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Research Article

Natural Nano-Biotechnologies

Boris Osovetsky*

Perm State University, Perm, Russia,

***Corresponding Author:** Boris Osovetsky, Perm State University, Perm, Russia.

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Abstract

The aim of the article is to show the opportunities of modern methods of nanogold investigation with application to biotechnologies. The main concept of the work is connected with the interpretation of the nature of complicated biogenic nanogold aggregates. The processes of their origin with participation of microorganisms are considered on the example of some areas in the Urals (Russia). These include zones with pseudomorphous aggregates after diatom algae, black shale strata, etc. The described processes are proposed to be considered as natural nano-biotechnologies that can be used to extract nanogold in the future. Besides, geological objects with biogenic nanogold aggregates may be new perspective source of gold.

Keywords: Nanogold; The Urals (Russia); Diatoms; Black Shale; Nano-Biotechnology

Introduction

Currently, biotechnology is widely used to extract fine (“invisible”) gold from ores. The effective use of this method is facilitated by the presence of bacteria in nature, which actively absorb gold from the environment in the course of their life activity. In addition to bacteria, some algae and fungi differ in their ability to actively absorb gold [3].

However, in recent years, ore occurrences with even smaller gold, most of which belong to a nano-sized metal, are increasingly being discovered. Numerous data indicate widespread nanogold in natural objects. It is released in large quantities in the weathered rocks of gold-sulfide formations, where the bulk of the metal dispersed in sulfides. The sizes of gold particles in sulfides reach tens of micrometers, but the predominant in mass is a much smaller metal, including nanoscale.

Particularly impressive are the data of a detailed study of the forms of gold occurrences in unique deposits using modern research methods. For example, in the Witwatersrand deposit among various types of gold nanoscale biogenic variety is present [2,4,11]. In the Carlin deposit, the bulk of nanogold particles is concentrated in sulfides, and its share in the total mass of the metal is estimated at 8% [5].

The study of various geological objects shows that the presence of nanogold in them is due to the processes associated with the vital activity of certain microorganisms that are able to actively extract nanogold from the environment. Bacterial biofilms on the surface of placer gold grains are fixed in many parts of the world [15]. For example, they include colloidal gold nanoparticles about 2–3 nm in size in the basin of the Rio Saldan River. The presence of four types of bacteria was established in these films [16].

The process of nanogold absorption by bacteria was confirmed by special experiments. In particular, the possibility of the formation of spherical aggregates consisting of octahedral gold nanoparticles was experimentally proved [7,8]. Spherules of nanogold sized 5–10 nm were found even inside the bacteria in the course of experimental studies [14]. Their formation is associated with metabolic processes that are widespread in nature. In subsequent special experiments, it was proved that the mass of newly formed biogenic gold can reach 10% of the mass of the primary metal [17].

The intense processes of the "new" gold growth on the surface of the primary metal were established in the paleoplacers and dumps of ancient gold placers. Using the example of the Otago region (New Zealand), it was found that the growths on the surface of the gold grains is due to a combination of inorganic chemical reactions and the microbiological activity of groundwater [18]. The presence of black films, which are bacteriomorphic structures with a large amount of nano-sized metal, is found on the surface of gold in placers of the Rich Hill (Arizona). The latter varies widely in the characteristics of the internal structure. In particular, there are amorphous spherical secretions, scales, well-formed octahedral crystals, etc. By dimension, newly formed nanoscale gold can be subdivided into several groups, which allows to conclude about the appropriate number of episodes of its dissolution and subsequent growth [9].

The example of the formation of nanogold concentrations due to the activity of microorganisms is the complex of gold-bearing deposits in the Vyatka-Kama Depression, confined to the marginal part of the East European Platform in close proximity to the Middle Urals. In tectonic terms, the Depression is a relatively young superimposed structure, the formation of which occurred in the Triassic-Jurassic time. The depression was filled mainly by the Lower Triassic and Middle Jurassic terrigenous gold-bearing sediments, the primary sources of which were the erosion products of the Urals rocks. It is known that the Urals is one of the largest gold-bearing provinces in the world with a large number of industrial alluvial deposits, mainly with small gold particles.

