

Typomorphic characteristic of gold from tailings of pyrite-polymetallic deposits of Siberian

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Abstract. The long-term stored tailings of the ore concentration of pyrite-polymetallic ore deposits are an ideal natural laboratory in which it is possible to study the gold transformation from primary ores to supergene with superimposed anthropogenic characteristics. The typomorphic characteristics of native gold are studied on the example of technogenic-mineral formations (TMF) of the Novo-Ursk, Belokluch and Zmeinogorsk deposits (Western Siberia). The grain size distribution of gold and its concentration, morphology, internal structure and chemical composition shows the features of gold conversion in the processes of dissolution, migration and secondary deposition at geochemical barriers.

As a result of a typomorphic analysis, external and internal signs were identified that prove that gold underwent supergene transformations directly in the body of the technogenic tailings. The growths and accumulations of nano- and micro-size gold, the formation of particles of aggregate structure, lamination, fine particles and veinlets, openwork edges, as well as the absence of physical damage on the surface of the golds, confirm the active mobility of gold at the scales of tailings and emphasize the complex nature of multi-stage processes of gold mobilization.

The gold formation of different chemical composition in TMF is explained by specific physical and chemical conditions for the section of the mound of stored waste, different sources of primary gold and geochemical barriers. $\text{Au}(\text{S}_2\text{O}_3)_n^{(1-2n)}$ and $\text{Au}(\text{HS})_2^-$ are the main complexes responsible for the mobility of gold. Gold of low and medium fineness is formed from thiosulfate complexes, whereas high-fineness gold is formed from hydrosulfide complexes.

Keywords: supergenegold, typomorphic features, technogenic mineral formations

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Introduction

The idea that gold remobilization in exogenous conditions was limited, which prevailed for many years, has now undergone a complete change. Evidence of the significant gold mobility in the supergene zone has been proven at a number of deposits in the weathering profiles (Freise, 1931; Petrovskaya, 1973; Roslyakov, 1981; Hong, Tie, 2005; Kalinin et al., 2006; Wierchowicz et al., 2018; Dunn et al., 2019; Kalinin et al., 2019 etc.). The phenomena of active gold redistribution in exogenous conditions are confirmed at the practice of placers mining. At the same time, no significant gold supergene enrichment was observed in a number of exploited deposits, although local concentration is observed almost everywhere.

All of the above applies to the tailing dump and waste, i.e. products of the processing of various sulfide ores (often called technogenic mineral formations (TMF) in Russia (Makarov, 2001; Naumov, 2010)).

The processes of dissolution, migration and growth of gold occurring in the oxidation zones of sulfide deposits and in weathering crusts are analogous to the processes in gold tailing dumps and placer deposits in near-surface conditions. The gold behavior in the tailing dumps depends on the gold forms in the rocks, the way of extracting and long-term storing of the substance (Kovlekov, 2002; Naumov, 2010; Litvintsev et al., 2016; Kuznetsova et al., 2019). Biological and chemical processes in combination with climate and geological conditions determine the physicochemical conditions in the environment and control the processes of dissolution, migration and growth of gold (Reith et al., 2012; Shuster, Reith, 2018; Dunn et al., 2019). The real difference between technogenic and natural processes is the rate of reactions in a limited space of crushed materials – millions of years are replaced by hundreds and tens.

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At the same time, the formed horizons of secondary concentration make it possible to consider waste and tailing dumps as potential (and often real) ore objects.

When studying the Au mobility with the other elements in various exogenous environments, the results of experimental studies, thermodynamic calculations, and direct study of the species of gold occurrence in surface and mine waters are widely used (Plyusnin, Pogrebnnyak, 1979; Roslyakov, 1981; Mann, 1984; Vlassopoulos, Wood, 1990; Shvartsev, Dutova, 2001; Xia, 2008; Zhuravkova et al., 2019). A significant number of publications are devoted to the study of typomorphic gold characteristics and accompanying mineral associations of supergene zones at various deposits (Mann, 1984; Kalinin et al., 2006; Khazov, Petrovskiy, 2007; Banshchikova et al., 2010; Fairbrother et al., 2012; Reith et al., 2012; Litvintsev et al., 2016; Shuster, Reith, 2018; Kuznetsova et al., 2019; Khusainova et al., 2019; Dunn et al., 2019; Khusainova et al., 2020 etc.). A review of the extensive literature on the supergene gold geochemistry shows that there are practically no studies devoted to the typomorphic gold characteristics in the tailing dumps.

The purpose of this work is to study the typomorphic gold characteristics to assess the degree of their transformation during the long-term storage of the Siberian tailing dumps. The following tasks have been solved: 1) to compare and trace the evolution of indicator characteristics of gold in the system “primary ores – oxidation zone – tailing dumps”; 2) to identify specific signs proving the processes of gold transformation in the supergene zone of various objects.

Methods

The work is based on the sampling conducted during field research in 2015–2019 by the Laboratory of Predictive Metallogenic Research (Institute of Geology and Mineralogy SB RAS).

The objects of our research were the embankment of processed ores stored (tailing dumps). The volume of each sample was at least 10 liters. In the laboratory, the substance was enriched by the gravitational method using a pan. The resulting concentrate (“black concentrate”) was brought to a “super concentrate” by washing it in a cup in water. For the convenience of viewing the sample under a binocular microscope (LOMO XC1422), magnetic and electromagnetic fractions were separated from the “superconcentrate” and sieve analysis was carried out according to classes: >1.0, 1.0–0.5, 0.5–0.25, 0.25–0.1, <0.1 mm.

Samples from the Zmeinogorsk tailing dumps are represented by V.P. Bondarenko (IGM SB RAS). Samples of primary and oxidized ores were taken by the authors directly at the quarry of the deposit.

The analytical research was conducted at the

Analytical Center of Multielement and Isotopic Research SB RAS (Novosibirsk). The Au and Ag contents were determined by atomic absorption spectrometry using a 3030 V spectrometer (Perkin-Elmer) and a Solar M6 photometer (Thermo Electron) (analyst V.N. Il'ina).

When studying native gold, specific morphological features were revealed, and signs of transformation were quantitatively evaluated: the nature of the surface, the presence of intergrowths and films. When describing gold, the authors relied on classical works (Petrovskaya, 1973; Nikolaeva, Yablokova, 2007; Osovetskiy, 2012, 2013; Nikolaeva et al., 2015). The study was carried out using a scanning electron microscope (SEM) “TESCAN MIRA 3LMU” (Czech Republic) with an INCA Energy 450+ XMax 80 microanalysis system (Oxford Instruments Ltd) (analysts N.S. Karmanov, M.V. Khlestov) and an electron probe microanalyzer Camebax micro (France), with accelerating voltage 20 Kv, probe current 70na (analyst O.S. Khmelnikova).

Objects of investigation

The objects of research are the tailing dumps from the Ursk ore field (Novo-Ursk (Fig. 1a) and Beloklyuch (Fig. 1b)) (Salair) and the tailings of the gold recovery plant of the Zmeinogorsk deposit (Fig. 1c) (Rudny Altai). The deposits belong to the sulfide type with a well-developed oxidation zone.

Tailing dumps of the Ursk ore field

The oxidation zone of the Novo-Ursk and Beloklyuch deposits was mined for Au and Ag in early 1930 using cyanide solutions.

Deposits (geological structure, morphology and composition of ore bodies, the sequence of mineral formation) has been described by many researchers. It is known that endogenous gold is found in native and bound form in sulfides (Bolgov, 1937; Cherepnin, 1957; Distanov, 1977), and in thin quartz veins. Its sizes do not exceed 0.015 mm. Gold was found in association with chalcopyrite, pyrite, and fahlores (Zerkalov, 1962; Kovalev, 1969), with argentite in quartz (Cherepnin, 1953). The Au content in pyrite is 5.8 ppm (Roslyakova et al., 1983). Pyrite contains inclusions of other ore minerals: galena, chalcopyrite, bornite, arsenopyrite, sphalerite, tennantite, altaite, geffroite, and mercury telluride. Naumannite and Hg selenide inclusions with significant Ag and S impurities were found in barite (Gustaytis et al., 2018). In addition, metallic gold (910 ‰) with Cu (28.6 wt. %) and Ag (61.4 wt. %) impurities was found in pyrite (Myagkaya et al., 2020). Tellurides of Au and Ag, altaite and hessite, are insignificantly developed (Distanov, 1977).

