022$
		13	2.95	112
30	2.91	19	2.90	420
30	4.31	14	2.90	42-2
		6	2.62	15-1
60	2.62	15	2.59	241
00	2.02	10	2.59	24-2
		7	2.59	202
		11	2.50	44-1
50	2.49	10	2.50	401
		19	2.50	40-3
5	2.14	5	2.13	600
		6	2.13	60-3
5	2.03	5	2.03	441
		8	2.03	44-3
10	1.929	7	1.926	062
		2	1.925	043
10	1 072	8 7 2 3 3	1.876	460
10	1.873	ა ე	1.875 1.872	$\frac{46-2}{42-4}$
10	1.801	10	1.800	80-2
30	1.730	10	1.738	080
30	1.750	5	1.734	004
		13	1.697	44-4
40	1.687	2	1.690	82-1
		$\bar{\overline{2}}$	1.690	82-3
		3	1.685	081
		8	1.558	84-1
20	1.558	3	1.557	820
		7	1.557	84-3
		2	1.526	48-2
10	1.522	2	1.524	423
		2 2 3 8 3 7 2 2 4 5 6 7 4 3	1.523	42-5
40	1 100	5	1.426	481
40	1.422	b 7	1.426	48-3
		<i>t</i>	1.425	443
30	1.297	4	1.297	4.101
30	1.29†	3	1.296 1.294	$\frac{482}{404}$
		ა	1.294	404

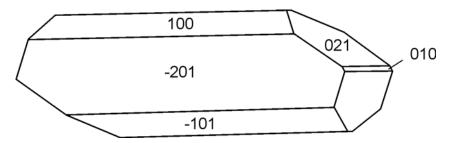


Fig. 1. Neskevaarite-Fe: a crystal from Khibiny

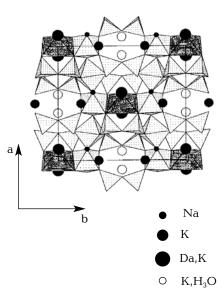


Fig. 2. Neskevaarite-Fe: the crystal structure; Fe octahedra are given in a dark tone, Ti and Nb — in a light tone.

a = 14.450(6), b = 13.910(6), c = 7.836(4) Å; β = 117.42(1)°, V = 1398(2) Å<sup>3</sup>.

Neskevaaraite-Fe is a member of the gutkovaite structural type which, in the labuntsovite group, is characterised by cation ordering in the split A site: A(I) and A(II). In labuntsovite and kuzmenkoite, instead, the A is unique and is occupied by Na and vacant in the two structural types, respectively. The split of the A site into A(I) and A(II) with different occupancy lowers the symmetry from C2/m [labuntsovite structural type, where A(I) and A(II) are related by an inversion centre] to Cm (gutkovaite structural type); that suggested to establish the gutkovaite subgroup within the labuntsovite group (Chukanov et al., 2002).

The framework of the structure of all the labuntsovite minerals is identical to that occurring, for example, in labuntsovite-Mn (Chukanov et al., 1999). It consists of corrugated columns of (Ti,Nb)-octahedra connected by (Si<sub>4</sub>O<sub>12</sub>) rings and additional D octahedra occupied by Mn2+ in gutkovaite-Mn, Zn in alsakharovite-Zn, and Fe in neskevaaraite-Fe. Alkali and alkali-earth cations and water molecules are situated in cavities of this framework. The main difference between the labuntsovite and gutkovaite structural types is represented by the A sites, as said above. The A(1) and A(2)sites located at 1.73 Å from each other and filled statistically with Na or K atoms, respectively. Potassium atoms occupy the positions, which in labuntsovite sensu strictu are filled

with  $\rm H_2O(1)$  molecules; this site, as well as the Sr site in alsakharovite-Zn, is dislocated towards Na. Reduced Na-H<sub>2</sub>O(2) distance (1.97 Å) is due to incomplete occupation of these sites both by cations and anions.

The split B-site in neskevaaraite-Fe is occupied by K+-ions and minor amounts of  $H_3O^+$  distributed between sub-positions; such configuration of the B-position is inherent in alsakharovite-Zn. A weak band at 1717 cm<sup>-1</sup> indicates the presence of  $H_3O^+$  in the neskevaaraite structure.

A crystallochemical formula of neskevaaraite-Fe, as calculated from structural data at Z=1, is:

$$\begin{split} [Na_{2,0}(K_{1,6}Na_{0,4})][K_{2,21,0}(H_3O)_{0,8}][K_{0,7}Ba_{0,5}(H_2O)_{2,2-0,6}]\\ [Fe_{0,7}Mg_{0,4}][Ti_{4,8}Nb_{3,2}(OH)_{5,27}O_{2,73}][Si_4O_{12}]_4 \bullet nH_2O, \end{split}$$

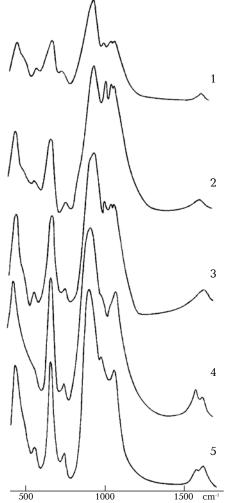


Fig. 3. IR-spectra of the gutkovaite and kuzmenkoite subgroup minerals: 1 — gutkovaite-Mn, 2 — alsakharovite-Zn, 3 — neskevaaraite-Fe, 4 — kuzmenkoite-Mn, 5 — kuzmenkoite-Zn

Table 3. The gutkovaite subgroup minerals: a comparison of crystallochemical characteristics

Mineral	Gutkovaite-Mn	Neskevaaraite-Fe	Alsakharovite-Zn
Simplified formula	$CaK_{2}Mn(Ti,Nb)_{4}$	$NaK_3Fe(Ti,Nb)_4$	$NaSrKZn(Ti,Nb)_4$
	$(Si_{4}O_{12})_{2}(O,OH)_{4}\cdot 5H_{2}O$	$(Si_4O_{12})_2(O,OH)_4\cdot 6H_2O$	$(Si_4O_{12})_2(O,OH)_4 \cdot 7H_2O$
Space group	Cm	Cm	Cm
- α, Å	14.365	14.45	14.49
b, Å	13.89	13.91	13.91
c, Å	7.81	7.84	7.82
β, °	117.4	117.4	117.6
	Prevailing	cations:	
A(1)	Ca	Na	Na
A(2)		K	Sr
B	K	K	K
D	Mn	Fe	Zn
M	Ti	Ti	Ti

where the compositions of the four key groups in the A, B, C, and D-positions are attributed to the first four pairs of brackets.

A partially ordered Ti and Nb distribution between different octahedral sites is a typical feature of neskevaaraite-Fe: in one site Ti prevails, whereas another one is occupied by equal amounts of Ti and Nb.

It is noteworthy that the role of water in the gutkovaite sub-group minerals is different from that in other labuntsovite-group minerals. In labutnsovite, two independent sites of the water molecules occur, of which  $H_2O(1)$  is coordinates the A and B cation sites, whereas  $H_2O(2)$  coordinates only the A site. Both sites of H<sub>2</sub>O can be displaced towards the A site, which is commonly occupied by Na. In tsepinite-Na both H<sub>2</sub>O positions are displaced and occupied by  $H_3O^+$ . In kuzmenkoite  $H_2O(1)$  is preserved, and  $H_2O(2)$  is replaced by  $H_3O^+$ . On the contrary, in gutkovaite-like structures  $H_2O(2)$  is preserved, whereas  $H_2O(1)$  is displaced and may be occupied by cations (e. g., Sr). In addition, in gutkovaite-type structures Ba selectively occupies only one vertices of the D-octahedon when the D site is vacant which is one of the reasons that the symmetry grade is lowered.

Rozenberg *et al.* (2002b) give the details of crystalline pattern of neskevaaraite-Fe. Table 3 presents the characteristics of the gutkovaite group minerals.

The wave numbers of the IR-spectrum bands are (cm<sup>-1</sup>; sh - shoulder, s - strong band): 3530, 3340, 1653, 1083 s, 1059 s 1025 s, 951 s, 930 sh, 770, 686 s, 584, 530 sh, 458. By the IR-spectra, the gutkovaite sub-group members can be distinguished from other labuntsovite group minerals, including members of the kuzmenkoite sub-group (Fig. 3).

As a conclusion we emphasize that the gutkovaite and labuntsovite (sensu strictu) -subgroup members are essentially different. The fact that intergrowth of neskevaaraite-Fe and labuntsovite-Fe was found to occur in Khibiny, suggests that these minerals as separate species consisting of the same chemical elements, but different in structural patterns. The individuality of neskevaaraite-Fe is demonstrated also by the admixture chemistry. Neskevaaraite-Fe is poor in Ba and Mg relative to associating labuntsovite-Fe, but it is rich in Mn and especially in Nb (see items 2 and 3 in Table 1). It is reasonable to assume that Nb stabilizes the neskevaaraite-Fe structure as well as structures of other kuzmenkoite-subgroup minerals.

Type specimen of neskevaaraite-Fe is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, Russia (reg. no. 2814/1).

The authors thank A.S. Podlesny for samples he collected in Khibiny and presented for studies.

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UDC 549.6

# PABSTITE FROM THE DARA-i-PIOZ MORAINE (TADJIKISTAN)

#### Leonid A. Pautov

Fersman Mineralogical Museum of the Russian Academy of Science, Moscow, pla@fmm.ru

Pabstite was discovered in the moraine of the Dara-i-Pioz glacier (Garmsky district, Tadjikistan) in a leucocratic rock mainly composed of microcline, quartz, and albite. Subordinated minerals are aegirine, titanite, astrophyllite, bafertisite, galena, sphalerite, ilmenite, pyrochlore, fluorite, zircon, fluorapatite, and calcite. Pabstite forms grains and well-faced crystals (0.1-0.5 mm), growing on quartz crystals in small cavities abundant in the rock. Its composition is close to the final member BaSnSi<sub>3</sub>O<sub>9</sub> in the series pabstite-benitoite. Microprobe analysis has shown:  $SiO_2 - 37.43$ ;  $TiO_2 - 0.19$ ;  $ZrO_2 - 0.16$ ;  $SnO_2 - 30.05$ ; BaO - 32.41; total 100.24. The empirical formula is  $Ba_{1.02}(Sn_{0.96}Ti_{0.01}Zr_{0.01})_{0.98}Si_{3.01}O_9$ . Refraction parameters of pabstite are  $n_o = 1.668(2)$ ;  $n_e = 1.657(2)$ , which is much lower than cited figures for pabstite from the type locality. Strong dependence of pabstite optical properties on titanium contents is shown. The find of pabstite at Dara-i-Pioze is the first find of pabstite in alkaline rocks and, apparently, the second find of this mineral in the world. 2 tables, 3 figures and 13 references.

Pabstite BaSnSi<sub>3</sub>O<sub>9</sub>, the tin analogue of benitoite, was described as a new mineral from Santa Cruz (California, USA), where it was met in cracks of silicified limestones in association with quartz, calcite, tremolite, witherite, phlogopite, diopside, forsterite, taramellite, cassiterite, franckeite, stannite, sphalerite, and galena (Gross et al., 1965). A separate publication (Dunning, Cooper, 1986) is devoted to the mineralogy of the Santa Cruz Quarry. Pabstite was discovered by the author of this paper in a quite different geological setting - in rocks of the Dara-i-Pioz alkaline complex - at laboratory studying of field collections of 1995, which have been made together with A.A.Agakhanov, V.Yu.Karpenko and P.V.Khvorov. Other references to pabstite finds are absent in the accessible literature. Other samples of pabstite, except for those from California, are also absent in the largest mineralogical collections of our country - the Fersman Mineralogical Museum of the Russian Academy of Science and Vernadsky State Geological Museum of the Russian Academy of Science. Apparently, the Santa Cruz Quarry in California was the unique place of finds of this rare mineral until recently.

#### Occurrence and Mineral Association

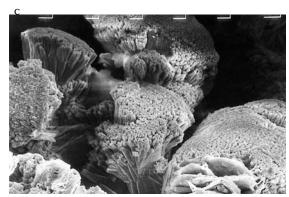
Pabstite was discovered in moraine material of the Dara-i-Pioz glacier located within the Upper Dara-i-Pioz alkaline massif (Garmsky district, Tadjikistan). The massif is located near the water-divide in the southern slope of the Alai Range, has a close to ring structure and is composed of biotite and tourmaline granites,

aegirine syenites and foyaites. The first data on the massif were received at works of Tadjik-Pamirs expedition of 1932 – 1936. The Dara-i-Pioz massif mineralogy is covered in a number of publications (Dusmatov, 1968; Dusmatov, 1971; Dusmatov, 1993; Semenov, 1975; Belakovsky, 1991, etc.). Most typical feature of the Dara-i-Pioz massif is an unusual for alkaline massifs enrichment with boron and lithium (Dusmatov et al., 1972) and «dryness» - absence or scarcity of minerals containing water or hydroxils. Mineralogically, this is manifested in the development of boron analogue of albite - reedmergnerite - and availability of numerous rare boron silicates (leucosphenite, stillwellite-(Ce), tienshanite, tajikite, calcibeborosilite-(Y), hyalotekite, etc.), wide distribution of lithium minerals (polylithionite, tainiolite, sogdianite, sugilite, neptunite, etc.). Other elements typical to Dara-i-Pioz and forming own minerals include rare earth elements and yttrium (stillwellite-(Ce), minerals of the tajikite group, kapitsaite-(Y), nordite-(Ce), monazite-(Ce), etc.), beryllium (leucophanite, epididymite, barylite, calcibeborosilite-(Y), hyalotekite, moskvinite, etc.), zirconium (sogdianite, zektzerite, bazirite, zircon, minerals of the eudialite group, etc.), niobium and tantalum (minerals of the pyrochlore group, baotite), thorium and uranium (thorite, turkestanite, uraninite), cesium (cesium-kupletskite, telyushenkoite) and tin [though only one tin mineral was met till now - this is pabstite, increased tin contents were earlier reported in titanite (Reguir et al., 1998; Reguir et al., 1999) and sogdianite (Pautov et al., 2000) from this massif].

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From the crystallochemical point of view, a remarkable feature of the Dara-i-Pioz massif is large presence and variety of ring silicates. Minerals of the eudialite group with nine-member rings of oxygen-silica tetrahedrons occur in microcline-reedmergnerite pegmatites and in verv original quartz-titanite-aegirine vein rocks. Silicates with six-member rings are represented by minerals of the tourmaline group; the axinite structural type is represented by ferroaxinite, extremely rare at Dara-i-Pioz. Silicates with dual six-member silica-oxygen rings of the milarite group are most various, many of them were first described from this massif - these are first of all sogdianite, which is a rock-forming mineral in some veined rocks, sugilite, darapiozite, dusmatovite, shibkovite, berezanskite. A representative of minerals with four-member silica-oxygen rings at Dara-i-Pioz is baotite, a silicate with dual four-member rings is turkestanite. The benitoite structural type (silicates with three-member silica-oxygen rings) is represented by bazirite and now has supplemented by pabstite. At last, quite recently a mineral with dual three-member rings (a new structural type) was discovered at Dara-i-Pioz - moskvinite.

Pabstite was discovered in medium-coarse grained inequigranular leucocratic rock, mainly composed of microcline, quartz, and albite. Subordinated minerals are aegirine, titanite, astrophyllite and bafertisite forming separate accumulations and lenses, that gives rock spotty, here and there banded texture. Accessory minerals are galena, sphalerite, ilmenite, pyrochlore, fluorite, zircon, fluorapatite, and calcite. The rock bears traces of plastic and fragile deformations expressed in bending of scaly astrophyllite and bafertisite grains, broken grains of microcline, lamellar calcite twins. Small (0.3-1 cm) cavities, encrusted with long-columnar transparent and colorless quartz crystals (1 to 5 mm long) with growing on them white spherical aggregates and short prismatic crystals of zircon and rarely single well formed fine crystals of pabstite, are rather abundant in the rock (Fig. 1). Pabstite as irregular grains also occurs and in albite-titanite-quartz-zircon aggregates (Fig. 2), disposed in immediately proximity to above cavities.

Fig. 1 a – fragment of pabstite crystal aggregate. In the upper part of image one can see a zircon crystal, x300; b – short prismatic pabstite crystal on quartz, x500; c, d – aggregates of split crystals of zircon from a cavity with pabstite, c-x200, d-x1000. REM-photos

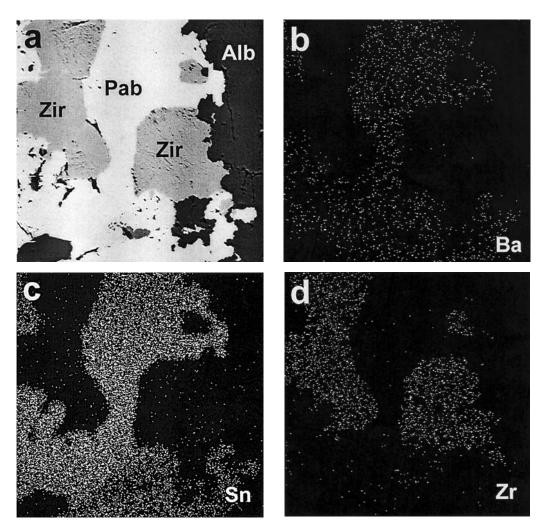


Fig. 2. An intergrowth of pabsite (Pab) with zircon (Zir) and albite (Alb.) a-COMPO regime; b, c, d-characteristic X-ray radiation of specified elements. Width of the field of vision is <math>600 microns.

#### **Physical Properties** and Optical Characteristics

Pabstite grains have white color and slightly greasy luster. Cleavage is absent. Mohs hardness is about 6. Crystals of pabstite (0.1 -0.5 mm) are colorless and transparent, their morphology is well visible in Fig. 1. In short-wave UV light, the mineral shows weak bluish fluorescence. Pabstite is optically uniaxial, negative. The refraction parameters measured on rotating needle are  $n_o$  = 1.668(2);  $n_e = 1.657(2)$ , that is much below the values for pabstite from the type locality. Refraction parameters of pabstite from California on the data of Gross et al., 1965 are

 $n_o = 1.685$ ;  $n_e = 1.674$ . Such essential distinctions in optical characteristics are explained by features of chemical composition of the mineral: pabstite from Santa Cruz considerably more enriched with titanium (TiO $_2$  – 3.8 wt.%) than mineral from Dara-i-Pioz (TiO $_2$  — 0.08 – 0.42 wt. %) and this has caused its higher refraction parameters. Empirical dependence of refraction parameters on composition in the series pabstite-benitoite is shown in Fig. 3. The deviation from the direct dependence in the field near the final member  $BaSnSi_3O_9$  is probably caused by the contribution of small admixture of zirconium into the increase of refraction parameters of pabstite from Dara-i-Pioz.

Table 1. X-ray powder pattern data for pabstite

Pabstite,	Dara-i-Pioz	Synthetic pabs	stite, JCPDS	43-0633
d	I	d	I	hkl
5.81	60	5.83	37	100
4.93	33	4.923	12	002
3.76	100	3.7625	95	102
3.36	90	3.3672	30	110
3.21	10	3.1842	9	111
2.92	28	2.9156	17	200
2.78	53	2.7793	100	112
2.52	5	2.5093	5	202
2.46	20	2.4633	10	004
2.34	3	2.3511	1	113
2.27	2	2.2692	2	104
2.21	2 5 3	2.2043	12	210
2.153	3	2.1509	4	211
		2.0117	6	212
1.983	11	1.9880	23	114
		1.9439	14	300
1.887	6	1.8818	13	204
		1.8302	1	213
1.810	8	1.8082	17	302
		1.6832	5	220
1.647	8	1.6421	12	006
1.614	2	1.6172	2	310
1.595	4	1.5928	10	222
		1.5804	4	106
1.541	3	1.5366	8	312
		1.5259	8	304
1.476	5	1.4758	10	116

Table 2. Chemical composition of pabstite

Oxide	Dara-i-Pioz, Tadjikistan 1	Santa Cruz, California 2	Theoretical composition 3
$SiO_2$	37.43	37.7	37.22
$TiO_2$	0.19	3.8	
$ZrO_2$	0.16	—	
SnO <sub>2</sub>	30.05	24.4	31.12
BaO	32.41	33.2	31.66
Total	100.24	99.1	100.00

Note: 1 — mean of 3 microprobe analyses. Analyst — L.A. Pautov. The empirical formula at calculation for 9 oxygen atoms is  $Ba_{1,02}(Sn_{0,96}Ti_{0,01}Zr_{0,01})o_{,99}Si_{3,01}O_{,97}$  2 — microprobe analysis.  $Ba_{1,03}(Sn_{0,77}Ti_{0,23})_{1,09}Si_{2,99}O_{,9}$  (Gross et al., 1965); 3 —  $BaSnSi_3O_{,9}$ 

## X-ray Data

The pabstite from Dara-i-Pioz was studied by the powder X-ray method on diffractometer DRON-2. Fe-radiation and graphite monochromator were used. Scanning speed of the counter was 1 degree/minute. Quality of received powder pattern could be considered satisfactory, which is caused by small quantity of mineral. Results of X-ray powder pattern calculation in Table 1 show affinity of the investigated mineral to BaSnSi $_3O_9$ . It should be noted that the mineral is inconvenient for pho-

tographic study because of strong fluorescence under X-rays.

#### **Chemical Composition**

The Dara-i-Pioz pabstite chemical composition was studied using X-ray microanalyzer JCXA-50A equipped with energy dispersion spectrometer Link-U and three wave spectrometers. The quantitative analysis was carried out using wave spectrometers at accelerating voltage U = 20 kV, probe current 20 nA and beam diameter 2 microns. Reference samples were benitoite USNM 86539 for Ba, Ti, Si; synthetic  $SnO_2$  – for Sn; synthetic  $ZrO_2$  – on Zr. Calculation of concentrations was made using the ZAF-correction method in the «PUMA» program. Table 2 gives the results of analyses. As noted above, the pabstite from Dara-i-Pioz is closer to the final member BaSnSi<sub>3</sub>O<sub>9</sub> than the mineral from the first description place. In addition, an insignificant admixture of zirconium is characteristic of the described pabstite.

#### Conclusions

Pabstite was discovered in a quite different geological setting, than at the reference site. It is the first find of pabstite in alkaline rocks and probably the second find of this mineral in the world. Pabstite is the first actually tin mineral at Dara-i-Pioz.

The Dara-i-Pioz pabstite has the composition close to final member  $BaSnSi_{3}O_{9}$  in the

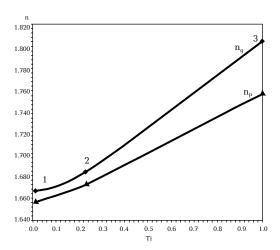


Fig. 3. Dependence of refraction parameters in pabstite-benitoite series on composition (Ti). 1 — pabstite from Dara-i-Pioz, 2 — pabstite from Santa Cruz (Gross et al., 1965); 3 — BaTiSi $_3$ O $_9$ .

series pabstite-benitoite. The zirconium admixture in Dara-i-Pioz pabstite probably indicates the existence of isomorph system pabstite-benitoite-bazirite.

A strong dependence of pabstite optical properties on the titanium content is shown, the fact to be considered at optical diagnostics of the mineral (pabstite refraction parameters cited in the majority of mineralogical directories refer to the mineral from California and are much higher, than refraction parameters of low-titanium pabstite).

The data on hydrothermal synthesis of  $BaSnSi_3O_9$  and  $CaSnSi_3O_9$  (Gross *et al.*, 1965; Nekrasov, 1973; Nekrasov, 1976) and mineral associations allow to assume that pabstite crystallization at Dara-i-Pioze occurred at final phases of albitization from alkaline solutions rich in silica and relatively poor in tin at temperature above 300°C. A probable source of  $Sn^{4+}$  is tin liberated from Sn-containing sogdianite at its replacement in the phase of its albitization by zektzerite.

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# RARE-METAL «ZEOLITES» OF THE HILAIRITE GROUP

Igor V. Pekov

Lomosov Moscow State University, Moscow, igorpekov@mtu-net.ru

#### Nikita V. Chukanov

Institute of Chemical Physics Problems of the RAS, Moscow Oblast, Chernogolovka, chukanov@icp.ac.ru

#### Natalia N. Kononkova

Institute of Geochemistry and Analytical Chemistry of RAS, Moscow

#### Dmitrii Yu. Pushcharovsky

Lomosov Moscow State University, Moscow

The hilairite group includes hilairite, calciohilairite, komkovite, sazykinaite-(Y) and pyatenkoite-(Y). Their unique structural type is based on a mixed framework of screwed chains  $(Si_3O_9)$  and isolated M-octahedra (M=Zr,Ti,Y+Ln); large cations (Na,Ca,Ba,andsubordinatedK,Sr) and water molecules settle down in extensive zeolite-like cages and channels. Some features of chemical composition and properties of hilairite-group minerals are easily explained if to consider them as specific rare-metal «zeolites». Hilairite-group minerals occur in hydrothermalites of the Khibiny-Lovozero alkaline complex, Kola Peninsula. This paper gives a review of publications on the hilairite group, describes new finds in Khibiny and Lovozero massifs, gives 29 chemical analyses of these minerals, including 17 analyses made by the authors. The isomorphous series hilairite — calciohilairite was established in material from Lovozero, as well as Ba-K- and Sr-containing varieties of calciohilairite. The first finds of hilairite and pyatenkoite-(Y) in Khibiny are described. The comparative analysis of IR spectra of all group members is given for the first time. Crystal chemistry, properties and genesis of hilairite-like minerals are discussed in view of their zeolite-like structure

4 tables, 2 figures and 27 references.

### Introduction

Hilairite crystallochemical group unites five minerals — trigonal (rhombohedral — R32) rare-metal silicates with a unique structural motive: hilairite, calciohilairite, komkovite, sazykinaite-(Y) and pyatenkoite-(Y) (Table 1). Infinite screwed chains (Si<sub>3</sub>O<sub>9</sub>) extended along the main axis make the basis of their structure. Si-tetrahedra are jointed by pendent apices with M-octahedra, forming a mixed framework  $\{M(Si_3O_9)\}$ , where dominant M-cations in different cases are Zr, Ti, and (Y + Ln). A step of  $(Si_3O_9)$  chain along the axis c is three Si-tetrahedra; M-octahedra, each of which is connected to three silica-oxygen chains, repeat with the same period. The structure contains channels. large cages and extra-framework alkaline and alkaline-earth cations (Na, Ca, Ba, and subordinated K and Sr) and water molecules settle down. The structure of hilairite-group minerals includes two nonequivalent octahedric positions of M. In hilairite, calciohilairite and komkovite, Zr sharply prevails in both M-positions, in sazykinaite-(Y) one of them (M1) is selectively occupied with atoms of

Y or Ln (with corresponding increase of M-O distance), whereas the second (M2) remains occupied by zirconium; pyaten-koite-(Y) is an isostructural analogue of sazy-kinaite-(Y), where Zr is replaced by Ti (Ilyushin et al., 1981; Sokolova et al., 1991; Rastsvetaeva and Khomyakov, 1992, 1996; Pushcharovsky et al., 2002).

Hilairite-group minerals are rather rare minerals of hydrothermal rocks related to diverse alkaline complexes: nepheline syenite, alkaline granite, and carbonatite. Despite of being rare, these minerals are very interesting in crystallochemical and genetic relation due to the original structural motif, wide variability of composition at preservation of the motif, unusual type of cation ordering (rare-earth members of the group) and a number of other specific features, which are easy to explain if to consider hilairite-like phases in view of their strongly pronounced zeolite-like structure.

The greatest variety of hilairite-group representatives is observed in hydrothermal rocks of the well-known Khibiny-Lovozero alkaline complex on the Kola Peninsula. All members of

the group, except for komkovite, are present here, the number of their finds comes to a dozen; in some cases these minerals are the main concentrators of zirconium, yttrium and heavy lantanides in late paragenesis. This paper is devoted to the description of hilairite-group minerals from new occurrences in Lovozero and Khibiny massifs, and also to the discussion of some interesting mineralogical and crystallochemical features of the entire group.

#### Occurrence

Hilairite Na<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O is the most widespread member of the group. It was discovered by G.Chao at al. (1974) in hydrothermal rocks related to nepheline syenites and alkali-rich pegmatites of agpaitic Mont Saint-Hilaire complex in Quebec, Canada. It associates here with gaidonnayite, elpidite, natrolite, microcline, analcite, albite, aegirine, rutile, zircon, fluorite, calcite, sulfides (Chao et al., 1974; Horvath and Gault, 1990; Horvath and Pfenninger-Horvath, 2000). Hilairite, in association with aegirine, natrolite, serandite, sphalerite, cordylite and zakharovite, also occurs in miarolitic cages of agpaitic nepheline syenite, which makes part

of the nearby Saint Amable sill (Horvath et al., 1998). This mineral in late pegmatite paragenesis is related to alkaline and nepheline syenites of Southern Norway: with pyrophanite, astrophyllite, catapleiite, analcite, boehmite, etc. in Bratthagen near Larvik and in Langesundsfjord - on islands Siktesце (with albite, gaidonnayite, zircon) and Vesle Arце (with aegirine and zircon) (Raade, Mladeck, 1977; Raade et al., 1980; Andersen et al., 1996). Hilairite in Vuoriyarvi alkaline-ultrabasic complex in Northern Karelia was described in cavities in dolomite carbonatites in association with carbonate-apatite and pyrite (Voloshin et al., 1989). Hilairite enriched with calcium settles between grains of albite, potassic feldspar, quartz, aenigmatite, and narsarsukite in alkaline granite of the southern part of Strange Lake complex (Quebec-Labrador, Canada). However, the data on chemistry of the mineral are absent because of small quantity of substance (Birkett et al., 1992). Hilairite was also found in alkaline complex Po3os de Caldas in Brazil (Horvath et al., 1998). In the majority of listed cases, this mineral occurs in cavities, where forms light (colorless, white, pink, cream, light brown) subisometric crystals up to 4 mm with faces  $\{11-20\}$  and  $\{01-12\}$ , sometimes also {-1-120} (class of symmetry

 ${\it Table~1.}\ {\bf Comparative~characteristics~of~hilairite-group~minerals}$ 

Mineral	Hilairite	Calciohilairite	Komkovite	Sazykinaite-(Y)	Pyatenkoite-(Y)
Idealized formula	Na <sub>2</sub> ZrSi <sub>3</sub> O <sub>9</sub> • 3H <sub>2</sub> O	CaZrSi <sub>3</sub> O <sub>9</sub> • 3H <sub>2</sub> O	BaZrSi <sub>3</sub> O <sub>9</sub> • 3H <sub>2</sub> O	Na <sub>5</sub> YZrS <sub>i6</sub> O <sub>18</sub> • 6H <sub>2</sub> O	Na <sub>5</sub> YTiSi <sub>6</sub> O <sub>18</sub> • 6H <sub>2</sub> O
Symmetry	Trigonal,	Trigonal,	Trigonal,	Trigonal,	Trigonal,
	<i>R</i> 32	<i>R</i> 32	<i>R</i> 32	R32	<i>R</i> 32
Unit cell para	meters				
a, Å	10.556	10.498	10.52	10.825	10.696
c, Å	15.855	7.975	15.72	15.809	15.728
V, Å <sup>3</sup>	1532	761	1507	1604	1558
Z	6	3	6	3	3
Framework d (number of fra atoms in 1000	amework 15.7	15.8	15.9	15.0	15.4
Refractive inc	lices				
$n_e$ $n_o$	1.596	1.619	1.644	1.578	1.607
	1.609	1.622	1.671	1.585	1.612
D <sub>meas</sub> ., g/cm <sup>3</sup>	2.72	2.68	3.31	2.67	2.68
D <sub>calc</sub> ., g/cm <sup>3</sup>	2.74	2.74	3.31	2.74	2.70
References	Chao <i>et al.,</i>	Boggs,	Voloshin <i>et al.</i> ,	Khomyakov <i>et al.,</i>	Khomyakov <i>et al.</i> ,
	1974;	1988;	1990;	1993;	1996;
	Ilyushin <i>et al.,</i>	Pushcharovsky <i>et al</i>	., Sokolova <i>et al.</i> ,	Rastsvetaeva and	Rastsvetaeva and
	1981	2002	1991	Khomyakov,1992	Khomyakov,1996

32), frequently twinned. Fine-grained masses are also present.

In the territory of the USSR, hilairite for the first time was described by A.P.Khomyakov and N.M.Chernitsova (1980) on the material of three finds in the Lovozero massif. In samples from underground workings in the Alluaiv Mountain, hilairite has been met as yellowish and brownish transparent rhombohedral crystals 0.5-1 mm in size, closely associating with neighborite in small cavities of pegmatoid ultra-alkaline rocks, which veined and streaky bodies occur in poikilitic cancrisilite-sodalite-nepheline syenite. Major minerals in these rocks are potassic feldspar, nepheline, sodalite, cancrisilite, aegirine, alkaline amphibole; typical minor and accessory minerals are analcite, natrolite, ussingite, lorenzenite, lamprophyllite, eudialyte, parakeldyshite, apatite, ilmenite, gaidonnayite, steenstrupine, loparite, sulfides, etc. This paragenesis includes villiaumite, kogarkoite, sidorenkite, thermonatrite. Hilairite in another association was found in borehole core from the same Alluaiv Mountain: here its pink crystals up to 1 mm occur on walls of cavities in albite rock associating with elpidite, siderite and hisingerite-like phase. At last, in a sheet-like pegmatite on the Karnasurt Mountain, hilairite was found as pink opal-like grains up to 1 cm in dense fine-grained albite rock with serandite and sphalerite. In all three cases the mineral is determined

X-ray powder patterns and by optical properties (Khomyakov and Chernitsova, 1980), the chemical composition was not studied. G.D.Ilyushin *et al.* (1981) studied the crystal structure of hilairite in a single crystal from the Alluaiv Mountain for the first time and described its structural type, which has appeared to be a new one.

We have discovered hilairite in the Khibiny massif, where it was not known before. Known collector A.S.Podlesnyi collected samples with hilairite in an underground working of the Kirovskiy apatite mine (level +252 m) in the Kukisvumchorr Mountain. The pegmatite where it was found out has received the name of «Hilairitovoye» after the find of fine specimens with hilairite. This is a lens more than 10 m in the extent and more than 1 m thick in ijolite-urtite the with near contact apatite-nepheline rock. We have determined 50 (!) mineral kinds, including more than 20 rare-metal minerals, from the « Hilairitovoye» body. The main components of pegmatite are microcline, nepheline, and aegirine; titanite,

pectolite, natrolite, eudialyte, rinkite, astrophyllite, apatite, fluorite, dawsonite, and sulfides are abundant. The richest hydrothermal mineralization is developed in small cavities in «pillows» of microcline. Walls of these cavities are covered with crystals of albite, calcite, quartz, ankerite, apatite and associated various rare-metal minerals - alkaline silicates of zirconium (hilairite, elpidite, catapleiite, gaidonnayite), beryllium (epididymite, eudidymite), niobium and titanium (nenadkevichite, vuoriyarvite-K, tsepinite-K, labuntsovite-Mg), carbonates of strontium, barium and rare-earth elements (strontianite, donmckelviyte-(Y), navite-(Y). ancylite-(Ce). synchysite-(Ce), kukharenkoite-(La), carbocernaite, burbankite). Anatase, barite, gobbinsite, celadonite, muscovite, hisingerite, thorite, hematite, etc. are also discovered here in late associations. Hilairite forms fine crystals up to 6 mm in the greatest dimension and have been made out by faces of rhombohedron {01-12} and trigonal prisms {11-20} and {-1-120}. The ratio of areas of these faces defines the habit and shape of crystals: most frequently there are isometric pseudo-rhombic dodecahedric individuals, sometimes extended along axis c, and rare rhombohedra almost without prism faces (Fig. 1b-e). Faces of hilairite crystals are usually smooth, brilliant, less often covered with complex figures of growth. Crystals are opaque, saturated with microinclusions, giving them different shades of brown color, from dark-chocolate to light-coffee. Clusters of hilairite crystals are frequent here, they even form brushes.

One more find of hilairite we made in the Lovozero massif. This mineral, represented by a high-calcium variety, composes core of some crystals of calciohilairite in cavities of albitized porphyraceous lujavrites on the Flora Mountain (Pekov, 2000). This occurrence is characterized in more detail below.

Calciohilairite CaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O was described as a new mineral from miarolitic cavities in boulders of alkaline granites of the Golden Horn batholith on the slope of Liberty Bell Mountain in the northern part of Cascade Range, Washington, USA. It was discovered as white and bluish crystals (up to 2 mm), formed by faces {11-20}, {-1-120} and {01-12} in association with microcline, quartz, albite, chlorite, fluorite, bastnaesite, zircon, malachite (Boggs, 1988). Calciohilairite was found in the latest paragenesis in cavities of nepheline syenite in Saint Amable as several beige and white prismatic-rhombohedral crystals 0.5 - 0.9 mm in size. In one case it grows on natrolite together with nenadkevichite, rhodochrosite, polylithionite, fluorite, aegirine and pyrite, in another it associates with astrophyllite, aegirine, eudialyte, microcline, manganneptunite, natrolite and birnessite pseudomorphs after serandite. The composition of mineral from Saint Amable, in the data of electron microprobe sounding is: (Ca\_{0.99}K\_{0.01})\_{\Sigma\_{1.00}}(Zr\_{0.96}Ti\_{0.02}Mn\_{0.01})\_{\Sigma\_{0.99}}(Si\_{3.00}Al\_{0.01})\_{\Sigma\_{3.01}}O\_{8.98}^{-3}3H\_2O (Horvath et~al.,~1998). At Mont Saint-Hilaire, calciohilairite was noted as aggregates to 1 mm in association with quartz in cavities in alkaline hornfels (Horvath and Pfenninger-Horvath, 2000).

The fourth in the world and the first in Russia find of calciohilairite was made by one of authors on the Flora Mountain in the northern endocontact of the Lovozero massif (Pekov, 2000). This is probably richest of all known occurrences of this mineral; calciohilairite here is the main Zr concentrator in hydrothermal rocks. It gives isometric, frequently split crystals to 0.5 mm formed by faces of rhombohedron {01-12} and prisms {11-20} and {-1-120} (Fig. 1c). Aggregates of split individuals, sometimes spherical, up to 1 mm in diameter, are usual here. Fresh crystals are transparent, of light brown (coffee) color. The altered varieties are turbid to completely opaque, milky-white or have color of ivory. Calciohilairite grows on walls of cavities in albitized porphyraceous murmanite-eudialyte and lorenzenite-eudialyte lujavrites near the contact with a pegmatite vein. It associates with aegirine, natrolite, lorenzenite, epididymite, carbonate-fluorapatite, pyrite, and especially close with minerals of labuntsovite-group: kuzmenkoite-Mn, labuntsovite-Mn, organovaite-Mn, vuoriyarvite-K. Core of some calciohilairite crystals correspond by composition high-calcium or high-potassium varieties of hilairite.

Other variety of enriched with barium calciohilairite is found in cavities in a hydrothermally altered zone of a large pegmatite in the Lepkhe-Nel'm Mountain in the same Lovozero massif. This body has an irregular form and occurs in feldspathoid poikilitic syenite. Marginal parts of pegmatite are mainly composed of potassic feldspar, aegirine, nepheline, eudialyte, magnesio-arfvedsonite, lamprophyllite, lorenzenite; the core has experienced an intensive hydrothermal alteration and contains, in addition to relics of the listed minerals, abundant halloysite and natrolite. Once abundant mineral of pectolite-serandite series is totally replaced with water oxides of Mn. Hydrothermal mineralization is also intensive in the intermediate zone of pegmatite, where fluorapatite, carbonate-apatite, tainiolite, polylithionite, neptunite, catapleiite, kupletskite, barytolamprophyllite, tundrite-(Ce), vinogradovite, Nb-titanite, minerals of labuntsovite group (tsepinite-Na, tsepinite-K, paratsepinite-Ba, kuzmenkoite-Zn, alsakharovite-Zn), harmotome, and Ba-containing calciohilairite develop in cavities. The last forms single translucent white rhombohedral crystals (Fig. 1a) to 0.5 mm together with natrolite growing on microcline, aegirine, and lorenzenite.

**Komkovite** BaZrSi $_3$ O $_9$ ·3H $_2$ O is only known in carbonatites of the Vuoriyarvi alkaline-ultrabasic massif in the Northern Karelia. It was described from the borehole core, in dolomite streaks cross-cutting metasomatically altered pyroxenite. Its brown rhombohedral crystals to 5 mm grow on dolomite in cavities of streaks together with phlogopite, strontianite, barite, georgechaoite, and pyrite (Voloshin *et al.*, 1990).

Sazykinaite-(Y) Na<sub>5</sub>(Y,HREE)ZrSi<sub>6</sub>O<sub>18</sub>·3H<sub>2</sub>O was discovered in hydrothermally altered ultra alkaline pegmatite, occurring on urtite/apatite-nepheline contact in the Koashva Mountain in the Khibiny massif. It forms yellowish-greenish rhombohedra up to 2 mm across, formed by faces {01-12}, closely associating with lemmleinite-K in cavities in essentially aegirinic zone of pegmatite containing also natrolite, potassic feldspar, pectolite, alkaline amphibole, lomonosovite, sphalerite, etc. (Khomyakov et al., 1993).

Recently sazykinaite-(Y) was also found in Saint-Hilaire, in cavities in essentially sodalite hyper alkaline rock as crystals formed by faces of rhombohedron {01-12} with a narrow band of prism {11-20}, in association with ussingite, serandite, mangan-neptunite, lintisite, erdite and vuonnemite (Horvath, Pfenninger-Horvath, 2000).

One of authors (I.V.P.) has found that sazykinaite-(Y) is rather common in the pegmatitic complex of the Koashva Mountain in Khibiny, formed by a series of morphologically and structurally similar bodies located strictly on the contact of urtite with a large deposit of apatite-nepheline rock. In addition to pegmatite, in which sazykinaite-(Y) was described for the first time by A.P.Khomyakov et al. (1993), this mineral was found in three bodies where it is not only the unique phase of Y and HREE, but also one of basic carriers of Zr in hydrothermal paragenesis (Pekov, 1998). Sazykinaite-(Y) only occur in cavities and most frequently - in dissolution hollows in eudialyte as doubtless source of Zr, Y, and HREE.

Rhombohedral crystals of sazykinaite-(Y) (Fig. 1a) usually do not exceed 1-2 mm, but occasionally up to 5-6 mm. They are very frequently split, have a blocky-mosaic structure. Other simple forms, except for {01-12}, were not revealed in the materal from Khibiny. It has light yellow, pale-brown or greenish color, sometimes almost colorless, and transparent. Sometimes sazykinaite-(Y) associates with other alkaline Zr-silicates - catapleiite, umbite, kostylevite, wadeite - but almost never in direct contact with them. Sazykinaite-(Y) associates with aegirine, natrolite, microcline, pectolite, lamprophyllite, magnesiumastrophyllite, sphalerite, sometimes lemmleinite-K, sitinakite, nacaphite, sodalite, lomonosovite, etc. Its association with minerals of light lantanides, practically deprived of Y and HREE (vitusite-(Ce), belovite-(Ce), petersenite-(Ce), remondite-(La), rinkite, potassic rhabdophane-(Ce), etc is characteristic. In some pegmatites it is possible to see sazykinaite-(Y) in the neighbourhood with «salt» minerals - villiaumite, Na-carbonates, soda-phosphate, in others they are completely leached.

**Pyatenkoite-(Y)**  $\rm Na_5(Y,HREE)TiSi_6O_{18}{}^{\circ}3H_2O$ , a titanium analogue of sazykinaite-(Y), was described as a new mineral from hydrothermal rocks of the Alluaiv Mountain in the Lovozero massif. Its colorless rhombohedral crystals formed by faces  $\{01\text{-}12\}$  and up to 0.5 mm, grow on walls of cavities and cracks in lomonosovite, associating with albite, natrolite, gonnardite, aegirine, neptunite and fluorite (Khomyakov *et al.*, 1996). No other finds of this mineral are known till now.

We have discovered pyatenkoite-(Y) in the Kukisvumchorr Mountain in the Khibiny massif. It is determined in sample #447 from A.S.Podlesny collection. This sample is a fragment of prospecting well core, drilled in an underground working at level +252 m in the

Kirovskii mine. Pyatenkoite-(Y) forms light gray with greasy luster translucent crystals up to 1.5 mm, quite often split, made out by rhombohedron faces {01-12}, with a band of prism faces {11-20} and {-1-120} (Fig. 1b). These crystals and their aggregates on walls of cavities occur in the axial zone of a pegmatite streak composed of white to colorless microcline with small amount of black needle-like aegirine. To walls, the streak is enriched with aegirine; nepheline and rinkite appear in it. In cavities, film and spheroidal grains of brown and black solid bitumen are observed together with pyatenkoite-(Y).

#### **Chemical Composition**

The chemical (cation) composition of minerals (Tables 2 and 3) was determined by electron microprobe using the Camebax SX 50 instrument at the Department of Mineralogy of the Lomonosov Moscow State University. In order to prevent destruction of samples, the analysis was carried out by a rastered beam from an area of  $10 \times 10$  microns at accelerating voltage 15 kV and beam current 20 nA. The standards were: albite (Na), orthoclase (K, Al, Si), andradite (Ca, Fe),  $\text{SrSO}_4$  (Sr),  $\text{BaSO}_4$  (Ba), amphibole (Mg),  $\text{MnTiO}_3$  (Mn, Ti), ZnO (Zn), phosphates of individual REE like (REE)PO $_4$  (REE = Y and lantanides),  $\text{ThO}_2$  (Th), Zr (Zr), Hf (Hf), Nb (Nb).

The basic features of composition of investigated minerals are given below.

Ratio  $Si/\Sigma M\approx 3$  was observed in all samples, which, undoubtedly, is related to precisely separated «building» functions of the cations forming a mixed framework.

Among M-cations, Zr dominates in hilairite, calciohilairite and sazykinaite-(Y), while Hf, Ti and Nb are only a small admixtures, down to

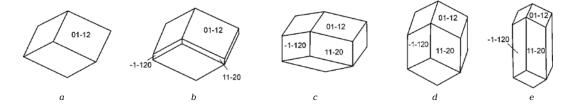


Fig. 1. Crystals of hilairite-group minerals from the Khibiny, Lovozero alkaline complex, Kola Peninsula

- a sazykinaite-(Y) from the Koashva Mountain, Khibiny, pyatenkoite-(Y) from the Alluaiv Mountain, Lovozero, and calciohilairite from the Lepkhe Nel'm Mountain, Lovozero;
- b pyatenkoite-(Y) from the Kukisvumchorr Mountain, Khibiny;
- c calciohilairite from the Flora Mountain, Lovozero;
- $d\!-\!e-$  hilairite from the Kukisvumchorr Mountain, Khibiny

Table 2. Chemical composition of hilairite, calciohilairite and komkovite

	1	2	3	4	5	6	7	8	9	10	11
wt. %											
Na <sub>2</sub> O	14.77	_	_	13.43	14.32	0.20	0.22	0.24	0.13	0.20	0.00
$K_2O$	_	_	_	0.52	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	0.13
CaO	_	13.56	_	0.20	n.c.	11.25	10.74	10.70	11.62	11.41	0.08
BaO	_	_	30.02	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	28.19
CuO	_	_	_	n.c.	n.c.	0.19	0.77	1.12	0.42	0.74	n.c.
FeO	_	_	_	0.03	n.c.	0.03	0.70	0.03	0.12	0.09	0.33
$Al_2O_3$	_	_	_	0.03	n.c.	2.61	2.59	1.06	0.05	0.28	n.c.
SiO <sub>2</sub>	42.97	43.58	35.28	42.08	44.12	38.81	39.03	39.74	41.16	41.37	34.44
TiO <sub>2</sub>	_	_	_	0.04	0.00	0.09	0.09	0.04	0.04	0.02	0.00
$ZrO_2$	29.37	29.79	24.12	29.72	30.43	31.64	32.37	33.37	33.58	32.02	24.94
HfO <sub>2</sub>	_	_	_	n.c.	0.21	n.c.	n.c.	n.c.	n.c.	n.c.	0.46
H <sub>2</sub> O	12.89	13.07	10.58	13.54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.70
Total	100.00	100.00	100.00	99.62	89.08	84.82	86.51	86.32	87.12	86.13	99.27
			Forn	nula units	, calculat	ion for 9 o	oxygen at	oms			
Na	2.00	_	_	1.85	1.89	0.03	0.03	0.03	0.02	0.03	_
K	_	_	_	0.05	_	_	_	_	_	_	0.01
Ca	_	1.00	_	0.02	_	0.86	0.81	0.82	0.87	0.86	0.01
Ba	_	_	1.00	_	_	_	_	_	_	_	0.95
Cu	_	_	_	_	_	0.01	0.04	0.06	0.02	0.04	_
Fe		_	_	_	_	_	0.04	_	0.01	0.01	0.02
efc	2.00	1.00	1.00	1.92	1.89	0.90	0.92	0.91	0.92	0.94	0.99
Al	_	_	_	_	_	0.22	0.22	0.09	_	0.02	_
Si	3.00	3.00	3.00	2.99	3.01	2.78	2.76	2.83	2.89	2.92	2.95
Zr	1.00	1.00	1.00	1.03	1.01	1.11	1.12	1.16	1.15	1.10	1.04
Hf	_	_	_	_	_	_	_	_	_	_	0.01
$H_2O$	3.00	3.00	3.00	3.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.08

- Notes:

  1 calculated composition of Na<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  2 calculated composition of CaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  3 calculated composition of BaZrSi<sub>3</sub>O<sub>3</sub>·3H<sub>2</sub>O;
  4 hilairite: Mont Saint-Hilaire, Quebec (Chao et al., 1974),
   the total also includes (wt. %): MgO 0.01, MnO 0.02;

  5 hilairite: Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  11 komkovite, Vuoriyarvi (Voloshin et al., 1990).
  2 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  3 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  4 hilairite: Odden Horn, Washington (Boggs, 1988);
  11 komkovite, Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  12 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  13 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  14 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  15 hilairite: Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  16 total of extra-framework cations;
  17 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  18 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  19 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  10 calciohilairite: Golden Horn, Washington (Boggs, 1988);
  11 komkovite, Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  12 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  13 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  14 hilairite: Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  16 total of extra-framework cations;
  17 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  18 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  19 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  10 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  11 komkovite, Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  12 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  13 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  14 hilairite: Vuoriyarvi, North Karelia (Voloshin et al., 1989);
  15 not calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;
  16 total of extra-framework cations;
  17 calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3H<sub>2</sub>O<sub>9</sub>·3

Table 2 – continued (new analyses)

	12	13	14	15	16	17	18	19	20	21	22
	12	13	14	13	wt.		10	19	20	21	22
Na <sub>2</sub> O	13.04	2.33	1.02	0.57	0.07	0.00	0.28	0.10	0.00	0.00	0.31
K₂Ô	0.66	3.08	3.13	3.02	3.00	1.58	2.09	2.03	1.43	0.43	0.46
CaO	0.05	4.09	4.97	5.19	5.65	6.19	6.96	7.54	9.38	11.47	6.89
SrO	0.00	0.00	0.00	0.00	0.43	0.54	0.67	1.34	1.24	0.62	0.00
BaO	0.40	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.15
MnO	0.52	0.49	0.35	0.41	0.42	0.14	0.25	0.29	0.13	0.01	0.31
FeO	0.53	0.05	0.00	0.00	0.04	0.05	0.03	0.00	0.05	0.08	0.07
ZnO	0.00	0.00	0.03	0.61	0.19	0.09	0.18	0.00	0.14	0.00	0.00
$Al_2O_3$	0.06	0.00	0.00	0.00	0.00	0.03	0.02	0.05	0.03	0.05	1.36
$SiO_2$	42.66	43.43	44.58	43.94	44.99	47.40	44.90	41.94	42.64	41.82	43.70
$TiO_2$	0.00	0.46	0.58	0.71	0.98	1.07	0.81	0.87	0.92	0.55	0.33
$ZrO_2$	28.92	27.41	28.27	28.76	30.41	29.89	29.23	29.51	29.17	29.57	26.46
HfO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.63	0.00	0.79	0.00
$Nb_2O_5$	0.74	3.34	3.11	2.39	1.08	2.26	1.76	1.41	1.30	1.34	0.00
Total	87.58	84.87	86.04	85.60	87.26	89.24	87.47	85.69	86.43	86.73	86.04
			Forn	nula units	, calculati	ion for 9 c	xygen at	oms			
Na	1.77	0.32	0.14	0.08	0.01	_	0.04	0.01	_	_	0.04
K	0.06	0.28	0.28	0.27	0.26	0.13	0.18	0.18	0.13	0.04	0.04
Ca	_	0.31	0.37	0.39	0.42	0.44	0.51	0.57	0.70	0.86	0.52
Sr	_	-	-	_	0.02	0.02	0.03	0.06	0.05	0.03	_
Ba	0.01	0.01	_	_	_	_		_		_	0.17
Mn	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.02	0.01	_	0.02
Fe	0.03	_	_		- 0.01	_	_	_	- 0.01	_	
Zn				0.03	0.01		0.01		0.01		
Eefc	1.99	0.95	0.81	0.79	0.74	0.60	0.78	0.84	0.90	0.93	0.79
Al											0.11
Si	2.99	3.07	3.09	3.08	3.09	3.13	3.07	2.98	2.98	2.93	3.10
Ti	_	0.02	0.03	0.04	0.05	0.05	0.04	0.05	0.05	0.03	0.02
Zr Hf	0.99	0.95	0.96	0.98	1.02	0.96	0.98	1.02	1.00	1.01	0.92
ні Nb	0.02	0.11	0.10	0.08	0.03	0.07	0.01 0.05	0.01 0.05	0.04	0.02 0.04	_
מאד	0.02	0.11	0.10	0.00	0.03	0.07	0.03	0.03	0.04	0.04	

- Notes:

  12 hilairite: the Kukisvumchorr Mountain, Khibiny;
  13 hilairite: the Flora Mountain, Lovozero (the core of calciohilairite trystal);
  14 21 calciohilairite: the Flora Mountain;
  22 calciohilairite: the Lepkhe Nel'm Mountain, Lovozero.
  In all analyses the contents of Mg, REE, Cl are below detection the limits by the electron microprobe;
  Σefc the sum of extra-framework cations.

Table 3. Chemical composition of sazykinaite-(Y) and pyatenkoite-(Y)

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		1	2	3	4	5	6	7	8	9	10	11	12
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $							wt. %						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$Na_2O$	18.02	18.98		15.45		14.07		13.80	12.54	17.25	17.16	16.02
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		_	_	3.05	2.49	2.55	4.06	1.82	4.19	2.12	0.14	0.13	0.13
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$Y_2O_3$	13.13	13.83	8.74	9.31	9.30	8.30	8.15	5.57	11.41	6.64	11.60	10.05
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		_	_	0.00	0.01	0.01	0.05	0.02	0.15	0.00	0.10	0.00	0.00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					0.25	0.66	0.23	0.12	2.65		0.34	0.00	0.00
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		_	_	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			_	0.25	0.06	0.63	0.24	0.17	2.16	0.24	0.60	0.00	0.00
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	2 0		_	0.38	0.48	0.95	0.63	0.24	0.79	0.32	1.14	0.00	0.32
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $													
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $													
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Tm <sub>o</sub> O <sub>o</sub>												
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Yh <sub>2</sub> O <sub>3</sub>												
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		_											
Nb <sub>2</sub> O <sub>5</sub>		14 33											
Na		_											
Total         100.00         100.00         98.81         86.17         86.17         85.82         85.83         90.16         84.78         87.26         85.73         86.36           Na         5.00         5.00         4.38         4.44         4.15         4.08         4.35         3.83         3.65         4.70         4.60         4.28           K         —         —         0.58         0.47         0.48         0.78         0.34         0.76         0.41         0.03         0.02         0.02           Y         1.00         1.00         0.69         0.73         0.73         0.66         0.64         0.42         0.91         0.50         0.85         0.74           La         —         —         —         —         —         0.01         0.02         0.02         —         —           Ce         —         —         0.01         0.04         0.01         0.005         0.14         0.02         0.02         —         —           Pr         —         —         —         —         —         0.01         0.01         —         —         —         —         0.02         0.02         —		12.58											
Na													
Na				For	mula un	its, calc	ulation f	for 18 ox	ygen at	oms			
K         -         -         0.58         0.47         0.48         0.78         0.34         0.76         0.41         0.03         0.02         0.02           Y         1.00         1.00         0.69         0.73         0.73         0.66         0.64         0.42         0.91         0.50         0.85         0.74           La         -         -         -         -         -         -         0.01         -         0.005         -         -           Ce         -         -         0.01         0.01         0.04         0.01         0.005         0.14         0.02         0.02         -         -           Pr         -         -         -         0.04         0.01         0.005         0.14         0.02         0.02         -         -           Sm         -         -         0.01         -         -         -         0.01         0.01         0.01         0.01         0.01         0.03         0.04         0.02         0.06         0.02           Eu         -         -         0.05         0.06         0.06         0.04         0.04         0.04         0.04         0.08         -	Na	5.00	5.00								4 70	4 60	4 28
Y         1.00         1.00         0.69         0.73         0.73         0.66         0.64         0.42         0.91         0.50         0.85         0.74           La         -         -         -         -         -         -         0.01         -         0.005         -         -           Ce         -         -         0.01         0.04         0.01         0.005         0.14         0.02         0.02         -         -           Pr         -         -         -         -         -         0.01         -         0.02         0.03         0.05         0.04         0.04         0.04         0.02         0.06         0.02         0.06         0.02         0.06         0.02         0.06         0.02         0.06         0.02         0.01         0.02         0.02         0.02         0.02         0.02         0.02         0.01         0.01         0.01													
La         -         -         -         -         -         -         0.01         -         0.005         -         -         -           Ce         -         -         0.01         0.04         0.01         0.005         0.14         0.02         0.02         -         -           Pr         -         -         -         -         -         0.01         -         0.02         -													
Ce         -         -         0.01         0.01         0.04         0.01         0.005         0.14         0.02         0.02         -         -           Pr         -         -         -         -         -         -         0.01         -         0.02         0.06         0.02         0.06         0.06         0.04         0.03         0.04         0.02         0.06         0.02         -         -         0.03         -         -         0.03         0.04         0.04         0.04         0.04         0.04         0.04         0.04         0.08         -         0.01         -         -         -         0.01         -         -         0.01         -         -         0.													
Pr         -         -         -         -         -         0.01         - <td></td>													
Nd         -         -         0.01         -         0.04         0.01         0.01         0.11         0.01         0.03         -         -           Sm         -         -         0.02         0.03         0.05         0.04         0.03         0.04         0.02         0.06         0.02           Eu         -         -         0.01         -         -         -         -         -         0.03         -         -           Gd         -         -         0.05         0.06         0.06         0.04         0.04         0.04         0.04         0.08         -         0.01           Tb         -         -         0.01         -         -         -         -         0.02         -         -           Dy         -         -         0.06         0.06         0.05         0.06         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         -         -         0.01         -         -         -         0.01         0.01         -         -         -         0.01         0.01         -											_		
Sm         -         -         0.02         0.03         0.05         0.04         0.03         0.04         0.02         0.06         0.02           Eu         -         -         0.01         -         -         -         -         -         0.03         -         -           Gd         -         -         0.05         0.06         0.06         0.04         0.04         0.04         0.04         0.08         -         0.01           Tb         -         -         0.01         -         -         -         -         0.02         -         -           Dy         -         -         0.06         0.06         0.05         0.06         0.04         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.04         0.03         0.03         0.03         0.03         0.04         0.04         0.04         0.04           Tm         -         -         0.03         0.03         0.02											0.03	_	
Eu         -         -         0.01         -         -         -         -         -         -         0.03         -         -           Gd         -         -         0.05         0.06         0.06         0.04         0.04         0.04         0.04         0.08         -         0.01           Tb         -         -         0.01         -         -         -         -         -         0.02         -         -           Dy         -         -         0.06         0.06         0.05         0.06         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.04         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         0.01         0.05         0.03           Th         -         -         0.03         0.03         0.02         0.03         0.01         0.05 <td></td>													
Gd         -         -         0.05         0.06         0.06         0.04         0.04         0.04         0.04         0.08         -         0.01           Tb         -         -         0.01         -         -         -         -         -         0.02         -         -           Dy         -         -         0.06         0.06         0.05         0.06         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.04         0.03         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         0.01         0.05         -         -           Yb         -         -         0.03         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         0.03         0.04         0.04         0.03         0.04         -         0.01												_	_
Tb         -         -         0.01         -         -         -         -         -         -         0.02         -         -           Dy         -         -         0.06         0.06         0.05         0.06         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.04         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         0.01         0.05         -         -           Yb         -         -         0.03         0.03         0.02         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         -         0.04           Si         6.00         6.00         6.03         6.15         6.12         6.06         6.06													0.01
Dy         -         -         0.06         0.06         0.06         0.05         0.06         0.04         0.06         0.11         0.03         0.03           Ho         -         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.03         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         0.01         0.05         -         -           Yb         -         -         0.03         0.02         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         -         0.04           Si         6.00         6.03         6.15         6.12         6.06         6.06         6.21         6.20         6.03         6.09         6.05           Ti         -         1.00         0.15         0.12         0.15													
Ho         -         -         -         -         -         -         -         0.01         0.01         -         -           Er         -         -         0.04         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         0.01         0.005         -         -           Yb         -         -         0.03         0.02         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         0.05         0.03           Si         6.00         6.03         6.15         6.12         6.06         6.06         6.21         6.20         6.03         6.09         6.05           Ti         -         1.00         0.15         0.12         0.15         0.01         0.04         0.04         0.08         0.86         1.00         0.99           Zr         1.00         -         0.07         0.09         0.07         - </td <td></td>													
Er         -         -         0.04         0.04         0.03         0.03         0.03         0.04         0.04         0.06         0.04           Tm         -         -         0.01         -         -         -         -         -         0.01         0.005         -         -           Yb         -         -         0.03         0.02         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         -         0.04           Si         6.00         6.00         6.03         6.15         6.12         6.06         6.06         6.21         6.20         6.03         6.09         6.05           Ti         -         1.00         0.15         0.12         0.15         0.01         0.04         0.04         0.08         0.86         1.00         0.99           Zr         1.00         -         0.74         0.68         0.67         1.02         1.01         0.95         0.73         0.03         -         -           Nb         -													
Tm         -         -         0.01         -         -         -         -         -         0.01         0.005         -         -           Yb         -         -         0.03         0.02         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         -         0.04           Si         6.00         6.00         6.03         6.15         6.12         6.06         6.06         6.21         6.20         6.03         6.09         6.05           Ti         -         1.00         0.15         0.12         0.15         0.01         0.04         0.04         0.08         0.86         1.00         0.99           Zr         1.00         -         0.74         0.68         0.67         1.02         1.01         0.95         0.73         0.03         -         -           Nb         -         -         0.09         0.07         -         0.02         -         0.08         0.17         0.01         0.15				0.04	0.04	0.03	0.03	0.03	0.03			0.06	0.04
Yb         -         -         0.03         0.03         0.02         0.03         0.02         0.03         0.02         0.03         0.01         0.05         0.03           Th         -         -         0.03         0.04         0.04         0.03         0.04         -         0.01         0.01         0.01         -         0.04           Si         6.00         6.00         6.03         6.15         6.12         6.06         6.06         6.21         6.20         6.03         6.09         6.05           Ti         -         1.00         0.15         0.12         0.15         0.01         0.04         0.04         0.08         0.86         1.00         0.99           Zr         1.00         -         0.74         0.68         0.67         1.02         1.01         0.95         0.73         0.03         -         -           Nb         -         -         0.09         0.07         -         0.02         -         0.08         0.17         0.01         0.15					_	_		_	_			_	_
Th					0.03	0.02		0.02	0.02			0.05	0.03
Si     6.00     6.00     6.03     6.15     6.12     6.06     6.06     6.21     6.20     6.03     6.09     6.05       Ti     -     1.00     0.15     0.12     0.15     0.01     0.04     0.04     0.08     0.86     1.00     0.99       Zr     1.00     -     0.74     0.68     0.67     1.02     1.01     0.95     0.73     0.03     -     -       Nb     -     -     0.09     0.09     0.07     -     0.02     -     0.08     0.17     0.01     0.15													
Ti - 1.00 0.15 0.12 0.15 0.01 0.04 0.04 0.08 0.86 1.00 0.99 Zr 1.00 - 0.74 0.68 0.67 1.02 1.01 0.95 0.73 0.03 Nb 0.09 0.09 0.07 - 0.02 - 0.08 0.17 0.01 0.15													
Zr 1.00 - 0.74 0.68 0.67 1.02 1.01 0.95 0.73 0.03 Nb - 0.09 0.09 0.07 - 0.02 - 0.08 0.17 0.01 0.15													
Nb 0.09 0.09 0.07 - 0.02 - 0.08 0.17 0.01 0.15													
$H_2O$ 6.00 6.00 6.25 n.d n.d n.d n.d n.d n.d n.d n.d		6.00	6.00										

### Notes:

- 1 calculated composition of Na<sub>5</sub>YZrSi<sub>6</sub>O<sub>18</sub>6H<sub>2</sub>O;
  2 calculated composition of Na<sub>5</sub>YTiSi<sub>6</sub>O<sub>18</sub>6H<sub>2</sub>O;
  3 9 sazykinaite-(Y) from the Koashva Mountain, Khibiny:
  3 Khomyakov *et al.*, 1993;
  4 7 Pekov, 1998 (4 and 5 zonal crystal: 4 core, 5 marginal zone);
  8 9 Yakovenchuk *et al.*, 1999 (the total also includes, wt. %: analysis 8 FeO 0.26; analysis
  9 CaO 0.07, SrO 0.08);
  10 pyatenkoite-(Y) the Alluaiv Mountain, Lovozero (Khomyakov *et al.*, 1996);
  11 12 pyatenkoite-(Y) from the Kukisvumchorr Mountain, Khibiny;
  n.d. water content was not detected

almost total absence. Yttrium and lantanides are absent in quantities determined by the electron microprobe (> 0.05 - 0.1 %) in hilairite and calciohilairite. These regularities are also fair for komkovite (Table 2).

Yttrium in all cases dominates among REE in sazykinaite and pyatenkoite. In investigated samples of these minerals from Khibiny, heavy lantanides sharply prevail in lantanide spectrum with DyGd-maximum in sazykinaite and Er-maximum in pyatenkoite.

In barium-containing calciohilairite from the Lepkhe Nel'm Mountain, Lovozero, the admixture of aluminum was discovered: 1.4 wt. % of  $Al_2O_3$  (analysis 22 in Table 2).

The structure of large (alkaline and alkaline-earth) cations in investigated hilairite and calciohilairite samples varies rather widely:  $Na_2O 0.0 - 13.0$  wt. %, CaO 0.7 - 11.5%, K<sub>2</sub>O 0.0-3.2 %, SrO 0.0-1.3 %, BaO 0.0 – 6.2 %. Such high contents of admixtures of K, Sr, and Ba in hilairite and calciohilairite were not known earlier. Amounts of others low-valent cations (Mg, Mn, Fe, Zn) are small less than 1 wt. % in all analyses. Zonal crystals whose core are enriched with Na and correspond to high-calcium variety of hilairite (analysis 13 in Table 2) while peripheral parts correspond calciohilairite (analysis 16 in Table 2) were discovered in Lovozero hydrothermal rocks. Transitions between zones are gradual, which allows to suppose continuous isomorphism between large extra-framework cations and, respectively, about isomorphous series hilairite - calciohilairite.

In sazykinaite-(Y) and pyatenkoite-(Y) alkaline-earth and other bivalent cations are practically absent and Na is the main extra-framework cation: pyatenkoite is almost purely sodic mineral; all samples of sazykinaite contain appreciable admixture of K  $(1.8-4.2 \text{ wt.} \% \text{ K}_2\text{O})$ .

The total contents of alkaline and alkaline-earth cations is variable in calciohilairite from Lovozero. In addition to stoichiometric varieties, there are also cation-deficient varieties, in which the total of extra-framework cations little exceeds 0.5 of formula unit (at calculation to  $\mathrm{Si}_3$ ).

#### The X-ray Data

The crystal structure of calciohilairite — the unique representative of the group, which structure remained unstudied until recently — was studied (Pushcharovsky *et al.*,

2002) in a single crystal from the Flora Mountain (Lovozero). Even the sizes of unit cell of this mineral were not authentically known. R.C.Boggs (1988) has stated a trigonal cell, twice as big in direction a than in other members of the group: a = 20.90, c = 16.05 Å. However, poor quality of single crystals from Golden Horn left doubts in correctness of these results. The data received for the Lovozero cation-deficient calciohilairite with the help of single crystal diffractometer Siemens P4 show that the unit cell of this mineral by a is the same as in all other representatives of the group, and by c is less: a =10.498, c = 7.975 Å (Pushcharovsky *et al.*, 2002). Thus, it appeared four times smaller in volume than R.C.Boggs (1988) supposed it. The space group of calciohilairite is R32, as well as of all other members of the group (Table 1), but the parameter c of its cell is equal to the repeatability period of M-octahedra (~8 Å) and, respectively, the «step» of a screwed chain (Si<sub>3</sub>O<sub>9</sub>), which includes three Si-tetrahedra. The other members of the group contain in cell two periods of chain in height and two M-octahedra, which is related to the arrangement of extra-framework cations and water molecules (see, for example, Ilyushin et al., 1981). In calciohilairite with disordered as compared to structure, one position extra-framework cations (with dominating Ca) is realized instead of two nonequivalent in other members of the group, which provokes halved parameter c.

A similar mixed framework of hilairite-group minerals results in similarity of their X-ray powder patterns. Only members containing large octahedron occupied with Y and Ln in the framework may be separated in X-ray powder patterns from REE-free members (Table 4). Obviously, as well as in case of alumosilicate zeolites, character of «filler» of extensive cages (alkaline and alkaline-earth cations and water molecules) does not render essential influence on parameters of cell and X-ray powder pattern.

Table 4 shows X-ray powder data for calciohilairite from the Flora Mountain (Lovozero), indicated in parameters of true, i.e. small cell determined by single crystal method in comparison with X-ray powder data of other members of the group. At choice of indices *hkl* for calciohilairite, the data on intensity, received from its crystal structure data, were taken into account.

 $\it Table~4.~X-ray~powder~data~for~hilairite-group~minerals$ 

	1		2			3		4		5	
I	d, Å	hkl	I	d, Å	I	d, Å	I	d, Å	I	d, Å	hkl
90	6.02	011	90	6.03	10	5.96	32	6.03	60	5.99	012
90	5.20	110	70	5.25	100	5.23	63	5.40	30	5.36	110
5	4.00	201			10	3.94					202
							2	3.776			113
5	3.65	102	5	3.62	80	3.59	4	3.645			104
							3	3.453	20	3.43	211
100	3.15	121	90	3.14	20	3.13	84	3.236	100	3.21	122
100	3.01	300, 022	100	3.01	80	3.02	88	3.127	40	3.093	300
					90	2.96	100	3.030	85	2.990	024
					10	2.880					123
					20	2.840					302
					40	2.615	19	2.708	40	2.661	220, 033
40	2.60	212	50	2.62	60	2.571	8	2.641	20	2.608	214, 205
							3	2.565			131
			10	2.41	30	2.393	9	2.472	5	2.439	312
							4	2.407			223
25	2.37	113	10	2.35	20	2.327	5	2.371	22	2.353	116
			10	2.19			7	2.248	10	2.210	042
35	2.12	132	20	2.13	20	2.124	14	2.175	24	2.148	134
					60	2.106	2	2.134			321, 230
			5	2.02	10	2.026	13	2.077	10	2.050	232
50	1.99	410, 303	70	2.00	30	1.984	7	2.046			410, 306
							18	2.018	55	1.998	404, 306
					30	1.960					800
					10	1.931	_				233
					10	1.911	3	1.909	17.5	1.881	217,143, 018
20	1.83	322, 024	40	1.86	40	1.841	13	1.890	17.5	1.870	324, 226
			4.0	4.00	20	1.829		4 005	4.0	4 000	500
		000	10	1.83	50	1.796	4	1.825	12	1.808	502, 208
20	1.74	330	20	1.755	20	1.750	21	1.805	24	1.781	330
					10	1 700			5	1.746	009, 241
10	1 71	404 404	10	1 71 1	10	1.736	1.1	1 700	10	1 710	235
10	1.71	421, 124	10	1.714	50	1.700	11	1.730	10	1.712	422, 128
15	1.68	052	10	1.693	10	1.656	12	1.696	26	1.676	054
20	1 65	1.5.1	20	1.660	20	1.640	4	1.640	5 5	1.648	511
30	1.65	151	30	1.660	30	1.642	4	1.648		1.627	152, 243
15	1.59 1.57	413 105	10 5	1.598	10	1.579 1.564	7	1.618	26 5	1.598 1.556	244, 416
5 5	1.51	600, 512	J	1.559	10 50	1.544	2 5	1.577 1.564	J	1.550	318, 1.0.10, 153
J	1.31	000, 312			10	1.546	J	1.304			131, 600 237
					20	1.527	4	1.549	5	1.532	514
			40	1.468	20	1.505	4 5	1.549	J	1.332	342, 253
			40	1.400	10	1.480	J	1.314			2.0.10
40	1.45	520, 333	30	1.442	20	1.460	13	1.503	44	1.481	520, 603
40	1.43	J40, JJJ	30	1.444	20	1.400	5	1.491	***	1.401	336
							J	1.491			330

## Notes:

- 1 calciohilairite, the Flora Mountain, Lovozero (camera RKD-57.3, FeK-radiation);
  2 hilairite, the Kukisvumchorr Mountain, Khibiny (camera RKD-57.3, FeK-radiation);
  3 komkovite, Vuoriyarvi (Voloshin *et al.*, 1990);
  4 sazykinaite-(Y), the Koashva Mountain, Khibiny (Khomyakov *et al.*, 1993);
  5 pyatenkoite-(Y), the Aluaiv Mountain, Lovozero (Khomyakov *et al.*, 1996).

