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To cite this article: L V Moskvitina *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **272** 022184

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Research of Nanoscale Gold by Methods of Tunneling and Atomic-Powered Microscopy with Chemical and Ion-Plasma Etching in the Kuchus Deposit (Republic Sakha (Yakutia))

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Abstract. Methods of scanning tunneling and atomic force microscopy, nano-gold deportment in sulfides was studied in carbonaceous shale deposits Kyuchus (Yakutia). Chemical and ion-plasma etching in oxygen and argon medium was used for nano-gold detection. It is shown when bombarding with oxygen ions pyrite and arsenic pyrite are etched layer by layer, revealing nano-gold particles. Deformation structures of adjacent sulfide and their interaction with gold separation had been investigated. In arsenic pyrite of early stage gold is found in patterned solid solution.

1. Introduction

The Kuchus deposit is one of large-scale gold deposits of Russia. According to its formation, geological and geochemical parameters and scales this gold mine belongs to a gold-sulfide type in carbonaceous slates [1]. The deposit is located in Kularsky district of the Kularo-Nersky black shale vein system, in the Yansky deep occasional break (Yakutia) [2].

For improvement and development of new technologies for extracting fine-grained gold it is necessary to find out a gold deportment and its chemical state in mineral concentrators. The main morphological type of the Kuchus gold-sulfide deposit is the sulfide streak-imbedded mineralization presented by a short-grained pyrite and arsenic pyrite impregnation in quartz silicified argilliferous shales.

The ore auriferous production is related to it. Most of gold contains in pyrite and arsenic pyrite of – 72.4%.

As known the presence of ‘invisible gold’ in early sulfite is mostly typical to the gold-sulfidic of ores of Karlinskiy type. The submicroscopic gold (10-100 nm) is considered to be invisible if it is indistinguishable in the optical or electronic microscope. It has been assumed that the gold in these minerals can be deployed in micro lattice imperfections or can penetrate isomorphically into crystal lattice of minerals and presented as a type of micro selections on the surface faces [7].

However, gold deportments are not still been identified and require further investigation.



The aim of the work is to study gold departments in sulfides by layer-by-layer preparation of enclosing sulfides by chemical, then ion-plasma etching by means of the methods of scanning tunneling and atomic-powered microscopy.

2. Materials and Methods

For study grains of selected pyrite and arsenic pyrite, the grains of 0.25 mm fraction were sealed in epoxy blocks. The polished sections from core of quartz-sulfide and gold-sulfide ores have been prepared as well. To reveal gold inclusions, sulfides in epoxy blocks had been etched for 8 hours in 30% hydrochloric acid. For deeper preparation of sulfides the polished sections undergo to two-stage etching: 1) etching for 4 hours in "Aqua Regia", 2) the ion-plasma etching (IPE) on the installation of Etna 100 PT. Technical specifications of etching: inductive plasma source-250 W., accelerating voltage- $U_C=200$ V., plasma: O + Ar 60:60 cm³/min, vacuum – 0.002 mbar, etching time 3 minutes. To purify etching patterns after the treatment the blocks were washed in the ultrasonic washing plant for 5 minutes. In the epoxy blocks 60 pieces of grains were found. In the sections there were 40 grains. All in all 60 grains were studied in the epoxy blocks and 40 grains of auriferous minerals in the polished sections.

The processed chemical and ion-plasma etched samples were investigated in the tunneling microscope of NT-MDT Integra Spectra 2011 (Russia, Zelenograd). Plotting characteristics: wavelength is 532 nm. The range under consideration is 150-2500 cm⁻¹. For studying the prepared sulfide structures an atomic-powered method was used by the microscope. The sizes of inclusions were measured by 2D images, the shapes of inclusions and structural structures of minerals were studied by 3D images. Raman spectroscopy was used to determine the phase composition. The chemical composition of the phases was studied by the micro-agent analysis on the microanalyzer «JEOL JSM-6480 LV Scanning Electron Microscope».