As a result of the formation of the oxidation zone, gold was released, forming native particles, while relative to the primary ores, Au was enriched by 7–20 times, Ag by

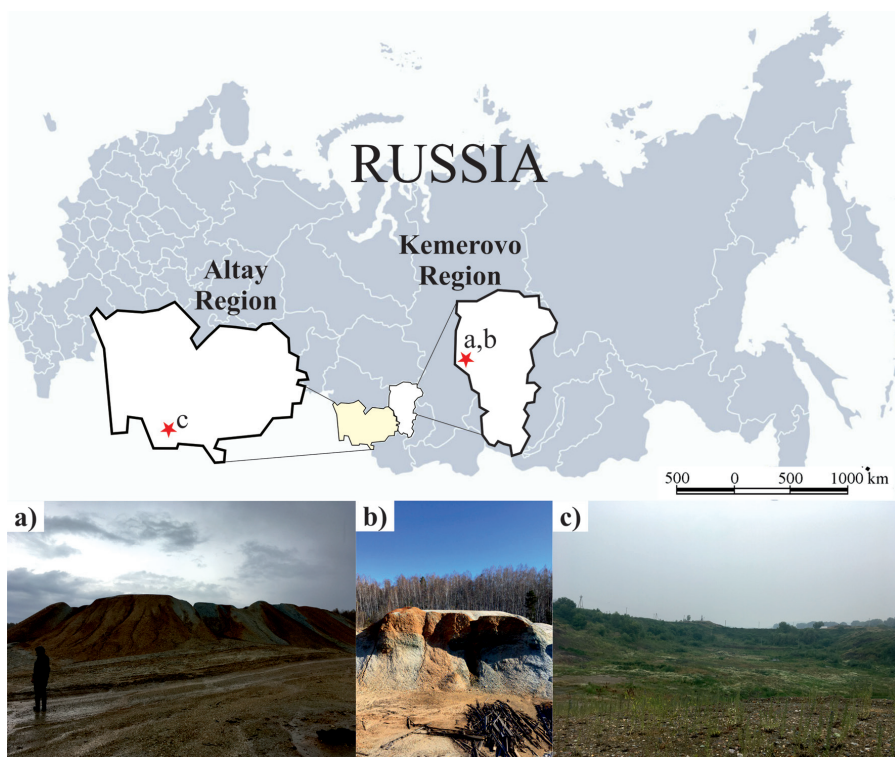


Fig. 1. Geographical location of research objects (marked with an asterisk) and general view of tailing dumps: a) Novo-Ursk; b) Belokluch; c) Zmeinogorsk

5–7 times and As by 2–3 times (Bolgov, 1937; Derbikov, 1937). The oxidation zone is characterized by a high content of Hg, manifested both in native form and in the form of cinnabar. The sources of mercury are fahlores and sphalerite (Kovalev, 1969), as well as tellurides and mercury selenides.

Modern tailing dumps of the Novo-Ursk and Beloklyuch deposits are represented by embankments 10-12 m high with Au content varies from 0.13 to 1.2 ppm; Ag – 0.72–31 ppm. Of the minerals, pyrite, barite and quartz predominate; jarosite, gypsum, goethite, less muscovite, albite, chlorite, and microcline are also present. The streams flowing in the territory of the tailings dump have the following composition: waters – TDS up to 4.8 g/L, strongly acidic (pH 1.8–2.7, Eh 665–760 mV), sulfate, Al-Fe-Ca and contain 2.5 mg/L Cu, 11 mg/L Zn, 110 µg/L Pb, 630 µg/L As, 440 µg/L Se, 28 µg/L Te, 11.4 µg/L Hg, and 18 µg/L Cd (Olenchenko et al., 2016; Myagkaya et al., 2016a, 2016b; Yurkevich et al., 2017). Au concentrations in the drainage brook from the dumps vary depending on the season from 0.2 to 1.2 µg/L, Ag – from 0.01 to 0.3 µg/L. With distance from the dumps in the drainage brook, the pH increases, and the concentration of Au decreases to 0.003 µg/L, Ag – to 0.008 µg/L (Myagkaya et al., 2013).

Ores and tailings dump of the Zmeinogorsk deposit

The tailing dumps of the Zmeinogorsk deposit were accumulated mainly in two stages: from 1904 to 1917 and from 1936 to 1956. The raw materials were gold-

bearing hornfelses, primary sulfide and oxidized ores, in the later period – tailings dumps. Extraction at the factory was carried out in two ways: separation of gravity concentrate followed by amalgamation and cyanidation in the first period and flotation with amalgamation in the second.

The concentrate for processing consisted of primary ores represented by pyrite, chalcopyrite, bornite, galena, gold, silver and oxidized ores including azurite, malachite, cerussite, smithsonite, Fe and Mn oxides and hydroxides (Fig. 2).

Large gold particles (up to 2–3 mm) was found mainly in oxidized ores. Primary sulfide ores contained up to 2.25 ppm Au, oxidized ores 3.2 ppm, and gold-bearing hornfels up to 3 ppm (Polovnikova, 2009). It is noted that the accumulated tailing dumps of ores have been repeatedly processed, the last time being in early 2000.

The tailing dumps of the Zmeinogorsk gold processing plant is located in a kind of “pit”, in the alluvial deposits of the first above-floodplain terrace

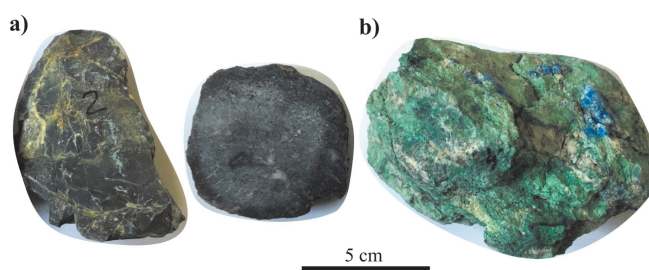


Fig. 2. Ores of Zmeinogorsk deposit: a) primary (gold-bearing cherts); b) oxidized.

of the Korbalikha river. As mentioned above, after the next mining of the tailing dumps in the 2000s, the embankments became low (up to 2 m), gentle, and covered with vegetation. The gold content in the tailing dumps reaches 0.87 ppm. The dump material consists mainly of quartz (50 %), mica, plagioclase, barite, and kaolinite. Sometimes hematite is found, often in the form of pyrite pseudomorphs. In concentrates, malachite is noted in small amounts, as well as oxides and hydroxides of Mn and Fe. Ore minerals include pyrite, chalcocopyrite, bornite, fahlore, and gold.

Results

When studying the typomorphic gold characteristics, special attention was paid to the following parameters: the Au content in the embankment, the size, shape, and micro sculptures of the particle surface, the chemical composition (fineness and trace elements), and Au microstructures (internal structure), which are presented in summary Tables 1 and 2.

Tailing dumps of the Novo-Ursk and Beloklyuch deposits

In the Novo-Ursk tailing dump fine gold prevails, the grade is <0.25 mm (Fig. 3a), while in the Beloklyuch tailing dump, it is > 0.25 mm (Fig. 3b).

Particle shapes include gold grains of isometric (49 %) (Fig. 4a, e, h), elongated (40 %) (Fig. 4 b-d, g, i),

less often flattened (8 %) (Fig. 4f) ones.

Among the micro-sculptures of gold surfaces, one can distinguish: 1) nano- and micron-sized Au build-ups of rounded, irregular, and scaly shapes on the surface of native gold particles and in association with supergene minerals in the form of single or multiple accumulations (Fig. 4d, f); 2) the presence on the Au surface of various supergene new-growth: films and crusts in a composition close to the Au-Ag-S-Se-Hg-phases (Fig. 4b, e); 3) gold intergrowths with grains of barite (Fig. 4g), iron hydroxides, chalcocopyrite, calcite, and quartz (Fig. 4b); 4) sculptures of dissolution in the form of a leached relief (Fig. 4 g-i). For gold from the Beloklyuch tailing dump, micro-laying was found.

