2016

Геология

# МИНЕРАЛОГИЯ, КРИСТАЛЛОГРАФИЯ

# удк 549.283 Superficial Nanotextures of Placer Gold

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The methods of high-resolution electron microscopy were applied to study nanotextures on the surface of placer gold grains (the Urals, Siberia, Altai in Russia, Yukon Territory in Canada, etc.). Among superficial nanotextures, the cracks, furrows, pores, films, inclusions, monolayers, complicated aggregates with gold of relevant size were described. It is supposed that the nanotextures on gold surface partly depend on internal structure of metal and afterwards reflect diverse influences of supergenic factors. Some of them (nanocracks, nanopores) are connected with defects of crystal lattice. A presence of nanolayers reflects instability of gold grain growth, as well as nanoinclusions point to its genesis. The secondary products of weathered rocks such as individual nanoparticles, their aggregates, nanofilms of Fe, Al, Si, and other compounds, coverings, and growths of "new" gold are discovered on a gold surface. There are the assumptions that gold surface nanotextures may promote remarkable changes in chemical, physical and mechanical properties of the metal, especially in the flotation activity, settling velocity and absorption capacity.

Keywords: placer gold, surface, electron microscopy, nanotextures, gold properties. DOI: 10.17072/psu.geol.32.34

# Introduction

At present, physics of solid surface has become the basis of achievements in micro- and nanoelectronics, new technologies in the chemical industry, etc. The processes that occur in crystal surface are the subject of intensive research. The positions and chemical ties of atoms in the surface layer and in the internal zone of gold are rather different. For example, on the surface, there are the so called "torn" electric ties which appear because of the breach of the usual atom coordination. As a result, atoms in the surface layer get closer to each other and the structure of the crystal lattice becomes rather distorted. Thus, the surface layer of gold is specific state of solid substance. Its typical features are unusual crystal chemistry and electric structure, as well as a great number of mechanical and crystal defects (vacations, dislocations, etc.) [3]. Thickness of gold surface layer usually varies from 0.1 to 0.001 mm.

The surface of gold grains has certain marks that indicate their origin or influence of environmental factors. It is very sensible to the activity of geochemical agents, conditions and migration way of ions, lithogenetic processes, etc. The reason is a unique combination of the properties of gold: low hardness, malleability, hydrophobicity, electric conductivity, great specific gravity, etc.

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The surface of placer gold is regarded as a prominent genetic indicator and reflects the distance of its migration from the source rocks. In particular, the surface roughness influences hydraulic equivalence and, as a result, influences the migration capacity of gold grains. The gold extraction rate of the enrichment process depends not only on the grain size and morphology but on its surface too. For example, iron oxides on the gold surface decrease its flotation properties.

There are different ways of studying the surface of gold. The surface of large gold grains may be studied visually or under a binocular microscope. This level of research gives the opportunity to comprehend the common relief (sculpture) of gold surface. The microsculpture of gold surface is the subject of electron microscopy observation. There were many publications on this topic in the 20<sup>th</sup> century [2, 5, 19, etc.]. For instance, the high porosity of gold surface layer was discovered. Various defects of gold surface (cracks, furrows, scratches, hollows, imprints of minerals, etc.) were also described and explained.

The nanosculpture of gold surface is the subject of high-resolusion electron microscopy. It has become the subject of research only recently. It has been found that many superficial nanotextures are part of a system comprising both micro- and nanoobjects. However, the latter have their original morphology, properties and other features. For instance, the first observations of gold surface under a scanning tunneling microscope showed superstructures and steps of monoatomic height. As a result, it was proved that the surface structure of gold was rather inhomogeneous [1]. The electron microscopy of high resolution gave the information about a very complex topography of phase distribution in the surface layer [9]. Great attention was paid to the problem of the reaction of gold surface to the physical factors of the environment (for instance, electric field) [8, 13]. Study of gold nanorelief has become a widespread method of surface layer research.