#### IR-spectroscopy

The IR-spectroscopic data on hilairite-group minerals are rather dispersed, and the IR-spectrum of calciohilairite was not published at all. A.V.Voloshin with co-authors (1989) gaves spectra of water alkaline Zr-silicates - catapleiite, gaidonnayite, georgechaoite and hilairite and fairly notes that the IR-spectroscopy is quite convenient for diagnostics of these minerals. A.P.Khomyakov with co-authors (1996) note that the IR-spectrum of pyatenkoite is generally close to the spectra of sazykinaite, hilairite and komkovite. However, it is difficult to agree without reserves with this statement. Fig. 2 shows IR-spectra of all members of hilairite group and serious distinctions between them are well visible.

Really, the IR-spectroscopy can be proposed as a reliable and fast method not only to distinguish hilairite-group minerals from representatives of other structural types, but also for their diagnostics inside the group. Only hilairite and calciohilairite can be confused by IR-spectra, whereas other minerals have individual sets of features expressed in appearance, disappearance, or shift of this or that spectrum band and/or redistribution of their intensities.

The IR-spectrum of pyatenkoite is most sharply distinguished, which is related to entry of Ti instead of Zr. The distinctions consist both in occurrence of own bands related to vibrations Ti-O (first of all, this is a doublet in the band 700 cm<sup>-1</sup> instead of single at zirconium minerals) and in strong polarization by Ti, as against Zr, bond Si-O that results in splitting the main Si-O band of stretching vibrations in pyatenkoite spectrum into two comparable by intensity components at ~900 and ~1020 cm<sup>-1</sup>. Such character of splitting gives completely individual structure to the main band in spectrum of pyatenkoite allowing to confidently distinguish this mineral from zirconium members of the group.

Very serious distinctions are observed in the area of absorption bands corresponding to vibrations of water molecules — stretching  $(2900-3550~{\rm cm}^{-1})$  and bending  $(\sim 1600~{\rm cm}^{-1})$ . So, splitting of the band of molecular water bending vibrations in komkovite and sazykinaite spectra indicates the presence in these minerals of water molecules at two structural positions, as against three other members of the group, where, considering single band near  $\sim 1600~{\rm cm}^{-1},~{\rm H}_2{\rm O}$  positions are of one type. An intensive wide band near  $\sim 2900~{\rm cm}^{-1}$  in the sazykinaite spectrum indicates the existence of

strong hydrogen bonds, which are not observed in pyatenkoite. At last, a wide band near  $\sim 3200~{\rm cm}^{-1}$  may indicate the presence of  $({\rm H_3O})^+$  in hilairite-group minerals; most strongly this band is manifested in hilairite and calciphilairite.

#### **Discussion**

New finds of hilairite-group minerals in the Khibiny-Lovozero complex show that these minerals are not so rare as it was supposed earlier. The received data on their cation composition appreciably expand our knowledge about isomorphous capacity of hilairite structural type. So, variations in crystals from the Flora Mountain (Lovozero) composition unequivocally show the existence in nature of extended isomorphous series hilairite—calciohilairite and also indicate possibility of entry of significant amounts of K and Sr admixtures in these minerals. Finds of

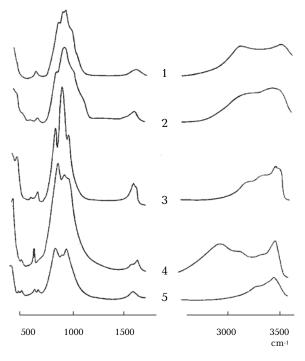


Fig. 2. IR spectra of hilairite-group minerals:

- 1 hilairite (Alluaive Mountain, Lovozero),
- 2 calciohilairite (Flora Mountain, Lovozero),
- 3 komkovite (Vuoriyarvi),
- 4 sazykinaite-(Y) (Koashva Mountain, Khibiny),
- 5 pyatenkoite-(Y) (Kukisvumchorr Mountain, Khibiny)

high-barium varieties of calciohilairite (Lepkhe Nel'm Mountain, Lovozero, — analysis 22 in Table 2) allows to assume the probability of realization of the isomorphous series calciohilairite — komkovite.

Results of study of cation-deficient calciohilairite structure from Lovozero (Pushcharovsky et al., 2002) enlightens the nature of non-stoichiometry in compounds with hilairite structural type. In addition to usual heterovalent replacements  $Ca^{2+}$  +  $\leftrightarrow$  2Na+, partial occupancy of cations (H<sub>3</sub>O)+ in the position usually only occupied with water molecules was revealed here. Significant sizes of cages in the framework allow to placed here such a large cation as hydronium, which compensate the lack of positive charge caused by the reduction of contents of «usual» cations — of alkaline and alkali-earth metals. The presence of hydronium is directly proved by IR-spectroscopy and indirectly - by overestimate of ratios for Si and M-cations at calculation of formulas of cation-deficient varieties by  $O_9$  (see analyses 14 through 18 and 22 in Table 2). As a result, the idealized general scheme of isomorphism resulting in observed compositions of cation-deficient calciohilairite may be written as:

 $2Na^+ + H_2O \rightarrow 0.5Ca_2^+ + 1.5 + (H_3O)^+$ . king into account that core of Taking cation-deficient calciohilairite crystals from the Flora Mountain are quite often appreciably enriched with Na in comparison with high-calcium peripheral zones (analyses 13 and 16 in Table 2), it is possible to assume that this scheme of isomorphism at the same time is also the scheme of reaction of natural ion-exchanging process, which results in transition of hilairite, crystallized from alkali-rich solutions, into calciohilairite at late hydrothermal phases in conditions of reduced alkalinity (as is known, reduction of activity of alkalis is rather typical of late phases of agpaitic system evolution). The presence of such open channels in hilairite type structure makes easy ionic exchange and it is thought that this phenomenon in general may be characteristic of hilairite-group minerals, responsible, in some cases, for the composition of extra-framework cations and water contents.

Isomorphism in the frame work is not so wide. So, strict order of two types of M-cations with different sizes — (Zr,Ti) and (Y,Ln) in structures of sazykinaite and pyatenkoite (Rastsvetaeva, Khomyakov, 1992, 1996), as well as absence of REE in hilairite, calciohilairite and komkovite, indicate that isomorphous series between rare-earth and rare-earth-free members of the group are absent.

Thus, in the hilairite group, it is possible to distinguish two independent subgroups: with the same filling of both M-octahedra (hilairite, calciohilairite and komkovite) and with the ordered distribution of M-cations of two types in positions M1 and M2 - sazykinaite-(Y) and pyatenkoite-(Y). Continuous isomorphism between Zr and Ti(Nb) even in isostructural sazykinaite and pyatenkoite is not discovered yet and it is possible that compete series between them are not realized at all owing to serious distinctions in crystallochemical features of Zr and Ti, in detail discussed by Yu.A. Pyatenko and A.A. Voronkov (1977). Presence of Al in hilairite-group minerals is only reported for calciohilairite: from the Golden Horn (Boggs, 1988, - see analyses 6-8 in Table 2) and from the Lepkhe Nel'm Mountain, Lovozero (analysis 22 in Table 2). The structure of Al-containing calciohilairite was not studied, it is only possible to note that the mineral from the Golden Horn has increased content of Al at some deficiency of Si, and in that from Lovozero – a deficiency of Zr.

Thus, stable composition of mixed octahedral-tetrahedral framework at widely varying contents and ratios of extra-framework cations (including hydronium) and a variable quantity of molecular water are characteristic of hilairite-group minerals. A number of attributes indicate easy ionic exchange and de-cationing in hilairite-like phases. All these features could be very well explained if to consider hilairite-group minerals as spcific zeolites with a combined framework.

Currently large scientific and practical interest call zeolite materials of new type, which framework includes five six-coordinated cations Ti, Nb, Al, Ga, V, etc. together with tetrahedral fragments (see, for example, the review of Rocha et al., 1996). These «zeolites» are characterized by wide spectrum of structural types and quite often have unique properties. Among minerals good example of microporous materials with combined octahedral-tetrahedral framework are Ti, Nb-silicates of the labuntsovite (Chukanov et al., 2002; Pekov et al., 2002).

Members of the hilairite group are also bright representatives of natural rare-metal "zeolites". They have a unique structure in which apex-connected silica tetrahedra form chains and isolated M-octahedra are occupied with atoms of Zr, less often Ti(Nb) and Y(HREE), joining to pendent apices of Si-tetrahedra, complete the framework. It is interesting that this picture is opposite to what is observed in labuntsovite-like minerals,

where chained motif is formed by interconnected by apices Ti, Nb-octahedra, while isolated four-member rings of Si-tetrahedra act as a binding element. These two contrast examples well illustrate the possibilities of topological variety of rare-metal «zeolite» structures. The density of framework of hilairite-group minerals varies from 15 to 16 framework atoms (Si+M) by  $1000~\mathring{A}^3$ ; such values are characteristic of «true» alumosilicate zeolites with «loose» frameworks.

The thermal data also unequivocally specify the zeolite character of hilairite-like minerals. So, dehydration of hilairite at heating completely terminate at 220° C and then dewatered material preserves the hilairite structure minimum to 855° C. At return cooling, rehydration also begins at 220° C and in 15 hours at room temperature the mineral absorbs about 95 % from initial quantity of water; the rehydration product is meat-red, porcelain-like, gives the X-ray diagram of hilairite (Chao et al., 1974). The main quantity of water from sazykinaite-(Y) flashes out below  $250^{\circ}$  C (more than 80 wt. % from all the loss, by the published thermal curve). After heating up to 500° C, grown white and turbid crystals give the X-ray powder pattern of sazykinaite with weakened diffusion lines (Khomyakov et al., 1993).

It is possible that massive pink to red opaland porcelaine-like varieties of hilairite described from Saint-Hilaire (Chao *et al.*, 1974) and Karnasurt Mountain in Lovozero (Khomyakov, Chernitsova, 1980) could arise owing to dewatering of «normal» crystalline hilairite at additional heating of a pegmatitic system after the crystallization of mineral and its rehydration at cooling.

Large enough Y cation participates in the sazykinaite and pyatenkoite framework, which is rare for similar «zeolites». Probably, the framework-forming role demanding in this case the minimization of coordination polyhedron volume interferes with entry of ions of light lantanides — largest of REE<sup>3+</sup> — into these phases in essential quantities. Only one analysis of sazykinaite is known where Ce prevails in Ln spectrum, but here Y remains dominant M2-cation (analysis 8 in Table 3). Zeolite nature of hilairite-group minerals is also proved by the ease of entry of additional Na+ cation (in relation to REE-free members of the group), necessary to compensate the deficiency of positive charge arising at heterovalent replacement  $(Zr,Ti)^{4+} \rightarrow Y^{3+}$  in channels of sazykinaite and pyatenkoite. As is known, just this is the charge balance mechanism in very

many «true» zeolites with wide limits of isomorphism between  $Si^{4+}$  and  $Al^{3+}$  in tetrahedra (Gottardi, Galli, 1985).

A triple system hilairite  $Na_2\{ZrSi_3O_9\} \cdot 3H_2O$  — calciohilairite  $Ca\{ZrSi_3O_9\} \cdot 3H_2O$  — komkovite  $Ba\{ZrSi_3O_9\} \cdot 3H_2O$  has a peculiar analogue by a set of extra-framework cations among «true» zeolites: natrolite  $Na_2\{Al_2Si_3O_{10}\} \cdot 2H_2O$  — scolecite  $Ca\{Al_2Si_3O_{10}\} \cdot 3H_2O$  — edingtonite  $Ba\{Al_2Si_3O_{10}\} \cdot 4H_2O$ . Moreover, isotructural natrolite and scolecite show a complete miscibility, while structurally close edingtonite rarely contains appreciable admixtures of other cations (see: Gottardi, Galli, 1985).

Due to its zeolite-like structure causing multicomponent composition and significant variations in contents of cations (especially extra-framework cations) and hilairite-group minerals are sensitive indicators of chemical environments at mineral formation. As shows the analysis of their occurrence conditions and paragenesis, the temperature interval of crystallization of these most rich in water Zr-silicate phases is narrow: appearance of hilairite-group minerals from hydrothermal solutions at temperatures above 150°C is little probable. At the same time, geochemical settings of their formation may differ strongly. So, the particular type of hydrothermal rocks related to carbonatites of the Vuoriyarvi massif has sharp barium specificity manifested, in particular, by the presence of komkovite; decomposition of abundant eudialyte containing admixtures of Y and HREE (Koashva, Khibiny) in hyperalkaline hydrothermal conditions has resulted in crystallization of sazykinaite-(Y) in leaching cavities — the mineral, which has concentrated these elements (Pekov, 1998).

In some cases the composition of hilairite-like minerals reflects the chemical environment of late solutions — the stage of decationing of these phases or ionic exchange. This could be the way of formation of the secondary concentric zonality — so we interpret the structure of crystals from the Flora Mountain in the Lovozero massif.

#### **Conclusions**

So, basing on the results of study of new finds of hilairite-group minerals in the Khibiny-Lovozero alkaline complex and on earlier published data from all known occurrences of the world, we attempted to illustrate zeolite character of these minerals and to characterize from this viewpoint their composition and some cry-

stallochemical features. Hilairite-group minerals form a very original type of natural rare-metal «zeolites» with a peculiar combined framework. Their properties demand detailed study: it is possible that they are not only unusual, but also interesting in practical application.

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#### ON THE CHEMICAL COMPOSITION OF GERMANITE

#### Svetlana N. Nenasheva

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, sn@fmm.ru

Germanite is a very rare mineral that commonly occurs as small segregations in association with bornite, renierite, fahlores, sphalerite, galena, and other sulfides and sulfosalts. Very fine structures of replacement of germanite for renierite are often observed. Such small segregations are difficult to study. Optical properties of germanite are slightly variable in different areas and in samples from different deposits. The chemical composition (concentrations of the principal elements) of germanite varies over a wide range. In addition, the mineral was revealed to contain a wide set of admixtures. Therefore, different researchers propose different formulas for germanite. Chemical and electron microprobe analyses of germanite, accessible in literature, were compiled by the author, and peculiarities of the chemical composition of germanite were studied. It has been revealed that 28 analyses from 37 ones are adequately recalculated to the formula with 66 atoms in the unit cell; 6 analyses, to the formula with 64 atoms; and 3 analyses, with 68 atoms. The Me/S ratio in the analyses varies from 32:32 to 34:32 and to 36:32; that is, this ratio in the real analyses is inconstant. This fact suggests that we deal either with solid solutions or with three different, but similar in the chemical composition and properties, minerals. The second assumption is more probable. It is concluded that there exist three mineral species close to germanite in the chemical composition.

8 tables, 3 figures and 22 references

Germanite has been known from the 1920s. It was discovered by G. Schneiderhuhn (1920) at the Tsumeb ore deposit, Namibia, and was described and named so by O. Pufahl (1920). Later, the mineral was found at the Bancairoun, France (Levy, 1966) and Radka, Bulgaria (Kovalenker, et al., 1986) ore deposits. Finds of complex Ge sulfides were reported from some Russian ore deposits, including the Pai-Khoi, Urup, Gai, III International, and Kurumsak ones, and from the Chelopech ore deposit, Bulgaria. However, these minerals contained large concentrations of either As or V, or,

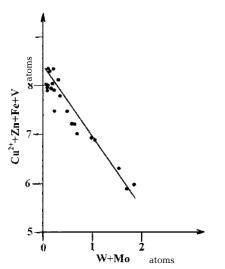


Fig. 1. Dependence between  $Cu^{2+} + Fe + Zn$  and W + Mo in analyses of germanite

sometimes, of As and V together. In this case, concentrations of these elements were comparable with that of Ge and sometimes exceeded it. We excluded these analyses from the consideration, because they were probably assigned to germanocolusite or colusite.

At all the ore deposits, germanite is associated with bornite, renierite, fahlores, and galena, being commonly intimately intergrown with these minerals. Very fine structures of replacement of germanite for renierite are often observed. Such small segregations are difficult to study. Optical properties of germanite are slightly variable in different areas and in samples from different deposits. Its color under reflected light is pink with violet tint, being very unequal. According to the optical features, L. Loginova (1960) distinguished three individual varieties of germanite.

The chemical composition (concentrations of the principal elements) of germanite varies over a wide range (in wt.%): Cu 40.9 - 51.0, Fe 0.0-10.7, Ge 3.0-11.0, Zn 0.0-5.5, and S 30.0-34.5. In addition, the mineral was revealed to contain a wide set of admixtures, including As, V, Ga, Sn, Sb, W, Mo, Pb, and Ag. Therefore, different researchers propose different formulas for germanite (Tables 1 and 2). These formulas are characterized by different cation/anion ratios equal to 1:1 (Sclar et al.,1957; Levy, 1966); 1 : 0.95 = 1.052 (Springer, 1969); 34:32 = 1.062 (Tettenhorst and Corbato, 1984; Spiridonov, 1987; Godovikov, 1997); and 36:32 = 1.125 (Spiridonov et al., 1992).

Table 1. Germanite formulae proposed by different researchers

Formula	Reference	Me/S
$Cu_3(Fe,Ge)S_4$	De Jong, 1930	1
$Cu_3(Fe,Ge,Zn,Ga)(S,As)_4$	Sclar et al., 1957	1
$Cu_6FeGeS_8 \rightarrow Cu_3Cu_{2+3}Fe_{3+}Ge_{4+}S_8$	Levy, 1966	1
(Cu,Fe,Zn,W,Mo,V,Ge,As Ga)S <sub>0.95</sub>	Springer, 1969	1.052
$Cu_{26}Fe_4Ge_4S_{32} \rightarrow Cu_{16}^+Cu_{16}^2Fe_{10}^3Fe_{3+4}^4Ge_{4+4}^4S_{32}$	Tettenhorst et al., 1984	1.062
$Cu_{20}(Cu_{2+},Fe_{2+},Zn)_{6}Fe_{3+}Ge_{6}S_{32}$	Spiridonov, 1987	1.062
$Cu^{+}_{22}(Cu^{2+},Fe^{2+},Zn)_{6}Fe^{3+}_{2}(Ge_{4}As)_{6}S_{32}Cu^{+}_{22}(Cu^{2+}_{2}Fe^{2+}_{2}Zn_{2})_{6}Fe^{3+}_{2}(Ge_{4}As_{2})_{6}S_{32}$	Spiridonov et al.,, 1992	1.125
$Cu_{8}^{+}Cu_{5}^{2}Fe_{3}^{+}Ce_{5}^{4}$	Godovikov, 1997	1.062

Table 2. Theoretical composition of germanite (in wt. %), based on formulae proposed by different researchers

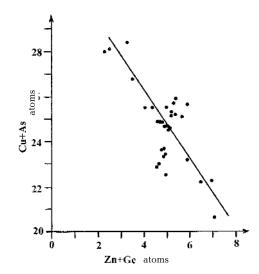
Authors	Cu	Cu+	Cu2+	Fe	Zn	Ge	As	S
Levy, 1966	49.76	24.88	24.88	7.29		9.47		33.48
Tettenhorst, Corbato, 1984	51.76	31.85	19.91	7.00		9.1		32.14
Spiridonov, 1987	43.50	39.55	3.95	6.95	4.07	13.55		31.93
Spiridonov, 1992	45.58	41.78	3.80	6.68	3.91	8.68	4.48	30.67
Godovikov,1997	51.76	31.85	19.91	7.00		9.1		32.14

The crystal structure of germanite is derivative from the crystal structure of sphalerite and is close to those of stannite and colusite. Based on this fact, R. Tettenhorst and C. Corbato (1984) proposed a formula of germanite, similar to that of colusite, namely Cu<sub>26</sub>Fe<sub>4</sub>Ge<sub>4</sub>S<sub>32</sub>. This formula is electrically neutral only on condition that it contains 10 atoms of divalent Cu and 4 atoms of trivalent Fe. The presence of 10 atoms of divalent Cu is also specified by a crystallochemical formula of germanite, proposed by A. Godovikov (1997),  $Cu_{8}^{+}Cu_{5}^{2}Fe_{5}^{3}+_{2}Ge_{5}^{4}$  $\rightarrow$  Cu<sup>+</sup><sub>16</sub>Cu<sup>2+</sup><sub>10</sub>Fe<sup>3+</sup><sub>4</sub>Ge<sup>4+</sup><sub>4</sub>S<sub>32</sub>. A crystallochemical formula of germanite, proposed by E. Spiridonov (1987),  $Cu_{20}^+(Cu_{2+},Fe_{2+},Zn)_6Fe_{3+}^ Ge^{4+}{}_{6}S_{32}$ , is not electrically neutral. Later, in the work on germanocolusite, E. Spiridonov with co-authors (1992) proposed another crystallochamical formula for germanite,  $Cu_{22}(Cu_{2}^{2}, Fe_{2}^{2}, Zn)_{6}Fe_{3}^{3}(Ge_{4}As)_{6}S_{32}$ . In this case, the formula is electrically neutral, but the sum of atoms in the unit cell is 68 rather than 66 as in colusite whose formula was adopted by E. Spiridonov as the basis for examination of the germanite formula; therefore, the Me/S ratio is equal to 36/32 rather than 34/32.

These contradictions prompted us to make an additional analysis of the literature data on germanite.

37 chemical and electron microprobe analyses of germanite were found and recalculated into formulae with regard to necessity of their electrical neutrality (Table 3 and 4). A formula was considered to be electrical neutral if it had the valence balance ( $\pm\Delta$ , the absolute value of the deviation from zero) no higher than 3%. To calculate the valence balance, it was necessary to understand the positions of admixtures in the crystal structure.

The p-elements, Ge, As, and Ga, are the neighbors in Mendeleev's Periodic Table and have similar electronic structures, therefore, they can be isomorphous. Other admixtures, V, Fe, Cu, Mo, and W are d-elements; so, it can be assumed that V, Mo, and W can substitute Fe and Cu, occupying the sites of divalent cations or trivalent Fe. The sum (W + Mo) depends inversely on the sum (Cu<sup>2+</sup> + Fe + Zn), which evidences in favor of the assumption that W and Mo occupy the sites of divalent cations or trivalent Fe (Fig. 1). The sum (Cu + As) inversely proportional to the sum (Zn + Ge), which is evidence for the isomorphism Zn<sup>2+</sup> + Ge<sup>4+</sup>  $\rightarrow$  Cu<sup>+</sup> + As<sup>5+</sup> (Fig. 2).



**Fig. 2.** Dependence between Cu + As and Zn + Ge in analyses of germanite

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Table 3. Electron microprobe and chemical (\*) analyses of germanite in wt. % (upper row) and in f.u. (lower row). Analyses 1, 6, 22, 23, 24, and 36 are recalculated based on 64 atoms in the unit cell; analyses 8, 21, and 35, based on 68 atoms; the remainder, based on 66 atoms

N.T.		ina 35, bas							3.4	C	-
№ os.	Cu	Fe	Zn	Ge	Ga	As	V	W	Mo	S	Σ
1	45.1	7.4	1.3	9.7	0.00	2.6				33.4	99.5
0.4	21.92	4.09	0.61 2.61	4.13		1.07				32.17 31.34	63.99
2*	45.4	4.09 7.22 4.23	2.61	4.13 6.20 2.79		1.07 5.03 2.20				31.34	63.99 99.246 66.00
2*	23.38	4.23	1.31	2.79	1.05	2.20				31.98 31.27	00.00
3*	42.12 21.57	7.80 4.55	3.93 1.96	10.2 4.57	1.85 0.86	1.37 0.60				31.27	99.49 66.00
4*		4.55 4.56	2.58	4.5 <i>t</i> 8.70	0.86	4.13				31.74	00.00
4	45.39 23.98	2.74	1.32	4.02		1.85				30.65 32.09	99.55 66.00
5*	39.44	10.7	3.56	7.04		4.86				31.44	99.98
3	20.38	6.29	1 79	3.18		2.13				32.19	99.98 66.00
6	44.20	6.70	3.56 1.79 1.50	9.70		3.30				34.60	100.0
Ü	21.25	3.66	0.70	4.08		1.35				32.96	64.00
7	46.5	8.5	0.70	9.4		4.2				31.6	100.26
-	23.50	4.89		4.16		1.80				31.65 30.03 32.30	64.00 100.26 66.00
8*	43.6	6.4	3.10	9.0		4.70				30.03	97.7
	23.67	3.95	1.64	4.28		2.16				32.30	68.0
9	45.5 23.19	7.20	1.2 0.59	9.8	0.1	3.5 1.51				31.8 32.11	99.1 66.00
	23.19	4.18	0.59	4.37	0.05	1.51				32.11	66.00
10	46.7	6.5	8.0	9.0		4.2 1.82		0.6		31.7	99.5 66.00 98.5
	23.83	3.77	0.40	4.02		1.82		0.10		32.06	66.00
11	45.5	6.8	1.2	9.6		3.3			0.5	31.6	98.5
10	23.36	3.97 5.5	0.60	4.31		1.44		1.0	0.17	32.15	hh ()()
12	46.5	5.5	0.9	9.0		4.0		1.8	0.5 0.17	31.8	100.0 65.99
10	23.81	3.20	0.45	4.03		1.74		0.32	0.17	32.27	05.99
13	45.4 23.20	5.8 3.37	1.3 0.65	9.9 4.43		3.3 1.43		3.4 0.06		31.9 32.31	101.0 65.99
14	47.1	3.6	1.4	10.1		1.43		0.00	3.0	31.8	100.99
14	24.06	2.09	0.69	4.52		3.2 1.39		0.2 0.03	1.02	32.20	100.4 66.00 100.3 65.98 101.4
15	47.5	3.5	1.4	9.6		3.1		0.03	2.8	32.20	100.00
15	24.22	2.03	0.69	4.28		1.34		0.3 0.05	0.94	32.43	65.98
16.	45.6	1.0	1.7	9.7	0.6	3.5		9.1	0.54	30.2	101.4
10.	24.39	0.61	0.88	4.54	0.29	1.59		1.68		32.01	65.99
17	44.9	1.3	2.2	9.7	0.4	2.6		9.0	0.5	30.4	101.0
	24.04	0.79	1.14	4.55	0.20	1.18		1.66	0.18	32.26	66.00
18	46.5	2.4	1.6	10.1		2.8	0.1		4.5	31.5	99.5 65.99
	24.06	1.41	0.80	4.58		2.8 1.23	0.06		1.54	32.31	65.99
19	48.8	1.4	0.1	5.4	0.8 0.37	7.4 3.21	1.9 1.21		2.0 0.68	31.9 32.31	99.7 66.00
	24.94	0.81	0.05	2.42	0.37	3.21	1.21		0.68	32.31	66.00
20	48.9	1.7	0.1	5.1	8.0	7.6 3.27	2.2 1.39		1.8	32.1	100.3 65.99 100.7
	24.80	0.98	0.05	2.26	0.37	3.27	1.39		0.60	32.27	65.99
21	50.9	3.2		7.2		4.9	2.9			31.6	100.7
00	26.37	1.89		3.26		2.15	1.87 2.0			32.44	67.98 101.2
22	48.1	5.5		11.0			2.0			34.6	101.2
22	22.79	2.96	1 17	4.56	0.12	1.00	1.18	0.60	0.22	32.50	63.99
23	46.99 22.37	8.31 4.50	1.17 0.54	9.67 4.03	0.12 0.05	1.09 0.44		0.68 0.11	0.33 0.10	33.61 31.78	102.4 64.00
24	45.81	5.22	2.38	10.0	0.03	1.43		0.11	0.10	32.72	09.50
24	22.60	2.93	1.14	10.9 4.73		0.60				32.72	98.50 64.00
25	45.6	6.61	1.14	9.42	0.12	3.27	0.13	0.05	0.20	32.00	99.5
20	23.10	3.81	1.94 0.96	4.18	0.06	3.27 1.40 2.88	0.13 0.08	0.03	0.07	32.2 32.33	99.5 66.00
26	43.8	8.69	1.34	9.19	0.20	2.88	0.12	0.29	0.81	31.7	99.0
	22.36	5.05	0.66	4.11	0.09	1.25 2.99	0.88	0.05	0.27 0.16	32.08	66.00 98.9
27	43.4	8.86	1.30	9.70	0.15	2.99	0.10	0.11	0.16	32.1	98.9
	22.07	5.13	0.64	4.32	0.07	1.29	0.06	0.02	0.05	32.35	66.00 99.73 65.99
28	45.55	6.35	1.88	8.81	0.63	3.55 1.54	Traces	1.28	0.03	31.65	99.73
	23.29	3.69	0.93	3.94	0.29	1.54		0.23	0.01	32.07	65.99
29	44.8	9.11	0.61 0.30	10.2 4.47	0.22	2.80 1.19	0.10	Traces	0.17	32.4	100.4 66.00
	22.45	5.19	0.30	4.47	0.10	1.19	0.06		0.06	32.18	66.00
30	46.1	7.15	1.81	9.61	0.25 0.11 0.13	3.19 1.37	0.10	0.01	0.25 0.08 1.10	31.8	100.3 66.00 101.4
	23.29	4.11	0.89	4.25	0.11	1.37	0.06 0.13		0.08	31.84	66.00
31	46.9	6.65	0.87	9.55	0.13	3.58	0.13	0.16	1.10	32.3	101.4
20	23.49	3.79	0.42	4.19	0.06	1.52	0.08	0.03	0.36	32.06	66.00
32	45.7	8.59	1.29	9.57	0.11	3.91	Traces	0.36	0.14	31.92	101.6
33	22.85	4.89	0.63	4.19	0.05	1.66	0.16	0.06	0.05	31.63	66.01
33	47.1 23.45	7.03 3.98	1.25 0.60	9.46 4.12	0.71 0.32	3.66 1.55	0.16	0.21 0.04	0.47 0.16	32.1 31.68	102.1 66.00
34	23.45 44.6	9.24	1.36	9.73	0.32	2.93	0.10 0.12	0.04	0.16	32.15	100.96
34	22.33	5.26	0.66	4.26	0.12	1.24	0.12	0.26	0.45	31.92	65.99
35	49.01	9.78	0.00	7.84	0.00	4.75	0.00	0.04	0.15	32.2	103.58
33	24.72	5.61		3.46		2.03				32.18	68.00
36	40.89	4.41	5.36	10.2		0.38	2.80			32.38	98.45
20	20.44	2.51	2.60	4.46		0.16	1.75			32.08	64.00
37	44.07	5.19	5.46	10.2		1.26	2.90			32.66	99.82
	21.76	2.92	2.62	4.42		0.53	1.79			31.96	66.00

Notes: (An. 2) Pb 0.69% (0.11 f.u.), insol. res. 0.75%; (An. 3) Pb 0.96% (0.15 f.u.); (An. 4) insol. res. 2.12%; (An. 5) Pb 0.26% (0.04 f.u.), insol. res. 1.68%; (An. 8) insol. res. 0.88%; (An. 23) Ag 0.11% (0.03 f.u.), Sn 0.16% (0.04 f.u.), Sb 0.14% (0.03 f.u.), Mn 0.03% (0.02 f.u.), (An. 7) analysis is sample from the Bancairoun deposit (Levy, 1966); (An. 24) analysis is sample from the Radka deposit (Kovalenker et al., 1966); (An. 36 and 37) analyses are samples from the Rajpura-Dariba deposit, India (Mozgova et al., 1992); other analyses are samples from the Tsumeb deposit: (An. 1 and 8) after Francotti et al., 1965; (An. 2) after Pufahl, 1922; (An. 3, 4, and 5) after Viene et al., 1968; (An. 6) after Levy, 1966; (An. 9—20) after Springer, 1969; (An. 21-22) after Geier et al., 1970; (An. 23) after Spiridonov, 1987; (An. 25-34) after Spiridonov et al., 1992; (An. 35) after Khoroshilova et al., 1988.

 $\it Table~4.~ \textbf{Formula based on recalculated germanite analyses}$ 

Nº	Formula	Valence ba ± Δ	Me/S	
1	$Cu+_{20}(Cu^{2+}{}_{1.92}Fe^{2+}{}_{2.09}Zn_{0.61})_{4.62}Fe^{3+}{}_{2}(Ge^{4+}{}_{4.13}As^{5+}{}_{1.07})_{5.2}S_{32}.$	-7.13	% 11.	0.990
	$Cu+_{16}(Cu^{2}+_{5.92}Zn_{0.61})_{6.53}Fe^{3}+_{4.09}(Ge^{4}+_{4.13}As^{5}+_{1.07})_{5.20}S_{32\cdot 17}$	-1.14	1.7	
2	$Cu+_{20}(Cu^{2+}{_{3.38}}Fe^{2+}{_{2.23}}Zn_{1.31}Pb^{2+}{_{0.11}})_{7.03}Fe^{3+}{_{2}(Ge^{4+}{_{2.79}}As^{5+}{_{2.20}})_{4.99}}S_{31\cdot 98}$	-1.74	2.7	1.064
3	$Cu +_{20} (Cu^{2+} +_{1.57} Fe^{2+} +_{2.55} Zn_{1.96} Pb^{2+} +_{0.15})_{6.23} Fe^{3+} +_{2} (Ge^{4+} +_{4.57} Ga^{3+} +_{0.86} As^{5+} +_{0.60})_{6.03} S_{31\cdot 74}$	-1.16	1.8	1.079
4	$Cu^{+}_{20}(Cu^{2+}_{3.98}Fe^{2+}_{0.74}Zn_{1.32})_{6.04}Fe^{3+}_{2}(Ge^{4+}_{4.02}As^{5+}_{1.85})_{5.87}S_{32\cdot09}$	-0.77	1.2	1.057
5	$Cu +_{20} (Cu^{2} +_{0.38} Fe^{2} +_{4.29} Zn_{1.79} Pb^{2} +_{0.04})_{6.5} Fe^{3} +_{2} (Ge^{4} +_{3.18} As^{5} +_{2.13})_{5.31} S_{32 \cdot 19}$	-2.01	3.1	1.049
6	$Cu +_{20} (Cu^{2} +_{1.91} Fe^{2} +_{1.78} Zn_{0.72})_{4.41} Fe^{3} +_{2} (Ge^{4} +_{4.21} As^{5} +_{1.39})_{5.60} S_{33 \cdot 99}$	-9.37	14.	
	$Cu+_{16}(Cu^{2+}{}_{5.91}Zn_{0.72})_{6.04}Fe^{3}+_{3.78}(Ge^{4}+_{4.21}As^{5}+_{1.39})_{5.60}S_{33\cdot 99}$	-3.59	5.3	0.941
7	$Cu+_{20}(Cu^{2}+_{3.50}Fe^{2}+_{2.89})_{6.39}Fe^{3}+_{2}(Ge^{4}+_{4.16}As^{5}+_{1.80})_{5.96}S_{31\cdot 65}$	+1.12	1.7	1.085
8	$Cu +_{20} (Cu^{2} +_{3.67} Fe^{2} +_{1.95} Zn_{1.64})_{7.26} Fe^{3} +_{2} (Ge^{4} +_{4.26} As^{5} +_{2.16})_{6.44} S_{32\cdot 30}$	+3.84	5.6	
	$Cu^{+}{}_{22}\!(Cu^{2+}{}_{1.67}\!Fe^{2+}{}_{1.95}\!Zn_{1.64})_{5.26}Fe^{3+}{}_{2}(Ge^{4+}{}_{4.26}\!As^{5+}{}_{2.16})_{6.44}\!S_{32\cdot30}$	+1.84	2.8	1.105
9	$Cu +_{20} (Cu^{2+} +_{3.19} Fe^{2+} +_{2.18} Zn_{0.59})_{5.96} Fe^{3+} +_{2} (Ge^{4+} +_{4.37} Ga^{3+} +_{0.05} As^{5+} +_{1.51})_{5.93} S_{32 \cdot 11}$	-1.12	1.7	1.055
10	$Cu +_{20} (Cu^{2+} +_{3.83} Fe^{2+} +_{1.87} Zn_{0.40})_{6.10} (Fe^{3+} +_{1.9} W^{4+} +_{0.10})_{2} (Ge^{4+} +_{4.02} As^{5+} +_{1.82})_{5.84} S_{32\cdot06}$	-0.64	1.0	1.059
11	$Cu^{+}{}_{20}(Cu^{2+}{}_{3.36}Fe^{2+}{}_{2.14}Zn_{0.60})_{6.10}(Fe^{3+}{}_{1.83}Mo^{4+}{}_{0.17})_{2}(Ge^{4+}{}_{4.31}As^{5+}{}_{1.44})_{5.75}S_{32\cdot15}$	-1.66	2.6	1.054
12	$Cu+_{20}(Cu^{2}+_{3.81}Fe^{2}+_{1.69}Zn_{0.45})_{5.95}(Fe^{3}+_{1.51}Mo^{4}+_{0.17}W^{4}+_{0.32})_{2}(Ge^{4}+_{4.03}As^{5}+_{1.74})_{5.77}S_{32\cdot 27}$	-1.5	2.3	1.045
13	$Cu +_{20} (Cu^{2+} +_{3.20} Fe^{2+} +_{1.97} Zn_{0.65})_{5.82} (Fe^{3+} +_{1.4} W^{4+} +_{0.60})_2 (Ge^{4+} +_{4.43} As^{5+} +_{1.43})_{5.86} S_{32\cdot 31}$	-1.51	2.3	1.042
14	$Cu +_{20} (Cu^{2+} +_{4.06} Fe^{2+} +_{1.14} Zn_{0.69})_{5.89} (Fe^{3+} +_{0.95} Mo^{4+} +_{1.02} W^{4+} +_{003})_2 (Ge^{4+} +_{4.52} As^{5+} +_{1.39})_{5.91} S_{32\cdot 20}$	-1.56	2.4	1.050
15	$Cu +_{20} (Cu^{2} +_{4.22} Fe^{2} +_{1.02} Zn_{0.69})_{5.93} (Fe^{3} +_{1.01} Mo^{4} +_{0.94} W^{4} +_{0.05})_{2} (Ge^{4} +_{4.28} As^{5} +_{1.34})_{5.62} S_{32 \cdot 43}$	-3.13	4.8	1.036
16	$Cu +_{20} (Cu^{2} +_{4.39} Fe^{2} +_{0.29} Zn_{0.88})_{5.56} (Fe^{3} +_{0.32} W^{4} +_{1.68})_{2} (Ge^{4} +_{4.54} Ga^{3} +_{0.29} As^{5} +_{1.59})_{6.42} S_{32 \cdot 01}$	+1.76	2.7	1.060
17	$Cu^{+}{}_{20}(Cu^{2+}{}_{4.04}Fe^{2+}{}_{0.63}Zn_{1.14})_{5.81}(Fe^{3+}{}_{0.16}Mo^{4+}{}_{0.18}W^{4+}{}_{1.66})_{2}(Ge^{4+}{}_{4.55}Ga^{3+}{}_{0.20}As^{5+}{}_{1.18})_{5.93}S_{32\cdot26}$	-0.54	0.8	1.046
18	$Cu +_{20} (Cu^{2} +_{4.06} Fe^{2} +_{1.01} Zn_{0.80})_{5.87} (Fe^{3} +_{0.40} V^{3} +_{0.06} Mo^{4} +_{1.54})_{2} (Ge^{4} +_{4.58} As^{5} +_{1.23})_{5.81} S_{32 \cdot 31}$	-2.41	3.7	1.043
19	$Cu +_{20} (Cu^{2} +_{4.94} Fe^2 +_{0.70} Zn_{0.05})_{5.69} (Fe^3 +_{0.11} V^3 +_{1.21} Mo^4 +_{0.68})_2 (Ge^4 +_{2.42} Ga^3 +_{0.37} As^5 +_{3.21})_{6.00} S_{32\cdot31}$	-0.56	0.9	1.042
20	$Cu+_{20}(Cu^{2+}+_{4.80}Fe^{2+}+_{0.97}Zn_{0.05})_{5.82}(Fe^{3+}+_{0.01}V^{3+}+_{1.39}Mo^{4+}+_{0.60})_2(Ge^{4+}+_{2.26}Ga^{3+}+_{0.37}As^{5+}+_{3.27})_{5.90}S_{32\cdot 27}$	-0.4	0.6	1.045
21	$Cu^{+}_{22}(Cu^{2+}_{4.37}Fe^{2+}_{1.76})_{6.13}(Fe^{3+}_{0.13}V^{3+}_{1.87})_{2}(Ge^{4+}_{3.26}As^{5+}_{2.15})_{5.41}S_{32\cdot 44}$	-0.83	1.3	1.096
22	$\text{Cu+}_{16}(\text{Cu}_{2}+_{6.79}\text{Fe}_{2}+_{2.14})_{8.93}(\text{Fe}_{3}+_{0.82}\text{V}_{5}+_{1.18})_{2}\text{Ge}_{4}+_{4.56}\text{S}_{32\cdot50}$	-6.9	11.	
	$Cu^{+}_{16}Cu^{2+}_{6.79}Fe^{3+}_{2.96}(Ge^{4+}_{4.56}V^{3+}_{1.18})_{5.74}S_{32\cdot 50}$	-2.4	3.6	0.969
23	$(Ag^{+}_{0.03}Cu^{+}_{16})_{16.03}(Cu^{2+}_{6.37}Mn^{2+}_{0.02}Zn_{0.54})_{6.93}(Fe^{3+}_{4.50}Mo^{4+}_{0.10}$			
	$W^{4+}{}_{0.11}Sb^{3+}{}_{0.03})_{4.74}(Ge^{4+}{}_{4.03}Sn^{4+}{}_{0.04}Ga^{3+}{}_{0.05}As^{5+}{}_{0.44})_{4.56}S_{31\cdot 78}$	-0.71	1.1	0.904
24	$Cu+_{16}(Cu^{2}+_{6.60}Zn_{0.14})_{7.74}Fe^{3}+_{2.93}(Ge^{4}+_{4.73}As^{5}+_{0.60})_{5.33}S_{32\cdot00}$	-1.81	2.8	1.00
25	$Cu+_{20}(Cu^2+_{3.1}Fe^2+_{1.97}Zn_{0.96})_{6.03}(Fe^3+_{1.84}V^3+_{0.06}W^4+_{0.01}Mo^3+_{0.07})_2(Ge^4+_{4.18}Ga^3+_{0.06}As^5+_{1.40})_{5.64}S_{32\cdot 33}$	-2.69	4.2	1.040
	$Cu+_{20}(Cu^{2+}+_{3.10}Fe^{2+}+_{1.81}Zn_{0.96})_{5.87}Fe^{3+}+_{2}$	-2.376	3.7	
	$(Ge^{4+}_{4.18}Ga^{3+}_{0.06}As^{5+}_{1.40}V^{5+}_{0.08}W^{4+}_{0.01}Mo^{3+}_{0.07})_{5.80}S_{32\cdot 33}$			
26	$Cu +_{20} (Cu^2 +_{2.36} Fe^2 +_{3.45} Zn_{0.66})_{6.47} (Fe^3 +_{1.6} V^3 +_{0.06} W^4 +_{0.05} Mo^3 +_{0.27})_2 (Ge^4 +_{4.11} Ga^3 +_{0.09} As^5 +_{1.25})_{5.45} S_{32\cdot08}$	-2.21	3.4	1.057
27	$\text{Cu+}_{20}(\text{Cu}^{2}+_{2.07}\text{Fe}^{2}+_{3.26}\text{Zn}_{0.64})_{5.97}(\text{Fe}^{3}+_{1.87}\text{V}^{3}+_{0.06}\text{W}^{4}+_{0.02}$	-2.8	4.3	1.040
	$Mo^{3+}_{0.05})_2(Ge^{4+}_{4.32}Ga^{3+}_{0.07}As^{5+}_{1.29})_{5.68}S_{32\cdot35}$			
	$Cu+_{20}(Cu^{2}+_{207}Fe^{2}+_{3.12}Zn_{0.64})_{5.84}Fe^{3}+_{2}(Ge^{4}+_{4.32}Ga^{3}+_{0.07}As^{5}+_{1.29}V^{5}+_{0.06}W^{4}+_{0.02}Mo^{3}+_{0.05})_{5.81}S_{32:35}$	-2.45	3.8	
28	$Cu^{+}{}_{20}(Cu^{2}+{}_{3.29}Fe^{2}+{}_{1.92}Zn_{0.93})_{6.15}(Fe^{3}+{}_{1.76}W^{4}+{}_{0.23}Mo^{3}+{}_{0.01})_{2}(Ge^{4}+{}_{3.94}Ga^{3}+{}_{0.29}As^{5}+{}_{1.54})_{5.77}S_{32\cdot07}$	-1.28	2.0	1.057
29	$\text{Cu+}_{20}(\text{Cu2+}_{2.45}\text{Fe2+}_{3.31}\text{Zn}_{0.3})_{6.06}(\text{Fe3+}_{1.88}\text{V3+}_{0.06}\text{Mo3+}_{0.06})_{2}(\text{Ge4+}_{4.47}\text{Ga3+}_{0.10}\text{As5+}_{1.19})_{5.76}\text{S}_{32*18}$	-2.11	3.3	1.051
	$Cu+{}_{20}(Cu^2+{}_{2.45}Fe^2+{}_{3.19}Zn_{0.3}){}_{5.94}Fe^3+{}_{2}(Ge^4+{}_{4.47}Ga^3+{}_{0.10}As^5+{}_{1.19}V^5+{}_{0.06}Mo^3+{}_{0.06}){}_{5.88}S_{32\cdot18}$	-1.87	2.9	
30	$Cu^{+}{}_{20}(Cu^{2}+{}_{3.29}Fe^{2}+{}_{2.25}Zn_{0.89})_{6.43}(Fe^{3}+{}_{1.86}V^{3}+{}_{0.06}Mo^{3}+{}_{0.08})_{2}(Ge^{4}+{}_{4.25}Ga^{3}+{}_{0.11}As^{5}+{}_{1.37})_{5.73}S_{31\cdot84}$	-0.64	1.0	1.071
31	$Cu^{+}{}_{20}(Cu^{2+}{}_{3.49}Fe^{2+}{}_{2.26}Zn_{0.42}){}_{6.17}(Fe^{3+}{}_{1.53}V^{3+}{}_{0.08}W^{4+}{}_{0.03}Mo^{3+}{}_{0.36}){}_{2}(Ge^{4+}{}_{4.19}Ga^{3+}{}_{0.06}As^{5+}{}_{1.52}){}_{5.77}S_{32\cdot06}$	-1.21	1.9	1.057
32	$\begin{array}{l} \text{Cu+}_{20}(\text{Cu}^2+_{2.85}\text{Fe}^2+_{3.00}\text{Zn}_{0.63})_{6.48}(\text{Fe}^3+_{1.89}\text{W}^4+_{0.06}\text{Mo}^3+_{0.05})_2(\text{Ge}^4+_{4.19}\text{Ga}^3+_{0.05}\text{As}^5+_{1.66})_{5.9}\text{S}_{31\cdot63} \end{array}$	+0.97	1.5	1.085
33	$Cu^{+}{}_{20}(Cu^{2+}{}_{3.45}Fe^{2+}{}_{2.28}Zn_{0.60})_{6.33}[Fe^{3+}{}_{1.70}V^{3+}{}_{0.10}W^{4+}{}_{0.04}Mo^{3+}{}_{0.16}]_2(Ge^{4+}{}_{4.12}Ga^{3+}{}_{0.32}As^{5+}{}_{1.55})_{5.99}S_{31\cdot68}$	-0.64	1.0	1.083
34	$\begin{array}{llllllllllllllllllllllllllllllllllll$	-1.37	2.1	1.069
35	$\begin{array}{llllllllllllllllllllllllllllllllllll$	+0.29	0.4	1.113
	$cu^{+}_{16}(cu^{2+}_{4.44}Zn_{2.60})_{7.04}Fe^{3+}_{2.51}(Ge^{4+}_{4.46}As^{5+}_{0.16}V^{5+}_{1.75})_{6.37}S_{32\cdot08}$	+0.84	1.3	0.995
	$\begin{array}{llllllllllllllllllllllllllllllllllll$	-2.66	4.1	
37	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	-3.41	5.3	1.065
	$\begin{array}{lll} \text{Cu+}_{20}(\text{Cu}^{2}+_{1.76}\text{Fe}^{2}+_{1.62}\text{Zn}_{2.62})_{6.00}(\text{Fe}^{3}+_{1.30}\text{V}^{3}+_{0.70})_{2}(\text{Ge}^{4}+_{4.42}\text{As}^{5}+_{0.53}\text{V}^{5}+_{1.09})_{6.04}\text{S}_{31.96} \end{array}$	-0.14	0.2	

**Notes:** All Cu over 16, 20, and 22 atoms in the analyses recalculated based on, respectively, 64, 66, and 68 atoms, is divalent;  $Sb^{3+}$ ,  $V^{3+}$ ,  $Mo^{3+}$ , and  $W^{4+}$  substitute  $Fe^{3+}$ ;  $Sn^{4+}$ ,  $As^{5+}$ ,  $Ga^{3+}$ , and  $V^{5+}$  substitute  $Ge^{4+}$ .

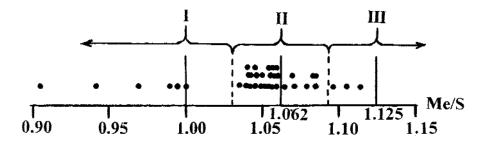


Fig. 3. Ratio Me/S in analyses of germanite. Groups of the analyses: (I) analyses with the relationship Me/S close to 1; (II) analyses with the relationship Me/S close to 1.062; and (III) analyses with the relationship Me/S close to 1.125.

This isomorphism was earlier revealed in another complex Ge sulfide, renierite (Bernstein, 1986). In renierite, this dependence is more clearly pronounced than in germanite, possibly due to a more complex character of isomorphism in the latter (because germanite contains admixtures of V, Mo, W, and Ga, which are absent in renierite). According to data of E. Spiridonov (1987), in germanite  $Fe^{3+}$  occupies the same site that is occupied by  $V^{3+}$  in colusite; therefore,  $V^{3+}$  can substitute  $Fe^{3+}$  in germanite as well.

A recalculation of the analyses has demonstrated that only 28 analyses from among 37 ones are adequately recalculated to the formula with 66 atoms in the unit cell (in 6 of them, the valence balance slightly exceeds 3%). Six analyses can only be recalculated to the formula with 64 atoms in the unit cell (in 2 of the 6 analyses, the valence balance slightly exceeds 3%), and 3 analyses are well recalculated only on condition that the unit cell contains 68 atoms (Table 4). The Me/S ratio in the analyses varies from 0.904 to 1.113, grouping about the values 1.00, 1.062, and 1.125, corresponding to the Me/S ratios equal to 32:32, 34:32, and 36:32 (Fig. 3). Thus, the cation/anion ratio in real analyses is not constant. This suggests that we deal either with solid solutions or with three different, but similar in the chemical composition and properties, minerals. The second assumption is more probable. Were there an area of solid solutions, the Me/S ratio would be continuous from 1 to 1.125.

So, the 37 analyses are subdivided into three groups calculated based on 64, 66, and 68 atoms in the unit cell. For each group, variations of the principal components (Table 5), their average values (Table 6), as well as the average values of the components occupying different sites in the crystal structure of the mineral (Table 7) are specified. The Cu content generally increases with increasing the number

of atoms in the unite cell; the content of Ge and divalent cations decreases in this same direction, which once more illustrates the existing obvious, although relatively slight, differences in the three groups of chemical analyses of germanite, as well as the presence of the isomorphism  $Zn^{2+} + Ge^{4+} \rightarrow Cu^+ + As^{5+}$ . Empirical formulae of the average analyses calculated based on different numbers (64, 66, and 68) of atoms in the unit cell will be as follows:

 $Cu^{+}_{16}(Cu^{2+}_{6.0}Fe^{2+}_{0.8})_{6.8}Fe^{3+}_{3.5}(Ge^{4+}_{4.4}As^{5+}_{1.1})_{5.5}S_{32.2}$  $\Delta = -1.2; 1.9\%$ 

 $Cu^{+}_{20}(Cu^{2+}_{3.3}Fe^{2+}_{2.0}Zn_{0.8})_{6.1}Fe^{3+}_{2.0}(Ge^{4+}_{4.2}As^{5+}_{1.6})_{5.8}S_{32.1}$   $\Delta=-1.2;\,1.9\%$ 

 $\text{Cu+}_{22}(\text{Cu}^{2}+_{29}\text{Fe}^{2}+_{24}\text{Zn}_{0.6})_{5.9}\text{Fe}^{3}+_{2.0}(\text{Ge}^{4}+_{4.0}\text{As}^{5}+_{2.1})_{5.1}\text{S}_{322}$   $\Delta=-1.9;\,2.9\%$ 

The conclusion on the existence of the three different mineral species can also be derived through drawing an analogy between germanite, on the one hand, and chalcopyrite, talnakhite, mooihoekite, and haycockite, on the other. Until the 1970s, the four last-mentioned minerals were mistaken as a single mineral, chalcopyrite, because of the closeness of their chemical composition and physical properties. In 1967, the work by L. Cabri (1967) was published on cubic chalcopyrite that was found to be an individual mineral species, talnakhite; within 5 years, 2 more mineral species, mooihoekite and haycockite, were discovered (Cabri et al., 1972). Their crystal structures, as well as that of germanite, represent superstructures from the sphalerite structure. As is seen from Table 8, their Me/S ratios are the same as those, around which these ratios are grouped in the real analyses of germanite. This suggests an existence of three independent minerals. Based on the above-presented formulae of chalcopyrite, talnakhite, and mooihoekite, it is easy to obtain germanite formulae with the Me/S ratio equal to 1, 1.062, and 1.125.

In case of substitution  $Fe^{3+}_{13} \rightarrow Me^{2+}_{7} + (Ge^{4+}_{5}As^{5+})_{6}$  in chalcopyrite  $-Cu^{+}Fe^{3+}S_{2} \rightarrow$ 

Table 5. Variations in concentrations of the principal components in the chemical composition of germanite, in wt. % (upper row) and in f.u. (lower row)

An.calc.,		Cu	F	₹e	Zn		(	Ge	Α	As	Ge + A	s+Ga
based on:	from	to	from	to								
64 atoms	40.9	48.1	5.2	8.3	0	5.4	9.7	10.9	0	2.6	11.0	13.4
	20.4	22.8	2.9	4.5	0	2.6	4.1	4.7	0	1.07	4.6	6.4
66 atoms	39.4	48.8	1.3	10.7	0	5.5	5.1	10.1	1.3	7.6	11.2	13.8
	20.4	24.9	8.0	6.3	0	2.6	2.3	4.6	0.5	3.27	4.9	6.0
68 atoms	43.6	50.9	3.2	9.8	0	3.10	7.2	9.0	4.7	4.9	12.1	13.7
	23.7	26.4	1.9	5.6	0	1.6	3.3	4.3	2.0	2.2	5.4	6.4

Table 6. Average concentrations of the principal components in the chemical composition of germanite, in wt. % (upper row) and in f.u. (lower row)

An.calc., based on:	Cu	Fe	Zn Fe	e+Zn	Ge	As Ge -	-As+Ga S		
64 atoms	45.2	6.3	1.95	8.2	10.2	1.5	12.6	33.6	
	23.3	3.4	0.9	4.3	4.3	0.6	5.4	32.2	
66 atoms	45.5	6.0	1.6	7.6	9.1	3.5	13.0	31.7	
	23.3	3.5	0.8	4.3	4.1	1.6	5.7	32.1	
68 atoms	47.8	6.5	1.0	7.5	8.0	4.8	12.8	31.1	
	24.9	3.8	0.5	4.3	3.7	2.1	5.8	32.2	

Table 7. Average concentrations of the principal components in the chemical composition of germanite, in f.u.

An.calc.,						Fe <sup>3+</sup> + V <sup>3+</sup>	+		Ge+As+
based on:	Cu+	Cu <sup>2+</sup>	Fe <sup>2+</sup>	$Zn^{2+}$	$\Sigma Me^{2+}$	Mo+W	Ge <sup>4+</sup>	$As^{5+}$	Ga + V <sup>5+</sup>
64 atoms	16	6.0	8.0	0.0	6.8	3.5	4.4	1.1	5.5
66 atoms	20	3.3	2.0	8.0	6.1	2.0	4.2	1.6	5.8
68 atoms	22	2.9	2.4	0.6	5.9	2.0	4.0	2.1	6.1

Table 8. Structural characteristics of germanite and minerals of the chalcopyrite group

Mineral	Formula	Sp. gr	Z	Unit cell par	rameters, i c	n Å Reference	Me/S
Chalcopyrite Talnakhite Mooihoekite Germanite	$\begin{array}{c} Cu^{+}Fe^{3} + S_{2} \rightarrow Cu^{+}_{16}Fe^{3} + {}_{16}S_{32} \\ Cu^{+}_{9}Fe_{8}S_{16} \rightarrow Cu^{+}_{18}Fe^{2} + {}_{2}Fe^{3} + {}_{14}S_{32} \\ Cu^{+}_{9}Fe_{9}S_{16} \rightarrow Cu^{+}_{18}Fe^{2} + {}_{8}Fe^{3} + {}_{10}S_{32} \\ Cu_{26}Fe_{4}Ge_{4}S_{32} \rightarrow Cu^{+}_{16}Cu^{2} + {}_{10}Fe^{3} + {}_{4}Ge_{4}S_{32} \end{array}$	I42 <u>d</u> I43 <u>m</u> P42m P43n	4 16 8 1	5.281 10.59 10.58 10.58	10.401 5.37 62(5)	Hall <i>et al.</i> ,1973 Cabri, 1967 Cabri <i>et al.</i> , 1972 Tettenhorst <i>et al.</i> , 19	1 1.062 1.125 84 1.062

 $Cu_{16}^{+}Fe_{3+}^{+}{}_{16}^{-}S_{32}$ , germanite —  $Cu_{16}^{+}Me_{2+}^{+}$ ,  $Fe_{3+}^{+}{}_{3}(Ge_{32}^{+}{}_{5}As_{32}^{5+})_{6}^{+}S_{32}$ , with the ratio Me/S = 1 is formed.

In case of substitution Fe³+ $_{12} \rightarrow Cu^+{}_2 + Me^2{}^+{}_4 + (Ge^4{}^+{}_4As^5{}^+{}_2)_6$  in talnakhite —  $Cu^+{}_9Fe^2{}^+Fe^3{}^+{}_7S_{16} \rightarrow Cu^+{}_{18}Fe^2{}^+{}_2Fe^3{}^+{}_{14}S_{32}$ , germanite  $Cu^+{}_{20}Me^2{}^+{}_6Fe^3{}^+{}_2(Ge^4{}^+{}_4As^5{}^+{}_2)_6S_{32}$  with the ratio Me/S = 1.062 is formed.

In case of substitution Fe²+²+Fe³+\*\* → Cu²+\* + Ge⁴+\*\* in mooihoekite Cu³+\*\* Ge²+\*\* Fe³+\*\* 5S₁6 → Cu³+\*\* Fe³+\*\* 6S₃2\*, germanite Cu³+\*2 Me²+\* 6Fe³+\*\* 2Ge⁴+\* 6S₃2\* with the ratio Me/S = 1.125 is formed. Taking into account the isomorphism Zn²+ + Ge⁴+ → Cu²+ + As⁵+\*, the formula appears as Cu³+\* 2Me²+\* 6Fe³+\*\* 2(Ge,AS)6S₃2\*, which corresponds to the formula by E. Spiridonov with co-authors (1992). In all the formulae, Me²+ is Cu²+\*, Fe²+\*, Zn²+\*.

The similarity between these formulae to those obtained through recalculation of the average analyses for each group is obvious.

That once more confirms the logic of the conclusion on the existence of three mineral species chemically close to germanite.

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### ON GERMANOCOLUSITE FROM KIPUSHI (KATANGA)

Svetlana N. Nenasheva

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, sn@fmm.ru

#### Leonid A. Pautov

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, sn@fmm.ru

Bornite from the Kipushi ore deposit was studied in Sample 64332 from the collection of the Fersman Mineralogical Museum. It was revealed to contain small oval inclusions of germanocolusite associated with renierite, tennantite, chalcopyrite, and sphalerite. Germanocolusite from Kipushi contains slightly more Zn and V and less As, as compared to germanocolusite from the type locality. A new crystallochemical formula proposed for germanocolusite takes into account the isomorphism  $Zn^{2+} + Ge^{4+} \rightarrow As^{5+} + Cu^+$ , characteristic for complex sulfides of Ge. This is the first find of germanocolusite at the Kipushi deposit. 5 tables and 7 references

Germanocolusite was approved as a mineral species in 1992 (Spiridonov et al., 1992); but even earlier, «yellow germanites» were distinguished among germanites, in whose composition significant amounts of V and As were determined and which referred to as vanadium or vanadium – arsenic germanites. Spiridonov et al. (1992) demonstrated that varieties of the V or V−As germanites, in whose formulas Ge prevailed over As, represented germanocolusites. These researchers (Spiridonov et al., 1992) presented 3 analyses of germanocolusite from the ore deposits Urup, Russia; Tsumeb, Namibia; and Chelopech, Bulgaria (Table 1, An. 1-3). Another analysis of a Ge sulfide from Urup, compositionally close to germanocolusite, was published by Kachalovskaya et al. (1975) and later repeated in the work by Spiridonov et al. (1986) under the name «colusite-Ge» (Table 1, An. 4). The concentration of Ge in this mineral exceeds that of As. The crystallochemical formula proposed for germanocolusite by Spiridonov et al. (1992) is as follows:  $Cu_{18}^{+}Cu_{2+4}^{2+}(Cu_{2+1}^{2+}Fe_{1}Zn)_{4}V_{3+2}^{3+}X_{4+6}^{4+}S_{32}$ where  $X^{4+} = Ge^{4+}$ ,  $(As, Sb^{5+} + As, Sb^{3+}) : 2$ ; Sn4+, Mo4+, Te4+.

A recalculation of the germanocolusite analyses presented in the work (Spiridonov et~al.,~1992) to this ideal formula revealed that 2 analyses from 3 ones were not electrically neutral (valence balances 4.2 and 3.5%) (Table 2, An. 1 and 3). Analyses are considered electrically neutral if their valence balances are no more than 3%. If to take into account the isomorphism  $Ge^{4+} + Zn^{2+} \rightarrow As^{5+} + Cu^+$ , characteristic for complex Ge sulfides, than the formula proposed by the discoverers can be presented as  $Cu^+_{18+x}Cu^{2+}_4(Cu^{2+},Fe,Zn)_{4-x}V^{3+}_2$  ( $Ge^{4+}_{6-x}As^{5+}_x)_6S_{32}$ , or  $Cu^+_{18+x}Cu^{2+}_4Me^2_{4-x}V^{3+}_2$  ( $Ge^{4+}_{6-x}As^{5+}_x)_6S_{32}$ , where  $0 \leqslant x \leqslant 3$ . On recal-

culation to this formula, all analyses from the work (Spiridonov *et al.*, 1992) are electrically neutral (Table 2), which is evidence in favor of the formula that takes into account the isomorphous substitution  $Ge^{4+} + Zn^{2+} \rightarrow As^{5+} + Cu^+$ .

We found germanocolusite in Sample 64332 that was registered as bornite from the Kipushi (Katanga) ore deposit in the collection of the Fersman Mineralogical Museum. The germanocolusite is present as small oval grains up to  $10-15~\mu m$  in size, confined as a rule to renierite that, in its turn, is enclosed in bornite associated with tennantite, sphalerite, and chalcopyrite. Under reflected light, the germanocolusite is pinkish lilac, isotropic. The reflection intensity is lower than that of chalcopyrite and tennantite and higher than that of bornite and sphalerite. The particles are so fine that their X-ray identification is impossible.

