L. MARCHENKO, L. KOMASHKO

(Institute of geological sciences named after K.I. Satpayev)

ON TRACE OF MICRO- AND NANOPARTICLES OF PRECIOUS METALS IN SULFIDES AND CARBONACEOUS MATTER

Annotation

The distribution of sulfides, micro-and nanoparticles of precious metals for gold deposits of Carlin and epithermal type (according to the literature), and sulfides, and carbonaceous matter to black shale type deposits (own data).

Key words: inclusions, precious metals, micro- and nanoparticles, gold deposits, energydispersive spectra, microdiffraction analysis, sample preparation, shungite, fullerene-like nanostructure, nanotube, native and mineral composition.

Кілт сөздер: қоспа, асыл элементтер, микро- және нанобөлшектер, алтынкенді кенорны, энергодис-персті спектрлер, микродиффракционды талдау, сынамадайындық, шунгит, фуллерентәрізді наноқұрылым, нанотүтік, табиғи және минералды құрам.

Ключевые слова: включения, благородные элементы, микро- и наночастицы, золоторудные месторождения, энергодисперсионные спектры, микродиффракционный анализ, пробоподготовка, шунгит, фуллереноподобная наноструктура, нанотрубка, самородный и минеральный состав.

Introduction. In many gold deposits which are related to different genetic types, the carrier and the hub of gold are considered mainly by sulphides, primarily pyrite and arsenopyrite. The goal of this article is to determine the nature of the distribution of inclusions of micro and nanosized particles of precious metals in minerals hub. Pyrite contains significant amounts of trace elements, including Au, Ag, Pt, Te, Se, and others that may be included in the micro-and nanoparticles. Our work aims are to study the status, composition and structure of these particles. Pyrite and arsenopyrite containing nanoparticles are found mainly in the low-temperature Carlin-type deposits (Nevada, USA), epithermal (Pueblo Viejo - Dominican Republic, Porgera - New Guinea) [15-18] and "black shale" type deposits (Bakyrchik, Vasilievsky, Kvartsitovye Gorki - Kazakhstan, Kyrgyzstan - Kumtor, Muruntau and others, Uzbekistan, Sukhoi Log - Russia and many others) The distinguishing feature of deposits of "black shale" type is that the micro-and nanoinclusions developed as precious metals in sulphides, and in carbonaceous matter [1-6, 20].

In Carlin-type deposits of pyrites (Lange, et al., 2009) [16] microscopic inclusions of native gold and tellurides are described. Most recently microinclusions of petzite (Ag₃AuTe₂), calaverite (AuTe₂), altaite (PbTe) and pure gold were reported in pyrites of Dongping and Huangtuliang (China) deposits. Arsenopyrite of Carlin-type deposits are enriched in gold and arsenic with compelled amount of antimony, mercury and thallium. Ores of this type of deposits are formed at a temperature of about 200°C (Cline et al., 2005) [16].

In epithermal deposit Pueblo Viejo are found nanoparticles containing Ni, As with variable content of silver and antimony in the form of Au-Ag-Ni-As-S (Fig. 1). Authors consider these are crystalline inclusions. In this field there are three types of pyrite: Cu-rich, As-saturated and "undoped". For the Cu-rich numerous nanoparticles of 5-50 nm are identified, containing various amounts of Sb, Te, Pb, Bi and Ag. Ag-Au nanoparticles are in the Cu-rich pyrites in contact with arsenopyrite. The authors [16] suggest the structural state of the particles in the form of minerals only on the basis of elemental composition, namely in the form petrovskaite (AuAgS), uytenbogaardtite (Ag₃AuS₂).

Pyrite of epithermal deposit Porgera has as inclusions of nanoparticles sized 5-20 nm consisting of Pb-Ag-Sb-S, as well as galena particles sized 200-500 nm.





Figure 1 – Distribution of nanoinclusives on pyrites (a,b), image of 1 AuTe(1) and AgAs(2)

of nanoinclusives in porous growth region of arsenopyrite. Pueblo-Viejo deposit [16]

Nanoparticles enriched with gold and silver were discovered in pyrites from Carlin-type and epithermal deposits, in the latter type, on example of the Pueblo Viejo deposit, nanoparticles of noble metals consist of silver with some gold, probably electrum. Pure silver without mixture of gold, but closely adjacent to the gold nanoparticles predominates in nanoparticles of Carlin-type. Sulfur, selenium and tellurium with formation of probably naumannite (Ag₂Se) or hessite (Ag₂Te)). Among the possible nanominerals that can "hold" gold and silver are petrovskaite uytenbogaardtite, rarely, lenaite and argentopyrite and sternbergite (AgFe₂S₃), which are difficult to distinguish from silver-bearing nanoparticles in pyrites matrix. With glance of the stability of gold and silver-bearing nanoparticles in Ag-Au-Ag-S systems of petrovskaite and yutenbogaardit are stable in the solid state below 181 ° C, and Au and S, while the Ag can react with them to create Ag2S. We can not exclude the presence of Au₂S, which is stable below 177 ° C.

The authors [16] show that most trace elements included in the nanoparticles are confined to the defective area, and not to monocrystals of pyrites. If also detected the presence of nanoparticles in one crystal of pyrite (Fig. 1b), even here there is some distortion of the crystal hub. In addition, the deficiency of sulfide stress porous structures, usually enriched with nanoparticles, which is typical for Carlin-type deposits. Porous structures with inclusions of gold and arsenopyrite were found by us at the center of the zonary arsenical pyrites of Bolshevik deposit of "black shale" type (Fig. 3). Origin of porous structures can not be explained only by the simultaneous origin of inclusions. It should be taken into account later process. On epithermal deposit Pueblo Viejo porous structures are similar to liquid inclusions, which are usually formed in the growth zone of nanoparticles.

According to the origin of the nanoparticles, such as the ones on Carlin-type deposits (Paleni, et al., 2004) [16] is proposed: 1) direct precipitation from hydrothermal solution, and 2) exsolution of the receiving pyrite during cooling. Most nanoparticles are very small on epithermal deposit Pueblo Viejo, (Fig. 1b), where Pb-Sb-Bi-Ag-Te-S nanoparticles have a size of less than 10 nm (shown by arrows), which are probably formed by exsolution (on crack of grain), to the same clusters of Pb-Te-Sb-Au-Ag-Bi-S nanoparticles are surrounded by undistorted "undoped" pyrite. Likely candidates for the direct deposition of the solutions are larger nanoparticles> 20 nm, were reported along the growth zones of pyrite (Pueblo Viejo deposit) that are associated with variable zoning of As and Cu. Porous and polycrystalline zone filled by Cu-Fe-S nanoparticles are another example of direct precipitation from solution. On the formation of larger Au nanoparticles on the surface of pyrite (Bakken et al., 1989) [16] interpret this as the result of simultaneous growth of nanoparticles and host pyrite. Similar conclusions were drawn (Yang et al., 1998) [16], which described the spherical gold nanoparticles sized 70-150 nm on the growing surface of pyrite (Fig.1c).

