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METACOLLOIDAL GOLD

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The processes of aggregation and crystallization of natural colloidal gold, formed by mechanic way during grinding of gold particles in contemporary placers and in process of the hydrothermal sol-gel synthesis, are studied. It is shown that, in the first case, the friable heterodispersed globular sediment transformed in the dendrite-like intergrowths and films with pores of hexagonal outlines was an initial form of coagulate. In the second case, that was the compact clots and films transformed during the process of syneresis and coalescence in the flat gold particles with a mosaic-block structure. The new aggregative type of core-shell structures of gold with blocks enriched by gold and inter-block space enriched by silver was found. The epitaxial correlations between gold and quartz by a law $(10\bar{1}1)_{SiO_2} \parallel (001)_{Au}$ и $[12\bar{1}0]_{SiO_2} \parallel [100]_{Au}$ was ascertained for the gold nanoparticles.
1 table, 7 figures, 18 references

The colloidal gold, by generally accepted determination, is the metal gold, consisting of hydrophobic, positive charged particles of nanometric size, which are located in the form of suspension in the liquid; the diphase system with a liquid dispersion medium and ultrasmall gold particles is the gold sol, and the falling flaky sediment is the gold gel. The process of the gold sol coagulation, beginning in the liquid phase under the influence of electrolytes, is accompanied by the rapid crystallization of the sediment, its ageing and syneresis with the isolation of the dispersed phases in a rest dispersion liquid, being still heterogeneous, with the following coalescence of the solid nanoparticles. The metacolloidal gold is the gold formed at the expense of crystallization of the gel sediment.

The process of formation of colloidal gold in nature conforms to the above-mentioned well-known scheme, which is realized mainly in two different geological environments. One of them is connected with formation of the thin colloidal layer with finest gold suspension over the surface of gold particles, which is grinded under influence of thin clastic material in a water stream in alluvium at normal temperature and pressure. The time of mechanical influence on gold, by the geological scale, is small (months, years), although, it significantly excels the duration (hours, days) of such type experiments. Another, the most distributed in nature, method is the hydrothermal sol-gel synthesis of colloidal gold, realized in the periods of the pressures decrease in hydrothermal system as a result of strong supersaturation of solutions in local parts of the forming gold-quartz ore bodies, mainly in the epithermal deposits. The fall of coagulates is caused by the reduction reactions of the high-concentrated dissolved gold salts with a formation of the unstable gold sol. The process takes place at high temperatures (~200 °C) and pressures up to 0.5 GPa, in multicomponent solutions with low salinity of alkaline type (pH 8.5 – 9.0) with dissolved salts (predominating $HSiO_3^- > HCO_3^-$) and gases $N_2 > CO_2 > H_2S$ (Laz'ko *et al.*, 1981). The rapidly proceeding initial stages of the natural sol-gel synthesis are changed by a long period of aggregation and transformation, which is estimated by tens of million years. The features of the initial gel nature of matter are entirely razed; their traces can be found by study of textural-structural correlations of mineral aggregates that was a theme of the special studies in the middle of the last century (Textures..., 1958).

The clarification of peculiarities of the colloidal gold aggregation in the natural processes was a purpose of present study. The samples of native gold from quartz veins of the epithermal deposits of Zabaikalie (Balei-Taseevskoe) and Kolyma (Agatovoe) and also the placer gold from the contemporary alluvial sediments of the Lena River basin (East Siberia) were the objects of study. The works were carried out with the electron microprobe analysis and method of analytical electron microscopy (scanning and transmission), with application of the aimed replicas from the fresh or etched fracture of samples.

Metacolloidal gold in river alluvium

The borders and outgrowths of redeposited gold on the gold particles from placers are known for a long time under a name of the new gold. It was studied long time, beginning from the early works of F. Freize (Freize, 1931), and later was described in the works of P. Ramdor (Ramdor, 1962), N.V. Petrovskaya (Petrovskaya, 1973), and many other researchers. It is known that processes of corrosion and refinement of the gold particles surface with formation of the high-fineness shells precede to formation of the new gold, containing, in contrast to the high-fineness shells, the significant amounts of the silver admixture. In contemporary placers, at the relatively short-time stay of gold particles in river alluvium, the high-fineness shell is often absent, and new gold precipitates on the corrosive surface of particles of initial gold.

