

Hydrogenic processes of autigenic mineralization of native gold of the Ural placers

Svetlana Kovrizhnykh¹, Vladimir Naumov², Dmitriy Abroskin³

¹Perm State National Research University, Bukireva, 15, 614990, Perm, Russia, sveti5@rambler.ru

²Natural Science Institute of Perm State University, Genkel, 4, 614990, Perm, Russia, naumov@psu.ru

³UralStroyProgress, Ekaterininskaya, 66, 614045 Perm, Russia, da@ohl-gut.ru

Abstract

In the article the processes of formation of “new” autigenic native gold are considered. The forms of manifestation of noble-metal mineralization in the Ural placers are also taken into consideration. The studies of gold deposition at cryogenic and evaporative geochemical barriers (Australia, New Zealand, Canada) are exemplified. The influence of microorganisms, bacteria and fungi on the processes of gold dissolution, transfer and accumulation are shown as well. The history of the Urals during the formation of Mesozoic weathering crusts and the development of peneplain with the formation of laterites is demonstrated. The mechanism of modern processes of technogeogenesis is given.

Key words: native gold, autigenic gold, cryogenic barrier, evaporative barrier.

Introduction

The natural processes of formation of “new” autigenic native gold are quite widespread, but it is difficult and ambiguous to identify them. Earlier it was noted that in the Ural gold - platinum placers noble-metal mineralization is almost always present in the several facies (forms of manifestation) - clastogenic and autigenic. The clastogenic mineralization is observed in the form of rounded clastic particles of native gold and platinoids. The nature of allotigenic clastogenic gold is determined by its mechanical release from hydrothermal veins of gold-quartz low-sulphide formation, from gold-bearing ores of gold-sulfide low-quartz formation at the orogenic and post-orogenic stages of formation of the folded system of the Urals. The autigenic form of precious metals is represented by gold pellicles passively growing on the clastic particles, and kelpite borders, metasomatically replacing clastic gold particles (Khazov et al., 2010). Autigenic gold is formed from the mineralized water due to the destruction of ores of the gold-sulphidic low-quartz and gold-pyrite formations. In some cases, the autigenic mineralization of gold is manifested in the form of independent clastogenic aggregates

of nano - and micro-gold or growths on the surface of gold particles and platinoids; microorganisms, bacteria and fungi are involved in its formation. The mineralization was established for the territory of the Upper-Kama depression (Naumov et al., 2003; Naumov, Osovetsky, 2013; Osovetsky, 2012, 2013) and the gold particles from technogenic-mineral formations and zones of noble-metal mineralization of the Ural placers (Naumov, 2010; Naumov, etc., 2011).

The problem of gold in the hydrosphere and the relationship of the liquid phase of hydrogenic gold with the solid phase placer gold is not new. The problem of “growth” and “destruction”, the dissolution and deposition of gold in placers, many studies are devoted and there are different opinions. The background and anomalous distribution of gold concentration in the surface and groundwater is uneven. The gold content in the hydrosphere for all types of fresh water is stable and makes up $3.0 \cdot 10^{-9}\%$. The increased content of the dissolved gold is found in slightly acidic, neutral or slightly alkaline bicarbonate and sulfate waters. In recent years, the works on the higherhydrogenic mineralization with the gold of surface and groundwater of the gold ore and gold placer

areas in the permafrost development zone, have appeared (Amosov, 2000; Alexandrov, 2007; Fedoseeva, 2000).

In the hydrochemical studies of the influence of cryogenic processes on the formation of water flows of gold scattering by A. V. Plyusnin and his colleagues (1979) is shown that its concentration in ordinary water is 6.6×10^{-7} g/L, increases to 11.2×10^{-7} g/L in melt water and reaches 15.0×10^{-7} g/L in the waters subject to pre-freezing to the temperature of -6°C . The increased acidity of the solutions contributes to the dissolution, migration of gold. Under certain geochemical conditions, it is deposited. The gold deposition is controlled by geochemical barriers: oxygen, reducing, sulphate, carbonate, alkaline, carbon, sulfide, evaporative, cryogenic, sorption or their combinations.

