

Chapter 2

Mineral–Concentrators of Nanogold

2.1 Sulfides

The issue of “invisible” gold in sulfides from hydrothermal deposits has long been studied by scientists. This gold is the main metal piece produced by mankind, as prevalent in the reserves of the largest world deposits (Witwatersrand, Tarkwa, Muruntau, etc.). They account for up to 40% of the total mass of metal in the deposits.

However, please note that sulfides of hydrothermal genesis do not always contain gold, and if they are, the latter is characterized by a rather broad grain-size range of particles. In this spectrum, probably the main place belongs to the gold of micrometer size, but always visible and possibly predominant proportion to sub-microscopic particles (smaller than 0.1 μm , i.e. nanoscale).

The role of sulfides as mineral–concentrators of gold indicated by many researchers (Maslennitskiy 1944, 1948; Kaimirasova 1968; Korobushkin 1970; Kalitkina 1971; Voitsekhovskiy et al. 1975; Sakharova et al. 1975; Mironov and Geletiy 1979; Gavrilov et al. 1979, 1982; Kozerenko et al. 1986; Cook and Chrysosoulis 1990; Sazonov et al. 1992; Wilson et al. 1995; Genkin 1998; Simon et al. 1999b; Bortnikov et al. 2003; Smagunov et al. 2004; Tauson et al. 2005; Koneev 2006a, b; Meretukov 2006; Zhmodik et al. 2007; Cepedal et al. 2008).

Many sulfides are not only the mineral–concentrators, but the main mineral–carriers of gold nanoparticles (especially pyrite and arsenopyrite, and to a lesser extent pyrrhotite, bismuthinite, galena, fahlore, covellite, etc.) (Zagainov 2009).

For example, the main mineral–carriers of gold in the Carlin deposit are arsenic pyrite and marcasite. In these sulfides free gold of powder in size is present, but the nanoparticles predominate (Wels and Mullens 1973; Fleet and Mumin 1997; Reich et al. 2005a, b). Determination of the regularities of gold nanoparticles distribution in Carlin ores, where they were also found on the surface of the galena and arsenopyrite grains, is seen as an important step in addressing the issue of invisible gold in sulfides (Palenik et al. 2004).

Gold nanoparticles recorded in the pyrite grains of the Pokrovskiy gold-silver deposit in the Pre-Amur region (Moiseenko et al. 2010a). The average gold content in the ore body presented by paleovolcanic rocks is estimated at 44.4 g/t, and nanogold in pyrite makes up to 9% of the total metal mass in the rock.

The presence of nanogold, in addition to arsenopyrite (especially needle-like shape) and pyrite, was found in pyrrhotite, chalcopyrite, galena, and sphalerite in gold ore deposits of Uzbekistan (Koneev et al. 2010). Novgorodova (2004) revealed nanocrystals of gold in sulfides of the deposits in the Southern Urals. Ozhogin (2009) when studying the material composition of gold-sulfide ores from Malomyr in the Pre-Amur region marked the presence of nanogold of 5–10 nm in size in pyrite and arsenopyrite.

The distribution of gold nanoparticles on the surface of sulfide minerals (pyrite, galena, pyrrhotite and arsenopyrite) is studied with the use of high-resolution electron microscopy (Zhmodik et al. 1989; Mikhlin et al. 2006b). The staff of the Institute of Geology and Nature Management FEB RAS established a presence of two nanogold types in ore deposits of the Far East: spheroidal from 5–250 nm in size with high fineness and in the form of monolayers of nano-sized thickness. They noted that the layers of native gold alternate with films of electrum containing carbon, uranium, and chlorine (Moiseenko et al. 2010b). The presence of gold nanoparticles has been established in tiny grains of galena also (Moiseenko and Kuznetsova 2010).

The main factors determining the concentration of gold in sulfides are their crystallochemical features (in particular, the presence of certain impurities, defects of the crystal lattice, etc.) and geochemical parameters of ore-forming environment (primarily temperature and fugacity of sulfur, etc.) (Badalov 1972; Arehart et al. 1993; Tauson et al. 1996; Zhmodik et al. 2010). The scientists of the Institute of Geology and Mineralogy SB RAS based the criteria that determined the presence of gold as isomorphic admixture in sulfide minerals with these features.

Currently the existence of different forms of the gold occurrence in sulfides assumes: isomorphic, in the form of gold sulfides, as a mechanical admixture of micro- and nanoparticles of gold and mixed. Isomorphism is observed both in the cationic positions (lattice sites occupied by iron cations) and anionic (in the place of the anions of sulfur, arsenic and other elements) (Schweigart 1965). Special studies have shown that the possible forms of gold occurrence in pyrite are isostructural compounds of the type AuS_2 or Au_2S .

However, most scientists believe that finding invisible gold in the pyrite structure is associated with defects in the crystal lattice. The positions of vacancies are the most favorable in this respect. This view is based on the endocrypty of trace elements concept, which theoretically justifies their occurrence in the crystal structure due to the presence of inherent defects (Urusov and Kravchuk 1978; Cabri et al. 1989, 2000; Abramovich et al. 1989, 1990; Tauson 1999a, b; den Besten et al. 1999). The application of this concept in relation to gold is fully justified, because it takes into account important crystallochemical peculiarity of this metal, which is manifested in his pronounced tendency to endocrypty. The presence of gold nanoparticles in vacant positions of the crystal lattices of the sulfides accounts for

their relatively rapid movement and the possibility of concentrating in different structural positions, due to the migration of vacancies. In addition to positions of vacancies, nanogold may be concentrated in zones of edge dislocations, micro- and nanocracks, etc.

Large widespread view that invisible gold is mainly concentrated on the surface of sulfide grains (Bancroft and Jean 1982; Jean and Bancroft 1985; Hyland and Bancroft 1989; Möller and Kersten 1994; Becker et al. 1997; Maddox et al. 1998). It is consistent with the known provision that a certain portion of the impurity atoms located in the vacant positions as a result of migration is to move in the direction of sub-surface zone. However, the process of adsorption of metal atoms from the environment plays the main role (Renders and Seward 1989; Widler and Seward 1998, 2002; Laptev and Rozov 2006). The concept of the existence in the sub-surface zone of sulfides with thickness less than 300 nm of the non-autonomous phases with a deficit of metals and the presence of specific chemical bonds, including S–O and S–S, is developed. Considerable number of them is dimers. Favorable conditions for absorption of trace elements, particularly nanoparticles, from the environment are created in this zone (Simon et al. 1999a; Smagunov 2007).

The findings of this conception are confirmed by experimental data (Mycroft et al. 1995). In particular, the surface properties of the pyrrhotite crystals have studied at the nanoscale. Pyrrhotite with lots of gold nanoparticles on the surface is distinguished by a lower ratio of Fe:S. It is assumed that iron deficiency in the sub-surface layer of pyrrhotite may be associated with the presence of not only sulfide and sulfur-containing compounds of iron, but also of the oxide and hydroxide. The latter are characterized by high sorption properties, which are manifested in the adherence of gold nanoparticles (Smagunov et al. 2004).

An artificial solution was used in one of the experiments. It included gold nanoparticles of 10–80 nm in size and the fine powder of pyrite particles in the tens of micrometers. Nanogold was obtained by artificial way, and the size of its particles was controlled by special methods. It was established experimentally that nanogold completely deposited on the surface of pyrite particles when its concentration in a solution reached about 50 mg/ml. The smallest particles of pyrite showed the high ability to adsorb gold nanoparticles. At the same time, the process was also influenced by the size of the gold particles: large nanogold had the higher adsorption ability (Fu et al. 2012).

Experiments also proved that nanoparticles of gold ranging from 2 to 50 nm in size and more were absorbed by the surface of sulfides in the process of spontaneous precipitation from chloride solutions under reducing conditions. Thus, the dimensions of the nanoparticles, their location on the surface of sulfide and the total number depend on the mineral species, surface condition of the grain and the external environment. By the ability to adsorb nanogold the sulfides are arranged in the following order: chalcopyrite, sphalerite, galena, arsenopyrite, pyrite, pyrrhotite. The state of the sulfide surface also affects the morphology of gold nanoparticles. The deposition of nanogold promotes moderate oxidation with origin thin oxide films on the mineral surface (Romanchenko 2007).

The possible range of gold occurrence in the crystal structure of sulfides was calculated by different methods (Tauson et al. 1998a, b). One of them obtained the limit by almost two orders of magnitude higher than theoretically installed isomorphic capacity of the mineral crystal lattice (Smagunov 2007). Thus, it is considerably influenced by the crystallochemical characteristics of the mineral and geochemical parameters of the environment (temperature, fugacity of sulfur, etc.). The influence of the energy amount of the metallic bond in the crystals of sulfides in the presence of invisible gold was experimentally proved also (Mironov et al. 1987). There is a direct correlation between these indicators.

A number of works devoted to the study of the question of particularly morphological aspects of gold nanoforms in sulfides. A detailed study with application of high-resolution electron microscopy showed that they are frequently the assemblies of nanoscale globules of gold. Some units can reach quite large sizes. This conclusion was made by Marchenko (2011) in the study of gold particles up to 20 μm present in the grains of arsenopyrite and arsenical pyrite from the rocks of black shale formations in Kazakhstan.

