

# Supergene Gold in the Gold-Bearing Wastes of Sulfide Deposits

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## Abstract

The dumps of the pyrite-barite-polymetallic deposits of the Ursk ore field (Salairsky Ridge) have been studied by author. As a result of research, it was found that secondary gold enrichment horizon was formed at the bottom of the dump, and it consists of supergene gold. Gold morphology was studied using scanning electron microscopy. This research makes an attempt to prove that this gold is newly formed, bearing traces of growth and consolidation. In addition, factors that contribute to the formation of this gold are considered. The obtained results are the evidence of the high mobility of the dissolved forms of gold in an acidic medium, followed by their deposition on the geochemical barrier.

**Keywords:** supergene gold, dumps, the secondary enrichment horizon

## Introduction

Scientists often investigate the behaviour of gold, namely, distribution, genesis and morphology from supergene zone (Hong Tie 2005; Kalinin et al. 2009; Reith et al. 2012; Osovetsky 2015; Shuster et al. 2017). However, they investigate the gold migration ways from wastes of gold-bearing deposits to prove high mobility of gold in nature and technogenic supergene zones (Myagkaya et al. 2016; Kirillov et al. 2018; Wierchowiec et al. 2018). Besides, the cycle of gold depends on the vital activity of microorganisms (Kuimova Moiseenko 2006; Reith et al. 2006; Shuster Reith, 2018).

It is known that in the supergene zone of sulfide deposits, as well as in the weathering crust, a horizon of secondary enrichment is formed (Smirnov 1951; Kreiter et al. 1958; Roslyakov 1981). The horizon of secondary enrichment is a zone highly enriched with metal, which is formed as a result of physical, chemical, biological and mechanical processes of differentiation and integration of substance in the supergene zone.

The author, in the example of the dumps of the Ursk ore field, studies the gold-bearing wastes and also explain reasons to the formation of supergene gold.

## Materials and methods

The Ursk ore field is located in the northern Salair Ridge (Kemerovo region, Russia). The ore field includes the Novo-Ursk, Belokluch, Samoilov and a number of ore formations. It is the pyrite-barite-polymetallic type of mineralization. The structure, morphology, and composition of the ore bodies, the sequence of mineral formation, and the history of mining have been studied and described by many researchers; thus, a brief description of the ore field is given in this articles (Bolgov 1937; Cherepnin 1953; Kovalev 1969).

The material was selected from the wastes of the Novo-Ursk and Belokluch deposits. The samples were collected from vertical sections in different “lithological” interlayers and were enriched by the gravity method by using a pan.

The tailings preserves wastes from cyaniding auriferous pyritic and complex ores (primary ore and ore from the gold-bearing weathering profile) of the Novo-Ursk deposit. Dumps have a height of 10-12 m. The ore mineralogy consists of pyrite, sphalerite, chalcocopyrite, galena, arsenical pyrite, fahlite, cinnabar, as well as quartz, barite, calcite, chlorite-group minerals, sericite, albite,

graphite, rutile, and fluorite (Myagkaya et al. 2016).

Samples were collected from two dumps. In the section of oxidized ores, three lithologically different layers (horizons) are distinguished (from top to bottom, Fig. 1A): 1. gray-blue clay horizon (30 cm) with sufficiently hard rocky material (with quartzite geodes, shale); 2. dark brown clay horizon (2-4 cm) containing a large amount (30-40%) of wood (such as wood chips); 3. light brownish horizon (30-40 cm thick), lying directly on the soil. The total number of samples – 19, 15 kg each. In the heap of primary ores, four samples were taken from a brown-ocher cemented horizon, lying directly on the soil (60-80 cm thick). The two dumps are separated by an "acidic" stream that was formed as a result of infiltration of atmospheric water through these dumps.

The wastes of the Belokluch deposit have a height of 10 m. In a vertical section, three lithologically distinct layers can be distinguished (from top to bottom) (Fig. 2A): barite material (60 cm); pyrite material (2 m); oxidized zone (> 60 cm). The total number of samples was eight, with a volume of 15 kg each.