The electron probe microanalysis was realized on a JEOL JXA-50A microprobe with a TRACOR-Xr energy-dispersive spectrometer (accelerating voltage 20 kV, beam current 30 • 10-9 A). The concentrations were calculated using the ZAF correction. The following standards (analytical lines) were used: ZnS  $\begin{array}{lll} (Zn_{K\alpha} \ \ and \ \ S_{K\alpha}) \text{,} & GaAs \ \ (As_{K\alpha} \ \ and \ \ Ga_{K\alpha}) \text{,} \\ Cu_2FeSnS_4 \left(Cu_{K\alpha}, Fe_{K\alpha}, Sn_{L\alpha}, S_{K\alpha} \right) \text{,} \ V \ and \ Ge \ me- \\ \end{array}$ tallic ( $V_{K\alpha'}$   $Ge_{K\alpha'}$   $Ge_{K\beta}$ ). The composition of germanocolusite from Kipushi is presented in Tables 3 and 4. A pronounced positive correlation is traced between Cu and As, also between Zn and Ge, and negative correlation is traced between Ge and As. All analyses calculated based on the formula taking into account the isomorphous substitution  $Ge^{4+} + Zn^{2+} \rightarrow As^{5+} + Cu^{+}$ are electrically neutral within the admissible range of 3%. As is seen from Table 5 that exhibits variations in the principal components of the germanocolusite composition, the

Table 1. Electron microprobe analyses of germanocolusite: in wt. % (upper row) and in f.u. (lower row). (An. 1-3) after (Spiridonov et al., 1992); (An. 4) after Kachalovskaya et al., 1975

Nº.				Element	contents				Σ	Me/S
	Cu	Fe	Zn	Ge	As	Sb	V	S		1110, 5
1	49.69	0.47	0.91	8.62	5.19	80.0	3.22	32.10	101.4	1.064
	24.96	0.27	0.44	3.79	2.21	0.02	2.02	31.96	66	
2	49.22	1.56	0.15	6.55	5.90	0.12	3.19	31.97	100.31	1.059
	24.91	0.90	0.07	2.90	2.53	0.03	2.01	32.06	65.99	
3	48.04	1.54	1.28	9.13	3.38	0.40	3.17	31.05	100.66	1.073
	24.50	0.89	0.63	4.08	1.46	0.11	2.02	31.39	65.99	
4	47.8	1.00	5.5	10.6	2.9		3.1	32.0	102.9	1.102
	23.66	0.56	2.65	4.59	1.22		1.91	31.40	65.99	

Notes: Trace elements: (An. 1): Sn 0.14% (0.04 f.u.), W 0.03 (0.01), Mo 0.67 (0.22), Ag 0.13 (0.04), and Bi 0.15 (0.02); (An. 2): Ga 0.35 (0.16), Sn 0.06 (0.02), W 0.06 (0.01), and Mo 1.18 (0.39); (An 3): Ga 0.17 (0.08), Sn 0.17 (0.08), Ag 0.09 (0.03), and Se 1.08 (0.44). (An. 1 and 4) from the Urup deposit, (An. 2) from Tsumeb, and (An. 3) from Chelopech

 $\it Table~2.$  Recalculated germanocolusite analyses presented in Table 1

Nº	Formulas calculated based on the ideal formula proposed by Spiridonov with co-authors (1992)	Vale: bala:	
	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}, Fe, Zn)_{4}V^{3}_{-2}X^{4}_{-6}S_{32}$	$\pm\Delta$	%
1	$(Cu^{+}_{18.00}Ag^{+}_{0.04})_{18.04}Cu^{2+}_{4}(Cu^{2+}_{2.96}Fe^{2+}_{0.27}Zn_{0.44})_{3.67}(V^{3+}_{2.02}W^{4+}_{0.01}Mo^{3+}_{0.22})_{2.25}$		
	$[Ge^{4+}_{3.79}Sn^{4+}_{0.04}(As^{5+}_{2.21}Sb^{5+}_{0.02}Bi^{5+}_{0.02})_{2.25}]_{6.08}S_{31\cdot 96}$	+2.79	4.2
2	$Cu + {}_{18}Cu^2 + {}_4(Cu^2 + {}_{2.91}Fe^2 + {}_{0.90}Zn_{0.07})_{3.88}(V^3 + {}_{2.01}W^4 + {}_{0.01}Mo^3 + {}_{0.39})_{2.41}$		
	$[Ge^{4+}_{2.90}Ga^{3+}_{0.16}Sn^{4+}_{0.02}(As^{5+}_{2.53}Sb^{5+}_{0.03})_{2.56}]_{5.64}S_{32\cdot 09}$	-1.78	2.7
3	$(Cu^{+}_{18.00}Ag^{+}_{0.03})_{18.3}Cu^{2}_{+4}(Cu^{2}_{+2.50}Fe^{2}_{+0.89}Zn_{0.63})_{4.02}V^{3}_{+2.02}$		
	$[Ge^{4+}{}_{4.08}Ga^{3+}{}_{0.08}Sn^{4+}{}_{0.36}(As^{5+}{}_{1.46}Sb^{5+}{}_{0.11})_{1.57}]_{6.09}(S_{31}_{39}Se_{044})_{31.83}$	+2.32	3.5
4	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{1.66}Fe^{2+}_{0.56}Zn_{2.65})_{4.87}V^{3+}_{1.91}$	+3.13	4.7
	$(Ge^{4+}_{4.59}As^{5+}_{1.22})_{5.81}S_{31\cdot 40}$		
	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{1.66}Fe^{2+}_{0.47}Zn_{2.65})_{4.78}(V^{3+}_{1.91}Fe^{3+}_{0.09})_{4.78}$	+3.22	4.9
	$(Ge^{4+}_{4.59}As^{5+}_{1.22})_{5.81}S_{31\cdot 40}$		
Nº	Formulas calculated based on the ideal formula	Vale	
	$Cu^{+}_{18+x}Cu^{2+}_{4}Me^{2+}_{4-x}V^{3+}_{2}Ge^{4+}_{6-x}As_{x}S_{32}$	bala	
_	(C - A - )	±Δ	%
1	$(Cu^{+}_{20.25}Ag^{+}_{0.04})_{20.29}Cu^{2+}_{4}(Cu^{2+}_{0.71}Fe^{2+}_{0.27}Zn_{0.44})_{1.42}(V^{3+}_{2.02}W^{4+}_{0.01}Mo^{3+}_{0.22})_{2.25}$	. 0 50	0.0
0	$[Ge^{4+}_{3.79}Sn^{4+}_{0.04}(As^{5+}_{2.21}Sb^{5+}_{0.02}Bi^{5+}_{0.02})_{2.25}]_{6.08}S_{31\cdot 96}$	+0.53	8.0
2	$Cu^{+}_{20.56}Cu^{2+}_{4}(Cu^{2+}_{0.35}Fe^{2+}_{0.90}Zn_{0.07})_{1.32}(V^{3+}_{2.01}W^{4+}_{0.01}Mo^{3+}_{0.39})_{2.41}$	0.70	1.0
3	$[Ge^{4+}_{2.90}Ga^{3+}_{0.16}Sn^{4+}_{0.02}(As^{5+}_{2.53}Sb^{5+}_{0.03})_{2.56}]_{5.64}S_{32\cdot 09}$	-0.78	1.2
3	$(Cu^{+}_{19.57}Ag^{+}_{0.03})_{19.6}Cu^{2+}_{4}(Cu^{2+}_{0.93}Fe^{2+}_{0.89}Zn_{0.63})_{2.45}V^{3+}_{2.02}$	+0.75	1.2
4	$[Ge^{4+}_{4.08}Ga^{3+}_{0.08}Sn^{4+}_{0.36}(As^{5+}_{1.46}Sb^{5+}_{0.11})_{1.57}]_{6.09}(S_{31\cdot39}Se_{0\cdot44})_{31.83}$	+0.73	1.2
4	$\begin{array}{l} Cu^{+}{}_{19.22}Cu^{2+}{}_{4}(Cu^{2+}{}_{0.44}Fe^{2+}{}_{0.47}Zn_{2.65})_{3.56}(V^{3+}{}_{1.91}Fe^{3+}{}_{0.09})_{2.00} \\ (Ge^{4+}{}_{4.59}As^{5+}{}_{1.22})_{5.81}S_{31\cdot40} \end{array}$	+2.0	3.1
	(GC · 4.59 · 1.22) 5.81 · 31 · 40	1 2.0	5.1

Table 3. Electron microprobe analyses of germanocolusite from the Kipushi deposit (Sample 64332) in wt. % (upper row) and in f.u. (lower row)

Nº			Elen	nent cont	tents			Σ	Me/S
	Cu	Fe	Zn	Ge	As	V	S		
1	50.14	0.30	3.75	7.98	3.89	3.53	32.17	101.76	1.047
	24.96	0.17	1.82	3.48	1.64	2.19	31.74	66	
2	49.41	0.29	4.31	8.03	4.11	3.68	32.35	102.18	1.045
	24.49	0.16	2.08	3.48	1.73	2.28	31.78	66	
3	49.37	0.50	4.69	8.75	3.57	3.19	31.74	101.81	1.099
	24.68	0.28	2.28	3.82	1.52	1.98	31.44	66	
1	48.94	0.12	4.11	8.79	3.15	3.63	32.37	101.11	1.060
	24.45	0.07	2.00	3.84	1.34	2.26	32.04	66	
5	48.21	0.39	4.24	8.68	2.79	3.43	31.43	99.17	1.076
	24.61	0.22	2.10	3.88	1.21	2.18	31.79	65.99	
6	48.11	0.35	4.91	8.68	2.84	3.58	32.47	100.95	1.062
	24.03	0.20	2.38	3.80	1.20	2.23	32.15	65.99	
!	48.10	0.56	4.84	8.93	2.96	3.65	32.38	101.42	1.065
	23.96	0.32	2.34	3.89	1.25	2.27	31.96	65.99	
3	47.76	0.53	4.89	8.63	2.86	3.44	32.36	100.47	1.050
	23.97	0.30	2.38	3.79	1.22	2.15	32.18	65.99	
)	47.75	0.54	4.87	9.11	2.70	3.47	31.89	100.33	1.072
	24.08	0.31	2.39	4.02	1.16	2.18	31.86	66	
0	47.12	0.36	5.03	9.00	2.90	3.16	31.71	99.27	1.061
	24.01	0.21	2.49	4.05	1.25	2.00	32.02	66	

 $\it Table~4.$  Recalculated analyses of germanocolusite from the Kipushi deposit

VΩ	Formulas calculated based on the ideal formula	Valence	balance
	$C{u^{+}}_{18+x}C{u^{2}}^{+}{}_{4}M{e^{2}}^{+}{}_{4\text{-}x}V^{3}{}^{+}{}_{2}G{e^{4}}^{+}{}_{6\text{-}x}As_{x}S_{32}$	$\pm\Delta$	%
	$Cu^{+}_{20.0}Cu^{2+}_{4}(Cu^{2+}_{0.96}Zn_{1.82})_{2.78}(V^{3+}_{1.83}Fe^{3+}_{0.17})_{2.00}$		
	$[Ge^{4+}_{3.48}(As^{5+}_{1.64}V^{5+}_{0.36})_{2.00}]_{5.48}S_{31\cdot74}$	0.0	0.0
2	$Cu^{+}_{20.17}Cu^{2+}_{4}(Cu^{2+}_{0.32}Zn_{2.08})_{2.40}(V^{3+}_{1.84}Fe^{3+}_{0.16})_{2.00}$		
	$[Ge^{4+}_{3.48}(As^{5+}_{1.73}V^{5+}_{0.44})_{2.17}]_{5.65}S_{31.78}$	+0.18	0.3
3	$Cu^{+}_{19.78}Cu^{2+}_{4}(Cu^{2+}_{0.90}Zn_{2.28})_{3.18}(V^{3+}_{1.72}Fe^{3+}_{0.28})_{2.00}$		
	$[Ge^{4+}_{3.82}(As^{5+}_{1.52}V^{5+}_{0.26})_{1.78}]_{5.60}S_{31\cdot 44}$	+1.44	2.2
4	$Cu^{+}_{19.67}Cu^{2+}_{4}(Cu^{2+}_{0.78}Zn_{2.00})_{2.78}(V^{3+}_{1.93}Fe^{3+}_{0.07})_{2.00}$		
	$[Ge^{4+}_{3.84}(As^{5+}_{1.34}V^{5+}_{0.33})_{1.67}]_{5.51}S_{32\cdot04}$	-1.14	1.8
5	$Cu^{+}_{19.61}Cu^{2+}_{4}(Cu^{2+}_{1.00}Zn_{2.10})_{3.10}(V^{3+}_{1.78}Fe^{3+}_{0.22})_{2.00}$		
	$[Ge^{4+}_{3.88}(As^{5+}_{1.21}V^{5+}_{0.40})_{1.61}]_{5.49}S_{31.79}$	- 0.2	0.3
6	$Cu^{+}_{19.63}Cu^{2+}_{4}(Cu^{2+}_{0.40}Zn_{2.38})_{2.78}(V^{3+}_{1.80}Fe^{3+}_{0.20})_{2.00}$		
	$[Ge^{4+}_{3.80}(As^{5+}_{1.20}V^{5+}_{0.43})_{1.63}]_{5.43}S_{32\cdot 15}$	- 1.76	2.7
7	$Cu^{+}_{19.84}Cu^{2+}_{4}(Cu^{2+}_{0.12}Zn_{2.34})_{2.46}(V^{3+}_{1.68}Fe^{3+}_{0.32})_{2.00}$		
	$[Ge^{4+}_{3.89}(As^{5+}_{1.25}V^{5+}_{0.59)})_{1.84}]_{5.73}S_{31.96}$	-0.4	0.6
8	$Cu^{+}_{19.67}Cu^{2+}_{4}(Cu^{2+}_{0.30}Zn_{2.38})_{2.68}(V^{3+}_{1.70}Fe^{3+}_{0.30})_{2.00}$		
	$[Ge^{4+}_{3.79}(As^{5+}_{1.22}V^{5+}_{0.45)})_{1.67}]_{5.46}S_{32\cdot 18}$	- 1.82	2.8
9	$Cu^{+}_{19.65}Cu^{2+}_{4}(Cu^{2+}_{0.43}Zn_{2.39})_{2.82}(V^{3+}_{1.69}Fe^{3+}_{0.32})_{2.00}$		
	$[Ge^{4+}_{4.02}(As^{5+}_{1.16}V^{5+}_{0.49})_{1.65}]_{5.67}S_{31.86}$	- 0.1	0.2
10	$Cu^{+}_{19.46}Cu^{2+}_{4}(Cu^{2+}_{0.55}Zn_{2.49})_{3.04}(V^{3+}_{1.79}Fe^{3+}_{0.21})_{2.00}$		
	$[Ge^{4+}_{4.02}(As^{5+}_{1.25}V^{5+}_{0.21)})_{1.46}]_{5.48}S_{32\cdot02}$	- 1.12	1.7
Fo	rmulas calculated on the ideal formula proposed by	Val	ence
Sp	iridonov with co-authors, 1992	bal	ance
Cι	$1_{18}^{+}Cu^{2}_{4}(Cu^{2}_{1}, Fe, Zn)_{4}V^{3}_{2}X^{4}_{6}S_{32}$	=	ΕΔ %
1	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{2.96}Fe^{2+}_{0.17}Zn_{1.82})_{4.95}V^{3+}_{2.19}$		
	$(Ge^{4+}_{3.48}As^{5+}_{1.64})_{5.12}S_{31\cdot74}$	+1.11	1.7
2	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{2.14}Fe^{2+}_{0.16}Zn_{2.04})_{4.34}V^{3+}_{2.24}$		
	$(Ge^{4+}_{3.44}As^{5+}_{1.70})_{5.14}S_{32\cdot 28}$	- 0.9	1.4
3	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{2.68}Fe^{2+}_{0.28}Zn_{2.28})_{5.24}V^{3+}_{1.98}$		
	(Ge <sup>4+</sup> <sub>3.82</sub> As <sup>5+</sup> <sub>1.52</sub> ) <sub>5.34</sub> S <sub>31·44</sub>	+2.42	3.7
4	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{2.45}Fe^{2+}_{0.07}Zn_{2.00})_{4.52}V^{3+}_{2.26}$		
	$(Ge^{4+}_{3.84}As^{5+}_{1.34})_{5.18}S_{32\cdot04}$	- 0.2	0.3
5	$Cu^{+}_{18}Cu^{2+}_{4}(Cu^{2+}_{261}Fe^{2+}_{0.22}Zn_{2.10})_{4.93}V^{3+}_{2.18}$		
			0.0
	$(Ge^{4+}_{3.88}As^{5+}_{1.21})_{5.09}S_{31\cdot 79}$	+0.39	0.6
6	$\begin{array}{l} (G{e^4}_{3.88}A{s^5}_{1.21})_{5.99}S_{31\cdot 79} \\ C{u^+}_{18}C{u^2}_{4}(C{u^2}_{+2.03}F{e^2}_{-0.20}Z{n_{2.38}})_{4.61}V^{3}_{+2.23} \end{array}$	+0.39	0.6
6		+ 0.39 - 1.19	1.8
	$\begin{array}{l} Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23} \\ (Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32^{*}15} \\ Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27} \end{array}$		
	$\begin{array}{l} Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23} \\ (Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32^{*}15} \\ Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27} \end{array}$		
7	$\begin{array}{l} Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23} \\ (Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32^{*}15} \\ Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27} \\ (Ge^{4+}{}_{3.89}As^{5+}{}_{1.25})_{5.14}S_{31\cdot 96} \end{array}$	- 1.19	1.8
7	$\begin{aligned} &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23}\\ &(Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32*15}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27}\\ &(Ge^{4+}{}_{3.89}As^{5+}{}_{1.25})_{5.14}S_{31*96}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.97}Fe^{2+}{}_{0.30}Zn_{2.38})_{4.65}V^{3+}{}_{2.15} \end{aligned}$	- 1.19	1.8
7 8	$\begin{array}{l} Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23} \\ (Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32^{*}15} \\ Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27} \\ (Ge^{4+}{}_{3.89}As^{5+}{}_{1.25})_{5.14}S_{31\cdot 96} \end{array}$	- 1.19 - 0.06	1.8
7 8	$\begin{aligned} &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23}\\ &(Ge^{4+}{}_{3.80}As^5{}^{+}{}_{1.20})_{5.00}S_{32+15}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27}\\ &(Ge^{4+}{}_{3.89}As^5{}^{+}{}_{1.20})_{5.14}S_{31+96}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.97}Fe^{2+}{}_{0.30}Zn_{2.38})_{4.65}V^{3+}{}_{2.15}\\ &(Ge^{4+}{}_{379}As^5{}^{+}{}_{1.20})_{5.01}S_{32+18}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.98}Fe^{2+}{}_{0.31}Zn_{2.39})_{4.78}V^{3+}{}_{2.18}\end{aligned}$	- 1.19 - 0.06	1.8
6 7 8 9	$\begin{aligned} &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{2.03}Fe^{2+}{}_{0.20}Zn_{2.38})_{4.61}V^{3+}{}_{2.23}\\ &(Ge^{4+}{}_{3.80}As^{5+}{}_{1.20})_{5.00}S_{32*15}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.96}Fe^{2+}{}_{0.32}Zn_{2.34})_{4.62}V^{3+}{}_{2.27}\\ &(Ge^{4+}{}_{3.89}As^{5+}{}_{1.25})_{5.14}S_{31*96}\\ &Cu^{+}{}_{18}Cu^{2+}{}_{4}(Cu^{2+}{}_{1.97}Fe^{2+}{}_{0.30}Zn_{2.38})_{4.65}V^{3+}{}_{2.15}\\ &(Ge^{4+}{}_{3.79}As^{5+}{}_{1.22})_{5.01}S_{32*18}\end{aligned}$	- 1.19 - 0.06 - 1.35	1.8 0.2 2.0

 $Table~5. \ \, \textbf{Variations in the concentrations of the principal elements (in wt.~\%) in germanocolusite:} \\ (1) from the Kipushi deposit and (2) from the Urup, Tsumeb, and Chelopech deposits$ 

Element	1	2
Cu	47.12 - 50.14	48.04 - 49.69
Fe	0.12 - 0.56	0.47 - 1.56
Zn	3.75 - 5.03	0.07 - 0.63
Ge	7.98 - 9.11	6.55 - 9.13
As	2.70 - 4.11	3.38 - 5.90
V	3.16 - 3.68	3.17 - 3.22
S	31.43 - 32.38	31.05 - 32.02

analyses of germanocolusite from the Kipushi deposit contains more Zn, less As, slightly more Ge, and less Fe, as compared to analyses of germanocolusite from the Urup, Tsumeb, and Chelopech deposits. The average analysis of 10 analyses of germanocolusite from Kipushi does not completely correspond to the crystallochemical formula that takes into account the isomorphism  $Ge^{4+}$  +  $Zn^{2+}$   $\rightarrow$   $As^{5+}$  +  $Cu^{+}$ :  $Cu^{+}_{19.75}Cu^{2+}_{4.0}(Cu^{2+}_{0.60}Zn_{2.22})_{2.82}(Fe^{3+},V^{3+})_{2}$  $[Ge^{4+}{}_{3.80}(As^{5+}{}_{1.35}V^{5+}{}_{0.40})_{1.75}]_{5.55}S_{31.90}, \ or \ Cu^{+}{}_{19.8}$  $Cu^{2+}{}_{4.0}(Cu^{2+}{}_{0.6}Zn_{2.2})_{2.8}(Fe^{3+},V^{3+})_2[Ge^{4+}{}_{3.8}(As^{5+}{}_{1.4}$  $V_{0.4}^{5+}$ <sub>0.4</sub>)<sub>1.8</sub>]<sub>5.6</sub>S<sub>32</sub>. The number of divalent cations is more and the sum of 4- and 5-valence cations is less by approximately the same value, than it is required according to this crystallochamical formula. It is probable that some of the divalent cations occupy positions of the 4- and 5-valence ones; that is, the isomorphism is more complicated. This assumption is based on investigation of the Fe position in renierite, using the Mussbauer spectroscopy. It was revealed that Fe occupied three different positions (Bernstein et al., 1989). The same was confirmed by studying the renierite structure using the Rietveld method (Bernstein et al., 1989). In this case, the crystallochemical formula of germanocolusite will as follows:

 $\begin{array}{l} Cu^{+}{}_{18+x}Cu^{2+}{}_{4}Me^{2+}{}_{4-x}Me^{3+}{}_{2}[Me^{4+}{}_{6-x-y}Me^{5+}{}_{x}\\ Me^{2+}{}_{y}){}_{6}S_{32}, \text{ where } Me^{2+} \text{ is } Cu^{2+}, \text{ } Fe^{2+}, \text{ } Zn^{2+};\\ Me^{3+} \text{ is } V^{3+}, \text{ } Fe^{3+}; \text{ } Me^{4+} \text{ is } Ge^{4+}, \text{ } Sn^{4+}, \text{ } Ga^{3+};\\ Me^{5+} \text{ is } As^{5+}, V^{5+}, \text{ } Sb^{5+}, \text{ } Bi^{5+}; \text{ } \text{at } 0 \stackrel{\checkmark}{=} x \stackrel{\checkmark}{=} 3.0\\ \text{ and } 0 \stackrel{\checkmark}{=} y \stackrel{\checkmark}{=} 0.5. \end{array}$ 

An examination of the literature data has demonstrated that none analysis of germanite or colusite from the Kipushi deposit has been published until the present. Germanium mineralization of Kipushi was studied by Viaene and Morean (Viaene et al., 1968). From among Ge-containing sulfides, they found briartite and renierite only. They noted neither germanite nor Ge-containing colusite. In his work on renierite, Bernstein (1986) placed germanite from the Kipushi deposit into the table; however, describing mineral assemblages of this

deposit, he noted none Ge sulfides except for renierite. In *Geological handbook on side-rophile and chalcophile rare metals* (1989), mention is made of the fact that renierite only is present at Kipushi. It seems likely that our find of germanocolusite is the first for the Kipushi deposit.

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# MINERALOGY OF EPITHERMAL GOLD-SULFIDE-TELLURIDE ORES OF THE KAIRAGACH GOLD DEPOSIT, (Uzbekistan)

#### Vladimir A. Kovalenker

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), RAS, Moscow, vak@igem.ru
Olga Yu. Plotinskaya

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), RAS, Moscow, plotin@igem.ru

#### Rustam I. Koneev

Ulugbek National University of Uzbekistan, Tashkent, Republic of Uzbekistan

The Kairagach ore deposit is situated on the northern slope of the Kurama Ridge (East Uzbekistan), 3.5 km northeast of the well-known Kochbulak gold-telluride ore deposit. According to specific mineralogical features of the ores and hydrothermal alterations, it was assigned to the high-sulfidation (or acid-sulfate) type of epithermal mineralization. However, in contrast to typical gold deposits of this type with a pronounced Au-Cu specialization, the ores of the Kairagach deposit are characterized by the Au-Sn-Bi-Se-Te geochemical profile. This paper briefly summarizes original and published data on the Kairagach deposit, including its geological features and ore characteristics, sequence of the mineral formation, and the main mineral assemblages. Occurrence conditions and chemical peculiarities of the essential minerals of the gold-sulfide-selenide-telluride mineralization are considered. Data on the abundance and compositional variations of native elements (gold, tellurium, and tin), fahlores, Bi and Sb sulfosalts, Cu and Fe sulfostannates, and various selenides and tellurides are presented.

It is shown that the unique diversity of the ore mineralization is determined by the variety of state and occurrence forms (native, isomorphous, sulfide, selenide, and telluride) of their contained chemical elements. 6 tables, 5 figures and 15 references.

The Kairagach epithermal gold ore deposit of Late Paleozoic age is situated in the northern spurs of the Kurama Ridge, eastern Uzbekistan, 3.5 km northeast of the well-known Kochbulak gold-telluride deposit (Kovalenker et al., 1997). In terms of its economic potential, the Kairagach deposit is not assigned to the rank of large objects: its resources are estimated to be 50 t Au and 150 t Ag (Islamov et al., 1999). However, this object is of significant interest for studying epithermal ore genesis regularities, since it belongs to the acid-sulfate (Heald et al., 1987), or high-sulfidation (White Hedenquist, 1991), type of epithermal ore mineralization, that is very rare in the former Soviet Union territory, and its ores are consist of a unique variety of minerals (sulfides, sulfosalts, tellurides, selenides, and oxides). Moreover, in contrast to typical high-sulfidation ore deposits characterized by Au-Cu specialization of their mineralization (Summitwill in the United States, El Indio in Chile, Nansatsu in Japan, Lepanto in Philippines, Chelopech in Bulgaria), the Kairagach deposit is characterized by a clearly prou n Au-Sn-Bi-Se-Te geochemical profile of the ore mineralization.

The unordinary and complex mineral composition of the ores caused the fact that, even at early stages of studying the Kairagach deposit, the paramount attention was given to comprehensive mineralogical investigations. These works revealed here a number of rare minerals, including new mineral species (Badalov and Spiridonov, 1983; Badalov et al., 1984; Kovalenker, 1986; Kovalenker and Geinke, 1984; Kovalenker et al., 1984, 1986, 1987; Spiridonov and Badalov, 1983; Spiridonov et al., 1983). At the same time, no summary work on the Kairagach ore mineralogy has been published until now. The present paper summarizes data accessible by the present time (including those we obtained in the last years), which generalize the occurrence conditions, parageneses, and variations of the chemical composition of minerals that form the unique ores of the Kairagach deposit (native gold and other native elements, various sulfosalts, tellurides, and selenides). It is believed that the data considered here substantially refine and expand the notion of mineralogical and geochemical features not only of the Kairagach deposit but also of epithermal ore mineralization as a whole.

#### Geology and Ores of the Kairagach deposit

The Kairagach deposit is confined to a Hercynian volcanic caldera. The caldera is composed of Middle and Late Carboniferous andesite, andesite-dacite, and dacite tuffs, lavas, and subvolcanic formations. In the central segment of the caldera effusive-pyroclastic rocks are intruded by the mushroom-shaped Kairagach subvolcanic extrusive stock of trachyandesite porphyrites (1.2 x 3 km in size), that supposedly fills the vent of an ancient stratovolcano. In the northern endocontact zone of the extrusive stock, NE-trending ore-bearing structures are located. The volcanosedimentary rocks are also intruded by dikes of diabase porphyrites and granodiorite porphyries of Late Carboniferous to Early Permian age. The deposit is bounded by the Karatash normal fault on the west and by the NE-trending Shaugaz (or Angren) thrust fault on the north (Kovalenker and Geinke, 1984). In the volcanic and subvolcanic rocks, weak propylitization (calcite-chlorite and albite-chlorite-calcite facies) is ubiquitously manifested.

The ore mineralization at the Kairagach deposit is concentrated within 3-5-km-long zones of metasomatic silicification: the Diabasic, First, Chukurkatan, and Bedrenget ones. The commercial-grade ore mineralization has only been revealed in the Diabasic and First zones. These zones represent intricately constructed branching bundles of quartz, quartz-barite, and barite veins, as well as lenticular, veinlet-like, and breccia bodies, all of which contain nest-type, disseminated, and veinlet-disseminated ore mineralization. The host volcanites and diabase porphyrite dikes were subjected to intensive silicification, sericitization, and pyritization. Gold-sulfide-selenide-telluride mineralization mainly occurs in ore bodies of the Diabasic zone that has been most comprehensively studied by the present time, the bulk of resources of precious metals of the Kairagach deposit being related to this zone. It is confined to the northern contact of the Kairagach subvolcanic stock of trachyandesite porphyrites.

According to the mineral composition, two principal types among the ores localized within the Diabasic zone were distinguished. The first, gold-quartz type is represented by essentially quartz ores, in which sulfides (predominantly pyrite) commonly do not exceed 3-5 vol % in abundance. They are spatially associated with zones of monoquartzites and are characterized by the massive structure and relatively low concentration of the useful components.

Quartz of this ore type is cryptocrystalline to flint-like; as a rule, it is characterized by numerous caverns and high porosity, leaching cavities and contains sporadically distributed relicts of the host volcanites. The second, complex gold-sulfide-selenide-telluride type of the mineralization is represented bv vein-shaped and lenticular bodies, veinlet-disseminated and nest-shaped accumulations of quartz, quartz-barite, and barite composition with sulfides, sulfosalts, selenides, and tellurides, that are unevenly distributed within the ore zone among both the monoquartzites and berisite-like formations. Ores of this type play an important role in the balance of reserves of the deposit. They are characterized by variable concentrations of gold, silver, and other useful components, as well as by a complex and variable mineral composition.

# Sequence of Mineralogenesis and the Main Mineral Assemblages

Studying the structural and textural peculiarities of the ores revealed a certain sequence in formation of the ore mineralization in the Diabasic zone. It is shown that mineral assemblages of the ores and hydrothermal wall rock alterations formed during four main stages, including the Preproductive Metasomatic, Early Productive (or quartz-pyrite), Main Productive (or gold-fahlore-sulfosalt-telluride), and Postproductive (or quartz-carbonatebarite) stages (Plotinskaya and Kovalenker, 1998).

The Preproductive Metasomatic Stage is characterized by formation of secondary quartzite-type rocks with pyrophyllite, diaspore, kaolinite, and alunite, as well as of beresite-like quartz-carbonate-sericite rocks with pyrite.

The Early Productive Stage mineralization is dominated by minerals of the gold-quartz-pyrite assemblage, that are present in form of sulfide dissemination in gray metasomatic quartz. The sulfides are represented by predominant pyrite; minor chalcopyrite, and rare sphalerite, galena, and fahlores of the early generation. Native gold is present as ultradispersed inclusions in quartz and pyrite.

The Main Productive Stage includes several mineral assemblages that are commonly closely time-related and are often spatially telescoped. The earliest of them is the gold-quartz-barite assemblage. It is represented by segregations of native gold of high fineness, enclosed in quartz-barite aggregates, and is characterized by practically simultaneous

deposition of the gold, quartz, and barite. The assemblages of goldfieldite and famatinite-luzonite, which is encontered at upper levels of the deposit, attributed to the early ones. Goldfieldite and famatinite-luzonite commonly form small (up to a few hundreds micrometers in size) segregations within barite and quartz, or are present as relicts in later minerals. They are characterized by an appreciable (up to 1-2 wt. %) Sn admixture. The presence of famatinite, luzonite, and enargite among the ore minerals is considered to be a diagnostic feature of the high-sulfidation mineral-forming environment (White and Hedenquist, 1991). We believe that goldfieldite may also be assigned with certainty to indicator minerals of ore mineralization of this type.

Relatively later mineral assemblages include an assemblage of native gold with early tellurides (mainly altaite and calaverite as well as sylvanite, frohbergite, coloradoite, tellurantimony, and others). This assemblage is distributed practically throughout the whole vertical interval of the ore mineralization, except for the very near surficial level. The gold-telluride assemblage is often spatially coincident with the native tellurium assemblage. This mineral is characterized by significant (up to 10 wt. %) admixture of Se. It forms small segregations (occasionally intergrowths with chalcopyrite) in barite or quartz. Another mineral association temporally close to and often spatially coincident with the telluride parageneses is the assemblage of Cu and Fe sulfostannates, that includes mawsonite, stannoidite, kesterite, nekrasovite, volfsonite, hemusite, as well as a number of poorly studied minerals with variable rations of Sn, Cu, and Fe.

The sulfobismuthite assemblage is represented by minerals compositionally close to those of the bismuthinite-aikinite series and of the junoite and pavonite homologue series, as well as by hodrushite. These minerals are characterized by wide variations in the chemical composition and by increased contents of Se. form close intergrowths Bi-containing fahlores. Minerals of the bismuth-sulfoselenide assemblage are relatively later. They are represented by native bismuth, laitakarite, tetradymite, and other sulfoselenides, sulfotellurides, and sulfoselenotellurides, as well as by chalcopyrite, that replaced the selenitic sulfobismuthites as a result of their decay caused by changing of physicochemical conditions of environment.

The most widespread mineral assemblage among products of the gold-fahlore-sulfosalt-telluride stage is the

assemblage of fahlores that are commonly intergrown with chalcopyrite to form relatively large (up to several millimeters) aggregates. Fahlores of the late generation commonly contain numerous inclusions of native gold, Bi-sulfosalts, sulfostannates, tellurides, and selenides.

One of the latest mineral formations of the Main Productive Stage is the assemblage of hessite, electrum, and chalcopyrite. Very fine particles of these minerals are commonly confined to barite or quartz.

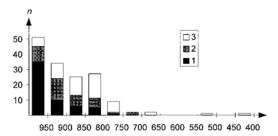
Mineralization of the Postproductive Stage is represented by thin veins or veinlets, transecting mineral formations of all the preceding stages. These veins and veinlets are composed of quartz, carbonates, and barite and occasionally contain variable amounts of sulfides, mainly of galena and sphalerite and more rarely of chalcopyrite, pyrite, and tetrahedrite.

#### Occurrence and Chemical Composition of the Essential Minerals of the Gold-Sulfide-Selenide-Telluride Ores

The chemical composition of the minerals was studied using the electron-probe microanalysis (EPMA) on Cameca MS-46 (analysts N.V. V.S. Malov and Troneva), Camebax-Micro (analyst Sandomirskaya), and SX-50 (analyst A.I. Tsepin) probes. The experimental conditions were as follows: (1) MS-46: accelerating voltage 20 kV; absorbed electron current 15-25 nA (depending on minerals analyzed); beam diameter  $1-2 \mu m$ ; analytical lines:  $K_{\alpha}$  (for S, Fe, Cu, and Zn),  $K_{\beta}$  (for As);  $L_{\alpha}$  (for Ag, Sb, Te, Bi, and Se); standards: stoichiometric FeS<sub>2</sub>, CuFeS<sub>2</sub>, NiAs, Ag<sub>8</sub>SnS<sub>6</sub>, and PbSe and metallic V, Zn, Sb, Ag, Te, and Bi; (2) Camebax-Micro: accelerating voltage 20 kV; absorbed electron current ~15 nA; beam diameter  $1-2\ \mu m;$  analytical lines:  $K_{\alpha}$  (for Cu, As, S, and Se) and  $L_{\alpha}$ (for other elements); standards: synthetic PbTe, CdSe, CuSbS<sub>2</sub>, and GaAs and chemically pure Au, Ag, and Bi; (3) SX-50: accelerating voltage 20 kV; absorbed electron current 20 nA; beam diameter  $1-2 \mu m$ ; analytical lines:  $K_{\alpha}$  (for Cu, As, S, and Se) and  $L_{\alpha}$  (for other elements); standards: synthetic PbTe, HgTe, FeS2, ZnS, and GaAs and chemically pure metals.

#### Native Gold, Tellurium, Bismuth, and Tin

The native gold particles are quite diverse in their morphology. There are xenomorphic,



Au/(Au+Aq+Cu+Hq+Te+S+Bi+Pb)

Fig. 1. Distribution of the fineness of native gold from different mineral assemblages of the Diabasic zone: (1) associated with quartz and barite, (2) with early tellurides and sulfobismuthites, and (3) with hessite, chalcopyrite, and tetrahedrite

elongated, cloddy, stringer, rounded, oval, and amoeboid particles of this mineral. More than 70% of the native gold particles are less than 20  $\mu$ m in size, while the number of relatively large (more than 100  $\mu$ m in size) gold particles does not exceed 10%.

Sulfides commonly contain isolated native gold inclusions, while the vein minerals host their aggregates often confined to the barite-quartz boundaries. The same parts of ore bodies contain, as a rule, increased amounts of minerals of the productive assemblages (tellurides, selenides, and sulfobismuthites).

A characteristic feature of native gold from ores of the Diabasic zone is its extremely high fineness determined as the ratio Au/(Au + Ag + Cu + Hg). The fineness varies from 992 to 900 in more than 50% of the gold particles studied and exceeds 800 in no less than 85% of the gold particles (Table 1, Fig. 1).

Gold particles characterized by the highest fineness are confined to quartz (fineness 937-965 on the upper levels and 974-995 on the lower ones) and to barite (795-946) and 880-989, respectively). The fineness of native gold associated with the early tellurides (altaite, calaverite, and others) increases from 806 – 944 to 971 with depth. Hessite, one of the late tellurides, is associated with electrum and gold of a relatively low fineness (from 670 to 850) on the upper levels and with gold of a higher fineness (950-960) at the lower levels. Later native gold that is present in intergrowths with minerals of the bismuthinite-aikinite series and Bi tellurides is characterized by a fineness of 838 – 943. Native gold associated with tetrahedrite and chalcopyrite exhibit wide variations of the fineness (790-956). Relatively small particles of native gold are, as a

rule, characterized by a low fineness; larger gold particles often possess a zonal structure: the central zones are represented by gold of high fineness, while the rims, by gold of low fineness, the differences in the Au concentrations reaching 27 wt.%. The highest Ag concentrations were registered in particles of electrum (fineness from 401 to 834) that forms veinlets in fahlore. As opposed to native gold from other mineral assemblages, this electrum additionally contains high concentrations of Hg (mainly 1-5 wt. %; up to 10-11 wt. % in rare cases).

In addition to gold, other native elements tellurium, bismuth, and tin - were revealed in the ores under consideration. Native tellurium forms small separate grains within barite or quartz; occasionally, it grows on segregations of earlier tellurides; in some cases, native tellurium was noted to be overgrown by chalcopyrite. Native tellurium that forms small segregations in barite is characterized by high (up to 10.25 wt. %) admixtures of Se. Native bismuth is represented by small segregations associated with Bi sulfosalts, Bi-containing fahlores, sulfostannates, and chalcopyrite. In its chemical composition, small admixtures of S, Cu, Fe, and Ag were revealed. Native tin forms very fine grains intimately intergrown with V-containing cassiterite and sulfostannates of Cu and Fe (Badalov et al., 1984).

#### **Fahlores**

Fahlores belong to widespread minerals of the Kairagach deposit. Their 4 principal generations were revealed with respect to the relative formation time, which are substantially different from each other in chemical composition (Table 2, Figs. 2 and 3). Fahlores of the early generation are predominantly represented by tennantite and As-reach varieties of the tennantite-tetrahedrite series minerals. They are rather rare and compose small segregations intergrown with pyrite formed during the early quartz-pyrite stage. Fahlores of the second generation represented by minerals of the goldfieldite-tennantite-tetrahedrite series are relatively more widespread. They predominantly occur at the upper levels of the deposit and intimately associated with calaverite, altaite, coloradoite, frohbergite, tellurantimony, native tellurium, and famatinite-luzonite. The Te content of these fahlores reaches 17 wt. % (decreasing up to 2-8 wt. % with depth); some their segregations are characterized by high concentrations of Ag (up to 11 wt. %) and Se (0.2wt. %). The high-Te goldfield-

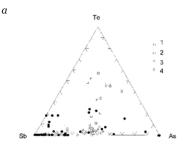
Table 1. Limits of variations of the chemical composition of native gold from the Kairagach ore deposit (wt. %).

Associated minerals	n*	Au	Ag	Cu	Bi	Te	Hg
Quartz	38	79.38-	0.12-	0.00-	0.00-	0.00-	0.00-
		99.41	17.77	0.21	1.46	0.62	0.30
Barite	11	79.19-	0.99-	0.00-	0.00-	0.00-	0.00-
		97.25	20.23	0.78	0.87	0.07	0.17
Early tellurides	19	84.64-	0.39-	0.00-	0.00-	0.00-	0.00-
(calaverite. altaite. frohbergite. petzite. etc.)		97.01	18.42	1.15	1.55	2.70	0.30
Late tellurides	12	67.11-	4.96-	0.00-	0.00-	0.00-	0.00-
(hessite) and chalcopyrite		94.05	29.26	1.87	0.61	1.11	0.09
Sulfobismuthites	18	71.78-	0.53-	0.0-	0.00-	0.00-	0.00-
and rare Bi		97.98	27.14	0.49	2.02	0.24	0.20
Fahlores.	28	79.01-	2.86-	0.26-	0.0-	0.0-	0.0-
sulfostannates. and chalcopyrites		95.56	22.05	2.52	1.11	0.19	1.28
Electrum stringers in fahlore	7	40.02-	14.42-	0.69-	_	_	0.00
•		83.44	46.58	2.35	_	_	11.26

Notes: ') n — number of determinations; (—) — not analyzed

ite-tennantite-tetrahedrite series minerals studied are characterized by a predominance (relative to the stoichiometry) of monovalent metals over divalent ones and of Fe over Zn among the latter (Fig. 3). In this case, As and Sb are present in approximately equivalent quantities (Fig. 2). It is important to note that Te in the chemical composition of the Te-containing varieties of fahlores is characterized by the positive charge 4+; therefore, this element is in the oxidized state here and, in contrast to its position in tellurides, belongs to the cationic part. Fahlores of the third generation are intimately associated with Bi sulfosalts as well as with native gold of high fineness, native bismuth, and selenides and are represented by minerals of the tennantite-tetrahedrite-annivite series (Fig. 2). They are characterized by high (up to 9 wt. %) contents of Bi (its concentration decreases up to 2-5 wt. % with depth), increased (1-3 wt. %) contents of Te, and low (<1 wt. %) contents of Ag (Table 2). Their As and Sb contents are approximately equal to each other, and Fe prevails over Zn (Figs. 2 and 3). As a rule, fahlores of the second and third generations occur as relicts within other minerals, including fahlores of the fourth generation. The latter are predominantly revealed in central zones of the ore bodies in form of rather large (up to several millimeters in size) segregations, often intergrown with chalcopyrite, sulfostannates, and chalcostibite and occasionally with bournonite. Fahlores of this generation usually contain segregations of native gold with relatively low fineness and some tellurides. The chemical composition of fahlores of the late generation is characterized by a prevalence of the tetrahedrite end member, by a predominance of Zn over Fe, and by low (<1 wt. %) Ag and Se concentrations (commonly on the order of 0.n wt. %) (Table 2, Figs. 2 and 3). However, the Ag content of tetrahedrites associated with bournonite and chalcostibite at deep levels of the deposit reachs up to 10 wt. %.

#### Sulfosalts of Bismuth and Antimony



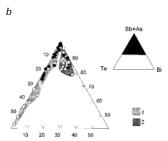


Fig. 2. Diagrams of the chemical composition of fahlore group minerals from the Kairagach deposit: (a) General variations of metalloids in fahlores of different (1-4) generations (at. %); (b) chemical composition of Bi- and Te-containing fahlores of the (1) second and (2) third generations. Open symbols are for the upper levels (+1340, +1300, and +1220 m); filled symbols are for the lower levels (+1100 and +1000 m)

 ${\it Table~2.} \ {\bf Limits~of~variations~of~the~chemical~composition~of~fahlore~group~minerals~of~different~generations~from~the~Kairagach~deposit}$ 

				Fahlore gene	eration			
	1 (n	=5)*	2 (n	= 23)	3 (n =	= 33)	4 (n	= 48)
	a	b	a	b	a	b	a	b
Cu	42.65-	10.28-	44.32-	11.29-	41.55-	10.56-	42.63-	10.96-
	40.42	9.40	34.27	9.35	36.67	9.50	30.99	8.62
Ag	0.78-	0.11-	11.18-	1.80-	0.60-	0.09-	9.53-	1.56-
Ü	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	5.68-	1.57-	7.11-	2.00-	6.84-	2.04-	5.89-	1.67-
	3.16	0.85	0.15	0.04	1.20	0.35	0.04	0.01
Zn	6.10-	1.39-	4.29-	1.04-	6.28-	1.59-	7.58-	1.90-
	2.89	0.64	0.03	0.01	0.08	0.02	0.41	0.10
Ге	1.78-	0.22-	17.16-	2.27-	2.26-	0.28-	4.89-	0.61-
	0.00	0.00	2.45	0.30	0.00	0.00	0.00	0.00
Sb	13.25-	1.68-	22.56-	2.98-	30.58-	4.19-	29.98-	4.17-
	0.06	0.01	2.94	0.40	12.50	1.62	10.54	1.32
As	19.45-	3.87-	12.86-	2.68-	9.95-	2.06-	12.94-	2.64-
	9.56	1.97	1.71	0.00	0.19	0.04	0.29	0.00
Bi	0.45-	0.03-	5.08-	0.40-	9.54-	0.77-	3.34-	0.26-
	0.00	0.00	0.00	0.00	0.55	0.04	0.00	0.00
S	29.31	13.50-	28.19-	14.17-	26.90-	13.21-	28.17-	14.08-
	26.87	12.92	22.92	12.10	23.42	12.19	22.25	12.00
Se	0.41	0.08-	1.28-	0.27-	0.59-	0.12-	0.58-	0.12-
	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00

Notes: (n) number of determinations, (a) wt. %; (b) formula coefficients (calculation based on 29 atoms in a formula unit).

 $\it Table~3.~ \textbf{Chemical composition of Bi sulfosalts (wt.~\%).}$ 

№ os.	Sample no.	Bi	Pb	Sb	As	S	Cu	Ag	Se	Total	+/- (%)*
1	27/85	62.49	12.32	0.33	0.00	17.56	3.66	0.00	1.12	97.50	-3.34
2	8/83	36.66	35.12	0.00	0.00	14.92	10.32	0.06	2.78	99.86	2.47
3	8/83	35.68	35.23	0.00	0.30	15.06	10.43	0.04	2.21	98.97	3.14
4	1050/82b	34.28	36.34	0.33	0.05	16.02	9.52	2.66	0.00	99.33	3.00
5	65/82	57.77	0.02	0.14	0.15	16.84	19.92	0.00	4.83	99.67	1.93
6	65/82	58.17	0.00	1.54	1.49	17.69	18.96	0.08	4.07	102.00	-1.89
7	65/82	58.80	0.00	0.22	0.16	17.52	18.97	0.08	2.78	98.53	0.87
8	42/85	55.31	19.68	0.09	0.00	16.20	4.36	0.08	3.12	98.87	3.38
9	147/81a	64.45	0.41	0.07	0.41	17.16	12.82	0.74	3.47	99.53	-1.17
10	8/83a	54.82	12.01	0.11	0.00	15.42	7.94	3.83	4.07	98.20	-0.25
11	8/83a	55.21	11.56	0.00	0.84	15.58	8.28	3.74	5.06	100.27	-0.09
12	8/83a	56.51	11.27	0.00	0.00	15.65	9.38	1.83	4.11	98.75	-0.46
13	8/83a	66.78	1.93	0.37	0.62	15.69	4.92	4.45	4.49	99.25	-3.54

Notes: (\*) valence balance; (1-4) bismuthinite-aikinite series, (5-7) emplectite, (8) junoite, (9) hodrushite, (10-12) cupropavonite, and (13) makovickite («Cu-benjaminite»).

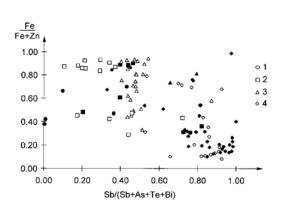


Fig. 3. Variations in the chemical composition of fahlores of different generations from the Kairagach deposit. Same symbols as in Fig. 2a

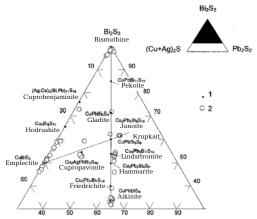


Fig. 4. Variations in the chemical composition of Bi sulfosalts (at. %): (1) theoretical compositions and (2) minerals from the Kairagach deposit

Bismuth sulfosalts belong to minerals widespread in ores of the Diabasic zone. Among different sulfobismuthites found here, we can distinguish emplectite, hodrushite, junoite, and several minerals assigned to the bismuthinite-aikinite series (Table 3, Fig. 4). Several natural phases of the Ag-Cu-Pb-Bi-S-Se system was also revealed here, whose chemical composition allows to assign them to the pavonite series. Because of the fact that minerals of the aikinite-bismuthinite and pavonite series commonly form intimate intergrowths with each other and with other ore and gangue minerals, it was impossible to extract pure material for their X-ray phase analysis. Therefore, they were mainly identified based on a closeness of the chemical composition of the phases studied to that of known minerals (Table 3, Fig. 4), because of which the identification of the sulfobismuthites considered here was substantially arbitrary. The sulfobismuthites are commonly characterized by high (up to 5 wt. %) contents of Se and are often intimately intergrown with native gold or contain its very fine (a few micrometers in size) inclusions; they are also associated with native bismuth, tetradymite, altaite, and other minerals of the productive assemblages. The bulk of the sulfobismuthites formed after the high-Te fahlores, together with the sulfostannates, but before the sulfoselenotellurides (Plotinskaya and Kovalenker, 1998)

Bismuthinite-aikinite series ( $Bi_2S_3$ -PbCuBiS<sub>3</sub>). The composition of the sulfobismuthites studied is grouped near figurative points of theoretical compositions of minerals of this series, including bismuthinite, aikinite, gladite, lindstrumite, krupkaite, hammarite, and friedrichite (Fig. 4). All of them are characterized by high contents of Se (up to 2 wt. %) and appreciable admixtures of As (up to 2-2.5 wt. % in bismuthinite and lindstrumite; up to 1 wt. % in aikinite). Substantial admixture of Sb were only revealed in bismuthinite: up to 1.5% Sb at the upper levels and up to 2-8 wt. % Sb at the lower ones. At deep levels of the Diabasic zone, the following mineral phases have also been revealed: a sulfosalt within the chemical composition (in wt. %): Bi 66.50, 66.17; Sb 14.07, 11.55; S 19.94, 16.42; and Se 0.00, 7.40, that is intermediate between bismuthinite ( $Bi_2S_3$ ) and chorobetsuite ( $\sim BiSbS_3$ ), and a mineral (Cu<sub>3</sub>Pb<sub>3</sub>Bi<sub>7</sub>S<sub>15</sub>) compositionally close to lindstrumite, that is intimately associated with native gold and tetradymite. It forms tabular segregations in barite and at the quartz-barite boundary. In peripheral zones of the ore bodies, sulfobismuthites are predominantly represented by aikinite that is intimately intergrown here with galena and contains practically no Se admixture.

Junoite series  $(Pb_3Cu_2Bi_8(S,Se)_{16}\text{-}CuBiS_2)$ .

The predominant mineral of this series is Se-containing emplectite (CuBiS<sub>2</sub>) associated with fahlores of the third generation. It forms large aggregates growing on fahlores, as well as intergrowths with Cu sulfostannates. The emplectite is characterized by admixtures of Sb and As and by high contents of Se (Table 3). At the deep levels, in common with the above-considered example with the bismuthinite-aikinite series minerals, Sb-containing (up 8 wt. % Sb) varieties of emplectite are found, which are also characterized by high Se contents (3-4 wt. %). Microprobe analysis for one of such minerals are as follows (wt %): Cu 22.67, Bi 26.78, Sb 25.27, S 22.36, and Se 0.79. Its idealized formula can be represented as  $Cu_5Sb_3Bi(S,Se)_{10}$  or as  $Cu(Sb_{0.6}Bi_{0.4})(S,Se)_2$ , if to consider this minerals as Bi-chalcostibite. High concentrations of Se (up to 3 wt. %) (Table 3) have also been revealed in junoite,  $Pb_3Cu_2Bi_8(S,Se)_{16}$ , that is significantly more rare mineral in the Kairagach ores than emplectite.

Pavonite group. To minerals of this group we can assign a mineral compositionally close to cupropavonite (AgPbCu<sub>2</sub>Bi<sub>5</sub>S<sub>10</sub>) (Table 3, Fig. 4). This mineral is associated with hodrushite and other Bi sulfosalts. It forms very fine  $(50-60 \ \mu m \ in \ size)$  rounded and oval segregations in Bi-Te-containing fahlores. We also found here rare small (no more than 30  $\mu m$  in size) grains of a mineral that, being generally close in chemical composition to benjaminite, was characterized by a predominance of Cu over Ag. Previously we named this «Cu-benjaminite». At the same time, its chemical composition at the compositional diagram (Fig. 4) is situated in the immediate proximity to the figurative point of makovickite (Zak et al., 1994). At the present time, however, a correct identification of the sulfosalt considered without additional investigations is impossible. Minerals of this group, in common with other sulfobismuthites developed in Kairagach ores, are characterized high by 5 wt. %) concentrations of Se.

Hodrushite ( $Cu_4Bi_\theta S_{1I}$ ) is closely similar in its chemical composition and crystal-chemical properties to the above-considered minerals of the pavonite series. It forms aggregates of acicular and tabular grains in quartz and barite or among fahlores of the late generation; it is

Table 4. Chemical composition of Au and Ag tellurides (wt. %)

Nº os.	Sample no	Te	Ag	Au	Cu	Se	Sb	S	Hq	Pb	Bi	Total
1	42/85	58.68	0.34	39.75	0.09	0.06	0.44	0.00	0.00	0.41	0.00	99.72
2	232-9	55.86	0.34	42.96	0.09	0.05	0.44	0.00	0.00	0.41	0.00	99.72
3	232-9	56.38	0.09	42.83	0.00	0.03	0.40	0.00	0.00	0.00	0.32	99.00
		55.95	0.02	42.03	0.01		0.37		0.00	0.00	0.00	98.66
4	Kai-32					0.14		0.00				
5	Kai-38	55.72	0.43	42.24	0.54	0.10	0.00	0.00	0.00	0.51	0.00	99.54
6	Kai-32	56.11	0.00	42.22	0.09	0.13	0.00	0.00	0.00	0.00	0.19	98.74
7	Kai-32	56.21	0.62	41.65	0.42	0.00	0.00	0.00	0.00	0.00	0.00	98.90
8	Kai-32	54.80	0.24	41.60	0.02	0.34	0.37	0.00	0.00	0.00	1.27	98.64
9	Kai-32	54.63	0.67	41.60	0.89	0.19	3.00	0.20	0.00	0.00	0.00	101.18
10	Kai-32	55.14	0.15	41.26	0.06	0.32	1.64	0.13	0.00	0.03	1.15	99.88
11	232-9	57.08	0.00	39.94	0.00	0.09	0.51	0.00	0.00	0.10	1.58	99.30
12	147/81	56.28	0.95	41.62	0.20	0.10	_	0.01	0.39	_	_	99.55
13	147/81	56.62	0.39	42.14	0.07	0.87	_	0.04	0.49	_	_	100.62
14	Kai-32	63.25	7.31	24.27	3.15	0.00	0.00	0.00	0.38	0.21	0.12	98.69
15	147/81	62.46	12.39	23.89	0.51	0.64	_	0.03	0.24	_	_	100.16
16	147/81	62.03	11.76	23.62	0.86	0.57	_	0.02	0.33	_	_	99.19
17	147/81	62.03	11.79	23.62	0.86	0.57	0.01	0.02	0.33	_	0.17	99.40
18	64/84	36.87	61.86	1.42	0.02	0.07	0.05	0.23	_	0.32	0.12	100.96
19	66/84	36.32	60.88	1.16	0.27	0.07	_	0.18	_	_	_	98.88
20	1050/82B	36.08	64.42	_	_	_	0.25	0.24	_	_	_	100.99
21	59/86	37.75	61.83	_	_	_	_	_	_	_	_	99.58
22	59/86	38.81	62.82	_	_	_	_	_	_	_	_	101.63
23	64/84	36.87	61.86	1.42	0.02	0.07	0.05	0.23	_	0.32	0.12	100.96
24	66/84	36.32	60.88	1.16	0.27	0.07	_	0.18	_	_	_	98.88
25	48/85	39.20	60.26	_	_	_	_	_	_	_	_	99.46
26	64a/84	39.06	60.63	0.17	0.58	0.20	0.38	0.22	_	_	_	101.24
27	27/85	36.82	61.55	0.24	0.08	0.04	0.24	0.10	0.00	0.26	0.14	99.47
28	147/81	41.01	57.39	_	_	0.06	_	0.03	0.71	_	_	99.20
29	64a/84	46.69	17.46	_	_	-	2.21	-	-	-	33.52	100.14

 $\textbf{\textit{Notes:}} \ \text{Analyzes:} \ (1-13) \ \text{ calaverite,} \ (14-17) \ \text{ sylvanite,} \ (18-27) \ \text{ hessite,} \ (28) \ \text{ stutzite,} \ \text{ and} \ (29) \ \text{ volynskite;} \ (-) \ \text{not analyzed.} \ \text{ and} \ \text{ support of the state of the support of$ 

often present in intergrowths with aikinite. Hodrushite from the Kairagach deposit is characterized by high concentrations of Se (up to 3.47 wt. %) and Ag (0.51-2.18 wt. %), as well as of Pb and As (up to 1.44 and 1.31 wt. %, respectively) (Table 3).

Sulfoantimonites are mainly represented in ores of Kairagach by bournonite and chalcostibite and occur here significantly more rarely than sulfobismuthites, predominantly in peripheral areas of the ore shoots. They are intimately associated with fahlores of the late generation, galena, and chalcopyrite. The chemical composition of the samples of chalcostibite and bournonite studied is close to stoichiometry of these minerals.

#### **Tellurides and Selenides**

Selenides and tellurides are widespread in ores of the Diabasic zone, although they do not form large accumulations here. They incorporate a large group of binary, ternary, and more complex compounds, including rare and, probably, new ones (Table 4), that can be described within the limits of the systems

Au-Ag-Te, Ag-Pb-Bi-Sb-Te, and Bi-Te-S-Se. The tellurides mainly occur as small (30-300  $\mu m$  in size) separate inclusions or aggregates in barite; at barite-quartz boundary; and, more rarely, among fahlore segregations. At deep levels of the deposit, they are commonly found in quartz.

Among minerals of the Au-Ag-Te system, revealed here, are calaverite, sylvanite, petzite, hessite, stutzite, native tellurium, and native gold. As a rule, these minerals form intimate intergrowths with each other among gangue and ore minerals; more rarely, they occur as separate segregations in barite, quartz, and sulfides. Peculiarities of their real chemical composition are presented in Table 4 and are demonstrated on a ternary compositional diagram (Fig. 5).

Calaverite. At upper levels of the deposit, calaverite is predominantly associated with native gold of high fineness and with petzite; at the lower levels, it is mainly associated with tellurantimony and frohbergite and, occasionally, with native tellurium and sylvanite. The mineral is characterized by stoichiometric ratios between the principal components (Table 4, Fig. 5). At the same time, it incorporates appre-

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ciable quantities of Ag whose concentrations increase with depth and commonly reach up to 1.7 - 1.8 wt. % at lower levels of the ore bodies. Small admixtures of Se (up to 0.34 wt. %) are practically permanently detected in the mineral composition; at the lower levels, admixtures of Cu (up to 0.5-0.9 wt. %) and Sb (up to 1.6-3.0 wt. %) are also noted. It is particularly remarkable that it is at the lower levels that several previously unknown natural mineral phases of the Au-Sb-Te composition with variable relationships between the components were found along with calaverite among minerals of the gold-productive assemblages. According to electron-microprobe data, the chemical composition of one of these phases is as follows (wt. %): Au -79.47, Ag -0.17, Te -10.61, and Sb - 9.05, which corresponds to the ideal formula Au5SbTe. Another Au-Sb-Te phase found here is composed of the same set of elements, but in the different ratios (wt. %): Au - 44.37, Te - 26.38, Sb - 28.04, and Se - 0.41. This analysis is well recalculated to the ideal formula AuSbTe. One more mineral phase found and studied at the deposit contains Bi in addition to Au, Sb, and Te and has the following chemical composition (wt. %): Au 31.58, Sb 8.87, Bi 5.81, and Te 54.23. The empirical formula of this compositionally complex mineral phase is close to the stoichiometry Au5Sb2Bi2Te13. It is possible that this mineral belongs to the nagyagite-buckhornite group; however, this question remains open now, since further investigations are impossible because of the very small ( $<20 \mu m$ ) size of its particles. Sylvanite predominantly occurs in ores of the deep levels and is substantially exceeded in abundance by calaverite. A small (no more than 0.4 wt. %) Cu admixture is constantly detected in its chemical composition. One of sylvanite segregations within barite has the chemical composition (in wt. %): Au 24.27, Ag 7.31, Cu 3.15, and Te 63.26, that corresponds to the ideal formula Au(Ag0.6Cu0.4)Te4; that is, this mineral occupies an intermediate position in the isomorphous series sylvanite (AuAgTe) - kostovite (AuCuTe4).

Minerals of the *Pb-Te-Se-S system* are represented in ores of the Diabasic zone by *altaite*, *clausthalite*, *and intermediate members of the galena-clausthalite series*. The most widespread of these minerals is altaite that belongs to early assemblages of the Main Productive Stage. Clausthalite and minerals of the galena-clausthalite series are associated with famatinite-luzonite, goldfieldite, chalcopyrite, and sulfostannates. The chemical composition of

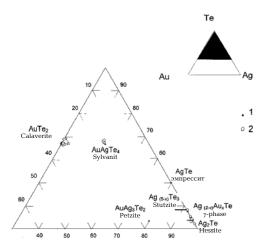


Fig. 5. Variations in the chemical composition of Au and Ag tellurides (at. %): (1) theoretical compositions and (2) minerals from the Kairagach deposit

the studied minerals of this system is presented in Table 5. Remarkable peculiarities of these minerals are as follows: the altaite contains appreciable admixtures of Ag, Cu, Fe, Sb, and, occasionally, Au; the galena-clausthalite series minerals are characterized by variable concentrations of Se and S and by the presence of small amounts of Bi (Table 5). In addition, *Bi-tellurantimony* was assigned to minerals of the early assemblages. Its chemical composition, according to electron-microprobe analysis, is as follows (wt. %): Bi 22.04, Sb 21.38, Te 55.82, and S 0.62.

Relatively later tellurides of the Kairagach deposit are represented by hessite, tetradymite, volynskite, and rucklidgeite, which are associated with gold of low fineness, sulfoselenotellurides, and selenides of Bi. It is worth to note that among the latter such rare minerals as kawazulite Bi<sub>2</sub>Te<sub>2</sub>Se; laitakarite Bi<sub>4</sub>(Se<sub>1</sub>S)<sub>3</sub>; nevskite Bi(Se<sub>1</sub>S), Se-sulphotsumoite  $Bi_3Te_2(S,Se)$ , and the phases Bi<sub>2</sub>(Te<sub>1</sub>Se<sub>1</sub>S)<sub>3</sub> and Bi(Se<sub>1</sub>S)<sub>2</sub>. All these minerals, whose chemical composition is presented in Table 6, occur as constituents of the gold-productive assemblages exclusively within ore shoots, mainly at the upper levels of the deposit. Although selenides proper are not widespread at deep levels of the deposit (a Bi selenotelluride, kawazulite, was only revealed there), some Bi sulfosalts, such as chorobetsuite-like minerals and Sb-emplectite, contain (along with appreciable amounts of Sb) significant (from 2.89 to 10.14 wt. %) concentrations of Se. Increased concentrations of Se are also characteristic for sulphotsumoite (chemical composition, wt. %: Bi 68.89, Sb 0.69, Te 24.06,

Table 5. Chemical composition of minerals of the system Pb-Te-Se-S (wt. %)

№ os.	Sample no	Pb	S	Se	Te	Sb	Fe	Cu	Ag	Au	Hg	Bi	Total
1	1020/86	59.41	0.00	0.03	38.25	0.24	0.36	0.66	2.40	0.00	0.00	0.00	101.35
2	130/87	61.67	0.00	0.22	36.34	0.29	0.58	0.78	0.17	0.18	0.00	0.00	100.23
3	130/87	60.79	0.03	0.30	36.86	0.30	0.70	0.66	0.15	0.60	0.00	0.00	100.39
4	1020/86	59.86	0.05	0.11	38.10	0.35	0.07	0.02	0.12	0.53	0.26	0.00	99.47
5	435/82	58.86	1.01	0.16	35.98	0.83	0.03	1.94	0.07	0.48	0.00	0.00	99.36
6	Kai-38	60.82	0.00	0.12	37.85	0.00	0.02	0.40	0.12	0.10	0.07	0.00	99.50
7	Kai-38	60.47	0.00	0.25	38.06	0.04	0.07	0.19	0.01	0.60	0.29	0.00	99.98
8	558/87	76.7	10.29	8.17	_	0.41	0.43	3.92	80.0	_	_	_	100.00
9	558/87	77.94	11.55	4.47	_	0.32	0.47	3.33	_	_	_	0.23	98.31
10	558/87	74.54	9.34	9.69	_	0.51	0.55	3.28	_	_	_	_	97.91
11	121/87	69.63	3.63	23.39	_	_	1.45	2.31	_	_	_	0.26	100.67
12	121/87	70.01	2.42	24.85	_	_	1.59	3.3	0.07	_	_	_	102.24
13	121/87	72.32	4.06	20.21	_	_	0.53	_	0.02	_	_	0.26	97.40

**Notes:** Analyzes: (1-7) altaite, (8-10) galenoclausthalite; (11-13) — clausthalite, (-) not analyzed

S 3.27, and Se 3.09), that was first revealed for the Kairagach deposit.

Sulfostannates represent one of mineral groups typomorphic for rich and bonanza ores. They include mawsonite, stannoidite, stannite, kesterite, nekrasovite, volfsonite, and hemusite, as well as several yet unnamed sulfosalts of Sn, Cu, and Fe, characterized by variable relationships between these elements (Kovalenker and Geinke, 1984; Kovalenker et al., 1986). We included Sn-containing colusite and stibiocolusite, interrelated with the isostructural nekrasovite through uninterrupted transitions, into this group as well (Kovalenker et al., 1984). Sulfostannates do not make up large accumulations in Kairagach ores and are commonly represented by small (up to  $50-100 \mu m$  in size) but numerous, rounded or xenomorphic segregations most often confined to fahlore, chalcopyrite, barite, or quartz. These minerals commonly occur in intimate intergrwths with each other, as well as with chalcopyrite, native gold, Se-emplectite, and other sulfobismuthites. Accumulations and separate grains V-containing (up to 1 wt. % V) cassiterite, as well as of native tin, are often confined to the aggregates of sulfostannates (Badalov et al., 1984). Chemism peculiarities and parageneses of sulfostannates in ores of the Kairagach deposit were comprehensively considered in special publications (Kovalenker and Geinke, 1984; Kovalenker et al., 1984 and 1986; Spiridonov et al., 1983); therefore, it would be sufficient to note here that the chemical composition of minerals of this group is characterized by permanent admixtures of Sb, As, and, to a lesser degree, Se, the typomorphic elements of the Kairagach ores.

#### **Conclusions**

1. In contrast to typical high-sulfidation epithermal ore deposits characterized by the

Au-Cu specialization of the ore mineralization, ores of the Kairagach deposit are complex, multicomponental, and exhibit a clearly pronounced Au-Bi-Sn-Se-Te geochemical profile.

- 2. The mineralogical complexity and originality of the Kairagach ores are caused by the variety of state and occurrence forms (native, isomorphous, sulfide, selenide, and telluride) of their contained chemical elements.
- 3. The typochemism of the Kairagach ores is determined by the presence of numerous and diverse minerals of Au, Ag, Bi, Sn, Sb, Se, and Te, that often possess a complex variable chemical composition and not infrequently make up series of solid solutions, or belong to homologue series.
- 4. Formation of the diverse, compositionally complex ore minerals of the Kairagach deposit was related to a high variability of the physicochemical parameters (T, P, pH, Eh, and component activities) under conditions of mineral-forming processes that dynamically developed near the Earth's surface.

#### Aknowledgements

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Table 6. Chemical composition of minerals of the system Bi-Pb-Te-Se-S (wt. %)

No o	os.Sample n	o. Bi	Pb	Sb	As	Cu	Ag	S	Se	Te	Au	Hg	Fe	Total
1	147/81	80.19	0.26	0.10	1.17	0.34	0.15	2.44	17.00	_	_		0.10	101.75
2	147/81	82.88	0.25	0.18	1.55	0.58	-	3.90	13.10	_	_	_	-	102.44
3	147/81	77.50	0.60	0.10	0.66	0.71	0.04	1.33	18.10	0.07	_	0.11	_	99.15
4	147/81	78.75	_	_	0.28	0.44	0.09	1.86	16.01	0.39	0.18	0.38	0.12	98.50
5	231/81	78.00	0.07	0.11	1.15	0.75	0.04	3.49	15.80	_	_	_	0.06	99.47
6	*	76.61	0.69	0.39	_	0.50	_	5.36	15.98	0.00	_	_	_	99.53
7	*	78.67	0.00	0.00	_	0.84	_	5.89	15.33	0.00	_	_	_	100.73
8	1031/86	66.15	6.48	_	_	3.80	3.80	13.90	6.24	0.61	_	_	_	100.98
9	1031/86	64.96	6.46	_	_	3.85	3.72	14.37	5.82	0.37	_	_	_	99.55
10	8/83	66.78	1.93	0.37	0.62	4.92	4.45	15.69	4.49	0.22	_	0.06	_	99.53
11	147/81	75.49	1.67	0.21	0.14	3.20	0.02	1.31	17.72	0.36	_	0.06	_	100.18
12	1020/86	56.28	0.12	0.25	0.00	0.00	0.45	4.36	0.13	37.04	0.19	0.00	0.01	98.83
13	1020/86	56.47	0.02	0.25	0.00	0.04	0.24	4.37	0.74	36.31	0.57	0.00	0.08	99.09
14	1020/86	55.74	0.00	0.26	0.00	0.00	0.07	4.46	1.03	36.44	0.25	0.00	0.48	98.73
15	42/85	54.59	0.07	0.56	0.32	0.03	_	3.69	0.99	34.44	-	_	_	94.69
16	232-9	56.02	0.00	0.73	0.00	0.00	0.00	4.11	1.15	36.91	0.37	0.00	0.04	99.33
17	232-9	56.78	0.00	1.05	0.00	0.00	0.00	3.96	1.24	36.94	0.00	0.00	0.00	99.97
18	Kai-38	56.27	0.00	0.00	0.00	0.07	0.00	4.30	1.84	35.38	0.81	0.23	0.02	98.92
19	27/85	50.74	3.50	0.26	0.00	1.01	0.63	4.31	2.69	34.55	0.00	0.00	0.76	98.45
20	*	73.64	2.04	0.61	_	_	_	0.91	5.79	18.16	_	_	_	101.15
21	147/81	55.92	_	0.44	_	1.39	0.29	1.75	9.12	30.58	0.37	0.71	_	100.57
22	Kai-38	57.07	0.00	0.03	0.00	1.10	0.00	2.52	9.51	29.69	0.00	0.33	0.00	100.25
23	8/83	52.88	_	0.86	0.02	3.22	0.57	2.91	7.32	29.73	0.60	_	0.63	98.74
24	K-12/ 1	56.42	-	0.81	-	1.06	_	3.25	6.11	33.01	-	-	_	100.66
25	K-12/2	68.89	_	0.69	_	_	_	3.27	3.09	24.06	_	_	_	100.00
26	232-9	53.86	0.03	1.37	0.00	0.04	0.00	2.64	7.04	32.42	0.72	0.11	0.00	98.23
27	Kai-38	53.39	0.00	0.00	0.00	0.78	0.14	3.71	3.75	32.62	4.72	0.28	0.07	99.46
28	Kai-38	55.74	0.00	0.00	0.00	0.90	0.06	2.96	6.40	32.19	0.19	0.00	0.36	98.80
29	*	62.58	1.48	0.50	_	_	_	2.94	6.23	28.08	_	_	_	101.81
30	64a/84	36.10	14.20	1.04	0.55	0.89	0.73	0.24	0.35	45.46	_	_	0.08	99.64

Notes: (1) after Spiridonov and Badalov, 1983; Analyzes: (1-5) laitakarite, (6-7) phase  $Bi_2SeS$ , (8-10) phase  $Cu_3Bi_3(S.Se)_5$ , (11) phase  $Cu_2Bi_1s(S.Se)_{11}$ , (12-19) tetradymite, (20) phase  $Bi_3TeSe$ , (21-24) kawazulite, (25) tsumoite, (26-29) phase  $Bi_3Te_2SeS$ , and (30) rucklidgeite; (-) not analyzed

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# CAVITATION MODEL OF MINERAL MICROSPHERULA FORMATION IN HYDROTHERMAL ORES

Margarita I. Novgorodova

Fersman Mineralogical Museum of the Russian Academy of Science, Moscow, min@fmm.ru

Stepan N. Andreev, Alexander A. Samokhin

Intitute of General Physics of the Russian Academy of Science, Moscow, asam@ran.gpi.ru

The cavitation model was considered to explain mineral microspherula formation conditions in ores of hydrothermal genesis. Microspherulas are treated as hardened and crystallized drops of melt. Thermodynamic calculations of thermal energy emitted during microseconds at gas bubble contraction in boiling up hydrothermal solution show that fusion of such refractory substances as quartz and gold is possible. 2 tables, 6 figures and 12 references

Mineral microspherulas of micrometer size (from 10 to 100  $\mu m$  in diameter) of different mineral composition were known from a long time (Vernadsky, 1955), but they have caused a special interest after were discovered directly in ores at a great depth (Gamyanin et al., 1999; Novgorodova et al., 2003). Earlier various reasons were used to explain their formation. So-called magnetic balls consisting of native iron with admixture of Ni, frequently completely or in part replaced with wastite or magnetite, were considered of cosmogenic origin; that found in mechanically crashed ores were considered as technogenous artifacts (Dilabio et al., 1988). Rounded concretion forms of mineral aggregates are well-known for sedimentary ores and mineral deposits of karst caves (cave pearls). None of these explanations can be used to explain conditions in which microspherulas of alumosilicate glasses and refractory metals, as well as sulfides settling down in voids and cracks of  $\alpha$ -quartz veins, were formed in mineralized zones of terrigenous and volcanosedimentary rocks metamorphosed to greenschist facies (gold deposits of Yakutia, West Uzbekistan, Alaska). Boundary parameters of greenschist metamorphism (T up to ~500°C, P up to ~2-8 kbar) do not suppose formation of conditions for partial melting of sulfide ores, as it was assumed by R. Frost (Frost et al, 2002) for deposits in rocks of amphibolitic and granulitic facies of metamorphism.

Actual data on physicochemical parameters of ore-forming solutions give thermobarometric studies of gas-liquid inclusions in minerals, in particular, in quartz. At the well studied Nezhdaninskoye deposits (Yakutia) it was established that ores were formed at T 175–360°C and P 1.2–1.7 kbar at participation from medium salted solutions with  $\rm H_2O>CO_2>CH_4=N_2>H_2S$ , separated into two phases: liquid water-carbon dioxide with  $\rm N_2$ ,  $\rm CH_4$ , dissolved chlorides, and

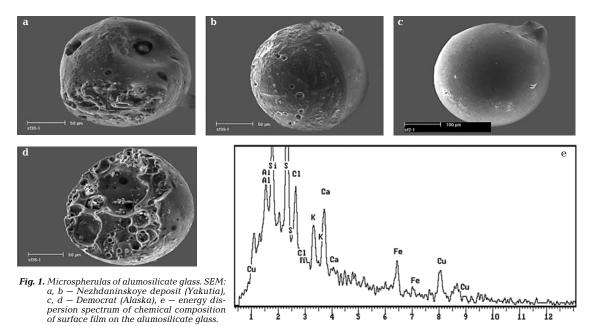
gaseous with prevailing  $CO_2$  and  $CH_4$  (Bortnikov *et al.*, 1998). Quartz grains do not show signs of fusion of quartz.

To explain formation of alumosilicate glass and refractory metal microspherulas with fusion points essentially exceeding temperature of hydrothermal solution at formation of gold-ore mesothermal deposits (Nezhdaninskoyee, Kellyam in Yakutia, Kokpatas in West Uzbekistan, Democrat on Alaska) a hypothesis on cavitation nature of the phenomenon was put forward (Novgorodova *et al.*, 2003<sub>1</sub>).

It was assumed that mineral microspherulas have been formed due to fast cooling and crystallization of melt drops arising in local zones of slightly open cracks and voids in the mineralization zone due to the phenomena of cavitation boiling up and heterogenization of hydrothermal solutions. The transition from a regime of slow infiltration of hydrothermal solutions through capillaries and pores in hosting rock to instant filling of cracks slightly opened at tectonic movements results in local pressure decrease, expansion of evolved gas bubbles and their collapse at returning to former conditions at full filling of slightly opened space. After the collapse, fine bubbles disappear, large are broken into a set of fine ones. Time of one bubble cycle is estimated at microseconds, however, heat and energy necessary for fusion of either solid particle in the impact zone of collapsing bubble are sufficient for fusion of such refractory matter, as quartz or gold. This is shown by the calculations below.

Fused state of microspherulas prior to their hardening and crystallization was established basing on the following facts and reasons (Novgorodova *et al.*,  $2003_{1,2}$ ).

Alumosilicate glasses of microspherulas (Fig. 1) are transparent, non-crystalline characterized by wide variety and discreteness in contents of rock-forming elements depleted in sili-



ca and alkalis as against the gold-hosting rocks and enriched with femic components (Fig. 2). The most part of analyses does not correspond to known chemical composition of any magmatic rock. The internal irregularity of microspherula chemical composition with inclusions of glass in glass was revealed; inclusions have low  ${\rm SiO}_2$  content and are represented by discrete compositions with high contents of  ${\rm Al}_2{\rm O}_3$ , MgO, CaO, FeO.

Microspherulas of monomineral composition were revealed among alumosilicate glasses. At the Nezhdaninskoye deposit, they are represented by glasses of almost pure  $\mathrm{SiO}_2$  (98.69 – 99.02 %) and pyroxene of enstatite-bronzite type with stoichiometric formula  $(\mathrm{Mg}_{1.4}\mathrm{Fe}_{0.6})_2(\mathrm{Si}_{1.9}\mathrm{Al}_{0.1})_2\mathrm{O}_6$ . Pyroxene is absent in terrigenous rocks containing gold-antimony ore in this deposit. All investigated glasses of the Democrat deposit have a similar formula of enstatite-bronzite.

The size of alumosilicate glass microspherulas is from 10 to 100  $\mu m$  (usually ~50  $\mu m$ ). Quartz glass microspherulas are the finest. All microspherulas are saturated with numerous gas vacuoles. Films and ingrowths of Ca, Cu, Zn, and Fe salts with ligands containing S, Cl, P, C were discovered on their surface by scanning electronic microscopy (SEM) using energy dispersion spectrometer Zink-860 (Fig. 1).

Microspherulas of ore minerals, which compositions are described by the system Pb-Sb-Au(Ag)-S(As), are monomineral (native

gold, galena, antimonite, boulangerite, pyrrhotite) and polymineral microspherulas of zonal structure with «gold» core and galena-boulangerite rims. Films of alumosilicate glasses and salts of Cu and Zn with ligands of Cl and S were discovered on their surface. Inside microspherulas, there are gas cavities and relics of quartz and arsenopyrite fragments.

Sliced and dendrite-like internal structure of monomineral microspherulas was established; contraction cracks, arising at reduction of volume at hardening and crystallization of melt gold drops (Fig. 3), are characteristic of microspherulas of native gold.

Zonal microspherulas show signs of liquation with separation of sulfide (Pb-Sb(As)-S) phase in marginal zones with eutectoid aggregates of galena and boulangerite and metal phase (Au(Ag)-Pb-Sb) part in the central zone (Fig. 4). The «gold» core is characterized by signs of stratification with sliced structure of phases differing in Pb contents and eutectoid aggregates of Au-Sb and Au-Pb-Sb phases (Table 1). The affinity of composition of natural Au-Pb-Sb phases to synthesized glasses of a new class of high-temperature superconductors was established for the first time (Nov-gorodova *et al.*, 2003<sub>2</sub>).

Using systems of invariant points in fluxion diagrams (Table 2), the interval of microspherula formation temperatures was evaluated between > 850°C (fusion of gold, galena, antimony, alumosilicates and quartz at pres-

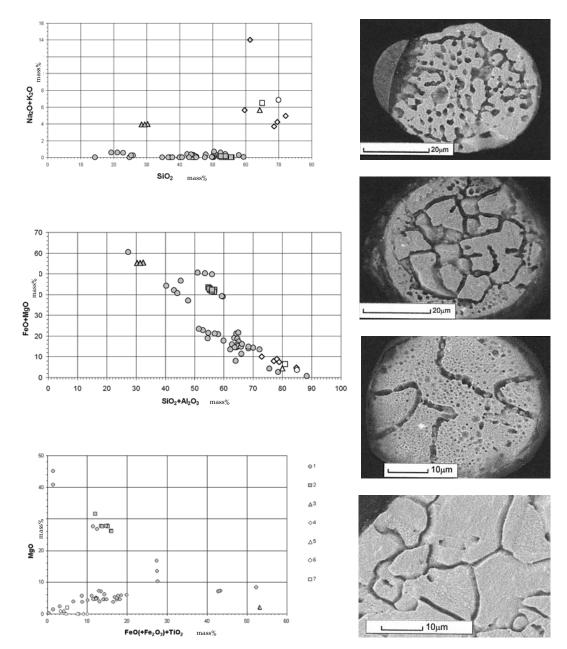


Fig. 2. Variational diagram of alumosilicate glass compositions: 1 — Nezhdaninskoye deposit, 2 — Democrat, 3 — Kellyam, 4 — Kokpatas, 5 — hosting siltstones, Nezhdaninskoye, 6 — hosting sandstones, Nezhdaninskoye, 7 — granodiorite, average after R.A. Daly.

Fig. 3. Contraction cracks seen in a cross sec $tion\ of\ a\ native\ gold\ microspherula.\ SEM.$ 

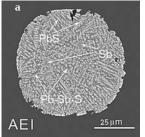
ence of natural fluxes and subsequent liquation of ore micromelts) and 650-400°C (fusion of galena-antimonite mixture with formation of boulangerite and galena through eutectoid disintegration of falkmanite protocompound) and to 300 - 250° C (fusion, stratification and eutectoid disintegration with formation of Au-Pb-Sb phases).