Fineness, chemical composition, and internal structure of gold from the Novo-Ursk and Beloklyuch tailing dumps have some differences. Novo-Ursk gold grains range widely from low- to very high-fineness composition with the constant impurity of Hg and Ag, while for the Beloklyuch deposit, only medium fineness gold is found with a complete absence of Hg. In some of the gold grains of these two objects, the Au fineness regularly decreases towards the edges. At the same time, Novo-Ursk grains were consisting of several components, the chemical composition of which varies from low to very high-grade gold. For gold grains of both objects, barite inclusions, openwork edges, and Au build-ups were noted.

<i>Characteristic</i>	<i>Novo-Ursk tailing dump</i>	<i>Beloklyuch tailing dump</i>
The concentration of Au and Ag (average)	Au – 1.1 ppm Ag – 15 ppm	Au – 0.60 ppm Ag – 17 ppm
Morphology of Au particles	1. The interstitial and crystalline forms; 2. Isometric flattened form; 3. Elongated tabular form.	
Surface sculpture of Au	1. Nano- and micron-sized Au particles on the surface of native particles and in association with supergene minerals; 2. Growth sculptures and microlayers; 3. «Sponge» forms; 4. Secondary mineralization, in the form of films (crusts, outgrowths), the composition of which is close to petrovskite, timannite, coloradoite, etc.;; 5. Inclusions of minerals and gold paragenesis with barite, chalcocopyrite, calcite, quartz.	1. Growth sculptures and microlayers; 2. Dissolution sculpture; 3. Porous relief (dissolution sculptures), which are filled with newly formed particles. 4. Inclusions of barite.
Chemical composition (microprobe analysis)	1. Low-grade gold: 643-794 ‰ Au, up to 5 wt. % Hg, up to 27 wt. % Ag; 2. Medium-grade gold: 805-860 ‰ Au, up to 3 wt. % Hg, up to 17 wt. % Ag; 3. Extremely fine gold: 973 ‰ Au, up to 3 wt. % Ag.	1 Medium-grade gold: 847-899 ‰ Au, up to 16 wt. % Ag; up to 0.4 wt. % Hg, up to 0.2 wt. % Cu.
The internal structure of Au	1. Nano- and micron Au outgrowths; 2. «Sponge» forms; 3. Inclusions of barite; 4. Reducing fineness from the center to the edges.	1. Inclusions of barite; 2. The openwork edges; 3. Reducing fineness from the center to the edges.

Table 1. Typomorphic characteristics of gold from the tailing dumps of the Ursk ore field

<i>Object Characteristic</i>	<i>Tailing dump</i>	<i>Primary ore</i>	<i>Oxidized ore</i>
The concentration of Au and Ag (average)	Au – 0.87 ppm; Ag – 21 ppm	Au – 0.7 ppm; Ag – 290 ppm	Au – 15 ppm; Ag – 100 ppm
Morphology of Au particles	1. Idiomorphic lumpy and irregular shape with elements of crystallinity; 2. Isometric flattened form; 3. Flattened micron-thick lamellar crystals; 4. Aggregate form («conglomerates»).	1. Idiomorphic flattened form, sometimes with elements of crystallinity; 2. Crystalline form (crystals, aggregates, interstitial); 3. Irregularly lumpy shaped.	1. Idiomorphic and irregularly lumpy shaped.
Surface sculpture of Au	1. «Sponge» forms; 2. Au outgrowth of nano- and micron-sized scaly, irregular and rounded shapes on Au particles surface and in association with supergene minerals; 3. «Mosaic» gold (in the form of separate blocks with pronounced cracks); 4. Dissolution sculpture; 5. Microlayers (step-growth); 6. Films of various compositions (Fe, Mn hydroxides), intergrowths with barite, muscovite, kaolinite.	1. Au outgrowth of nano- and micron-sized rounded and «sponge» shapes on Au particles surface and in association with supergene minerals; 2. Smooth flat surface; 3. Microlayers (step-growth); 3. Intergrowths of Au with Fe, Mn hydroxides, quartz, barite.	1. Au outgrowth of nano- and micron-sized rounded, «sponge» and irregular shapes on Au particles surface; 2. Intergrowths of Au with malachite and barite.
Chemical composition (microprobe analysis)	1. Particles with a block structure (2 phases): 1 (darker) –up to 42 wt. % Ag, up to 58 wt. % Au; 2 (lighter) –up to 25 wt. % Ag, up to 75 wt. % Au. 2. Particles with a homogeneous composition: 1 –up to 56 wt. % Ag, up to 44 wt. % Au; 2 –up to 34 wt. % Ag, up to 66 wt. % Au; 3 –up to 28 wt. % Ag, up to 74 wt. % Au. Rim –up to 13 wt. % Ag, up to 98 wt. % Au.	1. Particles with a block structure (2 phases): 1 (darker) –up to 66 wt. % Ag, up to 31 wt. % Au, up to 5 wt. % Hg; 2 (lighter) –up to 44 wt. % Ag, up to 50 wt. % Au, up to 6 wt. % Hg; veinlets –up to 16 wt. % Ag, up to 84 wt. % Au. 2. Particles with a homogeneous composition –up to 41 wt. % Ag, up to 72 wt. % Au, rim –up to 24 wt. % Ag, up to 90 wt. % Au. 3. In hydroxide films – inclusions up to 100 wt. % Au.	1. Particles with a block structure (2 phases): 1 (darker) –up to 56 wt. % Ag, up to 39 wt. % Au, up to 2 wt. % Hg; 2 (lighter) – up to 42 wt. % Ag, up to 58 wt. % Au. 2. Particles with a homogeneous composition –up to 44 wt. % Ag, up to 55 wt. % Au.
The internal structure of Au	1. <i>Block («mosaic»)</i> structure (12%); 2. <i>Homogeneous</i> structure (88%); 3. Rim and veinlets up to 10 microns thick; 4. Intergrowths Au with Mn, Fe hydroxides, barite, muscovite, quartz inclusions.	1. <i>Block («mosaic»)</i> structure (40 %); 2. <i>Homogeneous</i> structure (60 %); 3. Inclusions of barite, quartz, bromargentine, acanthine, phenakite, argyrodite, titanite, intergrowths with sphalerite, Mn, Fe hydroxides.	1. <i>Block («mosaic»)</i> structure (90 %), where there are veinlets of higher-grade gold between the parts (80 -90 wt. %); 2. <i>Homogeneous</i> structure (10 %); 3. Inclusions of galena, calcite, intergrowths and inclusions plattnerite in gold.

Table 2. Typomorphic characteristics of gold from Zmeinogorsk ore field

Zmeinogorsk ore field

At the Zmeinogorsk territory, visible native gold was found in primary and oxidized ores and tailing dumps. Using atomic absorption analysis, we have determined a high gold content in oxidized ores, which reaches 15 ppm (Table 2).

Compared to primary ores, the average silver content has decreased up to 10 times in the tailing dump. This is due to the higher migration capacity of silver. At the same time, a significant increase in the amount of fine gold occurs in the tailing dump, due to its predominant precipitation and gradual growth. The

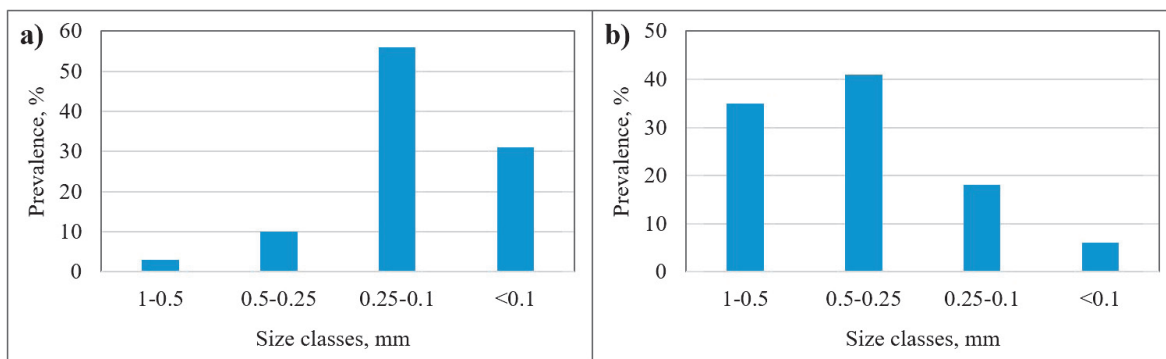


Fig. 3. Distribution of gold particles size classes (mm): a) the Novo-Ursk tailing dump; b) the Belochuch tailing dump

