

Matter-mineral characteristics of technogene placers – potential sources of precious metals (on the example of the Nizhneseledzhinsky gold-bearing node of Priamurye, Russia)

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Abstract. Over tens of years of mining and processing of ores and placers of gold in the world a huge amount of wastes originated in the form of spoil heaps and tailing dumps, in which the content of valuable components allow them to be considered a real additional resource of precious metals. The aim of the work was to establish the changes that took place in time in the spoil heaps of gold mining and to determine the prospects of the technogene placers as a potential source of the precious metal. The investigations were carried out with the use of the methods of the analytical raster electron microscopy and mineralogical and atomic-absorption analyses. On the example of the Nizhneseledzhinsky gold-bearing node of Priamurye we have done the comparative analysis of the mineral and granulometric composition of the original and developed placers. It is shown that through the technogenesis the mineral composition of the deposits changes including the process of decomposition of the lead and iron minerals with a partial reduction to a native metal.

In addition to the native gold in the technogene placers there have been found the following minerals with a high content of the precious metal: rutile, monazite, magnetite, metallic lead, galena, ilmenite, and zircon. The content of free gold in dumps is 190 mg/m³ in the average. The main amount of it (about 83%) consists of the fine gold (<0.5 mm).

We have studied the chemical composition of the native gold and associated rocks. It has been established that the gold has a multiphase composition. The phases are for the most part the gold amalgams and have two-, three-, and four-component compositions (Au-Hg, Au-Ag-Hg, Au-Hg-Pb, Au-Ag-Hg-Pb). About 30% of gold of the technogene placers have a high standard of fineness (~980‰). Almost all native gold is in close intergrowths with the rock-forming matrix of different composition: hydroalumosilicates, oxides, and hydroxides of Fe, Mn, and Pb, highly carbonaceous and carbon-bearing formations, and so on. Under the action of the physicochemical and biochemical process in the technogene placers different transformations of the native gold take place: purification at the expense of the silver evacuation; decomposition of the minerals-concentrators of gold; precipitation of micro- and nano-gold at the geochemical barriers with the formation of the so-called “new” gold (from nanoformations to micro- and macroforms).

Through the operation of the technogene placers one should take into account the fact that the ore minerals in them have high concentrations of heavy metals and radioactive elements, and the gold has a complicated multiphase and multicomponent composition, and 3/4 of it is amalgamated. The data obtained give the additional information for the elaboration of technologies for the development of the prospective gold-bearing technogene placers.

Keywords: technogene placers, native gold, phase composition, gold amalgam, fineness of gold

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Introduction

The history of global gold mining spans over more than one century. In the Russian Far East, the noble metal began to be extracted from placers more than 150 years

ago; private gold mining was officially authorized in the Amur Region in 1865. The enormous amount of waste in the form of dumps and tailing dumps was formed across the world thanks to decades of mining and processing of ore and rock mass of placers. It is thought there is only 12 billion tons of waste in the form of overburden rocks and mill tailings have been accumulated in Russia by now. They contain the valuable components, the amount of which allows them to be considered as a real additional

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resource of precious metals (Chanturiya, Vigdergauz, 2008). The resource potential of the man-made gold-bearing objects in Russia are hundreds of tons of Au, which corresponds to 55-60% of the volume of gold mined in the country. So, it is estimated that there is not less than 100-150 tons of tailings in the Republic of Sakha (Yakutia), and about 270 tons in the Amur Region (Mirzekhanova et al., 2016). Thus, the prospects of the technogene placer deposits of gold in the south Far East of Russia only can be estimated in the volume comparable to the already extracted reserves.

The loss of gold takes place through the extraction of it from the primary placers. This may be connected with both the technical imperfection of the equipment, resulted in the incomplete stripping of a placer, and the presence of the lenses of the persistent-frozen rocks, because of which some blocks of placers were left out (Shilo, 2000). With the available technologies the combined gold is poorly extracted, and, when the contents of clay minerals are high, the fine gold is evacuated with them into dumps.

With the improvement of gold recovery technologies, the tailings will undoubtedly be involved in the development. In this connection, the study of the matter-mineral state of these objects and features of the gold composition in them is an important task today. In addition, such investigations are important in terms of ecology of the environment, as over tens of years (up to 1988) in Russia, as over the world, mercury was used widely to extract the precious metal. It was used both at the stage of the heavy concentrate refining and to obtain a gravitation concentrate at the expense of the sluicing. Mercury together with gold arrived at the retreating devices and after the gold evacuation it came to "tailings" and was discharged into tailing dumps. The mercury contents in such dumps of fields and gold-digger artels reach several kilograms per ton (Akhmetov, 2013). Tailing dumps are usually located in the relief lows (creek and river valleys). When the river course is changed or with flooding waters the material, contaminated with mercury, comes to the river valleys and with the bottom sediments reaches the river mouth. Such tendency is observed in other countries also, where the gold mining was active (Alpers et al., 2005). In some countries up till now the gold is mined with the use of mercury. According to K. Telmer's data, as a result of such mining about 650 to 1350 tons of mercury a year enter the environment (Telmer, Veiga, 2008).

Besides mercury, the heavy metals (Pb, Zn, As, etc.) and radioactive elements (U, Th) combined in minerals are evacuated to the aeration zone (Sobolev et al., 1997; Tarasenko et al., 2017; Tarasenko et al., 2017a, 2017b).

Combination of the water-air action results in the break-down of many minerals that is accompanied by the increasing concentration of these elements in the

natural environment.

The matter of the exhausted placers (dumps) is a mechanical mixture of different rocks, of which the initial placer deposits of gold consisted. These are the rocks of alluvial, diluvial, eluvial and proluvial deposits. It should be noted that each technogenic deposit, as well as the primary placer has its own individual characteristics inherent only to the given deposit, which must be certainly factored into choosing the technology for its development. The mineral composition and mineralogical and geochemical features of legacy placers are usually inherited from the primary placer, but in the process of technogenesis experience certain changes.

The aim of the work was to establish the changes occurred with time in the gold mining dumps, on the example of the Nizhneselmdzhinsky gold-bearing node (NGN) of Priamurye to compare the matter-mineral composition of the primary and technogene placers, to study the chemical composition of native gold from the technogene placers, to define the ecological risks, and to consider the prospects of the technogene placers for the repeated development.

Short geological characteristics

The Nizhneselmdzhinsky gold-bearing node is located within the Chagoyan-Byssinskaya metallogenic zone of the Priamurskaya gold-ore province on the right bank of the Selmdzha River lower reaches (Fig. 1). Mineralization of predominantly gold-quartz, gold-polymetallic, and gold-silver types, as well as the placers with small-sized and fine-grained gold, is characteristic of the gold-bearing zones of this region (Kuznetsova, 2011).

Mainly the Riphean metamorphic schists and terrigenous formations of the Silurian age, broken by the different-age intrusions of acid and intermediate composition, participate in the structure of the Nizhneselmdzhinsky gold-bearing node.