The surface of gold nanoparticles is the subject of the most detailed study. Very

small oval-shaped nanoparticles of gold with smooth surface were found on grains of pyrite, galena and arsenopyrite with a help of an atomic force microscope [16]. Gold nanoparticles up to 10 nm in size were discovered in Karlin type deposits. They had a distorted hexagon shape [18]. A great achievement of high-resolution electron microscopy was the study of biogenic nanogold with very specific surface [7].

One of the most prominent problems associated with the research into gold surface is the origin of the so called "new" gold. This term was introduced by Freise [4] to refer to the re-depositional metal found in the wastes of ancient gold mines, where unusual forms of gold were observed on the surface of placer grains. Similar gold was afterwards discovered in some Russian placers too [17, 20].

The main peculiarities of the "new" gold are its morphological originality and variability. The most typical shapes are thin coats with a porous structure on the surface of gold grains, bud-like aggregates, and accumulations of fine crystals. Porous aggregates on the gold grains have a thickness of up to 15  $\mu$ m. Such forms are usually found only in certain parts of surface. Sometimes the "new" gold fills in the space between round particles of gold, forming a kind of small "conglomerates".

The "new" gold is a typical metal form found in weathered rocks deposits. Detailed studies have shown that it includes not only gold substance but also ferriferous hydroxide, tellurides of bismuth and iron, etc. [12]. Electron microscopy data gives us an opportunity to observe the spherical gold particles sized up to several micrometers or less in the structure of such aggregates.

Over the last few years, study of placer gold nanorelief with the use of highresolution electron microscopy has been the main subject of my research [14, 15]. As a result, the presence of "new" nanogold has been discovered in many deposits and ore bodies. Every object included various shapes, but all of them were aggregates of gold nanoparticles. The surface of placer gold undergoes transformation due to different exogenic processes. One of them is the formation of superficial layer with high fineness. During this process, usual impurity elements (such as silver, mercury, copper) migrate from the surface layer of gold particles to the environment. As a result, such layer becomes rather porous. Its width does not usually exceed several micrometers.

This article is devoted to aggregation of information on surface nanotextures of placer gold grains and their possible role in the change of the properties of gold.

# **Objects and methods**

The main object of the research is gold from placer deposits in different Russian regions (the Urals, European part of Russia, Kuzbass, Yakutia). Most samples come from the Urals placers (Andreevskaya, Eleninskaya, Nazarovskaya, Kazanskaya, Mikhailovskaya, Kolchinskaya, Chernoborskaya, Shakhmatovskaya, Chernorechenskaya, Kytlym placers) and wastes of their exploitation. Most of them are situated at the Mesozoic depressions stretching along the Ural Mountains. These placers appeared in the Late Mesozoic, Paleogene or Early Miocene. Their source rocks belong to goldsulfide-quartz and gold-sulfide formations. Among source rocks deposits, those of Karlin type were presented too. The Urals placers are characterized by rather small particles of gold. The chemical composition of gold usually included such admixture elements as silver, mercury, copper, palladium.

Great attention is also paid to the study of gold on the territory of Vyatka-Kama Depression situated in the eastern part of the East European Platform [10]. Here a Middle Jurassic intermediate collector of gold was formed by a basal coarse-grained horizon of ancient alluvium and underlying weathered rocks. Gold particles are very small (less than 0.25 mm) and flat. The "new" gold there is connected with the processes of natural amalgamation. Gold is discovered in modern alluvial sediments as well [14]. As for Siberian placers, the objects from the valleys of the Viluy River, the Sololi River and the Bodaibo River (Yakutia), the Kuklyanda River (Central Siberia), as well as the Kitat River and the Tutuyas River (Kuzbas) are presented.

Besides, the paper describes superficial nanotextures of gold from placers of the Yukon Territory (Canada). The gold grains were extracted from samples enriched during joint Canadian-Russian field expeditions in the Indian River valley organized by Canadian Geological Survey [6].

