First native silica findings in bismuth from garnet skarns of Ribny Log - 2 gold ore target in Topolninsk ore deposit (Gorny Altai)

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Abstract The nanomineralogic investigation results of ore minerals in metasomatites (garnet skarns) of Ribny Log- 2 gold ore in Topolninsk ore deposit (Gorny Altai) revealed the native silica impurities (Si) of 1 – 5 nm within the grains of native bismuth (Bi). Polished sections were examined by using Tescan Vega 3 scanning electron microscope (SEM) with Oxford energy-dispersive spectrometer at the Department of Geology and Mineral Exploration, Institute of Natural Resources, Tomsk Polytechnic University.

1. Introduction
The work is based on original nanomineralogic data obtained after the execution of commercial contract projects in examining substance composition of ore and wallrock metasomatite occurrences of Topolninsk ore field (Altai Territory). According to metallogeny Topolninsk ore deposit is within the Anuisk ore area of Altai-Kuznetsk gold - ore belt and is integrated constituent of Anuisk copper-gold placer cluster in North-Altai gold- ore belt [1]. Intrusive formations occupy from 30 to 35% of the total Topolninsk ore area and involve two solid massifs and numerous dikes of mottled Topolninsk gabbro-granodiorite-granitoid complex, stockworks and linear subvolcanic bodies of Kujagan rhyolite-dacite-andesite complex. The host rocks are strongly hornfelsed and skarnified within a significant deposit area of solid massif exocontacts. The Topolninsk ore deposit within the Sarasino-Insk zone is confined to Karaminsk transverse NW fault zone controlling the Topolninsk and Malo-Topolninsk intrusive bodies. In the above-mentioned solid massif contacts (dimensions of 4.5x2 and 2.5x1.5 km, respectively) there are skarn formations with different superimposed productive mineralization. The thickness of skarn lenses and bodies vary from 3 to 50 meters, extending along strike from 150 to 800 meters; total thickness of skarned rocks in the Western exocontact of Malo-Topolninsk massif is 500-1000 meters. The gold - ore mineralization as placer gold is identified throughout skarned rock cross-section [2]. According to A.I. Gusev data [3], the productive mineralization (4th hydrothermal cycle stage) formed after the intrusion of granodiorite-porphyry and granite-porphyry dikes into Topolninsk magma-ore-metasomatic system (MOMS) and dikes of syenites, granophyr-spherulyte leucogranites and moderately alkali leucogranites (primarily hybrid rocks) into Karaminsk magma-ore-metasomatic system (MOMS). Third- stage albite-quartz-epidote assemblage and fourth-stage mineral aggregates overlie these dikes.

The samples, including native bismuth grains with pure silica impurities, are garnet skarns with
specific granoblastic texture. Mineral composition: garnet~60%, calcite~20%, epidote~8%, chlorite~10%, ore mineral~2%, quartz – single grains. Besides, the secondary minerals that accompany the last productive stages of ore formation also include actinolite and ankerite.

Andradite garnets form anisotropic zoning crystals, the zoning of which is generated by varying iron content. The crystal form is idiomorphic, while sectoral twins are commonly observed. The grain sizes vary from 0.2 to 3 mm. The mineral is transparent or slightly yellow-brownish if reflected by the transmitted light through Nicol prism, and anisotropic in cross polarized light with a significant fringe. The grains are fractured and replaced by carbonates.

Calcite forms pelitomorphic and coarse-grained aggregates. The mineral is colorless and has bright pearly interference colors in cross polarized light. Another characteristic feature is twinkling.

Chlorite forms foliated and flaky aggregates of up to 0.2 mm spatially orientated towards garnet and calcite contact and localizes in garnet fractured cracks. Under conditions of one nicol, the mineral varies from greenish to yellow-colorless, while it has low abnormal interference colors of indigo-blue in cross polarized light.

Epidote is composed of small grains of up to 0.2 cm and is confined to happy occurrence zones. The mineral is yellow-brownish to pistache-green and has bright jet interference color in crosspolarized light with a significant fringe, the extinction of which is not more than 5 degrees. The sulphides detected by optic microscope include pyrite, chalcopyrite, cobaltite and arsenopyrite. Nanomineral phases of late mineralization stage: native bismuth, tetradymite, tellurobismuthite, sulphides (bismuthite), sulphasalts, sulphotellurides and selenides of Bi and Pb are of key importance. In most cases, the above-mentioned bismuth minerals are satellite resources and can be found in other similar targets within Soloneshensk ore cluster and other large gold deposits [3].

2. Methodology
To investigate the fine-dispersed composition phases of ore minerals is increasingly difficult as such phases comprise complex interrelations, the details and composition of which can be interpreted only at the micron level. The bismuth mineral samples (including native bismuth), in which pure silica was identified, were from metasomatic formations (garnet skarns) of Ribny Log-2 gold ore occurrence in Topolninsk ore deposit and were studied with Tescan Vega 3 electron scanning microscope and Oxword energy-dispersive spectrometer.