The inclusion of trace elements in the nanoparticles can be defined as an equilibrium process, so equally, and non-equilibrium [16]. Deposition of nanoparticles can also be caused by

changes of the chemical composition of the host pyrite. Gold and silver are going out of the pyrite structure and form into nanoparticles in connection with limits exceed of the pyrites solubility. That is, the nature of the structure of the pyrite surface can influence on the formation of nanoparticles.

Many experimental studies of a group of scientists were devoted to modes of occurrence and distribution of trace elements in natural and synthetic sulfides. [7-13, 21]. According to them, "sulphides which were formed under hydrothermal conditions (pyrrhotite, galena, pyrite, sphalerite) have a surface layer, thickness of 500 nm, differing in chemical composition, stoichiometry, and possibly the structure of the crystal volume." Nanocrystalline inclusions are formed in these "pre-surface" nanolayers. According to these authors, in the surface layer of the pyrite crystals there is pre-surface phase, the main components of which are Fe $^{+2}$, S²⁻, S²⁻ in varying relations, and oxidized forms of sulfur.

"Geochemical role of surface non-autonomous phase (NP) is to absorb trace elements incompatible with the structure of pyrite, but easily adaptable to a less rigid structure of non-autonomous phase" [13]. "NP layer in pyrites of epithermal deposits crystallizing in multi-phase systems in the presence of the impurity components (Zn, Pb, As, K, Cu, Tl, Ag, Au, etc.), is formed with the participation of additional elements, many of which are monovalent, which contributes the valence compensation in NP three-valent ferric iron by forming clusters of type AgFeS₂, KFeS₂, TIFeS₂, CuFeS₂». Experimentally established that pyrite in equilibrium condition can not contain more gold than 3 ± 1 g/t (at 500 ° C and 1 kbar.,) [9-12]. However, arsenic and tellurium-containing pyrites of some epithermal and Carlin type gold deposits can contain up to 500-700 g/t of structurally associated gold. Unusually high content of gold is typical for As - and Au-containing marcasite or Au-containing arsenopyrite, in which gold is in the structurally associated form[13]. "

Experimental studies [21] indicate that the surface concentration of gold passes through a maximum relations of Na2S to HAuCl4 in sulfide sols. The deposition of Au and Ag in the sulfide phases usually provide isolated pockets sized 10-30 nm. X-ray electron spectroscopy data show the presence of metallic gold, and the X-ray absorption spectroscopy data indicate the presence of disordered sulfide gold. Metal nanoparticles of gold and silver occur with increasing of reaction time [15,21].

Hanchuk A.I. and colleagues [14] in a study of quartz-sericite-graphitic schist of sutyrskaya formation (Far East, Russia) using electron microscopy (scanning electron microscopy) of polished thin sections and leachate, found microinclusions of native iron, silver, copper and micro-inclusions with different contents of gold, platinum, osmium, and iridium. "For inclusions of iron higher carbon (15,7-42,6 at.%), oxygen (5,2-5,3), sulfur (0.3) and silica (0.4) content are typical. In the studied inclusions the amount of atomic carbon (46-73 at.%) is higher than of natural iron carbide. In Cohen this amount is equal to 25 atomic %, indicating the possible presence in these carbon-rich phase (Fig. 2a). Inclusion of silver and copper were found in pure isolation and "combined" grains. These inclusions form a porous structure (Fig. 2b) and have the composition: Cu-58,5-64, 6; Ni-13,5-14, 2; Zn-17,8-18.0 and C-6,6-10, 2. Inclusion of silver (47,8-65,1) have lumpy structure with irregular edges (Fig. 2c) and impurities: Cu (1.8-20,5), U (up to 3,2), Zn (up to 7.1), S (up to 0,5), Si (6,2-8,7), Al (up to 0,8), O (5,9-15,1) and C (7,9-14,6). Combined grains have a tight structure (Fig. 2d). At the center of thee grains copper phase

was developed (Cu-64,3-64, 6; Ni-14,0-14, 1; Zn-21,3-21, 7). Copper phase wraps and cuts by streaks of silver phase: (Ag - 61,2; Cu-19, 4; U-12, 9); Ni-0, 9; Zn-7, 2; S-0, 7 and carbon C- 7.7 wt.%). Gold forms a flattened grains (Fig. 2e), with fineness 691-724, there is contaminant silver -7,3-16,4, copper - 8 ,6-12, 7 and carbon - 3,5-9,6. Platinoids are only recorded in the leachate. Grain platinoids sized 1-3 mm, in which Pt-17-39, 1, O-12.3-37, 3, and C-23 ,6-49, 6 plus impurity Fe-0 ,8-1, 6; K-0 ,6-1, 1; Al-3,3-6,6; Mg-0,3-0,6 and F-13 ,3-21, 7 "[14]. These inclusions were studied in a scanning electron microscope, X-ray microprobe (SEM EMP) in polished sections, thickness of 2-5mm over an area of 1 cm2.



Figure 2 – Distribution of micro-inclusions in polished sections in quartz-graphitic schists [15]

Inclusions of precious metals in the sulfides and carbonaceous matter have been studied on the example of "black shale" type fields of Kazakhstan (Bakyrchik Bolshevik, Vasilievsky, Kvartsitovye Gorki). We found a paragenesis of nanominerals of precious metals with pyrrhotite and tennantite in gold arsenopyrite and pyrite which is typical fo Bakyrchik area deposits, comprising nanominerals of precious metals: 1) Cooperite - platinum - PtS₂ unlike classical cooperite PtS, in our modification cooperite contains more sulfur. 2) palladium cooperate - PdS2. 3) Platinum-arsenide sperrylite - PtAs₂. 4) sternlergit - silver sulfosalts - AgFe₂S₃. 5) Arsenate arsenic AgAs₂O₃ • 1,5 H₂O. 6) silver fluoride AgF₂ • AsF₅. 7) petrovskaite - silver sulfide and gold - AgAuS. 8) palladoarsenid in two versions PdAs₂. 9) Ag₇AsS₆ and Ag₂AsS₂-billingsleit and devillit (Table 1).