Employees of the Amur Scientific Research Institute since 1992 have conducted systematic research of nanoscale gold. Overall, it was investigated gold from 48 alluvial and three coastal placers, which were located in the eastern areas of the country. The presence of gold in high quantities in pyrite, hydrogoethite and native metals (silver, copper, iron) has been determined by precision methods. Gold nanoparticles of spheroidal shape of 50–100 nm in size with the fineness of 800–820 were fixed by the methods of high-resolution electron microscopy in these minerals and kaolinite. Characteristically, nanoparticles of gold in these minerals formed the “staring” clusters, distributed very unevenly that significantly made difficulties for their detection. The proportion of nanoscale metal in the total its weight defined by vacuum filtration methods estimated at an amount of 31% (Moiseenko 2010).

Nanogold in sulfides in many deposits presents in several morphological types. For example, the discrete allocations of gold nanoparticles in pyrite and marcasite and films on the surface of the older sulfides without gold are observed in the Carlin deposit.

In the gold deposit, confined to the North China Craton, where gold mineralization is hosted by quartz veins in Archean metamorphic rocks of the amphibolite facies, invisible gold occurs in pyrite, on the one hand, in the form of isomorphic impurities, and, on the other hand, in the form of nanoparticles of native gold or electrum, and tellurides of gold. In addition, visible gold is presented hosted by grain boundaries or filled in microcracks in pyrite (Shi-Jian et al. 2011).

However, sulfides not always perform the role of mineral-concentrators and especially the mineral-carriers of gold. In this regard, great importance is attached to the problem of identifying of formation types of deposits, in which sulfides become the main mineral-carriers of gold.

It is believed that invisible gold in the greatest number concentrates in the sulfides of the Carlin-type deposits, as well as porphyry copper and pyritaceous (Vikentyev 2006; Vinokurov and Vikentyev 2009). The significant mass of the gold

is especially concentrated in gold-sulfide disseminated ores. The main mineral-carrier of gold is arsenopyrite. So, gold-sulfide mineralization in Olimpiadinskoe deposit is mainly represented by inclusions of nanogold in needle-like arsenopyrite. The industrial mineralization is presumably formed as a result of crystallization of gold-arsenic-sulphur complexes that were observed in gas phase by a zone of deep faults (Savichev 2004).

A more detailed examination reveals a different goldiferousness of separate generations of mineral-concentrators. The definition of invisible gold contents and associated elements in pyrite of the four gold-arsenic deposits using laser ablation ICP-MS (Large et al. 2009) has allowed to establish two phases of pyrite enrichment by gold in every deposit: early (sedimentary) and late (hydrothermal). In the first stage gold concentrates in arsenic-bearing diagenetic pyrite along with other trace elements (As, Ni, Pb, Zn, Ag, Te, V, Se), whereas in the second stage gold occurs as loose particles in the cracks of metamorphic or hydrothermal pyrite, and thin gold-arsenic edges on the protruding parts of the hydrothermal pyrite grains (for example, in the Carlin deposit). In hydrothermal pyrite not much Ni, V, Zn, Pb, Ag, but there are areas with abnormally high contents of Co and As. The increased contents of cobalt and nickel with low contents of arsenic and gold are also observed in the marginal edges on the ledges of hydrothermal pyrite grains of some deposits (Sukhoy Log).

Two generations of arsenopyrite grains are revealed in one of the gold-sulfide deposits of the Far East. The first of these is represented by large crystals without gold. The second generation of small arsenopyrite crystals has elongated prismatic shape. A significant amount of nanogold particles of a few tens of nanometers in size, forming clusters, is discovered in them by means of transmission electron microscopy (Ozhogina and Rogozhin 2010).

Thus, mineral-concentrator is capable to include nanogold often in a different measure in the same mineral deposit. So, one of the main mineral-carriers of gold in the Witwatersrand deposit is pyrite. However, the gold content in it varies in very wide limits (9–1440 ppm).

Some geochemical indicators of gold mineralization are revealed for sulfides. In particular, high arsenic and low iron contents are typical to them. Thus, the arsenic content in gold-bearing pyrite usually varies from 2 to 8 wt. % (Cline et al. 2005). The studies of some authors (Reich et al. 2005a, 2006) have shown that when the ratio $\text{Au}:\text{As} < 0.02$ gold is mainly present in pyrite in the form of a monovalent cation and isomorphically replaces the iron cations. The nanoparticles of native gold appear when a higher value of this relation is marked. All geochemical signs indicate that gold is adsorbed by pyrite from ore-bearing fluids, where it was in the form of complex $\text{Au}(\text{HS})_2$.

In Uzbekistan ores especially auriferous arsenopyrite with an increased S:As is discovered (Koneev et al. 2008). The mineral-carriers of invisible gold are pyrite and arsenopyrite in the skarn deposit El Valle (Spain). Gold-bearing pyrite (gold content up to 0.08 wt. %) has a high content of arsenic (up to 9.5 wt. %) and a large number of other trace elements (Sb, Ni, Tl, Cu, Hg, Se). The abundance of impurity

elements (Cu, Sb, Tl) is also characterized for arsenopyrite (gold content of 0.125–0.3 wt. %). Invisible gold concentrates on the parts of the surface of pyrite and arsenopyrite grains, characterized by iron deficiency (Cepedal et al. 2008).

The nature of distribution of gold nanoparticles in the crystal lattices of sulfides is also studied. In particular, a large amount of gold nanoparticles, the average size of which is about 4 nm, is detected when observed grains of arsenical pyrite in high-resolution electronic microscope. Their distribution in the bulk of pyrite grains is completely chaotic without any signs of a natural orientation.

A detailed study of the distribution of nanogold particles in sulfides is also in the process of their synthesis. In this case, it is possible to combine different conditions of mineral formation: the concentration of gold in solutions, their composition, external parameters, etc. (Bugueva 2006). These comprehensive studies revealed the effect of concentration of invisible gold on the border of nanoblocks of pyrite crystal lattice (planar defects) of 50–100 nm in size. It is manifested at relatively low temperatures (usually below 300 °C) and leads to the formation of high concentrations of gold (up to tens of grams per ton). The implementation of this effect in natural situations is quite probable in terms of the crystallization of mosaic structure pyrite from strongly saturated epithermal fluids that has been occurred during the formation of the Carlin deposit. Some gold-related elements, in particular arsenic, played the important role in intensifying of this effect. Arsenic ions participated in the transport of gold in hydrothermal solutions in the form of sulfide-arsenide complexes, and then the noble metal was selected from them as an independent mineral phase in the structures of arsenical pyrite or arsenopyrite. Arsenic often remains in the haloes of dissipation.

Modeling of the nanogold behavior in pyrite using the molecular dynamics method shows that from a hypothetical correct location in the matrix of pyrite at a temperature of 300 °C nanoparticles are rearranged in a random distribution at a temperature of 900 °C (Reich et al. 2006). During this process gold nanoparticles approach each other with origin of aggregates (Fig. 2.1).

Experiments have shown that with increasing temperature up to 370 °C the gold nanoparticles do not react to the state change of the environment. However, the process of aggregation and consolidation of nanoparticles begins above this temperature, which leads to their instability. By the way, approximately 100 primary gold nanoparticles smaller than 5 nm in size are transformed into several units of about 35 nm in size. The reason is melting of small nanoparticles, transition them to the solution, and then the deposition and aggregation.

The dependence of the melting temperature of free gold nanoparticles from their size is affected on these processes (Ercolessi et al. 1991). In particular, if you reduce the size to 4 nm, the melting point of gold is reduced with 1063 to 427 °C. The temperature limit of the existence of gold nanoparticles in arsenical pyrite was experimentally determined in the above results of studies. These data emphasized once again that a favourable condition for conservation of gold nanoparticles in sulfides is a relatively low temperature.

The behavior of gold nanoparticles in the structure of sulfide minerals depends significantly on their size that is experimentally proved also. In particular, the

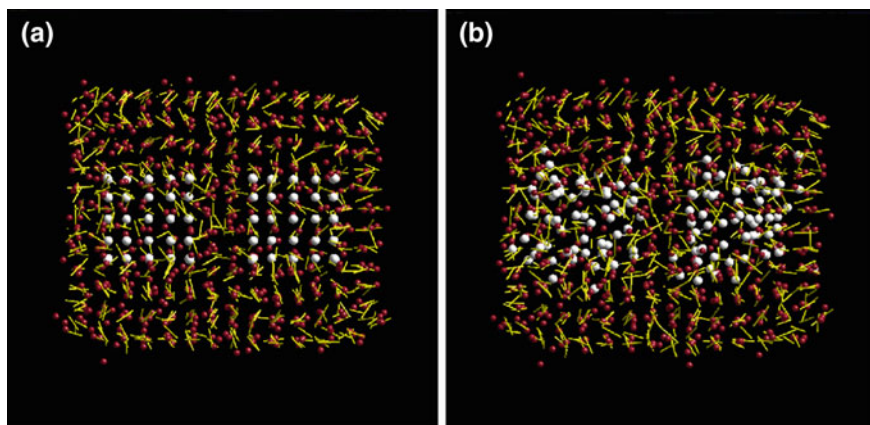


Fig. 2.1 The model of gold nanoparticles location in the structure of pyrite: **a**—primary at a temperature of 300 °C, **b**—redistribution of the nanoparticles at a temperature of 900 °C. (Reproduced from Reich et al. 2006)

binding energy of gold nanoparticles in the crystal lattice of the sulfide markedly increases when size decreases from 30 to 3 nm. There are also characteristic physical phenomena associated with the presence of nanogold (Mikhlin et al. 2006a).