In addition to small placer gold introduced from the Urals, clusters of metallic particles of an unusual morphological type were found in Middle Jurassic pebbles of the Depression and modern alluvium, which attracted attention because of the uneven surface and the characteristic globular-porous structure. Their sizes were mainly several tens of micrometers in length and up to 10 μm in width. The largest (100–200 μm) ones were the grains of a distinct aggregate structure.

The next places with biogenic gold were found on the western slope of the Middle Urals. These were coastal-marine facies with favorable conditions for accumulation of carbonaceous clay sediments, due to which black shale strata were subsequently formed. The gold of these sequences has long attracted the attention of scientists and is still not well understood. A large amount of nanogold in the composition of colloidal solutions is assumed to be carried out by the river systems from the adjacent land to the coastal zones.

Methods

Biogenic gold particles and aggregates were concentrated by the spiral separator from the samples (up to 0.1 m3) of sandy-gravel material of the Middle Jurassic and Upper Riphean rocks. The concentrates of separator were processed with application of different methods, such as sieving, settling in heavy liquid, magnetic and electromagnetic separation. The sieving process provided a considerable decrease of concentrate volume due to removal of large particles (more than 0.25 mm in size). Settling in heavy liquid (bromoform) gave the opportunity to subdivide concentrate into light (less than 2.89 g/cm^3) and heavy fractions. Magnetic separation with application of simple magnet was applied for removal of magnetite and minerals with its inclusions. At last, electromagnetic separation was a usual very effective way to extract gold particles and other minerals with analogous magnetic properties from concentrate. This operation was carried out with help of stationary electromagnetic separator EVS 10/5. Then gold particles were chosen using binocular microscope Nikon SMZ 745.

The electron microscopy methods were used for study of texture and chemical composition of gold particles. The images of particles were obtained when using the SEM with cool emission JSM 7500F ("Geol"). Determination of the chemical composition of gold particles was performed on energy-dispersive (INCA Energy 350) and wave (INCA Wave) spectrometers by "Oxford Instruments" as the prefixes to a JSM 6390LV ("Geol").

Results

The study of these particles under an electron microscope shows that they are aggregates of gold pseudomorphs after diatom algae, cemented by a secondary metal. The number of diatom pseudomorphs in a single grain of gold can probably reach several hundred (Figure 1). Their sizes are usually 5–10 μm. The presence of several generations of pseudomorphs in the grain, differing in degree of preservation, is clearly distinguished. The latest of them are represented by well-preserved individuals with distinct septa (Figure 2). With a higher magnification, the details of the internal structure of pseudomorphs and the presence of nanoscale fragments in them are revealed (Figure 3). Earlier generations are represented by severely damaged pseudomorphs with poorly visible septa and other details of the internal structure. Finally, only the outer shells are preserved from the earliest pseudomorphs (Figure 4).

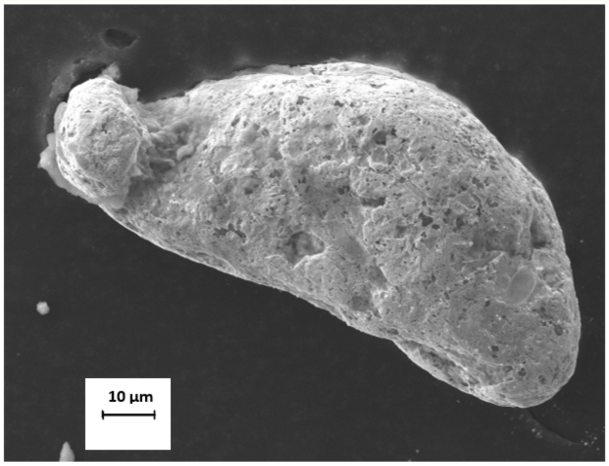

Figure 1: Biogenic gold from Middle Jurassic pebbles of the Vyatka-Kama Depression.