Table 1 – Inclusions of nanominerals of precious metals and their related of sulphide of Bakyrchik deposit

1. PtS_2 – cooperite, in the aggregate from particles sized 5-10 nm and more;	1. AgAuS – petrovskaite, in particles sized 20 nm,
2. PtS_2 – cooperite, in the aggregate from particles sized 30 nm;	structured fullerene-like crystal of hexagonal motif of cutting;
3. PdS_2 – palladium cooperite, in needle-shaped nanotube 75 nm in cross section;	2. PdS_2 – palladium cooperite, in translucent particles – 5 nm;
4. PdS_2 – palladium cooperite, in large crystal sized more than	3. AgAuS – petrovskaite in particles with a minimum size 5 nm;
200 nm (second modification);	4. PdAs ₂ - palladoarsenide in particles
5. $AgFe_2S_2$ – sternlergite, in nanotube sized 40 nm	with a minimum size 5 nm;
in cross section;	5. PtS_2 – cooperate in particles with minimum size 6-10 nm;
6. $AgAs_2S_3$ 1,5 H ₂ O, in nanocrystall with	$6 A \sigma A \sigma S \pm A \sigma A \sigma S = billingslowite$
nexagonal cutting sized ~ 10 min,	and devellit, in particles sized 5 nm;
7. AgF_2 As F_5 , in aggregate from translucent narticles of plate type sized 5-30 nm	7 PtAs ,sperryliteinevtended
particles of plate type sized 5-50 mill	nanotubes sized100 nm with seals along the extension (5 nm).
Attendant	Attendant
1. $\mathbf{Fe}_{1-\mathbf{X}}\mathbf{S}$ – pyrrhotite;	1. As_2O_3 – arsenolite, in large translucent
2. (Cu, Fe) ₁₂ As ₄ S ₁₃ – tennantite;	crystals prismatic type with shading along the elongation;

3. Смесь FeS ₂ и Fe _{1-x} S- marcasite and pyrrhotite;	2. $\mathbf{Fe_{1-x}S} - \mathbf{pyrrhotite};$
4. As_2O_3 – arsenolite;	3. FeS_2 – marcasite;
5. As – native arsenic;	4. FeAsO ₄ ;
6. KC ₈ - graphipotassium;	5. As – native arsenic;
7. SiAs, in crystal of pyramidal form sized 50x350 nm;	6. KC ₉ – graphipotassium.
8. Mixture FeAsS – arsenopyrite with As_4S_3 – dimorfit as spherical formations consisting of particles sized 4 nm.	

Note: The left

We first studied the inclusion of micro-and nanoparticles in carbonaceous matter (shungite) in "black shale" type deposits [6.20].

In shungite of Bakyrchik area deposits, along with nanominerals of sulphides and arsenides of platinum, palladium, silver and osmium, are widespread nanominerals of precious metal carbides. In samples of shungite from wallrock zone of Bolshevik deposit nanominerals of palladium - palladoarsenids, palladium cooperite and spinel are dominated. Silver in these samples of shungite is represented by nanominerals in chloride and sulphide forms or in the form of sulfosalts (Table 2).

In the carbonaceous matter at the microlayer of epienergy-dispersive spectra revealed a large variety of components-aggregates of precious metals following by pyrrhotite and tetrahedrite antimony ore (tetrahedrite) (Table 3), and identified a strong link of precious metals minerals with complex of "foreign" components, rare and scattered elements. Energy-dispersive spectra of platinum aggregate basically one hundred percent, but there is an evidence of the presence of Fe and S with pyrrhotite component ratio. Micron grains of platinum are often composed of fine nanoaggregate. Platinum is prevalent in Bakyrchik platinum group of deposits, it is often an impurity of Fe, Ti, Sn, Cu, which suggests other minerals intemetallids.

At the micro level, attracted to the sites of shungite, were found form of microinclusions of precious metal even more diverse than those included in the sulfides, and there were oxidized oxygen microphase with rare earths and rare elements (W, Sn, V, Nb, Ta, etc.), which differ significantly disruption of stoichiometry.

Table 2 – Nanomineraly precious metals and their related in nanostructured particles Shungite field Bolshevik

Mineral, formula	Size of, nm

	nanostructures
Orezone (1152)	
1. Pd ₅ Ti ₃	
2. PtAs ₂ - sperrylite	
3. PtCoO ₂ -N from 1 to 3 in one nanotube	125x13
4. Pt_2Y – dense nanotube	150x13
5. AgCl – hlorargirit, dense nanotube	100x5
6. (Pb , Ag) ₅ (Bi , As) ₆ (S , Se) ₁₄ -vittyte-argenshin microcrystal of prismatic form,	125x20
7. Fe ₃ PtC – carbide of glandular platinum - the aggregate of dense	~ 150
particles, forming a structured crystal with a hexagonal motif of cutting and small grains	~ 3
Attendant:	
1. (Cu, Fe) ₁₂ As ₄ S ₁₃ – tennantite in the (N_{2} 1-3) nanotubes, fig. a	125x13
2. $C_2 Ca O_4 2H_2O$ – vidiolit as inclusions in the "bubble" of polymeric formations (bitumens)	~10
Wallrock zone (867)	
1. Pd ₈₀ Si ₂₀ - large dense particles of prismatic form	100x60
2. $PtAsS_2$) – platarsite + OsS_2 – erlichmanite + FeC – ferric carbide in a large translucent crystallite	120x60
3. CoPt + AgClO ₄ + PdS ₂ – palladium cooperite + Ag ₃ AsS ₃ – xanthoconite, large translucent crystallites included in the aggregate "Asterisk" type, figure.5-v	120x100
4. Ag_3AsS_3 – xanthoconite + KC_8 - graphipotassium, large translucent particle with small dense formations	40x20
5. AlPtC _{0,5} +FePtC+Cr _{2,4} Pt _{1,7} C _{1-x} +AgFe ₂ O ₃ +AuSb ₂ (aurostibite)	75x25
6 $PtAs_2$ – sperrylite mixed with gold oxide in the aggregate of the large dense particles with signs of cutting	140x100
7. $Ag_4SeS - aquilorite + PdAs_2 - palladoarsenide, Pd_{80}Si_{20}$ in aggregate of large dense particles with signs of prismatic cutting	60x60
8. K_2PdO_2 in a large translucent particle	50x60
9 Pt ₁₆ S ₇ +Ag ₄ SeS Aquilorite in large dense particles with signs of cutting	100x80
9. AIPt ₃ C _{0,5} + Fe ₃ PtC + (Os, Ru)AsS - osarsite in the aggregate of dense	10x20

particles	
10. $PdAs_2+Ag_{1-x}S_8+Na_xPd_3O_4$ in the aggregate of translucent and solid particles	120x120

Table 3 – Distribution of trace minerals and their accosiates in shyngite of Bakyrchik region deposit (by energy dispersive spectra)

Deposit, zone (formation, well)	Name of mineral, formula	Grain size, microns	Number of grains per square1 2,5 mm ²
BOLSHEVIK	 Pt impure Fe, Ti, Sn, As, S, Cu, Zn Ag-native impure Fe, S, As, Cu, Zn Au native impure Ag, Fe Pt+Pd impure Sn and S 	5x5- 30x50 5x7-10- 30	35 65 5 1
Ore zone		2x5	
	Attendant: 1. (Cu, Fe) ₁₂ Sb ₄ S ₁₃ - tetrahedrite 2. (Fe, Mn) WO ₃ – wolframite 3. Tl, J, Ag, As, S – intermetallide of thallium, iodine and silver 4. Yb ₂ O ₃ – ytterbium oxide with ~ 2 % Tb	5x10- 30x40 3x5 	35 3 1
	 Pt – native with Fe, As Ag – impure Cu, S, Fe 	5x10 5x15	4 5
Ore zone (1152)	v 1. (Cu, Fe) ₁₂ Sb ₄ S ₁₃ - tetrahedrite	10x20	7
	 (Fe, Mn) WO₃ – wolframite (Y, Gd, Dy, Ho, Er)PO₄–xenotime (Y) with~20%TR 	4x6 —	1 2