The central part of the node is composed of large granitoid intrusions of the Ordovician granite complex and Middle-Late Carboniferous gabbro-granite complex as well as a series of small intrusions and dikes of granite-porphyrries, granodiorite-porphyrries, and diorite porphyrites of the Lower Cretaceous age.

Within the node, the occurrences of mineralization of gold, silver, lead, tin, niobium, and other elements have been recognized.

The most known gold occurrences – Khrabroe, Utesnoe, and Zagadochnoe, and most of the mineralization sites are represented by zones of the gold-quartz and gold-sulfide-quartz streaking in the quartz-mica, carbonaceous, and calcic shales of the Riphean. In addition, the mineralization areas were established among granitoids of the Paleozoic (Tatarka River and Geogriyevsky Creek). Among the ore minerals there

were found pyrite, arsenopyrite, galena, and native gold.

Gold-polymetallic (lead) ore occurrences of the Royal and Kosmatyi Creeks have been found in sandstones, aleurolites, and tuffs of the Silurian age, and the Veselyi occurrence is restricted to the Upper Proterozoic terrigenous-carbonaceous deposits. The presence of the non-oxidized galena in the heavy concentrates testifies to the near source of the original sulfide mineralization (Moiseenko, Kuznetsova, 2010). In the process of the dredging development of the Neklya River and Veselyi Creek placer the poorly rounded galena was met everywhere in the heavy concentrates (about 24% of the concentrate mass). The atomic-absorption analysis shows that galena contains Au – 67.75 g/t and Ag – 200 g/t, the Au/Ag ratio is 0.34. By this indicator the galena of the NGN is closer to the gold-ore and gold-polymetallic deposits of Priamurskaya Province than to the polymetallic proper (Moiseenko, Kuznetsova, 2011).

The tin and niobium occurrences (P. 8-10 Tatarka River, P. 12 Beznazvannyi Creek) are restricted to the metasomatically altered granites of Oktyabrsky complex. The mineralogical analysis shows that they contain columbite, pyrochlore, samarskite, and cassiterite. The tin content reaches 0.06% and niobium – 0.041% (Kuznetsova, 2011).

The deposits of the precious metal, corresponding by the productivity to numerous placers, have not been revealed as for now. This may be explained by the fact that the main source of gold of the NGN are the widely scattered over the area small gold-bearing quartz veinlets in the sedimentary rocks metamorphosed in the greenschist facies.

Within the node the alluvial gold placers are mainly occur, most of which are localized in the Upper Quaternary deposits. The gold-bearing beds are under the present alluvium at a depth of 2-5 to 12 m on the bedrock of original rocks composed of the weathered Upper Proterozoic-Lower Cambrian schists and Paleozoic granites (sometimes these are the clays of the crust of weathering).

The alluvial deposits are characterized by a great content of the clay and quartz material. The average mineralogical composition of the primary placers is given in Fig. 2.

The primary placers of the NGN demonstrate a significant spread of the heavy concentrate output – 0.2 to 9 kg/m³ of the washed rock. The study of the mineralogical composition of the heavy concentrate showed that the electromagnetic fraction (34-72% of the heavy concentrate mass) is composed for 50% of ilmenite, as well as garnet, monazite, and hematite are found also. The magnetic fraction (3-7% of the heavy concentrate mass) is composed for 90% of magnetite and martite. The non-magnetic fraction (4-29% of the heavy concentrate mass) is dominated by zircon (about 55%),

and rutile, sphene, cassiterite, galena, pyromorphite, and gold are present also (Kuznetsova, 2011).

The gold content in the primary placers is tens mg/m³ to 3946 mg/m³, in the average 282 mg/m³ for the mass. The main gold mass (about 70%) belongs to the class of -0.5 mm. Rarely gold nuggets 30 to 150 g in weight were found. The average Au standard* is 880 per mille (hereinafter Au/(Au+Ag)×1000). Fe, Zn, Sb, Zn, As, Pb, Ti, Mg, Mn, Ni, Co, and Bi are sometimes present as admixtures. The copper content in gold is stable within 0.01-0.03%. Significant variations have been established only for silver (4.1 to 13.9%) (Neronsky, Dobraya, 1975), whose amount depends on both the thermodynamic conditions of the ore formation and the duration of action on it of different factors under exogenic conditions. In the oxidation zone the electrochemical leaching of silver from the grain surface takes place resulting in the gold standard increase. Besides, in the primary placers the poorly rounded gold intergrown with quartz is constantly present.

By the present day practically all primary placers have been worked out and moved up into a class of the technogenic placers.

Methods of investigations

7 bulk samples (30-80 kg) were selected for the research of the following objects of the Nizhneselemdzhinsky gold-bearing node: the Neklya River (P. 1-5) with the Veselyi Creek inflow (P. 6, 7); the Tatarka River (P. 8-10); the Nadyga River (P. 11, 13) with the Beznazvannyi Creek inflow (P. 12), the Korean Creek (P. 14), the Kosmatyi Creek (P. 15); the Orlovka River (P. 16) with the Kuznetsovsky Creek inflow (P. 17), the Georgrgiyevsky Creek (P. 18) (Fig. 1). A heavy concentrate was obtained from samples by standard fractionation. The atomic-absorption and mineralogical analyses of samples were carried out at the IGNM FEB RAS. Native gold and minerals-concentrators of precious metals in the form of separate grains and intergrown pieces were separated according to a previously used technique (Moiseenko, 2007).

The element composition and morphological and microstructure features of minerals were studied with the method of the analytical raster electron microscopy (AREM) using the EVO 40XVP microscope («Carl Zeiss» Firm, Germany) equipped with the system of the power-dispersion X-ray (EDX) analysis INCA Energy («Oxford instruments» Firm, Great Britain) at the center of electron microscopy at the EGI FEB RAS.

Grains and intergrowths were fastened on special tables and studied under regimes of the secondary and backward scattered electrons and regime of EDX of microprobing with different magnifications (at the accelerating voltage of the electron beam of 20 kV). The samples were not sprayed with carbon as most of them