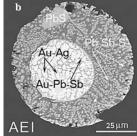
The fugitivity of sulfur and oxygen in gas phase equilibrated with sulfides of Pb and Sb was calculated by tabulated values of free Gibbs energy in reactions of sulfidization and

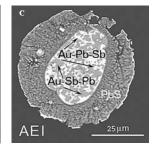
New data on minerals. M.: 2003. Volume 38

Table 1. Chemical composition (wt. %) of microspherula minerals

Nº	Mineral	Sample	Number of analyses	Au	Ag	Pb	Sb	Fe	As	S	Total	Formula
1	Arsenopyrite	92	3	_	_	_	_	34.39	46.23	19.52	100.14	$Fe_{1.00}As_{1.00}S_{1.00}$
2	_''_	82	5	_	_	_	_	34.32	45.99	19.79	100.10	Fe <sub>1.00</sub> As <sub>1.00</sub> S <sub>1.00</sub>
3	Pyrite	_"_	5	0.2	_	_	0.2	46.70	_	48.8	95.9	Fe <sub>1.06</sub> S <sub>1.93</sub>
4	Pyrrhotite	_"_	2	_	_	_	0.2	63.60	0.7	34.8	99.3	Fe <sub>1.02</sub> S <sub>0.97</sub> As <sub>0.01</sub>
5	Antimonite	_"_	3	0.2	_	_	69.6	0.30	0.5	27.9	98.5	Sb <sub>1.95</sub> S <sub>3.00</sub>
ô	Galena S <sub>0.99</sub> As <sub>0.02</sub>	-"-	6	0.7	1.0	83.3	0.2	_	0.5	13.4	99.1	$Pb_{0.96}Ag_{0.02}Au_{0.01}$
7	S <sub>0.99</sub> AS <sub>0.02</sub> Galena	105	1	_	_	86.58	_	_	_	14.03	100.61	Pb <sub>0.98</sub> S <sub>1.02</sub>
3	-"-	90	1	_	_	87.24	_	_	_	14.18	101.42	Pb <sub>0.98</sub> S <sub>1.02</sub>
)		96	1	_	_	86.32	_	_	_	14.10	100.37	Pb <sub>0.98</sub> S <sub>1.02</sub> Pb <sub>0.98</sub> S <sub>1.02</sub>
10		82	4	_	_	86.52	_	_	_	13.59	100.37	T 0 <sub>0.98</sub> S <sub>1.02</sub>
10		109	4	_	_	86.70	_	_	_	13.63	100.11	Pb <sub>0.99</sub> S <sub>1.01</sub>
12	 _"_	62	2			86.49	_			13.63	100.33	$Pb_{0.99}S_{1.01}$
3		62 82	4	-	_	55.46	25.55	_	_	13.71	99.84	Pb <sub>0.99</sub> S <sub>1.01</sub>
	Boulangerite		_	-	_				_			Pb <sub>5.03</sub> Sb <sub>3.94</sub> S <sub>11.03</sub>
4	-"-	109	4	_	_	55.54	25.38	_	_	19.12	100.04	Pb <sub>5.00</sub> Sb <sub>3.89</sub> S <sub>11.11</sub>
.5	_"_	-"-	4	0.3	_	56.9	24.1	_	1.4	17.6	100.30	$(Pb_{5.27}Au_{0.03})_{5.30}$ $Sb_{3.80}As_{0.36}S_{10.54}$
6	Gold	92	3	77.70	21.95	_	_	_	_	_	99.65	$Au_{1.98}Ag_{1.02}$
7	_"_	105	2	78.82	20.62	_	_	_	_	_	99.44	$Au_{2,03}Ag_{0,97}$
8	-"-	96	1	84.97	14.46	_	_	_	_	_	99.43	$Au_{3.05}Ag_{0.95}$
9	-"-	_"_	2	82.92	16.21	_	_	_	_	_	99.13	$Au_{2.96}Ag_{1.03}$
20	-"-	_"_	2	92.72	6.96	_	_	_	_	_	99.68	Au <sub>3.52</sub> Ag <sub>0.48</sub>
21	_"_	90	4	75.69	23.47	_	_	_	_	_	99.16	Au <sub>1.92</sub> Ag <sub>1.08</sub>
2	_"_	_"_	1	68.60	30.97	_	_	_	_	_	99.57	Au <sub>1.10</sub> Ag <sub>0.90</sub>
23	Au-Pb-Sb	92	1	70.98	_	2.90	25.08	_	_	_	98.96	Au <sub>0.72</sub> Sb <sub>0.23</sub> Pb <sub>0.03</sub>
24	_"_	62	3	42.46	_	12.06	45.65	_	_	_	100.17	Au <sub>0.33</sub> Sb <sub>0.58</sub> Pb <sub>0.09</sub>
25	_"_	_"_	3	41.89	_	44.30	13.58	_	_	_	99.77	Au <sub>0.39</sub> Sb <sub>0.21</sub> Pb <sub>0.40</sub>
26	_"_	_"_	5	42.3	0.6	45.3	11.3	-	1.1	-	100.6	$Au_{0.39}Ag_{0.01}Pb_{0.40}$
27	_"_	-"-	3	74.9	4.0	1.8	19.6	-	1.3	-	101.6	$Sb_{0.17}As_{0.03}  Au_{0.63}Ag_{0.06}Pb_{0.01}  Sb_{0.27}As_{0.03}$
28	_"_	_"_	3	62.8	1.1	0.9	31.1	-	3.3	_	99.2	$Au_{0.50}Ag_{0.02}Pb_{0.01} Sb_{0.40}As_{0.07}$
9	Arsenic	_"_	4	2.1	_	0.4	1.3	_	96.1	_	99.9	As <sub>0.98</sub> Sb <sub>0.01</sub> Au <sub>0.01</sub>
0	Au - Sb - As	_"_	3	59.2	_	0.9	25.1	_	14.9	_	100.1	$Au_{0.42}Pb_{0.01}Sb_{0.29}As_{0.2}$
31	Ag - Pb - S	105	1	_	24.24	60.72	_	_	_	15.91	100.87	Pb <sub>0.58</sub> Ag <sub>0.44</sub> S <sub>0.98</sub>
32	_"_	_"_	1	_	19.45	65.16	_	_	_	15.30	99.90	Pb <sub>0.65</sub> Ag <sub>0.37</sub> S <sub>0.98</sub>
3	_"_	_"_	1	_	22.10	62.86	_	_	_	15.43	100.39	Pb <sub>0.61</sub> Ag <sub>0.41</sub> S <sub>0.97</sub>
34	Sb-As	125	3	_	_	_	51.63	_	49.00	-	100.63	As <sub>3.03</sub> Sb <sub>1.97</sub>
35	Pb-Sb-Fe-0	90	1	_	_	72.54	20.38	6.14	-	_	99.07	Pb <sub>1.83</sub> Sb <sub>1.71</sub> Fe <sub>0.48</sub>
,,,	(PbO)	$(Sb_2O_5)$	(FeO)	O <sub>4.02</sub>		72.04	20.50	0.11			33.07	1 0 <sub>1.83</sub> 00 <sub>1.71</sub> 1 c <sub>0.48</sub>







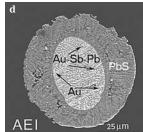


Fig. 4. Structure of ore microspherulas in section: galena dendrites in boulangerite matrix with irregular segregations of native antimony rimed by galena (a); zonal microspherulas with «gold» core: eutectoid aggregates of gold and Au-Pb-Sb phases with galena-boulangerite rim with a relic of unmelted galena (b); eutectoid aggregates of Au-Pb-Sb phase differing in Pb contents in galenite matrix with an admixture of boulangerite (c); sliced structures of Au-Pb-Sb phase and Au in «gold» core with galenite-boulangerite rim (d). The image in absorbed current (AEI). The scale ruler is 25 µm. Kellyam deposit.

oxidation (Novgorodova et al., 2003 $_2$ ). It was shown that the gas phase (molar shares of  $H_2 > H_2 O > H_2 S$ ) is saturated with hydrogen.

The initial stage of microspherula formation is the process of fusion of solid particles presenting as a suspension in the hydrothermal solution and got in cavitation field. Solid particles may form initial centers of cavitation bubbles. A necessary condition of transition of solid particles into the melt drops is the increase of their temperature up to values exceeding the fusion point. Such increase may be realized at collapse of a vapor-gas bubble. However, microsecond duration of the process requires discussion of its dynamics, amount of emitted energy and speed of solid particle heating.

Necessary calculations were made for quartz and gold, the most refractory minerals present in microspherulas, without taking into account natural additives decreasing fusion points. In other words, the task was to estimate the impact of maximum possible temperatures quickly arising at cavitation phenomena. For calculations, it was accepted that initial pressure  $P_1$  is 1.5 kbar, T is 250° C, gas bubbles during their maximal expansion have centimetric sizes, the size of native gold micrograins is 50  $\mu$ m, that of quartz 10  $\mu$ m. For simplification, it is also accepted that the liquid phase is water.

To evaluate the dynamics of gas-vapor bubble collapse in water we used the Rayleigh equation (Naugol'nykh and Ostrovsky, 1990):

$$R\frac{d^{2}R}{dt^{2}} + \frac{3}{2} \left(\frac{dR}{dt}\right)^{2} = \frac{1}{\rho_{1}} (P(t) - P_{1}), \tag{1}$$

where R - bubble radius, P(t) and  $P_1-$  pressure inside the bubble and initial pressure respectively,  $\rho_1-$  density of incompressible liquid environment of the bubble. Pressure P(t) was defined under formulas of adiabatic compression of non-ideal gas described by the Van der Vaals equation with a variable thermal capacity in calculation to one particle  $C_v=5/2$  for density of vapor  $\rho_v<\rho_c$  less than critical density  $\rho_c$  and  $C_v=3$  for density  $\rho_v>\rho_c$ .

The calculation under the formula (1) at  $P_1=1.5~kbar,\,\rho_1=1~g/cm^3$  and initial conditions  $P_0=40.5~bar$  and  $R_0=1~cm,\,where\,P_0-pressure of saturated vapor at <math display="inline">250^\circ$  C,  $R_0-radius$  of expanded bubble, shows that time  $t_m$  of existence of high temperature  $T>T_f$  in a bubble does not exceed 1.5 ms. The maximum temperature can rich  $T_{max}=7030^\circ$  C and minimum radius of a bubble  $R_{min}=0.15~cm.$  Values  $t_m$  and  $R_{min}$  appear approximately proportional to the initial radius of a bubble, at the same time  $T_{max}$  almost does not depend on  $R_0$ .

Elementary evaluation of  $l=\sqrt{\chi}t$ n case of quartz micrograin (thermal diffusivity  $\chi=0.02\,\mathrm{cm^2/s}$ ) shows that in time t ~1 ms the thickness of fused layer is relatively small l ~1.7  $\mu$ m, as comparison with the micrograin radius  $r_s=10~\mu$ m. At the same time, the appreciable excess of  $T_{max}$  over fusion point may provide energy input sufficient for deeper fusion of micrograins.

Solving the equation of heat conductivity for a spherical quartz microparticle with given thermal diffusivity  $\chi$ , thermal capacity  $C_s=70$  Joule/(Mole •°C), fusion point  $T_f=1610^{\circ}C$  and initial temperature  $T_{(r,o)}=250^{\circ}$  C, which surface temperature  $T_s=T(t)$  is determined from the decision of equation (1), it is possible to find out the complete energy input and distribution of temperature inside the micrograin at the given moment of time (Carslow, Eguer, 1964). Fig. 5 shows the complete energy input

$$\Delta Q = 4\pi c_s \int_{s}^{r_s} (T(r) - T_0) r^2 dr$$

and thickness of fused layer  $\Delta r$  in dependence on radius of extended cavitation bubble to the moment of time, when the bubble temperature T(t), after having past the maximum  $T_{max} = 7030^{\circ}$  C, decreases to the value  $T(t) = T_{\rm f}$ .

In Fig. 5 it is visible that the micrograin receives the energy necessary for its complete fusion  $\Delta Q=161\,\mathrm{erg}$  at  $R_{o}=1.4\,\mathrm{cm}$ , but actual temperature distribution is essentially irregular and the thickness of a fused layer at this moment only makes  $\Delta r=3.7~\mu m.$  At the subsequent moments of time the fusion depth may increase to 4.5  $\mu m.$  Full fusion may be realized at  $R_{o}>2~cm.$ 

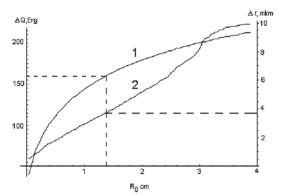
Thus, the quartz micrograin 10  $\mu m$  in size may be «dry» melted due to thermal energy arising at sharp adiabatic reduction of gas bubble with radius from 2 cm to 0.6 cm. So high temperatures (quartz  $T_f = 1610^\circ$  C) initiating the fusion of quartz micrograin surface may only be realized at centimetric sizes of extended gas bubble, that is apparently possible only at big volume of adiabatic cavity.

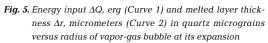
Similar calculations were also made for a 50  $\mu m$  native gold micrograin ( $T_{\rm f}=1063^{\circ}$  C, Cs = 25.23 Joule/(Mole  $^{\bullet}$  °C),  $\chi=1$  cm²/s), which results are shown in Fig 6. In this case the necessary for complete fusion energy input  $\Delta Q=1.06\cdot104$  erg is reached at  $R_{\rm 0}=0.2$  cm. At this,  $R_{\rm min}=0.06$  cm and fusion depth  $\Delta r=14$   $\mu m$ . The complete fusion of native gold micrograin within the framework of the given model requires  $R_{\rm 0}>0.5$  cm.

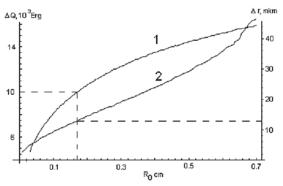
Equation (1) shows that temperature of solid particle and energy input of a compressed bub-

 $\it Table~2.~$  Invariant points of a natural system with Au, Pb, Sb, S, As, Fe (after Robinson, 1948; Craig et al., 1973; Gmelin Handbook...,1996)

Low-temperature association	High-temperature association	т°С
Quartz	Melt	1610
Galena	Melt	1115
Gold	Melt	1063.4
Galena-lead	Melt (stratified)	1041
Bronzite	Melt (1 kbar)	850
Antimony-melt (56% S)	Monotectic melt (~5,5% S)	800
Pyrite (+ sulfur)	Melt	743
Arsenopyrite	Pyrrhotite + loellingite + melt	702
Falkmanite (phase I after Craig et al.)	Galena + melt, Rich Sb <sub>2</sub> S <sub>3</sub>	642
Boulangerite	Falkmanite (phase I after Craig <i>et al.</i> 1973)	638
Gold – arsenic	Eutectic melt	636
Galena + antimony	Melt	622
Antimonite + antimony	Melt (stratified)	615
Boulangerite + galena	Falkmanite (phase I after Craig <i>et al.</i> 1973)	605
Ag <sub>2</sub> S + galena	Melt	605
Arsenic (25.5 %) + Antimony	Eutectic melt	602
Antimonite	Melt	556
Pyrite + arsenopyrite	Pyrrhotite + melt (AsS)	491
Aurostibite	Melt (congruent fusion)	460
Gold + silicon (6%)	Eutectic melt	370
Gold-aurostibite	Eutectic melt	360
Phase $Au_{0,36}Pb_{0,25}Sb_{0,39}$	Eutectic melt	250







 $\textbf{\it Fig. 6.} \ \textit{Energy input } \Delta \textit{Q}, \textit{erg (Curve 1)} \textit{ and melted layer thick-}$ ness  $\Delta r$ , micrometers (Curve 2) in gold micrograins versus initial radius of vapor-gas bubble

ble depend on its size at the moment of its greatest expansion. It is natural that more fusible matter of the majority of mineral microspherulas (Tables 1, 2) require 1-2 orders smaller bubbles.

It is necessary to remember that the used model is rather simplified and requires a number of specifications, in particular, more consistent consideration of dynamics of boundary processes liquid/vapor, real equation of state and process of heat transfer from the environment to a micrograin.

Nevertheless, the probability of sharp temperature fluctuations accompanied with generation of thermal energy sufficient for melting solid particles in a flow of boiling up hydrothermal solution is proved by the above calculations of cavitation models.

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#### ISOMORPHISM IN THE MINERALS OF STANNITE-FAMILY

Tat'yana L. Evstigneeva Institute of Geology of Ore Deposits (IGEM RAS), Moscow, evst@igem.ru

Vyacheslav S. Rusakov

Physics Department, Lomonosov Moscow State University, Moscow, rusakov@moss.phys.msu.su

Yurii K. Kabalov

 $Geology\ Department,\ Lomonosov\ Moscow\ State\ University,\ Moscow,\ kabalov@geol.msu.ru$ 

The crystals structures of stannite group minerals and mechanism of isomorphic substitution were studied using a complex of analytical techniques. Ten members of the kuramite-stannite series,  $Cu_{3-x}Fe_xSnS_4$  (0<x<1), synthesized by -0.1 formula units, pure stannite, and kesterite were chosen for this study. The methods used included microprobe and profile analysis (Rietveld method), Mö ssbauer spectroscopy, scanning and transmitting electron microscopy, and X-ray photoelectron spectroscopy. The intermediate members of the kuramite-stannite series are structurally similar homogeneous phases of tetragonal symmetry with regularly changing unit cell parameters (c/a-2). According to the structural analysis, four compounds of the series  $Cu_{3-x}Fe_xSnS_4$  with x=0.3, 0.6, 0.8, and 1.0 have tetragonal structures, which differ from stannite by their lower symmetry (I4) and distribution of atoms among tetrahedral positions.

According to the Mössbauer, the compounds of this mineral group contain divalent and trivalent iron atoms. Below the limiting iron atom concentration Fe (x) ~ 0.5 data shows that all Fe atoms are trivalent and occupy the sulfur octahedra. At 0<x<0.5, the substitution of atoms and the change of the structural positions and atom valence is carried out according to the scheme:  $2Cu^{2+}(T_d) \rightarrow Cu^{1+}(T_d) + (T_d) + Fe^{3+}(O_h)$ . The formula of the intermediate compounds can be expressed as

 $Cu^{1+}{}_2Cu^{2+}{}_{1\cdot 2x}Fe^{3+}{}_xCu^{1+}{}_xSn^{4+}S_4$ . The rend phase of this process is  $Cu^{1+}{}_2.5Fe^{3+}{}_{0.5}Sn^{4+}S_4$ . At the concentration (x>0.5), the mechanism of isomorphism is different:  $Cu^{1+}(T_d) + Fe^{3+}(O_h) + (T_d) \rightarrow 2Fe^{2+}(T_d)$ , and the end phase of this process is  $Cu^{1+}{}_2Fe^{2+}Sn^{4+}S_4$ .

Based on the results of the Mö ssbauer analysis, the structure of the intermediate phase  $Cu_{3*x}Fe_xSnS_4$  with x-0.6 was refined. It has been shown that  $Fe^{3+}$  atoms have octahedral coordination and occupy the positions that are free in the «normal» ordered sphalerite structure.

The Fe $^{3+}$ atoms (high-spin state) in kesterite with low Fe content are distributed among octahedral positions, which are vacant in the structure of pure  $Cu_2ZnSnS_4$ . This result is in good agreement with the complex scheme of isomorphism in  $Cu_{3-x}Fe_xSnS_4$  series.

 $2\ tables,\ 3\ figures\ and\ 11\ references.$ 

#### Introduction

Compared to the significant progress in studying the crystal structures of silicates and multi-atom compounds (organic substances, metalloorganic compounds, semiconductors of new types, etc.), the level of knowledge for structures of relatively simple compounds has not almost changed for the last 20 – 30 years. First of all this concerns intermetallides (Cu<sub>3</sub>Au, CuAu) or similar phases (NiAs, MnP, Fe<sub>2</sub>P, Ni<sub>2</sub>Si), sulfides (ZnS, CuFeS<sub>2</sub>, Cu<sub>2</sub>FeSnS<sub>4</sub>, FeS<sub>2</sub>), and their analogs. The main reason for this situation is the absence of high-quality material. Another reason is the widespread opinion about the «simplicity» of these crystal structures.

Most of the above-mentioned compounds have a high isomorphic capacity and always contain impurities (sometimes up to tens of atom percent). All these compounds are characterized by covalent or mixed (ionic-covalent, covalent-metallic, etc.) type of chemical bond. The presence of vacancies in many structural types and the different degree of ordering in the distribution of isomorphic components among structural positions are also typical for these minerals.

The problem of isomorphism in ore minerals, primarily sulfides, is quite important because many commercial elements are present as impurities and are now extracted from their host minerals. Investigation of the forms of occurrence of these elements is necessary to understand the reasons for the loss of useful components during ore processing and to develop new technologies. The different elements distribution in crystal structures, the possibility of isomorphic substitution of atoms, and, as a consequence, the ordering of atoms

Table 1. Stannite group minerals

Mineral	Formula	Sp.gr.	a (A)	b(A)	c(A)	Z	Reference
Stannite Kesterite Sakuraiite Okartite Briartite Gernyite Velikite Kuramite	Cu <sub>2</sub> FeSnS <sub>4</sub> Cu <sub>2</sub> ZnSnS <sub>4</sub> Cu <sub>2</sub> Zn(In,Sn)S <sub>4</sub> Ag <sub>2</sub> FeSnS <sub>4</sub> Cu <sub>2</sub> FeGeS <sub>4</sub> Cu <sub>2</sub> CdSnS <sub>4</sub> Cu <sub>2</sub> HgSnS <sub>4</sub>	I_42m I_4 I_42m* I_42m I_42m I_42m I_42 I_42m (I_4)	5.449 5.427 5.45 5.72 5.32 5.487 5.5749 5.445	5.449 5.427 5.45 5.72 5.32 5.487 5.5749 5.445	10.757 10.871 10.91 10.98 10.51 10.848 10.882 10.75	2 2 2 2 2 2 2 2 2	(Hall et al.,1978) (Hall et al.,1978; Kissin, 1989) (Chvileva et al.,1988) — «— «— « (Szymanski, 1978) (Evstigneeva et al., 1998)
Kuidillite	$Cu_2CuSnS_4$	1 42111 (1 4)	5.445	3.443	10.73	2	(Kovalenker <i>et al.</i> , 1979)

within the structure also need to be known to answer the question about the different behavior of atoms in the nature, further development of crystal chemistry, and synthesis of new compounds. This consideration involves both noble (Au, Ag, PGE) and common (Fe, Zn, Cu, Cd, Pb, etc.) metals.

There is a common opinion that the theory of isomorphism is well developed. Publications by L. Pauling, G. Goldshmidt, N. Belov, G. Bokii, V. Frank-Kamenetskii, and others are quite famous. Discussing chemical composition of minerals (especially ore minerals) mineralogists usually use the terms «substitution isomorphism», «compensation isomorphism», «intercalation isomorphism», «isomorphism of the ions of the same element with a charge change». However, in most cases, the data on the structures of particular compounds under discussion and on the crystallographic positions of the impurity elements are absent. Because of application Pauling's empirical rules, or of data interpolation for similar compounds many conclusions about the isomorphism in sulfides seem to be declarative. This problem primarily concerns the minerals with composition rich in impurities (MRSA) and non-stoichiometric; i.e. fahlores, stannite group, and their close derivatives. The X-ray analysis and spectroscopy techniques could help us to verify existing concepts and to collect new information about the real isomorphic sub-

The structure of stannite is derivative from the ZnS (sphalerite structure space group  $\overline{142m}$ ). The tetragonal unit cell of stannite is doubled c in comparison to ZnS: a=5.449, c=10.757 (4) Å, Z=2. Metal atoms occupy all sulfur tetrahedra with the similar orientation in the cubic close packing: Fe -2a (000), Sn -2b (1/2 1/2 0), Cu -4d (0 1/2 1/4), S -8i (xxz, x=0.7551, z=0.8702) (Hall et al., 1978).

The stannite-group minerals have the common formula  $A_2BSnS_4$ , where A = Cu,Ag; B = Fe,Cu,Zn,Cd,Ge,Hg etc. (Table 1). The stannite group includes kuramite ( $Cu_3SnS_4$ ) (Kovalenker *et al.*, 1979), kesterite ( $Cu_2ZnSnS_4$ ) (Kis-

sin 1989), okartite ( $Ag_2FeSnS_4$ ) (Chvileva et al., 1988), velikite ( $Cu_2HgSnS_4$ ) (Evstigneeva et al., 1998), cernyite ( $Cu_2CdSnS_4$ ) (Szymanski, 1978), and other species. Stannite minerals have a significant place among natural and synthetic sulfides. Many of those are abundant and characteristic minerals of pyrite, gold, copper-nickel, silver, and other ore deposits. The stannite compounds and their structural analogs are characterized by an extremely diverse composition, containing elements of the I, II, III, IV, V, VI, and VIII groups of the periodic system.

Minerals of the stannite family are characterized by a great number of isomorphic impurities. The most typical of which is iron in kuramite ( $\text{Cu}_3\text{SnS}_4$ ) (Kovalenker *et al.*, 1979) and kesterite ( $\text{Cu}_2\text{ZnSnS}_4$ ) (Kissin, 1989). The structures of these compounds are derivatives from the cubic sphalerite structure (ZnS). They differ in space symmetry ( $I\overline{42}m$ ,  $I\overline{4}$ ), distribution of metal atoms in the structural sheets perpendicular to the 4-order axis, and the degree of distortion of the coordination sulfur polyhedra.

The monocrystal method was only used for studying the structures of kesterite (Kissin, 1989) and Gernyite (Szymanski, 1978). These structures differ from the stannite one by the distribution of atoms among tetrahedral positions and by the absence of the diagonal mirror symmetry planes. The latter results in the reduced symmetry  $(I\overline{4})$ .

The study of synthetic compounds in the  $\text{Cu}_2\text{ZnSnS}_4 - \text{Cu}_2\text{FeSnS}_4$  system showed that the Fe-Zn substitution solid solutions exist in the whole range of compositions (Springer, 1979). Due to the close size of the divalent iron and zinc ions, the iron atoms were believed to substitute zinc atoms in the kesterite structure. However, it was suggested (Kissin, 1989) that the isomorphic series exists between kesterite and a polymorphic modification of stannite with kesterite structure. Thus, the problem of the substitution mechanism in the series  $\text{Cu}_2\text{ZnSnS}_4 - \text{Cu}_2\text{FeSnS}_4$  remains unsolved (Bernardini et al., 1979).

The existence of the stannite-kuramite series (limited?), with divalent iron substituting divalent copper in kuramite, was suggested according to the compositions, X-ray patterns, and properties (Kovalenker  $et\ al.$ , 1979). However, because of the different electron structures the Fe²+ and Cu²+ ions takes place should be interesting to know if the Fe-Cu substitution really takes place and, if it does, what is the mechanism of this process.

#### Subjects and methods of study

A complex investigation of the compounds of stannite group was carried out to refine the structural features of some sulfide phases and to determine the mechanism of isomorphic substitution. The kuramite-stannite system and kesterite were chosen as subjects for this study. Ten members of the kuramite-stannite series,  $Cu_{3-x}Fe_xSnS_4$  at 0 < x < 1 (step of  $x \sim 0.1$ formula unit), were synthesized from pure elements in evacuated quartz capsules (heating to 1150°C, annealing at 400°C, 960 hours, quenching in ice-cold water). The composition of kesterite from the Kester deposit (O. Stavrov's sample) was determined as follows (average of 10 analyses, wt.%): Cu 28.79 28.98; Zn 12.06 - 12.21; Fe 2.28 - 2.21; Sn 27.09 - 27.15; S 28.96 - 28.29;  $\Sigma$  99.18 -98.84; which yields the formula  $Cu_{2.00-2.03}$  $(Zn_{0.81\text{-}0.83}Fe_{0.18})Sn_{1.00\text{-}1.03}S_{3.99\text{-}3.94}.$ 

The valence and coordination of atoms in the crystal structures were concurrently determined by several methods: microprobe [MS-46 Cameca (IGEM RAS), Camebax Microbeam (Institute of Volcanology, RAS, Far East Branch), 20 kV-10 nA; standards:  $CuFeS_2$  (Cu,Fe),  $Sn_{met}$  (Sn),  $FeS_2$ (Fe)]; profile analysis (Rietveld method) - ADP-2 difractometer (CuKα, Ni filter), calculation by WIRIET program (version 3.3); Mössbauer spectroscopy (MS1001E, 57Co in Rh and <sup>119m</sup>Sn in BaSnO<sub>3</sub>; MSTools software complex); scanning (JSM-5300+Link ISIS) and transmitting (JEM-100C + Kevex 5100 EDD) electron microscopy; X-ray photoelectron spectroscopy [LAS-3000 «Riber» + OPX-150 semispherical photoelectron analyzer,  $AIK_{\alpha}$ (1486.6 eV) at U = 12 kV and I = 20 mA, calibration by carbon 1s-line (bond energy = 285 kV)]. Use of the modern analytic facilities and software for identification and decoding of experimental data enables determining the coordination and valence of Fe and Sn atoms in structures of common and rare sulfide minerals.

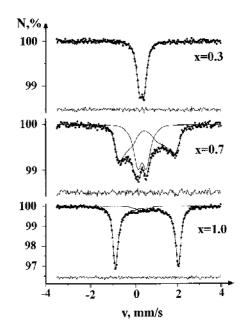


Fig. 1. Typical Mössbauer spectra of 57Fe for the compounds of the Cu₃₄FexSnS₄ series. N is the number of impulses (intensity), and v is the counting rate.

#### Results

According to SEM and transmitting electron microscopy data, all intermediate members of the kuramite-stannite series are structurally similar homogeneous phases with a tetragonal symmetry and regularly changing unit cell parameters (c/a-2).

The structural study of four phases of the  $Cu_{3-x}Fe_xSnS_4$  series (x = 0.3, 0.6, 0.8, and 1.0) by Rietveld method indicated that all of them have a tetragonal symmetry and differ from stannite ( $Cu_2FeSnS_4$ ,  $I\overline{4}2m$ ) by a lower symmetry ( $I\overline{4}$ ) and metal atom distribution among tetrahedral positions. The endmember of this series evidently is the synthetic polymorph of stannite. Attempts to determine how iron replaces copper in different tetrahedral positions in intermediate phases of the kuramite-stannite series lead to ambiguous results in spite of a good R-factor values (3.2-3.8%) (Evstigneeva et al., 2001a).

The Mössbauer analysis showed that the phases of this series contain both divalent and trivalent iron atoms (Fig. 1). It was found that below the limiting concentration (x)-0.5 iron is only trivalent and is octahedrally coordinated by the S atoms.

Within the whole isomorphic series, Sn atoms are tetravalent and have tetrahedral

Table 2. Composition (wt.%) of synthetic phases in the  $Cu_{3-x}Fe_xSnS_4$  system

x	Cu	Fe	Sn	S	Σ
0.08	41.74	1.08	34.11	24.72	101.65
0.14	42.71	1.56	31.04	23.85	99.16
0.29	39.68	3.79	29.62	29.32	102.41
0.40	40.50	4.83	28.96	23.36	97.65
0.51	39.16	6.60	29.39	26.31	101.46
0.58	35.28	7.88	30.00	29.33	102.49
0.71	35.89	8.89	28.96	27.07	100.81
0.84	32.03	11.18	29.65	29.70	102.56
0.97	33.77	11.52	28.21	25.69	99.16
0.96	29.80	12.88	26.5	29.9	98.1

 $\it Note: MS-46$  Cameca (IGEM RAS); Analyst: G.N. Muravitskaya; Conditions of analysis: 2 kV - 10 nA; standards: CuFeS $_2$  (Cu,Fe), Snmet (Sn), FeS $_2$  (Fe)

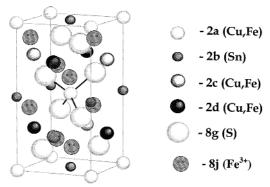
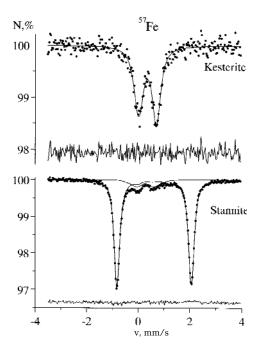


Fig. 2. Structure of an intermediate member of the kuramite-stannite series



 $\textbf{\it Fig. 3.}~\textrm{M\"o}~\textrm{ssbauer}~\textrm{spectra}~\textrm{of}~\textrm{\tiny 57}\textrm{Fe}~\textrm{for}~\textrm{natural}~\textrm{kesterite}~\textrm{and}~\textrm{stannite}$ 

coordination in the structure with a high degree of covalence (bonds with S atoms). As the concentration of the Fe atoms increases, the covalence degree of the Fe²+-S and Sn⁴+-S bonds decreases, while the covalence of the Fe³+-S bonds increases. The magnitude of the effective charge of the Sn atoms in the tetrahedral positions is  $Q_{\rm Sn}=3.38\pm0.08$  (Evstigneeva *et al.*, 2001a).

The structure of the intermediate phase  $Cu_{3-x}Fe_xSnS_4$  with x=0.6 was refined on the base of the Mössbauer data. The best results (R=2.69%) were obtained with  $Fe^{3+}$  distribution among the octahedral positions that are free in the «normal» ordered sphalerite structure: 8j - xxz ( $xFe^{3+}\sim1/4$ ,  $zFe^{3+}\sim0.126-0.128$ ,  $zFe^{3+}=zS/3+5/12$ , zS-z atoms of S-i in the structure) (Fig. 2). Correspondingly  $Me_{Oh}-Me_{Td}=2.31-2.34$  Å, that is comparable to the  $Me_{Td}-S$  distances but less than the  $Me_{Oh}-S$  distance (2.57–2.81 Å) (Td and Oh are tetrahedral and octahedral positions, respectively).

Two schemes of isomorphism in the  $Cu_{3-x}Fe_x$   $SnS_4$  series are proposed to explain the results obtained in this study:

At 0<x<0.5, the isomorphic substitution and the change of structural position and atom valence of occur as follows:  $2Cu^{2+}(T_d) \rightarrow Cu^{1+}(T_d) + (T_d) + Fe^{3+}(O_h)$ . The formula intermediate phases can be:  $Cu^{1+}_2Cu^{2+}_{1\cdot2x}Fe^{3+}_xCu^{1+}_xSn^{4+}S_4$ . The complete depletion of  $Cu^{2+}$  corresponds the formula  $Cu^{1+}_{2\cdot5}Fe^{3+}_{0.5}Sn^{4+}S_4$ .

Above the limiting concentration (x = 0.5), the scheme of isomorphism changes as follows: Cu+(T<sub>d</sub>) + Fe³+(O<sub>h</sub>) + (T<sub>d</sub>)  $\rightarrow$  2Fe²+(T<sub>d</sub>), and the end phase of this process is Cu¹+2Fe²+Sn⁴+S<sub>4</sub> (Evstigneeva *et al.*, 2001b).

The above-described mechanism of isomorphism could be indirectly confirmed by XPES results: the divalent copper content decreases (relative to monovalent copper) with increasing iron content.

The presence of the trivalent iron (high-spin state) in the octahedral coordination of sulfur atoms in the structure of kesterite pure in iron,  $Cu_{2.00-2.03}(Zn_{0.81-0.83}Fe_{0.18})Sn_{1.00-1.03}S_{3.99-3.94}$ , was proved by Mössbauer spectroscopy (Fig. 3; Rusakov *et al.*, 2001). This result contradicts the structural analysis data for kesterite, according which iron substitutes zinc in tetrahedral positions (Kissin, 1989).

Because the presence of trivalent iron atoms in octahedral positions is in good agreement with the scheme of isomorphism for Fe-poor members of the  $\text{Cu}_3\text{SnS}_4$  –  $\text{Cu}_2\text{FeSnS}_4$  series, a similar scheme could be suggested for the Fe-poor kesterite. The tetrahedral positions in

the structure become vacant:  $Cu^{1+}(T_d) + Zn^{2+}(T_d) \rightarrow (T_d) + Fe^{3+}(O_h)$ ; that correspond to the formula of the intermediate phases:  $Cu^{1+}_{2-x}Zn_{1-x}Fe^{3+}_xSn^{4+}S_4$ .

#### Conclusions

The isomorphism of Fe atoms in the stannite group compounds has a complex character and involves the formation of tetrahedral vacancies, occupation of octahedral positions, and change of the copper valence.

In the kuramite-stannite series there is the limiting concentration of Fe atoms, below which all Fe atoms are trivalent. In this concentration area, the number of Fe<sup>3+</sup> and Cu<sup>1+</sup> ions increases with x, while the number of Cu<sup>2+</sup> ions decreases. Above the  $x{>}0.5$  value, Fe<sup>2+</sup> ions appear, and their concentration increases with x, while the number of Fe<sup>3+</sup>and Cu<sup>1+</sup> atoms decreases.

The presence of trivalent iron atoms in the octahedral positions is also characteristic for Fe-kesterites (Fe < 0.5 formula units). That could prove the similar mechanism of substitution.

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## ADDITIVE MODELS OF OPTICAL PROPERTIES IN MINERALS OF HUMITE POLYSOMATIC SERIES

Boris B. Shkursky

Moscow State Prospecting University, Moscow, msgpa@msgpa.edu.ru

Additive models of optic properties of the Mg-F-humite minerals are proposed based on two schemes of structural partition. The recent scheme of structure partition with both forsterite and sellaite layers stacking is discussed and a new one with both norbergite and forsterite layers stacking is suggested. The essence of models is that weighted components of partial dielectric permeability tensors, belonging to different kinds of structural blocks, give an individual pays to average tensor and so they determine refractive indices of mineral. The partial tensor component values were estimated by least squares procedure and the calculated refractive are very close to those. Since both structure partition schemes provide a good agreement with real optical properties for models constructed by them, they seem to be correct and, therefore, the humite group minerals are members of a polysomatic series.

6 tables, 5 figures, 15 references.

Refraction parameters of humite group minerals are subject to appreciable joint influence of isomorph substitutions, both in cationic and anionic matrices of structure. This causes essential overlaps of refraction parameters values of different humite group mineral species.

The attempts to evaluate quantitative influence of chemical composition variations on optical characteristics by experimental data are considered as more or less unsuccessful (Deer et al., 1965, Minerals, 1972).

Theoretical calculations of the average refraction index for magnesium minerals of the group were made by V. Sahama (1953; see in Deer et al., 1965) taking into account the isomorphism  $F \leftrightarrow (OH)$  and using polarizability values. These calculations gave the results satisfactorily conformed to experimental data. However, there are deviations successively increasing in the row chondrodite - humite clinohumite. Refraction index is increased at the same row. In author's opinion, one of the possible steps to solve the above problem is the attempt to construct the additive model of indicatrix parameters variability for this mineral group according to principles discussed in the work by Yu. Punin (1989), that is devoted to optics of heterogeneous layered crystals. The condition of model applicability to humite group minerals is the presence in their crystal structures crystallochemically different layers or blocks, whose quantities changes from one mineral of another. Even now there is no common opinion among mineralogists regarding the existence of such layers or blocks in the crystal structures of humite group minerals (Bragg and Claringbull, 1967, Ribbe and Gibbs, 1969).

The purpose of this work is to construct additive models of optical properties for pure magnesium-fluorine minerals of the humite group. The results may affect the evaluation of traditional description principles applicability to the crystal structure of humite group minerals as the degree of efficiency of additive model of indicatrix in humite group minerals essentially depends on correct selection of structural fragments.

#### Optical indicatrix of Heterogeneous crystals

Heterogeneous crystals with irregularities much smaller than the wavelength are optically homogeneous (Punin, 1989). Optical properties of layered heterogeneous crystals are subject to the additivity rule: indicatrices of such crystals depend on volume ratios  $V_i$  of structural components characterized by an individual indicatrix and  $\Sigma V_i = 1$ . At the first stage, this work has to establish parameters of individual indicatrices for structural components, which contents in various humite group minerals are assumed known.

To solve the problem, we consider Fedorov-Pokkels and Hoiser-Wenk methods the most suitable out of three techniques of resulting indicatrix construction (Punin, 1989). The Mullar method, being convenient for establishment of component volume ratios by optical characteristics of a crystal, in our case should result in appreciable deviations of the form of resulting indicatrix from an ellipsoid. There are no reasons to doubt the ellipsoid form of indicatrices of humite group minerals as anomalies which might evidence the opposite are absent in the accessible publications.

In the Fedorov and Pokkels method (Punin, 1989), tensors of dielectric impermittivity of

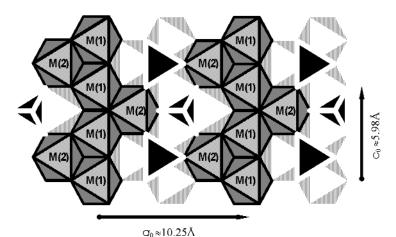


Fig. 1. The idealized structure of forsterite in the Pnam installation, the projection to (010)

components  $\epsilon_{j}^{-1}$  are averaged with the weights equal to volume parts  $V_{j}$ . Main values of resulting tensor  $\epsilon^{-1} = \Sigma V_{j} \epsilon_{j}^{-1}$  are equal to inverse square values of main refraction parameters — indicatrix semi-axes.

In the Hoiser and Wenk method, tensors of dielectric permittivity of components are exposed to weighted averaging. Squares of main refraction parameters — resulting indicatrix semi-axis — are equal to principal values of the resulting tensor  $\varepsilon = \Sigma V_{\mathcal{E}_i}$ .

Application of the optical properties additivity rule to humite group minerals assumes the availability of at least two types of structural components in their structures — diverse layers, which number in a cell changes regularly from mineral to mineral.

#### Selection of structural components

The most general formula of humite group minerals can be written down as follows (Jones, Ribbe *et al.*, 1969):

$$f\:Me_2[SiO_4] \bullet s\:Me_{1\text{--}t}\:Ti_t\:X_{2\text{--}2t}\:O_{2t}$$

were Me = Mg, Fe, Mn, Ca and X = F, OH, and factors f and s — positive counting numbers. Only minerals with s = 1 are currently known. In this case, the composition of titanium-free magnesium members of the group is described by factor f values:

Table 1. Values of factor f in formulas of humite group minerals

Mineral	Value f
Norbergite	1
Chondrodite	2
Humite	3
Clinohumite	4

At the end of the before last century, Penfield and Howe (1894) revealed relations between three known at that time (out of four) magnesium minerals of the humite group. This has allowed to identify variable ratio Mg<sub>2</sub>[SiO<sub>4</sub>]:Mg(OH,F)<sub>2</sub> as a morphotropy parameter. The roentgenostructural studies of all four minerals (Taylor and West, 1928) have shown that structures of humite group minerals are characterized by closest hexagonal packing (CHP) of anions and have much in common with the structure of olivine. Structures were interpreted as combination of forsterite Mg<sub>2</sub> [SiO<sub>4</sub>], and confined between them brucite-sellaite  $Mg(OH,F)_2$  layers, in certain ratios determined for every mineral.

Let's consider this method to distinguish key details in the idealized structure of humite group minerals basing on the system of designations accepted by Bragg and Claringbull (1967). To make comply the orientation of structure of various humite minerals and forsterite, we shall accept a single installation for cells of all minerals as it is proposed in Minerals (1972). In this case, the space group of rhombic forsterite, norbergite and humite will be expressed by symbol Pnam, and space group of monoclinic chondrodite and clinohumite — P12<sub>1</sub>/a1. The structures are represent in a projection to (010) in direction [ 100 ].

B the idealized forsterite structure (Fig. 1), the CHP plane, as well as in all humite minerals, coincides for the chosen projection with the drawing plane. The filled octahedric positions containing Mg are subdivided into two types — M(1) and M(2). Shown in Fig. 2 (a) forsterite blocks of A and B types are cut out from the forsterite structure and are layers as high as half forsterite  $c_0$  parameter, parallel to

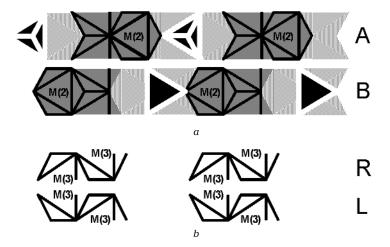


Fig. 2. Separation of structural fragments of the humite group minerals after Bragg (Bragg and Claringbull, 1967), the projection to (010) in the accepted installation: a) forsterite layers A and B, b) sellaite layers R and L

(001) and appear as tapes in the accepted projection.

Brucite-sellaite enantiomorphous blocks R and L (Fig. 2.b) are represented by layers about a quarter of forsterite  $c_0$  thick and contain half-octahedrons of M(3) type. They have a rutile-like structure and can be referred as brucite only because of usual presence of hydroxyl. Blocks are joined in such a manner that R and L never follow in succession whereas blocks A and B may adjoin each other.

If the blocks in the sequence along  $c^{\star}$  (hereinafter the vector of inverse lattice) to designate by letters A, B, R and L, than the resulting «words» — cyclic sequences of letters — the following combination rules will be observed: A only follows B or R, B — only A or L, and R and L — only B and A respectively. Each sequence unequivocally defines the mineral, but not on the contrary. Such a system of block designation, as well as blocks itself, N.V. Belov (1976) named Bragg blocks.

The sequence period corresponds to the period along  $\mathbf{c}^{\star}$ , equal to  $c_0 \sin \beta$  of the formed structure. Number of forsterite blocks in the period is always even. Parameters  $a_0$  and  $b_0$  are equal or very close to those of forsterite. In rhombic minerals number of blocks R and L coincides, in monoclinic it is different and the value of difference defines the total shift for the period and affects lattice parameter  $c_0$  and monoclinic angle B. In known monoclinic minerals of the group, the difference is 1. Blocks R should prevail to make the monoclinic angle blunt in the chosen installation and projections for monoclinic minerals. The resulting

ABRL-formulas for magnesium minerals of the group are:

Norbergite ALBR Chondrodite ABR Humite ABALBABR Clinohumite ABABR

The described scheme to distinguish structural fragments has found wide application and was used by many researchers of humite group, so it could be referred to as traditional. However, having specified the norbergite structure, Ribbe and Gibbs with co-authors (Gibbs and Ribbe, 1969), having confirmed the consistency of results to idealized structures determined by Taylor and West (1928), have made a conclusion that interpretation of structures by the last as an alternation of forsterite and sellaite layers is incorrect and serving a source of mistakes. So, it was found out that traditionally distinguished forsterite and sellaite layers do not correspond to forsterite and sellaite by composition (Jones, Ribbe et al, 1969). Completely denying a possibility and expediency to segregate similar layers, Ribbe, Gibbs et al. (1968) consider structures of humite minerals as essentially olivine-like with regular substitution of a part of oxygen atoms in CHP by fluorine and hydroxyl group with formation of vacancies in SiO<sub>4</sub>-tetrahedrons. Zigzag chains of edge-connected octahedrons are accepted as key details of the structure. Are there enough of reasons to completely deny the traditional structure description scheme or its modifications? If there is enough, then the humite group is a morphotropic homological series

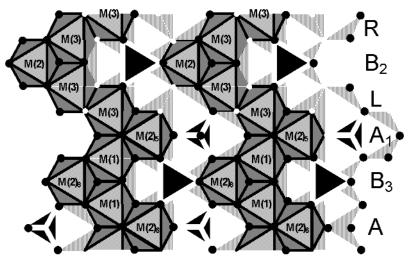


Fig. 3. Differences in the coordination of octahedric positions at various methods of combination ABRL blocks and three kinds of forsterite blocks.  $\bullet$  – Oxygen,  $\circ$  – fluorine

complicated by isomorphism, but if it is possible to distinguish blocks, the humite group can yet be considered a polysomatic series (Godovikov, 1997).

The analysis of octahedric position coordination features in blocks R(L) and A(B) with consideration of anion differences and options of block combination shows (Fig. 3) that composition of so-called brucite-sellaite blocks R and L is 2Mq(F,OH)O per cell, as was noted by Jones, Ribbe et al. (1969). There is to add that blocks A(B) have diverse composition depending on the surrounding and are subdivided into three kinds (Fig. 3).

In case of a norbergite, forsterite blocks are of kind  $A_1(B_1)$ , they are surrounded with blocks R and L from both sides. The M(2) octahedron preserves the designation as unique and has two F atoms on the ends of the not divided edge. Semi-octahedrons formed from M(1) octahedrons at cutting blocks A(B) from the forsterite structure are joined with half-octahedrons M(3) of sellaite blocks and resulting octahedrons receive a designation of M(3). Each block of kind  $A_1(B_1)$  contributes  $2Mq_2SiO_3F^+$  into a cell.

Forsterite blocks contacting with sellaite ones only at one side and adjoining on the other blocks similar to themselves are attributed to kind  $A_2(B_2)$ . Semi-octahedrons of blocks  $A_2(B_2)$  are half-octahedrons M(1) of forsterite, on the contact to block R or L they join half-octahedrons M(3) and this designation is applied to the resulting octahedrons. On the side of forsterite block, half-octahedrons are united with similar ones and are designated

M(1). Octahedrons M(2) of blocks  $A_2(B_2)$  on the contact to block R or L have F atom as one of ligands, the position inside such octahedron is designated M(2)<sub>5</sub>. The composition of such blocks per cell is  $Mg_4(SiO_4)SiO_3F^+$ .

At last, block  $A_3(B_3)$  surrounded with blocks  $B_2(A_2)$  or  $A_3(B_3)$  has a really forsterite composition and does not contain fluorine, its octahedric positions are designated M(1) and  $M(2)_6$ . The composition per cell is  $2Mg_2SiO_4$ .

Certainly, it is possible to make twisting boundaries of layers, not dissecting anions half-and-half, but attributing them entirely to one of next blocks and so to avoid formation of charged blocks and to bring compositions of layers to originally declared. But it will not change localization of connections Me-F and Me-O in blocks of different types. However, despite of revealed facts, the ABRL scheme, at due consideration of distinctions between block kinds and elimination of illusions about availability of fragments with sellaite composition and structure, unequivocally sets the composition and structure and correctly transfers topological features of atom coordination. But distinctions in grading blocks A(B) may affect individual contributions of these blocks in optical properties as the connections Me-O and Me-(F,OH) are different, concentrated in different kind blocks in unequal number.

Taking into account the above reserves, let us consider the alternative scheme of block selection (Fig. 4), which results in reduction of kind number to two, if to ignore enantiomorphism as it was made in the traditional scheme. Attaching from both sides to blocks R(L) thin

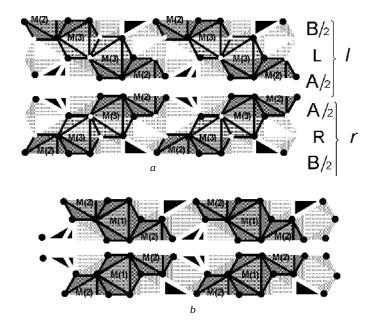


Fig. 4. Structural fragments under the abrl scheme: a) norbergite blocks r and l, b) forsterite blocks a and b.

● − Oxygen, ○ − fluorine

layers in height of a half-octahedron, separated from buffer blocks A(B), we receive blocks (designated respectively as r(I)) having composition of norbergite, in which all F(OH) atoms and connections with their participation are now collected (Fig. 4, a). The payment for this advantage is entry of Si atoms and their connections with oxygen in such blocks.

Two enantiomorphous blocks a and b of forsterite (Fig. 4, b) could be received by cutting layers from the forsterite structure with a shift by a half-octahedron in comparison with A and B. Such layers contain entirely octahedrons of M(1) and half-octahedrons M(2) positions, which, despite of getting the status of halves of M(2) $_5$  or M(2) $_6$  depending on neighbors, do not change the set of atoms and connections within the block. The proposed scheme of block interpretation has no weak points inherent to the traditional scheme and may serve for the description of structure and composition of any humite group mineral as

well as the traditional scheme until minerals with unusual R(L) inserts will be discovered, which is little probable.

Relation of traditional Bragg designations of ABRL sequences of elements to new *abrl* is expressed by the following symbolical formulas: r = B/2 + R + A/2, l = A/2 + L + B/2, a = B/2 + A/2 and b = A/2 + B/2, if to keep orientation and sequence of packing along  $\mathbf{c}^{\star}$ .

Combination rules change in the appropriate way. It is convenient for both schemes — traditional and proposed — to use the same letter designations to designate the number of different blocks in the period, as for proper blocks; distinctions in the use are easily established from the context. Interesting feature of quantitative ratio in the abrl scheme is equality of surpluses (r-l) and (b-a), whereas A=B in all cases and does not depend on (R-L). Table 2 shows options and quantitative characteristics in traditional and proposed schemes for humite group minerals and fo-

Table 2. Sequence and the maintenance(contents) of structural components in humite group minerals

Mineral	ABRL-scheme	A + B	R	L	abrl-scheme	a+b	r	1
Norbergite	ALBR	2	1	1	rl	0	1	1
Chondrodite	ABR	2	1	0	br	1	1	0
Humite	BABRABAL	6	1	1	abrbal	4	1	1
Clinohumite	ABABR	4	1	0	babr	3	1	0
Forsterite	AB	2	0	0	ab	0	0	0

75

rsterite, which is the final member of the polysomatic series forsterite-norbergite. These minerals should be considered as miscible components of the humite polysomatic series because compounds with more than 50 % of  $Mg(OH,F)_2$  are not known and sellaite does not belong to the series.

Volume ratio of structural components, which may be blocks AVRL or abrl, are related to the number of blocks in a cell and thickness of these of blocks. Using data on cell parameters of 10 humite group minerals (Jones, Ribbe et al., 1969) and least-squares method (LSM), we established individual contributions  $q_i$  of different blocks in the value of  $c_0sin\beta$  :  $q_A=3.018~\textrm{Å},~q_R=1.354~\textrm{Å},~q_a=3.018~\textrm{Å}$  and  $q_r=4.372~\textrm{Å}.$  Root-mean-square deviation (RMSD) of  $c_0 \sin \beta$  values calculated with these contributions from experimental values is 0.012 Å. Contributions  $q_i$  are evaluations of block thickness and may be considered their relative volumes.

#### Additive models of the indicatrix

The initial verification of the hypothesis on the additivity of optical indicatrix in minerals of humite polysomatic series was made on synthetic Mg-F representatives of the series, in which isomorph substitutions does not influence optical properties and their relation with the variable contents of structural components is not biased. The properties of synthetic minerals used at calculations were taken from Winchell and Winchell, 1967.

The right crystallophysical system of coordinates XYZ (hereinafter the basic), in which the listed axes coincide with directions of vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}^*$  of lattice in the accepted installation, was used for modelling an indicatrix. For rhombic minerals of the group, axis Z is directed by vector  $\mathbf{c}$ , conterminous with direction  $\mathbf{c}^*$ . In this system of coordinates, the value of main parameters of rhombic minerals will have the

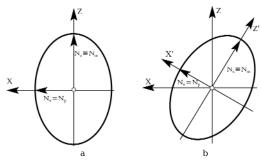


Fig. 5. The indicatrix orientation in relation to the basic axes in the projection to (010): a) rhombic minerals, b) monoclinic minerals

following designations:  $Ng = N_v$ ,  $Nm = N_z$ and  $Np = N_x$  (Fig. 5a).

For monoclinic minerals, the same conformities were conventionally accepted, considering that designations are attributed to the transformed system of coordinates X'Y'Z', revolved regarding the basic system around axis X through angle r counted in the positive direction. Taking into account that monoclinic minerals of the group have the Np axis of indicatrix located in a blunt angle  $\ensuremath{\mathtt{B}}$ , the extinction angle  $\Gamma$  is negative, that is, the system of coordinates X'Y'Z' for monoclinic minerals is revolved clockwise regarding the basic system (Fig. 5b).

Tensors of impermittivity  $\varepsilon^{-1}$  and permittivity  $\varepsilon$  of orthorhombic minerals in the basic system of coordinates and monoclinic minerals in the X'Y'Z' system have a canonical form, are characterized by three principal values and are noted as

$$\varepsilon = \begin{bmatrix} \varepsilon_{x} & 0 & 0 \\ 0 & \varepsilon_{y} & 0 \\ 0 & 0 & \varepsilon_{z} \end{bmatrix}, \qquad \varepsilon^{-1} = \begin{bmatrix} \varepsilon_{x}^{-1} & 0 & 0 \\ 0 & \varepsilon_{y}^{-1} & 0 \\ 0 & 0 & \varepsilon_{z}^{-1} \end{bmatrix}$$
(1,2)

Tensors of monoclinic minerals in the basic system of coordinates get a non-diagonal form related to their principal values

$$\varepsilon = \begin{vmatrix} \varepsilon_{11} & 0 & \varepsilon_{13} \\ 0 & \varepsilon_{22} & 0 \\ \varepsilon_{31} & 0 & \varepsilon_{33} \end{vmatrix} = \begin{vmatrix} \varepsilon_{\chi} \cos^{2} \gamma + \varepsilon_{z} \sin^{2} \gamma & 0 & (\varepsilon_{\chi} - \varepsilon_{z}) \cos \gamma \sin \gamma \\ 0 & \varepsilon_{\gamma} & 0 \\ (\varepsilon_{\chi} - \varepsilon_{z}) \cos \gamma \sin \gamma & 0 & \varepsilon_{z} \cos^{2} \gamma + \varepsilon_{x} \sin^{2} \gamma \end{vmatrix},$$
(3)

$$\varepsilon^{-1} = \begin{vmatrix} \varepsilon^{-1}_{11} & 0 & \varepsilon^{-1}_{13} \\ 0 & \varepsilon^{-1}_{22} & 0 \\ \varepsilon^{-1}_{31} & 0 & \varepsilon^{-1}_{33} \end{vmatrix} = \begin{vmatrix} \varepsilon^{-1}_{x} \cos^{2} \gamma + \varepsilon^{-1}_{z} \sin^{2} \gamma & 0 & (\varepsilon^{-1}_{x} - \varepsilon^{-1}_{z}) \cos \gamma \sin \gamma \\ 0 & \varepsilon^{-1}_{r} & 0 \\ (\varepsilon^{-1}_{x} - \varepsilon^{-1}_{z}) \cos \gamma \sin \gamma & 0 & \varepsilon^{-1}_{z} \cos^{2} \gamma + \varepsilon^{-1}_{x} \sin^{2} \gamma \end{vmatrix}$$

$$(4)$$

At absence of absorption, the corresponding main refraction parameters are connected with principal values  $\epsilon^{-1}_k$  and  $\epsilon_k$  of tensors  $\epsilon^{-1}$  and  $\epsilon$  at k=X,Y,Z, (Modern crystallography, 1981):

$$N_{k^{-2}} = \varepsilon^{-1}_{k} \text{ } \text{ } N_{k^{2}} = \varepsilon_{k}.$$
 (5,6)

Thus, certain values of tensor components correspond to each mineral with measured main refraction parameters. The tensor can be noted in the basic system of coordinates, but this requires knowing the orientation of indicatrix, in particular, the extinction angle r for monoclinic minerals. Using of Fedorov-Pokkels and Hoiser-Wenk methods allows writing down assumed linear dependencies of measured tensor components on evaluated unknown components of individual tensors describing different types of blocks. Definition of components of individual tensors from values of components of the resulting tensors evaluated with the use of measured refraction parameters becomes possible under the condition of availability of preliminary data or assumptions on the form of expression of individual tensors in the basic system of coordinates. Always when connection of components of tensors  $\varepsilon^{-1}$  and  $\varepsilon$  with refraction parameters is not directly taken into account, the expressions attributed to tensors of both types impermittivity and permittivity - are completely similar and to save the room it is enough to result expressions for tensors  $\epsilon$ .

Individual optical characteristics of each kind of structural components are described by tensors of the corresponding kind considering the symmetry features of structural components selected under schemes ABRL and abrl and regularities of their quantitative ratios in a cell. As enantiomorphous forsterite blocks A and B always occur in equal number, the same optical characteristic corresponding to a orthorhombic mineral can be formally attributed to any such block. Thus, tensors of blocks A and B in the basic system of coordinates have the canonic form and are characterized by three principal values. Symmetric pairs of individual indicatrices revolved around axis Y of the basic system in opposite directions on equal angles  $\alpha_{R_I}$   $\alpha_a$  and  $\alpha_r$  regarding axis Z correspond to monoclinic symmetry pairs of enantiomorphous blocks RL, ab and rl. In the transformed systems of coordinates revolved regarding the basic system through corresponding angles tensors of monoclinic blocks will have the canonic form and each will be characterized by three principal values. In the basic system of coordinates, tensors of monoclinic blocks get a non-diagonal form and their extra-diagonal components, if not compensated, enter into the resulting tensor of a mineral causing its oblique extinction. We shall only result the corresponding expressions for tensors  $\epsilon$  of blocks A(B), R and L as the last two are similar to expressions for others enantiomorphous monoclinic blocks

$$\varepsilon_{A} = \varepsilon_{B} = \begin{vmatrix} \varepsilon_{AX} & 0 & 0 \\ 0 & \varepsilon_{AY} & 0 \\ 0 & 0 & \varepsilon_{AZ} \end{vmatrix}, \tag{7}$$

$$\varepsilon_{R} = \begin{vmatrix} \varepsilon_{R11} & 0 & \varepsilon_{R13} \\ 0 & \varepsilon_{R22} & 0 \\ \varepsilon_{R31} & 0 & \varepsilon_{R33} \end{vmatrix} = \begin{vmatrix} \varepsilon_{RX} \cos^{2} \alpha_{R} + \varepsilon_{RZ} \sin^{2} \alpha_{R} & 0 & (\varepsilon_{RX} - \varepsilon_{RZ}) \cos \alpha_{R} \sin \alpha_{R} \\ 0 & \varepsilon_{RY} & 0 \\ (\varepsilon_{RX} - \varepsilon_{RZ}) \cos \alpha_{R} \sin \alpha_{R} & 0 & \varepsilon_{RZ} \cos^{2} \alpha_{R} + \varepsilon_{RX} \sin^{2} \alpha_{R} \end{vmatrix}, \tag{8}$$

$$\varepsilon_{L} = \begin{vmatrix} \varepsilon_{L11} & 0 & \varepsilon_{L13} \\ 0 & \varepsilon_{L22} & 0 \\ \varepsilon_{L31} & 0 & \varepsilon_{L33} \end{vmatrix} = \begin{vmatrix} \varepsilon_{RX} \cos^{2} \alpha_{R} + \varepsilon_{RZ} \sin^{2} \alpha_{R} & 0 & (\varepsilon_{RZ} - \varepsilon_{RX}) \cos \alpha_{R} \sin \alpha_{R} \\ 0 & \varepsilon_{RY} & 0 \\ (\varepsilon_{RZ} - \varepsilon_{RX}) \cos \alpha_{R} \sin \alpha_{R} & 0 & \varepsilon_{RZ} \cos^{2} \alpha_{R} + \varepsilon_{RX} \sin^{2} \alpha_{R} \end{vmatrix}$$
(9)

$$\varepsilon_{R} + \varepsilon_{L} = 2 \begin{vmatrix} \varepsilon_{R11} & 0 & 0 \\ 0 & \varepsilon_{R22} & 0 \\ 0 & 0 & \varepsilon_{P33} \end{vmatrix}$$

$$(10)$$

The diagonal form of the sum of tensors  $\varepsilon_R + \varepsilon_I$  corresponds to the rhombic system of minerals of the group with the equal number of blocks R and L, providing compensation of extra-diagonal components of the resulting tensor and, hence, the direct extinction. The equation (10) is also fair for tensors of other pairs of enantiomorphous monoclinic blocks ab and rl.

The contents of structural components in a cell of i mineral, depending on the used selection scheme of structural components, is characterized by values  $(A + B)_i$ ,  $R_i$  and  $L_i$ , or  $a_i$ ,  $b_i$ ,  $r_i$ and l<sub>i</sub> (Table 3), which, after multiplication by thickness q<sub>i</sub> of corresponding blocks and normalization by the total of all products, represent  $V_{ji}$  — volume parts of inputs of j blocks individual tensors into the resulting tensor of imineral of the group.

At structure interpretations under ABRL and abrl schemes, the resulting tensor is represent-

$$\varepsilon_{i} = V_{(A+B)i} \varepsilon_{A} + V_{Ri} \varepsilon_{R} + V_{Li} \varepsilon_{L'}$$
 (11.1)

$$\varepsilon_{i} = V_{ai}\varepsilon_{a} + V_{bi}\varepsilon_{b} + V_{ri}\varepsilon_{r} + V_{li}\varepsilon_{l}. \tag{11.2}$$

Equating separate components of the resulting tensor in (11.1) to sums of corresponding components in the right part, with the account of (7), (8), (9) and compensation of extra-diagonal components by equal number of enantiomorphous blocks R and L, we receive for the ABRL scheme

$$\varepsilon_{11i} = V_{(A+B)i} \varepsilon_{AX} + (V_{Ri} + V_{Li}) \varepsilon_{R11},$$
(12.1)

$$\varepsilon_{22i} = V_{(A+B)i}\varepsilon_{AY} + (V_{Ri} + V_{Li})\varepsilon_{RY}, \qquad (12.2)$$

$$\varepsilon_{33i} = V_{(A+B)i}\varepsilon_{AZ} + (V_{Ri} + V_{Li})\varepsilon_{R33}, \qquad (12.3)$$

$$\varepsilon_{13i} = \varepsilon_{31i} = (V_{Ri} - V_{Li}) \, \varepsilon_{R13}, \tag{12.4}$$

For the abrl scheme, in which all separate blocks are monoclinic, equating of separate components in the left and right parts in (11.2) with the account of (7), (8), and (9) results in more complex dependencies

$$\varepsilon_{11i} = (V_{ai} + V_{bi})\varepsilon_{a11} + (V_{ri} + V_{li})\varepsilon_{r11},$$
 (13.1)

$$\varepsilon_{22i} = (V_{ai} + V_{bi})\varepsilon_{ay} + (V_{ri} + V_{li})\varepsilon_{ry} \qquad (13.2)$$

$$\epsilon_{33i} = (V_{ai} + V_{bi})\epsilon_{a33} + (V_{ri} + V_{li})\epsilon_{r33}, \qquad (13.3)$$

$$\epsilon_{13i} = \epsilon_{31i} = (V_{ri} - V_{li}) (\epsilon_{a13} + \epsilon_{r13}). \eqno(13.4)$$

Prior to evaluation of individual tensor components, preliminary verification of fulfillment of one elementary consequence of the prospective model was carried out. Fedorov-Pokkels and Hoiser-Wenk methods were simultaneously compared and the second was preferred. Regarding tensors, the rule of trace invariancy (Il'in and Pozdnyak, 1984) is observed and values of traces of experimentally established tensors should be rather close to sums of individual tensor traces multiplied by corresponding V<sub>i</sub>. For schemes ABRL and abrl, conditions of traces equality is received by summarizing (12.1-3) and (13.1-3) respectively:

$$tr(\epsilon_i) \,=\, V_{\scriptscriptstyle (A+B)i}\,tr(\epsilon_A) \,+\, (V_{\scriptscriptstyle Ri}\,+\,V_{\scriptscriptstyle Li})\,\,tr(\epsilon_R) \text{,} \eqno(14)$$

$$tr(\epsilon_i) \,=\, V_{(a+b)i}\,tr(\epsilon_a) \,+\, (V_{ri} \!+\! V_{li})\,\,tr(\epsilon_r). \eqno(15)$$

Values of traces of tensor  $\varepsilon_{i}^{-1}$  of impermitivity  $tr(\epsilon_i^{-1}) = Nx_i^{-2} + Ny_i^{-2} + Nz_i^{-2}$  and traces of tensor  $\varepsilon_i$  of permittivity  $tr(\varepsilon_i) = Nx_i^2 + Ny_i^2 +$  $Nz_i^2$  were substituted in the left parts of equations (14) and (15) according to (5) and (6). Values of individual tensor traces were found by the LSM procedure and resulting tensor traces calculated with these values have shown a good consent with values of  $\epsilon_{\rm i}$  traces, received out of refraction parameters by Hoiser-Wenk method. The relative RMSD was 0.017 % for both schemes of selecting structural components. For traces of tensors  $\varepsilon_i^{-1}$ (Fedorov-Pokkels method) relative RMSD is 0.039 %, also for both selection schemes.

Under the ABRL scheme, principal values  $\epsilon_{AX}$  ,  $\epsilon_{AY}$  ,  $\epsilon_{AZ}$  and  $\epsilon_{RX}$  ,  $\epsilon_{RY}$  ,  $\epsilon_{RZ}$  of individual tensors  $\boldsymbol{e}_{\boldsymbol{A}}$  and  $\boldsymbol{e}_{\boldsymbol{R}}$  were determined by the Hoiser-Wenk method using LSM and equations (12), (8) and (9) with simultaneous formal search of angle

Table 3. Optical characteristics and contents of structural components in Mg-F humite group minerals

Mineral	$N_x = Np$	$N_y = Ng$	$N_z = Nm$	x∠Np	A+B	R	L	a	b	r	1
Norbergite	1,548	1,570	1,552	0	2	1	1	0	0	1	1
Chondrodite	1,582	1,612	1,594	-22	2	1	0	0	1	1	0
Humite	1,598	1,63	1,606	0	6	1	1	2	2	1	1
Clinohumite	1,608	1,636	1,618	-9	4	1	0	1	2	1	0

Table 4. Refraction parameters of Mg-F minerals of the humite group, designed using individual tensors of blocks under the ABRL scheme

Mineral	$N_x = Np$	N <sub>x</sub> calc.	$N_y = Ng$	N <sub>y</sub> calc.	$N_z = NM$	N <sub>z</sub> calc	x∠Np	x∠Npcalc.
Norbergite	1.548	1.5477	1,570	1,5704	1.552	1.5521	0	0
Chondrodite	1.582	1.5824	1,612	1,6115	1.594	1.5931	-22	-22.9
Humite	1.598	1.5990	1,630	1,6284	1.606	1.6078	0	0
Clinohumite	1.608	1.6068	1,636	1,6377	1.618	1.6171	-9	-11.9
RMSD	0.0	004	0,0	006	0.00	05	1.	52

Table 5. Individual refraction parameters of blocks under the ABRL scheme

		Main refraction <sub>l</sub>	parameters		
	ite» blocks calc.)	Sellaite (Minerals, 1963)		erite blocks (calc.)	Forsterite (Minerals, 1963)
$N_{\rm x}$ $N_{-}$	1.3519 1.3338	1,381 - 1,390 1,370 - 1,378	N <sub>x</sub> N	1.6352 1.6683	1,635 1.670
$N_z$	1.2991	1,370 – 1,378 1,370 – 1,378	$N_z$	1.6471	1,651

 $\alpha_R$ , optimal in terms of the minimum sum of square discrepancies of calculated resulting tensors and  $\epsilon_i$  tensors. The following principal values of tensors  $\epsilon_A$  and  $\epsilon_R$  were received:  $\epsilon_{AX}\!=\!2.6739,\,\epsilon_{AY}\!=\!2.7863,\,\epsilon_{AZ}\!=\!2.7129,\,\epsilon_{RX}\!=\!1.8276,\,\epsilon_{RY}\!=\!1.7791,\,\epsilon_{RZ}\!=\!1.6877$  and angle  $\alpha_R\!=\!72.11^\circ.$  The main refraction parameters of four and extinction angles of two minerals calculated using principal values of individual tensors  $\epsilon_A$  and  $\epsilon_R$  are well coherent with experimental data (Table 4).

Principal values of individual tensors of blocks A(B) and R(L) allow to estimate their main refraction parameters (Table 5). Difference of these parameters from those of minerals which names are assigned to blocks set under the ABRL scheme was expected because blocks are in interaction and their actual composition does not correspond to their conventional names as shown above.

LSM evaluations of components of tensors  $\varepsilon_{\rm b}$ and  $\varepsilon_r$  of structural blocks set under the abrl scheme also allow to calculate the main refraction parameters and extinction angles in good accordance with experimental: RMSD of calculated main parameters from Nx<sub>i</sub>, Ny<sub>i</sub>, and Nz<sub>i</sub> are 0.0004, 0.0006 and 0.0006 respectively and  $1.33^{\circ}$  for the extinction angle. However, the  $V_{ij}$ set realized in the used data file, results in unsolvability regarding principal values of tensors, except for  $\epsilon_{bY}=\epsilon_{b22}$  and  $\epsilon_{rY}=\epsilon_{r22}$ . As follows from equation (13.4), inputs of diagonal components  $\varepsilon_{b13}$  and  $\varepsilon_{r13}$  into the resulting tensors  $\varepsilon_i$  are made with identical factors, therefore the data on pure Mg-F minerals of the group only enable evaluation of  $(\varepsilon_{b13} + \varepsilon_{r13})$  which cannot be divided between tensors of blocks b and r. This circumstance does not allow to reduce unequivocally tensors  $\;\epsilon_{\scriptscriptstyle b}$  and  $\epsilon_{\scriptscriptstyle r}$  to the diagonal form and to estimate their principal values  $\epsilon_{bX}$ ,  $\epsilon_{rX}$ ,  $\epsilon_{bZ}$  and  $\epsilon_{rZ}$ . Nevertheless, the alone sum ( $\epsilon_{\text{b13}}$  +  $\epsilon_{\text{r13}}$ ) with inherent factors

 $(V_{ri}-V_{\it h})$  entirely forms extra-diagonal  $\epsilon_{13}$  component of the resulting tensor in monoclinic minerals of the group. It allows, using also evaluations  $\epsilon_{b11}$ ,  $\epsilon_{b33}$ ,  $\epsilon_{r11}$  and  $\epsilon_{r33}$ , to calculate all parameters of indicatrix, including the extinction angle. Table 6 shows evaluations of component of tensors  $\epsilon_b$  and  $\epsilon_r$ .