The value of the different mineral species of sulfides as mineral–concentrators of nanogold is not always consistent with their role as mineral–carriers of metal. The primary role as the mineral–carrier of gold from sulfide minerals belongs to pyrite in connection with its significant predominance in gold deposits, although the gold content in arsenopyrite and sometimes in some other sulfides may be higher than in pyrite. The proportion of the native nanogold mass in sulfides presumably increases proportionally to the increase in overall gold grade in ore.

2.2 Gold

The presence of gold nanoparticles in the sub-surface layer of matrix gold grains is widely common form of their existence in the weathered rocks of deposits and ore bodies of gold-sulfide and quartz-gold-sulfide formations. They can be found even on the surface of the grains of placer metal in alluvial deposits near source rocks, although their surface is subjected to strong mechanical deformations and abrasion during the transporting process. Gold nanoparticles are often met on the surface of gold particles in the placers of secondary collectors, re-deposited weathered rocks, etc.

2.2.1 Ensembles of Micro- and Nanoparticles

Gold nanoparticles typically present together with the microparticles of noble metal having the size somewhat more than $0.1\ \mu\text{m}$ (Fig. 2.2). The location of the micro- and nanoparticles is usually dispersed and chaotic within such ensembles, but sometimes there are clusters of them. However, only particles of nano-sized range can be distributed on the significant areas of the gold surface (Fig. 2.3).

2.2.2 The Morphology of Gold Nanoparticles

It is theoretically proved that the smallest size nanoparticles, including gold, usually have a spherical shape (Yushkin 2005). The reason for this phenomenon is the abundant surface energy of the nanoparticles.

Indeed, electron microscopic study of the gold surface of the numerous gold objects showed that metal nanoparticles were mainly represented by rounded up to spherical individuals (see Fig. 2.3). However, there were often other forms also: worm-like, angular and irregular. Nanoparticles of elongated shape, up to wire-like, were often presented on the surface of gold particles coated with hydroxides of iron (Fig. 2.4).

In addition to the above, even more complex morphological types of nanogold particles (for example, ameboidal) and a geometrically correct triangular, hexagonal, etc. are rarely observed (Figs. 2.5, 2.6).

The study of the structure of many nanoparticles under high magnification (up to 300–500 thousand times) does not detect the signs of heterogeneous structure (Fig. 2.7). Along with this, the complex structure of some nanogold particles, which represent the aggregates of tightly consolidated nanoparticles of different shapes and sizes, quite clearly manifests (Fig. 2.8).

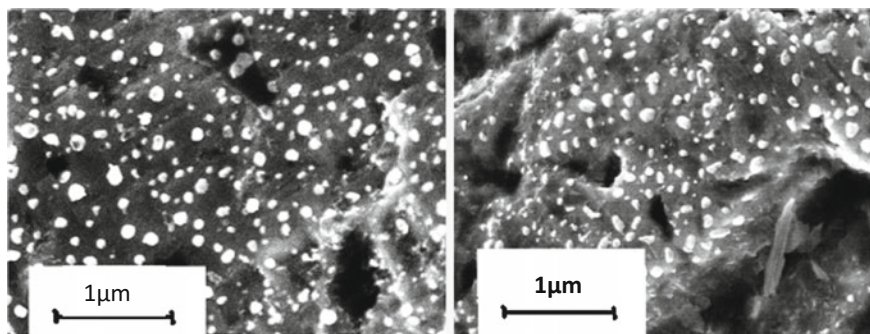


Fig. 2.2 Ensembles of micro- and nanoparticles of metal on the surface of placer gold grains

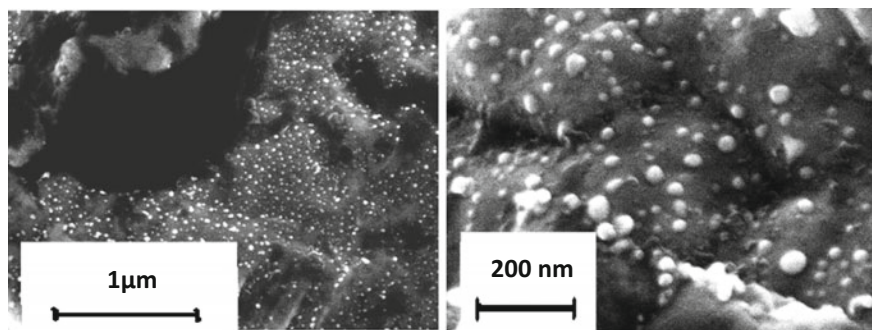


Fig. 2.3 Clusters of gold nanoparticles on the matrix metal surface

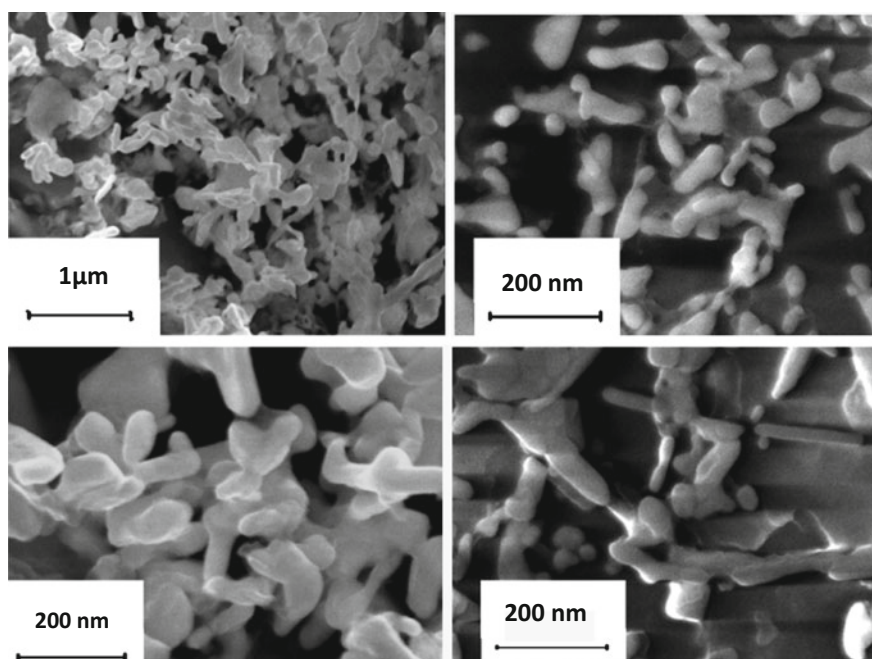


Fig. 2.4 Single and accumulations of gold nanoparticles of elongated shape

2.2.3 The Generations of Nanoparticles

Analysis of electronic microphotographs shows that it is possible to allocate among single gold nanoparticles the individuals being in different contacts with the surface of the matrix metal. For example, some nanoparticles barely touch the surface of matrix gold, the other root in a superficial gold layer to a definite depth (Fig. 2.9).

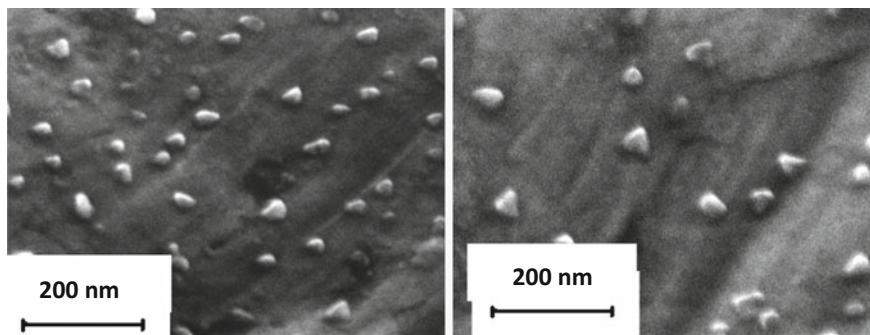


Fig. 2.5 Gold nanoparticles of the most common forms (the Vyatka-Kama Depression)

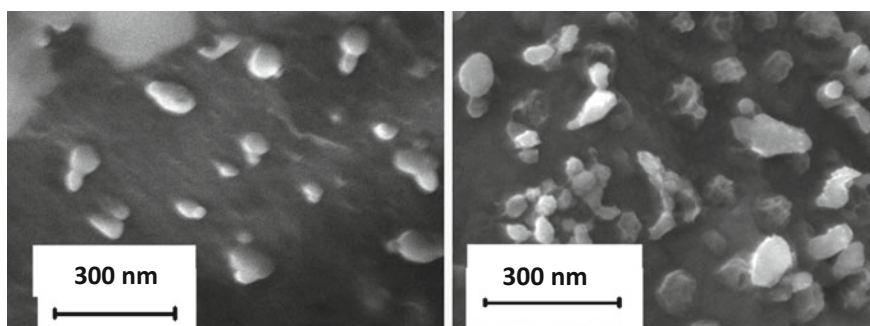


Fig. 2.6 Gold nanoparticles of various shapes

This fact indicates the time difference from the deposition of nanogold on the surface of the matrix gold. Probably, individual nanoparticles immerse into the sub-surface layer over time due to the diffusion of metal atoms. The most “ancient” of them probably do not differ in the pictures, being completely absorbed in the sub-surface layer.