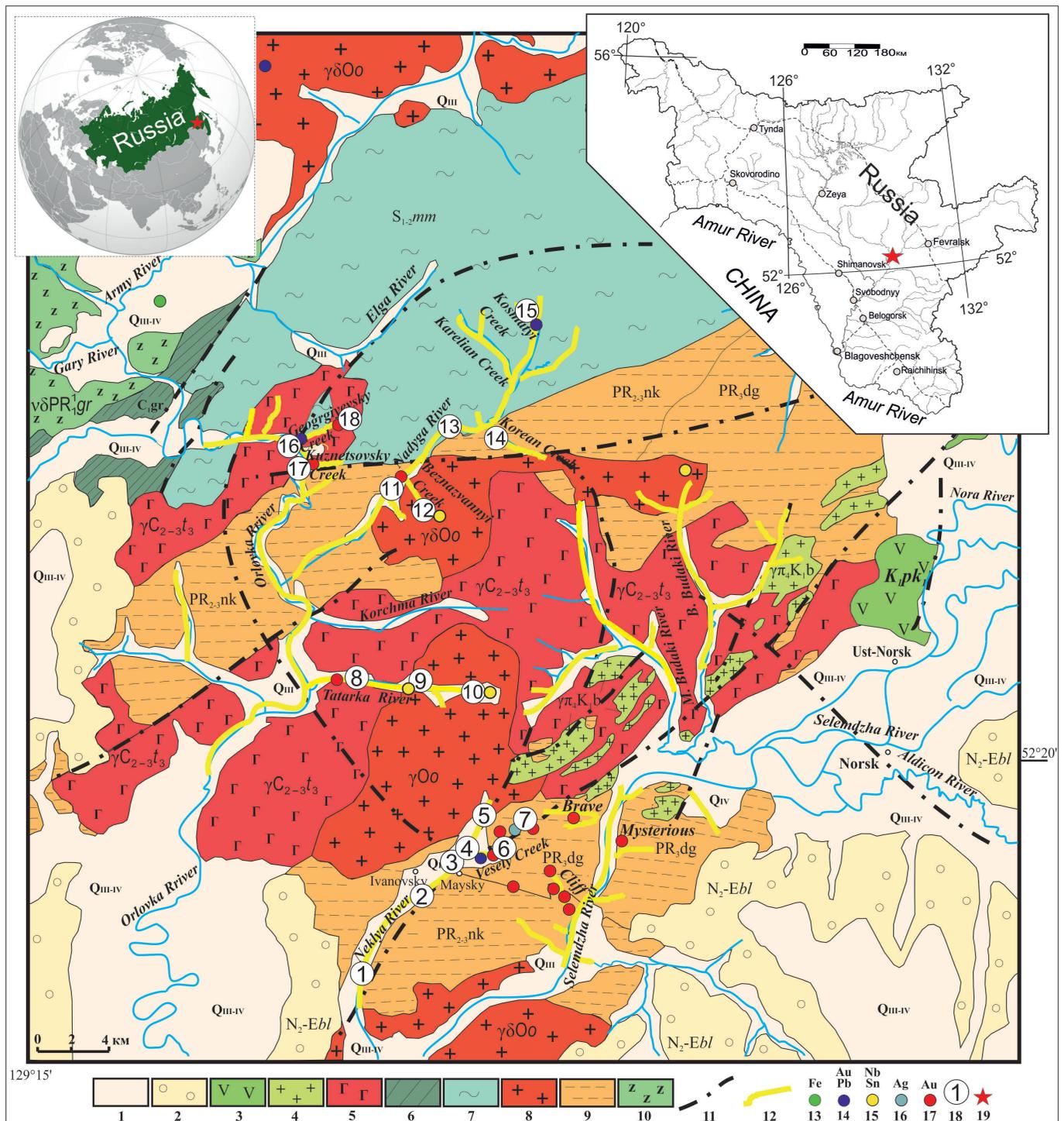


Fig. 1. Schematic map: geographic position (marked off on the inset), geological structure, and ore content of the Nizhneselemdzhinsky gold-bearing zone (the materials of V.F. Zubkov, 1980, and D.L. Vyunov, 2005, were used). Conventional signs: 1 – Quaternary formations (boulders, pebble, gravel); 2 – Neogene-Quaternary formations (clays, sand, pebble, siltstones); 3 – Early Cretaceous granite-porphyrries, granodiorite-porphyrries, and diorite porphyrites; 5 – granites and granodiorites of the Middle-Late Carboniferous age; 6 – Lower Carboniferous deposits (sandstones, limestones, siltstones); 7 – Silurian deposits (sandstones, siltstones, conglomerates, tuffs); 8 – Ordovician granites; 9 – Upper Proterozoic terrigenous-carbonaceous deposits (shales, limestones, sandstones); 10 – Early Proterozoic gabbrodiorites; 11 – faults; 12 – gold placers; 13–17 – ore occurrences and points of a mineralization: 13 – iron, 14 – lead, 15 – tin and niobium, 16 – silver, 17 – gold, 18 – point (place) of sample drawing; 18 – position Nizhneselemdzhinsky gold-bearing zone. P. 1-5 Neklya River; P. 6-7 Vesely Creek; P. 8-10 Tatarka River; P. 11, 13 Nadyga River; P. 12 Beznazvannyi Creek; P. 14 Korean Creek; P. 15 Kosmatyi Creek; Orlovka River (P. 16) and its inflows – P. 17 Kuznetsovsky Creek; P. 18 Georgrgiyevsky Creek.

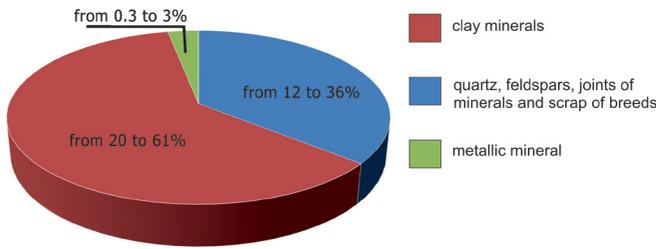


Fig. 2. Average mineral composition of the primary placers of the Nizhneselemdzhinsky gold-bearing node

are the current-conducting material. This allowed us in the analysis process to reveal unequivocally the carbon in the rocks (mineral mixtures) been closely intergrown with gold.

Results and discussion

The study of the technogenic placers of the NGN showed that in granulometric and mineralogical composition they differ from the primary placers. Through the development of the latter the clay minerals are washed out, and in the dumps a share of quartz and feldspars increases, and the percent of ore minerals grows also (Fig. 3).

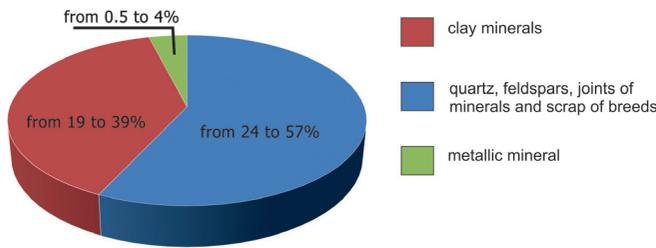


Fig. 3. Average mineral composition of the technogenic placers of the NGN

In the technogenic placers the output of a heavy concentrate is in the average 0.5 to 4% of the rock mass. The electromagnetic fraction (6 to 80%) is represented mainly by ilmenite (about 62%), monazite, siderite, garnet, and pyromorphite. The magnetic fraction (3-12%) is composed of the oxide conglomerates and iron hydroxides (about 80%), magnetite (about 25%), and martite. The non-magnetic fraction (2 to 29%) includes zircon (about 70%), cassiterite, rutile, native lead, gold, sphene, and galena.

The heavy concentrate of the technogenic placers of the Nizhneselemdzhinsky gold-bearing node is characterized by a higher radioactive background (about 170 mkR/h) that is explained by the presence (about 10%) in the concentrate of the thorium minerals (monazite) and uranium-bearing zircon (Kuznetsova et al., 2017; Moiseenko, Kuznetsova, 2017).