The grains of gold used for the research are mainly collected from concentrates received with the help of a spiral separator. They were obtained in the process of sample enrichment by gravity concentration method, which was applied in field expeditions. Gravity concentration was performed very carefully in order to extract small particles of gold (up to 30 µm). In the laboratory conditions, gold particles were picked up after a special concentration procedure (in heavy liquid, with the help of chemical treatment, etc.). Significant number of gold particles was studied under the electron microscope. For example, the quantity of gold grains from the Urals placers used for study were more than 1000 particles.

We studied the morphology and chemical composition of nanogold aggregates on the surface of matrix metal. The main results are obtained with the help of a scanning electron microscope with cool emission JSM 7500F (JEOL). These results are represented by electron microphotographs with magnification from 100,000 to 500,000. As a result, it is possible to distinguish on the gold surface details of up to 10 nm in size. The standard regime of operation: voltage - 15 kV, emission current  $-10 \mu A$ , working distance -8mm. The microprobe analysis was carried out under a scanning electron microscope JSM 6390LV (JEOL) with ED-spectrometer IN-CA ENERGY 350 (Oxford Instruments).

The study involved different particles of gold: big (more than 1 mm) and very small (up to 50 micrometers and less), flat and

bulky, of homogeneous and aggregate structure (Fig. 1).

# Results

The observation of gold grains under a high-resolution electron microscope revealed numerous different surface nanotextures.

Most of them may be regarded as surface defects. They are presented by different negative morphological features. A great number of such nanotextures on the surface of gold reflects the influence of environment factors. The last ones include mechanical damages (cracks, furrows), chemical etches (some pores, cavities), biological traces, etc.



Fig. 1. Typical large gold grains from the Urals placer

A certain part of them is a result of the adsorption process. This process reflects the active geochemical role of placer gold surface as an indicator of the environmental conditions. Some of gold superficial nanotextures are connected with the internal structure of metal grains. Such forms may be both positive and negative. They may help to explain specific behavior of separate gold particles during their migration and concentration in placers.

Below we discuss the most widespread nanotextures on placer gold surface and their probable role in gold behavior.

## Nanocracks

These are widespread nanotextures in the surface layer of gold. As usual, this layer is always overfilled with microcracks. The last may be connected, on the one hand, with the internal structure of gold matrix and, on the other hand, with surface transformation under the influence of external factors. Usually there is an unremitting line of micro- and nanocracks with the predominance of microcracks. However, some numerous nanocracks are not connected with the larger ones. It is an evident that nanocracks penetrate into the depth of surface layer in many parts of the grain (Fig. 2). Contours of nanocracks are mostly straight but occasionally they may be winding or branching.

Nanocracks are very often covered with gold rivets and other superficial deformations (Fig. 2B). Thus, a large amount of nanocracks may be located in the lower part of gold surface layer, which is inaccessible for observation. A part of space within nanocracks may be filled with secondary products such as colloidal gold, minerals of weathered rocks, etc. Many nanocracks may be completely "healed" by mineral substances.

The size of nanocracks reaches dozens of micrometers. Their width is rather variable:

in some segments, it remarkably enlarges up to 150–200 nm, but in their narrowest parts it is less than 10 nm.



**Fig. 2**. Fragments of nanocracks on the gold surface: A - long nanocrack, B - nanocrack, covered by surface gold layers

#### Nanofurrows

Elongated narrow furrows of less than 100 nm wide occur very rarely on the gold surface. They differ from nanocracks by their small depth and the presence of small mounds with flat rims on the sides (Fig. 3). These peculiarities indicate the origin of nanofurrows as a result of surface scratching. The height and the width of lateral bolsters depend on the depth of the cut into the surface. As a rule, the width of nanofurrows is rather constant (50–80 nm), and only in very short segments it is more than 100 nm. Narrow nanofurrows (less than 30 nm) present an insignificant part of their total number.

Scanning of the surface of many grains shows that nanofurrows are usually individual defects, but sometimes there are systems of nanofurrows oriented in different directions. Nanofurrows may contain different nanoinclusions, including nanogold particles (Fig. 4).