In case of humite and norbergite - rhombic minerals with direct extinction — contents of blocks and related factors  $V_{ii}$  are such that extra-diagonal components  $\epsilon_{\text{b13}}$  and  $\epsilon_{\text{r13}}$  of tensors  $\varepsilon_b$  and  $\varepsilon_r$  have zero value according to (10) or (13.4). Really, at a = b and r = l, pair half-forsterite enantiomorphous half-norbergite monoclinic blocks form quantitative combinations corresponding to rhombic forsterite and norbergite in equal number in humite and, apparently, to rhombic norbergite - in norbergite. Hence, diagonal components  $\epsilon_{b11}$ ,  $\epsilon_{b22}$  and  $\epsilon_{b33}$ ,  $\epsilon_{r11}$ ,  $\epsilon_{r22}$  and  $\epsilon_{r33}$  in themselves set individual main refraction parameters and are principal values of individual tensors  $\epsilon_{fo}$  and  $\epsilon_{n}$  for equivalents of forsterite and norbergite represented in the structure as pair combinations of even spatially separated blocks ab and rl. Table 6 shows individual main refraction parameters for equivalents of forsterite and norbergite corresponding to components  $\epsilon_{fo}$  and  $\epsilon_{n}$  n.

Good conformity of these values to actual parameters of forsterite and norbergite is natural as the blocks set under this scheme really have compositions of given minerals and similar structures in the specified pair combinations.

#### **Conclusions**

Comparing additive models of indicatrices of Mg-F humite group minerals constructed under two schemes of structural component

Table 6. Components of individual tensors of blocks in the abrl model and refraction parameters of forsterite and norbergite equivalents

Evaluations a co	emponent of tensors		raction parameters norbergite equivalents	Refraction parameters of forsterite and norbergite (Minerals, 1972))
$\varepsilon_{b11} = \varepsilon_{foX}$	2.6739	$N_{\text{foX}}$	1.6352	1,635
$\varepsilon_{\rm bY} = \varepsilon_{\rm b22} = \varepsilon_{\rm foY}$	2.7864	N <sub>foY</sub>	1.6692	1,670
$\varepsilon_{\rm b33} = \varepsilon_{\rm foZ}$	2.7129	$N_{foZ}$	1.6471	1,651
$\varepsilon_{r11} = \varepsilon_{nX}$	2.3955	$N_{nX}$	1.5477	1,548
$\varepsilon_{rY} = \varepsilon_{r22} = \varepsilon_{nY}$	2.4663	$N_{nY}$	1.5704	1,570
$\varepsilon_{r33} = \varepsilon_{nZ}$	2.4089	$N_{nZ}$	1.5521	1,552
$(\varepsilon_{\rm b13} + \varepsilon_{\rm r13})$	0.02071			

selection, it is possible to state that both models allow to predict optical characteristics of minerals with good precision proceeding from block presentation of their structure. The model under the abrl scheme gives a little bit better prediction of the extinction angle for monoclinic minerals. This is well understandable as in the ABRL model extra-diagonal component of the resulting tensor, responsible for oblique extinction, is entirely caused by inputs of blocks R(L), whereas in the abrl model the value of extra-diagonal components of the resulting tensor is formed by both norbergite and forsterite blocks. In the latter case, it is impossible to divide this responsibility between them only basing on magnesium-fluorine members of isomorph series. The construction of additive models of optical properties for minerals of the group with isomorphism under schemes  $Fe \rightarrow Mq$ , (OH)  $\rightarrow F$ and  $TiO_2 \rightarrow Mg(F_1(OH))_2$  is a subject for the further studies and will probably allow to divide influence of various types of blocks on the extinction angle value.

The additive models based on the assumption about cumulative influence of individual properties of structural components set by traditional and proposed in this work techniques on optical properties of a mineral adequately describe variability of indicatrix. This allows to make a conclusion that traditional interpretation of structures of humite group minerals is acceptable. The more correct from the crystallochemical point of view description of the structure gives the *abrl* scheme proposed in this work, which allows to consider humite group minerals as members of a polysomatic series, in which forsterite and norbergite blocks are combined in various proportions.

The constructed models may be used for prediction of optical characteristics of hypothetical minerals of the group, provided that their structure will be presented as a sequence of O or *abrl* blocks.

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# ARTICLES OF KOLYVAN GRINDING FACTORY IN THE FERSMAN MINERALOGICAL MUSEUM OF THE RUSSIAN ACADEMY OF SCIENCE

Marianna B. Chistyakova,

Mineralogical Museum of the Russian Academy of Science, Moscow, mineral@fmm.ru

Nina R. Budanova

Mineralogical Museum of the Russian Academy of Science, Moscow, mineral@fmm.ru

Brief history of decorative stone discovery and stonecutting development on Altai. Description of articles of Kolyvan grinding factory in the Museum's collection 10 color photos, 8 references.

The history of stonecutting art in Russia is rather original. Having arisen millenia after European and East arts, it has achieved amazing level in a short term since the  $17^{\rm th}-18^{\rm th}$  centuries. Such later development is related to the delayed formation of Russia as a united state and, respectively, to late interest to underground resources and their use.

At all their love to luxury, the Moscow sovereigns for a long time were compelled to be content with imported foreign-made jewels bought from East merchants going by the Great Silk Way far to the south from the boundaries of that time Russia. Respectively, the processing of jewels was absent. It was only reduced to fastening of bright gems to czar and church clothes and utensils.

However, it should be noted that soft stone in Russia was processed from the remote time and till association of isolated princedoms into a united state. It was compact soft white limestone — a widespread building material. Palaces, monasteries, temples, defensive walls and towers were erected from this stone. It was used not only as building material. Carving was very popular to ornament buildings. Remarkable monuments of architecture of many ancient cities of Russia (12th — 18th centuries) amaze till now with stone lacy patterns sometimes almost entirely covering walls (Vladimir, Yaroslavl, Rostov Great, Suzdal, ...).

Gradually brick replaced white stone as building material, but limestone for a long time was the unique natural material serving for dressing of buildings. Carved columns, platbands, kokoshniks, mythical creatures, vegetative ornament and other intricate details were traditionally made of this pliable to cutting trim stone. However, with time this art began to come to naught and by the

moment of stonecutting industry development in Russia it was forgotten.

Interest to patterned stones and their processing began to be clearly shown in Russia from the middle of the 17th century during the reign of the first sovereign from Romanovs' family — Michael (1613 — 1642). The foreign experts were invited for this purpose snf they even tried to organize prospecting for jewels in vicinities of Moscow and Tver (Valishevsky, 1911).

Prospecting in the central part of Russia had no success, but interest to earth riches of the country has not died away. In 1668 (Martynova, 1973) appeared authentic data on occurrences of rock crystal, blue topaz, amethyst, red tourmaline, and beryl in the Urals Mountains (near the Murzinka jail). But these were meanwhile only individual signals. A regular mining yet was absent and availability of decorative stones in Russia was not known at all.

Reforms of Peter the Great, which basically changed the life of Russia, have caused a close attention to the development of mineral riches of the country. Metals were necessary for the army and fleet. Construction of cities, and especially of the new capital on boggy banks of the Neva River, required huge quantities of building stone. Sharp shortage of it at erection of St. Petersburg has resulted in 1714 in the interdiction on stone construction in Russia and everyone coming to the place of the future capital should bring stones about him. Interiors of the first palaces were filled with foreign marble and European articles.

This could not last long. In 1717, Peter the Great has established the Berg-Collegium to organize prospecting for and extraction of national ores and stones. Gradually national

deposits of various metals, hard building materials, and later decorative stone were discovered and developed.

The development of stone-processing craft was rather complicated. Firstly, Russian masters only squared a stone and foreigners were called for more skilful work. Scales of works were negligible. It did not match grandiose projects in any way. There were no capacities to process not only stone, even glass.

Right at the end of the reign, in 1722, Peter issued the Decree on creation of the first in Russia state grinding mill intended for «sawing and polishing of marble and other stones» and polishing of glass in Peterhof (Budanov, 1980). It was burned down in 1731 and in 1735, under the Decree of Empress Anna, it was restored already for grinding and polishing «of diverse found in the country jasper and other stones...».

But Peterhof, being close to the capital, was very far from those places, where numerous deposits of marble and colored stones were discovered in the 18th century. And all these occurred on the «Stone» as the Urals were referred to at that time. There, in vicinities of already operating iron and copper factories, new and new stones were discovered. Almost simultaneously with the works at the Peterhof factory, in 1726, at Iset state-owned factory, stone processing was also begun. First only soft material was worked here, though by that time some hard stones - chalcedony and quartz — also were found. The further explosive development of mining on the Urals, discovery of deposits of various colored stones precious, industrial, building - has resulted in opening in 1751 of an independent stone-processing enterprise Ekaterinburg state-owned grinding factory.

At the same time, development of mineral riches in Russia also occurred far to the east of the Urals. At the end of the century, systematic study of Altai begins. Copper and silver ores were discovered, Lokot' copper and silver factory was constructed (1782 — 1784) on the Aley River. Interest to the region grew and, under the Decree of the Impress Katherine the Great, the intensive prospecting for «not only ores, but any sort of useful stones and minerals» began in vicinities of the factory.

In 1786, according to imperial commission, nine groups have gone for prospecting. One of them was headed by the doctor of Lokot factory Peter Ivanovich Shangin. This amazing person, who studied botany, cartography, ethnography and many other things in addition to medicine, has taken a great interest in stones

and as the award, he «had the luck» to survey upper reaches of the Charysh River and to get to the Korgon creek. Chalcedony and topaz were found, but the most important was the fact that jaspers and multi-colored porphyries, breccias, marbles were discovered (Rodionov, 1988, 2002). The Shangin's group discovered almost all well-known rocks of Altai. Later, only Revnev jasper (1789) and Beloretsk quartzite (1806) were discovered.

The samples sent to St. Petersburg hit the taste. Mining of porphyry began near the Lokot and the decision was made to build a grinding mill nearby «for manufacture of columns, vases, tables, fireplaces and others similar sings». In 1787 it has produced the first vase of one arshin in diameter (arshin -71.12 cm) of black Lokot porphyry (Rodionov, 1988, 2002). But possibilities of Lokot factory were limited. It mainly produced small goods and if there were large articled, they were turned «on the round table», i.e. on a lathe. They were monolithic, smooth, without carved ornaments. The Lokot was located far from the majority of the discovered deposits of ornamental stones of Altai. In 1800, the order of the Cabinet of His Imperial Majesty has come from St. Petersburg – «to close Kolyvan silver and copper factory and to arrange a grinding factory instead of it «. It was open in 1802. The new factory in the first half of  $19^{\text{th}}$  century produced large, even huge articles. By complexity, skill, art value they differ very much from Lokot articles (Budanov, 1980).

The history of Kolyvan factory is tragic. During the 19<sup>th</sup> century, having gone through intensive development, having made huge quantity of unsurpassed (in the global scale) masterpieces, by the end of century it appeared almost forgotten, and its surprising highly skilled masters unclaimed. The unique enterprise, which had and has no analogues in Russia or in the world, suddenly appeared outside of the sphere of interests of customers and owners. In the remarkable books of geologist-writer A.Rodionov «On wings of the craft» (1988) and «Kolyvan stonecutting» (2002) joyful and sad events of its history are fascinatingly described, as well as destinies of many unusual people, who discovered mineral treasures of the Altai and by improbable work mined and processed them.

We shall touch only a few moments from the interesting past of the factory, as it seems to us, by describing its articles stored in the Fersman Mineralogical Museum of the Russian Academy of Science.

<sup>&</sup>lt;sup>7</sup> From the Russian for «elbow» − an abrupt bend of a river

One distinctive feature of Kolyvan was that stonecutting art has arisen here literally on an empty place. If on the Urals even before opening of state workshop there were local skilled stonecutters and interest to colored stone and its handicraft processing was usual, stone on Altai never associated in minds with subjects of art. Therefore, it would seem that its builders and the more so masters — stonecutters should be (at list might be) foreigners, as well as under Peter the Great, who taught the craft to Peterhof masters and then have played some role in the development of stonecutting in Ekaterinburg. Russian masters constructed the Kolyvan factory and stonecutters were exclusively local. Only right at the beginning of organization of stonecutting on Altai - in 1786 – the St. Petersburg has sent some Peterhof masters to the Lokot factory. Moreover, there was no tradition of extraction and art processing of decorative stone on Altai.

And one more circumstance was typical of Kolyvan factory. From the very beginning of its existence, the enterprise was of the art industry. Building stones were not processed nor ground here. And, in contrast to Peterhof and Ekaterinburg, Kolyvan from the first steps began to process hard stone and in the most rational way.

The variety of the Altai ornamental stones is insignificant. These were only porphyries, jaspers and compact quartz (quartzite). However, each of these rocks has various colors. Porphyry has dark red, gray-violet, green, black varieties. Some of them (red, green) are very similar to rocks extracted yet in antique times in Egypt (red) and on Peloponnesus (green), which decorated palaces and temples of ancient Egyptians, and then Romans. Because of this similarity, the Altai rocks were also referred to as «antique» (Fersman, 1959). In the 18th century, porphyries and jasper of Altai were not distinguished. All stones were considered jasper, though even externally these rocks are easily recognized. In the 19th century the inventories of Kolyvan articles precisely and correctly designated the rock.

The jasper, hard rock, during all the history of mankind was used for small hand-made articles (amulets, ornaments, signets). Only in the 18th century, after the discovery of large jasper deposits on the Urals and on Altai, it began to be used for large decorative articles.

Altai jaspers are also various. The most well known among them is Revnev jasper (after the Revnevaya Mountain). Most often the reference to the Altai jasper means this jasper —

gray-green with spots and strips of greenish-gray and dark green color, named green-wavy from the very beginning. Basing on the pattern, wavy, banded and brocaded varieties are distinguished. Their mineral composition is similar and color intensity and pattern are only related to the prevalence of dark (epidote, actinolite, magnetite) or light (quartz, feldspars, etc.) minerals and their distribution (Barsanov, Yakovleva, 1978).

Besides the Revnev jasper, other varieties are rather widely known — Goltsov (greenish or bluish-gray) and Ridder (brecciated fabric with gray and pink irregular fragments in light-green cement). Very unusual jasper is the Korgon «coin» jasper. As a matter of fact, it is a dark gray quartz porphyry with inclusion of albite spherulites (Barsanov, Yakovleva, 1978), similar to small coins. The name was invented by Shangin, who has discovered it at Small Korgon. Articles of this rock are more rare than that of mentioned before. And one more variety of Altai jasper is the «dendrite» jasper. It almost entirely consists of fine grains of quartz, with occasional grains of topaz and magnetite. According to such composition, it has unusual for jaspers white or slightly yellowish color. On the light background black (presumably, organic matter) and brown (apparently, iron oxide) dendrites are well visible (Barsanov, Yakovleva, 1978). Its bodies are located along the Khair-Kumir creek (tributary of Charysh). Articles of it are not commonly known. Red jasper is known on Altai, but it is not very popular.

It is necessary to note that from petrographic perspective the Altai jaspers are a group of rocks of very different composition and genesis. Their common features are only fine grain and good polishing properties (Barsanov, Yakovleva, 1978).

One more remarkable Altai decorative stone is widely known — the Beloretsk quartzite (belorechite). Pure white, pink, yellow, inequigranular, locally semitransparent stone is good both for rather large articles and for small things. As unlike porphyries and jaspers, articles of which, but rare exceptions, were only produced at the Kolyvan factory, the Beloretsk quartzite was also used by other stonecutting workshops, state and private.

It is interesting that the attention to Altai among customers from St.-Patersburg was shown not only regarding articles of new rocks. Because of begun in the middle of the 18th century «general mineralogical illness» (the expression of the Berg-Collegium President P.A.Soimonov) people in capital were

also interested in Altai rocks, which varieties totaled in more than one hundred and half. The letter from St. Petersburg wrote: «His Imperial Majesty would kindly like to get samples of all porphyries, jaspers and others stones each time in two collections». Samples were also necessary for educational institutions of St. Petersburg. The Cabinet ordered 10 collections of 130 samples at once. Soimonov yet writes to Altai from St. Petersburg: «Here, all heads are infatuate with our porphyries. And that is why there is no any day without foreign application for delivery of samples for their courts...». He also asked to send material for the President of Academy of Science Ekatherine R. Dashkova: «The Princess has tortured me with the requirement of samples...» (Rodionov, 1988, 2002).

In the following 19th century, collections of Altai colored stones were also popular and highly appreciated. They were even used as diplomatic gifts (Rodionov, 1988, 2002). From the memoirs of the principal master of the Faberge Company F.P. Birbaum it is known that this so glorified company has ordered a collection of Altai rocks from Kolyvan (Faberge, Gorynya etc., 1997).

But the factory was certainly famous not for samples, but for the magnificent articles.

One of remarkable features of Altai deposits is that almost all rocks found there could be mined out in huge blocks enabling to cut out grandiose integral articles. Various colored stones of the Urals did not give large monoliths and were frequently fractured. The only exception is greenish-gray monophonic and compact jasper from the Kalkan Lake, of which very large vases of fantastic beauty were made.

The Kolyvan factory began to roughly develop right after the opening. There were strong preconditions for this. Stonecutters came here from the workshop of Lokot factory. They had flair and quite professional skills of artistic stone processing. The factory was headed by its practical founder — the former manager of Lokot shop, the gifted artist and technician, hereditary stonecutter Phillip Vasil'evich Strizhkov.

Numerous orders came from the Cabinet and, with rare exceptions, for very large articles capable to decorate huge halls of new imperial palaces. The material for work was mined nearby. It was difficult and dangerous to mine it in mountain conditions, but the factory did not depend on deliveries from other regions of the country. The work went uninterrupted at day and night. Because of huge

sizes of extracted blocks and ordered articles, and also because of poor road conditions, the material was dressed on-site and only then it was delivered to the factory. Usually this was only possible in the winter.

The victory over Napoleon has caused a powerful rise of spiritual forces in Russia. Patriotic sentiments find expression in solemn, heroic shape of works of art of that time. Especially brightly it was manifested in architecture. New majestic palaces and temples were erected. And this, in turn, entailed a burst of interest to large forms of stonecutting art. The Kolyvan factory is famous for just such works. It delivers unceasingly to St. Petersburg vases, bowls, tables, columns, and so forth. Huge articles with great precautions were transported both by land and water. At this particular time (1820-1843), the enormous (big diameter 5 m, height 2.6 m, weight approximately 10 tons) «Vase-Empress» - a miracle of stonecutting craft both in size and quality of processing - was manufactured from the Revnev jasper. With greatest precautions, thousands of kilometers of a difficult way were overcome and the vase was transported unhurt to St. Petersburg.

In the middle of the 19th century (1840—1850), the New Hermitage was under construction. And again the Kolyvan factory has many orders from St.-Petersburg, and unceasingly rotated shafts of machines and master were declined over articles with drawings, measuring devices; cut, polish, heal natural defects of stone and endlessly verifying accuracy of forms and quality of furnish.

In 1851, articles of Kolyvan factory were exhibited at the World Fair in London. Size and beauty of them amazed the public, which knew nothing about Siberian stonecutters. The commissioner-appraiser wrote: « ... dimensions and weight of these masses are those that I should confess - I do not know other similar pieces. I do not think even that so complicated and so well finished products were ever manufactured from times of Greeks and Romans» (Budanov, 1980). The participation in the London exhibition resulted for the Kolyvan factory in the Patent of Exhibition and the second grade medal. This was the world recognition. Then the factory successfully participated in other international and Russian exhibitions and received awards.

In second half of the 19<sup>th</sup> century, the interest of the Cabinet of His Imperial Majesty to large articles of stonecutters faded out. Their articles have already filled halls of palaces. Besides, the serfdom cancellation in 1861 has

caused a significant rise in labor price. The factory staff was reduced. The orders became lesser and lesser and not all ordered things were put in the overfull halls. Many of them were stored in warehouses of the Cabinet. By the end of century, on the World Fair arranged by Americans in Chicago (1893), the Kolyvan factory has shown nothing new. Only old things from warehouses of the Cabinet were sent there.

20th century was unsuccessful for the Kolyvan factory. World wars and revolutionary breaking have played its adverse role. The factory, which has brought the world glory to Russian Siberian stonecutting art, was deserted and almost was not used by the state under the destination. The Kolyvan factory repeatedly passed from one agency to another. It produced rollers, abrasive bars, facing slabs, and from time to time — small articles for daily use and souvenirs.

In the post-war time, some large vases were produced, but they appeared to be very expensive. Their manufacture was stopped. The hope for renewal of unique manufacture has only appeared now. But it is not known when it will come true.

Durability of the Altai stones and dimensions of articles of Kolyvan factory have protected many of them from damage and destruction. A significant amount of small vases, candelabrums, fireplaces and other articles decorates till now halls of museums and interiors of institution.

After the October revolution, a part of articles from stores of imperial palaces and apartments of supreme aristocracy was transferred to museums and other public organizations. Among them was the Mineralogical Museum, where these things draw attention by beauty of stone and quality of finishing.

It should be noted that attribution stone articles of even well-known factories is frequently rather difficult as they often bear no marks such as brands or hallmarks almost always available on metal things. This also refers to Kolyvan factory articles. The factory in different years had different rules of article registration. In the first half of the 19th century articles were not marked and if they were not noted in the log of made things with a detailed description and indication of sizes, the subsequent identity establishing of the listed article with the examined one is practically impossible. Only in 1853, the Cabinet by the circular of December 8 has ordered that «... the name of factory, date of beginning and termination of articles shall be indicated by cutting letters

on plinths of vases, bowls, candelabrums and pedestals, as well as the name of master, who managed the work».

At identification of manufacturing time of some our things we have met the mentioned above difficulties. So, the Museum displays two smooth jug-like vases of Revney jasper. Both consist of three mounted parts. A flat round profiled basis supports slightly flattened spherical body passing into a narrow open throat extending up. The boundary of the throat with the body is underlined by a thin vertical belt (Photo 6, 8). Vases are completely identical by size and form and only differ in jasper patterns. One of them is made of wavy jasper, another - of brocade variety. In difference to precise graphic pattern of wavy jasper, capricious outlines of dark and light spots of green tone in brocade jasper create an impression of a fantastic dynamical pattern.

An attempt to identify our vases under inventories of the "Books of stone articles manufactured at the Kolyvan grinding factory and sent to Saint Petersburg to the Cabinet of His Imperial Majesty since 1786" (Rodionov, 2002) had no success.

It is necessary to tell that the jug-like form of these vases does not correspond to the style of articles produced by the factory. The overwhelming majority of vases were of classical (or close to it) forms, which sketches made by outstanding architects of that time (Rossi, Quarengie, Galberg, Voronikhin, etc.) were sent from St. Petersburg. Therefore, it was not possible to compare even approximately our vases with known ones. Descriptions of several jug-like vases mentioned in the « Book ...» do not coincide with ours.

As things began to be signed since the 1850s, it is possible to assume that these vases were made earlier. May be for this reason the researcher of stonecutting art on Altai Sergai M. Budanov believed that they were made in the 1840s (Budanov, 1980). In 2002, A.Rodionov has published the book «Kolyvan stonecutting», which illustrations include the contour of vase of Revnev jasper in a jug form, presented by Alexander III to Turkish sultan Severet-bashaw in 1880. It practically coincides with the contour of Museum's vases. The slightly changed proportions could be explained that in the process of manufacture Kolyvan masters corrected their form, which happened more than once as proportions of separate parts in the sketch and in a ready large stone thing are perceived differently. The body of the presented vase, in contrast to ours, is covered by helicoid grooves. This,

together with the form, even more corresponds to the «east» style of an article. In a private conversation, A.Rodionov has stated the assumption that our vases are of 1870s. The issue has remained unclear.

Vases are shown in the Museum on pedestals of red Korgon porphyry as round smooth columns with carved spoons in the wider top part, supported on the base of a complicated form. On one of pedestals it is engraved «Kolyv. shlifov. fabrica (Kolyvan grinding factory). 1896».

If to consider the 40s years of 19<sup>th</sup> century as the date of manufacture of jug-like vases, the following them by time articles are fireplaces from the same Revnev jasper.

In 1840 – 1850, the New Hermitage was under construction. For it, Count L.A.Perovsky, being at that time the Head of the Cabinet, has ordered from the Kolyvan factory sixteen fireplaces of different rocks among other things. Under the Order of the Cabinet dated March 22, 1856 #2149, twelve of them were made by 1869, but only one was installed. The others were stored in a warehouse and two of them in the 20s years of 20th century were transferred to our collection (Photo 10).

Fireplaces are made from Revnev wavy jasper and are identical by the general composition, color, decoration, and size. Their decoration is extremely simple - low flat structures of separate parts, rounded tie-rods on the front and lateral walls, fastening of top board corners and pilaster extremities. The unique small carved ornament is located in the center of the front board. It is a vegetative motive in a medallion of a complex form, on which sides egg-like elements emerge on a smooth surface. The fireplace composition of laconic forms is enlivened by a combination of direct and curvilinear details of decor. The presence of large polished smooth planes does not break, but emphasizes beauty of stone increasing art effect of articles.

Fireplaces were manufactured at different time. This could explain some insignificant differences in their carved ornaments and in the degree of finishing of internal parts. The top boards of fireplaces bear texts with indication of place and time of their manufacture. The earlier one — «Kolyvan grinding factory. Processing began on March 8, 1861. Finished on February 24, 1863. The Manager — Court Counsellor Zlobin» (Photo 9). The second was manufactured since 1866 till 1869. The mentioned earlier «Book of manufactured articles» includes these fireplaces, the cost of ear-

lier one was 3,486 roubles and that of later 7,607 roubles.

Two more large signed articles of Kolyvan factory are shown in the Mineralogical Museum. These are a big pier-glass from gray-violet porphyry (Photo 5) and a vase from the same material on a gray-green porphyric pedestal. They were also ordered by the Imperial Cabinet. The order has come from the Cabinet under #1769 of June 22, 1871.

The pier-glass consists of four interconnected details: the basic middle part being a frame of a big oval mirror; rounded carved plate above; a flat horizontal table-top and carved pedestal with a rectangular mirror (Fig. 4). A pier-glass is made of fine-grained monophonic, having almost no pattern porphyry. Articles from such material were usually generously decorated with carving. The pier glass is not an exception. Its ideally smooth polished surface contrasts with the raised carving basically located above the mirror, on pedestal legs and also on the front side of table-top and pilasters. The most raised is the cartouche in the central part of the semi-circle top detail. Inside it, a flat surface of stone remained not ground (probably, under the plan of the artist, there should be a plug-in detail). The high cartouche topography is counterbalanced by relief terminations of lateral pilasters of the middle part of the pier-glass and convex carved details above it. Carved flowers come out of planes of pilasters and medallions. In the data of the «Book of manufactured articles...», the pier-glass cost was 40,180 roubles.

At the left in the bottom part of pedestal, the date of manufacturing of the article is engraved -1871-1874.

The mentioned above porphyric vase on a pedestal from the same order of the Cabinet rather differs from the majority of Kolyvan articles preserved to our time (Photo 3). Its form is nontraditional and disproportionate. Heavy, extending downward, as though melted body is supported by a low strongly profiled leg with a wide basis. The bottom, the heaviest part of body, is ornamented by carved concave spoons. Its central part bears two oval cartouches. The high open extending up throat somehow counterbalances the heavy bottom of the body. Handles going from body shoulders to the top of the throat balance all the composition. They are tracery, strongly bent, decorated by prominent carved flowers, which tie them to the middle part of the throat. As this vase is also made of monophonic material, it abounds in carved ornaments on all its parts - these are both vegetative motives and

geometrical ornament with ovals, small bolls, spoons and so forth. All these numerous details alternate with large enough smooth polished sites of the vase surface.

The vase was ordered together with a pedestal. It is reflected in the "Book of manufactures articles ...". The pedestal of rather light greenish-gray porphyry is a column on a wide profiled basis. The top is narrower than the base. It is profiled too and is decorated with concave spoons. The trunk of the column bears four pilasters with carved vegetative and geometrical motives.

By the time of creation of this vase, high classics, fashionable in the first half of the 19th century, began to be replaced by new trends. Even large stonecutting articles were decorated by florid details with numerous slots and openwork handles taken from saw cut window platbands of wooden architecture of that time. The highest skill of stonecutters was used for creation of masterly made articles, but of low art taste (Budanov, 1980). The vase with a pedestal was finished in 1875 and cost 25,294 roubles. At the end of 1875, as the «Book of manufactures stone articles...» testifies, it was sent to St. Petersburg. And there it had the same destiny as the majority of the above fireplaces. The overfilled imperial palaces have not found a room for it. It has also got to a warehouse. However, this was not the end of its history. In 1893, in honor to the 400th anniversary of America discovery by Columbus, among other actions, the World Fair of stonecutting articles was arranged in Chicago. The Kolyvan factory had received the invitation to the exhibition only three months prior to the opening. There was no time to make some article corresponding to the scale of the event. Then the articles stored in warehouses were remembered. This vase on a pedestal, one more vase of Korgon porphyry and a marble vase were sent over the ocean. Our vase, as is visible in a photo in the Exhibition Report, occupied the central place of the exposition. Kolyvan factory has received a bronze medal for these articles.

As follows from inscriptions on our articles and from records in the mentioned "Book...", the largest articles — the vase with tracery handles, its pedestal, the pier glass, fireplaces, and probably vases-jugs — were made by the Kolyvan factory in the period since 1861 till 1875, when Ivan Aleksandrovich Zlobin was the manager (1855 through 1885). He was formed architect and was the first class artist. He made a lot of drawings for various articles, including, probably, projects of the vase and

the pier glass of gray-violet porphyry (Budanov, 1980).

In addition to the mentioned large articles, the Museum has two small vases of dark-green Goltsov jasper and three of red Korgon porphyry.

These articles were transferred to the Museum in 1923 by the Museum of the City of Leningrad, which received them from imperial warehouses. The vases of Goltsov jasper decorated the Stroganov palace in St. Petersburg. After the October revolution, the Stroganov Palace-museum was organized there, afterwards liquidated. In 1926 these articles came to our Museum from this Palace-museum.

The vases are entirely identical. Wide, almost spherical body it is cut off by a wide, closed throat narrowed in the middle. The body is based upon a round leg with a prominent ring, supported on a smooth square base (Photo 1). These vases only differ in the pattern of stone.

Two vases of Korgon porphyry have a similar egg-like form. The first is based upon a square base of black marble. The short narrow throat was obviously closed by a cover now absent. The stone body of the second vase is fixed on a complicated ormolu base and has a bronze top (Photo 4). Different technologies were used for manufacturing bronze details — molding, pressure, engraving, gilding. Considering known works of Kolyvan factory, bronze details were made in another workshop. These vases were transferred to the Museum from the Hermitage in 1926.

The last art article of Kolyvan factory stored in the Museum is a small vase-bowl of the red Korgon porphyry, which came from State Museum Fund in 1927 (Photo 2). Earlier it was in the interior of Shuvalovs' private residence in St. Petersburg, which after the revolution was also used as a museum. After its closing in 1925, remarkable collections of painting and applied art were transferred to other museums.

And one more interesting showpiece from Kolyvan is stored in the museum. Not being a work of art, it nevertheless gives presentation of beauty and variety of the Altai ornamental stones. This is a collection of small (6 x 4.5 cm) rectangular polished plates, those «samples», which were popular still at the end of the 18<sup>th</sup> century (Photo 7). Unfortunately, there is no data, where from they have come to the Museum. Time of receipt is not known either. The corresponding columns in the inventory book are not filled. This is probably a collection, which was ordered from Altai by Faberge, or a collection of

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some high-ranking amateur of stone, from which palace it has got to the Museum in the 1920s. Many exhibits, which have got to the Museum at that time, have no description of history and wait for the researchers.

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## PETR A. KOCHUBEI AND HIS MINERAL COLLECTION IN A.E. FERSMAN MINERALOGICAL MUSEUM

Marina L. Moisseeva

Fersman Mineralogical Museum, Moscow, marina@fmm.ru

The article described the history of the unique mineral collection created by the Prince P.A. Kochubei in the nineteenth century.

18 color foto, 36 references.

In the autumn 1913, the «Priroda» magazine published a short information of the bill of purchasing, for the Academy of Sciences, of the Prince Kochubei large collection of minerals to have passed both chambers of the State Duma.

As was denoted in the Museum's account for the year 1913, this event took «an exclusive position not only amidst this year receipts but in the entire two hundred year history of our Museum». As A.E. Fersman wrote, this collection «had accumulated everything of the best given by the Russian nature in the last century« (Priroda, 1913). Due to this valuable acquisition, the Academy's mineralogical collection became one of the best of the European mineralogical museums, and its value increased almost twice (Collection..., 1914).

One of collecting aims may be further scientific study of the collection, in particular, looking for logical appropriateness of collected specimens. The primary selection of specimens for such a collection needs then a profound knowledge of the related branch, broad-mindedness, intuition, and inclination for the scientific analysis. Such an approach was likely inhering in the Prince P.A. Kochubei, a person who contributed much to practical applications of scientific achievements.

Prince Petr Arkad'evich Kochubei (1825—1892), the elder son of Arkadii Vasil'evich Kochubei, the Senator, and Sof'ya Nikolaevna, nee Princess V'yazemskaya', great-great-grandchild of the Malorossia (Ukraine) General Judge at the Hetman Mazepa, was known as an active public fig-

ure, a prominent Maecenas, a mineral great amateur, connoisseur, and collector.

Having graduated, in 1845, the Mikhailovskoe Artillery School, where mathematics and mechanics were lectured under the guidance of the Academician M.V. Ostrogradskii<sup>2</sup> and chemistry - Academician G.I. Gesse<sup>3</sup>, Kochubei continued his education abroad in 1846 – 47. In Löttich<sup>4</sup>, he studied military science, investigated percussion caps and cannon moulding. In Paris, he learned chemistry and physics from French professors Plouse, J.-B. Dumas<sup>5</sup>, A.-V. Regnault<sup>6</sup>. N.I. Raevskii, his Paris schoolfellow, was later known as a pedagogue-naturalist and the author of numerous geography, zoology, botany, and mineralogy textbooks. While learning, P.A. Kochubei took a great interest in mineralogy. Having returned from abroad, P.A. Kochubei graduated Officer Classes of the Mikhailovskaya Artillery Academy and «passed to the Guards Cavalry Artillery being also attached to the General-Feldzeichmeister Headquarters and appointed as a teacher of chemistry and practical mechanics at the Artillery Academy» (Sreznevskii, 1893). He taught for a while in the Academy but was soon appointed orderly and then aide-de-camp to the Emperor Alexander II. When accomplishing one of Emperor's errands, he «undertook a journey abroad with scientific aim, to familiarize himself with chemical laboratories in Belgium and Germany; after having returned, he published a description of these laboratories with an atlas of drawings»<sup>7</sup> (Khvostov, 1893). This let Kochubei establishing his own chemical laboratory, where he stud-

<sup>&</sup>lt;sup>1</sup> S.N. Vyazemskaya, the granddaughter of Count Petr Kirillovich Razumovskii, who gave her, as a dowry, several estates including the Zgurovka village that became P.A. Kochubei's family seat (Kochubei A.V., 1890).

village that became P.A. Kochubei's family seat (Kochubei A.V., 1890).

2 Ostrogradskii Mikhail Vasil'evich (1801 – 1861), known mathematician, Academician in Ordinary (Bol'shoi Russkii..., 2002).

<sup>&</sup>lt;sup>3</sup> Probably German Ivanovich Gess (Germain Henri, or Hermann Heinrich) (1802 – 1850), Russian chemist, founder of thermochemistry, Academician of the Petersburg Academy of Sciences (1830). Professor at the Petersburg Mining Institute (1832 – 1849). Discovered (1840) the Law of constancy of heat sums (the Hess Law). Discovered several new minerals (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>&</sup>lt;sup>5</sup> Dumas, Jean – Baptist Andrŭ (1800 – 1884), French chemist. In 1835 – 1840, professor of Ŭcole Polytechnique, in 1829 – 1852 – of the Art and Craft Central School, since 1839 – of the Medical School in Paris. In 1840, established training chemical laboratory, where the teaching was being led on the base of Ju.Liebig ideas. Foreign corresponding member of the Petersburg Acad. Sci. (1845) (Bol'shaya Rossiiskaya..., 2001 – 2002).

led on the base of Ju.Liebig ideas. Foreign corresponding member of the Petersburg Acad. Sci. (1845) (Bol'shaya Rossiiskaya..., 2001 – 2002).

6 Regnault, Henri-Victor, French physicist and chemist, professor of the Polytechnic school College de France. Foreign corresponding member of the Petersburg Acad. Sci. since 1848 (Brokgauz, Yefron, 2001 – 2002).

Kochubei, P.A., Opisanie zamechatel'nykh laboratorii Germanii i Bel'gii (A Description of German and Belgian Notable Laboratories), 1854.

ied inorganic and organic matters8. Later, he administered his chemical laboratory for studies to the Committee of Public Health and, then, for the work of the Russian Technical Society members.

In the summer 1855, P.A.Kochubei was charged with checking the rumors of grand larcenies of powder and cartridges from the Narva Fortress. He turned to with the inhering in him energy and devotedness to the call of duty» (Sreznevskii, 1893). After the errand was performed, Kochubei was received by the Emperor Aleksandr II. Kochubei reported the revision results as well as reforms of storing and registering at powder depots. However, no expected actions followed: some military officials were dismissed, and the system remained as formerly (Kochubei, 1890). Kochubei was disappointed very much and, despite of persuasion by his farther and uncle, retired in 1857. P.A.Kochubei settled in his estate Zgurovka9, Poltava Province, and «devoted himself wholly to his favorite engagements: agriculture, gardening, and forest cultivation»<sup>10</sup> (Sreznevskii, 1893).

Since 1859, P.A.Kochubei became a public figure. First, he attempted, together with N.F. Zdekauer<sup>11</sup> and E.V. Pelikan<sup>12</sup>, to establish a society for publishing a journal that would deal with the problems of public hygiene and food quality, for instance, the use of phosphoric matches, arsenic-containing paints, flour with sand admixture, and so on. This entailed establishing a commission chaired by the Home Secretary; however, most of proposals of the establishers were not accepted. These problems were being discussed at the meetings at the Kochubei's home, where many scientists were invited, for example, Academician N.N. Zinin<sup>13</sup>, the known chemist.

In the end of 1865, the idea arose among P.A.Kochubei's friends to establish a society which aim would be contribution to development of engineering and industry in Russia. P.A.Kochubei participated actively in organization of the Russian Technical Society created in 1866 and was elected at once the chairman of the first section of chemical works and metallurgy. In 1867, he was elected the Society Assistant Chairman and in 1870 through 1890 - its Chairman. His activities in the Russian Technical Society were perfectly corresponding with Kochubei's interests. The questions were being raised during «technical talks» that always interested him very much: steel, oil processing, cloth dying, photography, sewage disposal in Petersburg, organization of courses and schools for workers, and so on. Due to his efforts, the Russian Technical Society played an active role in development of applied science and technical education. Known scientists worked in the Society: D.I. Mendeleev<sup>14</sup>, L.E. Nobel<sup>'15</sup>, A.N. Engel'gardt<sup>16</sup>, A.V. Gadolin<sup>17</sup>, N.A. Iossa<sup>18</sup>, and others. P.A.Kochubei supported, both materially and mentally, the Society's many undertakings as if they were his own ones. He «could appreciate initiatives of his co-members whoever they were», «...everyone felt in him not only an ardent and energetic leader with a broad point of view but was imbued with assuredness in success, with his mental influence and ability to arouse energy in others too» (Sreznevskii, 1893). At the same time, P.A. Kochubei himself was often an initiator of investigation. Thanks to him new sections were established as ones of photography and its applications (1878), electrical engineering, aerostation (1880), railway techniques (1881), technical education (1884).

For instance, he was first to conduct chemical analysis of leadhillite from Nerchinsk (Koksharov, 1852 – 1855).

<sup>10</sup> The contemporaries marked P.A. Kochubei to «turn the steppe at his Zgurovka estate into forests and picturesque gardens» (Necrology..., 1892). 11 Zdekauer, Nikolai Fedorovich (1815–1895), known physician, in 1846–1863 professor of Medical Academy. Worked in the branch of public hygiene, contributed much to sanitary improvement of the Capital, was founder and chairman of the Society for public health preservation

nygiene, contributed much to sanitary improvement of the Capital, was founder and chairman of the Society for public health preservation (Brokgauz, Yefron, 2001 – 2002).

12 Pelikan, E.V. (1824 – 1884), physician, one of initiators of toxicology in Russia, founder of the journal «Arkhiv sudebnoi meditsiny i obshchestvennoi gigieny» (Archive of Forensic Medicine and Public Hygiene), 1865 (Bol'shaya Rossiiskaya..., 2001 – 2002).

13 Zinin, Nikolai Nikolaevich (1812 – 1880), prominent Russian organic chemist, Academician of the Petersburg Academy of Sciences (1865). He

synthesized substances that served a base to create industries of synthetic dyes, explosives, pharmaceuticals, etc. (Bol'shaya Rossiiskaya..., 2001 – 2002, Bol'shoi Russkii..., 2002).

<sup>&</sup>lt;sup>14</sup> On the RTO errand, D.I. Mendeleev studied elasticity of gases (The Systematic Index..., 1889).
<sup>15</sup> Nobel, Ludwig Emmanuel (1831 – 1888), enterpriser, lathe constructor. He converted the enterprise founded in Petersburg by his farther, Emmanuel Nobel, into a large machine shop «Ludwig Nobel» (now «Russkii Dizel'»). In 1876, founded, together with his brothers Robert and Alfred, an oil-industry enterprise in Baku (since 1879 — Brothers Nobel Partnership) that became the largest oil firm in Russia (Bol'shaya

<sup>16</sup> Engel'gart Aleksandr Nikolaevich (1828–1893), prominent scientist in agricultural chemistry and publicist. In 1866–1870, professor of chemistry at the Petersburg Agricultural Institute. Was arrested in 1870 for spreading democratic ideas amid students and imprisoned in the Petropavlovskaya Krepost'. Kochubei solicited of his release (Sreznevskii, 1893). In the beginning of 1871, was exiled to the Batishchevo village and subjected to police supervision. He created there a model farm using phosphorite meal as fertilizer. Author of a number of works on agriculture (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>&</sup>lt;sup>17</sup> Gadolin, Aksel' Vil'gel'movich (1828 – 1892), Russian scientist in artillery, metal machine processing, mineralogy, and crystallography, Full Member of Petersburg Academy of Sciences (1875), deduced 32 groups of crystal macro-symmetry, and proposed a method to represent these groups upon a sphere, which is in use up to the present time. The Petersburg Academy of Sciences awarded him in 1868 the Lomonosov Prize for the «Derivation of All Crystal Systems and Their Subdivisions from a Single Principle» (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>18</sup> Iossa, Nikolai Aleksandrovich (1845 – 1916(17)), Russian metallurgist. Graduated from the Institute of Corps of Mining Engineers (1865), worked at Ural plants. Since 1871, worked at the Petersburg Mining Institute (professor since 1882). In 1900 – 1907, Director of the Mining Department. In 1907, Chairman of the Mining Council and Mining Scientific Committee. Since 1920, first chairman of the Russian Metallurgical Society (Bol'shaya Rossiiskaya..., 2001 – 2002).

Since 1867, the Society's «Memoirs» were being published. During his leadership, the Russian Technical Society organized public lectures and talks to popularize technical knowledge, opened schools at works and factories providing general education, subsidized researches, sent students abroad for education. It organized congresses for technical branches, for example, the congresses of technicians (1875) and of technical and professional education (1889), participated actively in international congresses, meetings, and exhibitions. P.A. Kochubei solicited the Government and private persons<sup>19</sup> for allotting money for the Society's various initiatives, and also invested his own means.

P.A. Kochubei was especially concerned with creating «Technical Museum». The idea of collecting various objects as a reflection of the human civilization history was always appealing to him. He established in 1872-73, together with N.V. Isakov<sup>20</sup>, the Museum of Applied Knowledge. Later, he built photographic pavilion and donated there his own camera collection. He donated his own collection of lighting equipment for the historical section of lighting and oil industry, and added some new exhibits. He presented, at the exhibition, «the specimens of luminaires from most ancient and simple to the most elegant works of art» (Sreznevskii, 1893). They called sometimes the P.A. Kochubei's house «home museum». Various collections of «art and scientific rarities» were stored there including famous mineral collection.

The first mineral specimens collected not later than in 40ies of the nineteenth century. They were possibly bought in the August Krantz's mineral shop in Berlin, which the Kochubeis visited on their way to Krimnitz<sup>21</sup>. Later, P.A. Kochubei replenished his collection, purchasing and exchanging specimens. In the nineteenth century, mining in Russia developed rapidly, new deposits were being discovered, and their mining started. Collecting minerals was widely spread amid top aristocracy. There were a lot of known collectors among P.A. Kochubei's friends, including Count L.A. Perovskii<sup>22</sup>, Count S.G. Stroganov<sup>23</sup>, chemist A.B. Kemmerer, doctor E.I. Raukh, Professor A.I. Shrenk, and others. One of P.A. Kochubei friend was with the Duke N.M. Leuchtenbergskii $^{24}$  who used to visit his home and chemical laboratory. The Duke<sup>25</sup> presented one of topaz crystals to him. In 1848 P.A. Kochubei got acquainted with the Academician A.V. Gadolin, who lectured at that time physics in the cadet classes of the Mikhailovskoe School (<biblio>), and, later, probably in 1852-55 - with Academician N.I. Koksharov<sup>26</sup>. They stayed his best friends until the last days of his life27. In honor of his friend, Koksharov named the mineral kochubeite<sup>28</sup>. In 80ies, P.A. Kochubei organized «Mineralogical Fridays» at his home, where his friends, Academicians N.I. Koksharov and

P.A. Kochubei, jointly with N.V. Isakov, persuaded Baron A. Shtiglits to donate one million rubles for creation of a school for technical drawing (Necrology..., 1892). Aleksandr Shtiglits allotted 5.5 million rubles (Bol'shaya Rossiiskaya..., 2001 – 2002).
 Isakov, Nikolai Vasil'evich (1821 – 1891), adjutant General. Graduated from the Academy of General Staff. Participated in Caucasian expeditions

<sup>– 1848),</sup> Hungarian campaign (1849), Sevastopol' defense during the Eastern War. In 1859–1963, as warden of Moscow educational district, Isakov opened in the University chairs of world geography and state right of European countries, established pedagogical courses in the district, achieved the transfer of Rumyantsev Museum in Moscow and added there library and collections. Established «Pedagogicheskii sbornik» (Pedagogical One Shot), founded pedagogical library and Pedagogical Museum (Bol'shoi Russkii..., 2002).

<sup>&</sup>lt;sup>21</sup> Situated in 80 km to the Southwest of Berlin.
<sup>22</sup> Perovskii, Lev Alekseevich (1792 – 1856), Count, Russian statesman, Infantry General (1855). Count A.K. Razumovskii's flyblow, P.A. Kochubei's Perovskii, Lev Alekseevich (1792 – 1856), Count, Russian statesman, Inflantry General (1853). Count A.R. Razumovskii s hybrow, P.A. Rochuber's relative from mother side. Graduated from the Moscow University (1811). Participant of the Patriotic War of 1812 and foreign campaigns of 1813 – 1814. Was a member of first Decembrist organizations, but retired from the movement in 1821. In 1823 – 1826, served in the Collegium for foreign affaires, 1826 – 1840 – in Department and Ministry of Appanage. Minister for Internal Affaires in 1842 – 1852, advocate of gradual emancipation of peasants with land. In 1852 – 1856, headed the Ministry of Appanage, and was administrator of His Imperial Majesty's cabinet. Since 1850, headed the Commission for studying antiquities. Participated in excavatory archeology near Novgorod, at Suzdal', in Crimea. Assembled

a great numismatic collection that is stored now in Hermitage, and collection of old Russian silver as well as collection of minerals. Honorary member of Petersburg Academy of Sciences (1852) (Bol'shoi Russkii..., 2002). The mineral perovskite was named in his honor.

23 Stroganov Sergei Grigor evich (1794 – 1883), Count, Russian statesman and military man. One of richest Russian landowners. Participated in Patriotic War of 1812, distinguished himself in the Borodino Battle. In 1831 – 1834, fulfilled the duties of military governor in Riga and Minsk. In 1854 – 1855, participated in the Sevastopol' campaign; in 1859 – 1860, was Moscow military governor-general; in 1863 – 1865, chairman of the railway committee. Known as Maecenas, collector, and archaeologist. Was assigned, in 1835, curator of Moscow educational district. The period of his leadership (1835 – 1847) by common opinion of contemporaries was brilliant enoch for the Moscow University. He established in 1839 the of his leadership (1835 – 1847), by common opinion of contemporaries, was brilliant epoch for the Moscow University. He established in 1859 the Archaeological Commission whose chairman he remained to be until the end of his life; contributed to the excavations on the Black Sea beach, lifted interest for Russian numismatics, and compiled a very rich collection of Russian coins. In 1825, established in Moscow free art school (the Stroganov School) (Bol'shoi Russkii..., 2002). The S.G. Stroganov's mineral collection was purchased by the Mineralogical Museum of Academy of Sciences in 1877.

<sup>&</sup>lt;sup>24</sup> Duke Leuchtenbergskii, Prince Romanovskii, Nikolai Maximilianovich (1843—1891), son of Maximillian-Eugene-Joseph-Napoleon Duke v Leuchtenberg, son-in-law of Emperor Nikolai I. Adjutant General, mineralogist, made up a mineral collection, since 1865 the Chairman of Mineralogical Society, since 1866 the Honorary Chairman of Russian Technical Society. Author of several chemical and crystallographic studies (Brokgauz, Yefron, 2001 – 2002). His teachers were Academicians N.I. Koksharov and N.N. Zinin (Transactions...).

<sup>26</sup> Koksharov, Nikolai Ivanovich (1818—1892), prominent mineralogist, crystallographer, Academician of the Imperial Academy of Sciences (1866), Director of the Mineralogical Museum (1866–1873), Director of the Imperial Mineralogical Society. Geometrical constants found by him for prodigious number of minerals are considered, up to now, most precise ones. Lectured at various educational institutions including the Petersburg University and Mining Institute (Bol'shaya Rossiiskaya..., 2001–2002).

<sup>27</sup> P.A. Kochubei survived his friends: A.V. Gadolin for some days, and N.I. Koksharov for several hours. This impressed his contemporaries might-

ily (Khvostov, 1893). <sup>28</sup> A variety of clinochlore.

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A.V. Gadolin as well as Academician P.V. Yere-meev<sup>29</sup> and mining engineer Iossa met «just to talk science» (Sreznevskii, 1893).

In 1860, P.A. Kochubei entered the Imperial Mineralogical Society. He contributed minerals repeatedly to the collection of Mineralogical Society (Notes on Mineralogy ..., 1878, 1880) and to the Museum of Academy of Sciences, promoted, not sparing himself, scientific trips for searching minerals. For these merits, P.A. Kochubei was awarded, on 25 January 1872, the title of the Mineralogical Society Honorary member, and on 29 December 1876 the title of the Academy Honorary member as well (Sreznevskii, 1893).

Considerable means and wide circle of acquaintances amid mineralogists and geologists permitted P.A. Kochubei to buy extra class mineral specimens nearly at first hands. He managed to enrich his collection to great extent by means of purchasing the Count L.A. Perovskii's mineralogical collection after Count's death in 1856 (Koksharov, 1862). Lev Alekseevich Perovskii, Vice-President of the Appanage Department (1852-1856), contributed to development of mining industry in Russia, inspected supplies and working of lapidary works; many new deposits started to be mined by his initiative. At the same time, he was an ardent collector; one of his hobbies was minerals and precious stones. He used to take advantage of his rank to fill his collection. «All the best stones that went to the Appanage Department settled down in the Vice-President's collection. To get a certain specimen he used bribery and mean action. Many officials of the Appanage Department served agents for replenishing their head's collection» (Semenov, Shakinko, 1982). The L.A. Perovskii collection was notable for unique specimens of emerald and alexandrite from Izumrudnye Kopi, excellent topaz crystals from the Borshchevochnyi Range, Transbaikalia, remarkable beryl crystals from Murzinka, Urals, and Urul'ga, Transbaikalia (Koksharov, 1852 – 55).

P.A. Kochubei used every opportunity to fill his collection. When on the errand of the Russian Technical Society's, he visited the Paris World Exhibition to «enrich the Russian Technical Society's collection with the objects significant for techniques» (Sreznevskii, 1893). At the same time, he purchased for his «home museum» remarkable French artistic bronzes. «But P.A. Kochubei especially managed in Paris to enrich his mineral cabinet, partly by purchasing and partly by exchange for valuable specimens of Ural minerals which he had taken to Paris with this aim» (Sreznevskii, 1893).

The collection always amazed researchers with its exclusive quality of mineral specimens,. Academician N.I. Koksharov was first who applied it in and used many of its minerals for his work «The Materials for Mineralogy of Russia». Later, Academician A.V. Gadolin used the brookite crystals from the Atlya Placer, Urals, for his works. M.V. Yerofeev<sup>30</sup> appealed to collection of tourmalines. He studied their crystallographic and crystallo-optical properties, developing the theory of «crystal clustering» in his Ph. D Thesis<sup>31</sup> (Bol'shoi Russkii ..., 2001 – 2002). The Academician P.V. Yeremeev, N.A.E. Nordenskjold32, A.E. Arzruni<sup>33</sup> used P.A. Kochubei's collection (Excerpt..., 1910) for their research.

The collection included more than 3,000 specimens that presented more than 350 mineral species known in the nineteenth century. Topaz, beryl, tourmaline, chrysoberyl, corundum, quartz, orthoclase, gold, zircon, and apatite prevailed. At the same time, collection included some rare minerals. With great love and knowledge, P.A. Kochubei selected those specimens that expressed the diversity of the mineral world as well as of each mineral. Most of them are represented with well-faceted crystals differing in combinations of faces. The collection of topazes, beryls, and tourmalines are especially outstanding as well as the crystals of zircon, vesuvianite, orthoclase, and especially twins by various laws.

Topazes are the most brilliant and rich part the collection. Petr are collected topazes from ten deposits, mainly Russian ones. In A.E. Fersman's opinion, «Russia may be proud with its topazes as they occupy an exclusive place amid topazes of the whole world by their beauty of color, clear transparency water, and size of crystals» (Fersman, 1962). However, the beauty of

<sup>&</sup>lt;sup>29</sup> Yeremeev, Pavel Vladimirovich (1830 – 1899), mineralogist, Professor at the Mining Institute since 1866, Director of the Mineralogical Society since 1892, corresponding member of the St.-Petersburg Academy of Sciences (1875), extraordinary academician (1894). Editor of «Zapiski Mineralogicheskogo obshchestva» (Memoirs of the Mineralogical Society) and fourteen volumes of «Materials for Mineralogy of Russia» (Bol'shaya Rossiiskaya..., 2001 – 2002).
<sup>30</sup> Yerofeev, Mikhail Vasil'evich (1839 – 1888), mineralogist. Since 1879, Professor at the Warsaw University, then the Forestry Institute in

<sup>&</sup>lt;sup>30</sup> Yerofeev, Mikhail Vasil'evich (1839 – 1888), mineralogist. Since 1879, Professor at the Warsaw University, then the Forestry Institute in Petersburg (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>31 «</sup>Kistallograficheskie i kristalloopticheskie issledovaniya turmalinov» (Crystallographic and Crystallooptical Studies of Tourmalines), St.-Petersburg: 1870.

<sup>&</sup>lt;sup>32</sup> Nordenskjold, Nils Adolf-Eric (1832 – 1901), Baron, known Swedish traveler, geologist, geographer, Arctic explorer, sailor, and historian of mapmaking; bypassed Eurasia from the Northeast. Member of the Stockholm Academy of Sciences (1858), corresponding member of the St.-Petersburg Academy of Sciences (1879), Honorary Member of Russian Geographic Society (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>33</sup> Artsruni, Andreas (Andrei) Yeremeevich (1847 – 1898), Russian mineralogist. Corresponding member of the Petersburg Academy of Sciences (1895), Professor at the Breslavl' (Wroclaw) University (since 1883) and High Technical School in Achen, Germany (since 1884). Establisher of mineralogo-geological section of the Caucasian Museum in Tiflis. In his honor, the mineral artsrunite, double salt of lead sulfate and copper chloride, was named (Bol'shaya Rossiiskaya..., 2001 – 2002).

delicate blue topaz of Murzinka, reddish-purple tint of Sanarka and Kamenka topazes, and, finally, amber-colored topazes from the Borshchevochnyi Range, – all this is the pride of Russian color stones» (Fersman, 1962). Topaz is a widespread mineral; however, good crystals occur not often. In the Kochubei's collection. topazes are from Russian deposits of the Urals: Murzinka, Shaitanka, the Il'men Mountains, Kamenka River placers; deposits of Eastern Transbaikalia: Urul'ga River (Borshchevochnyi Range), Sherlovaya Gora, and Adun-Chilong, and also from foreign deposits: Brasil (Villa Rica) and Germany (Schneckenstein). Kochubei sought to include in his collection most typical specimens as well as non-typical ones for the

Beauty and perfectness is typical for the topaz crystals from the Urul'ga River. They are not the largest topazes, but they are marked out with transparency, multitude of faces, and diversity of crystal forms. Amid them, crystals occur of the Murzinka type with much developed pinacoid (001) and prism (120) (Cat. #31275 - photo 4; barrel-like crystals of the Il'men type with dipyramid faces that narrow the basal pinacoid; crystals of the Sherlovaya Gora type without pinacoid (Cat. #31266 photo 3) and with developed prisms (110), (120), (130), dihedron (011) (Cat. #31261); crystals of the Korosten' type without pinacoid and with well developed prisms (110), (120) (Cat. #31277 – photo 2). P.A. Kochubei was especially keen about rarely occurring faces to be present on the crystals. He wrote in a letter to N.I. Koksharov, «Recently I had got various minerals from Siberia, including a topaz from Urul'ga presenting a combination that I never met wherever. Your paper on topaz in «Materials for Mineralogy of Russia» does not, too, mention this combination»34 (Koksharov, 1856). Fairly rare faces are seen on some crystals, as r, v, r, and others. The crystals from Urul'ga consist about one third of the whole topaz selection. Primarily, all of them were of wine-yellow color, from pale yellow to deep reddish-yellow. Unfortunately, neither of them possesses now this color as they faded at the daylight. They measure from 1 cm to nearly 10 cm. A part of these specimens passed from the L.A. Perovskii's collection. The seven crystals are described (Koksharov, 1856) and sketched by N.I. Koksharov in «The Atlas» (Koksharov, 1853)<sup>35</sup>. Amidst them is the biggest crystal of this collection weighing 1.2 kg measuring 10.5 x 9.7 x 7.1 cm. By the N.I. Koksharov's description, this crystal «is especially remarkable with its absolute transparency, crystallization right-

ness, and significant size. Its color is wine-yellow (or, more rightly, between the Brasil topaz color and smoky quartz). Pleochroism is very distinct when it is displayed to the transmitted light: in the direction of the main or vertical axis it seems to be dark reddish-vellow, in the direction of macrodiagonal axis a bluish-green tint is visible, and in the direction of brachidiagonal axis the crystal retains its normal wine-yellow (Koksharov, 1856). It had lost its color yet in the previous century (Koksharov, 1862), and we only can admire perfectness of its form (Cat. #31262 - photo 5).

The topaz specimens from Sherlovaya Gora are the typical representatives of this deposit. They are clusters of well-shaped crystals measuring to 3 cm. Some crystals are very much transparent, they are often yellowish or colorless (Cat. #31320).

The topaz collection contains a great number of specimens from the Murzinka deposit. A.E. Fersman described four types of Murzinka topazes (Fersman, 1962); at the present time, three of them are described in this deposit (Popova et al., 2002):

«1) Crystals of «nearly cubical form» with basal pinacoid habit faces and almost quadrate prism 1 {120}; 2) crystals with hexagonal appearance due to the prevalence of m {110} prism, basal pinacoid is greatly narrowed with dipyramids, the faces are numerous; this type resembles the Il'menskii one», 3) «envelope-like» crystals with developed prism y {021} instead of disappearing basal pinacoid».

The biggest Murzinka crystals of this collection refer to the first type. Amidst them is a translucent crystal of superb blue color, about 10 cm long, intergrown with morion quartz, orthoclase, and albite-cleavelandite (Cat. #31327 - photo 8). Some crystals of the same type in this collection have a zonal white-blue color (Cat. ## 31294, 31295). The lesser crystals belong to the second type; some of them wear numerous faces (Cat. #31351 - photo 1). Some of the Murzinka crystals are double terminated, which is rare as they normally overgrow upon their matrix (Cat. ## 31291, 31310). Those crystals that overgrew with their side faces refer here too. In this case, one can also view both crystal heads (Cat. ## 31327 and 31328).

The crystals from the vicinities of the Shaitanka village «are notable for their water-like transparency and development of side f domes, which is, combined with strong corrosion of some of them, the most distinctive features of these, fairly rare, Shaitanka topazes» (Fersman,

<sup>&</sup>lt;sup>34</sup> The description and drawing of this topaz were given by Kochubei in the same letter; however, the specimen was not preserved. <sup>35</sup> To the present moment, five of seven crystals are identified exactly (Cat. # # 31262, 31266, 31269, 31275, 31277).

1962). There is an excellent representative of this type (Cat. #31302).

A.E. Fersman described topaz two types from the Il'men Mountains: «small free crystals sitting on the surface of vugs and crevices, or large crystals, so called «syrtsy», embedded in a mass of gangue quartz» (Fersman, 1962). N.I. Koksharov remarked that miners used to name such topazes «rotten» because of being strongly cracked they «draw in them moisture and so fragment easily to small pieces even at a slight pressure of fingers» (Koksharov, 1856). One of such crystals in the Kochubei's collection wears a rare k face<sup>36</sup>. Another crystals of the collection refer to the first type. They are transparent, colorless, well formed, and some are double terminated (Cat. ## 31306, 31308, 30309, 31311, 31312).

There is the only topaz crystal in the Kochubei's collection from the Kamenka River gold placer. It comes from the merchant Bakakin's gold mine and probably refers to the first finds of topaz in this site. The crystal is well-formed and very beautifully colored in deep violet-red (Cat. #31318).

The topazes from the placers of Villa Rica are typical for Brasil: most of them are dipyramidal crystals of yellow color. However, one of them is notable for unevenness of its color: yellow at its base passes gradually in crimson at the crystal head (Cat. #31315 — photo 7).

For the old Schneckenstein deposit in Germany, transparent colorless or pale yellow crystals are typical. The Kochubei's collection contains exactly such specimens: prismatic crystals overgrown upon a rock, measuring about 1 cm (Cat. ## 31331, 31332). The biggest crystal reaches 3 cm but is not transparent.

So P.A. Kochubei managed to represent completely enough the multitude of topaz crystallographic types and colors from the principal, known in the nineteenth century deposits. One may remark similar picture, too, in other minerals of this collection. Let us linger at some of them.

Chrysoberyl comprise in V.I. Vernadskii opinion (Collection..., 1914), one of the collection best parts, which was preserved almost completely: 48 of 50 specimens. Most of them are alexandrites from the Izumrudnye Kopi, Urals. «They are notable for dark green color with distinctly expressed and conspicuous pleochroism. The crystals usually occur as nice trillings» (Fersman, 1962). Alexandrite is mainly represented in the Kochubei's collection as separate trillings (more rarely as their intergrowths) up to 5—8 cm across (Cat. ## 30307, 30308 — photo 9, 30317, 30297). «Single crystals and

twins are very rare», marked A.E. Fersman (Fersman, 1962). Meanwhile, there is a fine twin in this collection of a heartlet shape, measuring about 1 cm (Cat. #30331). The chrysoberyls proper are mostly small and transparent, with well-developed faces. They represent five deposits, mainly in Russia (Izumrudnye Kopi and Bakakin's Mine in the Urals) and Brasil.

One of primary specimens is the alexandrite unique crystal cluster found in the Izumrudnye Kopi in 1840 (Fersman, 1961). It likely came to P.A. Kochubei from the L.A. Perovskii collection. The cluster consists of twenty-two dark green crystals of various sizes, translucent at the edges, the biggest one measuring 7.2 cm. There are mica scales and pale green opaque beryl prisms between them. The specimen measures 25 x 14 x 11 cm and weighs 5724 g. Its first description was made by N.I. Koksharov (Koksharov, 1857). Some crystals resemble those ones that were drawn by N.I. Koksharov in his Atlas Figs. 2, 4, 5 (Koksharov, 1853) (Cat. #30295 - photo 12). The first photograph of this specimen was taken by P.A. Kochubei and published by N.I. Koksharov in volume 4 of his «Materials for Mineralogy of Russia».

Excellent emeralds were preserved almost harmless up to the present time. It includes, mainly, the specimens from the Izumrudnye Kopi (33 Cat. # of 39, the entire number), the other being from deposits of Peru, Columbia, and Austria. In V.I. Vernadsky opinion, «many specimens should be evaluated as precious stones by their clarity and color intensity» (Collection..., 1914). The sizes of emeralds are from few centimeters to 20 cm. They are separate crystals and intergrowths of two crystals as well as various clusters, which are made up of subparallel, elongated or short-prismatic crystals diversely embedded in the mass of mica. The two crystals are notable for unevenness of their color. One of them, having had come from the Izumrudnye Kopi, wears a white stripe near its head (Cat. #31242). Another crystal is absolutely transparent and colorless, with a crosswise stripe of the emerald color (Cat. #31250).

This collection includes one of the first specimens found in 1831 at the Izumrudnye Kopi (Semenov, 2001). This is an excellent crystal of a very intense, dark green color with no yellowness, measuring  $12.5 \times 8.5 \, \mathrm{cm}$  and weighing  $2,225 \, \mathrm{g}$ , with some faces being perfect and its peripheral part being transparent almost everywhere. It contains numerous inclusions, and is broken with a large crack healed with mica. This emerald once associated wrongly with the tragedy of Yakov Kokovin, Director of the

<sup>36</sup> The crystal was not identified

Ekaterinburg lapidary works<sup>37</sup>. During a revision of 1835, many precious stones were disclosed in Kokovin's cabinet including an excellent emerald. Kokovin was accused of stealing them. The boxes with the stones were delivered to Petersburg to the Appanage Department that was entrusted with replenishing the Cabinet of His Imperial Majesty. However, the specimen appeared in the Cabinet. According to a version (Fersman, 1961), the unique emerald was stolen by Kokovin; by another version (Semenov, Shakinko, 1982), it was appropriated by the high-ranking official of the Appanage Department, Count L.A. Perovskii, an ardent collector. Both versions coincide in the emerald to be in the L.A. Perovskii's collection. Then its track is lost. The only description of the lost emerald was made by Yaroshevitskii, the councilor of State, in the revision report: «...and also one of the best virtue, of very grassy color, weighing a pound... most precious and hardly not exceeding, in its virtue, the emerald that was in the Julius Caesar crown» (Semenov, 1982) (Cat. #31219 photo 13).

The emerald mess was connected with «Sketches of the Stone History» published after the A.E. Fersman's death, where the editors did not notice the error: the emerald from Kochubei's collection was named «Kokovin's Emerald», and inaccurate information penetrated in literature. A mere comparison makes obvious the difference between these specimens: the emerald from Kochubei's collection, which is now in the Fersman Museum, weighs 2225g whereas the emerald subtracted from Kokovin – only 400 g. According to catalogues, there was in the Kochubei's collection no emerald portrayed by Yaroshevitskii.

As for the beryl only half of it have survived nevertheless, it contains many fine specimens even now. The aquamarine crystals are splendid, especially those ones from Adun-Chilong vicinities, of beautiful intense greenish-blue color (Cat. ## 31208, 32247), as well as large (Cat. ## 31204, 32046 - photo 11) and beryl small bluish-green, well-formed crystals, some of them opulently faceted (Cat. ## 32245, 31246), from the Urul'ga River, Borshchevochnyi Range, fine azure-blue beryls (Cat. ## 32251, 31212) and heliodor from the Sherlovaya Gora, Eastern Transbaikalia (Cat. #32250 - photo 10). The green and yellow-green crystals from Murzinka admirable. One of them is of a special interest

being double terminated; it was studied by N.I. Koksharov (Koksharov, 1852-1855). «In P.A. Kochubei's collection are two small, excellent beryl crystals terminated with flats on both ends. ...It is remarkable that hemimorphism is seen in them, which is a fact quite new for beryl. Anyway, hemimorphism seems to be only proper to the crystals from Murzinka, as all those crystals from Adun-Chilong and Borshchevochnyi that I happened to see to be picked at both ends, are quite symmetrical and no track of hemimorphism can be seen in them. ...The second crystal... is picked at the upper end with flats of hexagonal pyramids, main one t and one of the second kind s, and terminated with fairly developed straight flat P. At this crystal lower end are straight P end flat and only three alternating flats of the hexagonal s pyramid of the second kind. All flats of the crystal are bright» (Cat. # 32261) (Koksharov, 1852 - 1855).

V.I. Vernadskii and A.E. Fersman (Collection..., 1914) saw the collection value also in the fact that it contains minerals from most different paragenetic combinations. This relates greatly to the selection of calcite, to the minerals of the apatite group, and to vesuvianite. Some deposits are exhausted long ago, but the collection gives us opportunities to see native silver from Kongsberg (Norway), amalgam from Bavaria (Germany), fine crystal group of manganite from Ilmenau (Germany), hessite from the Zavodinskii mine in Altai (Kazakhstan), and azurite from Altai (Russia).

After P.A. Kochubei's decease, the collection was stored in his Zgurovka Estate being supplemented to the slight extent only.

The next stage in the collection history goes back to 1905, when it was damaged during peasant uprisings. The Kochubei's country estate was smashed and robbed by the crowds. «The Kochubei's house was burnt down, and his collection scattered all over the garden, some specimens being thrown in the pond. Eventually, after a long looking-for, nearly three-quarter of specimens were found», — so A.E. Fersman described this event (Fersman, 1961). Having had reassembled the collection, V.P. Kochubei<sup>38</sup>, the only son of P.A. Kochubei, transported it to Kiev. The specimens were being there sorted out and put in order by L. Kryzhanovskii<sup>39</sup>, the assistant at the Mineral cabinet of the Kiev University, under the guidance of P.Ya. Armashevskii, Professor at the same University (Excerpt..., 1910). Then the

<sup>37</sup> For further details, see «The Yakov Kokovin's Tragedy», in «Ural'skie samotsvety» (Gemstones of the Urals), pp. 71-78.

<sup>38</sup> Kochubei, Vasilii Petrovich (1868-?), graduated from the Petersburg University, was member of Russian Technical Society, participated efficiently in activities of its Fifth Section: Photography and Its Applications. During the Civil War of 1918, was attached to Skoropadskii, Hetman of Ukraine (Vernadskii, 1998).

<sup>🤋</sup> Possibly, Kryzhanovskii Leonid Il'ich, brother to Kryzhanovskii V.I. Was trading with minerals in Ekaterinburg.

owner transported the collection to Vienna and published there, in 1908, its catalogue and «began negotiations with the European and American biggest museums for its selling» (Fersman, 1961).

The Kochubei's collection is often mentioned in literature as auctioned in Vienna (Barsanov, Kornetova, 1989). Some specimens were possibly sold by V.P. Kochubei at an auction (by L.V. Bulgak's40 personal communication, the alexandrite crystal cluster was exhibited in the Vienna museum that belonged to Kochubei and had been purchased at the auction). However, the purchasing of the collection by the Russian (Petersburg's at that time) Academy of Sciences was dragged on for several years and has its own history.

In 1910, V.P. Kochubei «addressed Academy by a letter in which he proposed to buy his collection of minerals, setting price after it has been looked over by representatives of Academy of Sciences. In May 1910, a special commission was established in Academy of Sciences having included Academicians A.P. Karpinskii<sup>41</sup>, F.N. Chernyshev, S.F. Ol'denburg<sup>42</sup>, and V.I. Vernadskii. On 24 November 1910, the Academy Section of physical and mathematical sciences asked V.I. Vernadskii to go to Vienna to determine the collection's value» (Pis'ma..., 1985). This journey took place on 4 to 25 January 1911. V.I. Vernadskii wrote to his wife N.E. Vernadskaya 8/21 January 1911: «Arrived to Vienna today early in the morning and examined, together with Fersman, the Kochubei's collection. It seems to me (and Fersman thinks the same), it is not worth 20,0000 - 30,0000 rubles that Kochubei wants to get. It is worth considerably less, hardly more than 100,000 rubles» (Pages..., 1981). In the autumn of the same year, V.I. Vernadskii wrote on 5th November in the letter to A.E. Fersman: «Kochubei takes off - probably about 160,000 rubles, and we start the affair» (Pis'ma..., 1985). In addition, in another letter of 23 November he reported: «Today, the question of purchasing Kochubei's collection was settled in the Section» (Pis'ma..., 1985). The Academy had not enough money to purchase collection, so it addressed Government with petition. The question of allotting money was under consideration in the government for a long time, and the negotiations continued with the owner. Nevertheless, already in the spring of 1912, V.I. Kryzhanovskii<sup>43</sup>, custodian of the Museum mineralogical section, was detached in Vienna for formal acceptance of the collection. Perhaps, he made a detailed evaluation of specimens. Presumably, it was he who marked the value sums in the margins of the catalogue that is stored in our Museum. He appraised the collection at 141,550 rubles as minimum, and at 228,575 rubles as maximum. The average sum, which was written red, was 165,690 rubles (Katalog..., 1908). Though there was not yet the governmental resolution of purchasing the collection, in April of the same year 1912, the boxes with specimens already came in to Petersburg except one that was lost on the railway during transportation. V.I. Vernadskii reported A.E. Fersman in the letter of 25 April: «The collection arrived, but one box is absent, and we did not accept it. The Academy's solicitation is now in the Council of Ministers.  $Kryzhanovskii^{44}$  considers it as appraised too expensively but does not say this directly» (Pis'ma..., 1985). V.I. Vernadskii was always attending to the problem of allotting money. Eventually, his efforts were fruitful: V.I. Vernadskii wrote to A.E. Fersman in July 1912 from Losvida45: «The Ministry agrees to buy the Kochubei's collection in 1914. One should negotiate with Kochubei now, and I believe he will agree. The museum's nature would be altered at once» (Pis'ma..., 1985). A little later, in the letter of 3 August: «I wrote to Kochubei and almost do not doubt he will agree. Kokovtsev<sup>46</sup> is said to have urged, the government accepted the resolution» (Pis'ma..., 1985). But A.E. Fersman was in Borovichi<sup>47</sup>, so V.I. Vernadskii had written him there as well: «I wrote to Kochubei of the government assent to purchase his collection on condition of paying off the whole sum in 1913, if only legislature would agree» (Pis'ma..., 1985). One year more was spent for the question to be under consideration in legislatures. Only on 12 July 1913, a special law was accepted to allot 165690 rubles from the State Exchequer for purchasing this collection.