In the work process we carried out the comparative analysis of the heavy fractions of the primary and technogenic placers of the Veselyi Creek (Table 1).

mineral structure of the last cut of a concentrate	gold-alluvial-deluvial deposit %	technogenic placer deposit %
ilmenite	30	46
galenite	12	5
martit	8	gr.
hematite	6	–
limonite	5	gr.
garnet	3	2
rutile	3	1
magnetite	3	1.3
pyrite	2.3	gr.
tantaloniobata	1.4	–
oxides Mn	0.1	–
native Pb	–	15
monazite	1.4	10
conglomerates oxides Fe	0.3	8
zircon	4	5
Fe globules	–	4
cassiterite	0.5	1
siderite	–	0.2
scheelite	–	gr.
gold amalgam	–	0.5
the average content of Au in a concentrate, g/t	267	147
the average content of Au in the field on the weight, mg/m ³	329	187

Table 1. Composition of a heavy fraction of the primary and technogenic placer (Veselyi Creek)

Some placers of the NGN (Veselyi Creek, Kosmatyi and Georgrgiyevsky Creeks) are developed on the rocks with the gold-polymetallic (galenite) mineralization. In the hypergenesis zone galenite is disintegrated, but slower than other sulfides. Its content in the thecnogenic placers, as compared with the primary placer, decreases to 5%. The galenite is in part corroded with the formation on it of the local areas of oxides, hydroxides, and sulphates of lead. The lead minerals demonstrate a higher content of the precious metal. The AREM data show that the galena transformation products are found on the gold grains in the form of the incrustations of the copper-antimony-chloride-lead hydroxides. The anglesite separations (PbSO4) are rather common on gold.

In the dumps the amount of the metallic Pb reaches 15%. This is connected with the fact that under the redox conditions, produced by the destruction of the organic matter, swamping, and absence of oxygen, the galena and some minerals of iron decompose with a partial reduction up to a native metal (Myagkaya et al., 2016). The presence of 4% of the metallic Fe in the heavy fraction of the dumps is connected with these processes also.

In addition to the reduction conditions the technogenic placers are characterized primarily by the oxidation processes. In the hypergenesis zone the minerals, mainly

sulfides, are destructed with the formation of oxides and hydroxides of metals. Pyrite is intensively oxidized to oxides and hydroxides of iron. In the primary placers its share is several percents, then in the technogenic placers it is met in the mark quantities. As for the martite, hematite, and limonite under the technogenesis conditions they are redistributed with the formation of conglomerates and concretions. In the heavy concentrate the magnetite amount becomes less. The share of ilmenite increases to 46% and monazite – to 10%.

Gold amalgam is about 0.5%. Native gold is met, the average content of which in the concentrate is 187 g/t. In the dumps the native gold is represented usually by all fractions characteristic of the primary placers, but the contents of the intermediate fractions decrease, and they are most easily extracted through the initial development, so the percent of the finely dispersive and macroscopic gold grows (Shilo, 2000),

nuggets are met also. The histogram of the gold distribution on fractions in the primary and technogenic placers of the Veselyi Creek is given in Fig. 4, where it is seen that the gold bulk mass in the dumps (about 83%) belongs to the class of -0.5 mm, i.e. to the fine and fine-dispersive one.

Generally, minerals-concentrators with different contents of gold in them are found in waste placers. For

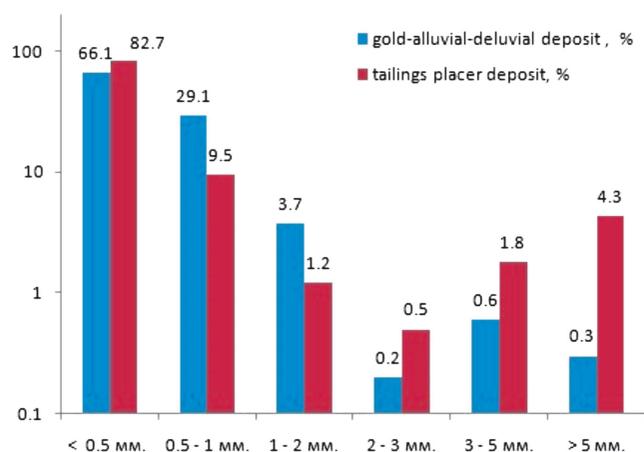


Fig 4. Histogram of distribution of native gold on fractions in primary and technogene placer deposit of gold (Veselyi Creek)

example, in the technogene placer of the Veselyi Creek are found: rutile (Au 1000 g/t, Ag 70 g/t), monazite (Au 680 g/t, Ag 600 g/t), magnetite (Au 300 g/t, Ag 100 g/t), chalcedonic quartz (Au 150 g/t, Ag 30 g/t), metallic lead (Au 140 g/t, Ag 50 g/t), and galena (Au 10 g/t, Ag <2 g/t). The deposition of nano-sized Au on the surface and along the defects in mineral structures (galena, rutile, monazite) evidences to the hypergene genesis of precious metals.

In the dumps of placers, where in the gold mining process the mercury was widely used, the amalgam active transformation takes place with release of the precious metal. In this case gold contaminates the typically accessory minerals of the placers, such as ilmenite (Au 110 g/t, Ag 50 g/t) and zircon (Au 280 g/t, Ag 560 g/t) (data of the atomic-absorption analysis) (Kuznetsova, 2011).

To determine the morphology, microstructure, and chemical composition of native gold from the technogenic placers of the Nizhneselemdzhinsky gold-bearing node in Priamurye we studied 396 samples using the methods of the raster electron microscopy and carried out several hundreds of the EDX analyses.

The data obtained (Table 2) show that native golds is heterogeneous in composition. In it there have been recognized the phases of practically pure gold, solid solutions of gold with silver, and amalgams on the Au, Ag, Hg, and Pb element base. The amalgam phases are found in most of the studied samples.

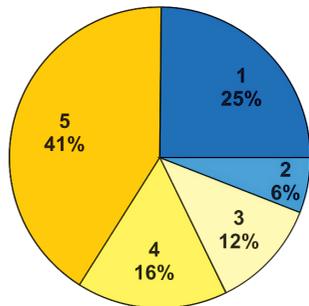
It should be noted that a specific feature of the studied technogene gold is the presence in its composition of a significant amount of the Pb-bearing amalgams. This may be a result of the fact that different minerals of lead, which are present in ores and enclosing rocks and often accompany gold in placers, were destructed in part or in full under the hypergenesis conditions with the formation of the mobile complex compounds of lead and, probably, its free monatomic forms. The latter are combined with Hg and Au to form the Pb- and Hg-bearing auric phases of different composition (Safronov, Kuznetsova, 2017).

Based on the element composition of the studied samples (Table 2), the authors by convention divided the native gold of the technogene placers into 2 groups

	system	Ranges of maintenance of elements			
		Au	Ag	Hg	Pb
Native gold	Au	100	-	-	-
	Au-Ag	88.9-99.3	0.7-11.1	-	-
Amalgam gold	Au-Hg ¹	87.8-99.3	-	0.7-12.2	-
	Au-Ag-Hg	73.3-93.0	1.0-13.7	1.7-22.3	-
	Au-Hg-Pb ²	42.3-95.1	-	2.2-16.7	1.4-50.4
	Au-Ag-Hg-Pb ³	60.0-90.2 ³	0.4-4.7	1.5-17.4	0.6-24.0

Table. 2. Chemical composition of native gold of the technogene placer of the Nizhneselemdzhinsky gold-bearing node in Priamurye according to the EDX analyses, wt. %. The blanks indicate that the element was not found. The impurities: ¹ Cu 0.5-1.7%; ² Sb 1.8-3.5%; ³ Zn 0.78-0.9%. All analyses are normalized, i.e. their sum is normalized to 100%.