#### Nanopores

Micropores are typical the defects of gold surface. Their sizes usually range from 10 to 1  $\mu$ m. The distribution of micropores on the

surface of gold may be well regular or chaotic. Their systems differ from each other in the density of their arrangement on the surface. The specific feature of micropores' location is their orientation in a chain in a certain direction. The directions of the chains may indicate the boundaries between microblocks in crystal lattice.

Nanopores are present in some systems of micropores. There are parts of gold surface with a big amount of both micro- and nanopores, as well as parts without nanopores. The boundary between these parts may reflect the zonal structure of gold or the elective influence of environmental factors. Micro- and nanopores have uneven depth and sometimes pierce several microlayers of gold. However, very often the independent systems of nanopores are formed. In that case, they are not accompanied by micropores. They usually have an oval contour, and are not very deep. Some of them differ from the majority of nanopores by a very specific profile (conical, wedge-like or cylindrical) (Fig. 5). Very rarely, there is a definite order in the arrangement of nanopores, which is usually linear or circular.

The diameters of nanopores usually range between 100–50 nm. Hollows sized less than

10 nm are rather uncommon. An exception is the surface of gold from weathered rocks from the Tykotlov polymetallic ore body (the territory of the Pre-Polar Urals), in which there are zones with predomination of nanopores of 10–30 nm of diameter. The density of the arrangement of nanopores on gold surface is rather different. As a rule, it is less than one nanopore per 1  $\mu$ m<sup>2</sup>. Gold in the oxidation zone of weathered rocks has a maximal density (160 nanopores/1  $\mu$ m<sup>2</sup>).



**Fig. 3.** *Fragment of a nanofurrow: on the left – common appearance, on the right – a part of nano-furrow* 



Fig. 4. Gold nanoparticles within nanofurrow



Fig. 5. The groups of nanopores on the gold surface: A - part of surface with low density of nanopores, B - surface with high nanopores density

However, this value for usual alluvial gold does not exceed 20 nanopores/1  $\mu$ m<sup>2</sup>.

# Microhollows with nanodefects

Besides the cracks and nanopores, there are numerous other deep negative defects on gold surface. They may be combined into the group of microcavities and microcaverns with nanohollows at the bottom. Such defects have irregular shapes and contours. They are very often connected with each other by narrow canals (Fig. 6).

Some microcavities may penetrate into the internal zone of a gold grain. The zones of surface with the accumulation of microcavities with nanodefects are presumably explained by defects of the crystal lattice. Overall, they may reflect the positions of weakened zones in the gold structure. Microcavities with nanohollows are very often filled with the products of weathering and gold of secondary origin. They may also contain nanoinclusions of different minerals.

### Nanofilms

Nanofilms are the usual features of gold from the weathered rocks. Some of them may be observed with the help of a highresolution electron microscope (Fig. 7). But very thin and transparent films are not visible. However, the microprobe analysis of the natural surface of placer gold (without polishing) usually reveals the presence of Fe, Al or Si in small quantities. At least some of these impurities are undoubtedly associated with substance of nanofilms (iron compounds, clay minerals, etc.). Besides, chlorides, phosphates, carbonates, sulfides and sulphates as well as oxides of Mn, Cu, Ti, intermetallic combinations of gold with Pb, Sn, Hg are found in chemical composition of nanofilms too (Table). After polishing, such chemical elements are no longer found in the same parts of the surface.

Nanofilms are the part of superficial systems of secondary products as well as microfilms. They differ from each other by the presence of unusual minerals in nanofilms, such as halite, monazite, amalgams, etc. As a rule, nanofilms are predominantly monomineral objects but microfilms may be polymineral ones.

Many nanofilms have fibrous or layered structure, which may by an evidence of their colloidal origin in weathered rocks.

#### Nanoinclusions

Scanning of gold surface gives us an opportunity to find different micro- and nanoinclusions. This research has revealed a large number of different nanominerals and even their aggregations in caverns and tracks on gold surface.