3. Results and Discussion

The study of the distribution of invisible gold in the ores of the Kuchus Deposit showed that early sulfides such as arsenic pyrite and pyrite are considered the main concentrators of gold. The most gold-bearing is a fine-grained needle arsenic pyrite, the lower gold content noted in pyrite. The gold content in arsenopyrite, depending on the modification, varies from 60 to 440 g/t and the average value is 201.33 g/t. The gold content in pyrite varies from 11.50 to 73 g/t. and the average value is 40.81 g/t. In earlier works by the electron microprobe analysis on the microprobe «JEOL JSM-6480 LV Scanning Electron Microscope» no gold inclusions have been identified without etching in the sulfides of the Kuchus deposit. [1].

The chemical etching of pyrite in 30% hydrochloric acid occurs by the following reaction:



H₂S₂– hydrogen disulfide (sulforan) is unstable and breaks at ultrasonic treatment.



Arsenic pyrite was prepared with "Aqua Regia" (a mixture of nitric and hydrochloric acids):



Reactive Ion Plasma Etching or RIPE (in the English literature-Reactive Ion Etching or RIE), is a kind of dry etching, in which an essential component of the process is ion-bombardment of the surface of the material in plasma. In reactive ion-plasma etching (synonym – reactive Ion etching), the treated samples are contacted with plasma and placed on an electrode connected to a radio-frequency voltage source. Material removal occurs both due to physical spraying by accelerated ions of chemically active

gases and as a result of chemical reactions between free atoms and radicals formed in the plasma and surface atoms of the treated material. Physical and chemical mechanisms are not independent: physical atomization activates the surface of the material, increasing the rate of chemical reactions, which in turn weaken the chemical bonds of surface atoms, thereby increasing the rate of physical atomization [3; 4].

Introduction of charged particles into the solid body causes ionization of lattice atoms and excitation of their electron shells. In precious metals with their high electrical conductivity, ionization caused by irradiation by charged particles is very quickly (during the time of 10-16-10-19 c) neutralized by conduction electrons, and this process does not lead to noticeable changes in their electrophysical properties [5]. This is the essence of selective etching of the sulfide matrix and nanoscale gold particles. In this case, oxygen as the strongest oxidizer, reacts with sulfide ions. The neutral gas argon bombarding the surface of sulfides sprays oxidation products, which are also known as volatile compounds pumped by the vacuum pump.

Sulfides in RIE are etched with oxygen by the following reactions:



In pyrites after chemical etching with hydrochloric acid, single gold inclusions are observed. The internal structure of the pyrite is identical to the parallel hatching on the crystal faces. Parallel structures are crossed by oblique cracks. Also, the faces of pyrite have a small block structure. The revealed gold particles in the pores formed in the intersections of cracks (figure 1a). The size of gold inclusions in pyrite №25 in a flat image was 15×25 nm., height 30 nm.

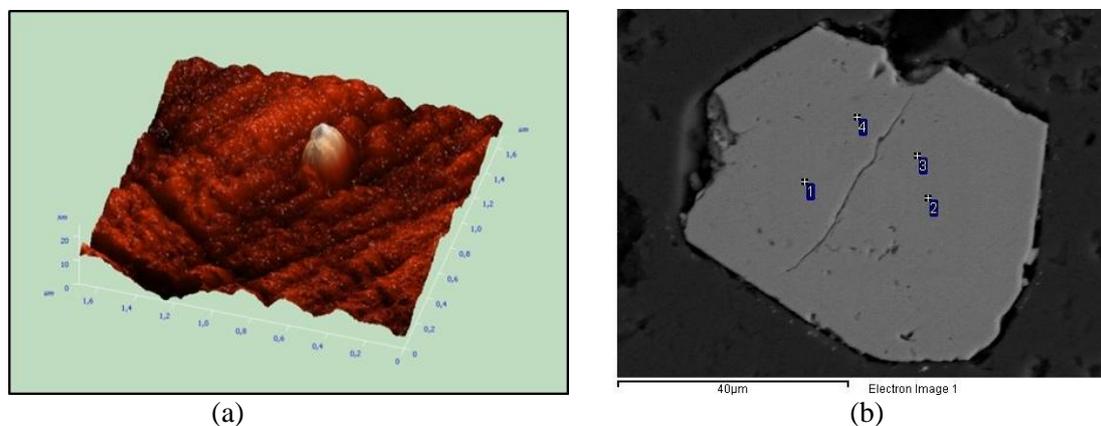


Figure 1. The gold inclusion in pyrite №25 on:

(a) – atomic force microscopy;