Studies of the chemical composition of samples were conducted in the Analytical Center of multi-elemental and isotopes research SB RAS (Novosibirsk). The concentration of gold and silver was

determined by the atomic absorption analysis (analyst Iliina V.N.). The main results are obtained by a scanning electron microscopy (SEM) a LEO VP 1430 (Carl Zeiss, Germany) INCA Energy SEM 350 (Oxford Instruments), spectrometer in the JEOL 01430VP. The finenesses of gold as well as its impurities was obtained by the microprobe analysis.

## Results

According to the atomic absorption analysis (analyst Iliina V.N.), the gold content for oxidized and primary ores varies in the range of 0.4 – 1.2 mg/kg at the Novo-Ursky tailing dump. We have found about 50 particles of nugget gold from horizon 1 from the dump of oxidized ores (Fig. 1A). Gold is fine, size <0.2 mm. Predominant grains are the grains of the crystalline form, elongated and rarely flattened. The surface combines a variety of sculptures. For example, there are nano- and micro-particles of gold in the form of growths on the surface of gold (Fig. 1B, C), in films of iron and manganese hydroxides, clay minerals, and also on the surface of barite grains. Often, gold particles have accumulations of nano- and micro-particles form spongy formations (Fig. 1B, C). Another characteristic of grains is the step structure of growth (Fig. 1D, E).

According to the microprobe analysis, gold of medium finenesses (703-984 ‰), silver impurities are presented – 12–27%;

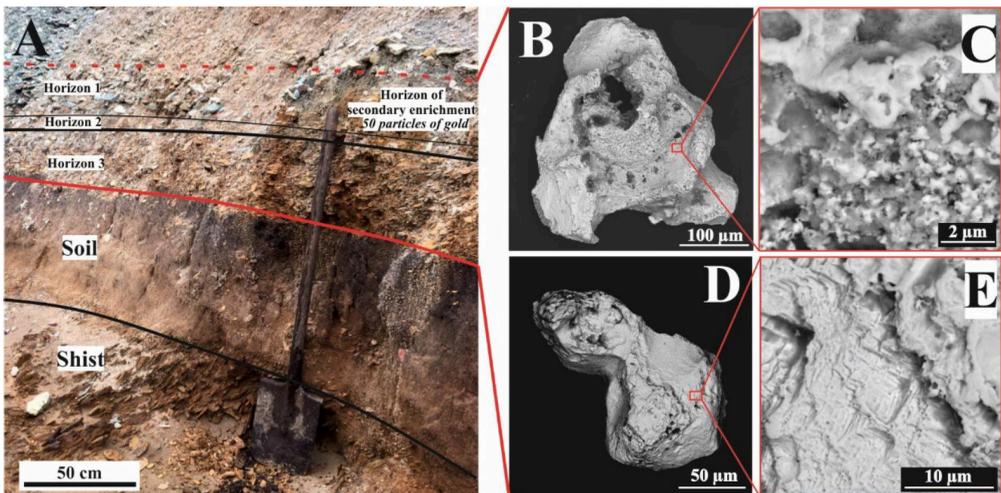
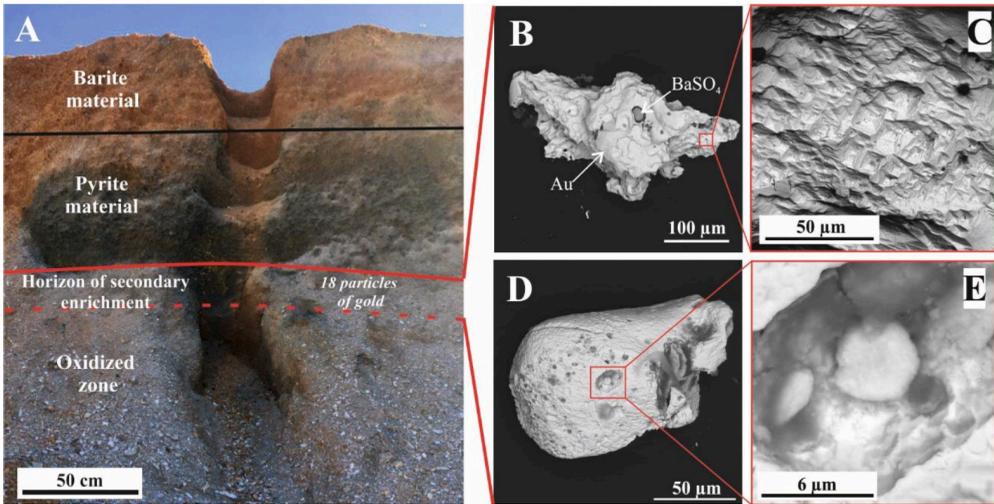