Different bioforms, microorganisms and fungi also participate in the process of dissolution, transfer and accumulation of gold. An example of this is the study by Jeremiah Shuster and et al. (2012). They studied gold in Australia (Queensland) and found that biogeochemical processes stimulate the cyclization of gold through dissolution and re-deposition reactions that lead to the conversion of gold into near-surface media. It was found that the microcracks on the surface of the grains are filled with organic and clay minerals, in which gold colloids and octahedral gold plates of nano- and micro-size are embedded. The formation of these secondary gold structures is explained by the deposition of gold due to the action of reducing agents such as microbiota, residual organic matter and clay.

The study of S. M. Zhmodik and others (2012) obtained new data on the role of micromycetes in the concentration and distribution of gold and platinum in the iron-manganese nodules of the world ocean. Inside the colony of fungi there are three forms of distribution of gold and platinum: 1) in the form of point concentrators (mainly for gold); 2) scattered without a clear dependence on the structure of the colony (manifested poorly for gold); 3) scattered with the concentration in the peripheral parts of the colonies and in spores (common for platinum).

The biogenic factor in the formation and

transformation of gold-bearing eluvium is undoubtedly included, but its role is still debatable. Some researchers believe that the participation of microorganisms in the transformation of matter, including native gold in the hypergenesis zone, is insignificant (Dilabio et al., 1988), others - emphasize its important role (Shkolnik et al., 2004; Southam et al., 2009; Mayorova et al., 2010; Bluman, Ibrahimova, 2010, etc.).

For arid conditions in the eight regions of Australia L. Fairbrother et al. (2012) investigated the influence of biogeochemical processes on the conversion of gold grains. In the subtropical and tropical climate there is a continuous processing, isolation and dispersion of gold and the subsequent deposition of gold nanoparticles to form biofilms on gold grains. In these parts, the availability of water and nutrients is limited and sporadic. Therefore, abiogenic evaporative mechanisms control the formation of secondary gold and especially gold nanoparticles. The biofilms able to transform grains of gold, are occasionally developed on the grains of gold in dry conditions. Their research shows that the processes involving microorganisms play an important role in the transformation of gold grains and contribute to the dissolution and deposition of gold. Microorganisms affect the formation of geochemical anomalies in arid conditions.

Frank Reith et al. (2012) studied the gold sampled in the six locations in the southern New Zealand. Based on the fact that biogeochemical processes lead to the transformation of gold in surface conditions, they evaluated the connection between the morphology of the surface of gold grains and the processes of conversing of supergen, paying special attention to the formation of gold nanoparticles in temperate climates. Signs indicating the dissolution of gold and silver were found, for example, dissolution of grain boundaries was observed on all grains, as well as a high content of tumors and gold aggregates. They revealed that climatic conditions with high rainfall enhance the transformation of gold grains (coating with bio pellicles, secondary gold, silica and carbon deposits on the surface of

transforming gold grains) and in the soil. Also they cleared up that the dissolution of gold in seawater and bio-mineralization with the participation of microorganisms are important factors affecting the change of gold in the sediments of beach placers. They found that the surface morphology of gold grains from New Zealand is the result of supergenic transformations occurring in modern conditions. The formation of gold nanoparticles, which was previously thought to be caused by evaporation occurring in high rainfall conditions, is likely to occur as a result of other mechanisms such as biomineralization.

Methods

Structural-tectonic and geomorphological analyzes were used at the regional and local levels to identify zones and areas favorable for the development of placer gold-bearing (Sigov, 1969; Naumov, 2010). Gold concentration studies have been conducted at placer development sites. Sampling, gravitational enrichment and extraction of free gold, including small and thin classes, were carried out according to the methods of Perm University (Lunev, Osovetsky, 1979; Lunev et al., 2000; 2003; Naumov et al., 2010). For particles of free gold and films, the mineral and chemical composition, structure, and structure were determined, including electron microscopy. Theoretical analysis and experimental work were carried out to determine the conditions and mechanisms for the dissolution, transfer and accumulation of gold-bearing phases in the evaporation and cryogenic barriers. (Naumov et al., 2010; Naumov, Husainova, 2017; Naumov, Osovetsky, 2017).

Results

The formation of natural gold placers in the Urals began at the post-construction stage of the folded system. The Mesozoic placer cycle clearly emerged, which appeared in the hot era of crust formation. The placers of gold of this time are characterized by increased productivity. A substantial role of the influence of the evaporation barrier, enlargement and formation of clastogenic gold particles is likely.