	Са	ontinuation	of table 3
Deposit, zone (formation, well)	Name of mineral, formula	Grain size, microns	Number of grains per square1 2,5 mm ²
	1. Pt – native	5x5	1
	2. Ag – impure Cu, Zn, Cl	5x7-	55
	3. Au –clear native	10x30	3
	4. Au – on brass (Cu+Zn)	3x5	7
		2 до 5	
Wallrock zone	Attendant:		
(867)	1. Re – rhenium with N and O ($ReO_3 \cdot NO_3$)?	5x15	1
	2. (Fe, Mn) WO ₃ – wolframite with molybdenum	30x40	1
	$3.MoS_3 - molybdenite$	2x5	1
	4. $Yb_2O_3 - yttrium$ oxide	2x4	1
	5. MnTa ₂ O ₆ - manganotantalite	3x5	4
	6. In, Sn, Ga, Cu – intermetallide of indium, stannum, gallium and copper	5x5	1
BAKYRCHI	1. Pt – clear large-scale	3x7-6x8	13
ĸ	2. Pt – impure Ti, Fe, Cu, As, S	5x10	13
	3. Au – with Ag, Ti, Fe, As, Ni, Cu, Zn	5x4	3
Ore zone	4. Ag – with Cu, Zn, S, F	2x5-	10
(2286)	5. Cu – with Ag, Zn	10x15	2
		5x10	
	Attendant:		
	1. (Cu, Fe) ₁₂ Sb ₄ S ₁₃ - tetrahedrite	7x10	20
	2. (Fe,Mn) Nb_2O_6 – columbite with Ti, S, Si	10x20	1
	3. HgSb ₄ S ₈ - livingstonite	6x6	1

	4. (Ce, La, Nd, Pr) FCO ₃ - b astnaesite (Ce) with 12 %	5x5	2
	TR	5x5	8
	5.(Y, Cd, Dy, Yb) PO_4 – xenotime (Y) with 10 % TR	_	1
	6. (Fe, Mn) Ta_2O_6 – tantalyte	_	4
	7. Y_2O_3 – yttrium oxide	_	1
	8. (Fe, Mn) WO ₃ – wolframite	_	1
	9. MoS ₃ – molybdenite		8
	10. PbS - galena		
	1. Pt – native	2x3-4x7	22
	2. Ag - native	5x6	18
Wallrock zone	Attendant:		
(813)	1. TiO_2 - rutile	prism	2
	2. ZrO - zircon	prism	3
	3. (Cu, Fe) ₁₂ Sb ₄ S ₁₃ – tetrahedrite	5x7-	10
	4.(Ce, La, Nd, Pr, Ho)PO ₄ - turnerite (Ce) with 15 %	10x15	13
	TR	5x2	3
	5. (Ce, La, Nd, Pr) FCO ₃ – b astnaesite (Ce) with 12-14 % TR		
	1. Pt - native	_	12
	2. Ag - native	_	16
Wallrock zone	Attendant:		
(790)	1. (Ce, La, Nd, Pr) FCO ₃ - bastnaesite (Ce) with 12 %	_	6
	IK	_	1
	2. Galena	_	1
	3. Sphalerite	_	1
	4. Stibnite	_	1
	5. Cassiterite		
	1. Pt impure Ni and Fe	4x3-4x8	6
INTERSTITI	2. Au with Ag	4x5	1
	3. Au with Pd, Sn, Cu	5x3	2

	4. Ag with Ta	10x6	1
Ore zone	5. Ag with S and Br		2
(2039)	Attendant:		
	 (Cu, Fe)₁₂Sb₄S₁₃ - tetrahedrite (Y, Cd, Dy, Yb) PO₄ - xenotime, (Ce) with 14 % TR 	2x5- 15x30 3x5-	10 7
		10X/	
Wallrock zone	1. Pt native	4x3	1
(2022)	2. Ag with Sn	3x5	1
	3. Cu with Zn	5x7	1



Figure 3 – Micron gold (Au - 87,3; Ag - 6,5) in defects of structure of zone arsenic pyrite. Bolshevik deposit. Photographed with a scanning electron microscope

For a large number of precious metals at the micro level (according to energy-dispersive spectra on shungite), especially for platinum and gold chemically combined elements are typical for nanolayer (sulfide, arsenide, etc.), followed by mostly native-metallic. Precious metals of micron size have the form of free thin aggregate distributed in shungite and is closely associated with pyrrhotite and tetrahedrite. High-grade gold with impure of silver (electrum) or copper (cuproauride). In addition, there is golden copper in which gold and silver are in separate compounds. Palladium goldis noted (porpezite). Silver is represented by sulphide and has impurity of bromine and chlorine (possibly due to the latest chemical analyses), but mostly silver is micron sized - native and in close association with gold (kustelite). Silver is also found as an impurity in antimonide tetrahedrite.

Nanoparticles of noble metals are usually incorporated into various nanostructures: nanotubes, fullerene-like particles and microspheres (Fig. 4), developed as in the sulfides and in schungite of ore and wallrock zones of Bakyrchik area deposits.

In fine-dispersed ores of precious metals deposits of Bakyrchik ore area we met hollow and filled nanotubes, spherical and faceted, single-layer and multi-layer, compacted, dense (opaque). Round or spherical formations filled with pure metal - "native" are generally opaque, and filled with nanoparticles of sulfides, arsenides, sulfosalts, carbides, oxides are translucent, and also transparent nanotubes, which include one or more nanominerals. They were met in the gold sulphides (arsenopyrite and pyrite) and in the environment of solid carbonaceous matter (shungite) situated in close paragenetic association with sulfides.

Nanomaterial represented by species with faceted fullerene-like structures we met in pentagoidodekahedrite gold-bearing pyrite of Bakyrchik deposits. Typically, these nanoparticles have the form of nanostructured crystals with six pentagonal outline (Fig. 4). Faceted varieties have dimensions with a large range - from the first nanometers to over 100 nm. They occur in the pyrite and arsenopyrite. Uncut - spherical translucent varieties with fullerene-like structures are more common in arsenopyrite and among shungite of the ore zone of Bakyrchik deposit. Spherical nanoparticles are o p a q u e and are widely developed in association with shungite of ore zone of Bakyrchik and Bolshevik deposits. They are usually filled with "native" metal - gold, silver, platinum, tantalum with silver, copper and other metals. Opaque varieties are represented by "sticky" rounded nanograins, growing into micrograin. There are complex structures, small size (the first nm) consisting of a combination of nanoparticles with fullerene-like structures and faceted nanotubes. Translucent and transparent, faceted and spherical nanoforms with fullerene-like structures and faceted nanotubes. Translucent and transparent, sulfides, arsenides, sulfosalts, oxides, carbides, precious, rare and trace elements.