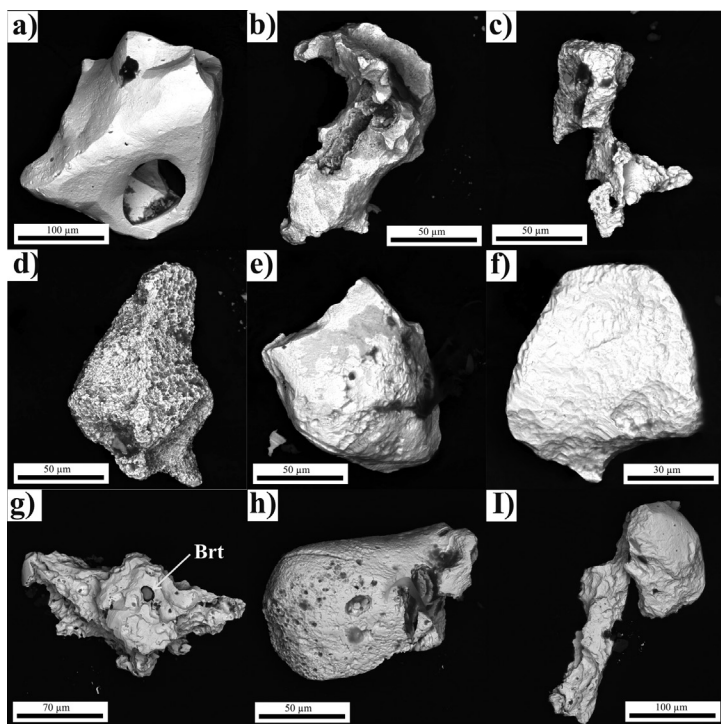


Fig. 4. Morphology of gold particles from the tailing dumps of the Ursk ore field: a-f) the Novo-Ursk tailing dump: a) gold of a crystalline form with a smooth surface and a hole; b) an elongated crystal-like particle coated with a film of Au-Ag-S-Se-Hg composition (gray); c) elongated gold grain of dendritic form; d) gold of a crystalline form and Au overgrowth on its faces; e) isometric gold form with a gray timmanite (HgSe) crust; f) isometric flattened particle; g-j) the Belochuch tailing dump: g) a massive particle with a smooth surface, shell-like fracture, and a barite inclusion (brt); h) a massive particle with a porous relief, in the depressions of which there are rounded new-growth; i) an aggregate particle, consisting of elongated and rounded gold parts.

predominant gold classes are 0.5–0.25 mm and <0.1 mm (Fig. 5).

Primary ores contain lumpy grains with elements of crystallinity, less often flattened particles (Fig. 6 d-f); in oxidized ores there are particles of irregular, lumpy shapes (Fig. 6 g-j). Among tailing dump gold, there is a variety of residual gold from natural ores that have undergone significant supergene transformations (Fig. 6 a-b), and newly formed grains (Fig. 6c).

The surface of gold from primary ores is very diverse due to the multiple transformation processes.

Au grains contain bizarre newly formed nano- and micro-particles of Au, and gold is also found in intergrowths with supergene minerals (barite, clay minerals, Fe hydroxides) in the dumps. The oxidized ores contain gold in association with malachite (Fig. 6i).

The chemical composition and internal structure of gold from the tailing dump is partially inherited from primary and oxidized ores (Table 2).

However, there is a noticeable increase in the thickness of edges and veins (up to 10 μm), a change in their fineness from 900 to 980 ‰.

The distribution patterns of silver are also reflected in the chemical composition of the particles.

For example, in a tailing dump in gold grains with a block structure, the amount of Ag impurity is about 30 %, in primary ores – more than 50 %, in oxidized ones – less than 50 %.

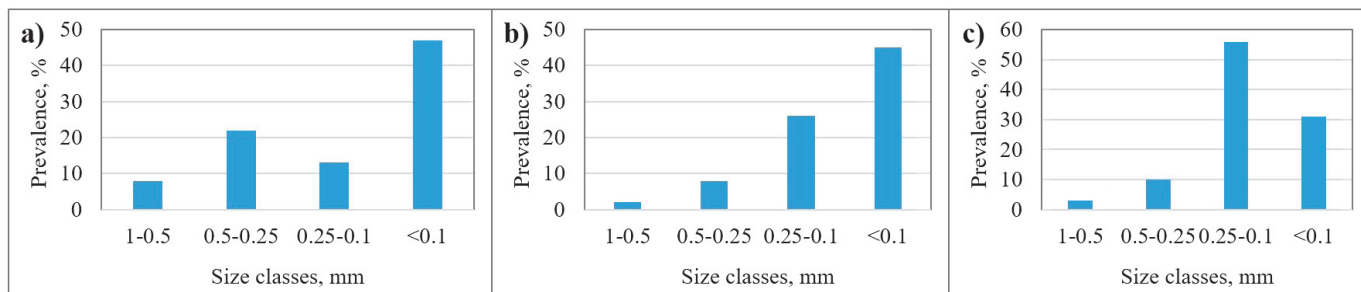


Fig. 5. Gold particle distribution by size classes (Zmeinogorsk deposit): a) tailings dump; b) primary ores; c) oxidized ores

Micro-sculptures of the growth and dissolution of Au particles

For gold from the tailing dumps of processed sulfide ores, the following features, which indicate the transformation of gold were identified. Nano- and microparticles of Au stand out among the growth sculptures.

Their formation is a direct evidence of gold mobility namely in a supergene environment (Osovetskiy, 2012, 2013; Reith et al., 2012; Kirillov et al., 2018; Wierchowiec et al., 2018; Dunn et al., 2019). Newly formed phases of gold on prior particle's surface are presented as single grains and/or clusters of nano- and micro-sizes of different morphological forms (round, oval, elongated). They both are found on flat, smooth surfaces of grains, and on elevations of the relief and depressions, irregularities. Their finding is often associated with secondary mineral associations (kaolinite, Fe hydroxides, and barite) (Fig. 7).

Figure 7e illustrates how grains of various minerals can be trapped during gold growth. For Novo-Ursk and Beloklyuch gold, barite inclusions within Au grains are frequent finding.

Another example showing how gold directly grows in the dump is shown in Figure 8. The newly formed phases of gold are deposited in the form of elongated (oval) particles and form “spongy” formations, which, subsequently, form larger particles.

In addition, “spongy” gold can manifest itself differently on the surface of native particles (Fig. 9).

The elements of layering and hatching on the surface of particles indicate the layer-by-layer growth of gold in the tailing dump (Fig. 10). Visual thickness is $<1 \mu\text{m}$. Layering elements are most often found on crystalline particles.

On the gold surface from the Novo-Ursk and Beloklyuch sites, peculiar funnel-shaped (octahedral) depressions are observed (Fig. 10 d-f). Such formations are called skeletal or Hopper crystals. Their peculiarity is that the edges of the crystals are fully developed, but the inner space is not filled. The funnel-shaped depressions appear when the diffusion limit predominates during growth (Krasnova, Petrov, 1997). The formation of skeletal forms occurs as a result of rapid crystal growth when the voltage is higher at the edges and corners of the crystals than in the center. The formation of skeletal crystals can also be influenced by the chemical composition of the medium, i.e. these processes also take place at a mixed limit of the growth process (with a predominance of the diffusion limit).

Dissolution structures include a pitted surface (Fig. 11) with a fine-meshed and dripstone relief, which is formed as a result of chemical etching of the surface gold layer under the influence of aggressive environmental components (pore solutions).