On corrosive surface of studied flat gold particle from the Ugakhan River placer (Lenskii region, East Siberia), the thickness of the new gold film is 20-30 microns. The broken film, incompletely covering surface of gold particle, is composed by a friable aggregate of heterodispersed globular particles, single or aggregated. The single globules with ideal spherical form are from 20 to 120 nm in diameter; they also form the doubled intergrowths with the point surface of contact (Fig. 1). The subsequent development of process of confluence (coalescence) of globules results in formation of the curved wire-like intergrowths with the side branches at angels close to 90° and 60°. At the ends of these dendrite-like intergrowths, the globular form rests. Formation of a porous film with uneven surface is the final result of aggregation of initially globular forms of gold. The largest pores up to 700 nm in size have typical hexagonal outlines inherited from the dendrite-like intergrowths with the side branches oriented at angels of 60° and 90° to the basis stem part.

In contrast to nanometric single globules, the larger (hundreds of nanometers in diameter) spherical ends of the side branches of dendritoids in a number of cases are covered by the small (10-20 nm in size) triangle vicinal forms or thin lamellar outgrowths curved at angles of 120°. A part of such spherical formations is badly polygonized. In spite of absence of clear crystallographic shape, both small and larger aggregated globules give the well-visible ring patterns of microdiffraction, which are characteristic for face-centred cubic structure of polycrystalline gold.

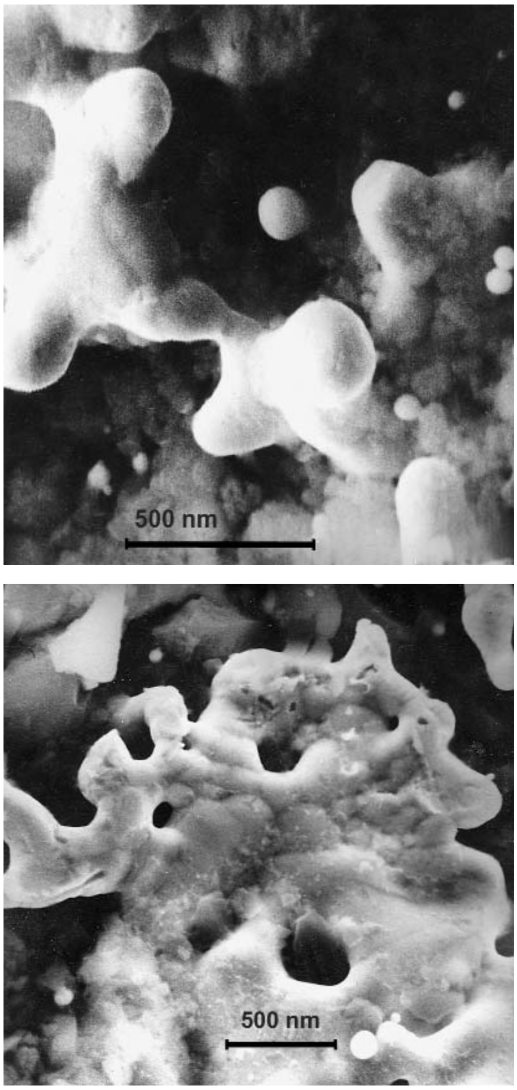


Fig. 1. Globular outgrowths on the surface of placer gold: a — dendrite-like intergrowths of globules with different size; b — film of intergrowing globules. REM. Length of scale lines is 100 and 500 nm

Metacolloidal gold in epithermal deposits

The metacolloidal gold is widespread in the gold-quartz and gold-sulphide-quartz ores of the epithermal gold-silver deposits within the quartz veins with banded and festoon-banded texture. The aggregations of gold are located according to thin-festoon curved layers of chalcedony-like quartz, or their thin inclusions saturate quartz aggregates, tincturing them in brownish and yellowish colours. Also the roundish ovoid aggregations of gold were noted (Petrovskaya, 1973), and in thin cavities of exfoliation are the friable aggregates of the thread-like and ribbon-like gold. In deposits of such type, known around the world, gold contains variable amount of the Ag admixture right up to high concentrations (usually 30-40% of Ag), it is remarkable by morphological diversi-