From precious metals minerals, which are filling nanotubes and nanoparticles with fullerenelike structure, a special place is occupied by sulfides and arsenides: PtS₂, PdS₂, PtAs₂, PdAs₂, Pt (As, S)₂, Ag3 AsS₃, AgAuS and others. As nanotubes and particle with fullerene-like structure (faceted and spherical) are often filled with carbides and sulfides of precious metals: Fe₃PtS; Cr₂Pt₂C. In spherical nanoparticles tungsten compound is found- tungstenit (WS₂), Li₂WO₄ and scheelite-CaWO₄. WS2 has a layered structure, resembling the structure of graphite and is used in experiments of nanotubes and nanoparticles creation with fullerene-like structures [17, 19]. A large number of microspheres - "bound together" aggregates, which are opaque and folded by metals (natives) are found in association with shungite ore zone of Bakyrchik and Bolshevik deposits and completed by platinum. [4] Micron grains of platinum consist of nanoparticles sized of several nm. Micron-sized particles of gold have a kind of "bound together" round nanoparticles. These structures show the closeness of the connection of nano-and micrograins which is typical for paragenetic mineral-ore associations.

In addition, there are nanostructured carbonaceous films that give a microdiffraction pattern with interplanar spacing $d_1 = 3,40 - 3,55$; $d_2 = 2,01-2,10$.

Carbon - graphene film has the highest surface energy. With the growth, it goes into the tube, cone, spiral, fullerene, spheroid, icosahedron etc. Due to its high surface energy carbon films hold on its surface (and their nano-structured formation) or capture nanoclusters inside in various mineral mode (sulfides, arsenides, oxides or native and intermetallic connection).



250 нм



b



Figure 4 – Nanostructured particles including precious metals from sulphides and carbonaceous matter (a-e)

On Kvartsitovye Gorki and Vasilievskoe deposits in the ore zone of pure monoshungite a large number of nanoparticles of precious and rare earth minerals are identified. Among platinoids on Vasilievskoe deposit nanominerals of platinum, palladium and iridium are equally developed. Among the rare earth minerals on this deposit is dominated by europium and proziodium (Eu, Pr), which have close links with gold, silver and palladium in the form of intermetallic compounds: AuPr, EuPd, PrAg₂, Au₃Eu, ErAu. Nanominerals of noble metals are widely presented in sulphide, arsenide forms and in connection with antimony: Pd₄S, Pd₁₀S₇, Pd₂Sb, Pd₄ (Sb, As)₄, Pd₈As₃, Ag₃Sb, AgSbF₆, AgHgAsS₃, PtAs₂, PtSb₂. Gold occurs in the oxide form (Table 4,5).

Table 4 – Nanominerals from shyngite of ore zone of Vasiliyevskoe deposit

N	Formula of mineral	Name of mineral	Description of nanostructured particles	The size of nanostructur es, nm
4122				
	IrTi ₃			
(19) a	AuO			
	Pd ₄ S			
	Al ₂ Pt		• Aggregates of elongated dense particles (nanotubes) with signs of cutting	20-80
	PtO		(
	Pd ₂ SnCu	Cabriite		
	FeC			
	AgHgAsS ₃	Laffittite		
(33)	IrLi ₂		Tight aggregate on the edge of which	20
б	Pt_5Zn_{21}		translucent particles are observed	
	PrZn			
(21)	Pd ₁₀ S ₇		Dendrite of dense nanotubes	20-80
В	Ag ₃ Sb	Dyscrasite		
	Nd ₂ O ₂ S			
	EuAs			
1	1	1		1

	Pr ₄ O ₇			
	PrAg ₂			
	AgSbF ₆			
	Pd ₂ Sb			
(23) г	AgHgAsS ₃	Laffittite	The aggregate is of compact elongated partially twisted graphene film type particles	10-20
(27)	Pd ₄ (SbAs) ₄		The aggregate of the large dense and	
(37) д	AgZr ₅		translucent graphene like particles of plate-type	20
	Pd ₈ As ₃	Stillolite		
	IrSe ₃			
	$Eu_3(PO_4)_2$			200
(25) e	PtZn ₅		Large dense elongated nanotube	200
	PtAs ₂	Sperrylite		
	EuS			

On Kvartsitovye Gorki deposit in rich ores where the content of gold in pyrite is 4 kg /t, in nanoform state in shungite gold is in oxide form or mixed with silver in petrovskaite and in intergrowth with rare earths (Au₃Eu, Au₂Er, Au₂Pr) in form of intermetallic compounds. Palladium is presented in mineral compound: Pd₃S, PdAs₂, AlPd, Pd₄S, Pd₁₀S₇. There are also widely represented minerals of iridium and platinum. Silver, as gold is often intimately intergrowth with rare earths in the form of intermetallic compounds.

Nanostructured formations developed in schungite mass and including nanominerals, precious metals on Kvartsitovye Gorki and Vasilievskoe deposits, differ significantly from nanostructures of Bakyrchik area deposits. On Kvartsitovye Gorki deposit fullerene-like structures are more developed differing by smaller dimensions and there is almost no cutting and by higher density. There are whole clusters of very small fullerene-like structures drawn into dendrides. Nanotubes which often form dense intergrowth of dendride are well developed on Vasilievskoe deposit (Fig. 4). All these structures are usually accompanied by carbon graphene films. Fragments of this relationship, as well as elements of outgrowing of grapheme-like films intp nanotubular and fullerene-like structures can be seen on many figures (Fig. 4, 5). You can watch the twist of these minifilms, scales and leaves, which were developed as in the ore and supra-ore zones, notably, the above active properties are illustrated which are typical for carbon graphene-like films.



250 нм



250 нм







Figure 5 – Nanostructured carbonaceous formations with nanoinclusions of precious and rareearth minerals (a,b) –

Bakyrchik and (c-e) – Kvartsitovye Gorki.