In the early Mesozoic (Triassic), in the period of intensive tectonic movements at the final stage of Hercynian orogenesis, erosion-denudation activity in the form of mechanical destruction and removal of material (physical weathering) substantially prevailed over the processes of chemical weathering. The release of the useful component from the bedrock was incomplete. The increased concentrations of gold were not formed. The average gold content in the terrigenous strata of the lower Mesozoic is close to its average content in eroded indigenous sources.

In the late Mesozoic tectonic stabilization of the territory and humid climate provided the predominance of chemical weathering processes, which led to intensive corrosion (peneplenization) with a very perfect mechanical sedimentary differentiation. Mainly alluvial placers were formed.

In the terms of humid climate and intensive chemical weathering the favorable conditions for the working out of erosion nets are created. The tectonically weakened zones of high-permeability faults, tectonic thrusts, ledge and other dislocations are the least resistant to the exogenous processes; zones of lithologic and stratigraphic contacts are represented by different physical properties of the rock complexes — development areas of carbonate, sandstone and shale strata.

The distribution of linearly weakened zones is subordinated to themeridional elongated Hercynian structures of the Urals. Therefore, the primary late Mesozoic river network began to form on them and has a meridional orientation (longitudinal valleys), often spatially coinciding with the zones of development of indigenous gold-platinum mineralization. The erosion-structural depressions are formed in the negative structures. They are filled with the late-Mesozoic terrigenous complexes of genetic series from eluvium to alluvium and preserved complex gold-platinum placers. Due to the substantial duration of these processes, Mesozoic erosion-structural depressions accumulated a substantial amount of released metal.

In the Cenozoic, especially in Pliocene-Quaternary time, as a result of the evolution of the river network and river interception

the transverse (relative to the Urals) valleys were being formed. In the process of erosion of Mesozoic deposits, there was a redeposition of useful components and their accumulation in the young strata of the Paleogene-Neogene-Quaternary age, often with the formation of industrial placers. Such placers linked with transverse valleys spatially coincide with the Eastern zone, which is the continuation of the Chusovskaya structural-erosion depression. Pliocene-Quaternary alluvial deposits (PP. Wilva, Srednyaya and Severnaya Rossoha, Bolshaya and Malaya Saldinka) - Promyslovsko-Kushvinskaya group, are distinguished by a good sort of gold and platinum, by large size, and are set in modern valleys Gornozavodskii district (Kopylov et al., 2015).

During seasonal freezing of alluvial precipitation in the Quaternary and in connection with the stages of glaciation and interglacial, the processes of authigenic mineral formation and the formation of golden crust and raids are probably also intensified. An example is the study conducted in Canada. Several Quaternary glaciations in the Yukon have been described, which are divided into three stages, commonly known as pre-RAID, Reid, and McConnell. The covers of pre-RAID glaciation are overlain by deposits, which are known in the Yukon as the White Channel Gravel and localized along the streams Hunker and Bonanza. Taking into account the morphology and nature of the surface, four types of gold particles are distinguished. First type are dense massive grains with rounded edges, numerous inclusions of quartz grains and geometrically correct replicas. The last ones record the location of the quartz crystals or gold of the next generation. The gold of this type is characterized by the relatively smooth surface. Its peculiarity is revealed in the presence of numerous thin-platy and lamellar bevels. This type of surface may appear in the result of the formation of gold from supersaturated gold-containing solutions at the cryogenic geochemical barrier. The formation of gold films on the grains of heavy and light fraction minerals in the white Chanel Gravel deposits was previously noted by different researchers (Patyk-Kara, 2008).

For the development of these concepts the mechanism of cryogenic gold deposition in glacial conditions is proposed. It manifests itself in the form of a "capture" by the gold matrix of grains of other minerals or by filling the voids with gold in the primary matrix of a heterogeneous material, where gold acts as cement and performs the intergranular space. On the surface of gold grains of this type there are raids, primers and aggregates of hypergenic minerals (Naumov et al., 2010).

The parallel geochemical bound process of crusts and raids formation of iron and manganese hydroxides is the result of surface interaction of gold-bearing phases with ore solutions enriched with these elements. Iron-manganese phases form raids and crusts on gold, act as cement, forming larger aggregates.

Modern processes of technogeogenesis are manifested in the areas of working out of copper gold-copper porphyry and related epithermal gold deposits. Man-made waste water enriched in siderophilic and chalcophile different elements are formed. They enter the horizons of groundwater and surface water. Along with them is dissolved gold in low concentration.