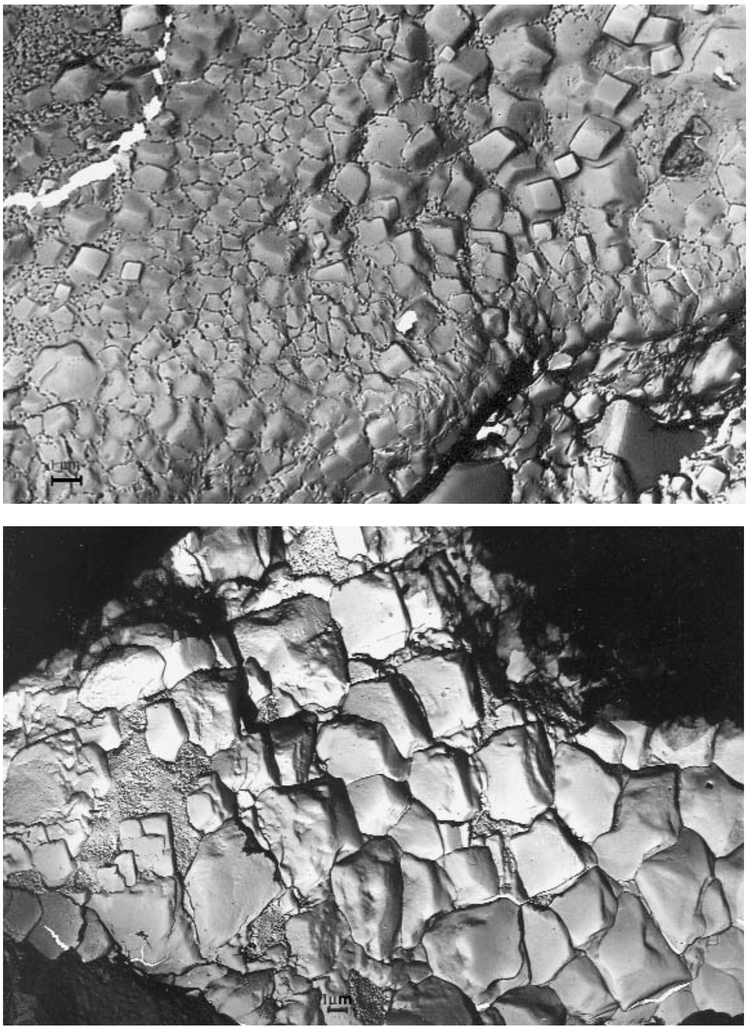


Fig. 2*. Porous cracks of syneresis and the cubic blocks in gold on quartz from the Agatovskoe deposit (Kolyma). PEM, etch., replica. Length of scale line is 1 micron*

ty, occurring in the form of crystals and their intergrowths, dendrites, skeletal formations, and xenomorphic lamellae. All particles of gold are characterized by the mosaic-block structure, which is absent in gold grains from deposits of other genetic types.

Mosaic structure of the high-silver gold was discovered in the second half of the last century, and thin details of inner structure of gold particles were minutely considered earlier (Petrovskaya, Frolova, 1969; Petrovskaya, 1973; Petrovskaya *et al.*, 1977). The genesis of mosaic-block structures was interpreted from general positions; polygene nature of them with accumulation of admixtures in front part of layer-growing faces and (or) with the post-crystallization transformations of the solid gold-silver solution, forming gold particles, was admitted (Petrovskaya, 1973).

New view on origin of the mosaic-block structures of gold, or a broad view, on origin of characteristic structures of aggregates of metacolloidal gold, that is stated in present work, is based on analysis of peculiarities of growth phenomena during process of natural sol-gel synthesis that took place at formation of the epithermal gold-silver deposits.

The multistage processes of ageing of coagulate, falling from solution on the mineral matrix in the form of the flat islet-like films or in the form of roundish or elongated clots play the leading role in formation of complex structures of metacolloidal gold.

Formation of syneresis cracks, that break the gel sediment on blocks bordered by the thin-porous rest matter is the initial stage of ageing (Ostwald ripening mechanism) of the flat spread films. The degree of porosity in borders reaches 50%; the form of pores is roundish; size of pore is 30-100 nm. The thickness of borders is from 100 nm to 2-3 microns. The blocks nearly 1 micron in size with the knob outlining in the centre are transformed in the crystalline polyhedra oriented by the threefold axis perpendicular to a plane (110) on the surface of matrix. The form of crystals is predominantly cubic; sometimes, it is complicated by the octahedron and dodecahedron faces (Fig. 2). The process of collective crystallization (coalescence) does not always reach the formation of the well-shaped crystal polyhedra, remaining separating blocks in the form of concretions of roundish and irregular shape, which are badly polygonized. The octahedral form of blocks was noted together with cubic form.