 $<sup>^{\</sup>rm 40}$  Bulgak, Lev Vasil'evich, scientific worker of the Fersman Mineralogical museum.

<sup>41</sup> Karpinskii, Aleksandr Petrovich (1847–1936), Academician (1896), the first elective President of Academy of Sciences (1917). President of Mineralogical Society in 1899–1936. One of those researchers who were the first to use microscope for studying rocks (1869). His works on tec-

tonics, paleogeography, and paleontology are widely known (Bol'shaya Rossiiskaya..., 2001 – 2002).

<sup>42</sup> Ol'denburg, Sergei Fedorovich (1863 – 1934), Orientalist, one of institutors of Russian school of indology, archaeologist, ethnographer, science organ-

izer, Academician of Academy of Sciences (1900), permanent secretary of Academy of Sciences (1904–1929) (Bol'shaya Rossiiskaya..., 2001–2002).

43 Kryzhanovskii, Vladimir Il'ich (1881–1947), professor; since 1907, custodian of mineralogical section of Academy of Sciences Museum; in

<sup>1932 – 1947,</sup> Director of the Mineralogical museum of Academy of Sciences.

44 here Kryzhanovskii, Vladimir Il'ich, is meant, custodian of museum mineralogical section.

<sup>&</sup>lt;sup>45</sup> The Lyuboshchinskiis' estate near Gorodok, the Vitebsk Province.
<sup>46</sup> Kokovtsev, Vladimir Nikolaevich (1853—1943), Count, statesman, financier. In 1911—1914, Chairman of the Council of Ministers. Since 1918, lived abroad (Bol'shaya Rossiiskaya..., 2001 - 2002).

<sup>&</sup>lt;sup>47</sup> The Proshkovo estate, Borovichi, the Novgorod Province.

After the devastation of 1905, the restored and catalogued part of collection numbered 2588 specimens. At the formal acceptance of collection by the museum, 100 numbers lacked: 11 specimens lacked yet at the collection evaluation in Vienna, 82 specimens were in the box that was lost on the way from Vienna. 7 specimens were accepted as fragments. Besides, 640 specimens were not mentioned in the catalogue, and it was possible to restore a part of them. In 1913, totally 2606 specimens were recorded in museum catalogues. Some specimens were lost in the following years during transportation from St.-Petersburg to Moscow in 1934, and several ones were written off as destroyed.

Now, museum contains 2,424 specimens from the collection of Count Petr A. Kochubei. They represent about 300 mineral species. 2,124 of them are included in the Systematic Collection, 150 in the Collection of crystals, 148 in the Collection of pseudomorphs, and two specimens in the Collection of deposits. About 350 specimens are exhibited in the museum expositions, and we may admire their perfectness.

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#### TEN TAELS MORE TO THE FUND OF THE MUSEUM

#### Mikhail E. Generalov

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. e-mail: mgeneralov@mail.ru

A silver ingot from the collection of the Fersman Mineralogical Museum has turned out to be a yamb, an ancient Chinese coin. Its description and information obtained from its marking stamps are presented. 4 color photos.

As an old English castle is unthinkable without ghosts rambling about its vaults, so any decent museum inevitably keeps some things of unclear history and purpose. One of such artifacts in the collection of the Fersman Mineralogical Museum was a curious silver ingot with the shape resembling a little boat (*Photo 1, 4*).

None worker of the museum had any notion of this article; it seemed likely that the ingot had been here from the earliest times. The entire absence of data on this specimen gave grounds to suspect that it had come here together with collections transferred to the museum by the government in the 1920s. The only characteristics of the ingot, that were revealed during an inventory of precious metals in the museum collection by a commission with participation of specialists of the State Depository of Valuables (Gokhran), were its weight (about 368 g) and fineness (silver 960). Its size is 62 x 40 x 40 mm.

The intent of this ingot was revealed by chance. The mineralogical museum with its exhibits related to the history of the last decades of the Russian royal dynasty was invited to an exhibition held in Copenhagen.

It was a chance to see the sights of the Danian capital, including, of course, the huge Historical Museum. Wondering over enfilades of the halls with Paleolithic tools, Viking barks, interiors of Middle Age dwellings, and posters of the fascist occupation period, it is easy to get lost and pass by the richest royal collection of coins and medals. It seems likely that this happens with many visitors; so, when I came to the halls where this collection was exposed, the local security guard was bored all alone. The showcases were crammed with treasures of all the times and nations, from Antic coins resembling golden grains to Sweden sealed copper plates weighing as much as 40 pounds. All of a sudden, something familiar, a pair of silver boat-shaped ingots, flashed in one of the showcases. The inscription on the label informed that they had been used as coins in China from

the early 18th through the early 20th centuries.

Sometimes later, we managed to learn more about these coin-ingots. Their principal peculiarity is the vivid individuality. There are no pair of absolutely identical ones among them. They were strongly different in shape and weight (value) and were issued in different times and in different China provinces by different silver stores, trading houses, jewelry firms, and banks. Among them there are square, rectangular, saddle-shaped, and rounded («drums») ingots, as well as «little boats», «flowers», etc. They vary in weight from several grams to almost 2 kg. Their value is expressed in taels that correspond to approximately 37 g silver, being commonly correspondent to 1, 3, 4, 5, 10, or 50 taels. In one form or other, they were in use in China during almost 1000 years. A custom to determine the value of silver ingots by their weight and metal purity led to the fact that foreign silver coins that came to China beginning from the 16th century were estimated according to the same principle. This approach made it possible to avoid denominations common for copper and paper currencies and to do them one of the most stable moneys in the world history.

These ingots are known under various names. The Chinese liang-bono and yuan bao gave rise to the Russian yamb. In Germany, they are named Packsattelmunzen («saddle-shaped moneys»). In Kyrgyzstan where they were also in use and mentioned in the Manas epos, they were named, depending on the weight, tai tuyak («horse's hoof») or koi tuyak («ram's hoof»). In the modern literature, they are referred to as sycee, from the Chine word for raw silk, because their surface is often covered with very fine lines resembling silk in the structure.

But let us return to the yamb that found its place in the collection of the Fersman Mineralogical Museum. As follows from its weight, its value corresponds to 10 taels. For information on its origin, We had to appeal to specialists and got the help of Steven Tai, a

collector and researcher from Taiwan, and of Nina Vladimirovna Ivochkina, the custodian of the Far East collection of the Department of Numismatics of the State Hermitage, the museum where the world second (only to the Chinese one) collection of yambs (700 specimens) is kept. Our joint efforts allowed to reveal the following. Our yamb was manufactured in the last years of government of the Tsin dynasty (1889 – 1913). One of the stamps in its hollow says that it was cast by a Beijing bank named Tszyui Shen, which can be approximately translated as «multiplying [the riches]» (Photo 3). This yamb is very similar to analogous ingots with a value of 10 taels, that were issued in the metropolitan province of Chaili (Hebei) in the late 19th century

Another stamp (damaged) contains a specification (typical for yambs) of a high quality of the silver used. «Shi tszi se», such the inscription was probably engraved on it, which may be translated as «the fineness is quite high». As is known, Chinese yambs were famous just for the purity of the metal they contained.

Small circle stamps (*Photo 2*) that are on the outer side of our ingot are traditional images of a round Chinese copper coin with a square hole, that was used as a goodwill symbol of enrichment and prosperity. This symbol was very widely used in folk patterns, in articles of applied art, and even in ancient assignations of the 11th century.

It is difficult to appreciate now, how valuable this find from the museum collection is.

Even experienced collectors say that the market price of yambs is still developing, and different dealers can sell analogous articles at prices differing by an order of magnitude. There is an evidence that one and the same yamb with a value of 50 taels, but in an extremely bad state, was bought in 1995 at a price of nearly \$1,000 and was resold two years later already at \$20,000.

What is undoubted, it is that the price of yambs is far from to be limited by the cost of their contained silver. An evidence for this statement is an existence of numerous recent imitations. Yambs have already long become a numismatic rarity, because most of them were melted to silver coins and adornments.

But even in the times when the silver equivalent of yamb was only appreciated, 10 taels were a serious sum of money. In the late 19th century, one silver tael corresponded to 1500-2000 copper coins. For our yamb with a value of 10 taels, one could purchase then more than 400 liters of rice, a true treasure in the permanently starving China of that time. As a whole, as opposed to copper coins that were used for everyday purchases, yambs served as a currency for large bargains.

Poverty was described in China as follows: «He has never taken a yamb in his hands.» However, we (workers of the museum) have already not assigned to this category of people.

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## NEW ACQUISITIONS OF THE FERSMAN MINERALOGICAL MUSEUM RUSSIAN ACADEMY OF SCIENCES (1997–2001)

Dmitriy I. Belakovskiy

Fersman Mineralogical Museum Russian Academy of Sciences, Moscow. dmz@fmm.ru; http://www.fmm.ru

Between 1997 and 2001, 3414 new mineral specimens were introduced into the inventories of the five major collections of the Fersman Mineralogical Museum RAS. These specimens represent 980 different mineral species from 73 countries. Among these, 372 are new species for the Museum, including 83 that were discovered during this period. Museum staff members discovered sixteen of these. Three of the new species were discovered in previously cataloged museum pieces that were acquired as other minerals. Of the minerals obtained, 93 are either type specimens or fragments of type specimens. By the end of 2001 the number of valid mineral species in the Museum fund reach 2700. Of the newly acquired items, 1197 were donated by 230 persons and by 12 organizations; 610 specimens were collected by the Museum staff, 600 were exchanged, 334 bought, 521 registered from previously collected materials, and 152 were obtained in other ways. A review of the new acquisitions is presented by mineral species, geography, acquisition type and source. The review is accompanied by a list of new species for the Museum along with a want list.

There is a common misconception on the part of many people that major mineralogical museums have already collected everything valuable and imaginable. People very often wonder why museums are interested in items that seem, in their eyes, quite ordinary. The notion that museum collections are complete is, in a way, similar to the broadly held idea, in the late 19th and early 20th centuries, that physics was a science nearly complete, lacking just a few finishing touches.

The fact that our old, authoritative Museum possesses only about 2800 of approximately the 4000 mineral known species should be enough to enlighten most people. This proportion is typical for many of the world's large mineralogical museums. Interestingly, more than ten private systematic mineral collections have more than 3000 mineral species; moreover, museum collections are expected to characterize numerous types and varieties of minerals, their morphological variations, assemblages and everything that illustrates the processes of mineral formation. It does not matter how rich, therefore, a museum collection is a work in progress. At the outset, I would like to thank all those who understand a museum's needs and responsibilities and who are committed to building our Museum collections; it is those people who have given meaning to a review such as this.

Reports on new acquisitions to the Museum have traditionally been published in the *NEW DATA ON MINERALS* issues. Due to a lapse in publication, however, the paper outlining the new acquisitions made between 1984 and 1996 was published in *AMONG THE MINERALS* almanac (2001). This paper can also be found on our web site (http://www.fmm.ru/novpost

frame.htm). The site also pictures the specimens indicated below by the www symbol.

In expanding the Museum's collections, we have been guided by the traditional structure of the collection that was introduced in the early 20th century by Acad. V. Vernadskiy. This structure is comprised of five major collections: systematic, deposits, crystals, formation and transformations of minerals, gems and stone art.

The largest is the systematic collection, which currently holds more then 90,000 items. Mineral species that are new for the Museum will be added to this collection, as will those specimens that are aesthetically appealing or that expand our knowledge of the variety of assemblages found for a given mineral species or of its chemical, morphological and other features.

The deposits collection (currently more then 30,000 items) is comprised of series of samples that illustrate the character and/or the originality of the mineral composition that is found inherently in a given mineral deposit (occurrence).

The crystal collection contains nearly 5000 items representing simple crystal forms as well as form combinations, habits, twinning and other crystallographic features.

The collection of formation and transformation of minerals holds more than 2000 samples, each of which portray some phenomenon related to the growth and dissolution or the destruction and transformation of minerals. The majority of this collection is made up of pseudomorphs.

The gem and lapidary arts collection is comprised of some 8000 gemstone minerals and items that have been crafted from these.

In general, new acquisitions are introduced into the collection in steps. They are first registered in the preliminary acquisitions book. They are then cleaned, identified (if necessary), labeled and recorded in the database. Finally, the Museum Commission on Funding and Purchase decides into which of the major collections that the article should be distributed; the Commission can also opt to place the article into the exchange fund or into another of the Museum's collections with less important status.

This review only includes data on those specimens that were logged into the inventory of the Museum's major collections between 1997 and 2001. Specimens that had not, at that time, been fully processed and assigned as well as specimens assigned to the exchange or research collections are not included in this review.

A total of 3414 specimens (3041 inventory numbers) were introduced into the Museum's inventory between 1997 and 2001. Of these, 2075 specimens (1964 inventory numbers) were assigned to the systematic collection, 334 (305) to the deposits collection, 300 (184) to the crystal collection, 501 (448) to the mineral formation and transformation collection and 204 (140) specimens were catalogued into the gem collection.

Relative to the previous years' acquisitions, the lot of specimens acquired during this period shows a significant decrease in the percentage acquired by Museum staff through expeditions. This decrease reflects a lack of funding that hindered the staff's ability to pursue its traditional fieldwork in the Former Soviet Republics. At the same time, however, the percentage of specimens acquired by personal donation increased relative to the previous five-year period.

## New Acquisitions as Classified by Mineral Species

Specimens catalogued between 1997 and 2001 represent 980 mineral species, 372 of which are new species for the Museum. These specimens include 83 of the approximately 250 new mineral species approved by the Commission on New Minerals and Mineral names of the International Mineralogical Association since 1997. Of these 83 species, 16 were discovered and described by Museum staff or in collaboration with museum staff. Three of the new mineral species were identified among the previously catalogued Museum specimens. Ninety-seven of the mineral species that are new to the Museum are type specimens (or fragments of type specimens), holotypes or co-types. By the end of 2001, the Museum listed some 2700 valid mineral species among its collections.

Of the 980 recently acquired mineral species, the majority (620) are represented by a single specimen. One hundred sixty species are represented by 2 specimens; 3 to 5 specimens represent each of 130 species; 40 species are represented by 6 to 10 specimens; 20 species by 11 to 20 specimens; 11 species by 21 to 100 items and just 3 species are represented by more than 100 specimens.

Quartz and calcite are almost always the best represented in museums and in private collections as a result of their endless diversity and prolific. This period was no exception: there were 190 newly acquired quartz specimens and 165 samples of calcite.

In addition to previously collected Russian quartz specimens, new rock crystal druzes were collected from Alpine klefts of Sub-Polar and South Urals. The obelisk-shaped crystals, up to 38 cm long are especially striking, along with groups of variously shaped crystals which Dmitriy Abramov collected at Astaf'yevskoe deposit. Yu. Pustov donated pseudodipyramidal quartz crystals of about 1 cm long on hedenbergite and a bunch of cleaved green (due to hedenbergite inclusions) quartz crystals on an andradite crust from Dal'negorsk, Russian Far East (photo 8). P. Bantsekov donated another representative of this area: a small druze of fine crystals pigmented orange-red by hematite inclusions. Many quartz samples collected at the ore deposits in Kamchatka and Russian Far East received from Central Scientific Geology-prospectical Institute. These samples are not aesthetic, but informative in term of ore deposition processes at these deposits. Quartz-calcite simplectites from torgolites of the Murun massif donated by V.Levitskiy are also genetically interesting.

New quartz acquisitions from FSU countries were supplied from a newly developed occurrence near Oni, Republic of Georgia. These are druzes of flattened rock crystal, among which Japanese twins occur, as well as zonal (due to decoration by green clinochlore) crystals with phantoms. Presence of rutile and brookite in some crystals emphasizes the Alpine vein type of mineralization (donations from A.Agafonov and purchases). The same sources supplied the Museum with recently collected quartz druzes and a bunch of splitted quartz with calcite crystals on magnetite from Dashkesan skarns, Azerbaijan. A.Kovalev donated beautiful strawberry quartz from Chimkent area of Kazakhstan. Red color of quartz and aventurescence are controlled by minute inclusions of hematite, goethite and, possibly, lepidocrocite (photo 9).

One of the most interesting specimens obtained abroad is a cluster of nested isometric quartz crystals, 3 to 4 cm long (the so-called Herkimer diamond, NY, USA). Among the purchased specimens from China are druzes of clear, strongly elongated quartz crystals with hematite inclusions and flattened hematite clusters between quartz crystals (Liu Zhon Guang Dag area). A 6-cm scepter-like amethyst crystal resting on quartz was obtained by exchange from Mangatobangy, Ambatofinandrahana, Madagascar (photo 7). Clear flattened quartz crystals were obtained from Pakistan; a skeleton quartz crystal from Nuevo Leon, Mexico, was purchased in 1999 at the Rocks and Minerals auction. A 15 cm radial cluster of pale lilac zoned quartz crystals looking like a flat blossom from the Rio Grande do Sul state, Brazil was obtained via trade. R.Currier donated quartz crystal with picturesque inclusions of carbonates and chlorite originating from the same country.

Synthetic quartz crystals of various shape and color were donated by the All-Russian Institute for Synthetic Minerals, Aleksandrov.

Chalcedony pseudomorphs after wood (Germany, Hungary, and the USA), after dinosaur bones (Colorado. USA, donated by T.Nipp), after fluorite (Zimbabwe), and after anhydrite (Vodino, the Volga basin, Russia) enlarged the collection of chalcedony varieties. A series of chalcedony and agate specimens represents a collection of pseudo-stalactites, membrane tubes, and other morphological types, which replenished a vast agate collection of the Museum and illustrates genetic concepts considered in Agates monograph (A.Godovikov et al, 1987). These are the specimens from Kazakhstan, Mongolia, Georgia, Brazil, and other countries, mainly from personal collection of A.Godovikov. Amateur mineralogist A.Katz, one of donators, gifted the Museum with a fine polished agate plate; the source occurrence was Mustakh, Sakha-Yakutia. The plate was named «Godovikov» www to memorize our late director, who contributed greatly to mineralogy and origin of this minerals.

Calcite goodies were obtained and registered from 37 deposits and occurrences. About one half of acquired calcite specimens represented by a splendid collection of glendonite (calcite pseudomorphs after ikaite) (photo 10-14). A.Nikiforov, A.Zakharov, M.Anosov and V.Levitskiy collected a larger part of this collection near Olenitsa village, Kola Peninsula, during several field trips organized by the Museum in 1997-1999. Another part (more than 20 pieces) of glendonite was col-

lected (and donated) by D. Sulerzhitskiy in the Bol'shaya Balakhnya river valley, Taimyr Peninsula, Russia. The Museum set of is a detailed illustration of the glendonite ontogenesis. It comprises individual crystals, twins, and intergrowths either grown separately or overgrowing pebbles of metamorphic or other rocks, petrified trees, shells, etc., The crystals or intergrowths are freestanding or covered with clay-carbonate concretions. Glendonite from Taimyr differs from that found in Kola Peninsula by shape of intergrowths; frequently, it is white. At the same time, some samples from these two localities are indistinguishable. The photographs of glendonite are located in the Web site of the Museum (http://www. fmm.ru/gallery.htm).

Among others calcite that encrusts the chambers cavity in the Ammonitoceras shell 36 cm in diameter. is worth mentioning. The piece was collected in the Belaya river basin, Caucasus. Russia, (photo 4). Among calcites acquired from Dal'negorsk the most attractive is a spherical crystal of Mn-calcite 12 cm in diameter (donated by V.Breckler). An unusual calcite piece that formed by sectorial pinacoidal-scalenohedral crystals of several generations was collected at Kukisvumchorr, Khibiny, Russia, by M. Dorfman. This mineral is a rarity in this locality. Interesting specimens were obtained from Sub-Polar Urals, Lower Tunguska basin, and Savvinskoe deposit in Transbaikal. Karstic forms of calcite collected from limestone at the village of Kol'tsovo, Kaluga oblast', are noteworthy. A fine cluster of 5 cm Iceland spar twined crystals from Sokolovskoe deposit, North Kazakhstan was donated by L.Bulgak.

Sphalerite (112 specimens) and galena (98) are on the 3rd and 4th places by the number of items acquired. This is mainly due to inventorying of proper sections of collections of V.Stepanov and A.Godovikov. These collections deserve individual consideration and description. Still, it should be noted that these sets present a very complete scope of sphalerite and galena varieties over the territories of FSU and some East European countries. Among those species acquisitions unrelated to the mentioned collections we should note a remarkable piece from Illinois, USA. It consists of two radial intergrowths of dark-colored sphaleritewww crystals, about 12 cm each, overgrowing a flattened quartzite fragment. Noteworthy also are small skeleton crystals of galena on argillite originated from hot sublimations fed by natural subterranean coal fire in Kukhi Malik, Central Tajikistan.

Pyrite takes the fifth place by the number of new acquisitions (82 samples). A good part of new samples originate from the Volga banks near Ul'yanovsk. In part these are small pyrite crystals crusts with very bright iridescence, encrusting fissures in spherical or elliptic septarian concretions (donations from A.Agafonov and A. Natarius). Another part consists of massive pyrite concretions, max. 20 cm in diameter, which form is so naturalistically phallic that even some experienced people believe them to be crafted by a man (donators L.Bulgak and A.Natarius) (photo 5). A pyrite pseudomorph after a jurassic stigmaria root collected in a coal pit near Borovichi, Novgorod oblast', Russia. Among other specimens of Russian origin a perfect cubic shape looking pentagonal dodecahedron of pyrite, about 11 cm in diameter, from Berezovsk, Middle Urals, along with deformed cubic crystals in chlorite schist from Dodo. Sub-Polar Urals, are noteworthy. A well-developed cubic pyrite crystal, 33 x 20 x 20 cm, with black fluorite aggregate adjoining one of its faces was obtained from Akchatau, Central Kazakhstan. This is the weightiest (about 80 pounds) specimen originating from the FSU countries for period described. Druzes of bright sparkling octahedral pyrite crystals www from Peru and as named «pyrite dollars» - discoid concretions from Sparta, Illinois, USA, are noteworthy among the foreign acquisitions.

Topaz (71 sample) and celestite (47) share the sixth and seventh positions. A part topaz was collected by the author of this paper in 1998 at Thomas Range, Utah. USA, due to a kind permission of J.Holfert who showed several good places at his claims. These are individual crystals up to 5 cm long, pinkish-brown, and intergrowths with bixbyite and pseudobrookite. Cut stones variously colored by treating in cobalt and titanium salt melts represent other part of new topaz specimens. These were included to the gem collection.

Among the new celestite specimens should be mentioned a splitted blue semi-transparent crystals associated with sulfur from Vodino, Samara oblast', Russia, collected by B.Shkurskiy. Celestite crystals, up to 5 cm of clear sky-blue color, were found at the Pinega River, Arkhangelsk oblast', within the voids in limestone. An interesting genesis small crystals of pale blue celestite on calcite helictites were collected in Promezhutochnaya cave, Kugitang Range, East Turkmenistan. Radial aggregate of gray celestite crystals hosted in dark argillite (so called stone chrysanthemum) was obtained from China.

The following table lists other mineral species acquired in quantity more than 7 specimens.

Mineral Num name of specime		Mineral Num name of specim	
Crossular	41	Copper	13
Isoferroplatinum	30	Rutile	13
Sperrylite	27	Fluorite	12
Barite	23	Bixbyite	11
Gypsum	23	Cinnabar	11
Muscovite	23	Orthoclase	11
Chalcopyrite	21	Erionite-K	11
Aragonite	20	Graphite	10
Berthrandite	19	Jadeite	10
Hematite	19	Sulfur	10
Siderite	18	Phlogopite	10
Fluorapophyllite	17	Sheelite	10
Charoite	15	Schorl	10
Spinel	15	Agrellite	9
Colemanite	14	Beryl	9
Magnetite	14	Betafite	9
Opal	14	Malachite	9
Stilbite	14	Miserite	9
Fluorapatite	14	Danburite	8
Andradite	13	Diopside	8
Vesuvianite	13	Clinochlore	8
Bismuth	13	Murmanite	8
Wollastonite	13	Chrysotile	8
Corundum	13	Aegirine	8

Isoimetrical and distorted green crystals up to 5 cm make a greater part of new grossular specimens collected at the Vilyui River, Sakha-Yakutia, Russia. Zoned rhombododecahedrons up to 5 cm are from Xalostok, Mexico, represent grossular of foreign localities, as well as faceted grossular from Sri Lanka included to gem collection.

Russian Government institutions supplied all «platinum» samples. All of them are from Konder massif and represented by more or less rounded nuggets from 20 to 350 grams. They mostly contain isoferroplatinum with some chromium spinelides and Cr-diopside.

All sperrylite specimens were collected by A.Ponomarenko during 1985-1988 at Oktyabrskiy mine, Talnakh deposit, Norilsk area. They represented by crystals up to 12 mm and intergrowths — freestanding or in mooikhoekite matrix. These were catalogued after determination of associated phases, which sometimes were more interesting, then sperrylite itself. Interesting specimens of other species will be characterized along with description of other categories of new acquisitions.

## New acquisition geography

The following table lists new acquisitions by their source countries.

Country	Number speciment		Country	Number specime	
Russia	1	386	Peru		7
United Sta	ates	368	Slovakia		7
Kazakhsta	an	148	Myanma	r (Burma)	6
Tajikistan		135	Hungary		6
Australia		80	Chili		6
Canada		72	Argentin	a	5
Brazil		61	Norway		5
Turkmeni	stan	60	South Afr	rica	5
Ukraine		54	Austria		4
Italy		51	Afghanis	tan	4
Azerbaija	n	50	Serbia		4
Czech Re	public	48	Tanzania		4
Georgia		46	I		3
Kyrgyzia		45	Portugal		3
Bulgaria		40	France		3
India		35	Algeria		2
China		35			2
Germany		34	PR Cong	0	2
Uzbekista	n	33	Oman		2
Mexico		30	South Ko	rea	2
Poland		24	Vietnam		1
Sri Lanka		21	Egypt		1
Denmark		20	Zimbabw	e	1
Rumania		18			1
Morocco		17	Malawi		1
Armenia		16			1
Great Brit	ain	13	Mali		1
Mozambi	que	13	New Zea	land	1
Zaire		12	Senegal		1
Sweden		12	Slovenia		1
Japan		12	Sierra Le	one	1
Madagaso	car	11	Turkey		1
Bolivia		8	Uruguay		1
Mongolia		8	Finland		1
Namibia		8	Chad		1
Switzerlar	nd	8	Antarctic	a	2
Greece		7	Oceans E	Bottom	5
Pakistan		7	Unspecif	ied	53

New materials originate from 73 countries. Plus; some were collected from the bottom of the Atlantic and Indian oceans and some from Antarctica. Fifteen countries supplied us with one specimen each; 2 to 5 specimens came from each of 14 countries; 6 to 10 from 13 countries; 11 to 20 from 9 countries; 21 to 40 from 8 countries. Ten countries gave 41 to 100 samples each, whereas 4 countries represented by more than 100 samples each. From 11 former Soviet Union Republics we obtained 1975 samples, of which 1386 were collected in Russia.

#### Russia

#### Kola Peninsula and Karelia

As usually, new acquisitions from this region are most abundant: a total of 348 samples. of which 83 are from Khibiny massif, 95 - from Lovozero massif, and 22 - from Kovdor. These three massifs gave 67 mineral species new for the Museum, including 43 type specimens. Major contributors of rare minerals of that area are I.Pekov (54), A.Khomyakov (36), and M.Dorfman (7). In addition, rare minerals were donated by Z.Shlyukova, V.Levitskiy, M.Anosov, S.Britvin, A.Zadov, R.Liferovich, N.Manaev, V.Yakovenchuk, N.Chukanov, A.Parashchenko, M.Moiseev, and others. The Museum staff collected twenty seven specimens, 25 were either purchased or exchanged. Besides new minerals, the Khibiny-massif presented us with an interesting item, a large cleaved blocks of red transparent villiaumite found at Koashva mine, Khibiny (photo 2). The mineral is clear enough to be cut. As far as we know, this was the only finding during the whole mining history in Khibiny. Unfortunately, most of this material was discarded to the dumps and

Unexpectedly large shomiokite-(Y) pieces and its dichroic crystals were donated by I.Pekov and A.Parashchenko. Fine lamprophyllite specimens from Khibiny, lorenzenite from Lovozero massif and diopside from Kovdor were donated by amateurs V.Silitskiy and L.Chikilyova. M. Moiseev collected at Kovdor quite remarkable specimens of new rare mineral, lemmleinite-Ba. These are bright red crystals up to 1 mm in cavities of calcite carbonatite. Among the stuff collected during Museum expeditions are large plates of purple murmanite in ussingite pegmatite (Karnasurt Mt., Lovozero). Very nice piece of elpidite from Alluaiv Mt., Lovozero massif was exchanged. (photo 19).

Other new acquisitions from Kola Peninsula were collected in the Keivy Heights (23 specimens). N.Pekova, I.Pekov, A.Voloshin, P.Kartashov, and V.Levitskiy donated rare minerals collected at Ploskaya Mt and massif Sakhariok. In addition V.Levitskiy donated a fine 8-cm staurolite twin («straight cross») hosted by muscovite schist (photo 24). More than 60 specimens were collected near Olenitsa village — mainly glendonite (see above).

An interesting new item from Karelia is a sphere cut from an almandine monocrystal found near Shueretskaya station (a donation from A.Scrafimovich). It exhibits an amazing type of asterism: fine light rings are distinguishable in several centimeters above the sphere. A

large prismatic crystal of red corundum hosted by gneiss was collected at Khit-ostrov.

#### **Ura1s**

This region gave us 211 new specimens. Forty-two of them came from Sub-Polar Ural. These are quartz, calcite, titanite, ferroaxinite, and hematite from Dodo, Puiva, and other deposits and occurrences along the east slope of the Urals. Among new things collected at the opposite slope (Yaruta Mt., Man-Khambo Range) very interesting an 8-mm crystal of recently discovered species tsaregorodtsevite sitting on quartz crystal face. A.Agafonov donated magnificent bright red corundum found at Rai-Iz massif.

Middle Urals supplied more then 70 new specimens. A.Zadov and A.Loskutov presented a series of samples, which characterize rodingite veins mineralisation at Bazhenovskoe asbestos deposit. These are idocrase crystals with reddish and pink zones, along with multicolored and colorless grossular, stilbite, xonotlite, and clinotobermorite (the first finding of the latter mineral in the region). Several vases made of serpentine from this deposit replenished the stone art collection.

M.Anosov donated interesting samples of green titanite twins up to 3.5 cm (photo 15) along with crusts of purple columnar crystals of Cr-amesite with alexandrite effect. Zoned masutomilite plates from Mokrusha pit donated by I.Pekov and elongated thin foitite crystals from Kazennitsa pit a gift from J.Patterson, represent Murzinka-Adui area. Rare minerals from the oxidation zone, phoenicochroite and embreyite were obtained from Berezovskiy mine along with previously mentioned pyrite.

South Urals gave more than 70 specimens. Among the most interesting objects we'd mention a rose shaped cluster of split blue corundum crystals, about 10 cm, from Ilmenskie Mts. (photo 3). S.Nikandrov who collected the mineral in the same area donated en cabochon-cut corundum that exhibits asterism. Other interesting findings comprise druzes with pseudocubo-octahedral crystals of perovskite up to 3 cm (photo 26) and magnetite from Zlatoust vicinity. Amazingly large (about 3-cm) hoegbomite crystal on clinochlore belongs to the same assemblage (photo 27). Unusual anorthoclase from Potaninskie Mts. that exhibits both sunstone and moonstone effects was purchased.

A total of 13 mineral species new for the Museum were obtained from South Urals, including 3 type specimens. In addition, B.Chesnokov donated a series of mineral phases he described from burning coal shafts dumps.

#### Russian Far East and Kamchatka Peninsula

Of 125 specimens obtained from this region, more than 100 represented Dal'negorsk area. Along with previously mentioned quartz and calcite, a large landscape piece of wollastonite skarn www is quite noteworthy. S. van Scriver donated original intergrowths of siderite spherocrystals (photo 23). Quite interesting hollow bertrandite-rhodochrosite pseudomorph after helvite up to 5cm originated from Zabytoe deposit, Khabarovskiy kray. Platinum nuggets from Konder massif already mentioned above.

Among 42 specimens from Kamchatka Peninsula are the sublimates of Tolbachik volcano fumaroles (donated by S.Filatov, S.Krivovichev, V.Popova, and N.Rudashevskiy), along with rare micro-minerals related to ultramafite-hosted PGM mineralisation. These minerals represent 2 species new for the Museum, including 7 recently discovered ones and 5 type specimens.

#### Krasnoyarskiy kray

A total of 128 new samples were obtained from here. These are related mainly to PGM minera1s, which occur in sulfide Cu-Ni ores of Noril'sk area. Beside previously mentioned sperrylite a collection contributed by A.Ponomarenko comprised rare minerals, including 7 species new for the Museum.

#### Sakha-Yakutia

Of 110 specimens, which included the above-mentioned grossular from Vilyuy, we obtained a series of polished charoite slabs from the Murun massif. The series illustrates textural and structural features of the mineral. Important specimens of rare minerals frankamenite, dalyite and others are also originate from Murun massif.

### The Baikal area and Transbaikal

More than 100 specimens were obtained from those regions. A crystal of blue apatite (40 x 14 cm) hosted by yellow calciphyre from Slyudyanka, Baikal area, is one of more attractive. From tourmaline pegmatites of Malkhan Ridge, Chita oblast' a 3.5 cm danburite crystal on smoky quartz and pink elbaite on quartz (donated by D.Abramov) are noteworthy. Buryatia, as well as northern and southern parts of the Baikal area supplied us with 12 species new for the Museum, including 10 type specimens.

#### **Northern Caucasus**

A total of 34 specimens were obtained from this region, including a 35 cm one represented by crust of bright orange-red orpiment on dolomite mined at the El'brusskiy mine, Karacha-evo-Cherkessia (photo 6).

#### **FSU** countries

The most significant acquisitions from FSU countries came from **Azerbaijan**. These are well-formed rutile crystals up to 3.5 cm with shiny faces on quartz recently mined at Kapydzhik (Kapudzhuk) Mt. near Nakhichevan' (photo 18). They are much higher by quality compare to previously obtained pieces from this occurrence. New stuff was obtained from Dashkesan iron deposit. Among them druzes of amphibole pseudomorphs after hedenbergite are notable, along with grayish-green apatite crystals on magnetite matrix with quartz, and calcite. Nearly all pieces from Azerbaijan were purchase from Stone Flower Co. for a special museum (actually symbolic) price.

The most notable pieces from **Kazakhstan** are several druzes of large goergeyite crystals from Inder Lake as well as inderborite and colemanite from the same deposit. Well-developed trillings of davidite-(La) up to 5 cm were obtained from Bektau-Ata massif, Balkhash area. We already mentioned above pyrite from Kara-Oba, and among specimens from Akchatau a bunch of bertrandite crystals about 4 cm frozen into a face of dark violet fluorite octahedron is quiet remarkable.

Most valuable materials from Tajikistan are series of specimens from Dara-i-Pioz alkaline massif, collected by the Museum stuff members (D.Belakovskiy and B.Shkurskiy), purchased, exchanged, donated to the Museum, or acquired as type specimens of new species (L.Pautov and A.Agakhanov). In some of these specimens new mineral species were discovered after they were cataloged to Museum inventory e.g., dusmatovite, shibkovite, and telyushenkoite (a new Cs mineral). Many of Dara-i-Pioz species have bright luminescence and it was a good addition for Museum fluorescent display case.

The unique thing among acquisition from **Uzbekistan** is a native tellurium crystal 8-cm size (donated by P.Goloshchukov) from Koch-Bulak gold deposit south of Tashkent (photo 1). Noteworthy is the crusts of dark green crystals of volbortite up to 1cm from Utch-Kuduk (donation from L.Pautov and A.Minko).

The brightest materials from **Kyrgyzia** are blue aggregates and radial intergrowths of khaidarkanite a new mineral discovered recently by museum stuff members in Khaidarkan mercury deposit.

#### Other countries

United States. Maximum number of new foreign acquisitions originated from this country Donations (131 sample) is one of the sources. A 67-specimens collection donated by A.Kidwell was finally catalogued. It comprises magnificent kidwellite specimens and a series of phosphates as well as a selection of minerals from Magnet Cove, Arkansas. P.Radomsky contributed a bunch of rare fluorescent minerals from Franklin, New Jersey. J.Patterson donated helvite, danburite, and other minerals from granite pegmatites of South California. Interesting examples of sogdianite and zektserite from Golden Horn batolith, Washington, were donated by R.Becker. and R.Boggs. Trona druzes and a series of borates from Boron, California were donated by J.Watson. The list of donators, maybe an incomplete one, includes G.Robinson, L.Ream, W.Simmons, P.Haynes, T.Brent, C.Korpi, W.Heller, T.Nipp, B.Cannon, A.Lelkes, and N. Medvedev. Other source of acquisitions was an inter-museum exchange, mainly with Smithsonian National Museum of Natural History, Washington, D.C., and exchange with private collectors. Forty-three species new for the Museum were obtained this way along with exquisite moganite secretions from New Mexico (photo 22). Field collecting carried out abroad by the Museum staff members makes the third source. Along with topaz from Thomas Range mentioned above, bixbyite crystals (photo 17) (max. 1.5 cm long), flattened crystals of red beryl. cassiterite and durangite, were collected in this area. Blue bertrandite-fluorite-hyalite nodules (photo 25) were found at Brush Wellman Be deposit, now totally re-cultivated. Recently discovered mineral formikaite was established in samples collected by A.Godovikov in 1965 in Cresmore, Califonia.

Canada. Most of the canadian new acquisitions originate from Mont Saint-Hilaire and De Mix-Varennes Quarry, Quebec (33 specimens). Private collectors donated a good part of these. L.&E. Horvath donated among other species, horvathite-(Y) named after them, and manganokhomyakovite - a Mn analogue of khomyakovite named after Dr. A.Khomyakov, a Russian mineralogist. The list of Canadian contributors includes also R.Rottenberg and P.Tarasoff, F.Spertini (spertiniite from Jeffrey Mine, Asbestos was obtained from him). A remarkable intergrowth of orange serandite 4-cm in size with a white spherolite of leifite was exchanged. Large hand specimens with agrellite, eudialite and vlasovite from Kipawa alkaline complex and large fluorapatite crystals from Yates mine, Quebec. also came that way. The Museum staff member in Silver Crater, Ontario, collected nice but hot betafite crystals up to 3 cm.

**Mexico**. Iridescent obsidian, transparent yellowish Labrador crystals from Labrador mine, Chihuahua, and spherical intergrowth of creedite from Navidad mine are the most notable specimens from that country.

**Brazil.** Among the acquisitions from this country there are large flattened crystals of eosphorite up to 10 cm long partially replaced by ernstite (photo 16), large crystal of hydroxylherderite from Linopolis, Minas Gerais, and stannomicrolite resting on surface of spherical stokesite intergrowth from Urucum mine, Minas Gerais.

Australia. A total of 80 samples were obtained from this country, including 11 species new for the Museum, a selection of specimens from Broken Hill (large bustamite crystals and acicular varieties of this mineral, spessartite and apatite in galena, an unusual bright-green orthoc1ase and other minerals. M.&L.Phelan donated a large sample of bright-colored stichtite from type locality in Tasmania.

**India.** Of 35 indian specimens the majority represented by diverse zeolites. An expressive bright-blue 2-cm cavansite spherolite and a 9 cm barrel-shaped red corundum from Mysore are of interest

China. A large (12-cm long) well-developed yellow partially transparent scheelite dipyramidal crystal is the most impressive sample among those 35 obtained from China (photo 20). A bright-green pyromorphite from Guangxi is highly attractive. Druzes of large barite and fluorite crystals from several deposits in Hunan province are quite notable. Fine examples of fluorite and agalmatolite curving replenished the gem collection.

Of other foreign samples I would mention kidney-shaped crusts and pseudostalaktite of malachite from Zaire, a red corundum from Sierra-Leone (donated by A.Belyakov), a transparent yellow meionite 8-cm crystal from Tanzania, a lepidolite spherocrystal (the so-called Barbot eye) from Mozambique, and curving on red corundum hosted by green zoisite (Tanzania) and chalcedony.

W.Pinch, an American collector, donated a fragment of the type specimen of andyrobertsite. Unfortunately, this publication is limited, so many other noteworthy specimens remained unmentioned.

### Types of new acquisitions and personalia

During 1997-2001, a total of 3414 specimens were cataloged to the main Museum fund collections. Of these 2180 came to the Museum during this period. Others were obtained earlier, but examined and cataloged during the period mentioned.

334 specimens were purchased, and 600 were obtained through exchange. Seventeen Museum staff members collected 610 specimens during field trips financed either by Museum or from other sources: D.Belakovskiy (140). A.Ponomarenko (92). A.Nikiforov (78), D.Abramov (63), A.Zakharov (46), B.Shkurskiy (41), D.Romanov (30) O.Sveshnikova (24), L.Pautov (20), A.Agakhanov (19), A.Evsecv (17), N.Pekova (13), M.Dorfman (11) and others.

A total of 521 specimens were cataloged as acquisitions from V.l.Stepanov's and A.A.Godovikov's collections.

Twelve organizations and 230 individuals donated 1197 samples (one-third of the total donation number). I.Pekov donated a maximum of 135 specimens. V.Levitskiy donated 101 specimen, A.Kidwell - 79. A significant number of specimens were donated by M.Anosov(58). D.Belakovskiy (42), A.Khomyakov (41), L.Bulgak (37), A.Zadov (29), D.Sulerzhitskiy (22), W.Heller (18), A.Nikiforov (18), L.Pautov (14), J.Patterson (13), E.Spiridonov (13), V.Karpenko (12), O.Sveshnikova (12), D.Abramov (11), D.Edwards (10), A.Agakhanov (10), E.Semenov (10), V.Silitskiy and L.Chikileva (10), A.Brusnitsyn (10). Other persons who donated specimens to the Museum at this period (directly or indirectly) are: A.Agafonov, A.Akimov, S.Aleksandrov, S.Anan'ev, V.Apollonov, V.Averin, E.Babkin, A.Badalov, R.Bagataev, A. Bakhchisaraitsev, P.Bantsekov, S.Baskakov, S.Baturov, A.Bazhenov, S.Belostotskiy, O.Belyaev, M.Bezsmertnaya, G.Bocharova, Yu.Bogdanov, P.Borisov, I.Bryzgalov, V.Bukanov, A.Bul'yenkov, A.Butler, V.Chalisov, V.Chernavtsev, B.Chesnokov, Yu.Chul'zhanov, I.Davidenko, M.Dobrovol'skaya, N.Erilova, V.Cekimyants, M.Generalov, I.Ginzburg, A.Godovikov, R.Gogoleva, P.Goloshehukov, P.Gorchakov, K.Cribakh, A.Gribanov, S.Gusev, I.Ilupin, M.Ismailov, A.Izergin, V.Kalachev, B.Kantor, G.Kapustkin, P.Kartashov, A.Katz, R.Khazov, K.Klopotov, Yu.Kobyashev, A.Konev, A.Koneva V.Kongarov, O.Kononov, A.Konoval, S.Konovalenko, V.Korolev, A.Kovalev,

Yu.Kozlov, S.Krivovichhev, E.Kutukov, E.Ku $varzina,\ V.Kuvshinov,\ V.Ladygin,\ A.Lapidus,$ A.Lapin, L.Lebedev, R.Liferovich, M.Litsarev, A.Loskutov, B.Magadeev, Kh.Magnishchan, V.Makarochkin, A.Makeev, M.Malev, S.Malinko, N.Manaev, B.Manucharyants, V.Markov, N.Medvedev, O.Mel'nikov, Yu.Men'shikov, A.Mineeva, A.Min'ko, A.Mochalov, P.Mochalov, M.Moiseev, N.Mozgova, Yu.Nadzhip, A.Natarius, B.Nenashev, S.Nikandrov, S.Nikitin, T.Nipp, T.Nishanbayev, E.Novgorodova, M.Novgorodova, M.Novikova, D.Novitskiy, N.Organova, Ya.Pakhomovskiy, E.Pankratova, A.Parashchenko, L.Pavlova, I.Peretyazhko, N.Pertsev, N.Petrovskaya, V.Pokusayev, Yu.Polekhovsky, V.Politov, O.Polyakov, A.Ponomarenko, V.Popov, M. Popov, V.Popova, L.Reznitskiy, O.Rippinen, D.Romanov, V.Rudnev, Yu.Samodurov, M.Samoylovich, S.Sandomirskaya, V.Sapegin, V.Savel'yeva, S.Savkevich, A.Serafimovich, M.Seredkin, L.Shabynin, A.Shevnin, B.Shkurskiy, Z.Shlyukova, E. Sklyarov, N.Skorobogatova M.Smirnova, N.Sobolev, A.Sokolov, V.Subbotin, O.Tananaeva, G.Tarnovskiy, I.Tkachenko, E.Tsukanov, S.Tsurin, V.Ushakovskiy, B.Vaintrub, L. Vergasova, A. Volchkov, A. Voloshin, V. Yakovenchuk, F.Yanshina, E.Zav'yalov, Yu.Zhdanov, O.Zhilina, B.Zlenko, I.Zotov and others.

Foreign donators were: A.Arnold, Arnot, C.Barbosa, R.Becker, I.Bernard, R.Boggs, V.Breckler, M.Bunno, G.Dowton, C.Garret, E.Grew, C.Hedergaard, L.&F. Horwath, J.Holfert, C.Korpi, R.Lavinsky, L.Gilberto, R.Kristiansen, F.Lewis, L.Menezes, E.Nickel, P.Haynes, J.Patterson, H.Penndorf, F.Pezzota, M.&E.Phelan, W.Pinch, L.Ream, G.Robinson, R.Currier,

J.Sharp, W.Simmons, P.Tarasoff, T.Brent, J.Vaidak, S.van Scriver, D.Varhegyi, J.Watson, C.Duszan, S.Petrussenko and others.

The following organizations donated specimens to the Museum: Central Scientific Geology-prospectical Institute (TSNIGRI), All-Russian Institute for Synthetic Minerals (VNIISIMS), Institute of Geology and Geophysics Siberian brunch of RAS, a school geological club «Geokompania», Ankersmith Holding, Waikato Mineralogical Museum, a School faculty of the Moscow Geology-Prospectical Academy (MGGA/MGRI), RAS Committee on Meteorites, Pyatigorsk Regional Studies Museum, Obninsk mineralogical association, Seventh Day Adventist group and others. Another sources, including unspecified, brought 152 samples.

On behalf of the Fersman Mineralogical Museum I would like to thank all donators and everybody who participate in replenishing of our Museum collections.

As for the nearest future, we are planning to expand the list of mineral species represented in the Museum. To do so we publish here our want list (Appendix 2). Along with species which are absent in Museum collection it includes the species needed for some particular scientific studies carried out in the Museum.

The author thanks L.Bulgak, M.Dorfman, A.Evseev, N.Mokhova, A.Nikiforov, M.Novgorodova, L.Pautov, I.Pekov, N.Pekova, G.Staebler and A.Cherkassov for discussions, valuable notes and assistance in preparation of this paper.

### Appendix 1

## A list of mineral species new for the Museum contributed during 1997-2001.

Mineral species approved by CNMMN IMA and published during 1997 – 2001 are set in bold.

- \* mineral species represented in Museum by type specimens or fragments of type specimens
- \*\* mineral species discovered by Museum staff or in collaboration with Museum staff.

Abernathyite
Abhurite *
Aeschynite-(Nd)
Agardite-(Y)
Aheylite
Alacranite
Altisite*
Alumoklyuchevskite
Alumopharmacosiderite
Ammonioalunite
Andyrobertsite*
Antimonpearceite
Archerite
Arhbarite
Arsenocrandallite
Arsenuranospathite
Ashburtonite
Atlasovite*
Auricupride
Avicennite
Babkinite*
Baksanite*
Bariumpharmacosiderite
Barrerite
Barroisite

	-
	sazhenovite sehierite selkovite' selkovite' selloite senyacarite serzanskite'' sergslagite sichulite sichulite sismuthopyrochlore sismuthopyrochlore sismutocolumbite' sismutomicrolite' slatonite sowieite stradachekite' stragite strzinite surpalite' suryalite' suryalite'
ŀ	Bradachekite* Braggite
I	Brizziite Burpalite*
I	Buttgenbachite Bystrite* Calcioancylite-(Ce) Calciohilairite

Camerolaite Cannonite
Cavsichite-(Y)
Cebollite
Chabazite-Sr*
Charlesite
Chayesite
Chengdeite
Chengdeite Cheralite
Cherepanovite Chernikovite*
Chernikovite*
Chiavennite
Chlorartinite
Chloromenite
Chromceladonite*
Chromphyllite*
Clinotobermorite
Clinotobermorite Cobaltlotharmeyerite
Clinotobermorite <b>Cobaltlotharmeyerite</b> Coquandite
Cobaltlotharmeyerite Coquandite Crawfordite*
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite
Cobaltlotharmeyerite Coquandite Crawfordite Cronusite Cryptohalite Cumengite
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite Cryptohalite Cumengite Cuproiridsite
Cobaltlotharmeyerite Coquandite Crawfordite Cronusite Cryptohalite Cumengite
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite Cryptohalite Cumengite Cuproiridsite
Cobaltlotharmeyerite Coquandite Crawfordite* Cronusite Cryptohalite Cumengite Cuproiridsite

Dashkovaite\*\*\*
Deferrite
Dellaite
Deloneite-(Ce)\*
Dorrite
Dusmatovite\*\*
Edgarbaileyite
Eddyarite
Englishite
Eriochalcite
Erichhacite
Erichmanite
Ershovite\*
Esperite
Eugenite
Feroxyhyte
Ferronordite-(Ce)
Ferronordite-(La)
Ferrorhodsite
Ferrotapiolite
Fervaite
Filipstadite
Filipstadite
Finnemanite

Fluorellestadite
Fluormagnesioarfvedsonite'
Fluornatromicrolite
Formicaite'
Frankamenite
Froodite
Gamophyllite
Gartrellite
Gasparite-(Ce)
Geminite
Georgiadesite
Germanocolusite'
Geversite
Gladiusite'
Gordaite
Grischunite
Gupeiite
Hammarite
Haradaite
Haynesite
Henrymeyerite
Heulandite-(Sr)
Hexaferrum
Heyrovskiite

Hibbingite Hochelagaite Hoernesite Hoernesite
Hollingworthite
Hongshiite
Horvathite-(Y)
Hsianghualite
Hunchunite Hutchinsonite Hydrohonessite Hydroxycancrinite'
Hydroxylclinohumite'
Hydroxylcllestadite
Ilinskite' Inaglyite Indium\* Insizwaite Intersilite Intersilite' Iquiqueite Iraqite-(La) Irhtemite Isomertieite Isovite'\* Iwakiite Jaffeite Jaffeite Jahnsite-(CaMnFe) **Jedwabite''** Jennite Jinshajiangite **Juanitaite** Juantatie
Juonniite
Kalifersite'
Kamiokite
Kanemite
Kapitsaite-(Y)\*\*
Karlite
Kashinite Keithconnite Khaidarkanite\* Khmaralite
Khristovite-(Ce)\*\*
Kipushite
Kochkarite
Komkovite Koragoite Korobitsynite\* Kosmochlor **Kozoite-(Nd)** Kremersite Krupkaite

Krutaite
Kuzmenkoite-Mn\*
Kyzylkumite
Labuntsovite-Fe'
Labuntsovite-Mg\*
Laffittite
Lanthanite-(La)
Lemmleinite-Ba\*
Lemmleinite-K\*
Ienaite Lemmieinite-r Lenaite Lermontovite\* Lesukite Letovicite Likasite Lindackerite Lintisite\* Lisitsinite\* Lisitsinite Listismite
Lithiowodginite\*
Litvinskite\*
Loudounite
Luanheite
Luddenite Lulzacite Lulzacite
Magnesiofoitite
Magnesiohastingsite
Magnesiokataphorite
Majakite
Makarochkinite'
Malanite
Malinkoite'
Manaksite Manakoite
Manaandonite
Manganokhomyakovite
Manganonauyakasite'
Manganonordite-(Ce)''
Manganosegelerite'
Manganotychite'
Mariopaifa Maričopaite Marrite Masutomilite Masutomilite Mawbyite Mazzite Megacyclite' Meixnerite Merenskyite Metteite-I Metamunirite Metarossite Michenerite Minasragrite

Mineevite-(Y)\*
Molybdophyllite
Monazite-(Nd)
Moolooite
Nafertisite\*
Natroxalate\*
Noltnerite Natroxalate'
Neltnerite
Nepskoeite'
Nickellokahydrite
Nickellotharmeyerite
Nickelschneebergite
Niobocarbide''
Nitrammite
Novgorodovaite'''
Nuffieldite
Olangaite'
Olekminskite'
Olkhonskite'
Organovaite-Mn' Organovaite-Mn\*
Organovaite-Zn\*
Orlandite
Orthominasragrite Orthoserpierite Padmaite\* Padmaite'
Palenzonaite
Paracelsian
Paranatisite'
Parapierrotite
Parasibirskite
Parallerrite Parasioniskite
Paulkerrite
Peisleyite
Pekoite
Penfieldite
Peprossiite-(Ce)
Petersenite-(Ce) Phoenicochroité Phuralumite Phuralumite
Phypite
Platarsite
Polyphite\*
Potasicferrisadanagaite\*
Powondraite
Preisingerite
Prismatine
Pseudoboleite
Pyatenkoite-(Y)\*
Quadruphite
Quintinite

Ramsbeckite Ramsbeckile
Reinhardbraunsite
Remondite-(La)\*
Rhodarsenide
Rimkorolgite
Robinsonite
Roggianite
Rorisite\*
Poscharita Roscherite Roshchinite Roshchinite\*
Rosaiate
Rosaiate
Roweite
Sabinaite
Saddlebackite
Sanjuanite
Sarcopside
Sazykinaite-(Y)\*
Schlossmacherite
Schmederite
Schuetleite
Schuetleite
Schumacherite
Scrutinyite
Segnitite Scrutinyte
Segnitite
Seidite-(Ce)\*
Shcherbinaite\*
Shibkovite\*\*
Shkatulkalite
Shomiokite-(Y)\* Sigloite Silvialite Silvalite
Sincosite
Skinnerite
Smithite
Sodium zippeite
Sofiite
Sopcheite
Sorosite
Sorosite Sorosite Spertiniite Squawcreekite Stannomicrolite Stetefeldtite Stibiocolusite\* Strakhovite\* Strakhovite\* Strontiowhitlockite\* Studenitsite\* Sudburyite Switzerite Takanelite Takanelite
Taneyamalite
Tantalcarbide
Tellurobismuthite
Telluropalladinite
Telyushenkoite\*\*\* Ternovite\* Tetraauricupride Thalfenisite Tiallenisite
Tiettaite\*
Tinsleyite
Tiragalloite
Tocornalite
Tolovkite
Triangulite
Tschernichite Tsnigriite\*
Tsumebite
Tuliokite\*
Turkestanite\*\* Ulrichite Urusovite Urvantsevite
Vajdakite
Varennesite
Vasilite
Vergasovaite\*
Vicanite-(Ce)
Vihorlatite
Villyaellenite Vihorlatite
Villyaellenite
Vistepite''
Wallisite
Weilite
Weinebeneite
Weissbergite
Widgiemoolthalite
Wilhite
Wilhite Wiluite Yanomamite
Zalesiite
Zemannite
Zhemchuzhnikovite Zincocopiapite Zincowoodwardite Znucalite Zvyagintsevite

## Appendix 2

## The Museum want list as for April 30 2003.

The most wanted mineral species are set in bold. Some mineral species listed are represented in Museum but needs better quality or for research programs.

Abelsonite Abenakiite-(Ce) Abswurmbachite Achavalite Acuminite Admontite
Aerugite
Akimotoite
Alarsite
Albrechtschraufite
Allorsite
Allorsite
Allorsite
Allorsite
Aluminobarroisite
Aluminobarroisite
Aluminobarroisite
Ammoniolorite
Ammoniolorite
Ammonioleucite
Amstallite
Anandite-2O
Andremeyerite
Androiste-(La)
Anduoite
Angelellite
Angelellite
Antroitie
Anthonyite
Anthonyite Admontite Antimonselite
Antimonselite
Aplowite
Arakiite
Aravaipaite
Arcubisite
Ardaite
Ardaelite
Ardulite
Arguite Argutite
Aristarainite
Armalcolite Armangite

Arsenbrackebuschite Arsenobismite Arsenoflorencite-(Ce) Arsenoflorencite-(Nd) Arsenogroceixite
Arsenogorceixite
Arsenogoyazite
Arsenohauchecornite
Arsenuranospathite
Artroeite
Arzakite
Arzunite
Aschamalmite
Aschamalmite Ashoverite Asnoverite
Assiste
Aspidolite
Asselbornite
Astrocyanite-(Ce)
Athabascaite
Aubortite Aubertite Auroantimonate Averievite Baghdadite Baghdadite
Baileychlore
Bailyuneboite-(Ce)
Ballpholite
Bamfordite
Banalsite
Bararite
Bariomicrolite
Bariomicrolite
Bariomicrolite
Bariosincosite
Barquillite
Barringtonite
Barringtonite
Barringtonite
Barstowite

Bartelkeite Bassetite Bastnaesite-(La) Bastnaesite-(Y) Baumstarkite Baylissite Bayarthita Bearthite Beartnite
Bechererite
Bederite
Bellorgite
Bellidoite
Bellidoite
Bellite Benauite Berdesinskiite Bernalite
Bernardite
Bernatite
Bideauxite Bideauxite
Bigcreekite
Bigcreekite
Biyoetite-(Y)
Billingsleyite
Bismutostibiconite
Blakeite
Bleasdaleite
Blossite
Bobkingite
Bonaccordite
Boralsilite
Borishanskiite
Bornhardtite
Bottinoite
Bottinoite
Brabantite Brabantite Bracewellite Bradleyite Braggite

Brandholzite Brendelite Brewsterite-Ba Brianite Brianroulstonite Brinrobertsite Brizziite Brodtkorbite Brokenhillite Bruggenite Brokenhillite
Bruggenite
Brunogeierite
Buchwaldite
Buckhornite
Bulachite
Bulachite
Bunsenite
Burnsite
Burssite
Burstite
Cabalzarite
Cadwaladerite
Calciooarvaiapaite
Calciootavaiapaite
Calcioopiapite
Calciarlite
Calcacite
Calcacite
Calcacite
Caldacrite Calciactte
Calderonite
Calkinsite-(Ce)
Cameronite
Camgasite
Canaphite
Canfieldite
Caoxite Capgaronnite Carboborite Carboirite

Caresite
Carlhintzeite
Carlinite
Carlosruizite
Carlsbergite
Carmichaelite Carmichaeite
Carobbiite
Carraraite
Cascandite
Cassedanneite
Cassidyite
Caswellsilverite Caswensiverine
Cavoite
Cebaite-(Ce)
Ceriopyrochlore-(Ce)
Cervelleite
Cesanite
Chadwickite
Chaidamuite
Changahite
Changchengite
Changchengite
Changite
Changaite
Chentempykhite Chenite
Cheremnykhite
Chernovite-(Y)
Chessexite
Chesterite
Chestermanite
Chillagite
Chiluite
Chladniite
Chloraluminite
Chlorbartonite

Chlorellestadite
Chlormanganokalite
Chlorocalcite
Chlorozincite
Choloalite
Chrisstanleyite
Christite
Chromatite
Chromatite
Chromatite Chrombismite
Chursinite
Chvaleticeite
Cianciulliite Clanculline
Ciprianite
Clairite
Claringbullite
Clearcreekite
Clerite
Clinocervantite
Clinoferrosilite
Clinojmthompsonite
Clinomimetite
Clinomimetite
Clinomemachite Clinomimetite
Clinoungemachite
Cobaltpentlandite
Cobaltzippeite
Cochromite
Comancheite
Comblainite
Complainite Comblainite
Compreignacite
Congolite
Coparsite
Coskrenite-(Ce)
Costibite
Coyoteite
Crerarite
Criddleite Criddleite Cualstibite Cuboargyrite
Cupoalite
Cupropavonite
Cuprorivaite
Cyanochroite
Damaraite Damaraite
Damiaoite
Danbaite
Danbaite
Danielsite
D'Ansite
Daomanite
Davidite-(Ce)
Davidite-(Y)
Deanesmithite
Deliansita Deanesmithite
Deliensite
Deloryite
Derbylite
Derriksite
Dervillite
Despujolsite
Dessauite
Diaoyudaoite Diagolida Dienerite
Dietzeite
Dimorphite
Dinite
Diomignite
Dissakisite-(Ce)
Dittmarite Dittmarite
Dixenite
Donarrisite
Donallcharite
Douglasite
Downeyite
Doyleite
Dozyite
Dreverite Dreverite Dreyerite
Drugmanite
Drysdallite
Dukeite
Duttonite
Earlandite Eastonite Ecandrewsite Ecandrewsite
Eckermannite
Effenbergerite
Ehrleite
Eifelite
Ekatite
Ellisite Emilite Ercitite
Erlianite
Ernienickelite
Erniggliite
Ertixiite
Eskimoite Esperanzaite Eugsterite Eveite Fabianite Faheyite

Fahleite
Fairbankite
Fairchildite
Falcondoite
Fangite
Farringtonite
Feinglosite
Feitknechtite
Felbertalite
Fencooperite
Fermorite
Fermorite
Ferrisatophorite
Ferrilotharmeyerite
Ferrilatrite
Ferrinatrite
Ferripatrizite Ferrilotharmeyerite
Ferrinatrite
Ferripedrizite
Ferristrunzite
Ferristrunzite
Ferristrunzite
Ferristrunzite
Ferristrunzite
Ferristrunzite
Ferristrunzite
Ferroakermanite
Ferroakermanite
Ferroaluminobarroisite
Ferroaluminotschermakite
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Jeanbandyite
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Lawsonbauerite
Leakeite
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Lehnerite
Leisingite
Lepersonnite-(Gd)
Levinsonite-(Y)
Levyclaudite
Lewisite
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Liebauite Lautenthalite

Liebenbergite Lindqvistite Lindsleyite Lishizhenite Lonecreekite **Loranskite-(Y)** Loseyite
Loveringite
Loveringite
Luberoite
Lucasite-(Ce)
Lukenchangite-(Ce)
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Macaulayite
Macedonite
Machatschkiite
Macphersonite
Macquartite
Madocite Madocitie

Maghagendorfite

Magnesioaluminotaramite

Magnesiochloritoid

Magnesiochloritoid

Magnesiocopiapite

Magnesiocopiapite

Magnesiocummingtonite

Magnesiodumortierite

Magnesioferrikatophorite

Magnesioferrikaromite

Magnesioferritaramite

Magnesioholmquistite

Magnesioholmquistite

Magnesiosadanagate

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Modderite
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Moeloite **Mohrite** 

Moluranite Molysite
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Monetite
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Montdorite
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Moreauite
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Morimotoite
Morozeviczite
Moschelite
Mottanaite-(Ce)
Mountkeithite
Moydite-(Y)
Mozartita Mozartite
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Muchuanite
Muckeite Mummeite Mundrabillaite Munirite Muskoxite **Muthmannite** Mutinaite Nabiasite Nabiasite
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Niahite
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Nickelbloedite
Nickelhexahydrite
Nickelphosphide
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Nioboaeschynite-(Nd)
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Nowackiite
Nukundamite
Nullaginite
Nyboeite
Obertiite
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Odinite Nimite Odinite
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Osarsite Oneillite Osarsite
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Palladoarsenide
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Palladseite Palmierite
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Paulkellerite
Paulmooreite Paxite **Pehrmanite-9R** Pehrmanite-9R
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Penobsquisite
Perryite
Peterbaylissite
Petroyskaite
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Petscheckite
Phillipsbornite
Philolithite
Phosphommite
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Phylotungstite
Pillaite
Pinalite Pinalite Pinchite Pingguite Pintadoite Piretite Piretite
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Redledgeite
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Refikite
Reichenbachite

Reidite Reinerite Remondite-(Ce) Rengeite Reppiaite Retzian-(Ce) Retzian-(La) Retzian-(Nd) Rhabdophane-(Nd) Rhodolumsite Rhodalsellide Rhodplumsite Richetite Rilandite Ringwoodite Ringwoodite
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Rossmanite Rossmanite Roubaultite Rouseite
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Shabaite-(Nd)
Shakhovite
Shandite
Sharpite Sharpite Sheldrickite Sherwoodite Sherwoodite Shigaite Shuangfengite Sicherite Sidpietersite Sidwillite Sieleckiite Sigismundite Silhydrite Silicon Silinaite Simmonsite Simonellite Simonite Simonite Simplotite Sinjarite Sinnerite Sinoite Skippenite Skippenite
Slawsonite
Sodium pharmacosiderite
Sopcheite
Spadaite
Sphaerobismoite
Spodiosite
Springcreekite
Srilankite
Stalderite
Standkite Stanekite Stanfieldite

Stanleyite
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Stetefeldtite Stibiobetafite Stilleite Stillwaterite Stishovite **Stoiberite** Stronalsite
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Uhligite
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Ungemachite
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Upalite **Uramphite** 

Urancalcarite
Uranosilite
Uranotungstite
Uricite
Ursilite

Utahite Vanadomalayaite Vanmeersscheite Vanoxite Vanuranylite Vaterite **Vaughanite** Veenite
Viaeneite
Viitaniemiite
Vikingite
Villamaninite
Vincentite Vincentite
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Virgilite
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Wallkilldellite-(Mn)
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#### GEOGRAPHICAL LOCATION OF MINERAL TYPE LOCALITIES

## Alexander A. Evseev

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, e-mail: evseev@fmm.ru

An inventory of mineral type localities at which more than three new mineral species were discovered (nearly 200 sites over the world) has been compiled. Their geographical locations have been refined (the coordinates are presented) using the multimedia Microsoft Encarta-2001 World Atlas. Examples of the earliest (regarding the year of the publication) and last finds of new minerals are presented for each of the type localities. These data can be used for expansion of museum collections at the expense of additions of type specimens.

The place of discovery, or the type locality (TL), is obligatorily specified in publications on new minerals. However, the geographical location is commonly the least precise characteristic in the descriptions of the finds. The geographical location of the finds determines their scientific and collectional value and, therefore, it is of particular importance for large world-class museums that are interesting in standards of new minerals with their TL.

The interest to the type localities has begun to increase from the 1960s. For example, comprehensive reviews of new minerals were already present in summaries on mineralogy of Colorado (Eckel, 1961), Japan (Introduction..., 1970), and other regions. In 1970, Embrey and Hey were the first to consider in detail the concept of type specimens (Embrey and Hey, 1970). In the 1990s, the international project was already being realized on compilation of the Catalogue of Type Mineral Specimens (CTMS); its parts were the work on Zair published in 1995 by M. Deliens and H.A. Stalder and others. A preliminary inventory including reliable new mineral species etc. from the United States (arranged by the states) was compiled by 1993 by V.T. King (remained unpublished). In 1998, Pekov published a summary on new minerals from the former Soviet Union, the most comprehensive work among publications on this subject. The first reference-book where an effort was made to specify the TL for each mineral species was probably the work by Nickel and Nichols (1991). The number of TL mentioned in this reference-book exceeds 1500. Using the summaries by Nickel and Nichols, Pekov, and Mandarino (1997), as well as other works, I have compiled the present inventory of type localities where more than three new mineral species were discovered (data are as of the late 1990s).

This inventory includes about 200 TL for which the geographical coordinates are presented with the use of the multimedia Microsoft Encarta-2001 World Atlas. The figures

preceding a TL name is the number of new species discovered here; the data borrowed from the work by Pekov (2000) are asterisked. For each TL, examples of finds of new minerals are provided from among the first (the year of the publication is specified) and last ones. In addition to the type locality proper, the inventory includes some districts 10-40 km across, if they incorporate several TL. It is obvious that comparing the objects in the number of new species and in the mineral diversity, it is important to take into account their sizes and surroundings, since finds derived from type localities different in name (or with different geographical locations) can belong to one and the same ore district, massif, and formation, or can be located very nearly to each other.

In this respect, it is useful to compile maps of regions (or countries), showing the TL location (see below). However, this problem is difficult to solve using ordinary geographical atlases, maps 1:500000, and reference-books on mineral deposits, since even many famous mineral type localities (Langban, Lengenbach, Ilimaussaq, etc.) are missing from them. The use of the Encarta-2001 World Atlas that contains 1.8 millions of geographical names facilitates the work, although the problem is not completely removed. Thus, the atlas does not contain some names (for example, Ilmeny = Ilmenskiye Mountains); on the other hand, it contains many names identical to each other, which hampers the search.

Thus, the name Panasqueira, Portugal, that is often encountered in mineralogical literature, is repeated 7 times in Encarta-2001. The same is true for Antisirabe, Madagascar (15 times); Mooihoek, South Africa (6 times); and Sar-e-Sang, Afghanistan (7 times, none of them being coincident with the famous lazurite deposit). The same problems persist with respect to finds of new minerals, made in the last few years. The TL of esperanzaite (the year 2000) is La Esperanza, Durango, Mexico; but the atlas refers to three populated localities La

Esperanza in this state. The TL of onite (1998), famous Tunaberg, is absent from the atlas, but there exists another point under the same name here. The TL of damiaoite (1997) is «the village of Damiao, 270 km apart from Beijing»; the atlas refers to 6 villages under this name in this region of China, but none of them is situated at the distance specified above. Another problem is related to an existence of different versions (including distorted ones) of Russian transcriptions for geographical names of foreign localities (for example, for the Italian names Leviglinani, Cetino, and Cerchiara). Incidentally, the name Cercharia is contained in Encarta-2001, but the locality it specifies is not the place where caoxite and mozartite were

The correctness of the names and locations is an individual issue (Evseev, 2000). Renamed TL, different TL under the same name, different spelling versions of the names, and dissimilar approaches to the location — all these complications make serious problems for many museums, collections, and publications. Significance of these problems can be estimated on the example of the inventory of 200 principal TL which comprise only a share of a percent of the total number of mineral localities.

#### Principal mineral type localities

Abbreviations:

(Dst.) district, area;

(Co.) county;

(m.) mine;

(Mf.) massif;

(Q.) quarry;

(N) north, northern latitude;

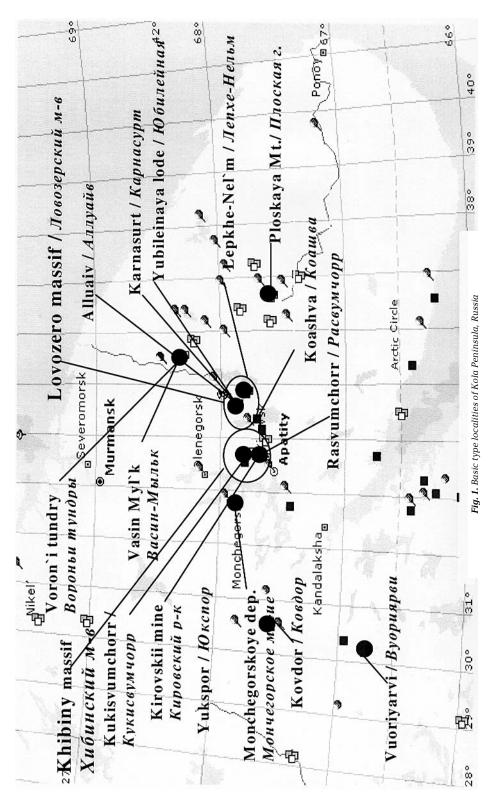
(S) south, southern latitude;

(W) west, western longitude;

(E) east, eastern longitude.