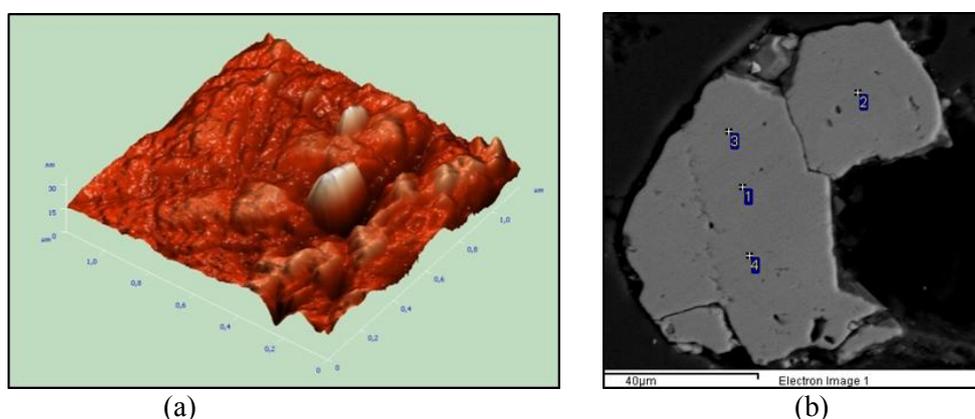
(b) – raster electron microscopy "JEOL JSM-6480 LV Scanning Electron Microscope".

After etching with hydrochloric acid, using x-ray spectral analysis in pyrite №25, the presence of gold was also recorded at four points (table 1).

Table 1. The X-ray spectral analysis of pyrite №25.

Spectrum	S	Fe	As	Au	Total
1	49.25	45.36	1.95	0.59	97.16
2	48.89	43.84	3.68	-1.42	94.99
3	52.02	41.18	2.53	-2.10	93.64
4	49.54	43.74	2.49	-0.042	95.35
Max	52.02	45.36	3.68	0.59	
Min	48.89	41.18	1/95	-2.10	

After etching in the «Aqua Regia» and ion-plasma etching in the flow of oxygen and argon in subsequent layers of pyrite in the atomic-force regime some gold inclusions were registered. The structure of the pyrite crystal is block. The gold inclusions were detected along boundaries of the blocks. The size of gold inclusions $40 \times 30 \times 62$ nm.

**Figure 2.** Gold inclusions in pyrite №22 on:

(a) – atomic force microscopy;

(b) – raster electron microscopy "JEOL JSM-6480 LV Scanning Electron Microscope".

The gold particles were also found in the observed points (table 2).

Table 2. The X-ray spectral analysis of pyrite №22.

Spectrum	S	Fe	As	Au	Total
1	52.23	40.58	1.56	0.42	94.79
2	49.55	40.90	2.94	-1.12	92.26
3	48.39	45.39	3.11	-0.64	96.25
4	51.85	43.00	3.47	2.83	101.15
Max	52.23	45.39	3.47	2.83	
Min	48.39	40.58	1.56	-1.12	

Table 2 shows the gold content from 0.42% to 2.83%. The highest gold content is recorded in pyrite with a high arsenic content [6].

In the polished sections there are 3 morphological varieties of arsenic pyrite: 1 - near the core quartz veins arsenic pyrite consists of disoriented blocks; 2 – rhombic with poor blockage; 3 – orthorhombic with gold-sulfide ores. When studying arsenopyrite1 in the atomic-powered mode some gold inclusions are registered along the block boundaries. The disorientation of the blocks is observed at all structural levels. The sizes of three measured gold inclusions: 1 - $24 \times 58 \times 42$ nm; 2 - $20 \times 58 \times 60$ nm; 3 - $27 \times 38 \times 25$ nm.