During precipitation and subsequent crystallization of the gold films on the surface of the quartz rhombohedron faces, the regular distribution of the gold cubic blocks by a law $(001)_{Au} \| (10\bar{1}1)_{SiO_2}$ was observed. The graphical comparison of two different adjoining planes (Fig. 3) shows the parallel orientation of the gold atoms in the rows $[\bar{1}00]$ and $[010]$ and the silica-oxide tetrahedra in the rows on $[\bar{1}2\bar{1}0]$ and $[10\bar{1}2]$. The sections in the same planes of the gold and quarts structures are congruent by area with a precision up to ±1.5% at superposition of 25 unit cells of gold on 12 unit cells of quartz. Taking into account the pseudocubic structure of the quartz crystals with rhombohedral habit, $rr(10\bar{1}1):(\bar{1}101) = 85°46'$, one can say about the epitaxis of gold and quartz, which is almost exactly maintained at sizes of the gold particles not less than 2 nm, overgrowing on the surface of the quartz rhombohedra. At increase of particle sizes, the parallelism of planes of two minerals is broken, the arising tensions results in the origin of the linear dislocations, which result in the twisting of planes (001) of gold that was mentioned earlier (Novgorodova, 2004).

The collective crystallization, accompanying the syneresis processes, also took place during transformation of the interblock rest matter. The thin-porous cellular structure of borders is changed by the dendrite-like or «knitted» forms of the curve enlarged (to 100-150 nm) gold particles (Fig. 4).

The complex nanostructures of metacolloidal gold mentioned in the previous work (Novgorodova, 2004) are also owed by their origin to phenomena of the gel ageing, which falls in the form of clots on the surface of the quartz grains. The typical structures of the kneed-shaped gold aggregations with one of more openings and radial dispersing cracks in the centre are formed, as it was ascertained ear-

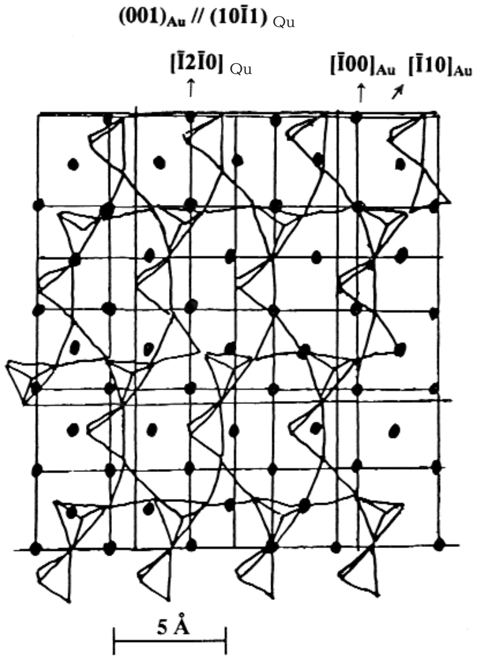


Fig. 3. Graphic superposition of planes (001) of gold and (10I1) of quartz

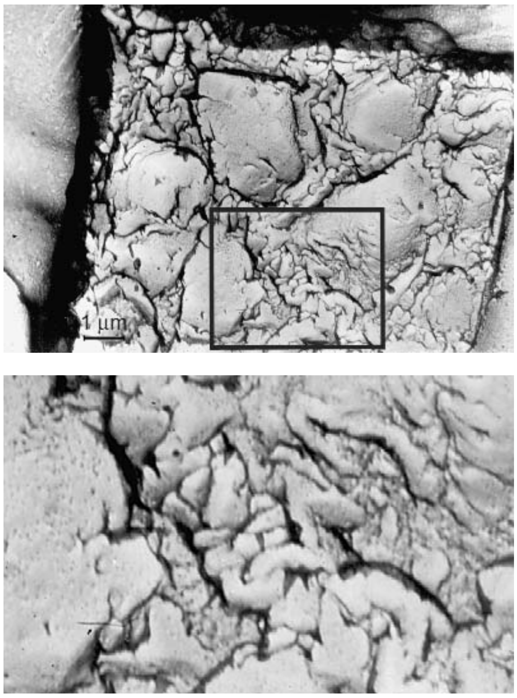


Fig. 4. Distorted «knitted» forms of nanoparticles of gold in the interblock space. PEM, etch., replica. Length of scale line is 1 micron (a) and 100 nm (b). Balei-Taseevskoe deposit (Zabaikalie)