Figure 1 The Novo-Ursk deposit: A – structure of dump; B – sponge gold of crystalline form; C – increased fragment B; D – the step structure of growth gold; E – increased fragment D



*Figure 2 The Belokluch deposit: A – structure of dump; B – crystalline form of gold with the step structure; C – increased fragment B; D – gold particle with a porous surface; E – increased fragment D newly formed phases*

mercury – up to 5%. High-grade gold (990) and grains with mercury impurity (up to 7.9%) were found. Gold is homogeneous in composition; no zonal structure or residual “cores” were noted.

According to the atomic absorption analysis, the distribution of gold at the Beloklyuyskoye deposit is even; the content varies from 0.12 to 0.17 mg/kg (average 0.15 mg/kg). We found 18 particles of gold from the horizon of oxidized ores. Gold is mostly fine, grade <0.2 mm. It is represented by crystalline gold particles with distinct edges, elongated prismatic crystals of tabular form. Morphological types of native gold, represented by aggregates of lumpy grains, have an irregular shape. The vertices of the faces are smoothed, and the edges of the particles are curved. A specific characteristic of the studied particles is the presence of mineral inclusions inside them, both on the surface and particles trapped inside (Fig. 2B). Sculptures of particles’ surfaces are very diverse. Almost all particles of gold have growth steps (Fig. 2B, C) and cross-hatching on the faces. Gold has a microlayers as well. In addition, a grain with a porous surface was found, which is filled with rounded aggregates of gold (Fig. 2D, E).

Gold has a homogeneous composition. The fineness varies from 826 to 901 ‰, silver

impurities are presented – 9-16 %; mercury – up to 0.4 %. The inner (central) part of the gold has, predominantly, a fineness higher than the edges. Fineness of gold decreases in the peripheral part of the gold, having a smooth, gradual transition. For grains of smaller classes (0.25–0.1 mm), curved edges were noted.

## Discussion

Physical, chemical and biological processes are bounded together and their influence determines the morphology of gold particles, as well as the distribution of gold concentrations. Biological and chemical processes in combination with climate and geological conditions determine the physical and chemical conditions in the environment and they control the processes of dissolution, migration and growth of gold. By the geological conditions author means not only the geological structure of the field and the form of gold, but also methods of its extraction and methods of storage of the substance. The importance of solving the gold substance of the supergene nature appeals to the analysis of its typomorphic features, such as granulometry, morphology, and chemical composition.

The Novo-Ursk and Beloklyuksk deposits belong to pyrite-barite-polymetallic type,

which has a powerful oxidation zone with free native gold. Endogenic gold mainly is in a bound form, in sulfides (Bolgov 1937; Cherepnin 1957; Kovalev 1969). Size of gold is 0,016 mm, gold found in chalcopyrite and pyrite (Bolgov 1937; Kovalev 1969) and also in argentite and quartz, tellurides of gold and silver – altaite and hessite (Cherepnin 1957). During the formation of the oxidation zone, gold was released. The highest concentrations of gold are in the oxidized zone. Barite zone, relative to primary ores, is enriched with gold (7-10 times), silver (5-7 times) and arsenic (2-3 times) (Bolgov 1937). In addition, the oxidation zone is characterized by high concentrations of mercury, presented both in the native form and in the form of cinnabar (Kovalev 1969).