The association of micro- and nanoinclusions enables us to make a conclusion about their connection with rocks that were the sources of placer gold. However, sometimes their position in the surface hollow indicates that they were pressed in it during the migration of gold.



**Fig. 6.** *Microcavities with nanopores at the bottom:* A – *narrow microcavity of complicated form,* B – *deep many-storeyed microcavity* 



Fig. 7. Nanofilm of monazite on the surface of the Urals placer gold

Nanoinclusions do not occur very often. This may be explained by the fact that in the process of surface grinding a great number of them were removed. Therefore, the usual places of their discovering are the micropores, microcracks and corresponding nanodefects, where they are protected from external impact. The most typical mineral nanoinclusions are quartz, pyrite, goetite and halite.

Chemical composition of gold with nanofilms on the surface, wt. %

| Element | 1     | 2     | 3     | 4      | 5     | 6     | 7     | 8     | 9      | 10    |
|---------|-------|-------|-------|--------|-------|-------|-------|-------|--------|-------|
| Au      | 87.58 | 61.82 | 69.31 | 83.34  | 93.98 | 85.78 | 86.82 | 90.70 | 67.83  | 66.24 |
| Ag      | 2.50  | 29.56 | 4.55  | 7.05   | 0     | 5.14  | 0     | 6.02  | 0      | 3.13  |
| Cu      | 0.16  | 5.96  | 0.96  | 0.37   | 0     | 0.81  | 4.01  | 0.94  | 0      | 2.50  |
| Hg      | 1.38  | 1.11  | 0     | 0      | 0     | 0     | 0     | 0     | 0      | 4.03  |
| Co      | 0     | 0     | 0     | 0.17   | 0     | 0     | 0.08  | 0     | 0      | 0     |
| As      | 0.17  | 0     | 0     | 0      | 0.25  | 0     | 0     | 0.14  | 0.37   | 0.14  |
| Bi      | 0.41  | 0     | 0     | 0      | 0     | 0     | 0     | 0     | 0      | 0     |
| Pb      | -     | -     | -     | -      | -     | -     | -     | -     | -      | 14.34 |
| Sn      | -     | -     | -     | -      | -     | -     | 2.36  | -     | -      | -     |
| Fe      | 4.08  | -     | 1.44  | 6.25   | 0.94  | 1.99  | 0     | 0.46  | 13.13  | 1.49  |
| Ti      | -     | -     | -     | -      | -     | -     | 0.09  | -     | 2.13   | -     |
| Cr      | -     | -     | -     | -      | -     | -     | -     | -     | -      | 1.25  |
| Mn      | -     | -     | -     | -      | -     | 0.18  | -     | 0.99  | 0      | -     |
| Al      | 0.66  | 1.55  | 0.14  | 1.28   | 0.76  | 2.44  | 0.36  | 0.44  | 9.49   | 0.77  |
| Si      | 1.01  | -     | 23.27 | 0.77   | 0.20  | 1.51  | 0.08  | 0.31  | 5.48   | -     |
| Na      | -     | -     | -     | 0.38   | 1.77  | 0.16  | -     | -     | -      | -     |
| K       | -     | -     | -     | -      | -     | 1.07  | -     | -     | 1.58   | -     |
| Cl      | -     | -     | -     | 0.40   | 2.10  | 0.90  | -     | -     | -      | 3.44  |
| Total   | 97.95 | 100   | 99.67 | 100.01 | 100   | 99.98 | 93.80 | 100   | 100.01 | 97.33 |

1 – the Yukon Territory; 2, 3 – the Sololi placer (Siberia, Russia); 4, 8 – the Elovka placer (the Urals, Russia); 5 – the Andreevskaya placer (the Urals); 6, 7 - the Kuklyanda River (Siberia); 9, 10 – the Kytlym placer (the Urals); - element does not determined.

#### Nanolayers

The study of placer gold grains with the layered internal structure under a scanning electron microscope shows that the details of their structure are revealed in their superficial forms. In particular, individual layers are distinctly expressed on the surface and sometimes complexes of layers may be visible. The thickness of layers varies in certain limits but overall they are usually measured in micrometers.