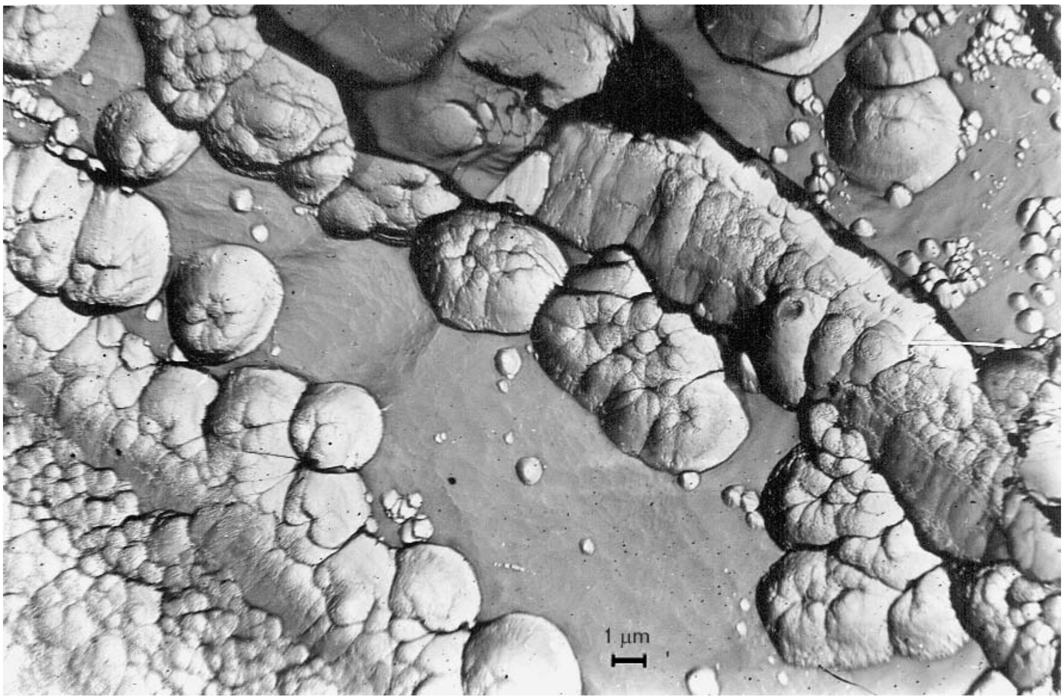
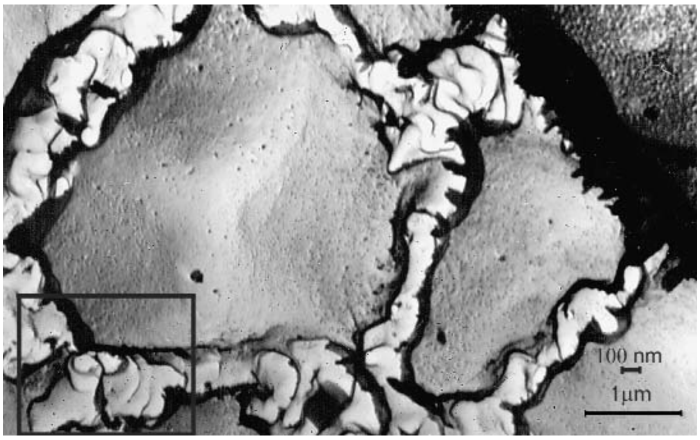


__Fig. 5__. Roundish and columnar aggregates of gold nanoparticles on quartz. PEM, etch., replica. Length of scale line is 1 micron. Agatovskoe deposit (Kolyma)



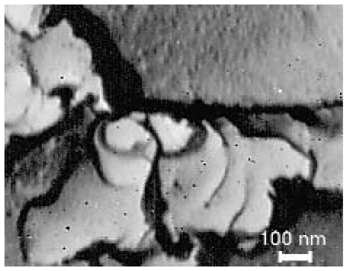


__Fig. 6__. Core-shell structure of native gold (a) and nanocone of gold in shell (b). PEM, etch., replica. Length of scale line is 1 micron and 100 nm. Agatovskoe deposit

lier (Chukhrov, 1955), as a result of separation of dispersion phase. Transformation of the high-viscous rest brings to formation of the zoned aggregates with the radial disposed blocks in the centre and the columnar aggregates at the periphery. Diversity of arising structures depends in many respects from a ratio of the dispersion medium and dispersed phase in the gold coagulate, i.e. from degree of its supersaturation. In a high-viscous central part of clot, the blocks separated at the borders of the syneresis radial cracks do not have crystallographic outlines; features of rotary rotation of these blocks are considered earlier (Novgorodova, 2004); that is an evidence that in process of coalescence, the coherence of borders of neighbouring blocks was not yet reached. In the less viscous rest matter of borders and interblock space, the thin dendrites and intergrowths of the larger distorted crystals border the blocks or form the columnar aggregates on the quartz matrix (Fig. 5). It is known that formation of nanocolumns can be a result of the growth on inclined plane of base (Karabacak