(Fig. 5). In the first group (I) there is the native gold, and in the second group (II) – gold amalgams. The first group includes the pure gold (1000‰) and solid solutions of gold with silver (Au-Ag) (979‰). The samples of the second group contain the mercury-bearing phases representing the amalgams of the two-component (Au-Ag), three-component (Au-Ag-Hg), (Au-Hg-Pb), and four-component (Au-Ag-Hg-Pb) compositions. The average gold standard of this group is 870‰. Among the three-component amalgams 12% belong to the Au-Ag-Hg system, and 16% – to the Au-Hg-Pb system. Among the three- and four-component compositions the authors have first distinguished the following compounds: $Au_1(Hg,Pb)_1$, $(Au,Ag)_2(Hg,Pb)_1$, $(Au,Ag)_4Hg_1$, $(Au,Ag)_4(Hg,Pb)_1$, $Au_3(Hg,Pb)_4$, $Au_4(Hg,Pb)_3$, $(Au,Ag)_9Hg_1$, and $(Au,Ag)_9(Hg,Pb)_1$ (Safronov, Kuznetsova, 2017). Admixtures of Cu, Zn, and Sb are met in gold.



Group	Phase of gold from the technogene placers	Gold standard, ‰
I	1 (Au-Ag) + (Au)	887 to 1000
	2 (Au-Ag)	average 979
II	3 (Au-Ag-Hg) + (Au-Hg) + (Au)	423 to 1000 average 870
	4 (Au-Hg-Pb) + (Au-Hg) + (Au)	
	5 (Au-Ag-Hg-Pb) + (Au-Hg-Pb) + (Au-Ag-Hg) + (Au-Hg) + (Au-Ag) + (Au)	

Fig. 5. Diagram of the quantitative ratio of native gold from the technogene placers with a different phase composition (Nizhneselemdzhinsky gold-bearing node of Priamurye)

The results of the investigations showed that 1/3 of the native gold of the technogene placers is the high-standard varieties and about 70% of samples are contaminated with mercury (Fig. 5). In some samples there were fixed the phases consisting for 97 mass% of Hg with an admixture of Pb ~ 2% and As < 1%. The presence of the free mercury indicates its occurrence in the dumps of the technogene placers.

In the placers of the Nizhneselemdzhinsky gold-bearing node “new” gold is common, which settles on the surface of the rounded gold grains (Petrovskaya, 1973; Reith et al., 2012; Hough et al., 2011; Shuster and Southam, 2015). The authigenic gold, found under microscope as the micro- and nano-sized phases, forms the tracery rims, hexahedral prisms, and spongy, globular,

and thread-like formations (Fig. 6), is characterized by a higher standard (до 1000‰), and in some cases forms the phases with mercury (Fig. 6 e). The formation of this gold under the technogenic conditions is indicated by both a high standard different from the main gold and the mercury admixture (Yesares et al., 2014).

The amalgamated gold comes to the dumps during its mining from placers. However, a part of the many-phase gold was formed or underwent the change of the composition immediately in the dumps due to the interaction of the residual mercury with the gold particles. As a rule, the surface of the amalgam separations of gold has a smoothed structure. But sometimes on the surface there are the corroded areas with a whimsical

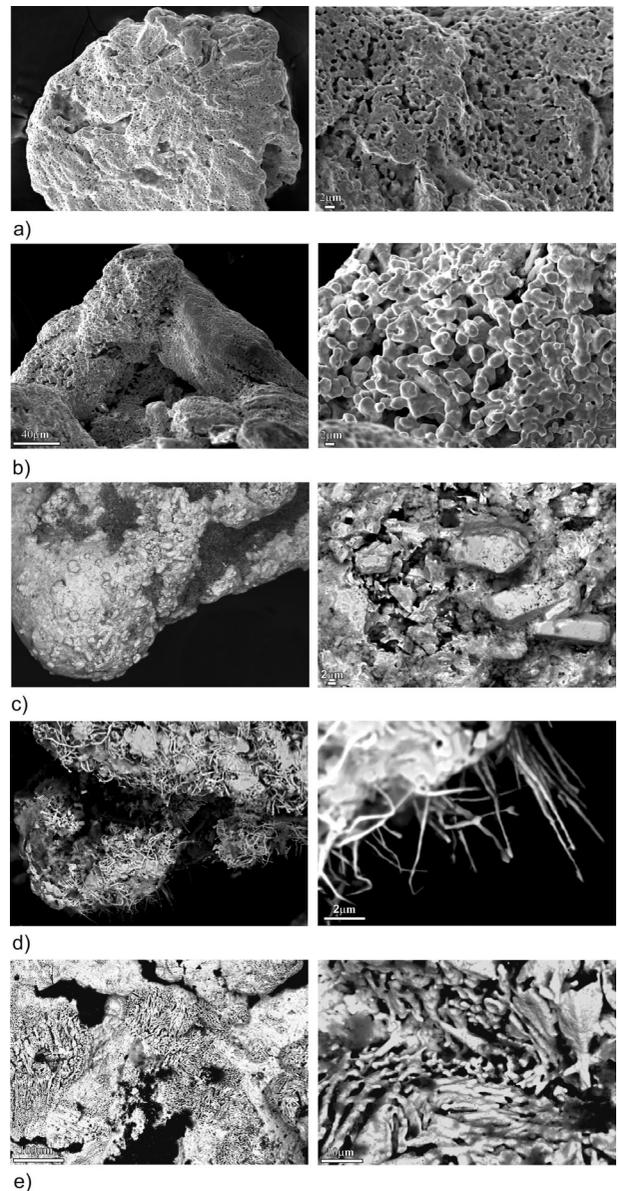


Fig. 6. Microstructure of native gold from the technogene placers of the Nizhneselemdzhinsky gold-bearing node of Priamurye: a) porous, b) globular, c) crystalline, d) filamentous, e) dendroid. Micrographs a, b were obtained in the secondary electrons; c, d, e – the photographs were taken in the backward scattered electrons.

microstructure that resulted apparently under the action of the aggressive solutions on gold (Fig. 6 e). The solutions most likely contained the lead complexes as in the corroded areas there was observed a higher content of Pb (6.27 mass%) and lower mercury (2.54 mass%) as compared with the less altered areas, where Pb was 1.89% and Hg 6.07%. In other words, in the corroded areas the mercury is in part dissolved (evacuated from them) and replaced by lead. Gold contents in both cases are practically the same – 91 and 92%.

