SUPERGENE MINERALS OF SHERLOVA GORA

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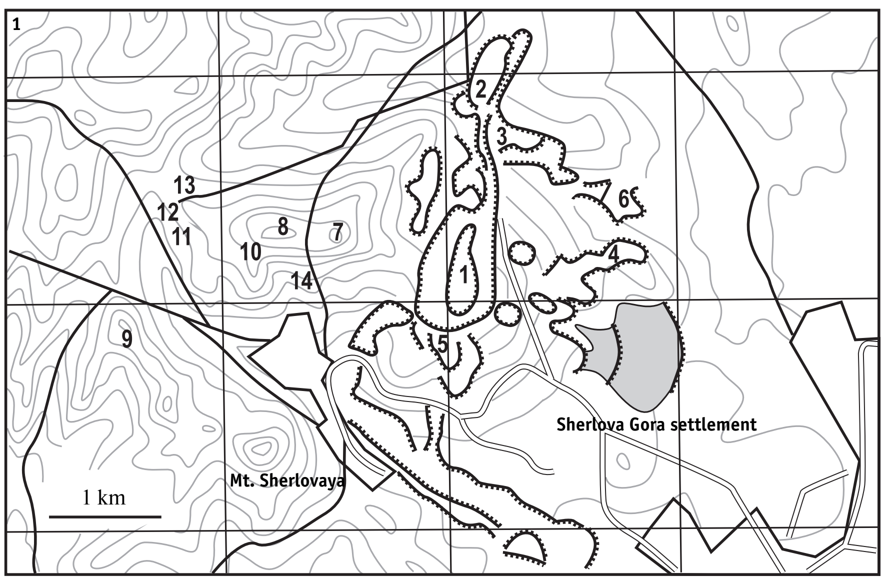
The Sherlovogorskoe deposit (Sherlova Gora, or Sherlovaya Gora[1]) is located near the Sherlova Gora settlement (*Figure* 1), 6 km from Sherlovaya railway station and 40 km to the north-west of the town of Borzya in the Borzinskiy district of the Zabaikalskiy krai (former Chita oblast'), Eastern-Siberian Region of Russia. It is one of the most famous gemstone deposits in Russia, known for almost three centuries. It is famous for its amazing crystals of beryl, including gem quality aquamarine and heliodor, as well as topaz and smoky quartz druses. Remarkable specimens of these minerals adorn many mineralogical collections both in Russia and around the world. Fluorite, ferberite, cassiterite, bismuthinite, molybdenite, native bismuth and tourmaline from Sherlova Gora can more rarely be found in collections as well. All other minerals from the deposit are usually represented only by occasional specimens and sporadic finds.

The deposit is characterized by a large and diverse mineralogy, and it has obvious interest and importance for mineralogists and species collectors, with special regard to supergene mineralization. However, despite the significant amount of geological literature dedicated to the deposit, there are only a very few publications studying its supergene formations. Our paper represents an attempt to fill this gap by compiling published information about all supergene minerals of the deposit known at the present time. We also bring greater focus to our recent finds made as a result of field trips and laboratory research throughout the 2011–2013 period. The rich arsenate mineralization that we discovered in the dumps of the



1. Sites of the Sherlova Gora deposit (square side is 2 km). Numbers show: (1) Tin open pit with technogene pond, (2) Northern dump, (3) North-Eastern dump, (4) Eastern dump, (5) Southern dump, (6) tailings storage facility, (7) top of the Lukavaya Hill, (8) top of the Obvinskaya Hill, (9) top of the Melekhinskaya Hill, (10) Novikov vein, (11) dumps of the Podnebesnykh prospect, (12) Novaya vein, (13) Karamyshevsky spur, (14) Zolotoi ("Golden") spur.

[1] – Following many researchers we use the terms "Sherlovogorskoe" and "Sherlova Gora" as synonyms. In writing "Gora", meaning *mountain* in Russian, with a capital letter we specify the actual deposit, in contrast to "Sherlovaya gora" (further in text – Mt. Sherlovaya) as a geographical site.

2. Panorama of Mt. Sherlovaya. Red numbers show: (1) Lukavaya Hill, (2) Obvinskaya Hill, (3) Melekhinskaya Hill, (4) Novikov vein. May, 2012. Photo: K.I. Klopotov.

Tin open pit of the former Sherlova Gora GOK (*GOK* is a Mining and Processing Plant), appears to be of particular interest. Here we have been able to identify a large number of rare arsenates, primarily from the mixite group and alunite supergroup. Two of these, plumboagardite and goudeyite, have never been found before within the territory of the Russian Federation. Moreover, rare minerals of tungsten (hydrotungstite), molybdenum (betpakdalite-CaMg) and bismuth (atelestite), found in the oxidation zone of the deposit, have been identified for the first time in Russia.

In this paper we also attempted to draft an exhaustive list of Sherlova Gora mineral species, based on the available literature and our new data. This list includes both supergene and hypogene minerals even though the latter are not described here in detail.

