Rare minerals of noble metals in the collection of the Mining Museum: new data

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Abstract. Modern analytical methods (optical and electron microscopy, X-ray microanalysis) were used to study the unique samples of sulfide ores from the Norilsk ore field from the Mining Museum collections of Saint Petersburg Mining University. Samples containing rare minerals of silver and platinum-group metals (sobolevskite, urvantsevite, sperrylite, argentopentlandite, froodite, kotulskite, and others) were studied. The chemical composition, grain sizes, aggregates, and mineral associations of more than ten noble metal minerals have been refined. The efficiency of combining various methods of electron microscopy and X-ray microanalysis for studying samples of this type is shown. The results of the work made it possible to obtain high-quality images of rare minerals, to detail information on museum objects, and to compile their scientific description. The conducted research showed the relevance of studying museum objects from known deposits of complex genesis and mineral composition in order to find and describe the samples with rare minerals.

Keywords: sulfide copper-nickel ores; Oktyabrskoye field; Talnakh deposit; noble metal minerals; Mining Museum

Received: 12.04.2022 Accepted: 25.05.2022 Online: 26.07.2022 Published: 26.07.2022

Introduction. The Norilsk ore field is known as a unique geological and mining object, also as the largest palladium deposit worldwide. A number of monographs and many articles are devoted to both the geology of this region [1] and the mineralogy of various types of its ores [2, 3]. Noble metal mineralization is concentrated in sulfide copper-nickel ores. The main ore minerals in these ores are pyrrhotite, chalcopyrite, pentlandite, cubanite, talnakhite, mooiihoekite, magnetite, as well as other sulfide minerals – bornite, chalcocite, covellite, heazlewoodite, millerite, and godlevskite [4]. Along with palladium, Norilsk ores are rich in platinum, gold, and silver, the Ag : Au : Pd : Pt content ratio is estimated as 20-40 : 1 : 20-50 : 5-15 [5]. Most of the noble metals in the Norilsk sulfide ores have their minerals, a smaller part is dispersed in sulfides (Pd and Ag in pentlandite, etc.) [5, 6].

Norilsk ores containing noble metals are widely represented in the collections of the Mining Museum, in particular, in the mineralogical collection, which currently includes more than 51,000 exhibits, reflecting the diversity of natural forms of 2222 mineral species. The vast majority of these specimens came to the Mining Museum quite a long time ago (in the second half of the 20th century) and require modern research for critical analysis and refinement of descriptions. At the same time, unique museum specimens cannot be destroyed or damaged in any way, which imposes significant restrictions on the choice of analytical methods. The solution to this problem could be the use of various electron microscopy and microanalysis techniques. With the implementation of high-precision methods of composite contrast and local microanalysis of minerals, it became possible to study ore aggregates of complex structure and genesis [7, 8]. The technique of using different modes of image contrast and X-ray microanalysis makes it possible to obtain express information on the composition, aggregates varieties, and heterogeneity of minerals [9]. Four sulfide ore samples (polished...
sections) from the Oktyabrsky and Talnakh deposits of the Norilsk ore district, which were transferred to the Mining Museum in 1976-1983, were selected for detailed study (see Table). They represent the following rare minerals in the Systematic Mineralogy collection of the Mining Museum: urvantsevite (MGS 1176/1), thalfenisite (MGS 1128/1), and putoranite (MGS 1289/1), and sobolevskite (MGS 1357/1).

<table>
<thead>
<tr>
<th>Inventory number</th>
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<th>Donator</th>
<th>Georeference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGS 1176/1</td>
<td>15.01.1976</td>
<td>N.S. Rudashevsky</td>
<td>Talnakh deposit, Mayak mine</td>
</tr>
<tr>
<td>MGS 1128/1</td>
<td>31.07.1980</td>
<td>N.S. Rudashevsky</td>
<td>Oktyabrkoye deposit, sahlbands of chalcopyrite veins</td>
</tr>
<tr>
<td>MGS 1289/1</td>
<td>28.10.1982</td>
<td>L.I. Emelina</td>
<td>Oktyabrkoye deposit</td>
</tr>
<tr>
<td>MGS 1357/1</td>
<td>05.04.1983</td>
<td>L.I. Emelina</td>
<td>Oktyabrkoye deposit</td>
</tr>
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</table>

*The data are given from the Mineralogy Department's primary registration book.

**Methodology.** Since the samples are museum items and their destruction is highly undesirable, research methods were limited by optical and scanning electron microscopy and X-ray microanalysis on the existing polished surfaces of polished sections. The studies were carried out at the Saint Petersburg Mining University at the Department of Mineralogy, Crystallography, and Petrography (optical microscopy) with the involvement of the laboratory facilities of the Common Use Center (electron microscopy and microanalysis).