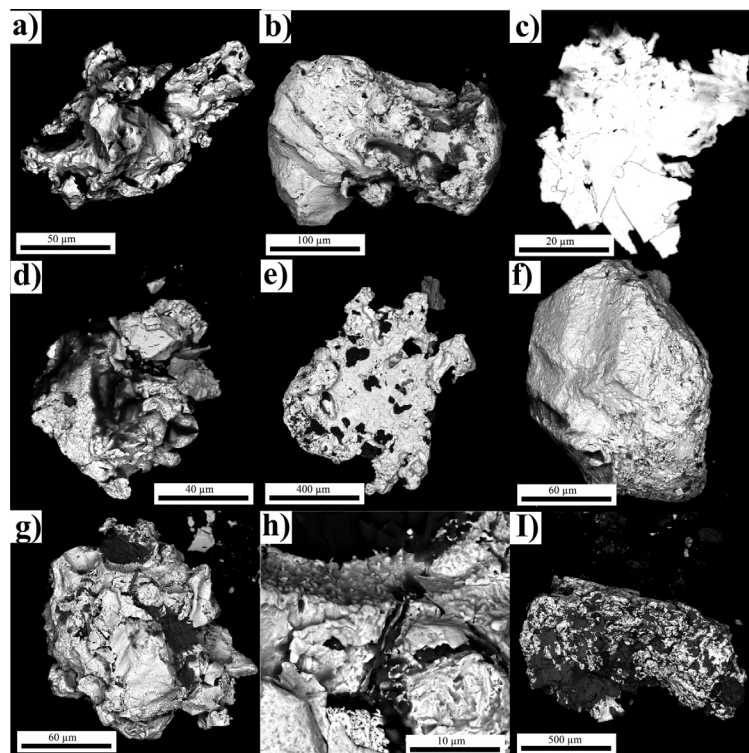


Fig. 6. Morphology of gold particles from the Zmeinogorsk ore field: **a-c) tailing dump**: a) an elongated particle of a lumpy form; b) massive gold grain with a transformed surface and films in depressions; c) flattened plate-like Au particles; **d-f) primary ores**: d) massive particle of lumpy form; e) flattened particle with a pitted surface; f) a grain of crystalline form with Au overgrowth on the surface; **g-i) oxidized ores**: g) massive lumpy grain; h) an enlarged fragment spongy gold; i) a massive particle in intergrowths with malachite.

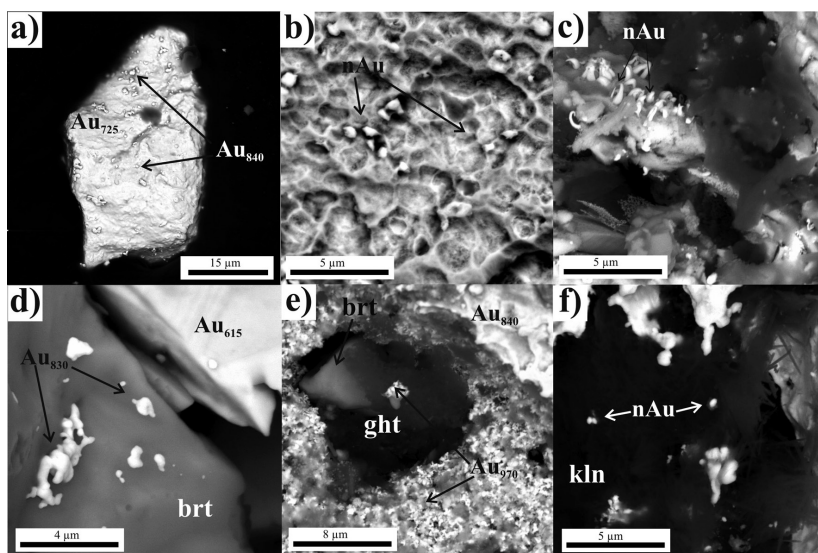


Fig. 7. New formed phases of gold on various surfaces: a) nano- and microparticles of Au, rounded and elongated, on a smooth gold surface; b) Au nanoparticles on the leached gold surface; c) elongated (dendritic) nanoparticles in a loose film of petrovskaite and Fe hydroxides; d) Au nano and microparticles on the barite surface (brt); e) Au nanoparticles of “spongy” shape overgrow on grain of barite (brt), which is covered with a film of Fe hydroxides (ght); f) association of nano- and microparticles of Au in kaolinite (kln).

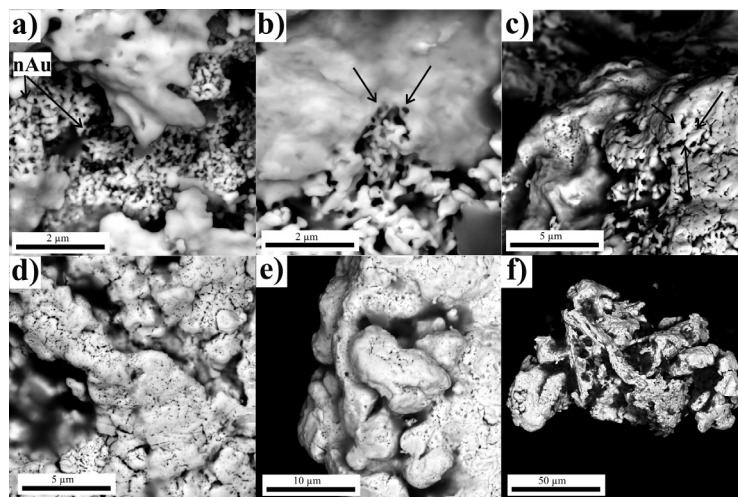


Fig. 8. The mechanism of growth of Au particles of aggregate (globular) structure from the tailing dump of the Zmeinogorsk deposit: a) an accumulation of Au nanoparticles, which, when enlarged and combined, form “spongy” forms; b-c) the combination of massive homogeneous gold and “spongy” accumulations; d) a porous surface on gold, formed as a result of combining nano- and microparticles; e) fragments of individual globules on the surface of the basic gold grain; f) general view of an aggregate structure particle, in the depressions of which films of Fe hydroxides are located.

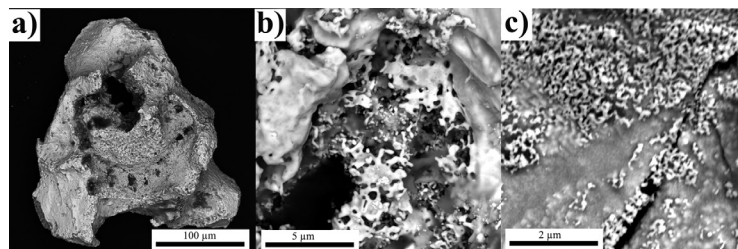


Fig. 9. Elements on native particles: a) the central part of gold consists of “spongy” gold, creating a particle of crystalline shape during growth, i.e. consolidation occurs from the edges to the center; b) amoeba-like forms of “spongy” gold; c) fine “sponginess”.

Supergene new-growth on the gold surface

Isolated films, crusts, outgrowths, and loose formations of different chemical compositions on the gold surface could be combined under the general name of supergene new-growth.

1) *Films and crusts.* Fragile, dark gray to black in color, varying in density. The thickness varies from 3 to 20 μm. Denser crusts (Fig. 10c) visually differ from fine-grained microporous aggregates (films, loose masses) (Fig. 12 a-b, j). Their location is confined to defects

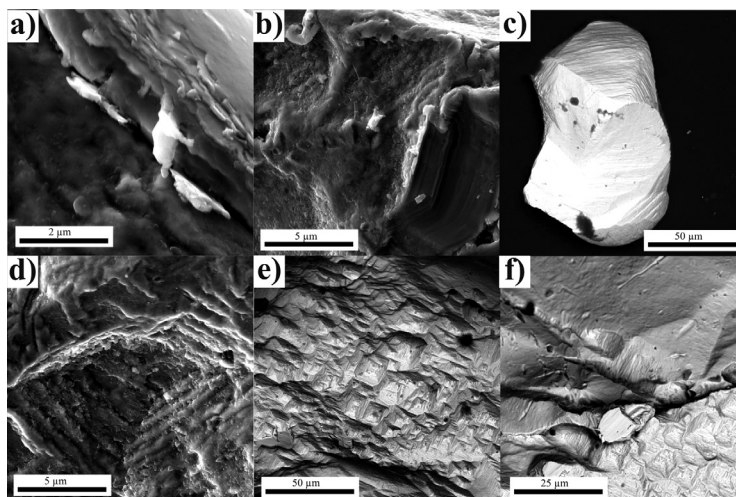


Fig. 10. Structures of layer-by-layer growth on the native particles surface: a-b) nanolayering; c) elements of layering on a gold crystal; d) an enlarged fragment of octahedral shapes, in which a layer-by-layer growth of matter is visible; e) general view of the gold grain surface with many depressions of octahedral shapes; f) transition of octahedral shapes into a smooth flat surface and smoothing (leveling) of layering.