The discovery of secondary minerals described in this paper, many of which are quite rare, was possible because of regular visits to the deposit during 1968 through 2013 by one of us (K.I.K.). Those efforts in selecting material containing diverse supergene products such as multicoloured incrustations, powdery and earthy ochres, films etc. led to many of these discoveries. Field trips to the Eastern, North-Eastern and Northern dumps of the Tin open pit and to the Obvinskaya and Melekhinskaya hills of Mt. Sherlovaya (*Figure* 2–5) during 2011–2013, have been particularly fruitful. Our study of the collected samples by electron microprobe, single-crystal and powder x-ray diffraction, infrared and Mossbauer spectroscopy, showed that the oxidation zone of the deposit contains an arsenate mineralization that is very rich and diverse in terms of cationic composition (Pb, Fe, Cu, etc.). Primary minerals widespread in the deposit (arsenopyrite, galena, pyrite and chalcopyrite) are the main source of the formation of such supergene mineralization. Many secondary minerals of the deposit were found in impressive samples.

Notes on History of Exploration and Studies of the Sherlova Gora Deposit[2]

The discovery of Sherlova Gora can be traced back to 1723 according to official sources when Ivan Gurkov, a Cossack from Nerchinskiy prison found "*coloured stones*" (beryl and topaz) on the Tutkhaltui Mountain – a discovery for which he was awarded five roubles by the Berg-Collegium in 1724. The deposit remained under the authority of the Governor of Irkutsk until 1788 and was then handed over to the Irkutsk Mining Administration. The latter officially renamed the mountain in the same year from Tutkhaltui to Sherlova, deriving its name from the word "scherl" used by the local miners of the time to describe all elongated transparent crystals (Yurgenson, 2001).

For a long time, Sherlova Gora was predominantly a source of gemstones, although some sources reported the discovery of wolframite there in 1788 (Barabanov, 1969), while the bismuth minerals, such as "bismuth glance" (bismuthinite) and native bismuth, had been identified already by the beginning of the 19th century (Kulibin, 1827). The large demand for wolframite which emerged at the end of the 19th century had

[2] For more detailed historical overview see paper by G.A. Yurgenson and O.V. Kononov in this *Mineralogical Almanac* issue (pp 12–93).

furic acid decomposition. In addition, the high concentration of As at the deposit resulted in the formation of rare Bi arsenate atelestite.

Supergene minerals of Mo are formed like Bi secondary minerals, i.e. either as pseudomorphs after molybdenite, or they are developed closely to the primary minerals. Ferrimolybdite, the most abundant supergene mineral of Mo in nature, is formed from input of Fe into the system (Smirnov, 1955). It is interesting, however, that at the Sherlova Gora deposit, supergene processes followed more complex pathways, but again with the key role of As: oxidation of arsenopyrite led to the input into the system, not only Fe^{3+} cations, but also AsO_4^{3-} anions, and this resulted in the formation of significantly more rare minerals of the betpakdalite group instead of ferrimolybdite.

Different chemical processes cause the precipitation of supergene minerals of W, tungstite at first. Levitskiy (1939) who mentioned it indicated that ferberite is the major hypogene carrier of W at Sherlova Gora, and it is usually replaced by Fe and Mn hydroxides with the absence of arsenopyrite. However, when crystals of ferberite are cemented by arsenopyrite partly altered to scorodite, Fe and Mn hydroxides are absent and canary-yellow tungstite is formed instead of them. It is obvious that in the first case, Fe and Mn hydroxides resulted from hydrolysis of ferberite with complete removal of W. In the second case, sulfuric acid released due to decomposition ("scoroditization") of arsenopyrite decomposes ferberite with Fe and Mn releasing as sulfate species and the precipitation *in situ* of solid tungsten acids – tungstite ($WO_3 \cdot H_2O = H_2WO_4$) and hydrotungstite ($WO_3 \cdot 2H_2O = H_2WO_4 \cdot H_2O$) at low pH value.

Tin supergene mineralization is absent at the deposit (with the exception of the information regarding the varlamoffite find), and that is caused by the extremely high stability of cassiterite as the major hypogene mineral under supergene environment and the rarity of easily oxidized stannite at the deposit.

Another group of supergene minerals at the Sherlovogorskoe deposit comprises products of recent mineral formation. These are water-soluble Mg, Zn, Cu, and Fe sulfates precipitated within the Tin open pit under surface water action. The evaporation of mining water in the dry period, or its freezing in winter time, causes crystallization of these minerals on the walls and in the coastal zone of the anthropogene pond at the bottom of the Tin open pit. These compounds are so called seasonal (ephemeral) minerals. They rise briefly and dissolve during rain, snow, or flood (Sergutskaya *et al.*, 2011). Minerals formed during recent years on technogene surfaces, for example on rock fragments and oxidized ores in the tailings storage facility of the processing plant of the former Sherlova Gora GOK as a result of interaction of unstable primary minerals with atmospheric agents should be also assigned to this group.