A particular role in the formation of authigenous gold in placer deposits belongs to bacteria. The presence of some types of bacteria in placer deposits was established long time ago, and the experiments showed that bacteria are able to concentrate the dissolved gold into visible particles, at least under an electron microscope (Marakushev et al., 1989; Reith et al., 2010; Southam et al., 2009; Shuster, et al., 2016, Rea et al., 2016). Moreover, in one of the deposits of the October gold-bearing zone, bacterial gold was discovered over time (Safronov et al., 1998).

When studying the gold of the technogene placers with the methods of the electron microscopy it was established that the most part of the precious metal represents the intergrowths composed of the grains of different composition and morphology cemented with each other by the polymineral matrix (Fig. 7 a),

often by gold amalgam. Almost all samples contain the inclusions of rocks of a complicated composition (Fig. 7 b). Below, as an example the demonstrative micrographs of gold samples are shown that contain the rock with the given points (spectra) of the EDX analyses and calculated compositions (Fig. 8, a, b, c; Table 3, 4, 5). Several hundreds of such areas have been looked over and studied, and more than 500 analyses have been done. As a whole, the rock inclusions in gold have a complicated composition and structure. In many rock formations, intergrown closely with native gold, the process of the formation of the authigenous precious metal is going on also. The inclusions of the nano-sized gold, invisible even with the greatest magnifications – so called cluster gold, are reliably fixed with the power-dispersive X-ray spectrometer (Safronov, Kuznetsova, 2016) (Fig. 8, micrograph 5, Table 4, pp. 2-5, Au ~ from 0.5 to 1.5%).

In the course of self-organization, larger isomeric, often sphere-shaped separations of the precious metal of various size are formed. The composition of such gold is simple – 100% Au (Table 4, micrograph 5, pp. 1). The size of nanoparticles ranges from 50-100 nm to 500-600 nm. Some particles are combined into groups of two, three or more individuals, and the size of such aggregates already extends beyond the nanometer range, and amounts – to several micrometers.

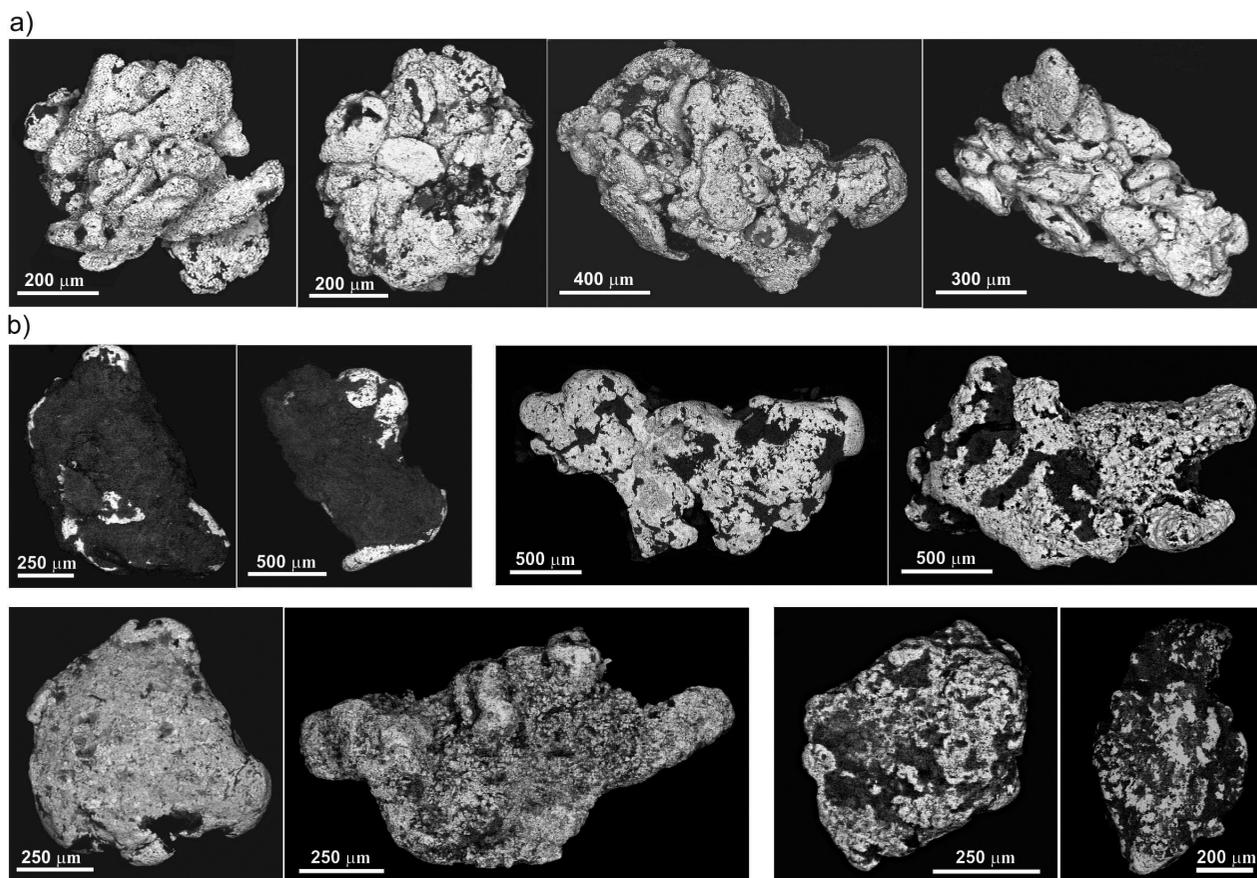


Fig. 7. Microphotographs of different morphological types of native gold from the technogene placers of the Nizhneselmdzhinsky gold-bearing node of Priamurye. The photographs were taken in the backward scattered electrons.