In this regard, we can distinguish the generations of different age for gold nanoparticles. The nanogold of the youngest generation that precipitates immediately at the nano- or microparticles of the previous one, forming a kind of tandem, looks especially pronounced in electronic microphotos (Fig. 2.10). It is characteristic that the particle size of the next generation, as a rule, smaller than the previous one. These tandems are usually the initial forms that precede the formation of aggregates.

Sometimes the morphological features of relatively large rounded gold nanoparticles indicate their concentric zonal structure due, perhaps, layer-by-layer growth of the shell in the range of some core (Fig. 2.11).

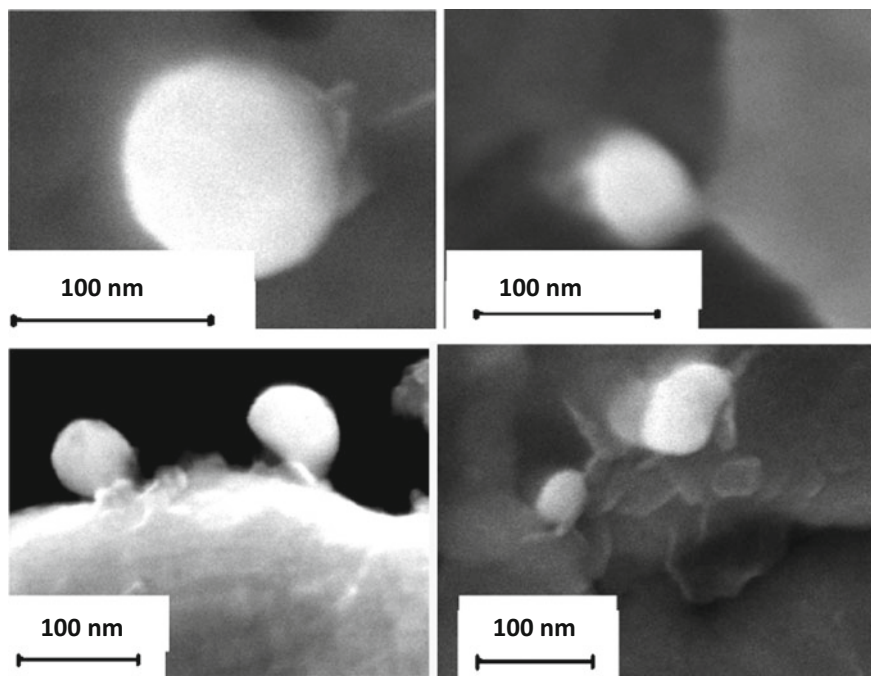


Fig. 2.7 Homogeneous roundish gold nanoparticles

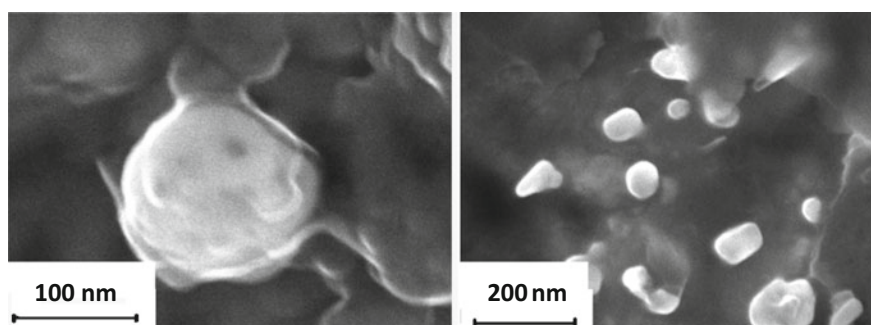


Fig. 2.8 Nanogold formed by the merging of smaller nanoparticles (the weathered rocks of black shales)

2.2.4 Regularities of Nanogold Location on the Surface of the Matrix Gold

Gold nanoparticles are usually not located uniformly on the surface of the matrix gold. The places of their local concentration are different hollows (cracks, pores,

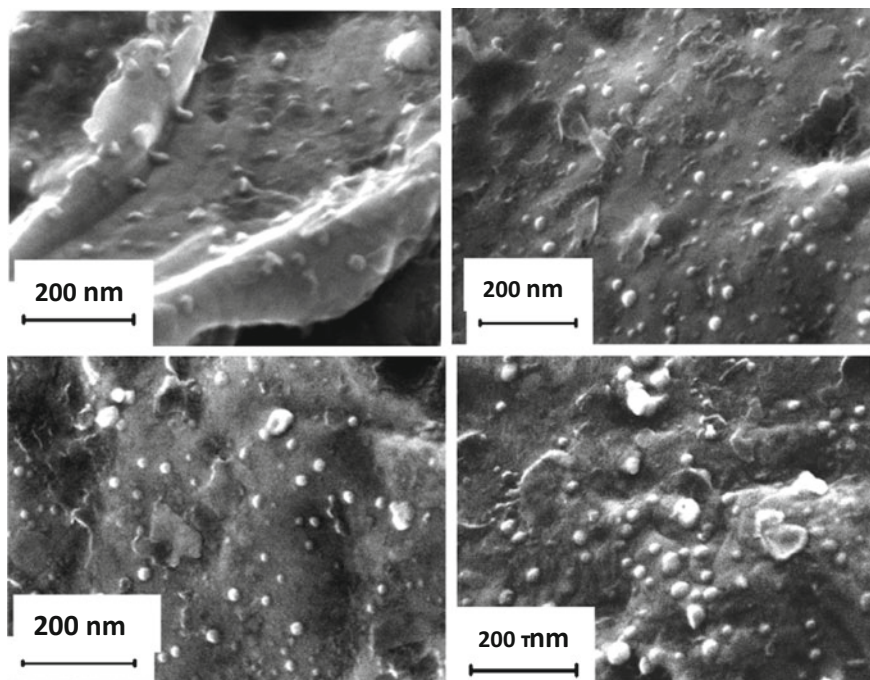


Fig. 2.9 Nanoparticles of different generations on the gold surface of the Vyatka-Kama Depression: buried in a surface layer of gold (*gray*) and the adjacent (*light*)

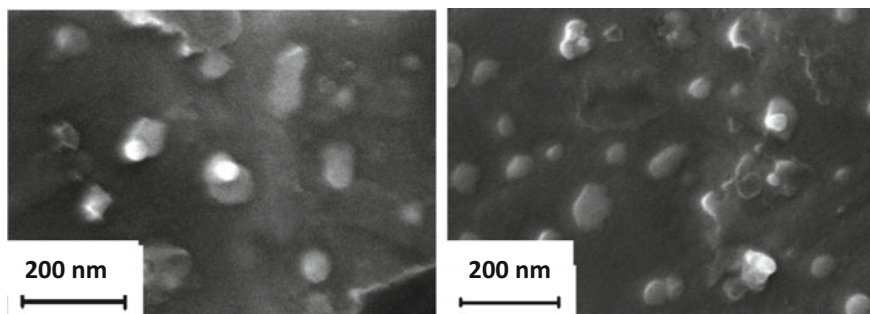


Fig. 2.10 “Tandems” of gold nanoparticles

scratches, etc.) or, on the contrary, the elevated parts of microrelief. In the first case, they are most often confined to the walls of the negative elements of the surface microrelief (Figs. 2.12, 2.13).

However, selective localization of gold nanoparticles with distinct boundaries of “populated” areas is observed even on a relatively flat surface of the matrix metal

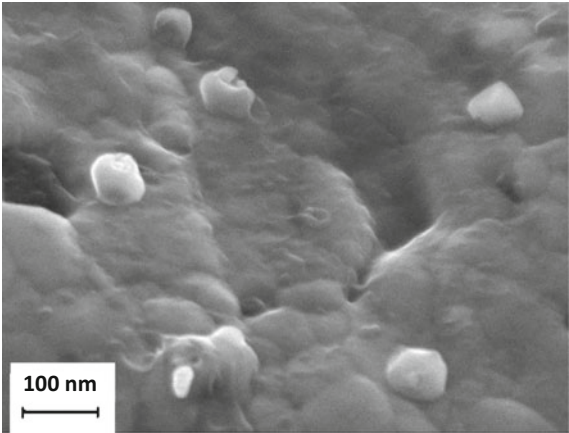


Fig. 2.11 Signs of concentric-zonal structure and growth of layered gold nanoparticles

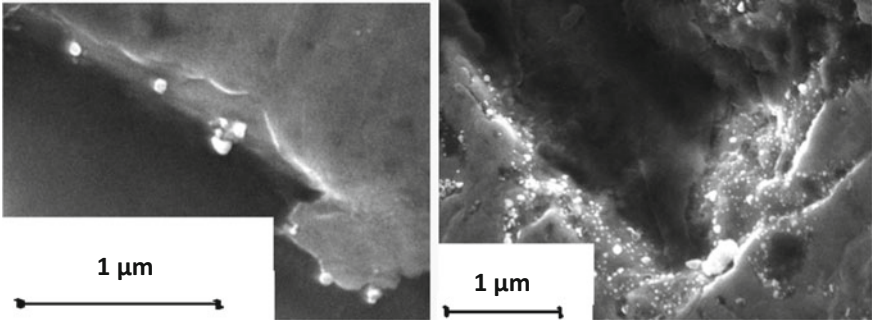


Fig. 2.12 The location of the nanoparticles on the walls of large hollows in surface microrelief of the matrix metal grains

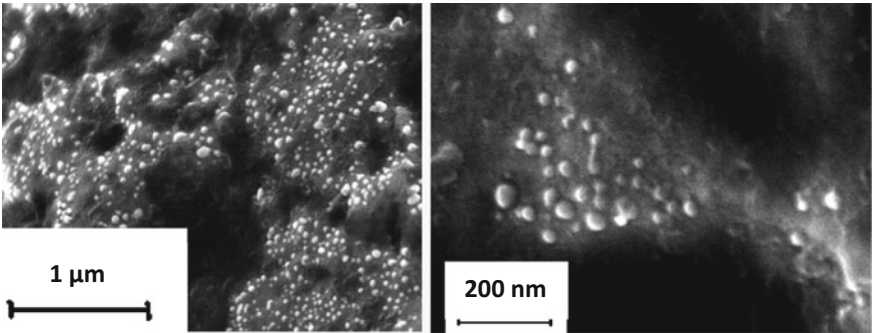


Fig. 2.13 The location of the nanoparticles on the elevated parts of the gold surface microrelief

(Fig. 2.14). Sometimes this is due to the availability of covering films of secondary substance (usually iron hydroxides). Nanoparticles also concentrate around the microinclusions on the surface of gold (Fig. 2.15).