As a result of such activities, solutions enriched with metals are formed, which are obtained during the leaching of ores during the technological processes of their enrichment. At the same time, they spend substantial energy resources to extract the rock from the Deposit, transport the ore to the ore-processing plant, conduct crushing, abrasion of the ore, and obtain gravitational and flotation concentrate. Then process the concentrate with transferring metals into the liquid phase and only after that extract the metals. Under waste and man-made waters actions on destruction, transfer and transfer metals in solutions are carried out by natural geological agents, activated by human technical activities. Thus formed solutions are human-activated hydromineral raw materials of different metals. When processing large volumes of hydromineral raw materials, it will be economically advantageous to extract it on an industrial scale using artificial geochemical barriers.

In the history of the Urals during the formation of Mesozoic weathering

crusts and the development of peneplains laterites are formed, within which for a much longer period of time such processes happened (destruction, transfer and metal accumulation). This mechanism of deposition and consolidation of gold can be illustrated by analogy while observing the salt evaporation from the drop of water saturated with different salts.

Conclusions

Based on the conditions of formation and transformation of gold-bearing phases due to the changes in tectonic, climatic and hydrochemical conditions of sedimentation, for gold-containing objects of the Urals can be concluded as follows.

1. Authigenic gold precipitated from solutions is represented by gold pellicles passively growing on detrital particles, and kelyphitic borders.

2. Authigenic pellicles and microcrusts cover the surface of detrital particles of both rocks and various minerals.

3. Native gold is formed not only in the hydrothermal process, but also the authigenic pellicles and shells are grown on, in the hot climate, in the tropical zone (evaporation barrier) and while freezing "cold" waters (cryogenic barrier) in the exogenous conditions (Khazov et al., 2010). The geochemical barriers (evaporative and cryogenic) contributed to the early (MZ-KZ) formation of increased concentrations of gold in the placers of the Urals in the form of authigenic and clastogenic gold and outgrowths on clastogenic gold.

The knowledge and accounting of natural processes of authigenic formation of gold from "ore-bearing man-made" solutions formed while working out sulfide ore deposits will allow to involve man-made ore, in-ground waters in the technological process of their enrichment and purification while ensuring the environmental safety of mining. The surface and underground waters of a number of waste deposits of gold-sulphide and gold-pyrite formations should be considered as a promising hydromineral raw material.

The creation of artificial geochemical barriers in various areas of working out gold-sulphide and gold-pyrite formations will allow

to extract gold from solutions. It is necessary to search for appropriate sorbents, extractants and other systems of gold deposition from solutions. It is necessary to search for sites and conditions for independent deposition of gold in modern technogenic and mineral formations.

Funding

The article presents the results of the work carried out within the framework of the scientific project by the international research team on the basis of the Perm State National Research University "Development of a nature-like technology for the formation of concentrations of useful components within man-made dumps by controlling the processes of technogenesis".

References

- Alexandrov SM (2007) Gold in the processes of endogenous and hypergenic changes of sulfides in magnesian skarns. *Geochemistry* 2:180—198.
- Amosov RA (2000) Cryogenic recrystallization and mechanisms of autigenic gold accumulation in alluvial deposits and weathering crust. Natural and man-made alluvial deposits at the turn of the Millennium. Moscow, p 18-20.
- Blueman BA, Ibragimova AK (2010) Biogenic and hydrobiogenic gold linear weathering crust. Mater. XIV international meeting. Geology of placers and deposits of weathering crust. Novosibirsk, p 103-106.
- Dilabio RNW, Newsome JW, McIvor D F, Lowenstein PL (1988) The spherical form of gold: man-made or secondary? *Econ. Geol.* 3:153-162.
- Fairbrother L, Brugger J, Shapter J, Laird JS, Southam G, Reith F (2012) Supergen gold transformation: Biogenic secondary and nanoparticulate gold from arid Australia. *Chemical geology*, p 17-31.
- Fedoseeva VI (2000) Physical and chemical regularities of migration of chemical elements in frozen soils and snow...Autoref.Diss. d-ra chem.sciences. Tomsk.
- Khazov AF, Silaev VI, Filippov VN (2010) Authigenic mineralization in fluvial placers as natural scientific phenomenon. *Journal of Komi scientific center of URO RAS* 2:54-60.