However, under a high-resolution electron microscope some individual microlayers turn out to be different combinations of nanolayers (fig. 8). Separate nanolayers are exposed on the surface as mound-like elevations and are remarkably distinguished in the surface nanorelief. The thickness of nanolayers is rather variable, which indicates changing conditions of the growth of gold in the source rock.

The thickness of many nanolayers gradually decreases in certain direction and then



they may disappear. Unlike microlayers, nanolayers often have different deformations and winding shapes. The possible reasons for such phenomenon may be the plastic deformations of the metal structure or defects of the crystal lattice.

The surface of gold is easily transformed during the migration and such insignificant elevations as nanolayers are smoothed out. That is why nanolayering is a very typical object of study only in the case of gold in weathered rocks.

# "New" nanogold

"New" gold is a mineral form of secondary metal that is absorbed by the surface of placer gold. This process begins with precipitation of nanogold particles in micro- and nanodefects of gold surface and sometimes ends with the formation of comparatively large growths, crystal accumulations, crusts, etc. Depending on the stage of this process, we may find on the gold surface the complex



**Fig. 8**. Nanolayers on the surface of gold grains (Kytlym placer, the Urals): A – deformed microlayers composed by nanolayers, B – nanolayers on a slope of gold grain

aggregates of nanogold particles, their growths, unusual porous microstructures, etc. [15].

The structure of "new" gold distinctly differs from that of gold matrix. It is characterized by the presence of variable colloidal and aggregate forms, a great number of pores, several gold-bearing generations, etc. This difference becomes visible under a scanning electron microscope applied for diametrical cuts of gold grains. The participation of nanosubstances in the process of "new" gold formation is revealed in nano-level of study (Fig. 9).

There are two large groups of "new" gold, which differ in their chemical composition, structure and genesis. The first group consists of metals and includes pure gold, gold with admixtures of silver, copper, mercury, palladium, lead or tin, electrum, amalgams, intermetallic compounds. Different features point to the colloidal origin of gold. The second group includes complex aggregates containing gold and silicon, ferriferous, clay and other compounds. They may be products of source rock weathering adsorbed by placer gold surface.

## Discussion

#### The origin of superficial nanotextures

The origin of nanotextures on the surface of placer gold is the result of different natural and technogenic processes. Firstly, superficial nanotextures are rather specific for gold from different source rocks. Secondly, they indicate some specific features of the internal structure of gold, namely defects of the crystal lattice. Thirdly, surface nanotextures may be the indicators of environmental geochemistry due to the variability of nanogold aggregates or nanofilms on the surface of gold. Therefore, they play a significant role in answering to many important questions concerning the gold grains. Furthermore, nanotextures of surface influence the physical and mechanical properties of gold grains.

Certain types of defects may reflect the influence of several factors. Thus, the origin

of nanocracks is rather variable. Most of them are presumably the results of mechanical deformation of gold grains during their transport by water flow. It has been proved that even intensive vibration of every crystal leads to the appearance of microcracks. Some of them may appear because of internal tension during the crystallization period. Finally, they may often fix the zones of crystal lattice defects (vacations, clusters, dislocations, etc.). The abundance of nanocracks indicates the presence of a vast empty nanospace in the structure of gold.

The origin of nanofurrows may be explained, first, in the following way: they may appear during the migration of gold particles in the bottom load of a river as a result of their scratching by mineral nanoparticles. The latter may slide on gold surface without deepening in it. But minerals with high hardness and sharp rims may leave imprints of their movements from time to time. Taking into account the high difference between the hardness of gold and that of widespread quartz, the result of their contact is rather predictable. The presence of systems of nanofurrows may rather reflect a long period of the migration of gold.