Fields have been discovered since the early 1930s. Gold mining was carried out from the oxidation zone, using cyanide. After enrichment, waste ores were stored directly on the soil layer in a specially designated area. Dumps have been stored there for over 80 years.

As a result of the research, it was found that grains of native gold are presented in the secondary enrichment horizon, which was formed at the contact of rock and soil. Since the studies were conducted on individual sections and the distribution of gold is extremely uneven, it is difficult to unambiguously determine the thickness of this horizon.

Gold is supergene, newly formed, as evidenced by the presence of particles of nano- and micron size, which form various growth structures, such as spongy gold or step forms.

We consider the possible conditions for the formation of gold in the secondary enrichment horizon. Sulfide wastes are stored in the open air undergoes weathering processes using water and wind, creating (bio)oxidative conditions. As a result of the oxidation of sulfides, "acidic drainage waters" (AMD) are formed. AMD has a high concentrations of metals and toxic elements. (Myagkaya et al. 2016; Yurkevich et al. 2017; Kirillov et al. 2018). The process of sulfide oxidation involves several stages, which reflects a gradual increase in the degree of

sulfur oxidation. Therefore, acid drainage (AMD) contains abundant sulfate anions and other sulfur ions, such as tetrathionate ( $S_4O_6^{2-}$ ) and thiosulfate ( $S_2O_3^{2-}$ ).

Gold in the dump can migrate in dissolved form or in the form of particles in a stream. Since the acidic environment prevails in the dumps, the dissolved gold is presented mainly in the composition of S-complexes, as well as in the form of mixed Au complexes. (Myagkaya et al. 2016; Yurkevich et al. 2017; Kirillov et al. 2018). Then, these complexes migrate with acidic drainage waters and precipitate on geochemical barriers, due to changes in the physico-chemical parameters of the environment, forming a secondary enrichment horizon with supergene gold.

Elements released using AMD waters are reprecipitated as other minerals, such as goethite, ferrihydrite, lepidocrocite, jarosite, schvertmannite and hydrogoethite. Therefore, a variety of other minerals predominates in the dumps, which form clusters, they are located in the horizon of secondary enrichment. Minor changes in pH-Eh can trigger a rapid changes in minerals, including dissolution, re-precipitation and structural changes (Marescotti et al. 2012).

In addition, microorganisms, bacteria and fungi are actively involved in the remobilization of gold, as well as in the gold formation, which accelerates the dissolution and transformation of sulfide minerals, as well as the processing, migration and deposition of gold and the formation of new gold (Kuimova Moiseenko 2006; Reith et al. 2006; Shuster Reith 2018).

## Conclusions

Thus, during more than 80 years, at the base of the dumps of the Novo-Ursk and Beloklyuisk deposits, the secondary enrichment horizon was formed with visible supergene gold. The abundance of sulfide minerals, as well as the size of the grains (about 0.2 mm), affected faster oxidation and release of gold.

The presence of gold particles of nano- and micron size, newly formed phases on the surface of earlier particles, as well as skeletal forms, indicate that gold grew in the wastes.