Previously, all the polished sections were studied in detail in reflected light (Leica DM 2700 optical microscope). The study showed that the ores are composed mainly of pyrrhotite, chalcopyrite, cubanite, pentlandite, galena, sphalerite, and magnetite, along with which there are a large number of grains of minerals previously classified as noble metal-bearing. Many of these minerals cannot be determined under an optical microscope due to their small size (tens to first hundreds of micrometers), complex intergrowths, and poor contrast of optical properties. Sections of polished sections with such minerals were selected for detailed study under an electron microscope.

Since the samples under study are non-conductive, polished sections were deposited with a thin carbon layer (no more than 15 nm). The carbon coating was carried out using a JEE-420 Vacuum Evaporator (Jeol, Japan). The previous experience has shown that such carbon film does not distort the morphological features of the sample and is safe for the preservation of exhibits when examined on scanning electron microscopes.

The samples were studied by scanning electron microscopy and X-ray microanalysis using two microscopes (Jeol, Japan) with different sources of electron emission: a tungsten cathode (JSM-6460LV) and a LaB₆ cathode (JIB-4500) with OXFORD semiconductor detectors.

Relevant is the use of SEM JSM-6460LV, which has several advantages: a five-axis motorized samples stage; semiconductor detector from B to U, operating at low currents of the electron beam; low vacuum mode, which allows studying dielectric or poorly deposited areas of the sample (microcracks and pores); the presence of high-contrast modes SEI, COMPO, TOPO, Shadow, providing an express analysis of the morphology and heterogeneity of minerals in complex aggregates; simultaneous areal mapping and linear scanning in x-rays for any set of elements.

The JIB-4500 MultiBeam provides, in addition to these characteristics, higher resolution, since a LaB₆ cathode is used, and a larger analytical working distance (18 mm) gives a more complete view of the sample. The use of an ion gun (Ga) makes it possible to correct the surface quality by removing a thin layer of the oxidation film (10-15 nm).

The study of the chemical features in the range of elements from C to U of the samples at an analytical point (3 μm) was carried out using an EDS spectrometer. Using the OXFORD software.
package for analyzing the X-ray spectrum, resolving complex X-ray line superpositions, and introducing corrections in quantitative calculations, the optimal conditions for measuring samples and calculating their composition were selected.

Depending on the size of mineral phases, the accelerating voltage varied from 10 to 25 kV, and the current on the sample ranged from $10^{-10}$ to $10^{-8}$ A. The best image resolution was achieved by changing the specified parameters and using the LaB$_6$ cathode (in addition to the W cathode). The working distance was standard (10 mm for JSM-6460 and 18 mm for JIB-4500) to obtain correct X-ray microanalysis results.

**Discussion.** As a result of the study, more than ten noble metal-bearing minerals were identified in the studied samples:

- palladium minerals – urvantsevite, sobolevskite, froodite, kotulskite, paolovite, sopcheite, and cabriite;
- platinum minerals – sperrylite, moncheite;
- silver minerals – native silver, hessite, argentopentlandite, sopcheite.

The distribution of noble metal minerals in the ore is extremely uneven; their complex intergrowths with each other and with the main sulfide minerals (primarily galena, pentlandite, and chalcopyrite) are typical. Most of the minerals were not recorded in the current museum description as individual items. At the same time, thalfenisite was not detected in MGS 1128/1 sample. Brief information on each of the mineral species detected and a description of its aggregates in the samples studied is given. The stoichiometric formulas of the minerals are given according to [10], and the mineral abbreviations in the images are according to [11].

**Native silver Ag, Au.** The most common silver mineral in all studied samples. It is represented by grains of irregular shape, often elongated, ranging in size from 30-50 to 150 μm. As a rule, it is located in galena or intergrowths with it; in association with galena and sphalerite in chalcopyrite, as well as in complex intergrowths with hessite (Fig. 1), moncheite, and kotulskite.

Significant variations of Ag and Au contents in the composition of native silver were observed between the studied samples: Ag 52.95-100.00 wt.%, Au 0-47.05 wt.%. Pure silver (close to 100 wt.% of Ag) was found in intergrowths with galena and in galena-sphalerite veinlets in pentlandite ore (MGS 1357/1 sample). In association with palladium bismuthides (sobolevskite, urvantsevite, and froodite in the MGS 1176/1 sample), the Ag content decreases to 78-88 wt.%, while Au, respectively, increases to 12-22 wt.%. Hessite veins in galena from sample MGS 1128/1 contain 53-57 wt.% Ag and 43-47 wt.% Au (composition variations are visible in brightness variations in high-contrast BSE images, e.g., Fig. 1). In the latter case, in reflected light, the mineral acquires a distinct golden color; nevertheless, according to the existing ideas [12], all the analyzed solid solutions belong to native silver.