**Fig. 9.** Growths of "new" gold in diametrical cuts of placer metal: A, C – with copper and mercury; B, D – details of structure in nano-level

There are several ways to explain the formation of nanopores. According to one point of view, nanopores are the former cavities of gas-liquid inclusions located near the surface of gold. Another widespread opinion is connected with the idea of elective chemical etching of gold surface. The typical places where such process may occur are intergranular space or a boundary of microblocks in the crystal lattice of gold. Nanopores may appear because of linear defects of the gold structure, too. Overall, the joint concentration of micro- and nanopores may be an indicator of the weakened zones in gold surface due to thickening of vacations in the crystal lattice. These zones may have very deep "roots" within the gold grain.

Finally, the locations of nanopores concentration are also considered as zones of intensive migration for admixture elements (silver, mercury, copper, etc.) through the surface layer of gold grain to the environment. At last, they may be imprints of external mechanical effects.

# The genesis of gold

Typical indicators of the genesis of gold are syngenetic mineral and gas-liquid inclusions. The most widespread mineral inclusions in placer gold are quartz and sulfides. The genetic information is contained in the morphology of quartz inclusions and the chemical composition of sulfides [17]. However, during the migration gold grains gradually lose superficial inclusions that narrow down the opportunities of electron microscopy. Nanoinclusions may remain on gold surface practically undamaged.

There are three groups of mineral nanoinclusions on gold surface: syngenetic, secondary and accompanying. Specific associations of minerals typical for source rocks represent the syngenetic nanoinclusions. It is obvious that many of such nanoparticles refer to quartz. Sulfide minerals represent the next widespread group. Syngenetic nanominerals usually have the ideal crystal shapes.

Among secondary minerals, there are various products of weathering, such as carbonates, chlorides, clay minerals, hydroxides of iron, manganese and aluminum, etc. The community of nanominerals on placer gold surface reflects the character of weathering processes in the deposit. For instance, the ferriferous aggregates with nanogold are very often found in cracks. It is a real proof of the decomposition of iron sulfide minerals that were the mineral-concentrators of nanogold. After their decomposition, nanogold particles often form complex compounds with ferriferous oxides as the most widespread products of weathered rocks.

Negative nanodefects of gold surface (nanocracks, nanofurrows, nanopores) are typical traps for the different mineral nanoparticles from weathered rocks. Among them, we have come across such minerals as quartz, baddeleite, staurolite, corundum, rutile, leicoxene, granate, chromite, and mica.

# Climate

Sometimes cubic or oval nanoparticles of salt (halite or silvite) are found in hollows of placer gold surface (Fig. 10A). They are formed because of filtration of underground waters through the weathered rocks. As is known, deposition of salt occurs in arid and warm climatic environment. Under favorable conditions, crystals of salt may grow to the large (in comparison with nanocrystals) sizes. For instance, a twined crystal of nanolayered halite was observed in a surface hollow of gold from the Urals placer, which was formed in the Oligocene in arid and hot environmental conditions (Fig. 10B).

# Internal structure and chemical composition

The study of diametrical cuts of placer gold grains under a high-resolution electron microscope has shown that such nanodefects as nanocracks and nanopores are typical not only of the surface layer, but also of the internal part of metal. It gives us a reason to assume that the damage of the surface layer is connected with defects of the internal structure of gold.

According to N. Petrovskaya [17], more than 40 elements can be found in gold in the

form of impurities. In many cases, chemical composition of gold grains shows the presence of elements for which mineral-bearers are not found. In particular, sometimes Fe is accompanied by S, which may be explained by the presence of undiscovered pyrite nanograins. In one of the deposits, the percentage of Fe in gold reaches 4.4, but there are no any visible inclusions (N. Petrovskaya suspects the presence of thin mechanical impurities in gold grains). G. Nesterenko [11] points out that many mechanical impurities in gold stay invisible though their presence is established with confidence by chemical analysis. Nanoinclusions in gold grains may undoubtedly have an impact on their chemical composition.

# Physical and mechanical properties

So far, no research has been conducted into the influence of nanodefects or nanoinclusions on the physical properties of metal grains. However, this phenomenon may be predicted based on theoretical and indirect data. In particular, many researchers have pointed out that some deflections of the physical properties of gold may be explained only if we take into account the peculiarities of thin metal structure.