- Kopylov IS, Naumov VA, Naumova OB, Kharitonov TV (2015) Gold-diamond cradle of Russia. Perm, 130 pp.
- Lunev BS, Naumov BA (2000) Small gold - the main gold of our planet. Geology of the Western Urals. Perm, p 50-56.
- Lunev BS, Naumov BA, Naumova OB (2003) Fine minerals in alluvium. Mountain Journal. Proceedings of higher educational institutions. Yekaterinburg, p 53-56.
- Lunev BS, Osovetsky BM (1979) Methodology for the gradual study of fine gold. *Kolyma* 11:36-37.
- Mayorova TP, Arteeva TA, Filippov VN (2010) Bacteriomorphic structures on native gold of the oxidation zone of the gold-quartz-sulfide Deposit of the Polar Urals. Mater. XIV international. meeting. Geology of placers and deposits of weathering crust. Novosibirsk, p 406-408.
- Naumov VA, Ilaldinov IJ, Osovetskiy BM, Goldyrev VV, Makeev AB (2003) Upper-Kama depression gold. Perm, 218 pp.
- Naumov VA, Kazimov KP, Osovetsky BM, LeBarge W (2010) Crystallomorphology and chemical composition of gold in the glacial region of the Yukon territory (Canada). *Bulletin of the Perm University* 1:24-32.
- Naumov BA, Lunev BS, Naumova OB (2010) Proceedings of higher educational institutions. North Caucasus region. A series of Natural Sciences. Rostov-on-Don, 4:123-126.
- Naumov VA, Lunev BS, Naumova OB (2011) Technogenic deposits - reserve of mineral base of Russia. *Bulletin of Perm University* 1:50-56
- Naumov VA, Osovetsky BM (2013) Mercuriferous gold and amalgams in mesozoic-cenozoic rocks of the Vyatsko-Kamskaya depression. *Lithology and Mineral Resources* 48(3):237-253.
- Naumov VA, Osovetsky BM (2017) The mechanisms of accumulation of gold on coal. Non-ferrous metals and minerals - 2017. Collection of reports of the Ninth International Congress. Krasnoyarsk, p 952-961.
- Naumov VA, Husainova AS (2017) Effect of seasonal freezing and warming of sulfides on gold particles in technogenic-mineral formations. Non-ferrous metals and minerals - 2017. Collection of reports of the Ninth International Congress. Krasnoyarsk, p 942-951.
- Osovetsky BM (2013) Pulverized gold at the nanoscale. Problems of Mineralogy, petrography and metallogeny. Science readings in memory of P. N. Chervinsky, Perm, p 3-9.
- Osovetskiy BM (2012) Nanosculpture of gold surface. Perm, 232 pp.
- Patyk-Kara NG (2008) Minerageny of placers: types of placer provinces. Moscow, 528 pp.
- Plusnin AM, Pogrebnyak YF, Tatyankina EM (1979) Influence of cryogenic processes on the formation of water flows of gold dispersion. Reports of the Academy of Sciences of the USSR. 247(3):700-703.
- Reith F, Stewart L, Wakelin SA (2012) Supergen gold transformation: Secondary and nanoparticulate gold from southern New Zealand. *Chemical geology*, p 32-45.
- Shkolnik EL, Zhegallo EA, Bogatyrev BA and etc. (2004) Biomorphic structures in bauxites (based on the results of electron microscopic study). Moscow.
- Shuster J, Reith F, Cornelis G, Parsons JE, Parsons JM, Southam G (2016) Secondary gold structures: Relics of past biogeochemical transformations and implementations for colloidal gold dispersion in subtropical environments. *Chemical geology* 10:154-164.
- SigovAP (1969) Metallogeny of the Mesozoic and Cenozoic of the Urals. Moscow, 269 pp.
- Southam G, Lengke MF, Fairbrother L, and Reith F (2009) The biogeochemistry of gold. *Elements* (5):303-307.
- Zhmodik SM, Kalinin YA, Roslyakov NA, Mironov AG, Mikhlin YL, Belyanin DK, Nemirovskaya NA, Spiridonov AM, Nesterenko GV, Airiyants EV, Moroz TN, Bulback TA (2012) Nanoparticles of noble metals in the hypergenesis zone. *Geology of ore deposits* 54(2):168-183.