- 9 Alsar \5 km NE from Rozden (41°11'N, 21° 57'E), F.Y.R.O. Macedonia \\1894-lorandite;...1989-bernardite; 1994-dorallcharite
- 5 Baia Sprie \ (47°39'N, 23°40'E), Romania \\1853-felsobanyaite (felsobanyite);...1929-klebelsbergite
- 5 Baita Bihorului \[=Baita: 46°29'N, 22°34'E], Romania \\1861-szaibelyite;...1985paderaite; 1994-makovickyite
- 5 Bambolla m. \Moctezuma (29°48'N, 109°41'W), Sonora, Mexico \\1972-bambollaite;...1989-cervelleite
- 7 Bambollita (=La Oriental) m. \Moctezuma (29°48'N, 109°41'W), Sonora, Mexico \\1973-quetzalcoatlite;...1979-tlapallite

- 9 Barberton district \(25°48'S, 31°03'E), Transvaal, South Africa \\1921-trevorite (Bon Accord 282 JU);...1978-nichromite (Bon Accord 282 JU)
- 4 **Bastnas** \Riddarhyttan (59°49'N, 15°33'E), Vastmanland, Sweden \\1841-bastnasite-(Ce);...1921-tornebohmite-(Ce)(toe rnebohmite-(Ce))
- 4 **Baveno** \(45°55'N, 8°30'E), Piemonte, Italy \\\* 1901-bavenite; 1998-scandiobabingtonite
- 12 Bayan Obo = Bayin Obo \(41°46'N, 109°58'E), Inner Mongolia, China \\1959-bafertisite;...1987-bajyneboite-(Ce)
- 10 Bellerberg q. \SE of Ettringen, 2 km N of Mayen (50°19'N, 7°13'E), Laacher See Area, Eifel, Germany \\1874-ettringite; ...1983-eifelite; 1999-schaferite
- 4 Bergen \(50°28'N, 12°16'E), 7 km W of Falkenstein, Saxony, Germany \\1877-Uranocircite ;...1984-Bergenite
- 4 **Big Chief m.** \[~5 km SE of] Keystone (43°53'N, 103°25'W), Pennington Co., South Dakota, USA \\1974-perloffite;...1984-sinkankasite
- 8 Big Creek and Rush Creek area \~8 km NE of Trimmer (36°54'N, 119°17 'W), Fresno Co., California, USA \\1965-fresnoite; ...2001-kampfite
- **4 Big Fish River** \(68°28'N, 136°30'W), Yukon, Canada \\1977-maricite;... 1981-wicksite
- 9 Big Fish River and Rapid Creek (see below) (area) \Yukon, Canada \\1976-baricite; ...1986-rapidcreekite
- 30 Binntal = Binnental = Val di Binn \E of Binn (46°22'N, 8°10'E), Valais (= Wallis), Switzerland (finds in area 6 x 6 km, including Cherbadung (= Pizzo Cervandone, Italy)) \\1845-dufrenoysite;...1994-fetiasite (Gorb); 1998-graeserite(Monte Leone thrust)
- 5 **Bisbee** \(31°26'N, 109°55'W) (area), Cochise Co., Arizona, USA \\1891-paramela-conite;...1983-henryite
- 22 Black Hills \ (area 160 x 88 km); pegmatites of area of Custer (43°46'N, 103°36'W) and Keystone (43°53'N, 103°25'W); Pennington\ Custer Co., South Dakota, USA \\1891-griphite;...1989-pararobertsite
- 7 Bon Accord \15 km NE from Barberton (25°48'S, 31°03'E) Distr., Transvaal, South Africa \\1921-trevorite;...1978-nichromite
- 5 **Bou Azzer** \(30°31'N, 6°54'W), Morocco \\1956-smolianinovite;...1987-wendwilsonite
- 9 Branchville \ about 6 km E of Redding (41°18'N, 73°23'W, Fairfield Co., Connecticut, USA \\1878-eosphorite;...1880-eucryptite
- 12 Broken Hill \(31°58'S, 141°28'E), New South Wales, Australia \\1892-marshite; ...1992-segnitite; Sutherland F.L., 2000



- 5 Buca della Vena m. \Stazzema (43°59'N, 10°18'E), Tuscany, Italy \\1979-apuanite; ...1997-dessauite; 1999-scainiite
- 4 Bultfontein m. \Kimberley (28°43'N, 24°45'W) area (SE), South Africa \\1932-bultfonteinite;... 1989-hawthorneite
- **4 Candoglia** \Val di Toce, ~2 km NE of Ornavasso (45°58'N, 8°24'E), Piemonte, Italy \\1905-paracelsian;...1984-titantaramellite
- 11 Cap Garonne \Le Pradet (43°06'N, 6°01'E), Var, France \\1910-cuproadamite; ...1997-pushcharovskite
- **4?** Carleton m. \Chester (43°16 `N, 72°36`W), Windsor Co., Vermont, USA \\1977-jimthompsonite;...1977-chesterite
- 5 Carlin m. (Au) \~15 km NW of Carlin (40°43'N, 116°06'W), Eureka Co., Nevada, USA \\1974-frankdicksonite;... 1979-ellisite
- 4 Cerny Dul \(50°37'N, 15°42'E), Krkonose, Czech Republic \\1958-koutekite;...1979-kutinaite
- 5 Cetine di Cotorniano \Rosia (43°15'N, 11°12'E), ~10 km SW of Siena, Tuscany, Italy \\1968-onoratoite;...1999-clinocervantite
- 4 Christmas m. (Cu) \(33°03'N, 110°44'W), 7 km NE of Hayden, Gila Co., Arizona, USA \\1976-junitoite;...1980-apachite
- 12 Chuquicamata \(22°18`S, 68°55`W), 15 km N of Calama, Antofagasta, Chile \\1908-natrochalcite;...1986-obradovicite
- 14 Clara m. \8 km NW of Wittichen (48°19'N, 8°20'E), Schwarzwald (= Black Forest), Germany \1966-barium-pharmacosiderite;...1984-cualstibite; 1993-arsenogorceixite
- 6 Clay Canyon \~2 km W of Fairfield (40°16'N, 112°06'W), Utah Co., Utah, USA \\1896-wardite;...1940-montgomeryite
- 7 Clear Creek claim \(36°23 N, 120°46 W), 10 km SW of Idria, San Benito Co., California, USA
- \\1990-edgarbaileyite;...1997-hanawaltite 6 — Cobalt (area) \(47^23^1N, 79^40^1W) (area), Ontario, Canada \\1924-ferrisymplesite (Hudson Bay m.);...1972-larosite (Foster m.)
- 4 Colquechaca (area) \(18°39'S, 66°01'W) (area), Potosi, Bolivia \\1926-penrose-ite;...1978-mandarinoite (both pacajake)
- 7 Copiapo (mining disrict) \(27^{\circ}21^{\circ}S, 70^{\circ}20^{\circ}W\) = (area), Atacama, Chile \\1833-copiapite;...1933-amarillite
- 4 Coyote Peak \SW of Orick (41°17'N, 124°03'W), Humboldt Co., California, USA \\1980-erdite;...1983-coyoteite
- 8 Crestmore q., \8 km NW of Riverside (33°59'N, 117°22'W), Riverside Co., California, USA \\1917-riversideite;...1966-jennite

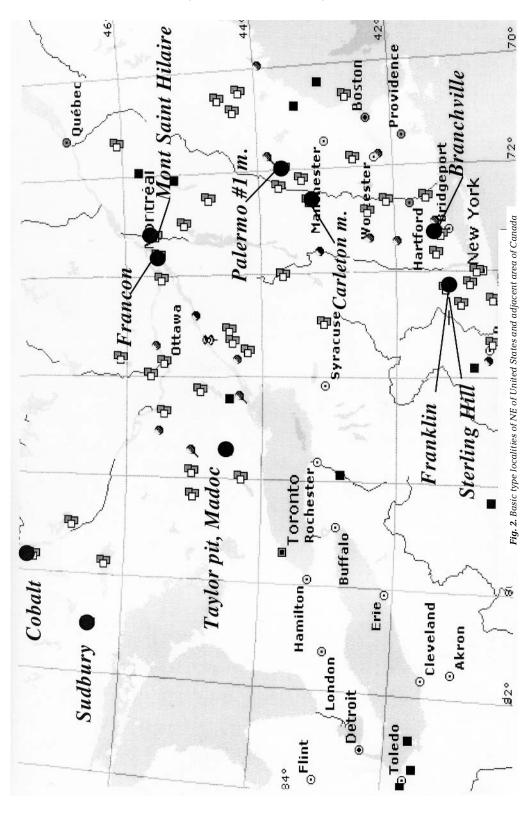
- 9 Death Valley \(area ~130 x 15 km), Inyo Co., California, USA \\1883-colemanite (Furnace Creek, 5-12 km NW of Ryan (36°19'N, 116°40'W);...1970-wardsmithite (Hardscrable Claim, Furnace Creek)
- 7 Elba Island \((central part:~ 42°47'N, 10°15'E), Italy \\1811-ilvaite (Rio Marina);... 1957-bonattite
- 9 Ettringer Bellerberg, 2 km N of Mayen (50°19'N, 7°13'E), Laacher See area, Eifel, Germany \\1964-mayenite;...1997-ternesite
- 6 Falun \(60°36'N, 15°38'E), Kopparberg, Sweden \\1828-botryogen;...1980-nordstromite
- 9 Foot Mineral Company m. \2 km SW of Kings Mountain (35°14'N, 81°20'W), Cleveland Co., North Carolina, USA \\1967-switzerite;...1990-lithiomarsturite
- 8 Francon q. \St. Michel Distr. (~46°31'N, 73°35'W), Montreal Island, Quebec, Canada \\1968-weloganite;...1990-voggite
- **45\* Franklin** \((41°07'N, 74°35'W), Sussex Co., New Jersey, USA \\1819-franklinite; ...1992-franklinphilite
- 65\* Franklin (area) \(41°07'N, 74°35'W), Sussex Co., New Jersey, USA \\1814-zincite; 1819-franklinite;...1994-samfowlerite
- 10 Franklin Furnace, Franklin (41°07'N, 74°35'W), Sussex Co., New Jersey, USA \\1830-willemite;...1928-larsenite
- 43 Franklin m., Franklin (41°07'N, 74°35'W), Sussex Co., New Jersey, USA \\1814-zincite;... 1994-samfowlerite
- 4 Fredriksvarn = Stavern (59°00'N, 10°02'E), Vestfold, Norway \\1826-pyrochlore; 1852-meliphanite
- 12 Freiberg and area \ (50°54'N, 13°20'E), Erzgebirge, Saxony, Germany \\1829-polybasite (Neuer Morgenstern m.);...1963-arsenpolybasite (Neuer Morgenstern m.)
- 7 Fuka m., = Bicchu = Bitchu (34°46'N, 133°26'E), Okayama Pref., Japan \\1973-bicchulite;...1992-clinotobermorite
- 7 Furnace Creek, Furnace Creek Wash (~36°23'N, 116°44'W), 5-12 km NW of Ryan (36°19'N, 116°40'W), Death Valley, Inyo Co., California, USA \\1883-colemanite; ...1965-mcallisterite
- 5 Gabe Gottes vein \ Ste.-Marie-aux-Mines (48°14'N, 7°10'E), Alsace, France \\1964-rauenthalite;...1982-phaunouxite)
- 4 Gambatesa m., Reppia (44°22'N, 9°26'E), Val Graveglia, Liguria, Italy \\1979-saneroite;...1992-reppiaite; 1994-vanadomalayaite
- 5 Good Hope m., Vulcan (38°20'N, 107°00'W), Gunnison Co., Colorado, USA

- \\1903-rickardite;...1986-cameronite
- 4 Grand Central m., Tombstone (31°43'N, 110°04'W), 30 km NNE of Bisbee, Cochise Co., Arizona, USA \\1979-girdite;...1979-winstanleyite
- 4 Grand Reef m., Aravaipa (32°57'N, 110°21'W) district, near Klondyke (32°50'N, 110°19'W), Graham Co., Arizona, USA \\1989-aravaipaite;...1989-grandreefite
- 8 Green River Formation \ (finds in area (wide of this area is up to 170 km): 1) Duchesne Co. and Uintah Co., Utah, USA 2) Sweetwater Co., Wyoming, USA \\1954-eitelite (Duchesne Co., Utah);...1978-abelsonite (Uintah Co., Utah)
- 4 Guanajuato \ (21°01'N, 101°16'W), mining district (area 200 sq. km), Guanajuato (state), Mexico \\1873-guanajuatite (Santa Catarina m.);...; [1963-antimonpearceite]
- 15 Hagendorf \(49°38'N, 12°27'E), 3 km NW of Waidhaus, Oberpfalz, Bavaria, Germany \\1920-phosphophyllite;...1988-lehnerite
- 11 Harstigen = Harstigsgrufvan \ [~3 km NE of] Persberg (59°45'N, 14°14'E), Varmland, Sweden \\1865-monimolite;...1891-svabite
- 5 Hatrurim \ W of Dead Sea (NW point: 31°46'N, 35°30'E), Israel \\1928-bayerite; ...1985-ye'elimite
- 4 Hillside m. \ (34°25'N, 112°54'W), Bagdad, Yavapai Co., Arizona, USA \\1951-andersonite;...1976-zinc-zippeite
- 4 Himmelsfurst m. \8 km SSW of Freiberg (50°54'N, 13°20'E), Erzgebirge, Saxony, Germany \\1840-xanthoconite;...1909-jordisite
- 25\* Ilimaussaq \(central part ~60°55'N, 45°52'W), ~25 km NNE of Julianehab (60°43'N, 45°52'W), Greenland (SW) \ 1 8 1 9 e u d i a lyte(Kangerdluarsuk);...1989-nacareniobsit e-(Ce)
- 4 Iquique \(20°13`S, 70°09`W) and area, Tarapaca, Chile \\1850-ulexite;...1986-iquiqueite
- 4 **Itabira** \(19°37`S, 43°13`W), Minas Gerais, Brazil \\1955-arsenopalladinite;...1977-palladseite
- **18\* Ivigtut** \(61°12`N, 48°10`W), Greenland (SW) \\1799-cryolite;...1997-jorgensenite
- 8 Izalco volcano \ (13°49'N, 89°38'W), El Salvador \\1979-stoiberite;...1988-howar-devansite
- 24\* Jachymov \(50°21'N, 12°55'E), Czech Republic \\1727-uraninite;...1996-jachymovite
- 6 Jakobsberg \S of Nordmark (59°49'N, 14°06'E), Varmland, Sweden \\1869-jacobsite;...1993-lindqvistite
- **4 Jas Roux m.** \(\(\frac{44^\circ 44^\circ 49^\circ N}\), 6\(^0 18^\circ E}\)), 12 km SSW of Mont Pelvoux (44\(^0 55^\circ N}\), 6\(^0 21^\circ E}\)),

- Hautes Alpes, France \\1970-pierrotite; ...1981-chabourneite
- 5 Jo Dandy m. \~10 km SE of Paradox (38°22'N, 108°57'W), Paradox Valley, Montrose Co., Colorado, USA \\1914-meta-hewettite;...1970-metadelrioite
- 7 Johanngeorgenstadt \(50°25'N, 12°44'E), Erzgebirge, Saxony, Germany \\1855-emplectite; ...2000-paganoite
- **4 Kamoto East m.** \[~5 km] S of Musonoi (10°40'N, 25°25'E), Shaba,Congo (DRC) \\1986-kamotoite-(Y);...1990-astrocyanite-(Ce)
- 7 Kangerdluarsuk \~15 km N of Julianehab (60°43'N, 45°52'W), Ilimaussaq, Greenland (SW) \\1819-eudialyte;...1967-tundrite-(Nd)
- 6 Kank \(49°58'N, 15°17'E), 3 km NE of Kutna Hora, Czech Republic \\1901-kutnohorite;...1999-parascorodite
- 7 Kasolo \ (11°03'S, 26°32'E), 5 km SW of Shinkolobwe, Shaba, Congo (DRC) \\1921-curite;...1923-schoepite
- 4 Keweenaw peninsula \ (80—100 x 20 25 km), NE of Houghton (47°06'N, 88°32'W), Lake Superior, Michigan, USA \\1925-pumpellyite -(Mg); 1963-anthonyite and calumetite (Centennial m., Calumet: 47°14'N, 88°27'W); 1979-macfallite (Copper Harbor)
- 4 **Keystone m.** \Magnolia Distr., 9 km SW of Boulder (40°01'N, 105°16'W), Boulder Co., Colorado, USA \\1877-coloradoite;...1988-keystoneite
- **14 Kobokobo** \(3°05'N, 28°08'E), Shaba, Congo (DRC) \\ *1958-lusungite*;... *1987-althupite*
- 7 Kombat \ (19°42'N, 17°42'E), ~50 km S of Tsumeb, Namibia \\1986-kombatite;...1990 -damaraite
- **5 Kuusamo** \ (65°57'N, 29°10'E), Finland \\ 1964-wilkmanite;...1964-trustedtite
- 68\* Langban \ (59°51'N, 14°15'E), 15 km NNE of Filipstad, Varmland, Sweden \\1830-hedyphane;...1998-philolithite
- 101 Langban \((59°51`N, 14°15`E)\) area (Harstigen, Nordmarken, Jakobsberg and others), Varmland, Sweden \\(1808-pyrosmalite;...1998-philolithite\)
- 23\* Langesundfjord \~5 10 km SE of Brevik (59°04'N, 9°41'E), Norway (S) \\1829-thorite (Lovo (=Laven) Isl.);...1890-hambergite (Helgeraen)
- 6 Larderello \(43°14'N, 10°52'E), Tuscany, Italy \\1854-larderellite;...1970-santite
- 16\* Lavrion = Laurium \(37°42'N, 24°03'E), Greece \\1881-serpierite;...1998-niedermayrite; 2000-zincwoodwardite
- 7 Leadhills \(55°24`N, 3°45`W), Scotland, Great Britain \\1832-caledonite;...1987-mattheddleite

- 25\* Lengenbach \(~46°21`N, 8°21`E), Binntal, Valais, Switzerland \\1845-dufrenoysite; ...1997-jentschite
- 5 Little Green Monster m. \Clay Canyon (40°16'N, 112°07'W), 2 km W of Fairfield, Utah Co., Utah, USA \\1930-englishite; ...1940-montgomeryite
- 5 Llallagua \((18°25`S, 66°38`W), Potosi, Bolivia \\1922-vauxite (Siglo XX m.); ...1982-jeanbandyite
- 7 Loven (= Laven =Lovo) Isl. \ ~5 km E of Langesund (59°00'N, 9°44'E), Langesundfjord, Norway (S) \\1829-thorite;...1885-lavenite
- 8 Madoc \ (44°30'N, 77°28'W), 45 km NE of Hastings, Ontario, Canada \\1967-veenite; ...1967-madocite
- 4 Magadi (Lake Magadi) \W of Magadi (1°53'S, 36°18'E), Kenya \\1909-uhligite; ...1970-makatite
- 8 Mammoth St. Anthony m. \(32°43'N, 110°37'W), Tiger, Pinal Co., Arizona, USA \\1950-wherryite;...1989-pinalite
- 6 Menzenschwand \ (47°49'N, 8°04'E), Schwarzwald, Germany \\1976-joliotite; ...1985-uranotungstite
- 4 Merume River \[compare Merume Mountains, Mazaruni River and Potaro River (sources: 5°16'N, 59°50'W), Guyana \\1967-guyanaite;...1976-mcconnellite
- **8 Minasragra** \ ~35 km SW of Cerro de Pasco (10°41'N, 76°15'W), Pasco, Peru \\1906-patronite;...1994-fernandinite
- 23 Moctezuma (area) \((29^{\circ}48\), \(109^{\circ}41\)\), Sonora, Mexico \\ \(1960\)-paratellurite; \(...1989\)-cervelleite
- 7 Moctezuma m. \[22 km] S of Moctezuma (29°48'N, 109°41'W), Sonora, Mexico \\1961-zemannite;...1979-burckhardtite
- 4 Molinello \9 km NE of Lavagna (44°21'N, 9°27'E), Val Graveglia, Liguria, Italy \1980-tiraqalloite;...1990-strontiopiemontite
- 41 Mont Saint Hilaire (area) \near Mont Saint Hilaire (45°31'N, 73°09'W) (area), 32 km ENE of Montreal, Quebec, Canada \\1967-lemoynite;...1999-khomyakovite; 2001-natrolemoynite
- 17 Monte Somma \Vesuvius (40°49'N, 14°25'E), near Naples, Campania, Italy \\1795-vesuvianite; 1800-nepheline;...1990-montesommaite
- **5 Moschellandsberg** \1km E of Obermoschel (49°43'N, 7°46'E), Rheinland-Pfalz, Germany \1972-schachnerite;...1992-belendorffite
- 4 Moss m. \near Nordmark (59°49'N, 14°06'E), Sweden \\1884-allactite;...1884-synadelphite
- 9 Mounana \((1^26 S, 13^09E), (U) deposit, 55 km NW of Franceville, Gabon

- \\1957-francevillite;...1971-bariandite
- **7 Musonoi m.** \(10°42`S, 25°23`E), W of Kolwezi (10°41`S, 25°39`E), Shaba, Congo (DRC) \\1965-guilleminite;...1971-derriksite
- 10 Musonoi m. Kolwezi m. (area) \ (10°42'S, 25°23'E) (~10°44'S, 25°27'E), W of Kolwezi (10°41'S, 25°39'E), Shaba Congo (DRC) \\1965-guilleminite (Musonoi m.); ...1990-astrocyanite-(Ce) (Kamoto-East pit)
- 15 Narssarssuk = Narsarsuk = Narsarsuaq, massif \-15 km SSE of Narsarsuaq (61°09'N, 45°25'W) or 10 km NE of Igaliko = Igaliku (60°59'N, 45°26'W), Greenland (SW) \\1893-neptunite;...1897-lorenzenite;...1953-rontgenite-( Ce)
- 8 Nordmarken = Nordmark \ (59°49'N, 14°06'E), Varmland, Sweden \\1808-pyrosmalite (Bjelkes Grufvan); 1835-safflorite; ...1917-katoptrite
- >100 Nordmark area \(Brattfors (20 km S of Nordmark), Harstigen, Jakobsberg, Langban (8 km ENE of Nordmark), Moss and other, Varmland, Sweden \\1808-pyrosmalite (Bjelkes Grufvan);...1998-philolithite (Langban)
- 5 Ojuela m. \Mapimi (25°50'N, 103°50'W), Durango, Mexico \\1956-paradamite; ...1983-lotharmeyerite (Mapimi)
- 4 Pacajake \Colquechaca (18°39'S, 66°01'W), bolivia \\1926-penroseite;...1978-mandarinoite
- 4 Pala District \ (Stewart m. and others), Pala (33°21'N, 117°04'W), San Diego Co., California, USA \\1912-sicklerite (Vanderberg m.); 1912-stewartite (Stewart m.)...1978-jahnsite-(MnMnMn) (Stewart m.)
- 8 Pala District Mesa Grande District Ramona District \(33°21'N, 117°04'W) (33°10'N, 116°46'W) (33°02'N, 116°52'W) (~40 x 20 km), San Diego Co., California, USA \\1912-sicklerite (Vanderberg m.); 1915-stibiocolumbite (Himalaya m.); ...1991-boromuscovite-1M (Little Three m.)
- 10 Palermo #1 m. (pegmatite) \1.6 km SW of North Groton (43°45'N, 71°52'W), Grafton Co., New Hampshire, USA \\1940-whitlockite;...1977-schoonerite; 1984-sinkankasite
- 4 Panasqueira \ (40°09'N, 7°45'W), 23 km W of Fundao, Portugal \\1966-berndtite-4H; ...1979-panasqueiraite
- 9 Paradox Valley \ (~40 x 15 km ), SE of Paradox (38°22'N, 108°57'W), Montrose Co., Colorado, USA \\1914-metahewettite (Jo Dandy Claim);...1962-hendersonite (J. J. mine)
- **4** − **Pitigliano** \ (42°37'N, 11°39'E), Grosseto,



- Tuscany, Italy \\1977-tuscanite;...1991-pitiglianoite
- >10 Poudrette q. \Mont Saint Hilaire (45°31'N, 73°09'W), Quebec, Canada \\1989-griceite;...2001-micheelsenite
- 5 Pribram \ (49°41'N, 14°00'E), Czech Republic \ \1820-cronstedtite;...1990-znucalite (Lill mine)
- **6 Rapid Creek** \(point A: 68°33'N, 136°47'W; point B: 68°31'N, 136°57'W), Yukon, Canada \\1976-baricite;...1986-rapidcreekite
- 5 Richelsdorf \ (~50°58'N, 10°00'E), Hessen, Germany \\1819-picropharmacolite;...1985simomkolleite
- 8 Sacaramb = Sacarimb = Nagyag (former) \ (44°57'N, 23°03'E), Romania \\ 1835-sylvanite;...1929-fuloppite
- **4 San Piero in Campo** \((42°54'N, 10°12'E), Elba, Italy \\1846-pollucite;...1993-uranopolycrase
- 7 Sapucaia \6 km SE of Sapucaia do Norte (18°50'S, 41°31'W), Minas Gerais, Brazil \1949-frondelite;...1958-roscherite
- 6 Scawt Hill \ near Larne (54°51'N, 5°50'W), Antrim Co., Northern Ireland, Great Britain \\1929-scawtite;...1973-ferrobustamite
- **38\* Schneeberg** \(50°36'N, 12°38'E), Erzgebirge, Saxony, Germany \\1786-meta-torbernite;...1998-brendelite
- **4 Scotia Talc m.** \ Bon Accord (~25°41'S, 31°10'E), 15 km NE of Barberton (25°48'S, 31°03'E), Transvaal, South Africa \\1968-nimite;...1974-bonaccordite
- 11 Searles Lake \ (15 x 12 km), near Trona (35°45'N, 117°22'W), San Bernardino Co., California, USA \\1878-tincalconite; 1885-hanksite;... 1963-galeite
- 4 Shaheru (Mt. Shaheru) volcano \(\(^1^22^9\)S, 29°14'E), ~5 km N of Nyiragongo, Nord-Kivu, Congo (DRC) \\\\1957-combeite;...1959-delhayelite
- **36 Shinkolobwe** \ (11°02'S, 26°34'E), Shaba, Congo (DRC) \\1921-curite;...1985-gysinite-(Nd); 1986-protasite
- 9 Sierra Gorda \ (22°53'S, 69°18'W) area (Caracoles [= Placilla de Caracoles: 23°02'S, 69°00'W] and others), Antofagasta, Chile \\1888-amarantite;...1999-changoite
- 5 **Sjo m. = Sjo Grufvan** \SE of Grythyttan (59°42'N, 14°32'E), Orebro, Sweden \\1888-arseniopleite;...1986-orebroite
- 4 Skipton Caves \ (37°41'S, 143°22'E), 45 km SW of Ballarat, Victoria, Australia \\1878-hannayite;...1887-dittmarite
- 5 Sophia m. \ (~48°20'N, 8°20'E), 300 m WSW of Kloster Wittichen (Weiss,1990), Schwarzwald, Germany \\1958-metakahlerite;...1998-chadwickite

- 5 Stassfurt \ (51°51'N, 11°35'E), Sachsen (= Saxony)-Anhalt, Germany \\1856-carnal-lite;...1884-pinnoite
- 8 Ste.-Marie-aux-Mines \ (48°14'N, 7°10'E), Alsace, France \\1941-dervillite;...1984-villyaellenite
- 22\* Sterling Hill \ Ogdensburg (41°05'N, 74°35'W), Sussex Co., New Jersey, USA \\1823-tephroite;...1987-parabrandtite
- 19 Sterling m., Sterling Hill, Ogdensburg (41°05'N, 74°35'W), Sussex Co., New Jersey, USA \\1823-tephroite;...1987-wendwilsonite
- 5 Stillwater Complex \ ~40 km across NW (~45°30'N, 110°15'W), Montana, USA \\1974-rhodium;...1979-telluropalladinite
- 7 Sudbury \ (46°29'N, 81°00'W), area 60 x 30 km, Ontario, Canada \\1889-sperrylite ( V e r m i l l i o n m.);...1980-tellurohauchecornite (Strathcona m.)
- 5 Tachgagalt = Tachguagalt \ (30°47'N, 6°51'W), near Quarzazate, Morocco \\1963-marokite;...1969-henrytermierite
- 4 Tanco pegmatite m. \ (50°26'N, 95°27'W), Bernic Lake, Manitoba, Canada \\1978-cernyite;...1992-titanowodginite
- 8 Taylor pit, Madoc \ (44°30'N, 77°28'W), Hastings Co., Ontario, Canada \\1967-veenite;...1967-twinnite
- 9 Temple Mountain (area) \ (38°41'N, 110°40'W), Emery Co., Utah, USA \\1914-uv-anite (Temple Rock);...2001-ortominasragrite
- 8 Terlingua (area) \(29°19'N, 103°36'W), Brewster Co., Texas, USA \\1900-terlinguaite;...1974-pinchite; 1981-Comancheite (Mariposa m.)
- **4 Tincalayu** \(25°07'S, 67°04'W), Salta, Argentina \\1957-ezcurrite;...1974-aristarainite
- 10 Tintic District \mining district (~ 10 x 5 km) from Tintic Junction (39°55'N, 112°09'W), Juab Co. Dividend (39°57'N, 112°03'W), Utah Co. , Utah, USA \\ 1916-arsenobismite (Mammoth m.);...1997-utahite and juabite (Centennial Eureka m.)
- 12 Tip Top m. \8.5 km SW of Custer (43°46'N, 103°36'W), Custer Co., Black Hills, South Dakota, USA \1974-robertsite;...1992-parafransoletite
- 11 Tombstone area \(31°43'N, 110°04'W), Cochise Co., Arizona, USA \\1885-emmonsite;...1980-schieffelinite (Joe m.)
- **4 Trogtal q.** \ 1 km N of Lautenthal (51°52'N, 10°17'E), Harz, Germany \\1955-trogtalite; ...1957-freboldite
- **57\* Tsumeb** \(19°14'S, 17°42'E), Namibia \ \ 1 9 1 2 t s u m e b i t e ;

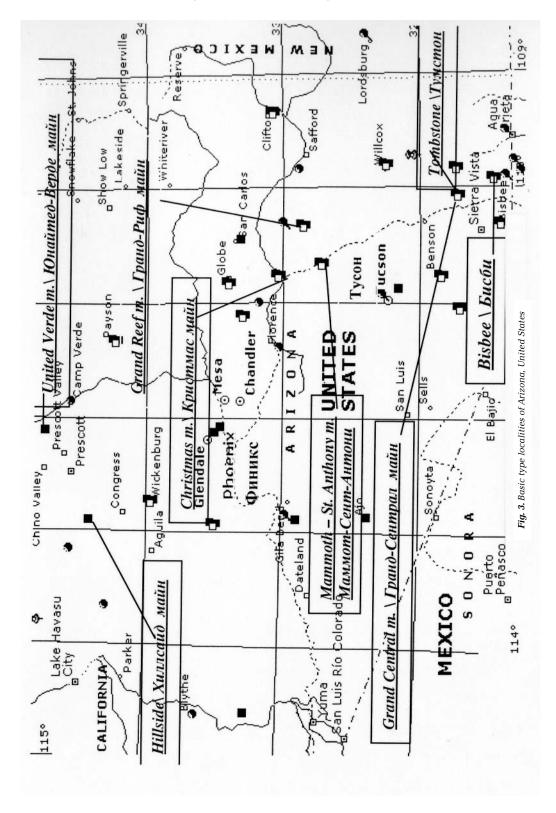
- 1920-duftite;...1999-wilhelmkleinite; 1999-sidpietersite
- 7 United Verde m. \near Jerome (34°45'N, 112°07'W), Yavapai Co., Arizona, USA \\1885-gerhardtite;...1959-yavapaiite
- 4 Utoe Isl. \(58°58 \text{ N, } 18°19 \text{ E), } 30 40 km SSE of Stockholm, Sweden \\1800-petalite; \[[1800-spodumene]...1978-magnesioholmquistite\]
- 5 Vestana = Vestane = Westana m. \ (56°10'N, 14°29'E), 1.5 km W of Nasum, Skane, Sweden \\1868-augelite;...1868-trolleite
- 60\* Vesuvius = Vesuvio \ (40°49'N, 14°25'E), near Naples, Italy \\1791-leucite; 1795-vesuvianite;...1988-panunzite; 1990-montesommaite (Monte Somma)
- 4 Viitaniemi \ [63°08'N, 28°30'E], Finland \\1954-vayrynenite;...1983-manganotapiolite
- 5 Vulcano Island \ (Island ~8 km across; volcano: 38°23'N, 14°58'E), Aeolian (= Eolie = Lipari) Islands, N of Sicily, Italy \\1882-hieratite;...2000-mozgovaite
- 6 Weisser Hirsch m. \ Neustadtel, Schneeberg (50°36'N, 12°38'E), Erzgebirge, Saxony, Germany \\1871-walpurgite; 1 8 7 1 - t r o g e r i t e (troegerite);...1983-asselbornite
- 8 Wessels m. \(~27^04\)S, 22°46\)E), NW of Kuruman, Northern Cape, South Africa \\1983-sturmanite;...1996-wesselsite
- >3 Wheal Gorland \-1 km N of St. Day (50°14'N, 5°10'W), Cornwall, England, Great Britain \\1787-olivenite; 1823-clinoclase
- 7 Wittichen \ (48°19'N, 8°20'E), Schwarzwald, Germany \\1800-pharmacolite;...1853-wittichenite; 1989-camgasite (Johann m.)
- 24 Wittichen (area) \ (48°19'N, 8°20'E) (Clara m., Sophia m. and others), Schwarzwald, Germany \\1800-pharmacolite; ...1998-chadwickite (Sophia m.)
- **4 Wolfsberg** \(51°32'N, 11°05'E), 8 km SW of Harzgerode, Harz, Germany \\1826-zinkenite (zinckenite);...1969-dadsonite
- 4 Xitieshan deposit \ (37°20'N, 95°32'E), Qinghai Prov., China \\1983-xitieshanite; ...1990-lishizhenite
- 4 Aginskoye deposit, near Aginskiy (55°28'N, 158°00'E), Kamchatka, Russia \\1978-bilibinskite;...1980-balyakinite
- 24 Alluaiv Mount, (~67°51'N, 34°32'E), ~27 km SW of Lovozero (68°01'N, 35°00'E), Lovozero massif, Kola Peninsula, Russia \\1979-sidorenkite;...2000-litvinskite («Shkatulka» vein); 2000-manganonaujakasite
- **4 Arzak,** deposit (Hg), [~20—25 km] NW of Terlig-Khaya (51°49'N, 93°28'E), Tuva,

- Middle Siberia (S), Russia \\1980-kuzne-tsovite;...1989-grechishchevite
- 7 Balasauskandyk (~44°32'N, 67°25'E), ~15 km NW of Aksumbe (44°27'N, 67°32'E), Karatau Range (NW), Kazakhstan \\1959-alvanite;...1989-kazakhstanite
- 7 Berezovskoye deposit, Berezovskiy (56°54'N, 60°47'E), 14 km NE of Yekaterinburg, Middle Ural, Russia \\1766-crocoite; ...1988-cassedanneite
- 4 Burpala massif, ~30 km NE from month Levaya Mama River (~56°14'N, 110°46'E), Lake Baikal Region (N), Russia \\1964-burpalite;...1969-plumbobetafite
- 9 Vasin-Myl'k, Voron'm tundry (~68°18'N, 35°32'E), Kola Peninsula, Russia \ 1 9 8 1 a 1 u m o t a n tite;...1992-manganosegelerite
- 4 Vishnevye gory (mountains), near Vishnevogorsk (56°00'N, 60°40'E), South Ural, Russia \1931-vishnevite;...1993-fluorrichterite (=fluororichterite)
- 11 Voron'm tundry (-68°18'N, 35°32'E), -13 km ENE of the mouth of the Uima River (68°15'N, 35°16'E), Kola Peninsula, Russia \\1957-lithiophosphate (Okhmyl'k Mount.);...1992-manganosegelerite
- 9 Vuonnemiok (Vuonnemiyok) river = (sources: ~67°39'N, 33°50'E), κ NE of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1929-fersmanite (the third Northern tributary);...1983-Kostylevite
- 10 Vuoriyarvi massif (~66°47'N, 30°10'E), Karelia (NW), Murmansk Oblast', Russia \\1961-carbocernaite;...1999-tumchaite
- 13 Dara-i-Pioz = Dara-Pioz massif (~39°28'N, 70°42'E), ~20 km E from month of Zeravshan River, Alaiskii Range, Tadzhikistan \\1963-calcybeborosilite-(Y); 1967-tienshanite;...2000-kapitsaite-(Y)
- 4 Zod deposit, near Zod (40°12'N, 45°51'E), Armenia \\1965-volynskite;...1987-chekhovichite
- 14 Ilmeny Mtns(~40x5 km), NNE of Miass (55°00'N, 60°05'E), South Ural, Russia \\1826-ilmenite;...1986-makarochkinite; 1993-fluorrichterite (=fluororichterite)
- 4 Inagli massif (~58° 44'N, 124° 56'E), ~30 km NW of Aldan, Yakutia, Russia \\1960-batisite;...1984-inaglyite
- 5 Inder deposit, ~15 km E of Inderborskiy (48°33'N, 51°44'E), Kazakhstan \\1937-inderite;...1966-volkovskite
- 4 Kadyrel'skoye deposit, ~23 km N of Shagonar (51°32'N, 92°48'E), Tuva, Middle Siberia (S), Russia \\1984-lavrentievite; ...1989-grechishchevite
- 10 Karatau Range (NW), Range (NW), Aksu-

- mbe (44°27'N, 67°32'E) area, Kazakhstan (S) \\1954-kurumsakite (Kurumsak); ...1989-kazakhstanite (Balasauskandyk)
- 31 Karnasurt Mount, (~67°53'N, 34°38'E), ~20 km SW of Lovozero (68°01'N, 35°00'E), Lovozero massif, Kola Peninsula, Russia \1954-beryllite; 1955-nenadkevichite; ...2000-malinkoite; 2000-organovaite-Mn
- 4 Kirovskii mine, Kukisvumchorr, ~5 km N of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1990-tuliokite; ...1997-isolueshite
- 12 Koashva Mount, ~13 km E of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1974-koashvite;...1999-lemmleinite; 2000-lisitsynite
- 13\* Kovdor (67°32'N, 30°30'E), Kola Peninsula, Russia \\1980-kovdorskite;...2000-[bakchisaraitsevite]; 2000-gladiusite; 2000-henrymeyerite
- 8 Kopeisk (55°07'N, 61°39'E), 15 km E of Chelyabinsk, South Ural, Russia \ \ 1 9 8 5 - s r e b r o d o l skite;...1990-dmisteinbergite; 1991-tinnunculite
- 3 Kochbulak deposit, [~10 km] E of Angren (41°01'N, 70°09'E), Uzbekistan \\1979-kuramite; 1981-chatkalite; 1982-mohite
- 8 Kukisvumchorr Mount, ~5-8 km N of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1959-magnesium astrophyllite;...1997-ancylite-(La)(Marchenko Peak)
- 4 Kuranakh deposit, near Kuranakh (58°45'N, 125°29'E), Aldan, Yakutia, Russia \\1975-kuranakhite;...1990-kuksite (Delbe orebody)
- 6 Kurumsak, ~20 km SW of Aksumbe (44°27'N, 67°32'E), Karatau Range (NW), K a z a k h s t a n \\1954-kurumsakite;...1989-kazakhstanite
- 4 Kyzylsai (=Kyzyl-Sai) ore field, [~30 km] SW of Chiganak (45°06'N, 73°58'E), Kazakhstan \\1962-mourite; 1965-sedovite; ...1975-sodium boltwoodite boltwoodite
- >5 Lepkhe-Nel'm Mount (~67° 48'N, 34° 48'E), ~25 km SW of Lovozero (68° 01'N, 35° 00'E), Lovozero massif, Kola Peninsula, Russia \\1956-kupletskite;...[2001-tsepinite-Na]
- 71\* Lovozero massif (central part: ~67°48'N, 34°43'E), SW of Lovozero (68°01'N, 35°00'E), Kola Peninsula, Russia \\1894-lamprophyllite;...2000-[litvinskite]
- 11 Mayak mine, Talnakh deposit, Talnakh (69°29'N, 88°26'E), Noril'sk district, Middle Siberia (N), Russia \\1969-godlevskite; ...1982-taimyrite
- **4 Monchegorskoye deposit**, near Monchegorsk (67°54'N, 32°49'E), Kola Peninsula,

- Russia \\1963-moncheite;...1964-imgreite; 1982-sopcheite
- 8 Murun massif, Murun Mount (~58°22'N, 118°53'E), ~50 km W of Torgo (58°28'N, 119°49'E), Aldan (NW), Yakutia\ Irkutsk Oblast, Russia \\1965-tinaksite; 1978-charoite;...1992-frankamenite; 1995-odintsovite
- 7 Novofrolovskoye deposit, near Krasnotur'insk (59°47'N, 60°30'E), North Ural, Russia \\1955-calciborite;...1968-vimsite
- 5 Noril'sk-I deposit, near Noril'sk (69°19'N, 88°11'E), Middle Siberia, Russia \\1962-vysotskite;...1969-godlevskite
- 30 Noril'sk district (including Talnakh), near Noril'sk (69° 19'N, 88° 11'E), Middle Siberia, Russia \\1947-stannopalladinite (Ugol'nyi Ruchei mine);...1992-vyalsovite (Komsomol'skii mine)
- 13 Oktyabr'skoye deposit, Talnakh (69°29'N, 88°26'E), Noril'sk district, Middle Siberia, Russia \1966-zvyagintsevite;...1983-cabriite
- 4 Pereval q., near Slyudyanka (51°38'N, 103°42'E), Lake Baikal Region (SW), Russia \ 1 9 8 5 k a l i n i nite;...1995-magnesiocoulsonite
- 6 Ploskaya Mount (~67°38'N, 36°42'E), ~35 km NNW of Krasnoshchel'ye, Keivy, Kola Peninsula, Russia \\1983-vyuntspakhkite-(Y); 1983-keiviite-(Y);...1997-fluorthalenite-(Y)
- >8 Rasvumchorr Mount, NE of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1954-shcherbakovite; ...1970 rasvumite;... 1993-megacyclite
- 7 Slyudyanka (51°38'N, 103°42'E) and area, Lake Baikal Region (SW), Russia \\1985-kalininite (Pereval q.);...1991-bystrite (Malo-Bystrinskoye lazurite deposit);...1997-chromphyllite (Kaber's Pit)
- 5\* Solov'yeva Mount (~57°41'N, 59°39'E), ~35 km SW of Nizhnii Tagil, Middle Ural, Russia \\1909-tantalcarbide («native tantalum»);...1997-jedwabite
- 4 Solongo deposit ,~20 km N Gunda (52°47'N, 111°43'E), Transbaikalia, Buryatia, Russia \\1965-kurchatovite;...1977-fedorovskite
- 15 Talnakhskoye deposit, Talnakh (69°29'N, 88°26'E), Noril'sk district, Middle Siberia, Russia \1968-talnakhite;...1992-vyalsovite (Komsomol'skii mine)
- 24 Tolbachik volcano (~55°49'N, 160°22'E), ~30 km S of Klyuchevskaya Sopka volcano, Kamchatka, Russia \\1983-tolbachite; ...2001-[bradachekite]
- 4 Trudovoye deposit, near Inyl'chek (= Enyl'chek) (42°01'N, 79°04'E), Kirg(h)i-

#### Geographical Location of Mineral Type Localities



- sia (= Kyrgyzstan)  $\1981-natan-ite;...1992-vistepite;$  1993-khristovite-(Ce)
- 6 Khardaikan deposit, Khaidarkan (39°56'N, 71°20'E), Kirg(h)isia (= Kyrgyzstan) \\1972-galkhaite; 1977-velikite;...1984-chursinite
- 136\* Khibiny-Lovozero complex (~80x40 km), between Kirovsk (67°36'N, 33°40'E) and Lovozero (68°01'N, 35°00'E), Kola Peninsula, Russia \\1894-Lamprophyllite;... 2001-tsepinite -(Na)
- 70\* Khibiny massif (central part: 67°43'N, 33°44'E), Kirovsk (67°36'N, 33°40'E) area, Kola Peninsula, Russia \\1923-mangan-neptunite (Malyi Mannepahk Mount); 1925-loparite-(Ce) (Malyi Mannepahk Mount);...2000-lisitsynite (Koashva Mount)
- 6 Khovu-Aksy deposit, near Khovu-Aksy (51°07'N, 93°40'E), Tuva, Middle Siberia (S), Russia \1953-vladimirite; 1953-shubnikovite;...1981-lazarenkoite
- 6 Chelkar (47°49'N, 59°37'E), 100 km SE from Ural'sk, Kazakhstan \\1960-strontioborite; 1962-halurgite;...1968-chelkarite
- 13 Yubileinaya pegmatite lode, Karnasurt Mount (~67°53'N, 34°38'E), Lovozero massif, Kola Peninsula, Russia \\1972-ilmajokite; 1973-zorite; 1973-lovdarite; 1973-raite;...1998-seidite-(Ce)
- >12 Yukspor Mount, ~8 km NW of Kirovsk (67°36'N, 33°40'E), Khibiny, Kola Peninsula, Russia \\1925-yuksporite;...1992-paranatisite (Material'naya Adit)

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## ARCHIVE OF THE MINERALOGICAL MUSEUM: REPLENISHMENT OF COLLECTIONS IN 1909–1914

#### Leo V. Bulgak

Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, mineral@fmm.ru

Information on replenishment of Museum's collections in 1909-1914 based on the study of archival sources. 6 figures.

In 1906, the Peter the Great Geological Museum, under the initiative of F.N. Chernyshev, was divided into two branches — geological and mineralogical. Academician V.I. Vernadsky headed the mineralogical branch occupying only one hall with 8 showcases. He has invited V.I. Kryzhanovsky to work in the Museum as the acting as keeper, who already in the beginning of 1907 has plunged into restoration of old collections, creation of new forms of records and accounting and replenishment of collections by new materials.

For more successful work in this direction, Vernadsky in 1909 sent this young specialist abroad to get acquainted with mineralogical museums of Berlin, Bonn, Munich, Dresden, Vienna, Geneva, where he studied collections and accounting and documenting methods of museum collections. Simultaneously, Kryzhanovsky got also acquainted with the work of foreign mineralogical offices engaged in trading minerals.

Having returned to Saint Petersburg, he started correspondence with these offices and purchased at them minerals new to the Museum. Minerals were sent from abroad by mail in parcels containing 15 to 50 samples. Kryzhanovsky selected the most interesting samples from each sent parcel and returned the staying. Frequently, all sent material was accepted. In this case the price of samples was discounted by 10 %. The postage on delivery of minerals and sending back the residues was born by a mineralogical office. Some samples were selected directly in offices at abroad missions of Fersman, Kryzhanovsky and Vernadsky.

The first parcel was received by the Museum on April 17, 1909 from the firm Grebel, Wendler and Co in Geneva. It contained 25 samples, mainly minerals of gold and silver from deposits of Peru, Mexico, USA, etc. at total amount of 249 Swiss Francs. Closest contacts were maintained with this firm. From 1909 to1914,

the Museum has received from Geneva 20 parcels with minerals of France, Spain, Portugal, Turkey, Hungary, Austria, Romania, Italy, Belgium, Norway, Greenland, USA, Australia, Madagascar, Turkey, Mexico and Brazil at the amount of 6,821 Swiss Francs.

Related to Vernadsky's interest to radioactive minerals and organization in 1912 of Radium Expedition of the Academy of Sciences, such minerals as uraninite, autunite, carnotite, uranothallite, torbernite, uranothorite, etc ware actively purchased.

The firm of Dr. F. Krantz (Bonn), in 1909 - 1914 has sent 11 parcels at the amount of 4,031 DM.

The firm of Julius Buhm (Vienna) has sent 16 parcels at the amount of 7,429 Austrian Crones in 1911-1914.

Six parcels came from the Freiberg Mining Academy (since 1909 till 1914) at the amount of 1, 705 Marks.

A set of betafite samples from Madagascar pegmatites, collected by A.E. Fersman during his stay in Vienna, was sent by doctor L. Eger from the Institute of Natural History.

A big parcel of silver minerals and rocks describing the Cobalt deposit in Canada was supplied upon Vernadsky's request by the mine management (also not free-of-charge). In addition, the Museum has received a parcel from USA (Philadelphia) from the firm Foot Mineral Co, containing, in particular, native tantalum from Altai and minerals from Colorado and California (amazonite, spodumene, kunzite, tourmaline, etc.). Some parcels came from Prague, from the mineralogical firm of V.Frie and one parcel at the amount of 1,252 Marks from Hamburg, from the firm of Ernst Winter & Sohn, containing 25 diamond crystals selected by Fersman.

Unfortunately, the World War I begun in August 1914 has interrupted these contacts and purchase of minerals from abroad has stopped.

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Fig. 1. The invoice (for 36 Rbl) drawn by Moscow collector R.R. Gassel'blat to the Museum for 8 samples with V.I. Kryzhanovsky's note on the disbursement

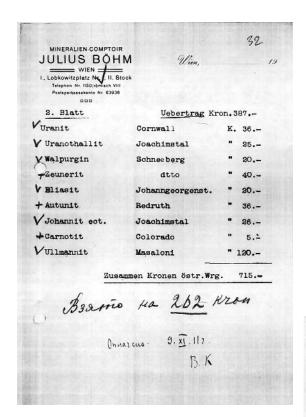


Fig. 2. The invoice of Austrian mineralogical office of Julius Böhm with V.I. Kryzhanovsky's note «Paid on November 9, 1911, V.K.»

The Museum was more intensively replenished by Russian minerals. So, in 1909, after long negotiations, the collection of Urals mining enterpriser K.A. Shishkovsky (100 samples for 4, 000 roubles) was purchased. At that time the Museum had enough of funds for this purpose. In addition to proceeds allocated annually by the Academy of Sciences, the Museum had in its account 200, 000 Rbl bequeathed by the deceased V.I. Vorob'ev for the Museum's development and purchase of minerals. The Shishkovsky collection was bought out of interest from this sum.

Additional funds were allocated to the Museum in 1912, when the Peter the Great Geological Museum was renamed into the Peter the Great Geological and Mineralogical Museum. The staff of the Museum was also increased. Fersman become the Senior Scientific Keeper of the Mineralogical Museum. The same year the Museum has acquired in Vienna the collection of P.A. Kochubei of about 2, 600 samples, including 300 unique pieces. The czarist gov-

ernment has allocated 169, 869 Rbl for this purpose.

Among many mineralogical firms of Russia, the Museum most closely cooperated with the Urals Mineralogical Office of L.I. Kryzhanovsky in Ekaterinburg. Since 1911 through 1917 this office has directed to the Museum about one hundred boxes (about 6000 kg) at the amount of 4, 527 Rbl.

The Urals Society of Naturalists in the same time has sent 8 boxes at the amount of 246 Rbl. Small purchases (at 30-40 Rbl) were made at other firms and individual collectors: A. Vyacheslov and Co (Saint Petersburg), R.R. Gassel'blat (Moscow), M.I. Rings (Perm), etc.

A large material came to the Museum as a result of own expeditions (A.E. Fersman and V.I. Kryzhanovsky missions to Middle and Southern Urals). So, L.I. Kryzhanovsky in the letter to the Museum dated September 27, 1912 wrote that «one of sent boxes in weight of

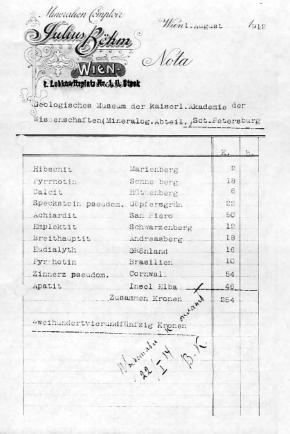


Fig. 3. The invoice of August 12, 1912 of Austrian mineralogical office of Julius Bö hm with V.I. Kryzhanovsky's note «To submit for payment on January 22, 1914, V.K.»

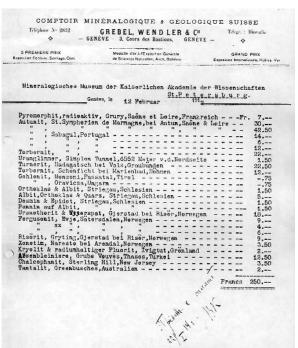


Fig. 4. The invoice of February, 12, 1912 of Swiss mineralogical firm GREBEL, WENDLER & Co with V.I.Kryzhanovsky's note «To submit for payment on January 22, 1914, V.K.»

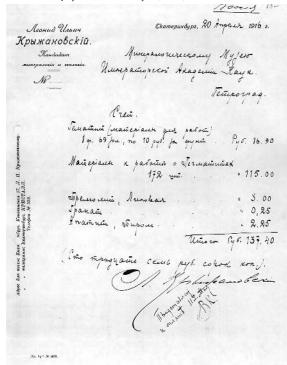


Fig. 5. The invoice for 137 Rbl 40 copecks of April 20, 1916, drawn by L.I.Kryzhanovsky on the Museum with V.I.Kryzhanovsky's note «Submitted for payment on May 11. V.K.»

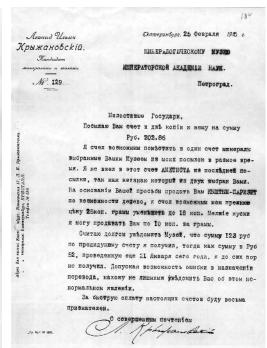


Fig. 6. Letter # 129 of L.I.Kryzhanovsky dated February 25, 1915 to the Mineralogical museum of the Imperial Academy of Sciences

4 poods and 7 pounds comprises minerals collected by Fersman and Kryzhanovsky during their summer expedition». A small amount of samples came as gifts. So, the same letter of L.I. Kryzhanovsky notes that «one box contains a collection gifted to the Museum from Emerald Mines of Mr. Kuznetsov located in quarter 220 of Berezovaya Dacha».

Gifts came from mine engineers, students, mine managers and collectors. However, the basic source of collection replenishment with diverse material was purchase of minerals at western firms and Russian collectors.

UDK 549:069

# THE ROLE OF A.E. FERSMAN IN THE MINERALOGICAL MUSEUM OF THE RUSSIAN ACADEMY OF SCIENCE

Tat'yana M. Pavlova A.E. Fersman Mineralogical museum, RAS, Moscow, pavlova@fmm.ru

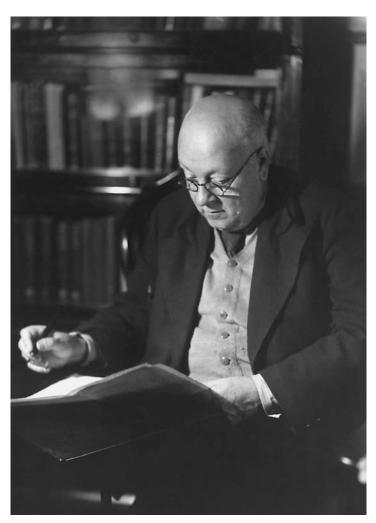
The paper portrays Academician A.E. Fersman as one of the founders and supporters of the Mineralogical Museum in Moscow; he guided the museum to form a new research center here. Photo, 8 references.

I came to be a passionate mineralogist when just six years old A.E. Fersman

In 2003 a community of mineralogists and geochemists will celebrate the 120th birthday of Academician Alexander E. Fersman.

«The first half of the  $20^{\text{th}}$ century was illuminated by names of outstanding scientists, who brought glory to the Russian and Soviet science. One of the first places belongs to Academician A.E.Fersman, a prominent geochemist and mineralogist. Several contemporaries were comparable by their scientific abilities, but it is hardly possible to find another scientist who combined his gift with improbable workableness, his public activities with practical studies on mineral resources, and scientific studies with popularization» (Perelman, 1968).

Life and work of A.E. Fersman was entwined with the Museum. The numerous field expeditions he led replenished the Museum collections. His broad scientific interests widened the thematic scope of the Museum staff: pegmatites of the Urals, Middle Asia, Transbaikalia, and Khibiny, mineralogy of diamond; jasper and gems, hypergene minerals, etc.



Academician Alexander E. Fersman in his study. Moscow, 1941, July,

A.E. Fersman was born on November 8, 1883, in St. Petersburg. He took the road to science as a six-year old boy, when he started with his first collection of minerals in Totaikoi (now Fersmanovo), Crimea, where his family used to spend summers. During 1901—1903 he was a student at Novorossiysk university, department of physics and mathematics. His education continued at Moscow university (1903—1907) where V.I. Vernadsky guided his mineralogical studies.

His love of minerals in all of their forms and a passion to collect grew into serious scientific interests, which covered the whole sphere of the natural and human history and culture. «All my life and further work was predetermined by this childish entertainment: instead of caring for a small personal collection came the tasks related to guidance of a large state museum of world reputation» he wrote later about himself. This was the Mineralogical Museum of the Russian Academy of Sciences which he headed from 1919 to 1945; later the Museum was named after him.

He started scientific studies when a student. «During this period, Vladimir I. Vernadsky introduced a notion on dispersed, non-mineral occurrence of chemical elements in nature. Vernadsky founded the principles of geochemistry, the science that studies the history of chemical elements in the Earth's crust. (Perelman, 1968). Due to his talent and deep knowledge of physics and chemistry, A.E. Fersman absorbed the pioneering ideas from his professor and joined him in developing the new scientific discipline. The academic studies of the young scientist came together with his museum work: in 1909 he was invited to join the staff of the Mineralogical bureau (Moscow university) as an assistant. At first he described minerals and arranged the collection systematically. In the same year he was elected a member of the Russian Mineralogical society and awarded the A.I. Antipov¹ medal for his studies in mineralogy. One year later at the age of 27 A.E. Fersman was elected a professor of Mineralogy in the A.L Shanyavsky People's university<sup>2</sup>. This was where the first course in geochemistry was read (Perelman, 1968).

In 1911, V.I. Vernadsky moved from St. Petersburg to Moscow and in 1912 he started work in the Peter the Great Geological Museum of the Russian Imperial Academy of Sciences leading its mineralogical branch. Fersman followed his teacher and at the end of 1912, became the senior custodian of the mineralogical branch. Academician F.N. Chernyshov was the director and head of the geological branch of this museum. In fact, the two branches of the Museum were individual research institutions. In 1912 the Museum was renamed to the Peter the Great Geological and Mineralogical Museum, it became the only academic institution in Russia which united the geological scientific disciplines. A new page was opened in the Museum's history, when new laboratories addressing or working with mineral chemistries and spectral analysis, started to bring interesting results. For the following fifty years, practically all mineralogical and geochemical research institutions of the national Academy of Sciences stemmed from these two laboratories (Barsanov, Kornetova, 1989). A.E. Fersman along with V.I. Vernadsky was the founder and builder of this grandiose scientific framework. Since then, the whole life and studies of A.E. Fersman became inseparable from the Museum.

In 1914, V.I. Vernadsky was appointed a director of the Peter the Great Geological and Mineralogical Museum. He organized a series of expeditions, and the materials and data obtained from these supplemented the mineralogical collections. Fersman actively participated in the formation of a substantial systematic collection and thematic collections (mineral deposits, natural crystals, pseudomorphs, and meteorites). A.E. Fersman, V.I. Vernadsky, and V.I. Kryzhanovsky as members of the Urals expedition visited the Ilmen Mountains and then the Murzinka mines. This field trip introduced the young scientist to pegmatites. From 1912 to 1918 Fersman published over one hundred papers and essays «having amazed everybody by his vivid style, wide scope, and fruitfulness» (Perelman, 1968). Many people of various ages and proffesions read these publications. For many geologists and mineralogists these books were the first which gave direction to the professionals.

In 1915, the Commission on Studies of Natural Productive Forces of Russia

<sup>&</sup>lt;sup>1</sup> Alexey I. Antipov (1833–1909), a Russian geologist, mining engineer, and businessman

<sup>&</sup>lt;sup>2</sup> The first non-government university in Russia funded by donation from Alfonce L. Shanyavsky (1837–1905), a businessman in the gold industry

(CONAPF) was established at the Russian Academy of Science, and Fersman became its scholarly secretary. His activities were aimed at the collection and evaluation of data on potential economic mineral deposits. New laboratories studied chemistries of the required ore components and estimated technological possibilities for their economic extraction. Geological expeditions were sent to Crimea, Middle Asia, the Urals, Transbaikalia, Altai, and Mongolia, and the Museum specialists joined the field teams. As a result, by 1917 the mineralogical collection of the Museum exceeded 25,000 samples.

In a Supreme Counsel for People's Economics, a new institution organized after the October revolution, Fersman, along with other scientists, discussed the problems of planning in a new way: formulation and solving of large national-scale problems come to the front stage. These giant amounts of public and management activities ran in parallel with research studies of the senior scholarly custodian of the Mineralogical Museum.

In February of 1919 at the age of 35 Fersman was elected a member of the Academy of Science of the USSR (Department of Physics and Mathematics). In *Notes on the Scientific Merits of Prof. A.E. Fersman* compiled by Academicians V.I. Vernadsky and A.P. Karpinsky wrote: «A.E. Fersman is one of the most talented mineralogists, a remarkable connoisseur of minerals, an energetic researcher of minerals in all relevant aspects, which display his close aptitude for other branches of knowledge, their origin and their role in the field sometimes named now geochemistry» (Perelman, 1968).

Being appointed a director of the Museum in 1919, Academician A.E. Fersman opened a new stage in its history. Along with purely museum work, i.e. replenishment of mineralogical collections, studies of the stored materials, preparations for new thematic exhibitions, he made research based upon modern laboratory techniques and methods a key task of the Museum staff. During that hard period, he used the CONAPF framework to carry out regional studies of the national mineral resources: significant expeditions were organized to visit Kola Peninsula, Pamir, East Siberia, and the European part of Russia.

Beginning in 1921, Fersman Thursdays (readings in mineralogy) were conducted at

the Museum. Among the members who attended or presented papers were F.Yu. Levinson-Lessing, D.S. Belyankin, S.M. Kurbatov, and other outstanding scientists. The Fersman Thursdays played a significant role in the progress of Russian mineralogy and geochemistry. «It has been a kind of university for us, young geochemists, for no special courses existed then. That's why we, geochemists, praised highly A.E. Fersman's presentations: we got the knowledge on the situation in geochemistry in the country and abroad,» A.A. Saukov recalled (Saukov, 1965). The tradition of scientific meetings in the Fersman Thursdays style lasted in the Mineralogical Museum until 1975. After the Museum building was closed for repairs, these meetings continued to be held at IGEM (the Academy of Sciences of the USSR). To keep the standards of research at the cutting edge, promising young specialists were invited to work in the Museum, among them B.M. Kupletsky, V.I. Vlodavets, D.I. Shcherbakov, I.D. Borneman-Starynkevich, E.M. Bonshtedt-Kupletskaya, N.N. Gutkova, E.E. Kostyleva, A.N. Labuntsov, and others. Being aware of the significance of crystal chemistry and solid state physics in the development of mineralogy, along with growing importance of crystals in technology, A.E. Fersman organized research groups of such profiles in the Museum and invited leading specialists, among them A.V. Shubnikov, G.G. Lemmlein, and N.V. Belov (Barsanov, Kornetova, 1989).

Fersman worked in investigation of colored stones and gems and as a leader of scientific management. In 1919, within the CONAPF framework he first offered the course, *Color Stones and Gems of Russia*, and in 1920 his monograph on the subject was published. This publication astonishes with the breadth of the subjects addressed, from the description of the gem and colored stone deposits, their mineralogy and geochemistry to the history of stone processing and its role in the cultural progress of mankind.

In subsequent years the Museum collections were being actively supplemented. On A.E. Fersman's initiative, numerous items from the State Fund of the Palace Articles and duplicate specimens from the State Hermitage collection of gems and colored stones were transferred to the Museum, along with the acquisition of formerly private collections (V.A. Ioss, E.O. Roma-

novsky, M.F. Norpe, the Stroganovs and Balashovs, etc.).

The wide scientific scope of A.E. Fersman defined new directions for the research being done by the Museum staff. Due to growing collections replenished by numerous expeditions, new exhibitions, e.g., mineral-forming processes, mineral parageneses, colored stones and gems, and the development of the laboratory base, in 1925 the Museum was divided into the Peter the Great Geological Museum and the Mineralogical Museum of the Academy of Sciences of the USSR. Having marked the 200th jubilee of the Academy of Sciences of the USSR, the Museum was re-opened, and the series of scientific publications was resumed, Proceedings of the Mineralogical Museum of the Academy of Sciences of the USSR (Godovikov, 1989)

Fersman cared much about the raising of the young researchers and maintaining the theoretical level of their studies. In 1925, the General Session of the Academy approved the program for the training of young researchers in academic museums, including the Geological, Mineralogical, Zoological, and other museums. In 1929, the postgraduate courses were established there. The admittance regulations and selection were carried out by a special commission that comprised academicians A.E. Fersman, A.F. Ioffe, and others (Komkov et al., 1977)

During the 1920's and 1930's Fersman wrote his best known popular books and essays on mineralogy and geochemistry based upon a treasury of his field and research experience. His *Popular Mineralogy* and *Popular Geochemistry* brought him glory as a classic in the popular science.

The Khibiny epopee played a very special role in Fersman's life, in the development of the Earth sciences and the world-class specialists in the USSR; it gave birth to a new industrial and research center located beyond the Polar Circle (Perelman, 1968). From 1920 to 1926 Fersman was the leader of the annual expeditions sent to the Kola Peninsula. He persuaded his colleagues from the Museum to join him in these expeditions. In 1926 the Khibiny apatite deposits were discovered, and in 1930 Fersman's team brought from Monche-Tundra the first samples of the massive sulfide Cu-Ni ore. During the course of the interdisciplinary studies in Khibiny, the geochemical regulations in the localization of apatite ore as related to

alkali magma were established. The first results were published in a book edited by A.E. Fersman, *The Khibiny apatite* (1922).

Taking much care about the museum work (replenishment and systematic studies of the collections exposures and exhibitions demonstrating the latest achievements in mineralogy), Fersman guided the activities of the research staff to solve problems of national-scale. priority was given to inter-disciplinary studies of the national mineral resources using the latest research methods. Fersman was a real leader both in scientific and management aspects of the Museum activities; he understood the need for development of new scientific institutions in mineralogy and geochemistry (Barsanov, Kornetova, 1989). To do so, the Institute of Mineralogy and Geochemistry was organized by the Soviet Academy of Sciences (1930), and Fersman was appointed its' director, whereas V.I. Kryzhanovsky, his colleague who had shared the hardships of museum work for many years, became the head of the Museum. The Museum became a department of the institute. Fersman remained a formal leader and continued his academic activities. While director, he completed his studies of pegmatites. Fersman considered these rocks to be a product of the magmatic melt evolution. He introduced a classification of pegmatites based upon the genetic features of its mineral constituents, their structure and chemistry. The first volume of his monograph *Pegmatites* was published in 1931. One year later, the institute he organized was restructured into the Lomonosov Institute of Geochemistry, Mineralogy, and Crystallography (LIGEM), and Fersman remained its director until his death (Godovikov. 1989).

In 1934 the Museum as a branch of LIGEM was moved to Moscow and occupied the former manege <hall for training in riding> in Count Orlov's manor, the Neskuchny Palace. Restructuring and repairs inevitably occurred. At the time, the collection of the Museum contained about 80,000 items. In 1937 another re-organization occurred in the Academy of Sciences, and the Museum was again re-named, the A.P. Karpinsky Geological Museum. As before, the Museum remained a branch of the institute, the latter was renamed to the Institute of Geological Sciences of the Academy of Sciences of the USSR. In fact, the Museum was an individual research center, for it had individual themes in research and was located separately from the head institute.

By the beginning of the  $17^{th}$  International Geological Congress in Moscow (1937) new thematic exhibitions were being prepared in the Museum Mineral Deposits of the USSR and New Discoveries during the Soviet Period. It should be emphasized that the principles of exhibiting minerals in compliance with their geochemical classification and by minerals representing individual chemical elements were new in the world practice. These exhibitions showed a historical sequence of mineral-forming processes in the Earth's crust (Barsanov, Kornetova, 1989). An exhibition that demonstrated the mineral wealth of the USSR was organized by the staff of Museum and Institute of Geological Sciences in the Moscow Conservatory where the IGC sessions occurred. Valuable samples were sent especially for this purpose from many mines and deposits of the country. Later these samples were incorporated into the collections of the Museum. This enormous work was done under the leadership and with the active participation of Fersman who was elected a Secretary General of the 17th IGC.

During WWII, the most valuable part of the Museum collection was evacuated to the Urals. As required by the Presidium of the Academy of Sciences of the USSR, Fersman left Moscow for Sverdlovsk (now Ekaterinburg) to mobilize the mineral wealth of the Urals for the needs of the national defense; he did much as a geologist and coordinator visiting mines and prospects (Perelman, 1968).

In 1943 Fersman was 60, and the Soviet government decorated him with the Labor Red Banner Order to honor the 40<sup>th</sup> anniversary of his fruitful scientific work. The London Mineralogical Society awarded him with the Wollastone palladium medal as the most prominent mineralogist.

In 1944 the research institutions of the Academy of Sciences started to return to Moscow. The Museum collections were back in Moscow, and intense work on the restoration of the expositions and restoration of the collections began. In 1942 Fersman had been appointed a director of Institute of Geological Sciences. Since then he formally ceased to be a leader of the Museum, but he always remained in contact with its staff. Further perspectives of research were outlined under his leader-

ship, along with a schedule of new exhibitions. The restoration period was short but intense, and on July 1, 1944, the Museum was again open to the public.

In January, 1945, V.I. Vernadsky died at the age of 82, and it was a heavy blow for Fersman. A.E. Fersman began working on V.I. Vernadsky's scientific biography, but failed to complete this work due to his own weakening health (Perelman, 1968).

Alexander E. Fersman died in Sochi on May 20, 1945. He was buried in the Novodevichye cemetery in Moscow. Prof. V.I. Kryzhanovsky was appointed the director of the Mineralogical branch of the A.P. Karpinsky Geological Museum.

In 1948 the Mineralogical branch of the museum became an individual research institution of the Academy of Sciences, and in 1955 it was re-named after A.E. Fersman.

The foundation of the Mineralogical Museum and its development as a new-type research institution was inseparable and unthinkable without A.E. Fersman. He believed that mineralogical collections should not just stimulate the development of the natural sciences, that they should match the latest approaches in these sciences and their greatest achievements. From the viewpoint of a museum associate, the problems of new geochemical studies of the Earth's crust requires proper systematic allocation and new theories for the objects represented in such a museum (Fersman, 1925).

A.E. Fersman's own collections registered in the Museum comprise more than 3000 species from Russia and abroad. «His collections, which represent the whole scope of mineralogy, represent Fersman both as a tireless explorer, thorough thinker, anefficient scientist and an author of numerous research publications» (Kryzhanovsky, 1965).

A memorial which includes A.E. Fersman's stud was organized in the Mineralogical Museum; it shows his working study previously located in Sretensky Blvd., Moscow. The exposition demonstrates personal possessions of Fersman (his writing set, spectacles, a knapsack and geological hammer, etc.), his books and a series of his publications. The Museum serves as an archive of his manuscripts and photographs, which were donated by his widow, Ekaterina M. Fersman (1903—1980).

Currently, the major collection of the A.E. Fersman Mineralogical Museum in-

cludes about 130,000 items; it is one of the five largest mineralogical museums in the world.

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## A.E. FERSMAN'S CONTRIBUTION TO THE SYSTEMATIC COLLECTION OF THE MINERALOGICAL MUSEUM OF THE RUSSIAN ACADEMY OF SCIENCES

## Vyacheslav D.Dusmatov

 $Fersman\ Mineralogical\ Museum\ of\ the\ Russian\ Academy\ of\ Sciences,\ dusmatov@fmm.ru$ 

The geography of A.E.Fersman's mineralogical collections, including samples surrendered to the systematic collection of the Mineralogical Museum of the Russian Academy of Sciences is described.

4 references.

«... stone owned myself, my ideas, desires, even dreams...» A.E. Fersman

Alexander Evgen'evich Fersman, during all the half-century period of scientific activity, after each trip to any region of Russia and Europe, brought interesting mineralogical material and mainly surrendered it to the Mineralogical Museum of the Russian Academy of Sciences. Besides, he handed collections to the Shanyavsky University, Simferopol Museum, and Moscow University. He maintained an intensive exchange of minerals with various scientists and museums of other countries. The only work devoted to the analysis of his activity in this direction is the work by V.I. Kryzhanovsky (1965), who worked with Fersman in the Mineralogical Museum for a very long time.

The illuminative chronicle of his trips begins in the childhood. Since being six-year old, Fersman almost each year took part in travels with parents, during which he collected minerals in Crimea, on Caucasus, on Black Sea coast, in Turkey, Greece, Italy, France, Switzerland, Czechia, Germany, Austria.

Recollecting these years, Fersman wrote: «... I have taken a great interest in mineralogy in original conditions of Crimea mountains, within scientific interests of a scientific family; yet a seven-year boy, for the first time having received as a gift a fine mineralogical collection, I have taken a great interest in stone, and down to 1912 was engaged in collecting mineralogical collection, which I then surrendered to the Shanyavsky Public University, in which I was the first figure in mineralogy...» (Fersman, 1927).

The student of the Moscow University since 1905, he visited open pits of Podolsk, stone quarry of Dorogomilovo, outcrops of Khoroshevo and Myachkovo. In the Podolsk open pit he has found palygorskite.

Fersman began the earliest independent scientific collections of minerals on the Elba Island in 1908. He wrote about this period: «for

the first time I have taken a great interest in gems when the destiny has brought me to the far Elba Island. Here, among caressing nature of the Mediterranean Sea, a wondrous pink tourmaline was so perfectly in harmony with gray granite rock, and the sparkling red hematite blinded eyes with the shine» (Fersman, 1974). From the Elba Island, Fersman has brought the biggest collection of samples, mainly from pegmatites. He studied and described these samples during five years and in 1913 has handed them to the Mineralogical Museum (Collection 1069 = 166 samples).

Being abroad in 1909, he studied diamond crystallography together with M. Goldschmidt. During studying, he bought diamonds in various shops, as it was impossible to visit the deposits. At that time he has got diamonds and carbonado from Brazil, black diamonds from German possession in Africa — Jagersfontein and common diamonds from Luderitz Bay (Coll. 562 = 18 samples).

During his trip to the Taurian province (Crimea, 1909), combining recreation in a manor of his relative E.A.Kessler with collecting minerals in vicinities of Simferopol, Fersman has visited stone quarries in Kurtsy and Cheshmedusi, where he has collected analcite, heulandite, prenite, leonhardite, wolchite, in which studying he was engaged earlier (Coll. 561 = 13 samples).