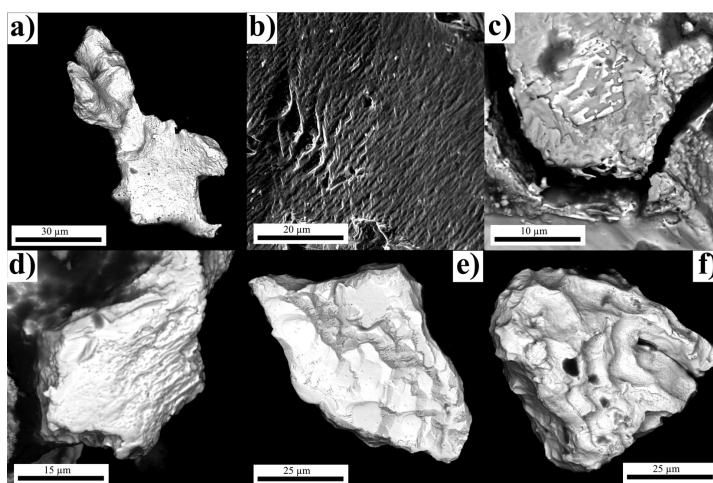


Fig. 11. Dissolution sculptures: a) depressions on the gold surface; b) dripstone surface, the direction of flow of solutions over the surface is shown; c-e) stepped elements formed as a result of dissolution, grooves stand out at the boundaries of the surface levels; f) dripstone surface of dissolution in the form of small ripples.

(depressions, pits) on Au surfaces (Fig. 12a), as well as grain faces (Fig. 12c).

In composition they are close to petrovskaita ($\text{AgAu}(\text{S},\text{Se})$), naumannite (Ag_2Se), and timannite (HgSe). Most often, these formations are poorly diagnosed, due to difficulties in determining the mineral stoichiometry. Sometimes this complexity is explained by the phase mixtures ($\text{Ag}_2\text{S} + \text{Ag}_3\text{AuS}_2$, $\text{AgAuS} + \text{Ag}_3\text{AuS}_2$) or the existence of $\text{Ag}_{2-x}\text{Au}_x\text{S}$ solid solutions (Pal'yanova et al., 2011; Tauson et al., 2018). In addition, the underestimation of the sum in the analyzes is associated with the microporosity of these mineral phases, as well as the appearance of additional mineral phases and products of their subsequent transformations (Nesterenko et al., 1984).

In loose masses one can observe gold micro-dissemination (light particles) (Fig.12b). The films contain impurities of I (3.2 wt. %), Br (3.8 wt. %), Cl (3.9 wt. %), Sb (2.4 wt. %), Pb (3.9 wt. %), Bi

(3.6 wt. %). In addition, utenbogaardite (Ag_3AuS_2) (Fig. 12d) were found in the petrovskaita film and fishesserite (Ag_3AuSe_2) (Fig. 12g) on the gold surface.

2) *Outgrowths*. These are single grains and clusters of irregularly rounded particles, ranging in size from 1-2 to 10 μm . In composition, they correspond to coloradoite (HgTe) (Fig. 12f), montrodoite (HgO) (Fig. 12f) and metacinnabarite (HgS).

3) Loose mineral formations on the gold surface in the form of oxides and hydroxides of Fe, Mn and Pb (Fig. 12i), clay minerals (kaolinite) (Fig. 7f), in which there are single segregations of native gold.

Gold fineness, chemical composition, internal structure

The internal structure of gold particles is a reflection of transformations in the process of growth and dissolution in the environment. The research revealed “spongy” formations, openwork edges and

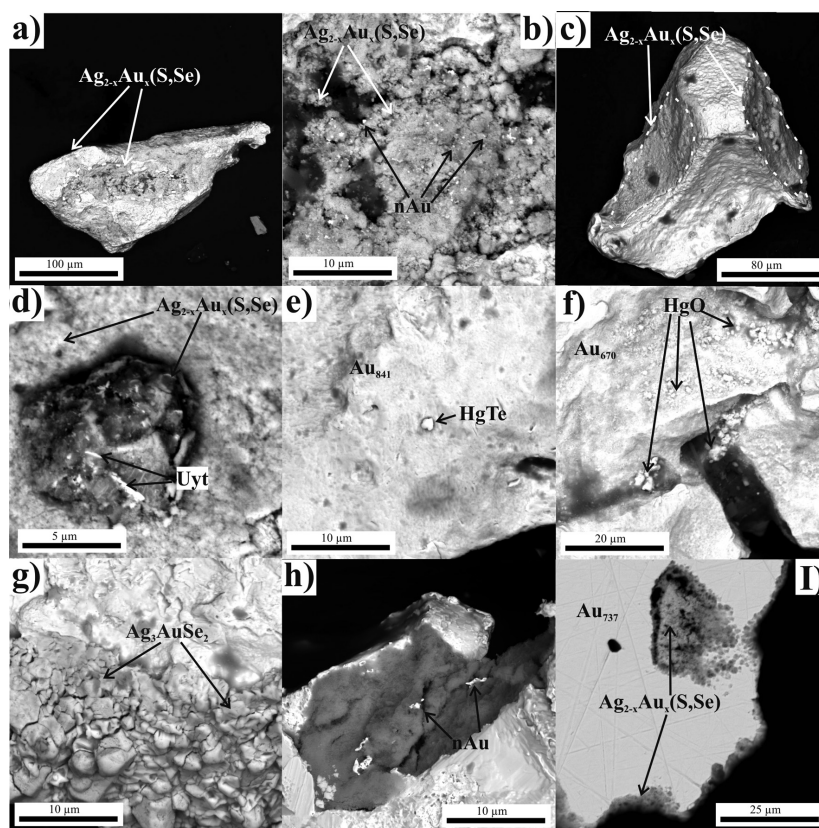


Fig. 12. Supergene new-growths on the native gold surface: a) loose film of Au-Ag-S-Se-Hg composition; b) enlarged fragment “a” with highlighted Au micro-inclusions; c) crusts Au-Ag-S-Se-Hg composition on the edges of gold; d) utenbogaardite inclusion in the $Ag_{2-x}Au(S, Se)$ film; e) outgrowth of coloradoite; f) outgrowth of the montroidite phase; g) outgrowth of fishesserite; h) Fe (Pb, Mn) hydroxides in depressions on the surface of gold with nano-Au precipitates; i) a polished section of gold, in which a small thickness of loose Au-Ag-S-Se-Hg-film can be traced

outgrowths, as well as high-fineness veins and edges (Fig. 13).

For the native gold of Ursk ore field, no characteristic residual cores and high-fineness rims and veinlets were found. The presence of residual particles would prove that the particles under study grew on residual gold grains, as on seeds. Moreover, the presence of high-fineness edges and veinlets could serve as evidence of gold self-purification due to the impurities removal. On the contrary, the opposite pattern is revealed – the gold fineness decreases towards the edges from medium to low fineness (Fig. 13c). At the same time, the aggregate structure of gold grains, consisting of various grains-parts, can be noted (Fig. 13a). Since the chemical composition directly depends on the gold source, the transport mode, and the specificity of the geochemical barrier (Kim, 1975; Osovetskiy, 2013; Nikolaeva et al., 2015), only the presence of a high-fineness composition cannot be an indicator of its “new formation”.

For the Zmeinogorsk object, the following regularity is revealed: in the tailing dump, there is 88 % of gold with a homogeneous composition, while in the primary – 60 % and oxidized ores – only 10 %. Moreover, the characteristic block (mosaic) structure of gold grains in oxidized ores (up to 90 %) is noticeably reduced to 12 % in tailing dump. This indicates an increase in the

gold fineness in the tailing dumps conditions of this composition.

Discussion

In supergene zone, gold is residual (allogenic) and newly formed authigenic. Au undergoes the processes of consolidation and destruction, which are manifested, in sculptures of growth and dissolution respectively. It is often difficult to establish the true nature of the particle’s micro-sculpture and their internal heterogeneous structure (Petrovskaya, 1973; Kirillov et al., 2018; Wierchowicz et al., 2018). However, the key difference between these processes is that dissolution acts primarily on surface defects and sub-grain boundaries, while growth occurs as a result of repeated nucleation of Au nanoparticles followed by their aggregation (Falconer, Craw, 2009).