Table1. **Variations of chemical composition (wt %) of gold with mosaic-block structure.**

No. of, sample-deposit	Phase	Au	Ag	Total	Stoichiometry Empirical	Theoretical
KS 1390	6-1	83.94	13.60	97.53	$Au_{3.08}Ag_{0.92}$	Au_3Ag
Balei-	6-2 block	99.69	1.10	100.79	$Au_{3.92}Ag_{0.08}$	Au
Taseev-	6-3	85.17	13.28	98.45	$Au_{3.11}Ag_{0.89}$	Au_3Ag
skoe	6-4	73.38	25.33	98.66	$Au_{4.90}Ag_{3.10}$	Au_5Ag_3
	6-5	81.34	17.02	98.36	$Au_{3.17}Ag_{0.83}$	Au_3Ag
KS 845	8 block	89.14	9.00	98.14	$Au_{3.37}Ag_{0.62}$	Au
Balei-	10	87.83	10.99	98.82	$Au_{3.25}Ag_{0.75}$	Au_3Ag
Taseev-	11	74.84	24.37	99.21	$Au_{5.00}Ag_{3.00}$	Au_5Ag_3
skoe	12 block	92.15	5.33	97.48	$Au_{3.62}Ag_{0.38}$	Au
	13	80.86	17.95	98.81	$Au_{2.85}Ag_{1.15}$	Au_3Ag
	14	71.15	27.57	98.72	$Au_{4.68}Ag_{3.32}$	Au_5Ag_3
A-1234	A-1 block	63.14	36.42	99.56	$Au_{1.95}Ag_{2.05}$	AuAg
Agatov-	A-1'	54.70	44.25	98.95	$Au_{3.22}Ag_{4.78}$	Au_3Ag_5
skoe	A-2 block	64.12	35.21	99.33	$Au_{1.99}Ag_{2.00}$	AuAg
	A-3 block	64.10	35.71	99.81	$Au_{1.98}Ag_{2.02}$	AuAg
	A-3'	53.15	46.80	99.95	$Au_{3.06}Ag_{4.93}$	Au_3Ag_5
	A-4 block	63.23	36.18	99.41	$Au_{1.96}Ag_{2.04}$	AuAg

et al., 2003).

Core–shell structures of metacolloidal gold

The core-shell structures are the zoned structures of nanoparticles with core and shell, which are distinguished by chemical composition. Such structures are known for many pairs of metals and compounds synthesized for different purposes of nanotechnologies. The core-shell structures of gold with a silver shell were synthesized in the form of nanoparticles with a size nearly 20 nm and more; it is noted that at decrease of the nanoparticles size the core-shell structures cannot be formed. The reasons of immixability of gold and silver at formation of the core-shell structures in a range of the nanoparticles sizes of ~20 nm remain uncertain (Shibata *et al.*, 2002).

Arising at crystallization of natural gels, the polycrystalline constructions have the zoned structure with the poly- and monoblock core and a border composed by aggregate of the smaller, crystallographically distorted particles. The distortion of forms is especially visible in the case, when blocks are brought together and borders are narrow (150-200 nm). In conditions of the constrained space, such unusual forms as nanotubes and nanocones are formed, which were not earlier known both for natural and synthesized gold. The diameter of the gold nanocone at the basis is ~100 nm, in upper part it is -200 nm (Fig. 6). By analogy with the synthesized nanoparticles, one can suppose that a process of the planes twisting is determined by the dislocation mechanism, for nanotubes it is determined by dislocations with angle and screw components, and for nanocones it is determined by disclines (Pokropivny, Pokropivny, 2003).