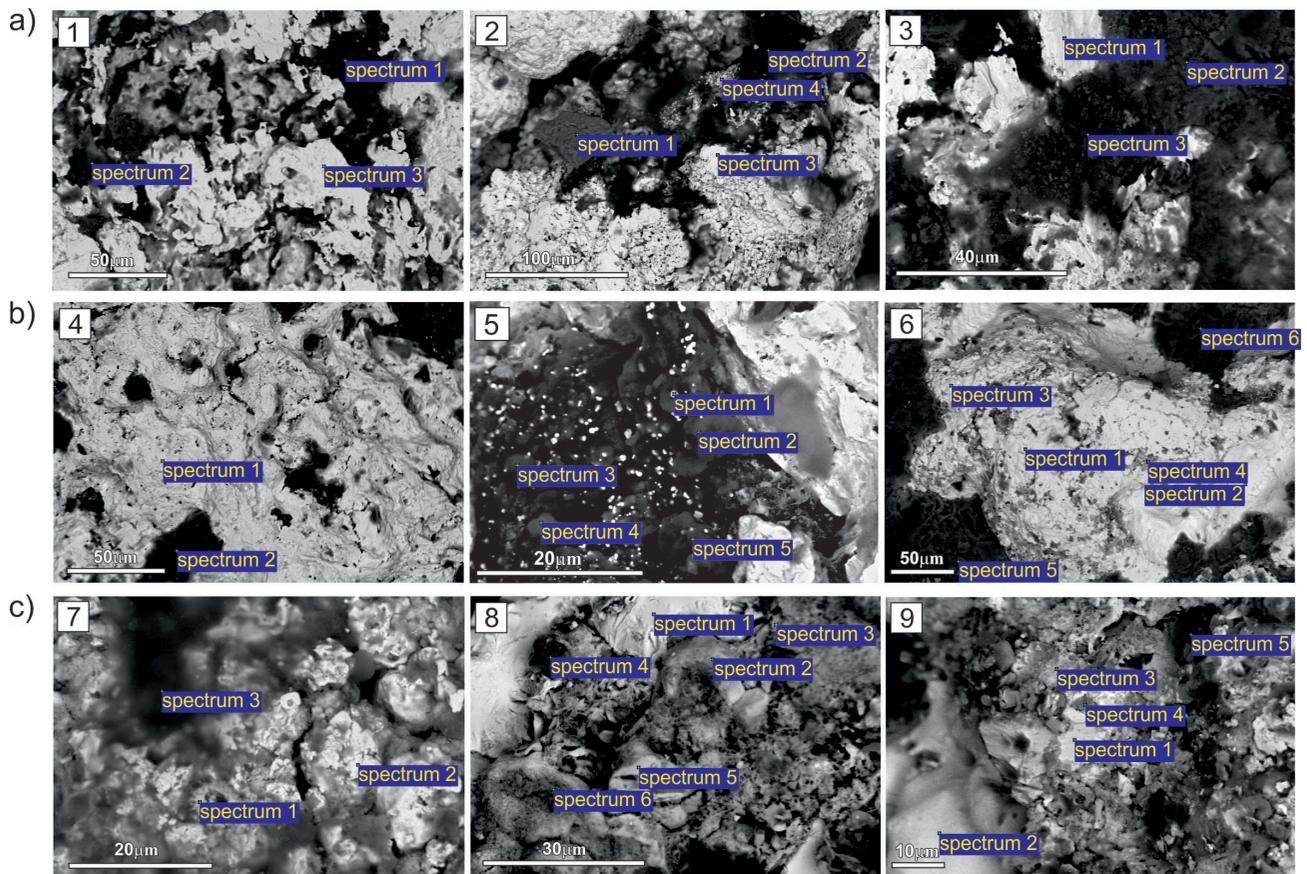


Fig. 8. Microphotographs of 9 gold grains containing the rock with the given points (spectra) of the EDX analyses. The calculated compositions are shown in Tables 3, 4, 5.

microphotograph element	1			2			3		
	spectrum			spectrum			spectrum		
	Sp 1	Sp 2	Sp 3	Sp 1	Sp 2	Sp 3	Sp 1	Sp 2	Sp 3
C		63.51			85.64			18.52	38.02
N		18.16							
O	65.19	16.63		58.55	11.57			53.18	44.93
Na				0.87					
Al	15.18	0.28			0.48			1.13	1.15
Si	15.94	0.35		0.50	0.77			1.41	2.06
S				0.60				0.75	0.44
Cl				0.78					
K	0.13			0.46	0.10				
Ti	0.64								
Mn									0.13
Fe	2.61	0.56		38.05	0.34			23.60	12.58
Ag					0.09		13.48	0.49	
Au		0.41	100	0.19	0.87	100	86.52		
Hg	0.12	0.05						0.69	0.52
Pb	0.19	0.05			0.15			0.24	0.19

Table. 3. Composition of the rocks associated with native gold according to data of the EDX analysis, atomic. % (Fig. 8, micrographs 1-3). To micrograph 1: Sp 1 – inclusion of kaolinite in interstitial of native gold; In the kaolinite there is a hydrogoethite impurity; Sp 2 – carbonaceous formation with Au, Ag, and Pb; Sp 3 – gold (1000%). To micrograph 2: Sp 1 – hematite; Sp 2 – carbonaceous rock with Au, Ag, and Pb; Sp 3 – gold (1000%). To micrograph 3: Sp 1 – high-standard gold; Sp 2 and Sp 3 – a carboniferous fine-dispersive mixture of limonite and hydroalunosilicate with Hg and Pb.

microphotograph element	4		5					6					
	spectrum		spectrum					spectrum					
	Sp 1	Sp 2	Sp 1	Sp 2	Sp 3	Sp 4	Sp 5	Sp 1	Sp 2	Sp 3	Sp 4	Sp 5	Sp 6
C											27.13		
O		64.66		62.93	69.51	69.17	63.55				52.88	63.15	64.03
Na				0.37	0.39	0.24	0.19						
Mg		0.77		0.72	0.31		0.33					1.03	2.65
Al		12.06		10.56	11.39	10.18	11.84				5.43	10.85	11.16
Si		14.05		10.73	11.65	9.80	10.83				5.96	17.71	13.81
P				0.20	0.19	0.33	0.25						
S					0.17	0.27	0.02						
Cl		0.27		0.34	0.44	0.41	0.27						
K		0.91		1.62	0.70	0.42	0.75					2.34	0.30
Ca		0.21		0.56	0.26	0.47	0.43					0.24	0.41
Ti		0.15		0.26	0.12	0.24	0.27					0.19	
Mn		2.66		1.74	1.68	1.23	1.47				0.98	2.24	1.07
Fe		2.35		8.83	2.24	5.30	9.01				0.43	1.84	6.26
Ag	11.75							1.88	6.59	4.36			
Sn	3.05												
Au	55.78		100	0.68	0.70	1.54	0.47	90.30	78.74	85.37	0.54		
Hg	15.93	0.56		0.30	0.12	0.14	0.13	7.82	9.85	6.60		0.34	0.30
Pb	13.48	1.35		0.17	0.13	0.25	0.17		4.82	3.67	6.63	0.07	

Table 4. Composition of the rocks associated with native gold according to data of the EDX analysis. Atomic % (Fig. 8, micrographs 4-6). To micrograph 4: Sp 1 – gold amalgam with Pb and Sn; Sp 2 – mixture of hydro-alumosilicates and Mn and Fe hydroxides. To micrograph 5: Sp 1 – nanogold (1000‰); Sp 2, Sp 3, Sp 4, Sp 5 – fine-dispersive mixture of hydro-alumosilicates and Fe and Mn hydroxides with particles of nanogold. To micrograph 6: Sp 1 – high-standard gold amalgam; Sp 2 and Sp 3 – gold amalgam with Pb impurity; Sp 4 – Pb carbonate with kaolinite; Sp 5 and 6 – hydroalumosilicate with Hg and Pb impurity.

Such nano-gold was observed in the study of ore deposits (Moiseenko et al., 2010; Safronov et al., 2011; Moiseenko, Kuznetsova, 2014; Moiseenko V.G., Moiseenko N.V., 2012).