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## References

- Bolgov GP (1937) Salair sulfides, Ursk group of polymetallic deposits *Izv. Tomsk. Polytechnic Inst.*, №53 (11), p. 45-96 (in Russian)
- Cherepnin VK (1953) The question of the composition and genesis of the ores of the Ursk deposits (Salair) *Izv. Tomsk. Polytechnic Inst.*, 90 p (in Russian)
- Hong H, Tie L (2005) Characteristics of the minerals associated with gold in the Shewushan supergene gold deposit, China. *Clays Clay Minerals*. 53, p 162–170, doi:10.1346/CCMN.2005.0530206
- Kalinin YA, Kovalev KR, Naumov EA, Kirillov MV (2009) Gold in the weathering crust at the Suzdal' deposit (Kazakhstan). *Russian Geology and Geophysics* 50 (3), 174–187, doi:10.1016/j.rgg.2008.09.002
- Kirillov MV, Bortnikov SB, Gaskova OL, Shevko EP (2018) Authigenic Gold in Stale Tailings of Cyanide Leaching of Gold–Sulfide–Quartz Ores (Komsomol'skii Gold-Extracting Factory, Kemerovo Region) *Doklady Earth Sciences*, 481 (2), p. 1091–1094. doi:10.1134/S1028334X18080299
- Kreiter VM, Aristov VV, Volynskii IS, Kreslovnikov AB, Kuvichinskii VV (1958) Behavior of gold in the zone of oxidation of auriferous sulphide deposits *Gosgeoltekhizdat, Moscow*, 268 p (in Russian)
- Kuimova NG, Moiseenko VG (2006) Biogenic gold mineralization in nature and in experiment *Lithosphere* (3), p. 83-95 (in Russian)
- Kovalev KR (1969) Features of the formation of ores of pyrite-polymetallic deposits of the North-Eastern Salair and East Tuva // Candidate's dissertation of geol. mineral. sciences. Novosibirsk, 32 p (in Russian)
- Marescotti P, Carbone C, Comodi P, Frondini F, Lucchetti G (2012) Mineralogical and chemical evolution of ochreous precipitates from the libiola Fe-Cu-sulfide mine (Eastern Liguria, Italy) *Appl. Geochem.* 27 (3), p. 577–589, doi:10.1016/j.apgeochem.2011.12.024
- Myagkaya IN, Lazareva EV, Gustaytis MA, Zhmodik SM (2016) Gold and silver in a system of sulfide tailings. Part 1: Migration in water flow *Journal of Geochemical Exploration*, 160, p. 16–30, doi:10.1016/j.gexplo.2015.10.004
- Nesterenko GV (1991) Forecast of Gold Mineralization by Placers *Nauka, Novosibirsk*, 191 p (in Russian)
- Osovetsky BM (2015) Aggregation of Nanogold Particles in the Environment *Natural Resources Research*, 25(2), p. 241–253, doi:10.1007/s11053-015-9277-9
- Roslyakov NA (1981) The geochemistry of gold in the supergene zone *Nauka, Novosibirsk*, p. 240 (in Russian)
- Reith F, Rogers SL, McPhail DC, Webb D (2006) Biomineralization of Gold: Biofilms on Bacterioform Gold. *SCIENCE VOL 313*, p. 233-236, doi:10.1126/science.1125878
- Reith F, Stewart L, Wakelin SA (2012) Supergene gold transformation: Secondary and nanoparticulate gold from southern New Zealand *Chemical Geology* 320-321, p. 32–45. doi:10.1016/j.chemgeo.2012.05.021
- Smirnov S (1955) The Supergene Zone of Sulphide Deposits. *Academy of Science, USSR, Leningrad*. 332 p (in Russian)
- Shuster J, Reith F, Cornelis G, Parsons JE, Parson JM, Southam G (2017) Secondary gold structures: relics of past biogeochemical transformations and implications for colloidal gold dispersion in subtropical environments. *Chemical Geology* 450, p 154–164, doi:10.1016/j.chemgeo.2016.12.027
- Shuster J, Reith F (2018) Reflecting on Gold Geomicrobiology Research: Thoughts and Considerations for Future Endeavors *Minerals* 2018, 8:401, doi:10.3390/min8090401
- Wierchowicz J, Mikulski SZ, Gąsiński A (2018) Nanoforms of gold from abandoned placer deposits of Wądroże Wielkie, Lower Silesia, Poland – The evidence of authigenic gold mineralization *Ore Geology Reviews* 101, p. 211–220, doi:10.1016/j.oregeorev.2018.07.009
- Yurkevich N, Bortnikova S, Olenchenko V, Abrosimova N, Saeva O, Karin Y (2017) Study of Water-rock Interaction in Sulfide Mining Tailings using Geochemical and Geoelectrical Methods *Procedia Earth and Planetary Science*, 17, p. 112–115, doi:10.1016/j.proeps.2016.12.019