Differing by sizes, which are larger at two-three orders than the synthesized nanoparticles with core-shell structure, the natural polycrystalline constructions show the morphological similarity to them. One failed to obtain, with necessary precision, the difference in chemical composition of core and shell of the zoned polycrystalline constructions, by electron microprobe analysis method because of low locality of the method. Estimation of chemical composition in the first approximation was made by the method of microprobe scanning along the profile with a step in 1 micron. Relatively large blocks and their aggregations and also the interblock space with size in several microns were studied. The obtained data (Table, Fig. 7) reflect with convincingness the tendency to enrichment of the interblock space and borders by silver around cores with increased content of gold. The calculated chemical compositions approach to stoichiometric ones. In relatively high-fineness (average fineness is 750-850) lamellar gold from the Tasseevskii region of the Baleiskoe deposit, the aggregations of blocks of

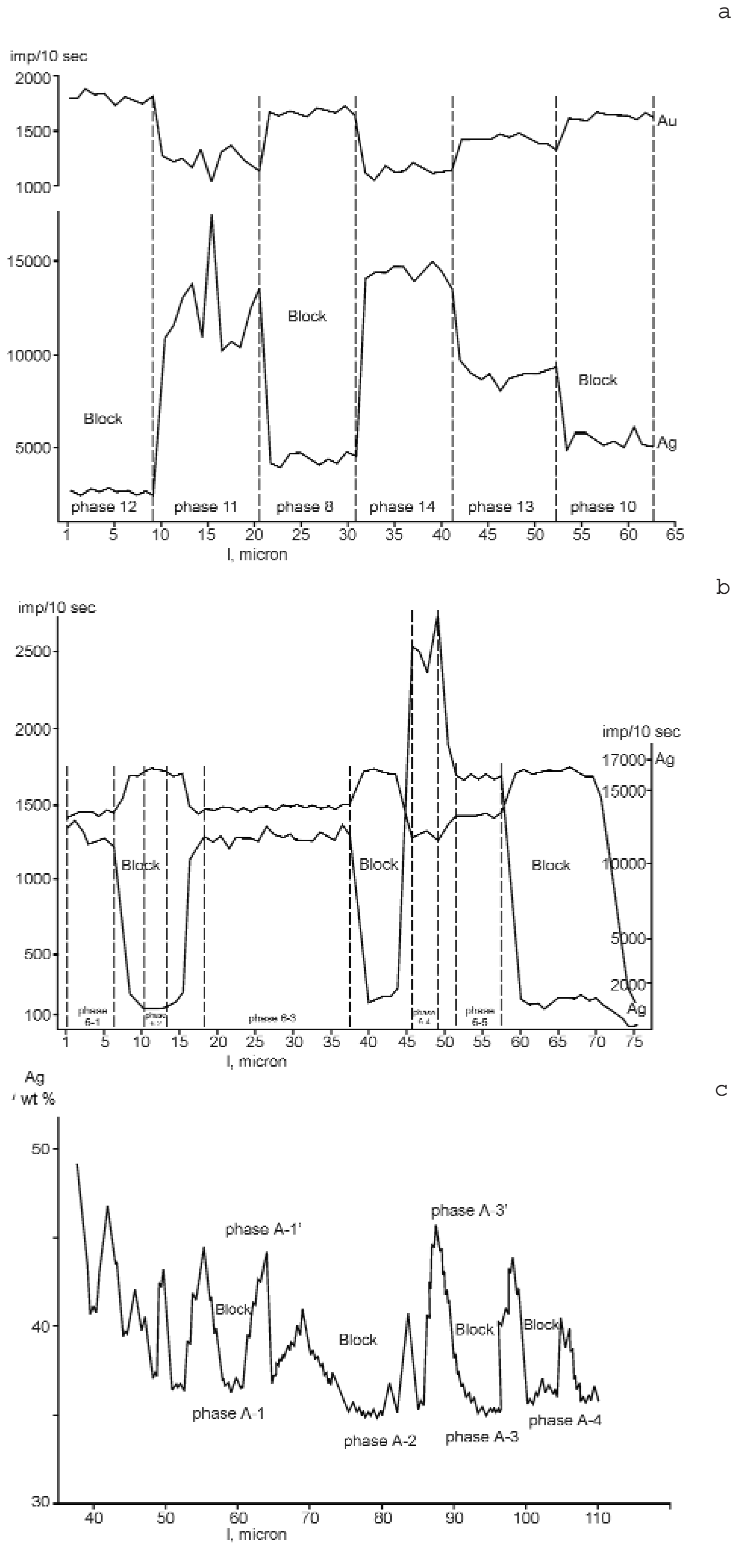


Fig. 7. *Variations of chemical composition along profile through gold particle with mosaic-block structure: a, b — Balei-Taseevskoe deposit; c — Agatovskoe deposit. Numbers of phases correspond to numbers in Table*