On the surface of the matrix metal with ridged or stepped microrelief due to the projections of microlayers nanogold particles are oriented along the directions of layering and mainly in the lower zones of microlayers junction (Fig. 2.16). As a result, there is a linear orientation of the nanoparticles parallel to the projections of stepped microrelief.

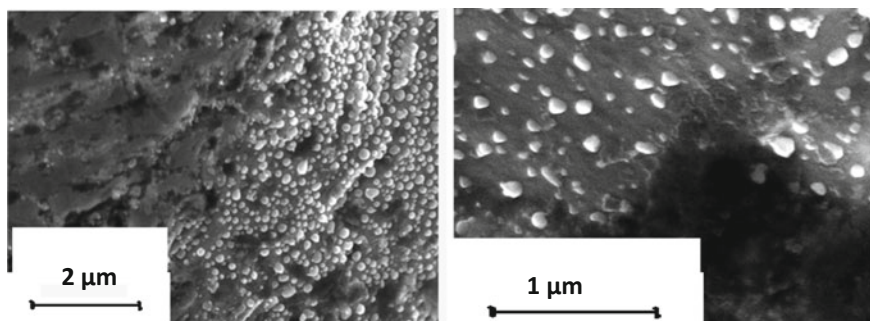


Fig. 2.14 The boundaries of the concentration zones of gold micro- and nanoparticles on the matrix surface

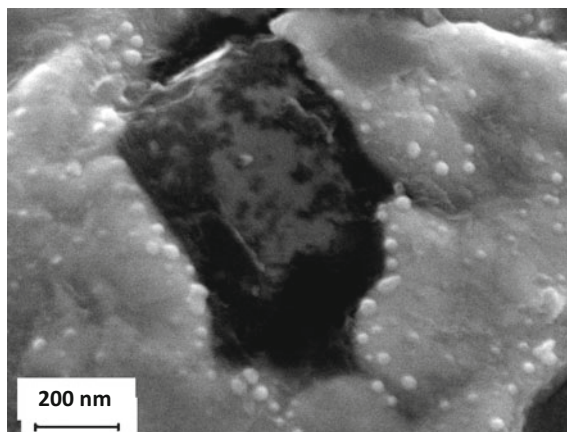
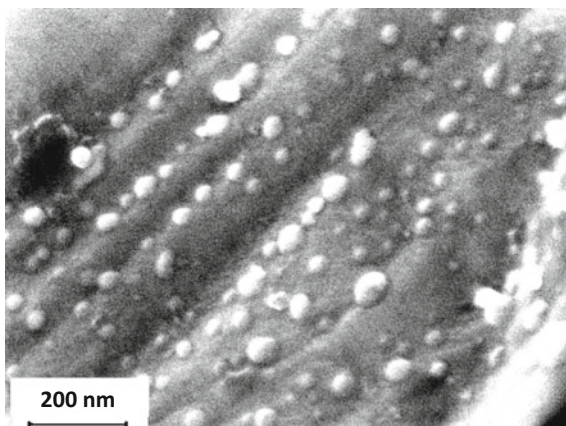


Fig. 2.15 The location of gold nanoparticles around the microinclusion

Fig. 2.16 Subparallel arrangement of gold nanoparticles on the surface of layered metal



2.2.5 The Density of Gold Nanoparticles on the Surface

Comparative analysis of electron microphotographs of the gold surface covered by metal nanoparticles shows that the density of the latter is considerably different. It can be quantified in the value of nanoparticles per unit surface area. Specific measurements show that the density of the gold nanoparticles on the matrix surface varies from a few to 150 nanoparticles per 1 mm^2 . It is controlled by the surface microrelief, especially the presence of microdefects (scratches, hollows, cracks, etc.).

2.2.6 The Chemical Composition of Gold Nanoparticles

Microprobe analysis gives the opportunity to determine the chemical composition of individual microparticles in the one-dimensional cluster with nanoparticles, which suggests their ordinary genesis. Thus, we can define the average chemical composition of nanoparticles taking into opinion a sufficiently dense arrangement of gold nanoparticles.

The results of microprobe analysis have allowed conclude wide variations in the chemical composition of nano- and microparticles of gold (Table 2.1). The identity of chemical composition of the matrix metal and particles of gold on its surface is marked in some cases, too.

Table 2.1 The chemical composition of gold microparticles (Vagran deposit), wt. %

Element	Grain 1					Grain 2		
	matrix	1 ^a	2	3	4	matrix	1	2
Au	72.53	72.90	64.27	86.59	71.25	96.12	94.79	95.30
Ag	27.02	26.54	35.30	12.62	27.88	0.46	1.12	0.24
Cu	0.25	0.36	0.21	0.49	0.28	1.71	1.82	2.19
Zn	–	–	–	–	–	1.27	1.40	1.81
Hg	0	0	0	0	0	0	0	0
Ni	0	0	0	0	0	0	0	0
Co	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	0	0	0
Sb	0	0	0	0	0	0	0	0
As	0	0	0	0	0	0	0	0
Bi	0	0	0	0	0	0	0	0
Pd	0	0	0	0	0	0	0	0
Pt	0	0	0	0	0	0	0	0
Fe	0.20	0.20	0.22	0.30	0.59	0.44	0.87	0.46
Total	100	100	100	100	100	100	100	100

^a1, 2, etc.—individual microparticles of gold

2.2.7 Nanoscale Particles in the Internal Structure of Gold

The nanoparticles present in the internal zones of gold as constituents of a granular structure of metal. Petrovskaya (1973) noted wide variations in the dimensions of the grains that make up the structure of granular gold (from 10 nm to 2 μm). It was established an important regularity, namely, to directly depending the values of grain diameters in internal structure from the particle size of gold.

We investigated fine-grained gold in the Jurassic sediments of the Vyatka-Kama Depression. There were the smallest individuals, the size of which usually did not exceed 500 nm. Gold particles were etched in alkali at the temperature up to 500 °C for a more distinct observation of their grained internal structure, which simultaneously led to the removal of gold nanoparticles from the surface.

The individual micrograins composing the internal structure of gold are distinctly distinguished on electron microscopic pictures of high resolution. Nanoparticles that promote the formation of a very dense packing of grains in the metal structure are found in the gaps between relatively large individuals (200–300 nm) (Fig. 2.17, 2.18). Fragments of granular structure of very fine particles of gold in different deposits with the participation of nano-sized individuals can be seen in other photos, too (see Figs. 2.3, 2.11).