Minerals

Dolomanova (1963) published the first detailed list of the Sherlova Gora minerals and mentioned that within the granite pluton and near contact ore bodies, 72 hypogene and 43 supergene minerals were found. However, her list comprises only 106 mineral species, 34 of which are referred to supergene. Ontoev (1974) mentioned 76 hypogene minerals. More recent publications (Abramov and Yurgenson, 2007; Sergutskaya, 2010, Sergutskaya *et al.,* 2011) report that the total number of mineral species at Sherlovogorskoe deposit reaches 100; however, they offer no lists of minerals found there. Taking all the above in mind, we consider it useful to present our own list of all hypogene and supergene minerals of the deposit (Table 1) that combines literature information, personal communications of our colleagues, and our data.

Since primary minerals are beyond this study, we only note here that according to the literature data the major ore minerals of the deposit are (in alphabetical order): arsenopyrite, cassiterite, chalcopyrite, ferberite, galena, and sphalerite; minor minerals are native bismuth, bismuthinite, molybdenite, pyrrhotite, and siderite; all other minerals are found in small amounts. Beryl, chlorites, feldspars, muscovite, quartz, siderophyllite, topaz, and tourmaline are the major "non-ore" constituents; amphiboles, ankerite, biotite, calcite, dolomite, fluorite, phlogopite, and zoisite are the minor ones (see Table 1).

Among the 200 mineral species shown in Table 1, 109 should be considered as supergene, and that is slightly greater than half. Unfortunately, for 53 among these 109 species, analytical data are completely missing in the literature or are insufficient for reliable determination.

Taking into account all the above, we mention in this paper all supergene minerals given in Table 1, but characterize in detail only those identified by analytical means. Apart from the description of a mineral species, its visual appearance is extremely important; therefore, we tried to accompany our description and analytical data with photos of the samples studied here. We believe that our findings of rare minerals of the mixite group and alunite supergroup are of special interest and importance, and therefore, we describe these minerals in separate sections. All other supergene minerals identified at the deposit are traditionally described by the chemical classes.

7. Fine-crystalline crust of turquoise-coloured **agardite-(Y)** associated with black kidney-like Cu-bearing **coronadite**. North-Eastern dump of Tin open pit. 5.5 x 3.5 x 2 cm.
Specimen: A.V. Kasatkin # 714A.
Photo: A.A. Kalinkin.

8. Crust of fine integrown spherulites of **agardite-(Y)**. Eastern dump of Tin open pit. 5.5 x 3 x 2 cm.
Specimen: A.V. Kasatkin # 766A.
Photo: A.A. Kalinkin.

9. Spherulites of **agardite-(Y)**. Eastern dump of Tin open pit. Fragment of specimen # 2-28.
Field of view: 10 x 8 mm.
Specimen: A.V. Kasatkin.
Photo: A.A. Kalinkin.

10. Spherulites composed of fine acicular crystals of **agardite-(Y)**. Eastern dump of Tin open pit. Fragment of specimen # 2-27.
Field of view: 10 x 8 mm.
Specimen: A.V. Kasatkin.
Photo: A.A. Kalinkin.

The mixite group unifies hexagonal arsenates and phosphates of copper with the idealized formula $ACu_6(TO_4,TO_3OH)_3(OH)_6 \cdot 3H_2O$, where species-defining constituents are octahedrally coordinated Cu cations, tetrahedrally coordinated $T = As^{5+}$, P^{5+}, and large cations in the structural channels $A = REE^{3+}$, Bi^{3+}, Al^{3+}, Ca^{2+}, Pb^{2+}.

Three members of this group, **agardite-(Y)**, $YCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$, **plumboagardite**, $PbCu_6[(AsO_4)_2(AsO_3OH)(OH)_6] \cdot 3H_2O$ and **goudeyite**, $AlCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$ were identified by us in the samples collected in 2011–2013 at the Eastern (GPS N 50°33'070" E 116°17'376"), North-Eastern (GPS N 50°33'636" E 116°16'431"), and Northern (GPS N 50°33'836" E 116°16'225") dumps of the Tin open pit. In addition, agardite-(Y) and goudeyite were confirmed in the samples collected at the Southern dumps (GPS N 50°32'508" E 116°16'103") in 1970 by one of us (K.I.K.) and, since then, stored in his collection as unknown minerals.

Agardite-(Y) occurs as thin turquoise coloured crusts up to a few cm in area (*Figure* 7) including crusts of fine spherulites (*Figures* 8, 9, 10), and chaotic segregations and clusters of various tints of green – from pale green and grass-green to light bluish green and vivid turquoise (*Figure* 11). The length of individual crystals does not exceed 0.6 mm (*Figure* 12); common thickness is 1–5 µm, rarely up to 10 µm. The crystals are transparent, with vitreous luster, often grouped in fine-fibrous aggregates (*Figure* 13). In the aggregates, the luster of the mineral is silky.

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MINERAL INDEX

*D*number is number page with description of the mineral species;
*A*number is number page with analytical data for the mineral species;
Fnumber is number page with illustration (photo or drawing) specimen of the mineral species;
Tnumber is number page where in Table 1. *Minerals of Sherlova Gora deposit* (pp 102–105) the mineral species are mentioned.