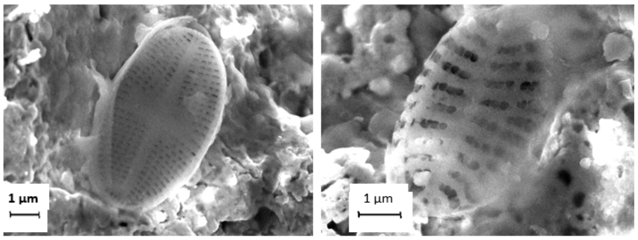

Figure 2: Pseudomorphs of gold after diatoms (the latest generation).

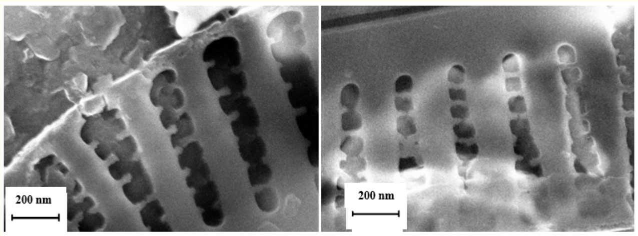

Figure 3: Fragments of gold pseudomorphs with nanoscale details of the structure.

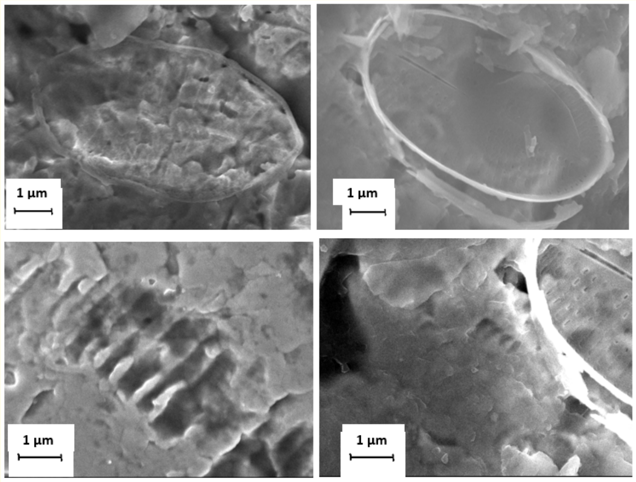

Figure 4: Fragments of the early generations of gold pseudomorphs after diatoms.

Thus, the process of formation of accumulations including a lot of particles of biogenic gold was a phased and rather long. However, to connect them together with the formation of pseudomorphous aggregates, it was necessary to impose additional secondary processes, which could be the diffusion of gold atoms between adjacent pseudomorphs and the formation of secondary gold from colloidal solutions. Due to these processes, cementation of individual pseudomorphs took place with the formation of aggregates with a size of up to 100 µm and more.

Finally, it is necessary to pay attention to the rather high degree of rounding of the biogenic gold grains (see Figure 1), which indicates a rather long transport in the aquatic environment from the place of their formation. Their accumulation with the formation of high concentrations occurred in the river beds at the Middle Jurassic with the active dynamics of the water flow as a part of coarse gravel-pebble alluvium under the influence of mechanical differentiation processes.

As to biogenic gold in black shales, various microbial communities were widely represented in the zones with various sorbents of nanogold (carbonaceous matter, sulfides, ferrous, siliceous and aluminous components, etc.). The formation of black shale strata usually covers a very long period of geological time (especially for Precambrian rocks). The combination of these factors creates favorable prerequisites for the formation of biogenic gold particles and their consolidation during subsequent secondary chemical processes. Many researchers point to the promise of black shale rocks as a source of gold for future generations [10,19].