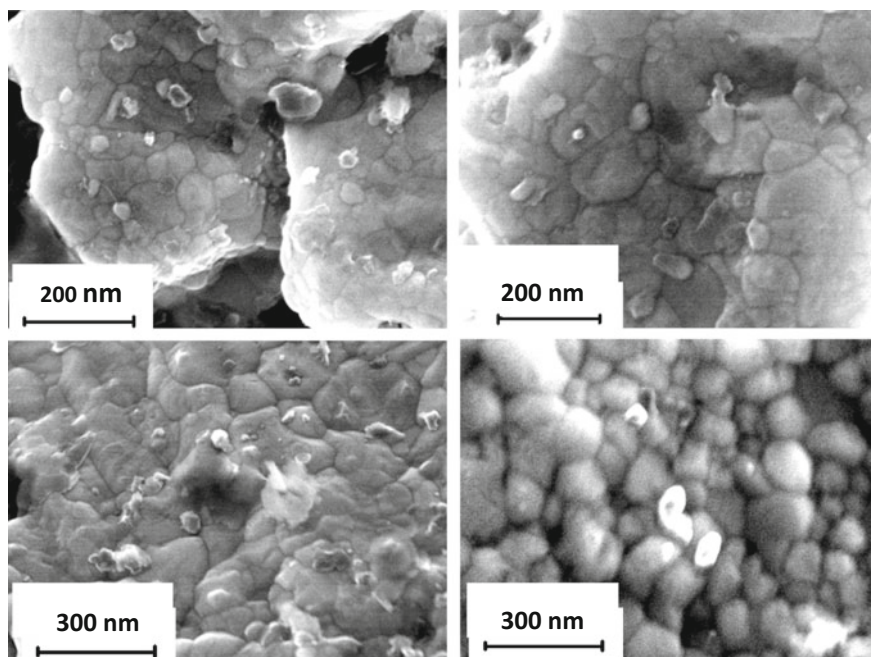


Fig. 2.17 Fragments of fine-grained gold structure with nanoscale inclusions

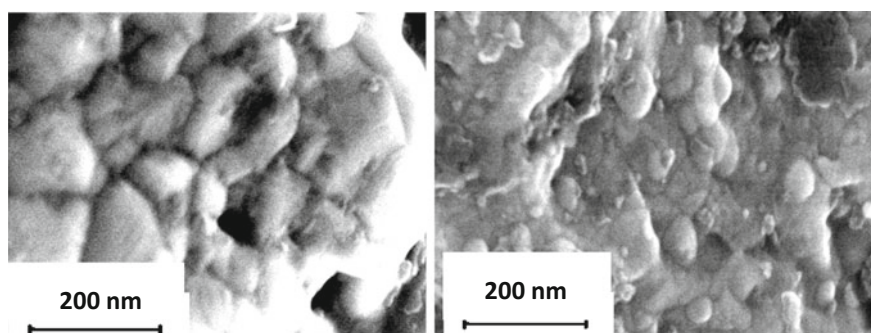


Fig. 2.18 Micro- and nano-grained structure of gold (the Vyatka-Kama Depression)

2.3 Platinum Group Metals

With the use of high-resolution electron microscopy and microprobe analysis we studied the many grains of platinum group metals from various objects, especially the Urals, with an attempt to detect gold nanoparticles on their surface. However, the composition of films of the usual golden color covering the surface of platinum grains in the most cases corresponded to the hydroxides of iron.

Only in several objects (Kuryinskaya placer in the Middle Urals, the weathered rocks of black shales in the Mining district of the Perm Region) nanoparticles of native gold and amalgams were detected in the hollows of isoferroplatinum and tetraferroplatinum surface (Figs. 2.19, 2.20, 2.21).

The gold amalgams of composition Au_3Hg_2 are the most common on the surface of Kuryinskaya placer platinoids. They are presented by microglobules of a few micrometers in size composed of nanoparticles (Fig. 2.22), multilayer continuous crusts of close-packed nanoparticles (Fig. 2.23) or other kinds of aggregates of nanoparticles (Fig. 2.24).

The nanoparticles of 10–20 nm in size differ with a large magnification in the composition of these clusters, which probably make up the bulk of nanoscale individuals (Fig. 2.25).

Fig. 2.19 Gold aggregates in a hollow of the surface of the isoferroplatinum grain

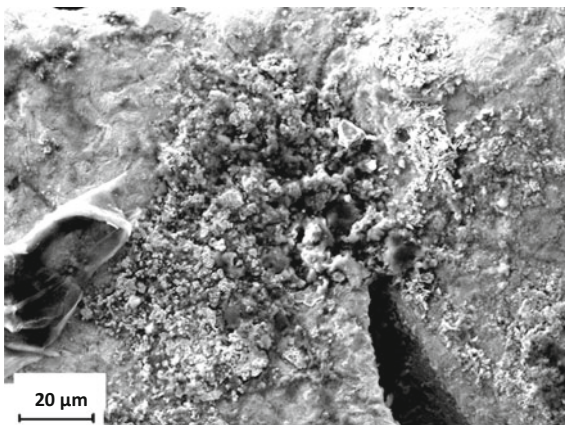
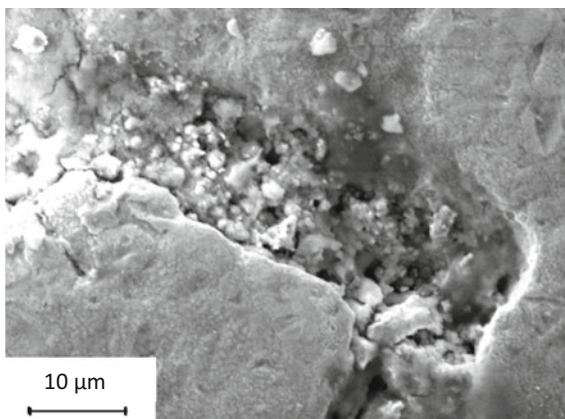


Fig. 2.20 The aggregates of gold amalgams on the isoferroplatinum grain



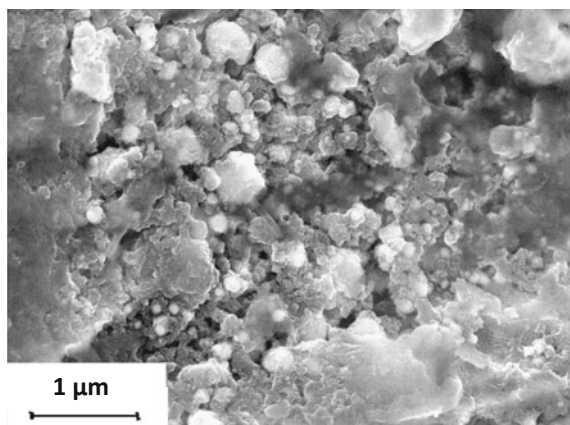


Fig. 2.21 The fragment of isoferroplatinum grain surface with nanogold

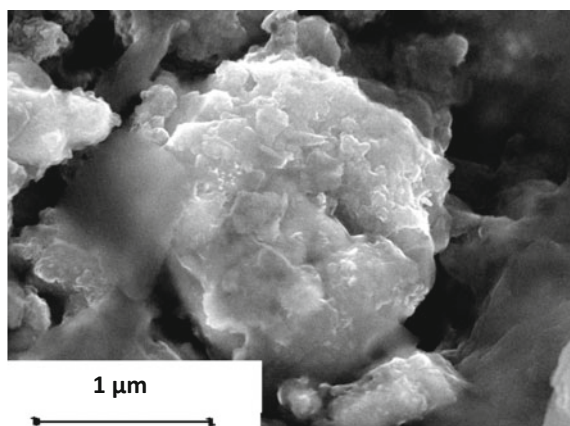


Fig. 2.22 Gold amalgam of about 2 μm in size on the isoferroplatinum grain

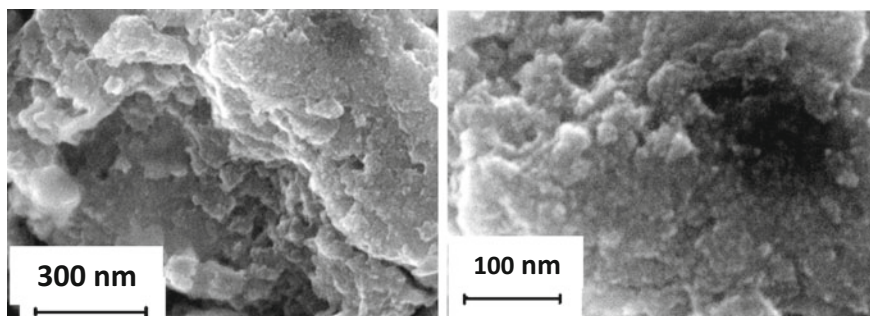


Fig. 2.23 Dense covers of nanogold particles in hollows of the isoferroplatinum surface

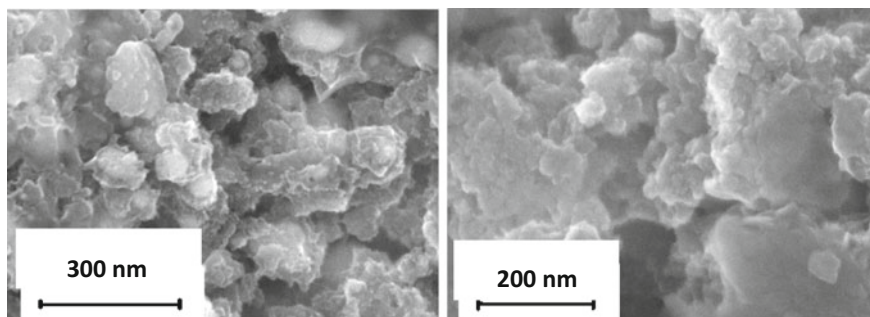


Fig. 2.24 Films of gold nanoparticles on the surface of platinumoids

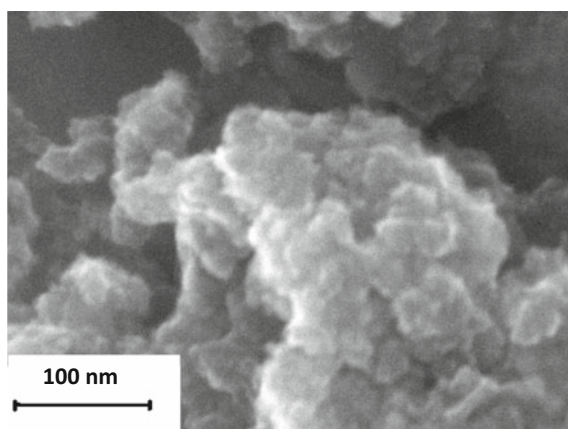


Fig. 2.25 Dense aggregates of gold nanoparticles up to 10–20 nm in size in the hollow of the tetraferroplatinum grain surface

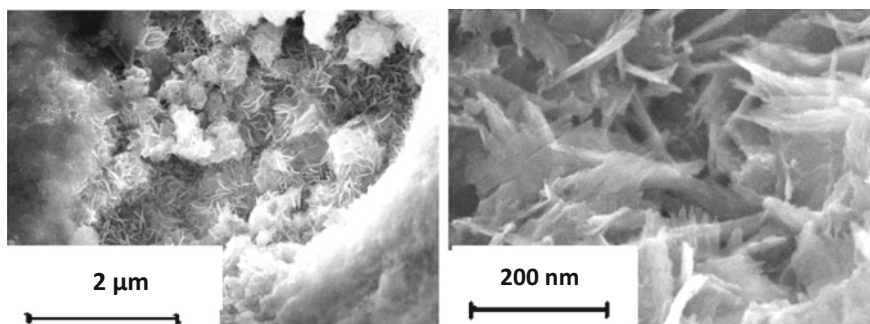


Fig. 2.26 Gold-ferriferous compounds in the hollows of the isoferroplatinum grain surface

The platinum grains, on the surface of which there are needle-shaped and star-shaped aggregates of gold-ferriferous composition, are characterized for the weathered rocks developed on the black shales (Fig. 2.26).