In May 1911, Fersman carried out excursions with students to Moscow area — Podolsk, Tsementny Zavod, Ratovka-Nikitskoye (Verepectu Mountain) where has collected *ratoffkite¹* (earthy fluorite), quartz, *ferriallophane*, *shanyavskite*, beraunit, calcite and, certainly, beloved palygorskite (Coll. 733 = 11 samples).

At the end of 1911 and in the beginning of 1912, he has finished one of stages in the study of magnesium silicates collected by him in the Nizhniy Novgorod province. These are mainly palygorskite and *spherosiderite* (botryoidal siderite) from the Buklovsky mine at Vyksy,

<sup>&</sup>lt;sup>1</sup> Italic designates the names given by A.E.Fersman, but currently not having the status of a mineral species. The accepted names of minerals are in brackets.

near the city of Gorbatov. He has also surrendered to the Museum sepioliths, *tsilerites* (rock cork), *tsermatites* (matted-fibrous chrysotile) from Switzerland, collected by him and sent by V.I. Vernadsky (Coll. 825 = 25 samples).

At the same time Fersman has finished studying of bought abroad diamonds and surrendered them to the Museum. These were diamonds from Kimberley and Jagersfontein, South Africa, and also diamonds from Brazil and from Bingara, Austria (Coll. 816 = 19 samples)

In the spring of 1912, Vernadsky, Fersman and engineer-geologist A.G. Kitaev have visited the Blyumov mine (Southern Urals), from which they have extracted 10 poods of samarskite for M. Curie, who worked at that time in Paris. Local miner Andrey Lobachev greatly helped them showing the richest zones.

Later, the Imperial Academy has sent Fersman, as a member of Radium Expedition headed by Academician V.I.Vernadsky, to the Urals since May 25 till August 25, 1912 for studying radioactive minerals within the limits of Perm, Ufa, and Orenburg provinces. During this time, they have visited Troitsky Stone, stone quarries on the Tura River, Verkhoturie and vicinities of the female monastery. From this trip Fersman has surrendered to the Museum orthite, biotite, microcline, chalcopyrite (Coll. 832 = 5 samples, Coll. 835 = 17 samples).

In the autumn of 1912, Vernadsky, Fersman, and Kitaev have visited Kochkar gold mines and Semenovsky mine. They have examined monazites and in mines along the Kamenka and Sanarka rivers have collected blue euclases, amethysts, aquamarines, pink topazes, rock crystal. At the Proroko-Il'insky mine, they have collected and partially bought pink topazes, in the region of Sokolinye Sopki — beryl.

In the same year, together with V.I.Kryzhanovsky, he has visited Murzinka: Buzheninov Log, Mokrusha, Yuzhakov mine, villages of Shaitanka, Kaltashi, and Komarovo. As a result of this trip, they have brought beryls, tourmaline and other minerals of pegmatites (Coll. 844 = 10 samples, Coll. 846 = 12 samples, Coll. 868 = 15 samples).

In the beginning of 1913, Fersman and A. Sergeev have collected *ratoffkite* and calcite near villages Korotnevo and Nyushchino in the Tver province (Coll.1032 = 12 samples), and since June 25 till July 25, 1913, Fersman and B.A.Lindener have made a trip to the Urals and visited Verkhoturie, Vysokaya Mountain, Lebyazhinsky mine, Kipovka, Adui, Alapayevsk and other regions. Fersman managed to visit the village of Reshety and has collected stilbite in an intergrowth with feldspars from

gabbroids and near the village Palkino - primary and secondary laumontites and leonhardites (Coll. 868 = 15 samples).

In addition to own collecting, Fersman has bought calcite brushes, *green vitriol* (melanterite). He and B.A.Lindener, in the region of Podenny mine, have collected chromites, uvarovites, chalcedonies, *orthites* (allanites), serpentines, have visited a maximum number of mines with pegmatites and have collected a lot of samples to replenish the collection of Urals minerals already available at the Museum (Coll.1043 = 102 samples)

In 1913, Fersman has presented a collection of minerals and a collapsible human skull from his personal collection to the Shanyavsky Public University. For this, of April 2, 1913, the Board of Guardians and Board of University have expressed him the acknowledgment.

During visiting Crimea in 1914, he, during vacations, has collected from the Kurtsy stone quarry, near the summer residence of Golovninsky (Kastel), palygorskite and calcite, and from the region of Eski Orda - anthraconite (calcite polluted with bitumen) and apherosiderite (Coll. 1104 = 12 samples). Then, during June and July, he has visited Urals within the Orenburg province: Tsarevo-Alexandrovsky mine, Iletskaya Zashchita, village of Klyuchi, where has collected and bought minerals. Here we shall note that prices for minerals, according to records in Fersman's diary, was as follows: tourmaline from Savvateyev -1 Rbl; brookite, topaz from Kochkar -4 Rbl, rhodusite (crossite), chalcedony, tourmaline (Shabry), clinochlore and rutile -21 Rbl, beryl and volosatik (quartz) (Sherlovaya Gora) — 18 Rbl (for comparison – the ticket to Miass costed 26 Rbl 40 copecks) (Coll. 1169 = 25 samples). Then, on July 3 - July 16, he, accompanied by M.E.Vladimirova, visited Tel'kossky and Garevoznesensky mines, where have collected pyrite, limonite and kaolin (Coll. 1170 = 5 samples). After that, he has left for Sweden, where has visited mainly pegmatites at Falun, Finbo, Skarpo, Uto, Langban, Stromsberg, Ytterby, etc. Here he has collected very extensive collection of minerals, first of all gadolonite, fergusonite, petalite, langbanite, yttrotantalite and other minerals of pegmatites (Coll. 1165 = 45 samples).

At last, his dream has come true — he has visited the Transbaikalian region in 1915. During this trip, Fersman has visited along the line Nerchinsk, village of Savvateyeva on the Urguchan River, village Gutai on the Chikoi River, village Utochkino on the Selenga River, many villages on the Khilka River, the Malkhan

Range, and Ust'-Kyakhta. All collection can be divided into two groups: minerals of pegmatites (Coll. 1343 = 66 samples) and minerals of zeolite group (Coll. 1344 = 85 samples).

So as Russia needed titanium, Fersman has organized prospecting of titanium ore on the Urals and for the Museum he has visited mines of Adui and Karas'e Lake, where has collected euxenite, orthite, beryl, and spessartine (Coll.1341 = 10 samples). In the summer, he has arranged time for rest and has gone to visit relatives in the town of Borovichi, where was situated the manor of his wife (village of Proshkovo). He has combined the rest with collection of minerals in this area. He has found sphalerite, galena, pyrite in coals on rivers Msta and Krupa, near the villages of Bolshoi Porog and Bobrovik (Coll. 1345 = 25 samples, Coll. 1388 = 5 samples). In 1916, Fersman and Vernadsky have gone on excursion to Altai, they have visited various mines: Ridder, Zmeinogorsk, Bolshoi Raznos, Cherepanovsky, and Zavodinsky, respectively, the collection basically included sulfides and oxides. (Coll. 1399 = 25 samples). After returning, A.E.Fersman, V.I.Kryzhanovsky and L.A.Kulik have collected ratoffkite, palygorskite and quartzes in the Tver province at villages Korotnevo and Fomino Gorodishche (Coll. 1494 = 22 samples) and samples from Rezh factory (Coll. 1398 = 19 samples). Later this year Fersman has visited Crimea; close to Feodosiya (Opuk Mountain) and Karadag (Kara-Agach Mountain) he has collected sulfur, calcite, celadonite (Coll. 1398

Because of intensive work, the Fersman's health deteriorated and in 1917 he went to Crimea to join his family staying there. However, in process of recovery, he was charged to inspect the chemical plant of I.P.Balashov in Saki to get acquainted with bromine and bromine-benzil production. In addition, with Professor P.A.Kashinsky, he has visited the Saki Lake, where has collected gypsum and halite. After that, in vicinities of Feodosiya, on the Lysaya Mountain, he has collected strontianite, quartz and calcite (Coll. 1518 = 10 samples).

Since 1918 till 1920, he made no trips and was only engaged in organizational affairs. Unique minerals which he has surrendered to the Museum were sulfides from the Urals and bought earlier five topaz crystals from Mongolia and pink fluorite (Coll. 1519 = 5 samples and Coll. 1547 = 5 samples).

In the beginning of 1920, the governmental Commission was formed to resolve the further destiny of the Murmansk railway under the presidency of A.P. Karpinsky, A.E. Fersman and J.M. Shokal'sky, and in May that year they have gone to Murmansk; geologist A.P. Gerasimov has joined them. At Imandra Station, during the compelled stop, they have made a reconnaissance itinerary, examined rocks and minerals, among which they have discovered apatite. At Kandalaksha, they have collected pegmatite minerals (Coll. 1576 = 5 samples).

Closer to summer, A.E. Fersman and E.M. Bonschtedt have visited the Tver province and along Vazuza and Derzha rivers, near villages Lesnichina and Vysokina, have collected *ratoffkite*, flint and quartz (Coll. 1577 = 10 samples). From earlier collection from villages Lipovka and Bayevka (the Urals), Fersman has surrendered aquamarine, fluorite with zinnwaldite and phacolite (chabasite) from the Selenga River basin (Coll. 1578 and Coll.1583 = 3 samples).

In the autumn of that year, an expedition to Khibiny was organized, which began grandiose study of this area. It is necessary to note the fact, that all collections were only surrendered to the Museum in the name of Khibiny Expedition, irrespective of who has collected the material. This rule was observed for many years (till 1930), therefore, not so many samples from Khibiny are attributed to personally Fersman, though he has collected very large material. After 1930, Fersman has surrendered titanomagnetite, fluorite, sphene, nepheline from Khibily (Coll. 2383, 2455, 2519 = 11 samples)

In May 1921, the Commission on Study of Natural Productive Forces of Russia under V.A.Vernadsky's initiative, sent Fersman for one month to the Urals for studying pegmatite veins and collection of samples in the region of Rezh factory and Emerald Mines. E.E.Kostyleva accompanied him in this trip and this time they have visited Lipovka (have collected vorobyevite, topazes, quartz), Lyublinsky mine, Sarapulka, Troitsky mine, etc. They have casually visited asbestos mines and collected a lot of minerals — part of them was left for studying and the other part has got to the Museum (Coll.1599 = 34 samples).

1925 for Fersman was the most abundant in expeditions. January — inspection of some mines on the Urals: Emerald Mines, Kyshtym, Bazhenovo, Shadrinsk, Bogdanovichi. During this fortnight mission, Fersman has found time and has collected some minerals — emeralds, beryl, corundum and others (Coll.1699 = 10 samples, Coll.2004, 2048, 2250 = 3 samples).

Two summer months he spent in a mission abroad — in Germany and Scandinavian countries. The primary goal was to familiarize with the organization of scientific work in institutes. During this short time, Fersman has visited

Norwegian pegmatites and gletschers, pegmatites of Sweden and has organized, speaking in Fersman's words, «a big supply» of samples (Coll. 2018 = 168 samples), twice as much as he has brought from the Elba Island. All samples can be divided into two groups: granite pegmatites mainly from the region of Langesundfiord and Krageroe and alkaline pegmatites of Norway. Collection of alkaline rock minerals has allowed discovering many minerals later in Khibiny. In 1928, he has added orangite (thorite), cryolite, xenotime, zircon, fizelyite (Coll.2275 = 10 samples) to the earlier surrendered Norway material.

After that, Fersman has visited radioactive occurrences in Karelia, Kyshtym group of deposits on the Urals and in the autumn, from Leningrad through Tashkent, has left for Fergana, where, together with D.I. Shcherbakov, has visited radium deposit Tyuya Muyun, sulfur deposit Shor Su, celestine deposit Lyakkan and chert outcrops at the village of Tul'. Naturally, the basic collection of minerals was specific — *uzbekite* (volborthite), celestite, barite, sulfur (Coll. 2065 = 18 samples).

In the same year the Museum received minerals, which he collected earlier — three emeralds from Habachtal (Austria), seven topaz crystals from Gorikho (Mongolia) (Coll. 2058 = 10 samples) and zeolites from Transbaikalia (Coll. 1344 = 24 samples)

In the period 1925-1929, Fersman has surrendered minerals from Sarapulka, Monetnaya Dacha, Kyshtsm and other regions of the Urals (Coll. 2044, 2053, 2113, 2198, 2250, 2256, 2324, 3164 = total of 25 samples)

In 1926, passing by the Military Georgian Road, he has collected antimonite and molybdenite near the Kazbek Station, and after visiting Murzinka in the Urals he has brought amethysts, corundums, and garnets (Coll. 2104 = 21 samples).

Multiple visits to Turkmenia (1928-1935) have replenished the Museum's collection with samples of sulfur, gypsum, witherite and some sulfides (Coll. 2252 = 12 samples, Coll. 2364 = 16 samples, Coll. 2600 = 2 samples, Coll. 2653 = 1 sample, Coll. 3056 = 3 samples). Fersman has visited Naboshar, Adrasman and Lyakkan in Tadjikistan and Kuperlisai and Maili-Su in Kirghizia and has collected torbernite, thorite, and carnotite (Coll. 2361 = 4 samples, Coll. 3056 = 8 samples, Coll. 3065 = 5 samples).

Fersman has visited Silesia in 1927, mainly the Striegau deposit (nowadays Strzegom, Poland), whence he has taken *strigovite* (chamoisite variety), smoky quartz, sulfides, etc. (Coll.2367 = 30 samples).

He has brought xonotlite and talc (Coll. 2387 = 2 samples) from Lopansky region of South Ossetia in 1931 and has also collected garnet (Coll. 2415 = 3 samples) on the Dzirul Range (Transcaucasia).

In the same year, Fersman has surrendered to the Museum some samples from Czechoslovakia — Jachymov, Linnwald — and Germany — Harz and Saxony (Coll. 2525 = 14 samples).

Fersman was in Czechoslovakia three times (1934, 1936, and 1939), mainly on treatment, but despite of illness, he repeatedly went to brief excursions on vicinities of Karlovy Vary and has visited Pribram, North Bohemia, Moravia, Remnitsa, etc. On the Jahimov deposit, he has collected radioactive minerals: uraninite, zippeite, *uranothallite* (liebigite), and cuprosklodowskite, from other places he has collected sulfides, carbonates, zeolites, and tourmaline (Coll. 2744 = 42 samples, Coll. 2746 = 35 samples, Coll. 2822 = 21 samples).

For the period 1929-1934, minerals from Transbaikalia, mainly from the Belukha deposit — wolframite, *lavrovite* (vanadium-bearing diopside), garnet, and pyrite (Coll. 2031, 2329, 2440, 2528 = only 29 samples) came from Fersman to the museum.

A.E. Fersman and V.I. Kryzhanovsky, making part of a small group, have made in 1935 a automobile route over the Urals (Fersman, 1936). Except for acquaintance to industrial facilities, a small number of minerals were collected, from which Fersman has surrendered 20 samples to the Museum (Coll. 2542, 2600, and 2646).

During treatment in Kislovodsk (1938), he has found celestite 4 km south of the Castle «Wiliness and Love» and was so enthusiastic in collecting minerals, that has brought 40 samples of only celestite, but he also collected associated sphalerite, pyrite, and chalcedony (Coll. 2807 = 74 samples).

In Kiev, in May 1939, a conference on Ukrainian pegmatites was held. Fersman with a group of colleagues — E.E. Kostyleva, K.A. Vlasov, V.I. Gerasimovsky and V.V. Shcherbina — took active part both in the meeting and in excursion to pegmatites of Volhynia — Volodarsk-Pisarevka near Zhitomir (Korosten' pluton) and pegmatites on the Teterev River near the village of Shumsk. After Kiev, he has visited Monchetundra (Kola Peninsula) and has collected pentlandite and pyrrhotite (Coll. 2907 = 8 samples).

In 1940, after an automobile trip to the Tyrnyauz deposit and Malka River on Caucasus and Adrasman, Maliysai and Uigursai deposits in Central Asia, Fersman has brought tuyamunite and sulfides (Coll. 3065 = 17 samples).

From a big expedition on inspection of Pechora-Ukhta deposits in 1940 (Coll. 2994), he has brought some minerals — amethyst, analcite, calcite and others.

These were the last receipts of minerals from Fersman. In 1941—1945, because of war and poor health, he was engaged basically in generalization of materials on mineral resources of the country being of strategic importance for needs of defense.

Currently the Systematic Collection of the Mineralogical Museum of the Russian Academy of Sciences has 102 thematic collections including 304 mineral kinds and their varieties (1658 samples), which came from Fersman.

Total number of samples surrendered personally by Fersman to collections of the Museum counts over 3000 samples.

In closing, the author expresses his most sincere gratitude to M.E. Generalov and E.A. Borisova for the help in preparing and writing this work.

#### Geography of Fersman's Mineralogical Collections

(names of geographical regions are given by Fersman's records, in brackets — numbers of a thematic collection registered in the Systematic collection of the Museum, bold figures — number of samples)

AFRICA [562, 816, 2525-7]

ALTAI, Tomsk province [1399-25]

AMERICA [562-18, 816-2]

AREA of the DON ARMY [2146-2] ARKHANGELSK province [1576-5]

AUSTRIA [816-**19**, 2058-**4**] BURYATIA-MONGOLIA [2058-**4**] CAUCASUS [2104-**17**, 2387-**2**, 2415-**3**, 3065-**14**]

CHELYABINSK oblast [2600-1, 3164-1] CRIMEA [561-13, 825-15, 1104-12, 1398-38, 1519-5]

CZECHOSLOVAKIA [825-2, 2525-21, 2744-43, 2746-36, 2822-23]

DENMARK [2275-10] ELBA [1069-166] SW part of Luderitz Bay (samples were bought in Europe)

Mines: Ridder, Zmeinigorsk, Nikolaev, Cherepanovsky and Bolshoi Raznos

Brazil, Uruguay (samples were bought in Europe)

Dolomitic Quarry, Yama

Kemsky district, Kandalaksha, Murmansk, Alexandrovka

Bingara, Habachtal

Selenga River

Kabardino-Balkariya, Tyrnyauz, Malka River, Kazbek Station, South Ossetia, Lopansky district, Chargany village, Dzhirul Range, Vishneviye Mountains, Shabrovskoe deposit Kurtsy, Cheshmedusi, Katel, Eski Orda, Feodosiya, Opuk, Lysaya Mountain, Karadag, Karagach, Saki Lake, Bulganak, Koktebel North Bohemia, Rothan near Falkenan, Slavkov, Podolya Prahy, Karlovy Vary, Muhebrum, Vridlo, Repcice Litomerik, Zalesly, Marianska hora, Seeberg, Haguenstein, Cerhovicka, Pribram, Jachymov, Oelsnitz hinnwald, Cerrniky, Beloves, Nachoda, Turnov, Krandorf, Kastalora, Zelechavsre udol, Kladio Kremnica, Chomutov Liliana, Liboris u Chomutova, Lebeik, Kozakov, Caslan, Riden, Cyrilov, Denica, Elbogen

Ivigtut

St. Mario, Grotta Doeci, Cava della Speranza, Rio Marina, Penta della Cannelle, Terranera Capo Bianco, Punta in Sansoni Calanita, S.Piero in Campa, Biodola golfo, Pontoferraio, Monte Bello, Lamaia golfo Biodala, val Valdana, Procchio, Porto feraio, Jamaio, Punto de Calamite, Capo Bianco, Ferranera, val Agwa viva, Marina in Campo, Spiaggio di Margidor, Scoglictto focta stella, Spiaggia del Liolo, Capo Calamita, Terre del Rio, Capo Norsi, San Jllario, Forte Falcole, Loll di, Palombia

EKATERINBURG province [1599-**39**, 2004, 2044-**3**, 2113-**8**, 2198-**5**, 2250-**2**, 2256-**3**]

FINLAND [2600-4] FRANCE [733-1] GERMANY [2525-7] HUNGARY [733-1] ITALY [558-6] KHIBINY [2383-2, 2415-3, 2455-2, 2519-4, 2907-8, 3036-2] KIRGHIZIA [2065-15, 2361-4, 3056-11]

KISLOVODSK [2807-59] KOLA PENINSULA [3036-2] KOMI [2994-4] MONGOLIA [1547-1, 1583-1] MOSCOW OBLAST [733-12, 793-3, 1699-4] NIZHNI NOVGOROD [825-6]

NORWAY [2018-156, 2048-13, 2275-5]

NOVGOROD [1345-25, 1388-5]

ORENBURG province [1043-**50**, 1169-**28**, 1519-**2**, 2053-**1**]

PERM province [832-5, 835-12, 844-10, 846-166, 868-15, 1043-54, 1170-5, 1341-10, 1578-2, 1699-2]

SEMIPALATINSK Oblast [5]

SIBERIA [1398-**12**] SILESIA SWEDEN [1165-**45**] Emerald Mines, Monetnaya Dacha, Adui, Sarapulka, Bayevka, Troitsky mine, Nizhneiset' Dacha, Lipovka, Voznesensk mines, Corundum mine, Rez factory, Lyublinsky mine, Nauruzova village, Asbestos mines, mines of Poklevsk, Kamyshinsk, Bazhenovo

Sordavala Pmrinili Sahsen, Harz Vacko

Tuscany, Campiglia, Marittime Kukisvumchorr, Rasvumchorr, an item. Olenjya, YUkspor, Gakman, Vudjyavrchorr Maili-Su, Kuperlisai, Kadamjai, Tyuya-Muyun, Shor-Su Castle «Wiliness and Love»

Kovdor, Monchetundra Ukhta district, Yarek deposit YArekskoe Urga, Gotikho River, External Mongolia Ratovka, Podolsk, Shamardino

Veliky Vrag, Ardatov, Vyksa, Gorbatov, Buklovsky mine

Gierrestad Fogue, Tvedestrand, Jarvik, Jangen-Kragere, Laven, Lagesund fiord, Fredrikkvarn, Baule, Srudesundes Kjar, Kjeo, Stoko, Ovre ako, Arendal, Eker, Piratholmen, Srudesundskjan, Eikaholmen, Bergen, Halvossrod, Raade, Oelegaardens, Kristiasand, Erje aarvold ost, Bergen ulro Reumassiv, Tonsen plads, Linderm jstle, Giallebaek, Felemarken, Odegaardens

Borovichi, Msta River, Krupa River, Vittsy riffle, Coal Mine, Svyatoslav Mine, Veliky Porog village, Bobrovik

Troirsky mine, Kosaya Mountain, Tsarevo-Alexandrovsky mine, Iletsk Zashchita, Klyuchi village, Plissovaja Mountain

Kyshtym, Kasli, Verkhoturie, Troitsky Stone, Adui River, Garevoznesensky, Tel'kosky, Solikamsk, village Komarovo, village Kaltash, Murzinka, Mokrusha, Shaitanka village, Bayevka, Alabashka, Reshety village, Palkino village, Khrustalnaya Station, Alapayevsk, Krivki village, Vatikha, (Murmanka village), Evropeiskaya Station, Susana, Sizikovo, Repevnya, Neivo-Shaitanka factory, Lebyazhensky mine, Lipovka, Byzovaya village. Saranka, Bisert factory, Rezh factory, Kamentka village, Tochil'naya Mountain, Alunite mine

Pavlodar, left bank of the Irtysh River, Ekibastuz, Kalkan Lake

Kuznetsk Ala Tau, Tel'bes

Striegau

Falun Korarfet, Uto, Jaugbau Nerike Janna, Stromsborg or Ebro, West manland Sala, Fahlum Frinnbo, Srarpo, Ytterby, Alno Poltang, Alno Smedegarden, Hollandi, Smedsgarlen, Alno Langorsholmen, Fahlung Ammeberg SWITZERLAND [793-3, 825-5] TADJIKISTAN [3056-11, 3065-14] TVER province [1032-13, 1494-22, 1577-10]

TURKMENIA [2252-12, 2364-17, 2600-7, 2653-1, 3056-11] TRANSBAIKALIAN REGION [1343-61, 1344-82, 1699-6, 2031-1, 2324-3, 2329-26]

UFA province [2152-3] UKRAINE [2907-8] URALS [2542-5, 2646-8]

UZBEKISTAN [2065-3, 3056-10, 3065-17]

#### Willis Zermatt

Taboshar, Adrasman, Lyakkan

Zubtsovsky district, villages Korotnevo and Fomino Gorodishche, Vazuza River, village Lesnichina, Derzha River, Rzhev, villages Vysokina and Tyushchino

Cheleken Island, Gaurdak, Sary-Bugor, Darvaz, Kara-Bogaz, Chemmerli Hill, Arpaklen Khilka River (Kupalei village), Chikoi River (Beregovaya village), Slyudyanka, Ust'-Kyakhta, village of Malyshevo, Myl'nikovo and Novonikolskoye, Yamarovka spring, villages of Utochkino, Korotkovo, Savvateyeva, Urguchan River, Ivkova village, Selenga River, Small Soktui. Belukha Mountain, Gutai, Bakhal Range, Bukuka, Onon-Borzya, Kara-Nor, Zavitaya River, Mandryk Rock, Malkhan Range the Chuvash steppe, Zlatoustovskoe deposit Volodarsk — Pisarevka

Adui, Nizhneisetskaya Dacha, Karas'e Lake, Alabashka, Gumbeika, Khalilovskoe, Magnitka, Kochkarskoe deposit Uigursai, Katta-Dali, Kara-Chagyr

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## PHOTOGRAPHING MINERALS

#### Boris Z. Kantor

For art or technical photographing minerals in non-professional conditions, high quality of medium magnifications can be ensured by means of miniature single lens reflex (SLR) cameras of general use and ordinary photographic materials. To apply long-focus macro lenses and avoid diaphragm excessive closing is recommended. To reproduce morphological features of a mineral, flexible and multi-functional artificial lighting is necessary. For negatives, daylight film in combination with light-conversion filter is recommended. Adequate reproducing of mineral complicated color involves accurate matching of color temperatures and selection of light sources, preferably halogen low-power cold-light lamps, corresponding the given combination of photographic material and color-conversion filter. 7 color photos, 2 references.

Photography expands appreciably our notion of the mineral kingdom. In skillful hands, even a plain shatter may be lifted, in its information and esthetic value, from the waste bin up to the level of museum specimen. An experienced photographer would never disregard those fragments, miniatures, and unpretentious petty crystals that are usually ignored by museums and collectors. At the same time, a large specimen attracting general admiration and exposed in its own separate showcase would hardly look equally spectacular on its small or medium size photo. Photography also gives full scope for any kind of interesting art-experiments with minerals.

Provided a well tooled-up professional studio is available, the technique of photographing minerals differs little from the ordinary close-up photography (Scovil, 1996). However, mineralogist and photographer professions combine only seldom in the same person. More often, a mineralogist - specialist or hobbyist - has no access to the expensive special cameras as well as studio lamps and other professional equipment. To illustrate a book or a paper or simply to picture minerals occasionally for his own pleasure, he is obliged to accommodate to the homely schedule of the so-called pop photography: picturing with a general use camera with succeeding processing and printing in a minilab.

Setting aside purely pictorial problems, whose solving depends entirely on the photographer's taste, competence, and mineralogical interests, let us define technical preconditions of mineral successful photography under these «amateur» conditions.

A mineral photo should be sufficiently sharp. Viewing, from the usual reading distance (25-30 cm), a picture up to 15 or 20 cm in size, a person with normal eyesight discerns not more than 8 or 10 lines per mm (400-500 dpi). Accordingly demanded resolution of a miniature  $(24 \times 36 \text{ mm})$  negative is 50-60 lines per mm (2500-3000 dpi) maximum. This is fairly achievable with the present-time photographic lenses and medium speed films (ISO 100-200). Technically perfect pictures can be made, so, with an ordinary miniature SLR camera, including any one of the amateur class, and ordinary photographic materials of general

A medium format camera even enables creating a «reserve» of resolution for an occasion of manufacturing larger magnification. However, popular roll-film cameras (e.g., Pentacon-Six or Exacta-66) have comparably massive mirrors which entails harmful vibrations during the process of exposure. As a result, the resolution is appreciably diminished and so the medium format advantage reduces to nothing. A good tripod diminishes vibration but cannot eliminate it entirely. It is less noticeable on condition of short enough (not more than 1/100-1/180 s) or long enough (not

less than 2-3 s) shutter speed, which is, however, not always accessible. Another way is to expose by switching the light on for the metered time after the shutter has been previously opened in darkness. The latter may entail, however, a shift of color in the red side because of the light source thermal lag.

So the balance of advantage should be lain with miniature cameras. On condition of using a tripod, the vibration in this case is inconspicuous. In addition, some miniature cameras are provided with the option of shutter release delay after the mirror has been lifted, which gives additional assurance

At the same time, the larger format is preferable for slides, as they need, in this case, no magnification to be viewed.

Minerals are mostly photographed in close-up regime, i.e. with magnifications up to 1:1, sometimes greater. As the camera standard lens cannot be focused from the demanded short distances, one lengthens it with an extension tube or bellows or provides with a close-up lens. However, both mentioned entail deterioration in the image quality, since the camera standard lens is corrected for «infinite» distance and does not, in the mentioned case, answer its purpose. Essentially better images can be produced with a macro lens as its optical system is specially corrected for close-up distances. In particular, not too expensive lenses of the Sigma EX macro series are noteworthy; they are put out for all the basic SLR cameras of modern generation (Canon, Nikon, Minolta, and Pentax) and produce high quality images.

For mineral photography, a macro lens with focal length about 100 mm is the best. It facilitates well the illusion of third dimension and perspective, is accommodative in operation, and, compared with short-focus lens, less liable to light diffraction in the diaphragm hole.

Despite of the common opinion, the use of a long-focus lens does not entail diminishing of the depth of field. According to calculations, the depth of field at close-up photography is proportionate to

$$f(M+1)/M^2$$
,

where f is diaphragm number and M is image magnification. Therefore the depth of field does not depend on the focal length.

The possibility of the lens aperture to be closed down at least to f=32 is advisable. However, closing down should not be overused. Sometimes, it contradicts the pictorial task; in addition, it affects adversely image quality. According to our data, the resolution of  $Canon\ EF$  as well as  $Sigma\ EX$  macro lenses is maximal at f=8 and drops by 20-25 per cent at f=22, and even by 40 per cent for the  $Sigma\ EX\ 2,8/50\ macro$  lens.

To choose the type of light sources is a primary task. In photographic sense, minerals are fairly complicated objects. This implies the use of not less than three or four autonomous light sources supplemented with reflecting cards of white paper and aluminium foil. The gleams of faces and the whole light pattern are very much sensitive to the illuminator positions. This implies a literally precision setup of light. It can be achieved on condition the illuminators are enough mobile.

By this reason, the «non-controlled» sunlight only finds a limited use, and so electronic flash without pilot light. The tungsten low-powered lamps are mostly used, as they do not provoke photographer's weariness of too intensive light and heat radiation that is also ruinous for some minerals like native sulfur or realgar. Mounted on miniature stands, the lamps may be easily moved along the surface of the table, an improvised shooting stage. A miniature remote-control station with individual toggle switches for illuminators would enable photographer to set up lighting not drawing away from the camera viewfinder.

Adequate reproducing of mineral complicated and whimsical colors is a most urgent problem.

In the process of minilab printing, color rendition errors of a negative can be corrected to a small degree only; besides, this is only possible after the draft copies have been made and studied. As to color slides, they cannot be corrected at all. To correct color completely is not always possible even by means of editing files obtained by scanning original photographs. So it is very important to avoid errors when taking pictures or, at least, to minimize them. The pledge of success is the proper choice of film, light filter, and light source types with matched color parameters:

$$10^5/T_1 - M_{\rm lf} = 10^5/T_{\rm f}$$

where  $T_{\rm l}$ ,  $T_{\rm f}$  — color temperatures, Kelvin (K), of light sources and film,  $M_{\rm lf}$  — filter conversion degree, decamired.

The film choice is only confined to two types balanced either for day (sun) light or tungsten light with color temperatures, accordingly, 5500 K and 3400 K. The choice of light-conversion filters is also limited. Purplish-blue filters are usually used with conversion degree either 12 or 15 decamired (marked as B12, B15 or Wratten 80B, Wratten 80A). On the other hand, the market assortment of lamps is fairly rich, and, furthermore, they are much cheaper than light-conversion filters. So it is reasonable to select lamp type matching one or two film — filter type fixed combinations.

Slides are usually taken on a reversible film for the light of incandescent lamps (tungsten light). As to negative films for tungsten light, they belong to the category of relatively expensive materials of narrow assortment and are intended mainly for portrait studio photography. At the same time, color correct rendition can be also achieved with daylight film on condition that the lamps are selected correctly and the light is conversed with the proper filter.

Unfortunately, lamp manufacturers do not indicate, as a rule, their color temperatures. According to our data, they are diverse within fairly wide bounds. The light temperatures of the majority of miniature halogen lamps are at the level of 2700 -2800 K, like domestic low-powered lamps. More promising are the halogen lamps of «cold light». In particular, «Radium» Company (Germany) produces miniature halogen lamps for 12 V and 50 W that can be matched satisfactorily with daylight film and 12B or 15B conversion filter. So do, as well, home-produced mirror photolamps of the ZK 220-250 type for 220 V and 250 W. To diminish fatiguing radiation, the latter's voltage can be reduced for the period of light setup (which is inadmissible for halogen lamps).

For the lack of a special light-colorimeter, color temperature of a light source may be estimated even in domestic conditions (Kantor, 1999). Of course, obtained data should be verified by means of control picturing of chromatic scale and colored and color-free objects (malachite, crocoite, quartz, etc.).

The background — a sheet of paper, cardboard, cloth — should be even, of subdued color, congruous with that of the speci-

men, with no pattern, spot, and texture. A neutral gray background is universal. A highlight spot on the background behind the photographed object would «lift» it and intensify volume illusion. A photo-printer file printout of gradual passage from white to dark gray color, with the dark side up, is a successful solution. The background should be placed at a sufficient distance to avoid shadow falling from the specimen.

All the modern miniature SLR cameras are provided with automatic exposure metering. Having chosen the aperture priority function and set up the proper diaphragm number, one lets the camera to set up the proper shutter speed. On the condition of light-shadow contrast being sufficiently evened, the option of integral (polysegment) metering should be selected.

When viewing a specimen, one turns it absent-mindedly with various sides to himself, lingering at some details of especial interest, and thereby a cumulative three-dimensional visual image is being formed in one's consciousness. The photographer's task is to imitate this image on the picture plane emphasizing, at the same time, either detail important for the given object, e.g., etching form, twinning seam, or face striation. For all this, only two pictorial means are actually available: specimen orientation and lighting setup. It is useful to study the specimen previously under the desk lamp in order to outline pictorial solution and select the object pole position and directions of main and accessory lighting. In the process of this procedure, it is better to view the specimen by single eye only, likewise camera does. On the shooting stage, the illuminators and reflecting screens should be set up one after another to light up, successively, the entire shape, brilliance and sculpture of faces etc. A reflecting screen of sufficiently large size can partly imitate the source of diffused light, which may be problematic for the home studio. At the final stage, the general light—shadow contrast should be regulated. A powerful tubular halogen lamp directed a sufficient distance from the front would do for this aim.

It is very important to check the specimen cleanness. Being left on its surface, dirt, dust, fingerprints will inevitably be visible on the picture.

All the illustrations have been taken with Canon EOS 50E camera with Sigma EX

2.8/105 mm macro lens and light-conversion filter Schneider 80B, using the mirror two-second blocking option, on Kodak ProFoto 100 and Fuji Superia 200 films; the lighting with «Radium» miniature halogen lamps 12 V 50 W.

Author's specimens and photos.

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#### Moisei D. Dorfman

A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, dorfman@fmm.ru

The veteran research worker of the A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, described his meetings with N.A. Smolyaninov, P.P. Pilipenko, and Yu.A. Bilibin, prominent mineralogists and geologists.

**About the author.** Moisei Davidovich Dorfman (born 6 February 1908) is the veteran research worker of the A.E. Fersman Mineralogical Museum, Doctor of Geology and Mineralogy, honorary member of the All-Russia Mineralogical Society, author of 135 scientific works including three monographs.

At the start of the Moissei Davidovich's creative development, his scientific work was concentrated on mineralogical study of tungsten deposits in Transbaikalia (Belukha, Bukuka) and Kazakhstan (Akchatau), but his scientific interests were mostly in alkaline rocks and minerals of the Khibiny Massif. His study of mineralogy and pegmatites of the Khibiny Massif led to the discovery of a number of new mineral species and varieties as well as minerals not known there before. The study of so-called ruined zones brought out the development of products of preglacial weathering in Khibiny (including more than 30 minerals not known there before) and let to discover a zirconium (zirfesite) area weathering crust. As a member of the Soviet – Mongolian geological Expedition, M.D. Dorfman studied alkaline rocks of Mongolia for several years and prepared materials for the monograph «The Minerals of Mongolia».



Since 1957, Moise Davidovich works at the Mineralogical Museum. He has made up several exhibits that show the results of his multiyear works. In the context of great exhibit "Types of Mineral Associations in the Earth's Crust", he created expositions to mineralogy of alkaline pegmatites and weathering crust minerals as well as showcases with minerals of chlorine, fluorine, phosphorus, sulfur, and selenium in the exhibit "Mineralogy of Chemical Elements".

For the two-volume monograph «The Mineralogy of Khibiny Massif», M.D. Dorfman with his co-authors were rewarded with A.E. Fersman Prize established by the Presidium of Academy of Sciences. On the occasion of fiftieth anniversary of the Kola Filial of Russian Academy of Sciences, M.D. Dorfman was awarded with « Transpolar Scientist Veteran» diploma.

In honor of M.D. Dorfman, the mineral dorfmanite was named.

When you are more than ninety and continue to work, you are more and more often tempted by the thought to impress your long life experience on paper: to begin writing memoirs. So I decided, too, to undertake my memoirs, by my friends and colleagues advice.

My geological long activities were various and proceeded in the regions with thousands of kilometers one from another: from Middle Asia to Kola Transpolar area. My memory saved interesting and even funny events associated with everyday life of geologists and expedition works, and also with meetings with some leading geologists and mineralogists, brilliant and original persons who knew their job excellently. However, when I took up the pen, it turned to be not so simple to recount all this. Therefore

I decided to follow my memory, not too much worrying of chronology and significance of events depicted, but invariably dwelling on my impressions of those remarkable personalities whom the fate brought me together.

#### Pavel Prokofyevich Pilipenko

Born 23 October 1877, died 3 February 1940.

Mineralogist and geochemist, Doctor of Geology and Mineralogy, Professor of Saratov, Tomsk, and Moscow universities, Head of the chair of mineralogy and geology in the Tomsk university, Head of the chair of mineralogy and crystallography in Moscow Institute of geological survey, vice-rector (for educational and scientific work) of the Moscow Institute of geological survey, director of mineralogical and petrographic

scientific department of Moscow university; creator and curator of Mineralogical museums in the Tomsk and Saratov universities. Awarded with the Akhmatov Great academic Prize.

The first bright recollections of my geological activities are associated with my entering the post-graduate study of the Moscow Institute of geological survey in 1939. By this time, I have already worked in some geological institutions and participated in expeditions. One of latest was the Akchatau wolframite deposit in Kazakhstan.

There were a lot of persons who wished to enter the post-graduate study of the Moscow Institute of geological survey that year. Professor P.P. Pilipenko, a disciple of Academician V.I. Vernadskii, was taking the entering examinations. I was examined in mineralogy, then the questions on crystallography, geochemistry, geology, petrography, and other parts of geological science followed. Each my answer was followed with Professor's remark: «What's the matter with you, really?» Abandoning the Institute after this prolonged and exhausting examination, I was fully confident of my complete illiteracy. It was clear to me that I could not be accepted to the post-graduate study. However, I had to pass another examination, on philosophy this time. My friends advised me to go for this examination despite my report of Prof. Pilipenko's reaction upon my answers when examined in profession.

A week later, Prof. Pilipenko uttered at the senate session: «After competitive examinations, Dorfman is accepted to the Chair of mineralogy...», which was a great and, should be said, very pleasing surprise for me.

My future dissertation related to the genesis of the Akchatau wolframite deposit in Kazakhstan. Having worked there for three seasons and made a careful study of local geology and mineralogy, I reported of my results at the Chair session. I accounted the deposit genesis not for the zoning of hydrothermal process that proceeds in a closed space but for repeated actions of high- to low-temperature solutions. The five types of various age mineralization were found. My conclusions I based persuasively, as I believed, on the paragenesis of each stage of the process. Prof. Pilipenko, the Chair head, turned out to be my opponent. Each my thesis and argument was defeated by him utterly. His critical remarks were so persuasive that it was very difficult to disprove them in the course of discussion... Naturally, I was terribly downcast: it turned out that all my genetic conclusions were incorrect.

But after the session, having analyzed professor's remarks calmly and carefully, I felt I could disprove them easily. Two weeks later, I came to my opponent to share my considerations. Pavel Prokofyevich listened to me attentively and then said, smiling, «Unless you have not come to me with all this, you will have nothing to do at the post-graduate study!»

It should be said that the Professor's original manner manifested in many other things. A year later, having become the Chair instructor, I had to train the students in using blowpipe. To check my lessons, Pavel Prokofyevich edged into the laboratory and, pretending to seeking for something, watched my working...

P.P. Pilipenko was a brilliant and original person who possessed thorough knowledge. A non-standard approach to geological problems was in his nature: it was not in vain that he was a disciple of V.I. Vernadskii, one of the most profound minds of the twentieth century.

## Nikolai Alekseevich Smol'yaninov

Born 21 May 1885, died 6 April 1957.

Honored Science Worker of R.S.F.S.R, USSR State Prize winner, Doctor of geology and mineralogy, Professor, Head of the mineralogy chairs in Moscow State university and Moscow Institute of geological survey, head of mineralogical section of Lomonosov Institute of Academy of Sciences of the USSR, curator of mineralogical museums in Moscow university and Moscow Mining academy, establisher (together with V.I. Vernadskii and A.E. Fersman) of mineralogical museum in the Moscow Institute of geological survey (on the base of collections of Moscow university and Moscow Mining academy; now the V.I. Vernadskii State Geological museum of Russian Academy of Sciences). Decorated with Order of Lenin and the Badge of Honor.

In his honor mineral smolianinovite was named.

A friend, a teacher, a comrade, — so I remember N.A. Smol'yaninov. I knew him for many years, but got in with him when I became a postgraduate in the Chair of mineralogy in Moscow Institute of geological survey (MGRI). When a postgraduate, I was invited in 1941 to participate in studying the new-discovered fluorite deposit in the Zeravshan Range, Tajikistan. The journey we had to undertake would have been a hard one since the deposit was at 6000 meters above sea level.

It was also decided to visit the Kulikolon well-known deposit of optical fluorite as it was at the route of our expedition. To familiarize with this deposit was of great interest as it

opened the possibility of comparative studying the known and new-discovered deposits.

At the height of field season, we suddenly got to know by radio of Hitler's treacherous aggression against our country. The party was decided to stop working. The students engaged in practical works left immediately for Moscow; as to us, the Institute workers, we were ordered to go to Semipalatinsk where the Institute was evacuated by that time.

In Semipalatinsk, the building for the Institute did not do for educational process. The chair of mineralogy needed a training collection of specimens, a laboratory, textbooks, handbooks to identify minerals, but there was nearly nothing of this available. In these complicated circumstances, administrative ability of Nikolai Alekseevich Smol'yaninov proved out. The local geologists' resources were mobilized, blowpipes were made of glass or copper pipes, and a room for practical training was prepared... All the possible had been done in short time to begin a normal academic year. The lessons proceeded at three faculties, the teaching load was maximum, but there were only two persons in the chair staff: N.A. Smol'yaninov and an assistant lecturer, i.e. me. However, Nikolai Alekseevich held chair meetings as if the entire educational Moscow staff was present. And he used to summarize resolutions with the words, «The Chair supposes...» or «By the Chair's decision...», though, I repeat, there were two of us only.

Shortly, I got to know that during evacuation of the Institute, when the Germans were near Moscow, many documents have been burnt down including the text of my dissertation, «The Mineralogy of Akchatau Wolframite Deposit, Kazakhstan», that was prepared to be defended. One can easily imagine what a hard blow turned to be this news for me. Nikolai Alekseevich showed maximal attention, called me to be courageous, and suggested to restore the manuscript since the analytical data as well as the short report were passed in Alma-Ata, to the funds of Kazakhstan geological service. Though being fully busy, Nikolai Alekseevich watched tirelessly over my work, and, as soon as it was completed and reported at the regular chair meeting, the chair resolution of the work readiness to be defended was entered in the minutes. Later, I defended it successfully in the Tashkent Middle Asia University.

In 1943, MGRI returned to Moscow. The N.A. Smol'yaninov's administrative remarkable ability manifested here again. For the first time in our country, Nikolai Alekseevich began his course of mineralogy in accordance with the

new crystallochemical systematics that was brought forward by Prof. Strunz in Germany. As a brilliant connoisseur of minerals, Nikolai Alekseevich was in the habit to give in his lectures a spacious material, which could not be found in any textbook. The mineral collection of MGRI that was headed by him for more than 20 years served an excellent illustration for his lectures.

An extraordinary event in N.A. Smol'yaninov's work was his discovery of scheelite, a valuable tungsten-containing mineral, amidst specimens of an old and non-ordered collection from Chorukh-Dairon, Tajikistan. One should clear up whether this was a casual find or scheelite is widespread in this deposit. With this aim, the Chair equipped a special party that confirmed the fact that there are industrial reserves of scheelite in the Chorukh-Dairon deposit. Just so a new deposit was discovered of this valuable mineral.

#### Yurii Aleksandrovich Bilibin

Born 19 May 1901, died 4 May 1952.

Geologist, specialized in placers, petrologist, initiator of home school of metallogeny, corresponding member of the Academy of Sciences of the USSR, professor, head of the Chair of ore minerals of the Leningrad State university, head of the sector of metallogeny of VSEGEI, head of the East-Siberian expedition of Academy of Sciences, one of initiators and head of the First Kolyma Expedition of 1928 – 1929. State Prize winner.

In his honor were named: mineral *bilibinskite*, range in the Cherskii Mountain system, Bilibino township in Magadan oblast', streets in Magadan and Aldan, and mine in Magadan oblast'.

The acquaintance with Yurii Aleksandrovich Bilibin took place in the autumn of 1942 in Tashkent, soon after my candidate dissertation defense at the Middle-Asia University. Earlier, I only knew Bilibin by his very interesting works on geology of the North of our country. We got acquainted at the «Glavzoloto» office. Yurii Aleksandrovich turned to be an amiable, big, and tall person. I had got to know soon that he was offered to work as chief geologist at the Koitash rare-earth deposit of scheelite near the Samarkand City. As there was no geological service at this mine, Yurii Aleksandrovich offered me to work as a mining geologist. It would have been of great interest to work with this prominent scientist, and I gave my consent. When I arrived at the mine, Bilibin already lived there with his family: Tat'yana Vasil'evna, his wife, and Sasha, their newborn son. Yurii Aleksandrovich familiarized me promptly with the deposit geological features. I was amazed with his shrewd observation. For instance, once he saw an inappreciable stripe of bare earth in the grass cover; it was, by his opinion, a surface trace of a fracture zone. Later, this fracture zone was actually established during the deposit mining.

The disposition towards humor was Yurii Aleksandrovich's characteristic feature. There was no forest in the deposit vicinities, only sparse odd bushes. Kizyak, pressed dung, served the only fuel. Bilibin once reported: he found a large «deposit» of kizyak; however, someone had already been successful in taking off the «cream» of it.

As it was wartime, the wages were very low at the mine, so the administration permitted the workers to mine scheelite in off-duty time and to change it for foods, in particular, wheat grain. Yurii Aleksandrovich and me seized this opportunity. We carried bags with ore from the mountain and then washed it in a butara, a sort of washing drum. The grain exchanged for scheelite I drove to Samarkand where my wife and two-year-old son lived then with my parents.

Yurii Aleksandrovich was a remarkable narrator. His narrations of placer geology, gold deposits, some geological objects were interesting and amusing every time.

In 1945, Yu.A. Bilibin was elected corresponding member of Academy of Sciences of the USSR. Soon after the war finished, he returned to Leningrad. One day, answering to my new-year congratulation, he wrote me in a letter: «I only regret that, according to our tradition, as soon as the merits of a scientific worker are recognized officially, he is loaded with so many duties that becomes unable to engage in his scientific work…»

It was said that Yurii Aleksandrovich's lectures were so interesting that they were attended not only by his students but also by the lecturers.

# The MEMORY (instead of epilogue)

The memory! Like a time machine, it carries you instantly in the past, and you begin to live again in that remote time that fell into oblivion long ago. And if you hold in your hands an object retained from those times, this sensation becomes especially realistic...

As a mineralogist, I always wished to retain for memory a small specimen of a mineral or rock from those distant lands where my life brought me. So a dozen of specimens was accumulated, the witnesses of remote times. Each one is connected with some kind of event, and that is why every one is dear to me.

For example, here is a scepter quartz crystal. It was brought from post-war Kazakhstan where I came across it at unusual circumstances.

The year 1949... The time of restoration after the post-war devastation, of putting deposits into operation and reconstruction of old, disabled ones. I was offered to be at the head of Kazakhstan inspection party and to conduct, at the same time, searches for new deposits.

We were threading on our truck by the Betpak-Dala desert to the site of forthcoming work. It was terribly hot, and to find a place for a camp was not easy. However, we suddenly saw on the horizon a small oasis of abundant greenery. Of course, we hurried there.

A geophysical party settled shortly earlier under the fresh shade of trees; they led systematic large-scale survey of the region. Having had pitched, side by side, our tents and also a big canvas canopy, under which, later, collected materials were being treated and food cooked, we outlined the plan of the works to be fulfilled. Thereafter I decided to go immediately in my own reconnaissance rout.

It should be said that our camp was situated aside of the former granite massif that had turned into an almost even granite field under the influence of constant winds, heat, sandstorms, and wild frosts in winter times for millions of years. I went just to this massif taking with me my knapsack, geologist's peak, and compass. In some three kilometers from the camp, in a pile-up of granite blocks, I found a large enough pocket — a vug with its sides covered with crystals of scepter quartz. The best, well faceted and transparent, crystals were unapproachable, and I felt the natural desire to obtain them. But the crystals prevented me from penetrating into the pocket by the usual way, i.e. feet-first. So I decided to creep into the vug with my head first. My attempt had been successful, and the pocket turned to be more capacious than I expected. In my excitement, I began to break off the best, most spectacular specimens. But after my mineralogical appetite had been satisfied, it became clear that it was not so easy to get out from the rock bag: those fine crystals that I liked so prevented me now from getting out. They stuck into my body like thorns and inflicted acute pain. Only after many attempts, I managed to scramble out of the trap having had compacted my body to the full breathing out. Covered with bleeding scratches, chivied, but with the happy

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phiz and the knapsack filled with trophies, I reached at last the camp.

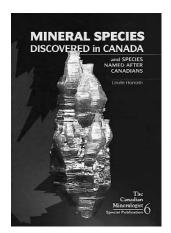
Having rested and put myself in order, I started to examine the specimens obtained so hardly. Scrutinizing the quartz crystals and granite pieces, I noted diminutive transparent bladed crystals that resembled very much bertrandite, a beryllium-containing mineral. Their composition was confirmed by spectral analysis. So the massif should be explored, and this work promised to be interesting.

Further studies confirmed unordinary beryllium mineralization of this massif. They had led initially to the discovery of a system of thin veins with bertrandite and helvite. As a result of prospecting in the shale. the quartz-hematite-helvite lenses were stripped about 10 meters in size containing more than 30 per cent of helvite. That was a new, not known earlier, type of hydrothermal genesis. But the most surprising were the lens edgings up to 10 cm thick. The constituting mineral resembled fine-grained amazonite feldspar, but being studied in detail, turned to be beryl! Do you know what means «uzunkulak»? In uzbek, it is «long ear», something alike wireless telegraph. You depart somewhere from the

camp, and, virtually, nobody knows your way; but when you reach your destination, the whole kishlak is already aware of your arrival. We got to know uzunkulak operation from our own experience. Soon after we made our interesting finds, the automobile drove up to our camp with a group of geologists from the Kazakhstan Geological service headed by academician F.V. Chukhrov. And then... We were being literally assailed by the planes of geological service. They used to land nearly our tents, a pile of probes was being thrown out upon the ground, then appeal to consult the accompanying geologist followed. They were the most extraordinary consultation in my life.

In autumn, we sent to Moscow 40 boxes of the valuable load. Alas, the specimens did not reach their destination. Evidently, the stones were not, to railroaders' opinion, of great value, and were simply thrown away. The searches were of no result... And only the quartz small specimen, which I hold in my hands, enables me to pass mentally into the hard-to-reach region of our works, and I feel myself again in that period of my life that is impossible to restore otherwise than in the memory.

New Data on Minerals, M., 2003, Volume 38



Laszlo Horvath "Mineral Species Discovered in Canada and Species Named after Canadians". The Canadian Mineralogist Special Publication 6, 2003. Editor Robert F. Martin. 372 pages, hardcover, 3 parts, 7 appendixes, index. Price \$45 (postage includes)

#### Order online at www.mineralogicalassosiation.ca or by fax 1-418 226-4651 or Mineralogical Assosiation of Canada

P.O. box 78087, Meriline Postal Outlet, 1460 Merival Road, Ottawa On Canada The main part of this book describes the 206 minerals that were first studied on the territory of Canada. Canada holds the fourth place after USA, Russia, and Germany in mineral discoveries. Description of each mineral appears on a separate page and includes the chemical formula, symmetry, detailed geography of type locality, brief description of the occurrence (bedrocks, mineral size, morphology, colour, associated minerals, etc.), origin of the mineral name, type specimens depository, and complete references to the first study and, in some cases, to other significant works. If the discovery of a mineral has a history, it is given in the "Comments" section, which also includes other additional

information on this mineral. The pages presenting the mineral species named after people contain not only some facts about those persons, but also their portraits (which seems to be very important!). Other illustrations in the book include black-and-white photographs of minerals (basically SEM images), crystal drawings, and scenic pictures of the type localities. An insert features 39 colour photos of specimens of the most beautiful Canadian minerals.

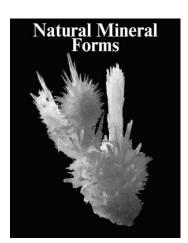
The history of new mineral discoveries in Canada, covering more than 220 years, is briefly described in the introduction. Appendices in the end of the book include the chronology of discoveries, geographic schemes of type localities, distribution of the mineral species among chemical classes, and the author index. Another section of the book is very interesting by discussing the names that were first introduced to the mineralogical literature based on studies of Canadian minerals (even though these names are considered obsolete from the standpoint of the current mineralogical nomenclature).

A separate section describes 30 mineral species discovered outside Canada but named after Canadians - mineralogists, crystallographers, and geologists. The descriptions in this section are structured similarly to those in the main part, and here we can also see the portraits of all those people.

The book is very complete and detailed. These qualities are absolutely crucial for this kind of a reference edition. Having experience of preparation of an analogous review for the former USSR territory, I can fully understand what an enormous effort has been made by the author to collect all the information and (especially!) illustration materials for this book. It is a very interesting and captivating reading, and, in spite of high saturation with facts, information is easily accessible due to clear and convenient organization of the material within each section. This remarkable work is a fundamental contribution to the history of mineralogy and can be recommended for reading by both professionals and amateurs.

Igor V. Pekov, PhD.

Department of Mineralogy,
Lomonosov Moscow State University



Natural Mineral Forms: Exhibition in Fersman Mineralogiacl Museum, RAS. Text: Alexander A. Godovikov and Victor I. Stepanov.

Editor: Margaruta I. Novgorodova.

64 pages, 153 color photos, softcover, fullcolor. Price \$35 (postage includes) **Order from US Representative of Mineralogical Almanac - Mr. Terry Huizing,** 5341 Thrasher Drive, Cincinnatti, OH 45247 USA.

www.minbook.com,minbooks@online.ru

The book involves systematization and description of various mineral forms known in the nature. This is the first published well-illustrated course that tracks the evolution of the crystal perfectness over the wide range of mineralization conditions. It proceeds from almost ideal crystals to highly defective ones, which can be rightly identified as both individual forms and aggregates. Regularly and irregularly formed aggregates of minerals are also considered.

The comparison the mineral forms crystallizing in fluid (gas, liquid), viscous (melt), and solid (rock) media is of great interest.



Photo Michael Leibov







Fig. 5. Pier glass of gray-violet Korgon porphyry. Height 240 cm. Kolyvan grinding factory, 1871—1874. Cat. #PDK-1721

Fig. 6. Vase-jug of Revnev brocade jasper. Height 69 cm. Kolyvan grinding factory. 19<sup>th</sup> century. Cat. #PDK-1722. Pedestal of red Korgon porphyry . Height 123 cm. Kolyvan grinding factory, 1876. Cat. #PDK-1702

Fig. 7. Part of collection of decorative stones of Altai. Size 65 x 50 cm. Size of samples is 6.5 x 4.5 cm. Cat. #PDK-4170

Fig. 8. Vase-jug of Revnev brocade jasper. Height 69 cm. Kolyvan grinding factory. 19th century. Cat. #PDK-1722. Pedestal of red Korgon porphyry . Height 123 cm. Kolyvan grinding factory, 1876. Cat. #PDK-1702

**Fig. 9.** Inscription engraved on one of jasper fire-places. Cat. #PDK-1706

**Fig. 10.** Fireplace of green wavy Revnev jasper. Height 130 cm. Kolyvan grinding factory, 1866—1869. Cat. #PDK-1705







Photo Michael Leibov











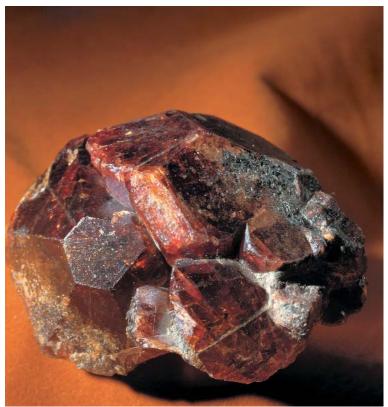
- 1. Topaz. Excellently formed, first-water crystal, blue, with faces c (001), m (110), l (120), b (010), f (011), o (111), u (112), i (113), d (101), g (130), 3 cm. Murzinka, Central Urals, Russia. Cat.~#31351
- **2. Topaz.** Crystal of Korosten' type with faces m (110), l (120), y (021), o (111), u (112), d (101), X (023), g (130), b (010), transparent, pale blue,  $5.3 \times 3.5 \times 2.3$  cm, Urul'ga River, Eastern Transbaikalia, Russia. From Perovskii's collection. *Cat.* #31277
- **3. Topaz.** Crystal of Il'men type with faces c (001), m (110), l (120), y (021), f (011), o (111), u (112), i (113), d (101), transparent, blue,  $6.5 \times 4.5 \times 2.1$  cm, 159 gramm weight, Urul'ga River, Eastern Transbaikalia, Russia. From Perovskii's collection. *Cat.* #31266
- **4. Topaz.** Crystal of Murzinka type with faces c (001) , m (110), 1 (120), y (021), transparent, pale blue,  $5 \times 4.3 \times 4.1$  cm, 153 gramm weight, Urul'ga River, Eastern Transbaikalia, Russia. From Perovskii's collection. *Cat #31275*.
- **5. Topaz.** Crystal with faces m (110), l (120), y (021), o (111), d (101), transparent, pale blue,  $10.5 \times 9.7 \times 7.1$  cm, Urul'ga River, Eastern Transbaikalia, Russia. From Perovskii's collection. *Cat. #31262*
- **6. Topaz.** Dipyramidal crystal of reddish-yellow, transparent, with dissolution traces. Villa Rica, Brasil. *Cat. # 31315*
- **7. Topaz.** Dipyramidal crystals ofzonal pink-red, transparent, with dissolution traces. Villa Rica, Brasil. *Cat. # 32143*
- **8. Topaz.** Crystal with faces c (001), m (110), 1 (120), y (021), u (112), i (113), transparent, blue, 8 x 3 x 2.5 cm, in intergrowth with morion, orthoclase, and albite (cleavelandite). Murzinka, Central Urals, Russia. Cat. #31327





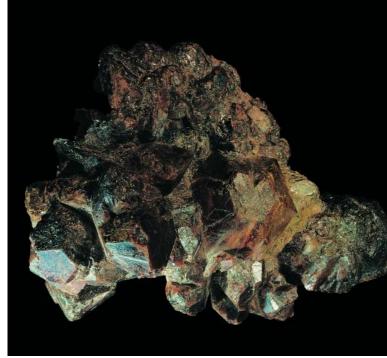












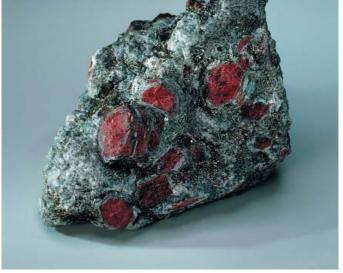
#### 9. Chrysoberyl (alexandrite).

Intergrowth of two trillings of 5 cm and 4 cm across. Izumrudnye Kopi, Central Urals, Russia. Cat. #30308

- 10. Beryl (heliodor). Crystal of deep yellow color, transparent, 3.5 cm. Sherlovaya Gora, Eastern Transbaikalia, Russia. Cat. #32250
- 11. Beryl (aquamarine). Blue, transparent crystal  $13 \times 4$  cm. Urul'ga River, Eastern Transbaikalia, Russia. Cat. #32046
- 12. Chrysoberyl (alexandrite). Crystal cluster.25 x14 x 11 cm, weight 5,724 gramm. Izumrudnye Kopi, Central Urals, Russia. Cat. #30295
- 13. Beryl (emerald). Crystal 12.5 x 8.5 cm, weight 2225 gramm. Izumrudnye Kopi, Central Urals, Russia. Cat. #31219
- 14. Perovskite. Crystal cluster with mica and chlorite on blue calcite. Specimen 17 x 10 x 8 cm. Akhmatovskaya kop', South Urals, Russia. Cat. #30737
- 15. Beryl (emerald). Crystal of deep green color, translucent at edges, 7.5 x 4.3 cm, weight 198 gramm. Faces are polished. Izumrudnye Kopi, Central Urals, Russia. Cat. #31228















16. Beryl (emerald). Subparallel crystal cluster, 9 x 3.5 cm, weight 78 gramm. Izumrudnye Kopi, Central Urals, Russia. Cat.~#31238

- 17. Beryl (aquamarine). Three intergrown crystals, transparent, blue, 11.8 cm high, weight 593 gramm. Urul'ga River, Eastern Transbaikalia, Russia. *Cat. #31203*
- 18. Beryl (emerald). Intergrowth of two well-formed crystals,  $8 \times 6$  cm, weight 452 gramm. Izumrudnye Kopi, Central Urals, Russia. Cat.~#31223

Photo M. Leibov



- 1. General view of yamb
- **2.** Small stamps on the side surface of the yamb
- 3. Stamps in the hollow on the yamb
- 4. General view of yamb

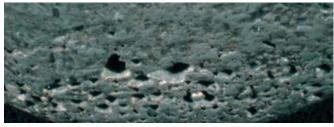


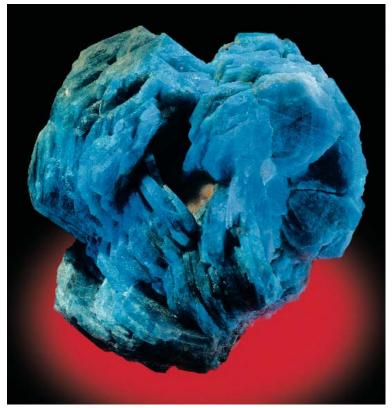
Photo M. Leibov







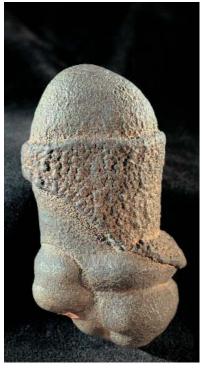




- 1. Native tellurium. crystal fragment 8 x 2.5cm with intergrowings of joseite, tennantite, empressite, sylvanite. Kochbulak gold deposit, near town of Angren, Kuraminskiy Range of Tien'-Shan' Mts., Uzbekistan. FMM #89884, donation of P.M. Goloshchukov.
- 2. Viliaumite, transparent fragment of crystal. Size of specimen 4.5 cm. Koashva mine, Khibiny, Kola Peninsula, Russia. FMM #90217, 2000.
- 3. Corundum (sapphire), A rose-shaped splitted blue corundum crystals. 10 cm high. llmenskie Mts., Ural, Russia. FMM # OP2076, 1999.

Photo M. Leibov





### 4. Calcite,

Calcite encrusting cameras inside the Ammonitoeeras shell. 36 cm in diameter. Belaya river basin, Caucasus, Russia FMM # OP2081, 1999.

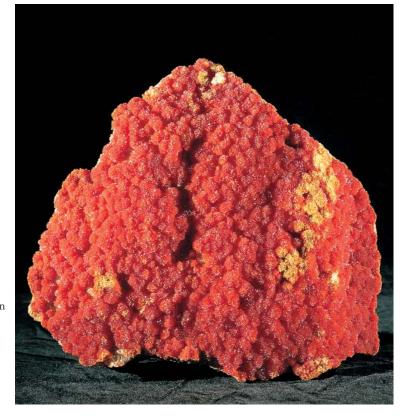
## 5. Pyrite, concretion.

Size 10 cm.

Volga River basin, near city of Ul'yanovsk, Russia. FMM # OP2033, donation of L.V. Bulgak, 1999.

**6. Orpiment.** Crust of small bright orange-red crystals on dolomite. Size of specimen 3 cm. El'brusskiy mine, Northern Caucasus, Russia. FMM #90000, 2001.

Photo M. Leibov









- 7. Amethyst, scepter on rock crystal. Size 11cm. Mangatobangy, Ambatofinandrahana, Madagaskar. FMM OP1825, exchange, 1997.
- 8. Quartz, druze of splitted green (because of thin hedenbergite inclusions) quartz crystals on an andradite. Size 10 cm.
  Sinerechenskoye occurrence, near Kavalerovo, Primorskiy kray, Russia.
  FMM #90264. donaton of Yu. Pustov, 2001.
- 9. Strawberry quartz, druze, size 11 cm, Chimkent area, Tyan'-Shan' Mts., South Kazakhstan, FMM #88615, donation of A.V. Kovalev, 1997.

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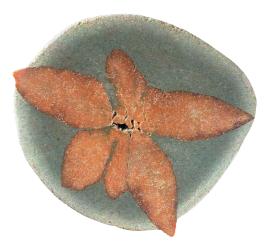








- 10. **Glendonite** (calcite pseudomorph after ikaite). Size 15 cm. Olenitsa river, near Olenitsa village, Terskiy shore of White See, Russia. FMM OP1951, Museum expedition, 1998
- 11. **Glendonite** (calcite pseudomorph after ikaite). Radial crystal cluster 3.5 cm. Size of specimen 9 cm. Bol'shaya Balakhnya river, Khatanga, Taimyr Peninsula, Russia. FMM # OP2124, donation of D.L.Sulerzhitsky, 2000.
- 12. **Glendonite** (calcite pseudomorph after ikaite). Crystal clusters in the centers of intergrown clay-carbonate concretions. Size 9 cm. Olenitsa river, near Olenitsa village, Terskiy shore of White See, Kola, Russia. FMM OP1953, Museum expedition, 1998.
- 13. **Glendonite** (calcite pseudomorph after ikaite). Twin intergrowth in clay-carbonate concretion. Size 9 cm. Olenitsa river, near Olenitsa village, Terskiy shore of White See, Kola, Russia. FMM K4727, Museum expedition, 1998.
- 14. **Glendonite** (calcite pseudomorph after ikaite). Cut of the crystal cluster in clay-carbonate concretion. Size 6 cm. Olenitsa river, near Olenitsa village, Terskiy shore of White See, Kola, Russia. FMM OP1900, donation of D.I. Belakovskiy, 1998.





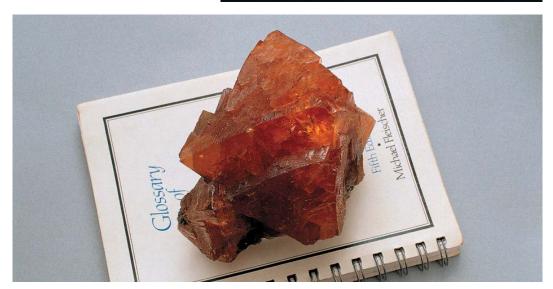




- 15. **Titanite,** Twin intergrowth 3.5 cm in size with kaemmererite on massive chromite. Size of specimen 10cm. Saranovskoe deposit, Ural, Russia. FMM #90045, donation of M.Yu. Anosov. 2000.
- **16. Eosphorite**, Slightly splitted crystal 9.5cm partly replaced by ernstite. Linopolis, Divino das Laranjeiras, Minas Gerais, FMM # 90319. Exchange, 2001.
- 17. Bixbyite, Cubic crystal 1.2 cm on topaz from the rhyolite cavity. Bixbyite site, Thomas Range, Juab Co., Utah, USA. FMM #89227. 1998.
- 18. Rutile . Twin crystal (4 cm long) on quartz. Kapydzhik Mt., Nakhichevan' near, Zanzezur Range, Azerbaijan. FMM#89806, 1999.
- 19. **Elpidite,** Intergrowth of columnar crystals bunches on natrolite. Size 15cm. Alluaiv Mt., Lovozero massif, Kola Peninsula, Russia. FMM # 90236, Exchange, 2000.
- 20. **Scheelite**, Blocky dipyramidal crystal, 12 cm. Xuebaoding Pingwu, Sichuan, China. FMM # 89909, exchange, 2000.









- **21. Corundum** (ruby), Corundum crystals in plagioclase-biotite rock. Size of specimen 13 cm. Rai-Iz massif, Polar Ural, Russia FMM #89011, Exchange. 1997.
- **22. Moganite.** Chalcedony containing moganite in rhyolite lithophyse. Geronimo Area, 100 miles NE of Lordsburg, New Mexico, USA. FMM # OP-1914, 1998.
- **23.** Siderite, intergrowths of spherocrystals. Size of specimen -3.5 cm. Dal'negorsk, Primorskiy Kray, Russia. FMM #OP2108, donation of Star Van Scriver, 2000.
- **24. Staurolite,** right cross shaped twin in mica schist, size 11cm, Keivy, Kola Peninsula, Russia. FMM # 88824, donation of V.Levitskiy, 1997.
- **25. Bertrandite**, opal-bertrandite-fluorite nodule. Brush-Wellman berylium mine, Spor Mt., Juab Co., Utah, USA. 1998.
- **26. Perovskite,** pseudocubic crystal 3 cm in size. Medvedevka, near Ziatoust city, South Ural. FMM #89480.
- **27. Hoegbomite,** intergrowth of hoegbomite crystals up to 3 cm on clinochiore. Size of specimen 6 cm. Medvedevka, near Zlatoust city, South Ural, Russia. FMM #89863, 1999.













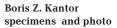


**Corundum,** 2.5 cm high. Mysore, India. Diffused light exposes face sculpture

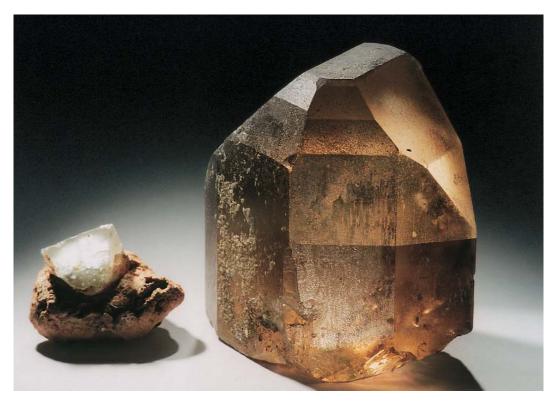
Cr-titanite twin, 3.5 mm. Sarany, Urals. The diaphragm moderate closing down facilitates to throw out the twin from the background of surrounding calcite colored with chromous chlorite

Topaz, 8 x 8.5 x 5 cm. Volodarsk-Volynskii, Ukraine. The light setup emphasizes crystal clarity and cleavage cracks. The color rendition of the larger crystal is adequate; however, blue color of the left one is much deprayed

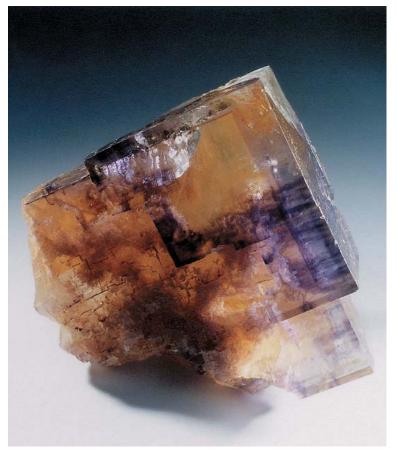
Vanadinite, 4 cm. Touissit, Morocco. The specimen orientation manifests parallel and fan-like arrangement of subindividuals; front faces were lit up











with two reflecting screens Fluorite, 6 cm. Denton Mine, Illinois. The light setup was aimed to show zoning and inner coloration; the front face sculpture is slightly marked in order to not to dead the main pattern

Sanidine Carlsbad twin, 3 cm. Bulgaria. The diaphragm «insufficient» closing draws one's attention away from the details of specimen attaching in the picture lower part and facilitates at the same the image plasticity

Gypsum, pseudomorphous after shell, 3.5 cm. Kertch Penisula, Ukraine. The light exposes macrocrystalline texture of the pseudomorph

Boris Z. Kantor specimens and photo