The features of gold-bearing black shale rocks are investigated on the example of the Riphean strata of the western slope of the Middle Urals [13]. Here there are different forms of gold occurrences: small scaly gold with rounded edges, which are the products of sedimentation in the Riphean time, well-formed octahedral crystals of secondary gold up to 0.2 mm in size, aggregates on the surface of gold and, finally, biogenic nanogold.

The most interesting of these are micro- and nanoscale aggregates, the internal structure of which indicates their origin due to the aggregation of gold nanoparticles. It is here that we encountered unusual gold-carbon phases, the nature of the composition and structure of which is unclear. Microprobe analysis shows the presence in them, in addition to gold (25–75%) and silver (1–24%), carbon (15-25%), impurities of other metals (Zn, Cu, Fe, etc.), SiO_2 and Al_2O_3. The presence of organometallic compounds in these phases, pseudomorphs of nanogold after microbial communities, etc. is assumed.

The consolidation of previously formed aggregates with the participation of natural amalgamation processes has been continuing in the weathered rocks on the black shale. As a result, rather dense aggregates with a size of up to 0.15 mm were formed, consisting of smaller aggregates with a size of 5–10 μm (Figure 5). The last are composed by nano-aggregates or nano-particles. In the chemical composition of the aggregates Au content is 70–90%, mercury – 5–10% (sometimes up to 20%). Impurities of Cu (up to 15%), Fe, Cl, etc. are also typical.

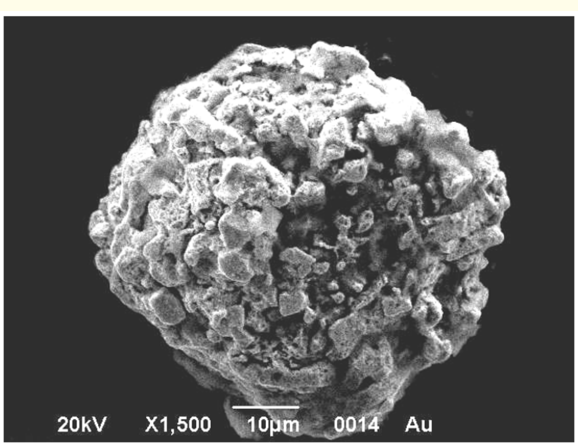

Figure 5: Aggregate gold from the weathered rocks of black shale.

Discussion

A detailed study of alluvial gold at numerous placers in the Urals and other territories at the nanoscale level [13] showed that, due to morphological features, a certain part of it may be of biogenic, sometimes with participation of chemical processes (Figure 6).

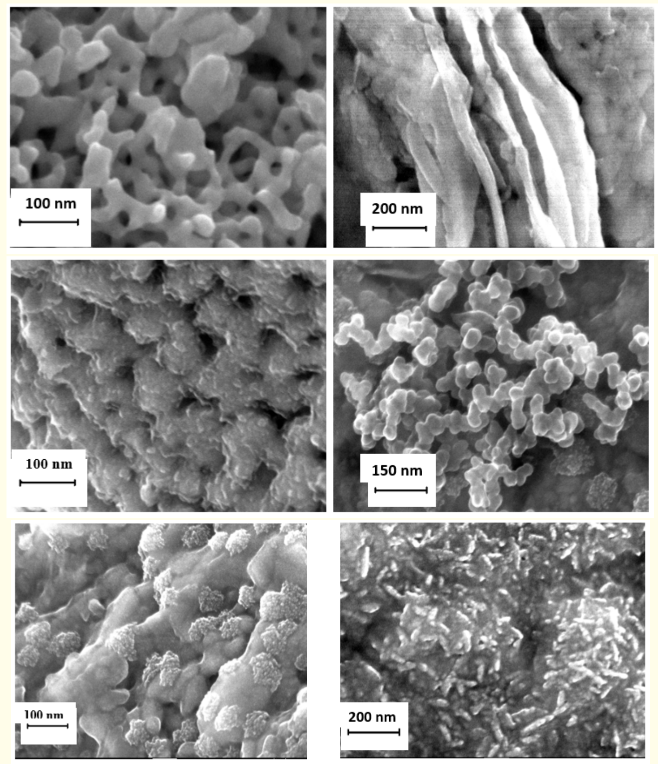

Figure 6: The varieties of presumably biomorphic nanogold in placers of the Urals.