Gold, iron and oxygen, the total content of which is from 80 to 98%, are presented in variable amounts in chemical composition of the gold-ferriferous aggregates on the surface of platinum group metals. Silicon and almost always aluminum are presented also. We can assume that the bulk of these aggregates are composed by nanoscale native gold, iron hydroxides, and subordinate amounts of clay minerals. The presence of lead and niobium at abnormally high contents in

Table 2.2 Chemical composition of platinoids and nanoscale gold-ferriferous aggregates on their surface, wt. %

Element	1	2	3	4	5	6	7	8
Pt	89.22	83.40	—	87.03	—	—	—	—
Au	—	—	64.70	—	45.21	68.37	23.16	15.88
Ag	—	—	1.50	—	0.33	0.49	4.06	2.02
Hg	—	—	33.54	—	—	—	—	—
Pd	0	0.40	—	1.47	—	—	—	—
Ir	0	—	—	0	—	—	—	—
Rh	0.32	—	—	0.39	—	—	—	—
Ru	0	—	—	0.22	—	—	—	—
Os	0	—	—	0.76	—	—	—	—
Fe	9.71	15.25	—	9.24	16.60	11.70	32.76	40.70
Sb	—	—	0.26	—	—	—	—	—
Cu	0.58	0.77	—	1.17	0.73	—	0.80	1.54
As	—	—	—	—	0.15	0	0.16	—
Pb	—	—	—	—	—	—	—	6.91
Ni	0.16	0.17	—	0	—	—	—	—
Nb	—	—	—	—	—	—	6.28	—
Si	—	—	—	—	5.16	1.10	1.95	3.89
Na	—	—	—	—	0.12	—	—	—
K	—	—	—	—	0.38	—	—	—
Al	—	—	—	—	3.73	0.98	2.08	3.24
Mg	—	—	—	—	0.44	—	—	0.19
Ti	—	—	—	—	0.08	—	—	0.13
Ca	—	—	—	—	0.26	—	0.37	0.30
Mn	—	—	—	—	0	0	—	0.13
O	—	—	—	—	26.82	17.36	26.38	24.69
Cl	—	—	—	—	—	—	—	0.37
Total	100	100	100	100,28	100	100	100	100

Kuryinskaya placer: 1—isoferroplatinum, 2—tetraferroplatinum, 3—gold amalgam; Perm Region, the weathered rocks of black shales: 4—isoferroplatinum, 5–8—gold-ferriferous aggregates on the platinoids

some places indicates the participation of the corresponding mineral phases reflecting the specific geochemical environment of the weathered rocks above the black shales (Table 2.2).

2.4 Goethite

The close geochemical connection between goethite and gold in the weathered rocks on the deposits of gold-sulfide and gold-sulfide-quartz formations is observed in almost all sites. Primarily, it is due to their close relationship with minerals of the primary sources of gold—iron-bearing sulfides (arsenopyrite, pyrite, pyrrhotite, chalcopyrite). Ferriferous hydroxides were formed in the process of oxidation of sulfides, and at the same time gold was released from crystal lattice of primary minerals.

Simultaneous deposition of gold nanoparticles on the surface of pyrite and goethite was recorded in detailed examination of a number of objects with a usage of radiotracer atoms (Schoomen et al. 1992). In the deposits of Hetai gold ore field (the Southern China) goethite particles of needle-like or spherical shape, spherical aluminum particles and crystals of calcite are the main mineral-concentrators of

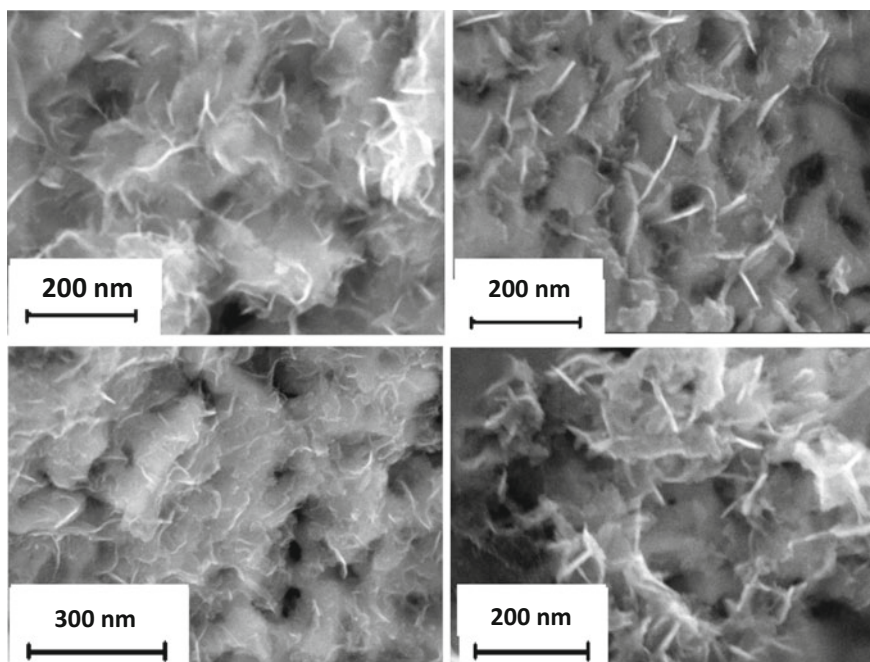


Fig. 2.27 Nanogold (light needle-shaped) in the goethite of different objects

gold nanoparticles. On the whole, the gold nanoparticles of 18 to 20 nm in size form aggregates together with the needle-like microparticles of goethite or they are concentrated on their surface (Shui 1991).

The presence of nanogold particles on the surface of iron hydroxides or their intergrowths are discovered by the author in the study of many objects, too (Fig. 2.27). There are exotic gold-feriferous aggregates on platinoids in the weathered rocks of black shale units described above. Nanogold in intergrowths with goethite has most often needle-like shape, which is probably the result of its growth in a certain direction. The density of gold nanoparticles disposition in feriferous aggregates varies markedly in different objects, which may be correlated with the degree of gold mineralization in the primary sulfides.

Other features of the gold-feriferous aggregates and their chemical composition will be discussed further in Chap. 3.

2.5 Quartz

Zagainov (2009) considers quartz as the second most important mineral-carrier of gold after sulfides. This is due to their joint origin in various types of deposits in a wide range of temperatures and the usual predominance of quartz in percentage quantities over the other mineral-concentrators. Visible gold is constantly observed in quartz of various occurrences. There were not so many researches on inclusions of gold nanoparticles in quartz, but they made on the example of some the largest deposits that allow confidently distinguish the quartz as the most important mineral-concentrator of nanogold. For example, quartz is one of the main mineral-carriers of gold in the Carlin deposit. It is proved for this deposit that a large proportion of the metal mass in quartz is presented by invisible gold (Cline et al. 2005). The same conclusion is drawn for many other objects.

The presence of fine and ultra-fine (dispersed) gold is found in the metasomatic quartz of the early generation in the Mnogovershinnoe deposit (the Lower Amur ore district). It is presented by drop-shaped forms, scattered throughout the mass of quartz metasomatites. The ore bodies in this deposit at 95–97% are composed of quartz that reveals its role as the main mineral-carrier of gold (Borodaevskaya and Rozhkov 1974).

The presence of gold nanoparticles in chalcedon-like quartz, filling up sub-veins and veins in metasomatites of Sovetskoe deposit (the Yenisei Ridge) is found by Novgorodova (2004). The sizes of gold nanocrystals, which usually have a cubic shape, are tens of nanometers. They often form the twin intergrowths. In addition, the allocations of colloidal gold, represented by clusters of globular particles of 1–3 μm in size are observed. Ozhogin (2009) noted the presence of gold nanoparticles in quartz of gold-sulfide ores of Malomyr deposit in the Pre-Amur region also.

It is found during the phase analysis of gold distribution in the Pokrovskoe gold-silver deposit in the Pre-Amur region that the largest proportion of its mass is

confined to the chalcedon-like colloform quartz (81%), which is one of the main mineral-carriers of metal (Moiseenko et al. 2010b).