**Hessite Ag$_2$Te.** One of the common silver tellurides [12]. Occurs in chalcopyrite ore, associates with galena, forming scattered inclusions 10-15 μm in size. It is represented by grains of a rounded or elongated (oval) shape with a size of 30-50 μm. In addition to galena, it associates with native silver (Fig. 1), moncheite, and kotulskite. The chemical composition of hessite, wt.%: Ag 61.46-64.52, Te 35.48-38.54, no impurities were found.

**argentopentlandite AgFe$_8$S$_8$.** It was first identified as a separate mineral species in the ores of the Norilsk region in 1977 [13] and was also described in the deposits of the USSR, Finland [14], Canada [15], the Czech Republic [16] and other countries as silver-enriched
pentlandite or a distinct mineral species. Argentopentlandite is represented by lamellar grains and their aggregates 100-150 μm in size in chalcopyrite ore near galena grains, as well as irregularly shaped grains 20-30 μm in size in pentlandite (Fig.2).

Chemical compositions of argentopentlandite, wt.%%: Ag 12.14-15.42, Fe 28.72-39.01, S 32.81-37.21, Ni 15.66-18.66, Cu (was found in single grain) – 0.71.

**Palladium bismuthides.** Palladium bismuthides are represented by several mineral species: sobolevskite, froodite, urvantsevite, and, possibly, polarite. Often, they form complex mutual intergrowths, enclosed in galena. To accurately distinguish palladium bismuthides from each other, a comparison of optical and electron microscopy data is required.

**Froodite PdBi₂ (monoclinic).** It was first described at the Sudbury deposit in Canada [17, 18] and subsequently found at similar deposits in Russia [4], Germany [19], South Africa, the USA, and other countries. In the studied samples, it occurs in intergrowths with urvantsevite, sobolevskite, and native silver enclosed within galena. In these intergrowths, it forms the central part (Fig.3) up to 300 × 500 μm in size. The chemical composition of froodite, wt.%%: Pd 24.26-25.57, Bi 74.43-75.74.

**Urvantsevite PdBi₂ (tetragonal).** It is much less widespread in the world than froodite and sobolevskite. First described in the ores of the Talnakh deposit in 1976 [20], later found in Karelia and Irkutsk regions [21]. In the studied samples, it forms intergrowths with froodite, sobolevskite, and native silver within galena. The grain size of urvantsevite is 50-100 μm. Chemical composition, wt.%%: Pd 24.30-24.36, Bi 61.27-61.85, Pb 13.85-14.37. In terms of chemical composition, urvantsevite differs from froodite by a noticeable impurity of lead, but, despite this, differs poorly from it in compositional contrast imaging. On the contrary, in reflected light under an optical microscope, it is quite well distinguished from froodite by its darker color and noticeable double reflection.

**Sobolevskite PdBi (hexagonal).** It was first identified as a specific mineral species in the Norilsk ores in 1975 [22]. Subsequently, the mineral was discovered in deposits and occurrences of the Northern Baikal region [23], Karelia [24], the Kola Peninsula [25], as well as in Canada [26], Greece [27], and a number of other countries (over 30 founds worldwide).
The studied samples contain sobolevskite grains of various shapes and sizes. In sample 1176/1, sobolevskite was found in the above-described intergrowths with froodite and urvantsevite, where it is confined to the boundaries with galena. The size of sobolevskite aggregates is 50-100 µm. In contrast to urvantsevite, sobolevskite differs little from froodite in reflected light but contrasts with it in BSE images due to the lower average atomic number.

In sample 1357/1, a small (30 µm) Sobolevskite grain with sperrylite inclusions in the central part was found at the magnetite-cubanite boundary (Fig.4). The shape of the grain is close to oval with uneven edges. The grain is surrounded by a thin (3-5 µm) rim consisting of altaite (PbTe) and, presumably, taimyrite and polarite.

The chemical composition of sobolevskite, wt.%: Pd 35.89-40.31, Bi 59.69-61.66; in grain from sample 1357/1, an impurity of Te is noted at the level of 3.76 wt.%.

Polarite PdBi (orthorhombic). It was first described in the ores of the Oktyabrskoye deposit in Norilsk in 1969 [28], by now it is known in about ten deposits and occurrences all over the world. It is noted in the marginal parts of the sobolevskite grain described above, in the form of a rim up to 5 µm thick. Because of the small thickness of the rim, accurate diagnosis by chemical composition is difficult. In composition, polarite differs from sobolevskite in a noticeable lead impurity level.