Table 5 – Nanominerals and including their nanostructured particles from shyngite of ore zone of Kvartsivotye Gorki deposit

N	Formula of mineral	Name of mineral	Description of nanostructured particles	The size of nanostructur es, nm
3018		I		1
(58) a	AgHgAsS ₂	Laffittite	The aggregate is made of thick fullerene particles	30-40
	AgAuS	Petrovskaite		
	Pd ₃ Si			
	$(Cu,Fe)_{12}As_2S_{11}$	Tennantite		
(66) б	PdAs ₂		Distorted tight aggregate	to 1000
	AlPd			
(64) в	AuO		Filled nanotube	50
	Al ₂ Pt			
	$(Cu,Fe)_{12}As_2S_{11}$			
(33) г	PtZn ₂		Large particle with signs of cutting and sealing	50-100
(35) д	PtSn	Niggliite	The aggregate of translucent graphene flakes	15-20
	AuZn ₃			
(29) e	Au₃Eu		On the background of translucent graphene particles dense rounded fullerene particles are developed	10-20
	Al ₂ Pt ₆			
(31) ж	PrO ₄		The aggregate is made of thick fullerene particles with a hexagonal signs of motif of cutting	60-80 and more
	IrCl ₃			
	Re(CO) ₅ Cl			
(00) 3	AlPd		The edge of a dense aggregate with translucent and dense particles with signs of cutting	80-100

	AuO		
	Pt ₃ Tl ₂		
	PdAs		
3270			
(02) и	Pd ₄ S	Clustered aggregates of fullerene particles constituting dendrides ("Octopus")	20-40 and < 60-80
(10) к	AgZr ₃ J ₁₂	Dense aggregates of elongated crystals with signs of cutting	100-200

The main mechanism of distribution of micro-and nanoparticles of gold and platinoids on complex deposits of "black shale" type of Kazakhstan is:

- confinement of micro-and nanoparticles of precious metals not only to sulfides, but also to the carbonaceous matter;

- in sulfides at the microlayer gold occupies defects of host mineral structure, according to electron microprobe analysis);

- gold and platinoids are developed in sulfides and in shungite in nano-and micron-sized form, native or mineral states (see Figure 3);

- nanominerals of gold and platinum enter (included or are on the surface) at certain nanostructured formations: nanotubes (carbonaceous and non-carbonaceous), fullerene-like nanostructures (carbonaceous and non-carbonaceous) and grapheme-like nanostructures;

- "bound together" aggregates are typical for micron sizes developed within shungite matter;

- there are precious metals on microlayer, often native, but the presence of high contents in some microprobes of sulfur, iron, arsenic, copper, zinc, tin, titanium, show on their possible existence in the form of intermetallic compounds, or other conditions (Fig. 6).



Figure 6. Microinclusions of platinum and gold in shungite ore zone of Bakyrchik, Promezhutochnoye and Bolshevik fields. Photographed with a scanning electron microscope.

Electron microscopic study of inclusions of metallic micro-and mineral nanoparticles in "black shale" type deposits began with analytical studies of chemical and elemental analysis of monominerals of sulphides and carbonaceous matter on the content of impurities of gold, silver, platinum and rare earth elements in them. The content of these elements studied by spectral, and atom-sorptographic and neutron-activation analyzes. Element analysis is applied to the electrical probe microanalyzer Superprobe 733 JEOL (Japan) and X-ray fluorescence spectrometer Focus-2M RTI Russia.

Study of inclusions of nano- and micromatter in sulphide and solid carbonaceous matter, selected from different zones of "black shale" type deposits (supra-ore, and wellrock and internal ore layer.) was performed with the use of electron microscopy to the light and X-ray microanalysis on electroprobe microanalyzer Superprobe 733 JEOL (Japan).

Deciphering of microdiffraction patterns of nanoinclusions conducted by us using the set of interplanar spacing of standard values, taken from ASTM on 8 lines (Table 6-8). Some phases are found in different microdiffraction patterns, often microdiffraction patterns can be the mixture of several phases, because the particles are small and are presented in clusters. [2] Our technique allows us (in the absence of the latest modern high-voltage equipment with energydispersive attachments) to use the possibilities of the conventional electron microscope of translucent type EM-125K (Ukraine) to obtain microdiffraction patterns of small particles sized 2-3 nm. The test samples were prepared by a special method. They were selected under a binocular of sulphides, arsenides and small layers uniform of carbonaceous matter. The samples were crumbled in an agate mortar, allowing the release of small inclusions from bulk crystalshub. The samples were studied in the form of dry suspensions deposited on collodion film. Small inclusions appear as clusters of dense or translucent particles. Microdiffraction patterns from these clusters of particles are performed by large sets of rings and some reflections that can be attributed to a mixture of different phases. Beforehand, element composition of powders was conducted on electron probe microanalyzer Superprobe 733 JEOL (Japan) and X-ray fluorescence spectrometer Focus-IRO 2M (Russia). So we had a "total" elemental composition of inclusions. Of course, we are dealing not with a single hub crystal and immediate inclusions, but we have a true mineral composition of inclusions on samples of sulfides, arsenides and carbonaceous matter in general. Particularly evident is the study of carbonaceous matter. Here there are some solid phases, as well as "contained polymer (liquid) capsules", some of which "burn" under the electron beam). Among the carbonaceous matter there are various forms of scales (thick, thin, hollow), which include small mineral phases. Thus, a special sample preparation and the possibilities of microdiffraction analysis allowed us to identify interesting parts for similar samples on different "black shale" type deposits (Bakyrchik Bolshevik, Vasilievsky, Kvartsitovye) Gorki.

Table 6 – Sets of the interplanar space of nanoform minerals from sulphides of Bakyrchik deposit

N	Formul	Name	of Interplanar space, Å	Interplanar space, Å	
	a of mineral	mineral	Design	Standard, on 8 lines	ASTM card
1	PtS ₂	cooperite	4,75-3,03-2,56-2,07-1,9- 1,73-1,67-1,59-1,49- 1 32-1 1	5,03-3,06-2,62-2,52- 1,95-1,77-1,67-1,47	18-973
2	PdS ₂	cooperite	3,53 -3,04-1,76-1,69-1,52	3,53-3,43-2,77-2,19-	22-774

				1,96-1,71-1,51-1,41	
3	AgFe ₂ S	sternlergyte	6,56-5,86-4,46- 4,24 - 3,33- 3,19 -2,86- 2,7 -2,2- 2,12-2,0- 1,97 -1,57-1,38	4,29-3,42-3,22-2,79- 2,63-1,94-1,9-1,79	11-61
4	AgAs ₂ O ₃		3,37-3,11-2,22-2,19-1,48	3,52-3,37-2,46-2,11- 2,05-2,0-1,57-1,43	33-1174
5	KC ₈	graphitopotas sium		5,3-5,1-4,2-3,01-2,67- 2,04-1,4-1,24-1,13	4-221
6	AgF ₂ ·A sF ₅		4,53 -2,67 -2,26 -1,66- 1,52-1,33	4,52-3,87-3,51-2,97- 2,78-2,48-2,26-1,43	36-564
7	AgAuS	petrovskaite	7,15-3,76-3,6-2,76-2,49- 2,37-2,11 7,12-4,18-3,58-2,82- 2,75-2,73-2,47-2,36- 2,08-1,56	7,16-3,96-2,77-2,63- 2,45-2,39-2,23-2,12	19-1149
8	PdAs ₂	palladoarseni de	3,06-2,74- 2,21- 2,11- 1,79- 1,7- 1,59- 1,47-1,39- 1,32 4,22-4,04- 3,03-2,62- 2,04-1,66	3,01-2,69-2,48-2,11- 1,8-1,6-1,22-1,15	3-1194
9	PtAs ₂	sperrylite	3,49-3,17-3,03-2,92- 2,42- 2,32 -2,12-1,89- 1,74-1,6-1,26	3,43-2,98-2,11-1,8- 1,33-1,15-0,8-0,78	9-452
1 0	Ag7AsS	billingsleyite		6,06-3,49-3,16-3,03- 2,91-2,8-2,47-1,85	21-1334
1	KC9	graphitopotas sium	7,42-6,36- 3,98-3,14- 3,07-2,98 -2,59-2,18- 1,74-1,66-1,6-1,52 4,22-4,09-3,03-2,62- 2,04-1,66		27-378
1 2	Ag ₂ AsS ²	devillit		3,25-3,17-3,08-3,02- 2,84-2,74-2,68-2,07	
13	PtS ₂	cooperite	5,05 -3,66- 2,62 -1,74- 1,67 -1,55- 1,50 -1,28- 1,22-1,14	5,03-3,06-2,62-2,52- 1,95-1,77-1,67-1,47	18-973