almost pure gold are bordered by the porous or dendrite-like interblock matter with chemical compositions close to Au_3Ag and Au_5Ag_3. In low-fineness gold from the Agatovskoe deposit, the blocks have chemical composition AuAg, and borders around them are Au_3Ag_5. Since microprobe analyses, which results are given in Table, were calculated with averaging by several, not less than 10, measurements, the more precision studies of chemical composition with locality J100 nm are necessary, and the above-mentioned data should be considered as preliminary.

Discussion

The evident differences in morphology of metacolloidal gold precipitated of the surface of placer gold in river alluvium and occurring in the gold-quartz veins of epithermal deposits are caused by the differences in kinetics of sedimentation and subsequent aggregation of colloidal nanoparticles, which is connected, in its turn, with obvious differences in physical-chemical parameters of the mineral-forming medium. The slow precipitation of colloidal particles of new gold, formed by mechanic way during grinding of gold particles in water stream, results in formation of the friable branched forms (Brechignac *et al.*, 2001), and their heterodispersed state reduces coalescence (Hoogenboom *et al.*, 2002) and prevents to formation of the large coherent domains. The polycrystalline patterns of microdiffraction of electrons obtained from such gold confirm this conclusion. The wire-like forms, as it is shown in the work (Hui *et al.*, 2003), usually consist of the incoherent domains of polyhedral form (distorted icosahedral polyhedra of Frank-Kasper and hollow polyhedra of Bernal), however, it is impossible to check it on natural samples.

The compact clots and films of gold, falling from the supersaturated hydrothermal solutions, have the long history of ageing, aggregation and recrystallization, which final result is formation of the mosaic-block structures of gold with heterogeneous distribution of silver admixture. Following experimentally ascertained facts require discussion.

1. In the process of syneresis and coalescence at early stages of ageing of coagulate penetrated on quartz matrix, the gold blocks of cubic form are quite often formed, whereas, at texturation of sediment, it was necessary to expect the primary orientation of particles on most compact packing plane of octahedron (111). The reason of that, as it was shown above, is in epitaxial correlations between atomic structure of face (001) of gold and pseudocubic structure of face of rhombohedron of quartz, at that $(10\bar{1}\bar{1})$ of quartz $\parallel$ (001) of gold and $[\bar{1}2\bar{1}0]$ of quartz $\parallel$ [100] of gold. The orienting influence of square base on growth of cubes of face-centred metals is also ascertained experimentally; it is shown that first 50 atomic layers in cubes have the ideal perfect structure (Zhang *et al.*, 2002). We should also note that contact between Au (metal) and SiO_2 (insulator) provides with the tunnel effect at current passing through solder with chemical composition Au-SiO_2-Si, unfortunately, the state of the boundary layer remains unknown (Pal *et al.*, 2004). Nevertheless, probability of the tunnel effect rise in the gold-quartz intergrowths is interesting for elaboration of electroimpulse methods of ore concentration.

2. The process of coalescence with separation of blocks and interblock space are accompanied by the clearly pronounced heterogeneity in distribution of gold and silver. Blocks in all analysed samples have increased content of Au. Since diffusion of particles in viscous matter of gels is troubled and even practically impossible (Chukhrov, 1955), it is necessary to admit that regrouping of initially heterogeneous by chemical composition nanoparticles with forward and rotary movement along thin cracks of membrane type, arising during syneresis, causes such effect. In that case, the membrane permeability for nanoparticles with high contents of Au must be higher than for the high-silver nanoparticles. Formed by this way, the aggregative core-shell structures are distinguished from synthesized ones not only by sizes but also by way of formation. In synthesis of core-shell nanostructures, the method of consecutive penetration of the Ag salts on already formed gold nanoparticles is applied; whereas in natural matter, the processes of self-organization of colloidal coagulate prevail.

3. It is accepted to consider that coalescence of nanoparticles in colloidal coagulate is realized under influence of the weak long-ranged forces of Van-der-Vaals type. However, recently for explanation of complicated movements of nanoparticles, joining in crystalline constructions, the formalism of thermal and statistic models of Casimir is engaged, which is used in quantum electrodynamics (Gopinathan *et al.*, 2002).

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