Confinement of metal nanoparticles (researchers often call them “colloidal gold”) to the forms of chalcedon-like quartz is also typical for many other occurrences, which indicates the need to maintain low temperature conditions for the formation and stability of nanogold. It is assumed that the presence of this gold colors quartz in a green or dark-green (Amosov and Vasin 1995).

2.6 Halides

The possibility of deposition of gold embryos on the surface of halite crystals can be seen in some experiments (Trofimov and Lukyanovich 1968). The presence of gold in the saline rocks of the Verkhnekamskoe deposit was established in 1984 (Smetannikov and Kudryashov 1995; Smetannikov 2008). Several forms of gold occurrence in the composition of sylvite and carnallite, including native gold particles of 70 μm to 300 nm in size, have been identified when performing phase analysis.

One of the forms of gold occurrence in salts of this deposit becomes organo-metallic. There are about 70 organic compounds here. They represent the stereochemical volume structures with the active reaction centers of 1–4 nm in size. The aromatical heterociclicies of nitrogen (aziridines, azocines, phthalocyanines) with ability to form sustainable coordination compounds with metal ions, presumably including gold, are discovered among them. Bacteria were probably involved in the formation of nanoparticles in the organic compounds with participation of sulfur. To date, they have identified organo-metallic structures that contain atoms of Zn, Sn, Hg, Ti, Fe, Co, Ni, Zr, Rh, and their study continues (Odintsova 2011; Bachurin et al. 2012).

Further studies of gold in salts of this deposit using the methods of high-resolution electron microscopy can lead to a detection of gold nanoparticles. Favorable preconditions for this exist due to the close proximity of the deposit to one of the world’s largest goldiferous province of the Urals.

2.7 Clay Minerals

Confinement of gold nanoparticles to the hydromica minerals is directly recorded in several natural objects (Guo et al. 2001). Sub-micron (invisible) gold is discovered in several mineral species (kaolinite, dickite, illite) of the clay minerals in the Carlin deposit. It accounts a significant portion of the total metal mass of this unique deposit (Cline et al. 2005).

The particles of nanogold are fixed in kaolinite by employees of the Amur Scientific Research Institute using the methods of high-resolution electron

microscopy. They differ spheroidal shape, have a size of 50–100 nm and a fineness of 800–820. The gold nanoparticles form clusters characterized by the star-like shape. They are distributed very unevenly in the clay mass, which significantly prevents their identification (Moiseenko 2010).

Special studies to determine the gold content by atomic absorption method in clay fraction (particles less than 1 micrometer in size) of Cenozoic sediments of the Kular and Kharaulakh areas were made by the members of the Institute of Diamond Geology and Noble Metals SB RAS (Yakutsk). The usual gold content in the clay fraction of sediments of different ages for these areas was on the order of 20–170 mg/t. However, the metal content increases and reaches in average of 4.4 g/t, and in one sample is 17 g/t, in the interlayer of the Middle-Upper Eocene clayey siltstones of Ulakhansisskoy gold ore zone in the Kular area (Sergeenko 2010). It is likely the presence of nanoscale gold in the clay fraction of these sediments.

The observations on clayey products of weathering the presence of gold nanoparticles, which are absorbed by defective crystals of hydromicas, has been discovered in deposits of vein-disseminated gold-sulfide ores (Yablokova et al. 1986). The indicators of important role of clay minerals as gold concentrators are the results of special tests of refractory clays in April deposit (Urskoe ore field, Salair Ridge). The presence of large quantities of fine-dispersed native gold is established here under the enrichment of technological samples (Nesterenko 1991).

2.8 Magnetite

The increased ability of the crystal lattice of magnetite to absorb gold is proved by the basic researches and the results of experiments (Ovchinnikova et al. 1998, Sazonov et al. 2008). According to some researchers, magnetite, in some cases, becomes more efficient concentrator of gold than pyrrhotite and pyrite (Smagunov and Tauson 2003). This is due to a wider isomorphic capacity of crystal lattice of magnetite, which allows him to have the isomorphic replaces of iron cations by many elements (especially titanium, vanadium, manganese, etc.). The causes are valent transitions of iron cations and the consequent presence in the mineral structure of a large number of cationic vacancies. The ability of magnetite to include gold as isomorphic admixture is proved by experiments (Mironov et al. 1986). Evidence of adaptation of the gold basic mass to sulfides in many deposits is explained by the broader their spreading in the ores of hydrothermal genesis.

The presence of gold microparticles in magnetites of several large deposits is established. The most gold-rich are titanomagnetite and skarn-magnetite ores. Thus, the share of gold in magnetites of some skarn ores of Turyinsk group accounts for up to 85% of the total mass of gold with content in the mineral up to 1 g/t, in magnetites of Peschanskoe skarn deposit is up to 16% of its total mass. Very fine particles of gold are found in titanomagnetites of Pudozhgorskoe deposit (Trofimov 2002).

Table 2.3 Magnetite as a mineral-concentrator of gold in the rocks of Kondoma district (Malikov and Malikova 1990)

Rock	Gold content in rock, mg/t	Magnetite content in rock, %	Gold content in magnetite, mg/t	Concentration ratio for gold	Share of gold mass in magnetite, %
Andesite-basalts	1.9(51) ^a	1.30	12.8(14)	6.7	7.3
Sienites	1.8(64)	1.29	7.8(25)	4.3	8.2
Granitoids	1.6(67)	1.12	21.6(24)	13.5	22.4
Scarn-magnetite ores	3.8(21)	—	8.5	2.2	—

^ain brackets—number of analyses

The gold content in accessory grains of magnetite of magmatic genesis is relatively small and ranges from 19 to 78 mg/t. However, they account for 16–24% of the gold mass in the rock. Presumably, this gold presents in magnetite as isomorphic admixture. The concentration of gold in hydrothermal magnetite is higher in 2–3 orders. It is proved that this is due to the release of microparticles (and possibly nanoparticles) of gold as a separate mineral phase (Shcherbakov 1974).

The role of magnetite as the mineral-concentrator of gold is studied in detail at the example of different rocks in Kondoma district of the Mountain Shoria (Malikov and Malikova 1990) (Table 2.3).

The ability of magnetite to adsorb gold chloride from corresponding solution is studied in experiments. This ability depends on pH, time and concentration of gold. The appearance of gold-bearing precipitate on the surface of magnetite is proved with use of electron microscopy (Alorro et al. 2010).

Experimental research on sorption of gold by magnetite is held with the use of its natural grains extracted from placers of the Aldan district (Ovchinnikova et al. 1998; Starkov 1998). It is found in the result of experiments that placer magnetite has the ability to adsorb gold from colloidal solutions. This promotes mechano-chemical activation of the magnetite surface. As a result, the absorbed gold is concentrated in certain areas on the surface of magnetite grains, which have a particular electronic state of iron atoms and the presence of surface defects.

The successful experiments on the creation of magnetite nanoparticles with a gold shell show the ability of the crystal lattice of magnetite to absorb nanogold. Such nanoparticles have found the application in medical practice, the manufacture of substrates for Raman spectroscopy, etc. In the process of their obtaining the magnetite nanoparticles are used as nucleation sites for gold (Semenova et al. 2010). The end result of the experiments is to get nanoparticles of spherical shape, consisting of a magnetite core with an average diameter of 10.4 nm and gold shell thickness of about 1.2 nm.

2.9 Carbonates

The presence of gold in ankerite, manganese and ferrous-magnesium carbonates is found; however, the data about its dimensions are absent (Sazonov et al. 2008). There is also information about the prospects of strontium ores (celestine) on the discovery of fine-dispersed gold (Lushchakov et al. 2004).

Siderite ores of the Vyatka-Kama Depression, which were previously exploited as raw material for iron plants, contain very fine gold. The genesis of these ores is considered to be sedimentary (lacustrine and bog environments). Fine-dispersed gold has been adsorbing from colloidal solutions in the nodules of siderite. It can be assumed that a considerable part of this gold is in the nanoscale particles.

The major mineral-concentrators of gold nanoparticles in deposits of gold ore field of Hetai (the Southern China) are small crystals of calcite, along with goethite (Shui 1991).

The balance distribution of gold in minerals of a number of deposits shows that a certain part of the total mass of metal belongs to carbonate minerals. For example, there is 23% of the total mass of gold in calcite of andradite skarn with disseminated magnetite of Peschanskoe skarn deposit (Grigoryev et al. 1991). However, there is no information what portion of this mass is nanoscale.

2.10 Feldspars

It is proved that the role of feldspars as mineral-carriers of gold, and possibly nanoscale, in the balance of metal distribution is particularly marked amid the minerals of metamorphic rocks (Table 2.4).

The nanogold inclusions of 50–100 nm in size of spheroidal shape were found in adularia of the Pokrovskoe gold-silver deposit in the Pre-Amur region (Moiseenko et al. 2010a). As it known, this variety of orthoclase crystallizes from low-temperature hydrothermal solutions, which are consistent with the necessary conditions for formation and stability of gold nanoparticles.

Table 2.4 The balance of the gold mass distribution in minerals of metamorphic rocks of the Northern Pre-Ladoga region (Sazonov and Kremenetskiy 1994), %

The type of rocks	Plagioclase	K feldspars	Biotite	Quartz	Muscovite	Total
Methapelites of amphibolite facies, feldspar-sillimanite zone	21	50	20	9	–	100
The same, transitional zone	45	24	24,5	6	0,5	100
The same, granate-cordierite zone	48	13	15	24	–	100

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