Table 7 – Sets of the interplanar space of nanoform minerals from shyngite of Bolshevik deposit

			Interplanar space, Å		
N	Formula of mineral	Name of mineral	Design	Standard	N of AST M card
0 r	e (1152)	Į			
1	(Cu,Fe) ₁₂ As ₄ S ₁ 3	tennantite	2,97; 2,51; 2,36; 2,12; 1,92; 1,43; 1,30; 1,24; 1,18; 1,09; 1,05; 0,82;	2,94; 2,55; 2,40; 1,99; 1,80; 1,54; 1,17; 1,04;	11- 102
2	Pd ₅ Ti			3,14; 2,31; 2,15; 1,63; 1,43: 1,30: 1,22: 1,15:	21-
3	PtAs ₂	sperrylite		3,43; 2,98; 2,11; 1,80; 1,33; 1,15; 0,80; 0,78;	
4	PtCoO ₂			5,95; 2,97; 2,43; 2,36; 2,15; 1,98; 1,65; 1,44;	27- 1330
5	Pt ₂ Y		4,33; 2,36; 2,14; 1,97; 1,53; 1,43;	4,31; 2,28; 2,18; 1.46; 1,34; 1,14; 0,80; 0,77;	12- 333
6	AgCl	chlorargyrit e	2,73; 2,37; 1,98; 1,92; 1,70; 1,66; 1,18;	3,20; 2,77; 1,96; 1,67; 1,60; 1,39; 1,24; 1,13;	31- 1238
7	(Pb,Ag)5(Bi,As)6(S,Se)14	vittyte- argenshyne	3,41; 3,10; 2,92; 1,75; 1,53;	3,63; 3,38; 2,99; 2,90; 2,75; 2,13; 2,04; 1,75	25- 460
8	Fe ₃ PtC		3,84; 2,79; 1,75; 1,61; 1,56;	3,81; 2,73; 2,23; 1,98; 1,73; 1,58; 1,37; 1,16;	
9	C ₂ CaO ₄ •2H ₂ O	videllite	4,39; 3,39; 2,36; 2,21; 1,89;		
W a	llrock (867)	1	1	I	L
10	Pd ₈₀ Si ₂₀				
11	Pt(As,S) ₂	platarsite	3,29; 2,05; 1,56; 1,22; 1,19	3,34; 2,89; 2,59; 2,36; 1,75; 1,61; 1,55; 1,26	33- 979
	OsS ₂	erlichmanite	1,22, 1,17	3,24; 2,81; 1,99; 1,69;	19-

				1,29; 1,08; 0,79; 0,78	882
	FtC			3,37; 2,14; 2,09; 1,7; 1,69; 1,5; 1,24; 1,12	3-411
12	CoPt		4,03; 3,66; 3,55;	3,68; 2,68; 2,17; 1,9;	29-
	AgClO ₄		3,38; 2,65; 2,12;	4,0; 3,51; 3,36; 2,49;	<u>492</u> 31-
	PdS ₂	coonerite		2,43; 2,14; 2,04; 2,0	1239
	1 4.52			3,58; 3,43; 2,77; 2,19;	22-
13	Ag.AsS.	_nalladium		5,5; 4,02; 3,38; 3,14;	<u> </u>
15	Ag3A853	xanthoconne		3,1; 2,82; 2,13; 1,98	0-134
			4,32; 3,81; 3,38;	3,83; 2,75; 2,25; 1,98;	
			3,18; 3,07; 3,0; 2,75; 2,63: 2,27: 1,96:	1,74; 1,59; 1,38 ; 1,17	29-71
	AIPtCar		1,72; $1,53;$ $1,47;$		2, 11
	An tC _{0,5}		1,44; 1,31; 1,26		
				3,86; 2,73; 2,23; 1,93;	
14	Fe ₃ PtC			1,73; 1,58; 1,37; 1,16	26-
	$Cr_{2,4}Pt_{1,7}C_{1-x}$			3,83; 2,7; 2,2; 1,91;	793
	AgFe ₂ O _#	aurostibite		1,71; 1,56; 1,35; 1,15	18-39
	AuSha			4,29; 3,42; 3,22; 2,79;	11-61
				2,63; 1,94; 1,9; 1,79	8-460
				3,85; 3,33; 2,98; 2,72;	0 100
				2,36; 2,0; 1,78; 1,28	
				3,43; 2,98; 2,11; 1,8;	9-452
	PtAs ₂	3,43; 1,8; 1,69; 1,56; 1,33; 1	1,33; 1,15; 0,8; 0,78		
15	sperrylite	1,52; 1,29; 1,19;			
	AuO		1,12; 0,83	3,48; 2,75; 2,63; 2,54;	23- 278
				2,22; 1,84; 1,7; 1,54	270
				Continuation of	ftable 7
		1 • /	2,95; 2,41; 1,9; 1,46;	2,88; 2,67; 2,59; 2,43 ;	27-
16	Ag4SeS3	aqualerite	1,21; 0,86	2,23; 1,73; 1,6; 1,48	620
	PdAs ₂	sperrylite		3,01; 2,69; 2,4; 2,11;	3-
				1,0, 1,0, 1,22; 1,13	1194
17	K ₂ PdO ₂		4,92; 4,61; 3,41; 2 56: 2 28: 2 03: 1 7:	4,97; 4,26; 3,04; 2,99; 2,58: 2,13: 1,56: 1,5 2	
	Na _x Pd ₃ O ₄		2,20, 2,20, 2,00, 1,7,	<i>2,00, 2,10, 1,00, 1,02</i>	27-