Therefore, there are a number of external and internal signs proving that gold has been transformed. The first includes such morphological changes as:

1) *presence of Au nanoparticles* (Osovetskiy, 2013; Shuster and Reith, 2018; Wierchowicz et al., 2018). Nanoforms are components of colloidal or ionic solutions that precipitate at various geochemical barriers and contribute to the formation of geochemical anomalies in the form of secondary enrichment horizons.

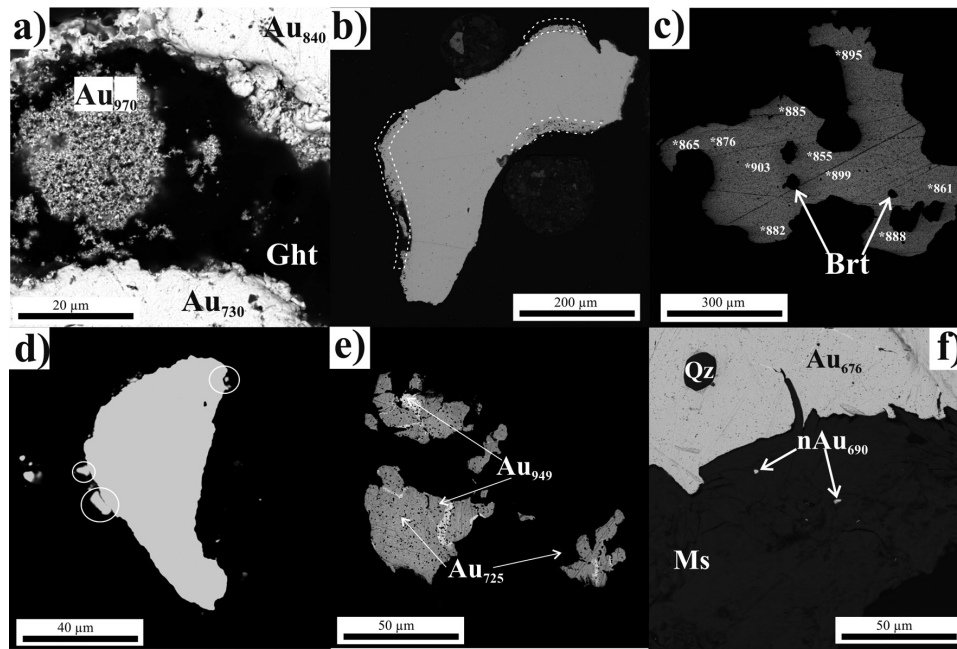


Fig. 13. Internal structure of particles: a) massive particle gold, inside which there is a fragment of “spongy” gold in a loose mass of Fe (Ght) hydroxides. Along the boundaries of massive gold, an increase in “spongy” Au is seen; b) openwork edges; c) inclusion of barite (Brt) inside the particle and distribution of fineness; d) nano- and micro-growth of Au on the surface of gold; e) streaks of high-grade gold inside the particle; f) Au microinclusions in muscovite (Ms).

They can be confined both to the surfaces of native gold particles and to secondary mineralization (films, clay minerals, etc.). Nanogold is most often considered to be of high fineness (Reith et al., 2012; Wierchowicz et al., 2018). However, it has been shown (Kim, 1975; Osovetskiy, 2013; Nikolaeva et al., 2015) that gold nanophases have a wide range of chemical composition, not always tending to 100 % pure Au. In this case, the chemical composition of gold matrix and nanoparticles on its surface may coincide.

2) *presence of various types of Au new-growth of different shapes and sizes on the Au grains surface.* They can have worm-like, rounded, needle-like, crystalline, “spongy” and other forms (Osovetskiy, 2012; Litvintsev et al., 2016; Shuster et al., 2017; Dunn et al., 2019). Their sequential concentration and enlargement occurs from nanosized to visible precipitates, namely, clusters form spheroids, spheroids – aggregates, and the latter form independent precipitates of complex and simple forms (Falconer, Craw, 2009; Osovetskiy, 2013; Kuznetsova et al., 2019).

3) *layering and crystalline particles form* (Krasnova, Petrov, 1997; Khazov, Petrovskiy, 2007; Osovetskiy, 2012). One of the signs of newly formed gold is the absence of mechanical deformation and the retention of the shape acquired during crystallization. This shape is determined by the age ratio of gold to the surrounding minerals. Layering indicates the stagewise growth of new portions of the substance.

4) *“aggregate” and granular particle structure* (Naumov, 2010; Osovetskiy, 2012; Kuznetsova et al., 2019). These gold grains show a visual mechanism

for the consolidation and gold growth in a supergene environment. Consolidation can occur both through mechanical and biochemical processes. The particles of different ages are interconnected with the help of unstructured gold and are very fragile and difficult to diagnose (Osovetskiy, 2013).

5) *presence of newly formed gold phases in association with supergene minerals* (Kalinin et al., 2009; Nikolaeva, Yablokova, 2007; Osovetskiy, 2012, 2013; Reith et al., 2012; Nikolaeva et al., 2015). This paragenesis point to joint growth and similar physicochemical conditions of existence in a supergene environment. For example, during the oxidation of sulfides, iron hydroxides are simultaneously formed and the gold contained in them is released. In addition, clay minerals are capable of sorbing gold on crystal lattice defects.

6) *presence of secondary (Au-Ag-S-Se-Hg) mineral paragenesis on the gold surface in the form of films, crusts.* Their formation occurs as a result of the interaction of gold layer surface with a specific technogenic fluid, consisting of a mixture of liquid and gas phases. The vapor-gas flows released from the Ursk and Beloklyuchevsk tailing dumps contain sulfur-, selenium- and nitrogen-containing gases (Yurkevich et al., 2019), which, in combination with pore solutions, actively transform gold grains, dissolving their surfaces and redeposited new mineral phases. Gold microparticles in petrovskaitite films play a significant role in Au mobility. The presence of Cl, Br, I in these mineral parageneses proves the role of supergene processes (Kuzhuget, 2014, 2018).

However, it cannot be ruled out that this passivating

layer (Au-Ag-S-Se-Hg composition) on the surface of native gold can be formed as a result of the technological extraction of gold (Senanayake, 2004; Birich et al., 2019; Wang et al., 2019).

7) Among the internal changes, the *formation of high-grade rims and veinlets* is most often distinguished (Petrovskaya, 1973; Nesterenko, 1991), which are characteristic of gold grains in placers and oxidation zones. Their formation is explained by the electrochemical process of gold purifying from impurity elements. In this process the behavior of Au and Ag is different and is explained by the fact that the dissolution of Ag occurs in the diffusion model, while for Au it is the result of the solubilization process. The presence of high-fineness veins and rims on gold from the dump proves particle transformation processes. In addition, the discovered openwork edges, inclusions of grains, intergrowths of microparticles with the surface, and “spongy” formations can also be attributed to the internal signs of gold transformation, which indicate active particle growth.

All of the above features are evidence of significant supergene gold transformations directly in the tailing dumps, including its remobilization and precipitation up to the formation of horizons of secondary gold enrichment.

The use of cyanidation and amalgamation for gold recovery has a direct impact on the transformation of gold during the long-term storage of processed ores. Cyanides and mercury in the dump are catalysts for chemical interactions since they persist under buried conditions for tens or more years (Gas’kova et al., 2000; Naumov, 2010; Kuznetsova et al., 2019, etc.). However, it is often difficult to identify the role of certain factors in gold transformation.

The results of the carried out studies make it possible to expand the understanding of the conditions of gold migration and forms of its redeposition, as well as to suggest the physicochemical mechanisms of this process. In essence, they are similar to those that appear in natural oxidation zones. However, they lead to a wider variety of mineral species and morphology of precipitates. An abrupt change in redox conditions in such dumps has a pronounced seasonal component (Dunn et al., 2019), which makes a significant contribution to the transformation of processed ores.