Quantitatively, the predominant bismuth-containing mineral was native bismuth, which is composed of rather large grains of up to 150 nm (figure 1). Bismuth tellurides and selenides include significantly smaller grains, apparently, forming internally solids, the proof of which is the changing content of selenium and tellurium in different grains. Sulphotellurides and sulphosalts of bismuth have practically the same grain size (from 1 ...10 nm). The smallest grains can be found in bismuthite where silver impurities are identified. These grains are fixed on the fringe region of native bismuth, rimming them as acicular crystals, filling in microcracks and voids within ankerite and actinolite (figure 1). The characteristic feature of actinolite and ankerite from studied metasomatic formations indicated manganese impurities, which, in its turn, is also specific for epidote.

Native bismuth is composed of round or, sometimes, idiomorphic grains enclosed in pyrite grains or contacting these grains (figures 1 and 2). It is considered that in most cases, native bismuth is a result of aqueous fluid-saturated solution precipitation, usually hot and containing SiO₂. Pure silica inclusions in native bismuth were not observed either in studied ore occurrence, or in other geological targets. Pure silica inclusions form isometric crystals of 1 ... 7 nm (figure 2). Oxygen (O) of 3.7% and iron (Fe) of 0.5% are impurities in pure silica.

3. Results and discussion
Recomposed gold-bearing systems spatially and paragenetically interrelated with gabbro-granitoid intrusive bodies generate specific diverse gold – ore deposits, i.e. from small to super gigantic ones, including such global gold deposits as Muruntau (Uzbekistan), Sukhoy Log (Transbaikal), Nezhdaninsko (Yakutia), Olimpiadinsko (Yenisei range), Berezovsko, Vorontsovo (Urals), Kumtor
(Kirgizia), Bakyrchik (Kazakhstan) and others [3]. Reducing medium in the fluids of ore-generating granitoids is characterized by the fact that the principal gold carriers are chlorine and sulfur complexes. Deep reduced state of melts provides the crystallization conditions for accessory minerals - menaccanite and pyrite [3].

**Figure 1.** Electronic image of garnet skarn area containing pyrite ore mineralization, which including native bismuth grains with native silica crystals (Ribny Log - 2 gold ore occurrence in Topolninsk ore deposit): 1) bismuth selenides and tellurides; 2) actinolite including manganese impurities; 3) ankerite including manganese impurities; 4) bismuthite.

**Figure 2.** Electronic image of native bismuth area with impurities of pure silica crystals. Energy-dispersive spectrum of native silica.
Such minerals were continually identified within the studied targets. It has been established that sulfur as HS is present in highly-reduced gabbro granitic magmas – in this case, sulfur is more soluble in silicate melts and furthers the formation of sulfide globules, which, in its turn, isolate gold from the melt. Pyrite globular formations from metasomatic formations of Topolninsk ore deposit were found in several samples. Reduced intrusion-related gold-ore systems are frequently encountered in many countries and regions. For example, in Canada, these deposits are Dublin Gulch, Scheelite Dome, Clear Creek that are localized within the Tombstone gold belt [4-6], while in the USA; they are the reduced Fort Knox gold systems [7]. Within these gold-ore targets native bismuth and bismuth-containing sulphosalts display late paragenesis and are represented by typical alloys with Te, Pb, Sb and Au. Tellurobismuthine, tetradymite, native bismuth, boulangerite and Bi-Pb sulphosalts are abundant minerals in Fort Knox deposits [8]. Almost 40% of gold in the ores of Dublin Gulch are complex intergrowths with native bismuth [9], bismuthite, tetradymite and tellurobismuthite [4].

Reduced gold systems can also be found in eastern Australia: Timbarra and Kidston [10]. In Gorny Altai, there are several gold magma-ore-metasomatic systems (MOMS) of this type: Karaminsk, Baranchinsk, Bazlinsk and Choisk [3, 11]. It is assumed that natural reduced systems are mechanism carriers in gold deposition by chlorine and hydrosulfide complexes of magmagene fluids to ore concentration areas. In most cases, it is the fluid-saturated environment of ore-generating formation systems that generate reduced native phases of metals and their alloys [12]. The reduced magma-ore-metasomatic systems include the largest (in terms of metal reserves) global gold deposits. They are characterized by ore “complexity”, where gold is accompanied by W, Bi, Te, Pt and Pd [13].

4. Conclusion

Natural reduced magma-ore-metasomatic systems that are sources of noble metal deposits and ore occurrences could apparently be a source of pure silica. Only a few cases of elemental silica findings have been observed which were formed in extremely reducing conditions. Pure silica was observed in the intergrowths with moissanite from Yakutia kimberlutes [14,15], in terrestrial iron from serpentinites [16], in the intergrowths with Fe$_2$Si from Lower Cambrian carbonaceous sedimentation [17], as well as in associations with native gold (Au) [18] and natural phase Au$_2$Al [19]. Moreover, pure silica was found as microscopic crystals in fumaroles of Tolbachik and Kudryavy volcanoes (Kamchatka) in association with other native metals (Al, Ti, Fe and Pt), formed during the high activity of halogens [20]. Pure silica inclusions in fulgurites associated with iron silicides were also investigated [21]. Pure silica associated with iron silicides was found twice in the lunar regolith 61501, 22 sample from Apollo 16 [22] and in iron silicides of lunar meteorite DHOFAR 280 [23]. The above-mentioned findings of pure silica indicate its specific formation conditions within an increased fluid-saturated system.

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