18	Pt ₁₆ S ₇ Ag ₄ SeS ₃	aqualerite	4,42; 2,57; 2,42; 2,25; 2,19; 1,7; 1,5; 1,47; 1,24	2,65; 2,58; 2,39; 2,23; 2,1 ; 1,82; 1,45; 1,22 2,88; 2,67; 2,59; 2,43; 2,23; 1,73; 1,6; 1,48	30- 884 27- 620
19	AlPt ₃ C _{0,5}		4,35; 3,81; 3,58; 3,38; 3,0; 2,77; 2,54; 2,48; 1,9; 1,84; 1,75; 1,69; 1,47; 1,39; 1,35; 1,27; 1,12	3,83; 2,75; 2,25; 1,95; 1,74; 1,59; 1,38; 1,17	29-72 26-
20	Pd ₂ As	палладо- арсенид	6,1; 3,05; 2,56; 2,12; 2,03; 1,64; 1,51; 1,45; 1,41; 1,38; 1 29	3,01; 2,69; 2,4; 2,11; 1,8; 1,6; 1,22; 1,15	3- 1194
20	Ag _{1-x} S ₈ Na _x Pd ₃ O ₄		1,21; 1,17; 1,1; 1,08	6,06; 5,25; 3,71; 3,17; 3,02; 2,02; 1,86; 1,07 2,51; 2,29; 1,63; 1,56; 1,51; 1,41; 1,23; 1,05	28- 406 12-31

Table 8 – Sets of the interplanar space of nanoform minerals from shyngite of Kvartsitovye Gorki deposit

NN	Formula of mineral	Name of	Interplan	ar distance, A	N of
p/p		mineral	Design	Standard	ASTM
				on 8 lines	card
1	2	3	4	5	6
3018	sample negative N 58	to the figure	5e		
1	AgHgAsS ₂	Laffitiite	4,07; 3,59; 3,24;	3,63; 3,51; 3,2; 3,02;	35-566
			3,08; 3,05; 2,91; 2,77; 2,54; 2,44; 2,18; 2,03; 1,97; 1,88; 1,79; 1,695; 1,52; 1,2	2,69; 2,14; 1,9; 1,89	
2	AgAuS	Petrovskite		2,9; 2,51; 2,04; 1,77;	26-78
3	Pd ₃ Si			2,71 ; 2,52 ; 2,39 ; 2,29;	36-932

			2,27; 2,16 ; 2,12; 1,89
4	$(Cu,Fe)_{12}As_2S_{11}$	Tonnantite	2,94 ; 2,55 ; 2,4 ; 1,99 ; 11-102
			1,8 ; 1,54 ; 1,17 ; 1,04
5	KHCO ₄		3,58 ; 2,91 ; 2,77 ; 2,58 ; 22-1222
			2,0 ; 1,82 ; 1,77 ; 1,73
6	MoC		2,74 ; 2,54 ; 2,47 ; 2,09 ; 6-546
			1,86 ; 1,66 ; 1,29
7	PtEuSi ₂		2,91 ; 2,06 ; 1,88 ; 1,77 ; 31-948
			1,60 ; 1,45; 1,43; 1,26
8	Ir ₄ NdB ₄		3,20; 2,59;2,41; 2,23; 35-1028
9	PrO		2,91; 2,52; 1,78; 33-1076
10	AgInTe ₂		3,58; 2,20; 1,88; 23-638

Whereas the application to determine the composition of the inclusions of the electron microscope with high resolution, secured by energy dispersive X-ray spectrometer with a resolution of 4 nm and the probe size of 1.0 nm reveals only the elemental composition and in some cases suggests the mineral composition of the inclusions. Significant difference of host mineral signal from the signal of the included nanoparticles is complicated, allowing only assume the phase composition of the inclusions [16].

In conclusion, it should be emphasized that all the types of gold deposits contain carbonaceous material that carries a significant number of micro-and nanoinclusions of precious metals. Their total content in this material is sufficiently high. For example, Carlin deposit contains gold in carbonaceous matter at a higher value. Gold content in the carbonaceous material in Bakyrchik area deposits is 150 g/t and plaginoids are more than 10 g/t. A significant portion of platinum tends to areas which are enriched by carbonaceous matter, which is observed in "black shale" type deposits (Kumtor Muruntau, Bakyrchik, Kvartsitovye Gorki). These data are obliged to study the distribution of micro-and nanoinclusions of precious metals not only in sulfides, but in the carbonaceous matter in different genetic types of gold deposits.

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Резюме

Л.Г. Марченко, Л.В. Комашко

(Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Алматы қ.)

СУЛЬФИДТЕР МЕН КӨМІРТЕКТІ ЗАТТАҒЫ АСЫЛ МЕТАЛДАРДЫҢ МИКРО-ЖӘНЕ НАНОБӨЛШЕКТЕРІНІҢ ТАРАЛУЫ ТУРАЛЫ

Карлин және эпитермалды түрдегі (Пуэбло-Вьехо және Поргера) кенорындарда микро-және наноқоспалар сульфидтерде басым болады, нанобөлшектердің құрылымдық жағдайы элементтік талдау кезінде ғана минералдар ретінде жорамалданады.

«Қаратақтатасты» түрдегі кенорындарда (Қазақстан) асыл металдардың наноминералы сульфидтерде де, сондай-ақ көміртекті затта да дамыған **парагенезі** байқалады. Микрожәне нанобөлшектер қоспалары наноминералдар түрінде наноқұрылымдық бөлшектерде «капсуландырылған». Сульфидтер мен көміртекті заттағы микро- және нанобөлшектер қоспасын зерттеу электрондықозондты талдаудағы микродифрак-ционды талдау мен рентгеноспектрлі микроталдауды қолдану арқылы жүргізілді.

Кілт сөздер: қоспа, асыл элементтер, микро- және нанобөлшектер, алтынкенді кенорны, энергодисперсті спектрлер, микродиффракционды талдау, сынамадайындық, шунгит, фуллерентәрізді наноқұрылым, нанотүтік, табиғи және минералды құрам.

Резюме

Л.Г.Марченко, Л.В.Комашко

(Институт геологических наук им. К.И.Сатпаева)

О РАСПРЕДЕЛЕНИИ МИКРО- И НАНОЧАСТИЦ БЛАГОРОДНЫХ МЕТАЛЛОВ В СУЛЬФИДАХ И УГЛЕРОДИСТОМ ВЕЩЕСТВЕ

На месторождениях карлинского типа и эпитермальных (Пуэбло-Вьехо и Поргера) микро- и нановключения фиксируются в сульфидах, структурное состояние наночастиц предполагается в виде минералов только на основании элементного анализа.

На месторождениях «черносланцевого» типа (Казахстан) выделяются **парагенезы** наночастиц благородных металлов развитые как в сульфидах, так и в углеродистом веществе. Включения микро- и наночастиц в виде наноминералов «закапсулированы» в наноструктурированные частицы. Изучение включений микро- и наночастиц в сульфидах и углеродистом веществе проводилось с применением микродифракционного анализа и рентгеноспектрального микроанализа на электроннозондовом анализаторе.

Ключевые слова: включения, благородные элементы, микро- и наночастицы, золоторудные месторождения, энергодисперсионные спектры, микродиффракционный анализ, пробоподготовка, шунгит, фуллереноподобная наноструктура, нанотрубка, самородный и минеральный состав.

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