The chemical composition of the polarite, wt.%.: Pd 35.80, Bi 49.28, Pb 14.92, Pd 36.55, Bi 44.59, Pb 18.87; Pd 36.49, Bi 56.48.

Sperrylite PtAs2. One of the most common platinum minerals. It is found in the central part of the described sobolevskite grain as two euhedral (close to octahedral?) grains about 3-5 µm each (Fig.4).

Chemical compositions of sperrylite grains, wt.%.: Pt 57.60, As 42.40 and Pt 56.36, As 42.55, Fe 1.09.

Moncheite PtTe2 and kotulskite PdTe. Both minerals were first described in the ores of the Monchegorsk deposit in 1963 [29]. Subsequently, they were found in many platinum-metal deposits and occurrences in Russia, Brazil [30, 31], Canada [18, 32], Japan [33], and India [34].

In the studied samples, both minerals show irregularly shaped isometric grains 10-20 µm in size in intergrowths with hessite and native silver, and moncheite occasionally forming overgrowth rims on kotulskite grains (Fig.5). Kotulskite is also found in association with galena, paolovite, and sopcheite (Fig.6).

The chemical composition of moncheite, wt.%.: Pt 42.54, Te 42.61, Bi 14.85 and Pt 42.50, Te 50.58, Bi 6.91. The chemical composition of kotulskite, wt.%.: Pd 37.70-43.58, Te 27.53-29.70, Bi 25.37-30.81, Pt was noted in one grain – 7.23 wt.%.
Paolovit Pd2Sn. It was first described in the ores of the Oktyabrskoe deposit in Norilsk in 1974 [35]. Currently found in a number of deposits in Russia, Canada, South Africa, and some other countries. It is found in chalcopyrite-galena ore, where it associates with hessite, sopcheite, pyrrhotite, and argentopentlandite, forming polymineral intergrowths and individual grains (see Fig. 2, 6). The sizes of aggregates are from 5 to 30 µm.

The chemical composition of paolovite, wt.%: Pd 66.72-67.95, Sn 29.61-33.28; in one grain, an admixture of Pt was noted – 2.44 wt.%.

Sopcheite Ag4Pd3Te4. Discovered in copper-nickel ores of the Monchegorsk deposit in 1982 [36]. To date, it is known in several deposits in Russia [25, 37], South Africa [38], Tanzania [39], and some other countries. It has associations with paolovite, kotulskite, and hessite in galena-chalcopyrite ore (Fig. 6). The grains are isometric and vary within 10-40 µm in size.

The chemical composition of sopcheite, wt.%: Ag 27.96-34.12, Pd 31.81-38.87, Te 27.22-31.92, Sn was noted in two grains – 5.27 and 6.85 wt.% (possibly due to the presence of paolovite nearby).

Cabriite Pd2SnCu. It was first described in the ores of the Norilsk region in 1983 [40], later found in several deposits in Russia, Canada, the USA, and South Africa [21, 41]. In the studied samples, it was found in a single grain of irregular shape 250-300 µm in size (Fig. 7), intergrown with high-grade native silver, galena, and bastnäsite-Ce in chalcopyrite.

The chemical composition of cabriite, wt.%: Pd 52.20, Sn 29.17, Cu 13.92, Pt 4.71.

Conclusions. The data obtained have both fundamental and applied significance. The collections of the Mining Museum currently lack samples with rare minerals of the following mineral species: taimyrite, paolovite, sopcheite, froodite, sperrylite, and cabriite. These minerals are not singled out in the Systematic Mineralogy collection as independent units; they are an integral part of complex polymineral formations, being present in grains of small size. Many of the above minerals (palladium bismuthides, palladium and platinum tellurides, gold-silver intermetallics), being close to each other in chemical composition and/or optical properties, are not always detectable in routine studies with an optical or electron microscope. Various approaches have been proposed to study such objects [42]. A detailed study of complex ore aggregates using high-precision composite contrast and local microanalysis methods allows us to solve this problem and expand our knowledge of the mineral composition of both already known [43, 44] and newly discovered noble metal deposits [45, 46].

As a result of the study, qualitative images of rare minerals were obtained, allowing us to detail information on the museum objects and compile their scientific description. This will make it possible to use these polished sections with rare minerals and other items from the collections of the Mining Museum as educational and practical material to improve the quality of education for university students. The results of the study can be used to improve methods for extracting precious metals from copper-nickel ores [47, 48], including using the latest beneficiation technologies [49, 50].
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The authors declare no conflict of interests.