**Fig. 10**. Halite in the superficial hollows on the gold surface: A - aggregate of micro- and nanograins, B - nanolayered twinned crystal

First, it is necessary to consider the properties that depend on the character of gold grain surface. One of such properties is the settling velocity of grains, which is responsible for the hydraulic equivalence and migration capacity of gold. The settling velocity may be determined in experiments showing its dependence on such factors as the grain size, specific gravity, shape and character of surface. For instance, grains with smooth and rough surfaces have different settling velocities. As a result, they migrate in bottom load into the different distance. During migration, some of them may be disseminated in river sediments instead of being concentrated. Hence, gold particles with many superficial nanodefects have not analogues conditions for concentration than grains without them. The same result is expected in the case of enrichment operations with gold, especially those based on gravitation methods.

It is important to take into consideration a character of gold surface in technologies with flotation. Flotation is usually applied for extraction of thin gold. It is possible to suggest that nanofilms of ferroxides, carbonates, etc. change the rheological properties of gold surface and may influence the results of flotation.

The abundance of nanoinclusions may undoubtedly influence the physical properties of gold grains. It has been established that the actual specific gravity of gold particles (usually less than 18 g/cm<sup>3</sup>) is remarkably smaller than the theoretical (around 19.3 g/cm<sup>3</sup>). All nanodefects of gold matrix may increase this difference, especially gas-liquid and quartz nanoinclusions, as well as nanopores and nanocracks.

The other noticeable changes of metal physical properties (hardness, electric, thermal, etc.) may be caused by the presence of empty space within the gold matrix. Certain its part refers to nanopores and nanocracks.

The abundance of nanodefects in addition to macro- and microdefects may promote the appearance of unusual mechanical properties of gold. For instance, the origin of fragile plate gold in some placers of Siberia is explained by their microstructure and their formation in result of the coagulation of submicrometer metal particles [12].

Our experience on enrichment of samples with thin gold has shown that under weak mechanical impact instead of flattening, metal grains sometimes disintegrate into smaller particles. Experiments have revealed elastic deformations in the gold structure [17]. The intensity of elastic deformations varies from one part of grain to another and usually increases towards the rims of the grain. This phenomenon may be caused by superficial nanodefects.

#### Acknowledgements

The author expresses his gratitude to those who placed their own grains of gold for the purposes of this research (Alexandr G. Barannikov, Yuriy A. Kisin, Vladimir A. Naumov, Alexei Y. Konopatkin), and colleagues from the Department of Mineralogy and Petrography of Perm State University for participation in field expeditions and extraction of gold grains under laboratory conditions.

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# Нанотекстуры поверхности россыпного золота

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Методы высокоразрешающей электронной микроскопии применены для изучения нанотекстур поверхности россыпного золота (Урал, Сибирь, Алтай в России, территория Юкон в Канаде и др.). Среди поверхностных нанотекстур описаны трещины, борозды, поры, пленки, включения, монослойки, сложные агрегаты с золотом соответствующих размеров. Обосновано, что нанотекстуры на поверхности золота частично зависят от внутреннего строения металла и в то же время отражают влияние различных гипергенных факторов. Некоторые из них (нанотрещины, нанопоры) связаны с дефектами кристаллической решетки. Присутствие нанослойков отражает нестабильность условий роста зерна, а нановключения указывают на его генезис. На поверхности золота обнаружены вторичные продукты кор выветривания, такие как индивидуальные наночастицы, их агрегаты, нанопленки с Fe, Al, Si и др. компонентами, корочки и наросты «нового» золота. Предполагается, что поверхностные нанотекстуры золота обусловливают заметные изменения химических, физических и механических свойств металла, особенно флотационную активность, гидравлическую крупность и адсорбционную способность.

Ключевые слова: россыпное золото, поверхность, электронная микроскопия, нанотекстуры, свойства золота.

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