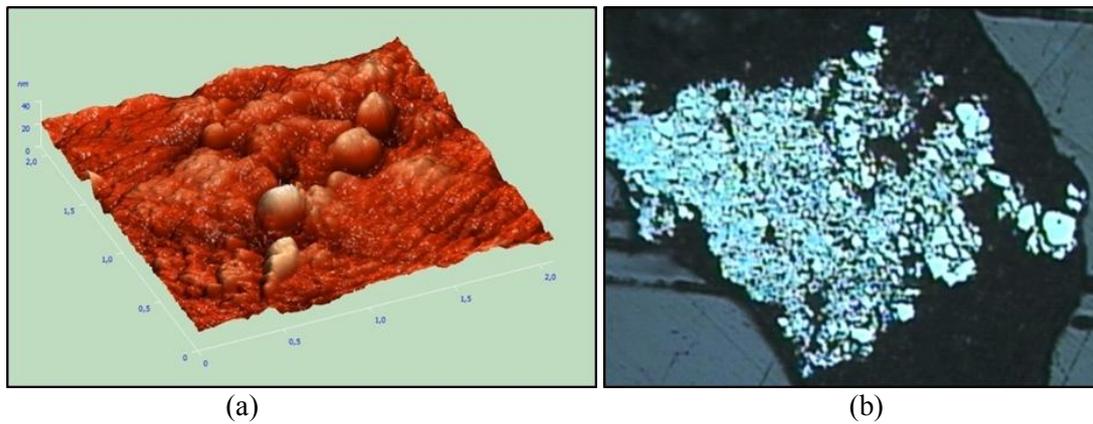


Figure 3. Block arsenic pyrite:

(a) – atomic force regime;

(b) – scanning tunneling microscopy.

In rhombic arsenic pyrite, gold is in the form of an ordered solid solution. After etching in the «Aqua Regia» and the use of RIE, gold inclusions are found in the cracks along the boundaries of the blocks. Flattened form of inclusions, repeating the form of the cracks. Dimensions of inclusions. $5 \times 12 \times 45$ from $3 \times 6 \times 30$.

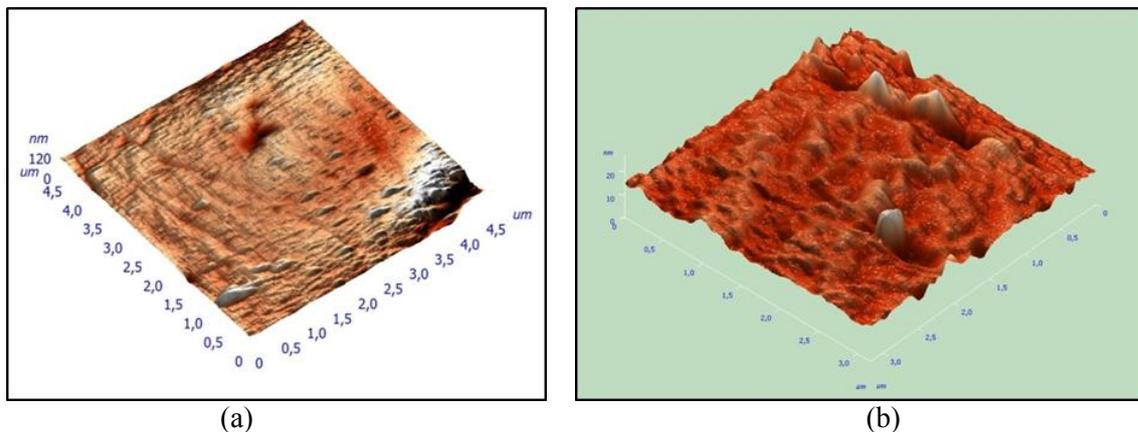


Figure 4. The gold inclusion in a rhombic arsenic pyrite:

(a) – arsenic pyrite before etching;

(b) – rhombic arsenic pyrite after etching in «Aqua Regia» and RIE.

In the etched rhombic arsenic pyrite a weakly disoriented block structure is detected.