The above-described forms of nanogold occurrence and processes of their origin are of great importance in assessing the prospects for gold-bearing territories. The fact is that the bulk of gold nanoparticles released from sulfides in the weathered rocks, has been scattering in sedimentary formations. The reasons are the specific chemical and physical properties of nanogold: high chemical activity, electric charge on the surface, sorption ability, high migration capacity, etc. Due to these properties and the presence of a large number of various natural sorbents in the environment, nanogold is actively absorbed by clay, ferrous, carbonaceous, silica, aluminous and other substances, being distributed almost evenly in a large amount of natural sediments. In particular, many gold nanoparticles are captured by colloidal solutions and are transporting over considerable distances, dissipating in natural waters.

Comparatively rarely, in special biogeochemical environments, the necessary conditions for the concentration of gold nanoparticles are created. In particular, nanogold in large quantities is deposited on the surface of the placer metal [9,13,16,18]. Metacolloid mineralization with the participation of nanogold is widespread in nature. In recent years, a lot of information has appeared on the active manifestation of natural amalgamation processes with the formation of nanogold aggregates [12]. In this series, one of the most effective natural processes of nanogold concentration is the vital activity of specific microorganisms, examples of which are given in numerous publications [1,3,5,6,8] and in this article. It should be emphasized that due to intensive processes of gold atoms diffusion, signs of its biogenic origin gradually disappear. It can be assumed that a significantly larger part of gold is biogenic than is currently known.

Biotechnological methods for extracting gold are currently being successfully applied to the enrichment of ores with fine metal. However, nanogold remains inaccessible for extraction by modern technologies. Although the size of bacteria used in biotechnology is commensurate with gold nanoparticles, there are still numerous problems associated with fine crushing of gold-bearing ore, etc.

In fact, in the examples above, we are dealing with effective mechanisms that can be considered as natural nano-biotechnologies. Their long-term functioning and practical significance are associated with the imposition of other biogeochemical processes. In addition, a rich source of continuous or intermittent entrance of nanogold is needed. As a result, along with the concentration of gold nanoparticles, their simultaneous enlargement occurs up to the dimension available for extraction by the cheapest gravity methods.

Forecasting of new promising sources of mineral raw materials is currently one of the urgent problems of modern geology. Mastering of the objects with nanogold is a part of this problem. Based on the results of our research, it is recommended at the initial stage, on the one hand, to identify the areas that in the geological past were favorable for the life of those organisms that were able to actively absorb gold. On the other hand, in such areas there should be geological objects with nanogold and other conditions necessary for the operation of natural nano-biotechnologies similar to those described above. The perspective geological objects have to be tested using special field and laboratory methods for sampling and processing of samples.

A detailed study of the morphology, composition and structure of nanogold aggregates, the origin of which was initiated by microorganisms, will also contribute to the improvement of biotechnological methods for extracting gold, including nanoscale.

Conclusion

Biogenic gold is widespread in specific sedimentary rocks with presence of carbonaceous, clay, ferrous, silica, aluminous substances. It has unusual and variable forms, which are often presented by aggregates. Their investigation under the scanning electron microscope of high resolution shows that a lot of aggregates is composed by biogenic nanogold particles.

In some geobiochemical environments there are conditions for not only consolidation of nanogold particles but either for their enlargement under the influence of additional processes (cementing, diffusion, nature amalgamation, etc.). The result of such processes is origin of complex aggregates up to 100 μm in size and more.

Further study of similar natural processes with the concentration of gold nanoparticles and the active participation of microorganisms can be very useful for improving industrial biotechnologies. May be, using natural nano-biotechnologies as an example, it is possible to create enrichment complexes for nanogold concentration.

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