Gold is dissolved by a number of oxidizing agents in the presence of a number of ligands (L), with the formation of compounds of the type $Au(I)L_2$ and/or $Au(III)L_4$. Under supergene conditions, chloride, thiosulfate, and high molecular weight organic humic and fulvic acids predominate (Boyle, 1979; Roslyakov, 1981; Mann, 1984; Hough et al., 2007; Shuster, Reith, 2018). In this case, the thiosulfate ligand plays a significant role only in the short-term mobilization in a supergene environment due to their oxidation (Craw,

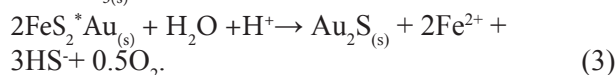
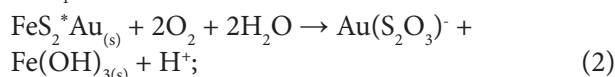
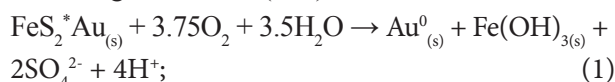
Lilly, 2016; Kharlamova, 2018; Liua et al., 2020). When ores are cyanidized in alkaline solutions (pH 11), cyanide and hydroxo- complexes will be stable for a long time in the tailing dumps systems (Gas’kova et al., 2000).

As studies (Naumov, 2010; Litvintsev et al., 2016; Wierchowicz et al., 2018; Kuznetsova et al., 2019; Khusainova et al., 2020 etc.), have shown, the main factor in gold solubilization is the particle size and form of occurrence in primary ores. This transition depends on the solubility of gold itself, the chemical activity of the medium, and the resistance to chemical weathering of its carrier minerals. Mainly, finely dispersed gold with a particle size of less than 0.1 μm passes into the solution, and grains with a size of 2-3 μm to 0.2 mm do not undergo dissolution, since they have increased stability (Roslyakov, 1981).

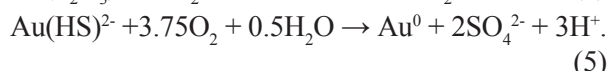
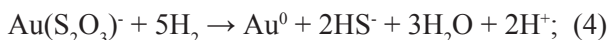
Because of the gold transition into solution, there is differentiation by mobility into difficult, easy and mobile forms (Roslyakov, 1981). The first gold is firmly bound to clay minerals and migrates with them due to mechanical movements under the action of gravitational forces. Mobile gold is found in pore solutions in the form of stable organo-complex compounds. In general, pore solutions contain a variety of electrolytes that promote the coagulation of colloidal gold particles and the formation of different particles morphology. Highly mobile gold is represented by the inorganic complex compounds and true colloids, and it is most influenced by Eh-pH conditions.

When the physical and chemical parameters of the medium change, gold is deposited, forming native solid phases. Only with sharp change in these conditions secondary gold enrichment horizons can be formed. Since Ag is a more mobile element, it can either form Ag-containing mineral phases or be carried away from this system, subsequently concentrating on another geochemical barriers.

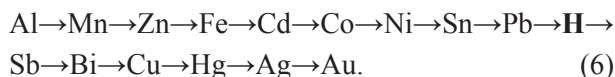
Au leaching from residual sulfide minerals acts as a continuous source of Au in the environment. In this case, gold will be released from pyrites as Au^0 and Au_2S as follows, respectively, under oxidizing, intermediate and reducing conditions (1–3):



Thiosulfate complexes are oxidized to sulfate or hydrosulfide ions and native gold, depending on the Eh-pH of environmental conditions (4, 5). This will lead to the enlargement of gold grains or the formation of aggregates, depending on the presence of seeds and the diffusion filtration mode of the solution.

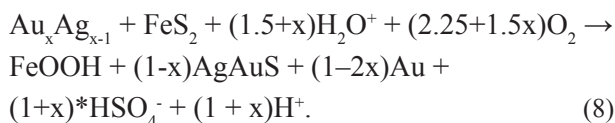
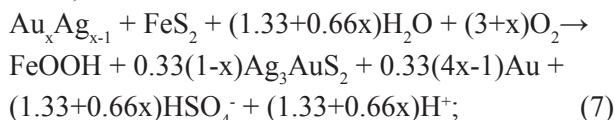


Comparing the reaction (4, 5) and fragments of the electrochemical series of activities of metals (6) that it can be understood that in the case when inert gold is already crystallizing, other metals migrate in the solution and will fall out only in the order of their sequence.



As mentioned above, $\text{Au}(\text{S}_2\text{O}_3)_n^{(1-2n)}$, where $(1-2n)$ is the valence of the complex, are metastable and can be transported over short distances within the sediment profile, and destabilization occurs through: 1) thiosulfate-oxidizing bacteria that use thiosulfate as an energy source (reductive biomineralization of gold) (Lengke, Southam, 2005; Etschmann et al., 2016; Shuster et al., 2017); 2) the presence of such reducing agents as organic matter and Fe^{2+} ions; 3) with a decrease in pH, when gold is reduced with the deposition of native particles on the already existing surface (Hyland, Bancroft, 1989; Mycroft et al., 1995).

These processes, enhanced by the gas phase participation, explain the presence of Au-Ag-S-Se-Hg film mineralization on gold particles surface in the dumps, represented by such minerals as petrovskaite, yutenbogaardite, naumant, timannite, and fishesserite. Their formation occurs by reactions (6, 7) (Savva et al., 2010):



The formation of different gold generations is influenced by the geochemical barriers (Kirillov et al., 2018, Khusainova et al., 2020). The formation of Ag-containing (14-20 wt. % Ag) native Au is the result of the decomposition of mixed thiosulfate complexes of the type $(\text{Au},\text{Ag})(\text{S}_2\text{O}_3)_2^{3-}$. The evidence is provided by films of $\text{Ag}_{2-x}\text{Au}_x\text{S}$ composition on the surface of gold grains with nAu inclusions (Fig.12b). Upon further exposure to acidic solutions, Ag-containing secondary Au undergoes redissolution in the form of hydrosulfide complexes and redeposition. The higher solubility of Au under acidic oxidizing conditions leads to the deposition of several generations of extremely high-fineness Au of different morphology upon changing conditions. This is confirmed by the association of “spongy” gold with Fe hydroxides on the surface of massive gold (Fig. 9a, 13a).

Conclusion

The main typomorphic gold characteristics from processed sulfide ores of Siberian deposits are considered. The results confirm supergene gold mobility inside the tailing dumps and the complex multistage processes of gold dissolution and re-precipitation.

Among the typomorphic similarities, the following stand out: 1) an increase in the amount of the fine gold; 2) the presence of well-preserved Au outgrowths of nano- and microscopic forms; 3) variable chemical composition of newly formed phases (from low to very high fineness); the composition of new precipitates and matrix gold can be the same or radically different; 4) the presence of layer-by-layer growth; 5) the absence of physical damage on the newly formed particles.

Among the typomorphic differences, the following stand out: 1) for the Novo-Ursk and Beloklyuchevsk tailing dumps: a) the presence of Au-Ag-S-Se-Hg mineralization on the surface of the gold grains, which indicates a specific physicochemical conditions of gold migration as thiosulfate complexes; b) the zoning of the chemical composition (fineness decreases towards the edges), there are no residual cores; c) inclusions of barite grains and its overgrowth with gold both on the surface and inside the particles. 2) for the Zmeinogorsk tailings dump: a) a significant decrease in the Ag content in ores: in primary (290 ppm) and oxidized (100 ppm) ores and processed (21 ppm); b) the formation of aggregate gold grains, which are absent in primary and oxidized ores; c) the increase in the thickness of veinlets and their chemical composition (up to 98 wt. % Au) in the particles.

Because of the long storage of tailing dumps containing pyrite and other sulfide minerals, there was a significant transformation of the tailing dumps and redistribution of precious metals (Au and Ag) during water-rock interaction. The presence of gold-bearing sulfide minerals, as well as small size of their grains, contributed to rapid oxidation and deposition of gold when changing physicochemical conditions.

The chemical composition of newly formed gold phases directly depends on the gold-containing association of minerals. The tailing dumps of pyrite-polymetallic deposits contain gold of different chemical composition: from low-grade to very high-grade. Due to the moderately acidic and fluctuating redox nature of tailing sediments, $\text{Au}(\text{HS})_2^-$ and $\text{Au}(\text{S}_2\text{O}_3)_n^{(1-2n)}$ are the main complexes responsible for gold mobility. Mixed thiosulfate complexes can be responsible for the precipitation of medium fineness gold, and hydrosulfide complexes - of high fineness gold.

The obtained typomorphic gold characteristics can be used by enterprises to create schemes for enrichment and extraction of metals, as well as to control the formation of zones with local (increased) metal concentrations.

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