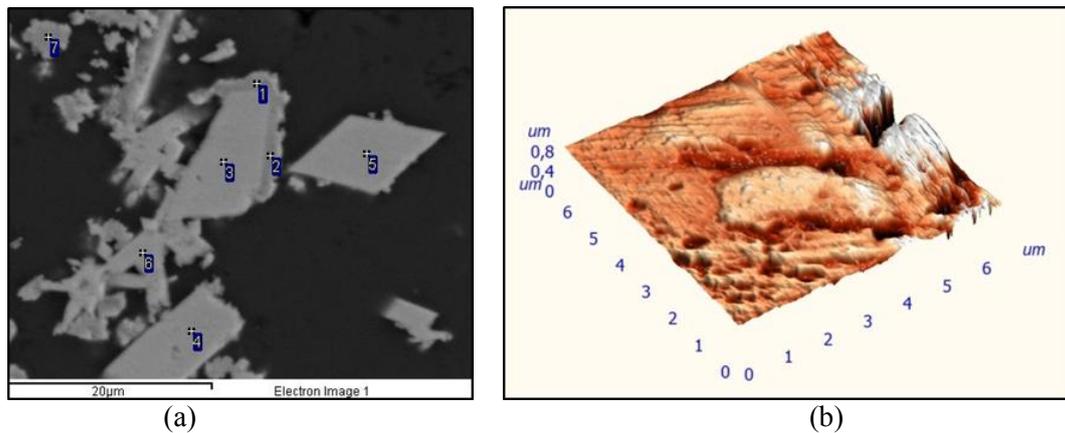


Figure 5. Rhombic and prismatic arsenic pyrites:

(a) – in a scanning mode of the X-ray analyzer «JEOL JSM-6480 LV Scanning Electron Microscope»;
 (b) – the prismatic arsenic pyrite in a atomic in an atomic-powered mode.

Table 3. The X-ray analysis of orthorhombic and prismatic arsenopyrite. %

Spectrum	O	Si	S	Ti	Fe	As	Ag	Au	Total
1			33.16		38.48	27.09		2.11	100.83
2	11.00	4.91	31.81		37.37	22.45		2.00	109.55
3			23.59		33.47	41.96	0.56	2.42	102.01
4			24.16		32.05	39.60	0.63	2.35	98.79
5			23.99		31.82	41.72	0.00	0.79	98.32
6			22.61		28.62	42.39	0.36	2.73	96.72
7		3.03	29.21	2.47	33.86	26.61	1.23	-1.37	95.03
Max	11.00	4.91	33.16	2.47	38.48	42.39	1.23	2.73	109.55.
Min	11.00	3.03	22.61	2.47	28.62	22.45	0.00	-1.37	95.03.

Inclusions in prismatic arsenic pyrites, based on the composition, are close to electrum and only shells comprise high-grade gold. The rhombic arsenic pyrite includes gold without silver (table 3). In the prismatic arsenic pyrite after etching in the “Aqua Regia” and RIE, fragments of the primary needle arsenic pyrite with gold inclusions are distinguished (figure 5b). The size of large gold inclusions were $10 \times 30 \times 90$ nm. In early prismatic arsenic pyrites gold is dispersed in the form of small emulsions. In the absence or low blockage the gold is not enlarged.

As the result of the experimental work we found out that the etching with 30% hydrochloric acid in pyrites revealed gold inclusions, which are fixed in the atomic-powered mode of the scanning tunneling microscope, as well as the micro-analysis of the raster microscope «JEOL JSM-6480 LV Scanning Electron Microscope».

During the chemical etching in “Aqua Regia” and subsequent RIE ions of oxygen and argon molecules of pyrite and arsenic pyrite are etched layer by layer. This shows the distribution of gold throughout the grain volume. The observed gold inclusions are enclosed in cracks and pores of the block structure of sulfide crystals. The crystal blockage is observed at different structural levels. Depending on the location in relation to the late core quartz veins with gold sulfide mineralization, the intensity of deformational changes varies from stronger to weaker ones. In early prismatic arsenic pyrites, gold particles found as patterned solid solution. As shown in [7], it is possible that under the influence of temperature influences and dynamometamorphism, gold particles are transferred by dislocations to the boundaries of block structures, where they become larger. The applied method of analysis can be used to identify types of ores and adjust the enrichment of deposits of this type.

4. Conclusions

1. In arsenic pyrite and pyrite the nano-gold is located on the boundaries of the block structure.
2. The crystal blockage is observed at different structural levels. Depending on the location in relation to the late core quartz veins with gold-sulfide mineralization, the intensity of deformation changes varies from stronger to weaker ones.
3. The layer-by-layer preparation of sulfides showed the distribution of gold throughout the grain volume.
4. In the early prismatic arsenic pyrite the gold is characterized as the patterned solid solution.

5. References

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Acknowledgments

The research was carried out according to the plan of research Diamond and Precious Metal Geology Institute of the SB of RAS, project No. 0381-2016-0004.