Under certain conditions (metasomatism, hypergenesis, etc.) the primary minerals-concentrators of gold are destructed, with the release of the precious metal (Naumov, Naumova, 2013; Hough et al., 2011; Reith et al., 2010; Lengke et al., 2006a, 2006b; Craw, Lilly, 2016; Fairbrother et al., 2012; Kuznetsova et al., 2015). Then, the self-organization of gold nanoparticles through clusters to spheroids, from spheroids to aggregates up to the formation of independent phases takes places, that is sequential concentration and coarsening of Au from nano-sized to visible precipitates (Moiseenko, 2007; Moiseenko V.G., Moiseenko N.V., 2012; Shuster and Southam, 2015; Shuster et al., 2017; Hough et al., 2011).

The rock inclusions in gold grains, studied with the analytical raster electron microscope, represent as a rule a fine-dispersive (sometimes fine-grained) mixture of some minerals and carbonaceous matter. The most common rock formations in the samples of the precious metal are the following mineral varieties: hydro-alumosilicates (clay minerals, hydromicas, chlorites,

and others) (Fig. 8 a, b; Tables 3, 4), hydroxides of Fe, and hydroxides of Mn (Fig. 8 a, b; Tables 3, 4). High-carbonaceous and carbon-bearing formations (Fig. 8 a, c; Tables 3, 5) occur in the form of films, accumulations, and graphitized matter.

In the rock component of gold both the native lead and its compounds are often found: oxides and hydroxides of Pb (minium, massicot) and sulphates (anglesite) and carbonates of Pb (cerussite, phosgenite). Rarer are chlorides of Pb (cotunnite, mendipite), phosphates (pyromorphite), and sulfides (galena). There are observed also the U-Pb-carbonate-phosphate compounds of a complicated composition and hardly diagnosed mineral mixtures of the Pb-bearing hydro-alumosilicates (Fig. 8 b,c; Tables 3, 5).

In the composition of inclusions the following silicates have been found: kaolinite, halloysite, chlorite, and sericite. Sulfides are represented by the oxidized pyrite, and oxides and hydroxides of iron – hematite, goethite and hydrogoethite (limonite). Among the manganese hydroxides there are romanecite and hollandite. The main rock-forming minerals of the inclusions in gold are quartz and adularia.

Practically in all phases of the rock components there

microphotograph element	7			8						9				
	spectrum			spectrum						spectrum				
	Sp 1	Sp 2	Sp 3	Sp 1	Sp 2	Sp 3	Sp 4	Sp 5	Sp 6	Sp 1	Sp 2	Sp 3	Sp 4	Sp 5
C	48.34		76.8		47.25	39.69	85.02		35.75			27.11	88.64	89.13
O	30.53		14.41		22.43	40.57	10.42		43.41			48.05	5.79	7.00
Na	1.50		0.94											
Al	0.52		0.14			0.96			2.77					
Si	0.42		0.12						2.99					
P	4.13		0.84											
S					12.73	0.81		48.62	2.68					
Cl	3.55		0.48						1.69			2.26		
K	1.64		2.05											
Ca			0.17											
Mn			0.15						0.72					
Fe	0.61		0.66						1.14					
Cu		2.66	0.43		1.63				0.51					
Zn	0.21		0.26											
As			0.01	0.66										0.01
Ag		5.62								5.89	5.21			
Sb					1.28	2.17			0.87					
Au	1.32	81.1	1.31							81.28	72.76	2.42	2.26	0.72
Hg		8.24	0.26	97.02			0.35		0.39	9.53	10.82			
Pb	7.23	2.38	0.98	2.32	14.68	15.79	4.21	51.38	7.09	3.31	11.20	20.17	3.30	3.14

Table. 5 Composition of the rocks associated with native gold according to data of the EDX analysis. Atomic % (Fig. 8, micrographs 7-9). To micrograph 7: Sp 1 – pyromorphite; Sp 2 – gold amalgam with Pb and Cu; Sp 3 – high-carbon rock with Au, Hg, Pb, Cu, and Zn. To micrograph 8: Sp 1 – free mercury; Sp 2 – copper-antimony anglezit in a carboniferous matrix; Sp 3 – hydrocerussite with Pb hydroxide; Sp 4 – carbon film with Pb and Hg impurity; Sp 5 – galenite; Sp 6 – Pb hydroalumosilicate with Cu u Sb. To micrograph 9: Sp 1 and Sp 2 – gold amalgam containing Pb; Sp 3 – mixture of cerussite and phosgenite; Sp 4 – inclusion of graphite with lead; Sp 5 – graphite inclusion containing Pb and Au.

is the organic (and/or inorganic) carbon containing small amounts of Au, Ag, Pb, and Hg.

Gold of the technogenic placers is characterized by micro- and nano-phases of amalgams of gold and lead, which are fixed in most of inclusions.

In the dumps the processes of the dissolution, transfer, and redeposition of the rock and ore elements took place (Saryg-ool et al., 2017). Such processes through the silver leaching resulted in a higher standard of some gold (Larizzatti et al., 2008). Besides, some minerals could be transformed, for example, galena into the sulphate and hydro-carbonate-sulphate forms. This is confirmed by the observed separations of anglesite and Pb-bearing alumosilicate mixtures of a complicated composition. Some minerals passed into the water-saturated varieties: kaolinite into halloysite, goethite into hydrogoethite, and so on. The complexes of oxides and hydroxides of Fe (limonite) and Mn act as sorbents, on which the gold, lead (including the native one), mercury, and other compounds precipitate. The clay minerals (kaolinite and others) also act as sorbents.

The presence of carbon testifies to the bacterial processes that produce the reduction conditions and favor the deposition, concentration, and enlargement of the precious metal (Moiseenko, 2007; Moiseenko, Kuznetsova, 2014).

The foregoing indicates the changes of the mineral-matter state of placers under the technogenesis conditions and testifies to the technogenic origin of the studied mineral associations.

Conclusion

The study of the matter composition of the technogenic placers of the Nizhneselemdzhinsky gold-bearing node in Priamurye has established the following facts:

Through the technogenesis process the mineral composition of the placers is actively changed.

The technogenic placers contain about 190 mg/m³ of the residual native gold, and about 30% of this metal is a high-standard one.

About 83% of gold in the dumps is fine and fine-dispersive.

Precious metal is very heterogeneous in composition. It contains numerous phases, ranging from practically pure gold, solid solutions of gold with silver, and ending with amalgams based on two-, three- and four-component systems of elements, including Au, Ag, Hg, and Pb.

Up to 70% of the examined gold samples are to some extent contaminated with mercury, and even the release of free mercury takes place, which indicates a high contamination of the technogene placers with this element.

All native gold is closely associated with a rock of different composition (hydroalumosilicates, oxides and hydroxides of Fe, Mn and Pb, high-carbon and carbon-containing formations, etc.).

Under the influence of the physicochemical and biochemical processes, various transformations of native gold take place in the technogenic placers: purification by the removal of silver; destruction of gold minerals-concentrators, deposition of micro- and nano-gold on geochemical barriers, and the formation of so-called "new" gold (from nano- to micro- and macro-forms).

When developing new technologies for more complete extraction of the precious metal from the technogenic placers it is necessary to consider that ore minerals in them have the increased concentration of heavy metals and radioelements, gold has the complex multiphase and multicomponent structure, and $\frac{3}{4}$ of gold is amalgamated.

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