Natural Clusters as the Source of Ore Material Formation in Noble Metals Deposits: Case Study of Gold Fields in the Republic of Kazakhstan, Russia, Uzbekistan, and Kyrgyzstan

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Abstract: The detailed study of the natural clusters and colloidal forms of noble metals in ores in order to use the results thereof to create a technology for extraction of nano- and cluster gold forms has been attempted. It was found that in the ores of black-shale gold-sulfide geological industrial type the cluster (colloidal) and ionic gold phase dominated, but the native gold phase is mostly presented by fine-dispersed gold. The maximum number of native gold phase is discovered in often disseminated and massive pyrite-arsenopyrite ores of the field. Most frequently high concentrations of native phases of fine-sized gold are identified in the early layered pyrite-arsenopyrite ores. Simultaneously, according to pyro-alkali analysis in the most ores samples from Bakyrchik field studied. The tens g/t of the ionic and cluster (colloidal) gold phase, were discovered. Discovery of precious metals in form of clusters helps to explain the likely source of the majority of gold, silver, palladium, platinum, and others in ore deposits; the difference in the gold fineness in endogenous ores; the possible presence both of gold and silver, and also platinum and other metals in the ores of many gold deposits. In particular, from the above explanation of the cluster nature, palladium, platinum and rhodium in ores of Bakyrchik and Zharkulak fields, and palladium and rhodium in ores of Arkharly field; and platinum in ores of Enbekshi field ores have been identified.
[Matvienko V.N., Kalashnikov Y.D., Goncharov A.A. **Natural Clusters as the Source of Ore Material Formation in Noble Metals Deposits: Case Study of Gold Fields in the Republic of Kazakhstan, Russia, Uzbekistan, and Kyrgyzstan**. *Life Sci J* 2014;11(1):269-281] (ISSN:1097-8135). http://www.lifesciencesite.com. 41

Keywords: Gold deposits, gold concentrates, gold, cluster gold form, pyro-alkali analysis method, fire assay test, cluster forms, colloidal forms, pyrites, arsenopyrites, noble metals natural clusters, organometallic compounds, proto-cluster forms, electronic microscopy.

1. Introduction

In late 70's and early 80's of the previous century, large-scale works were started to study typomorphism and phase composition of gold, carbon material and silica in ores of the most important geological and industrial gold deposits types in the USSR at the Institute of Geological Sciences of the Kazakh SSR under the initiative and with direct participation of V.N. Matvienko. Without going into details, we note that it was the first time we [1] found that the analyses used to determine noble metals at that time (assay and atomic absorption) underestimated significantly the "true" amount thereof in the analyzed ores. In early 80s a "**pyro-alkali analysis method**" [1] was developed and tested in a number of chemical laboratories in Kazakhstan and Kyrgyzstan. The method enabled a several fold increase in the gold content definition (as compared to fire assay test) due to previously unknown natural form of gold (we provisionally called at that time "colloidal"). Suffice it to say that the average underestimation of the gold amount in gold-ore deposits in black shale sequences demonstrated by assay test was up to 300-400% (at the maximum up to 800%) and in quartz veins it was up to 150-200%.

Moreover, the methods of native noble metals extraction preserving natural forms (nano-scale inclusive) thereof as well as the methods of native gold cluster forms metallization were established.

Application of such developments allowed the analysis of natural native gold in all its natural diversity of more than 50 gold deposits in the Republic of Kazakhstan, Russia, Uzbekistan and Kyrgyzstan by 1990. Concurrently, detailed electron microscope studies of carbonaceous matter and siliceous rock matrix consisting of native gold phase in gold- sulphide black shale, gold-sulphide quartz and epithermal gold deposits, including finely divided phase as well as cluster and nano-gold within the near-ore rocks (especially black shale rocks) were performed.

The outcome of the research was a three-volume Atlas of Standard Morphological Characteristics of Natural Gold of all grain size classes based on microprobe studies in and analysis of more than 5,500 gold grains of ore from the main gold deposits industrial types in the USSR. As a result of the research the "morphogenetic method" of assessment of the prospects of gold fields on the stage of assessment work was developed.

Only in 25 years after the publication of articles in the "National Geology", № 3 in 2000 [2] and afterwards in the "Ores and Metals", № 5 in 2004 [3], that many researchers, mainly in Russia (the group of scientists under the direction of A.H. Hanchuk and V.G. Moiseenko, R.I. Koneev, N.V. Berdnikov, etc.) and abroad [**4, 5, 6, 7, 8, 9**], based on modern analytical methods began to confirm and surpass the results that were obtained a quarter of a century earlier.

In the course of the research the enormous factual material was accumulated. Such data have not lost relevance today.

Now with **Ecolive Technologies Ltd** (www.ecolive-technologies.com) financial support we have an opportunity to publish the enormous scientific material that has been unused for more than 10 years. No doubt, it will be useful in modern research in gold deposits and the development of nano- and cluster gold as well as other noble metals extraction technologies.

The authors plan to publish the full (extended) version of the article, that was published in the "Ores and Metals", № 4 in 2004, pp. 28-36. M. **[3]** in its abridged variant.

After that we plan to publish a series of articles dealing with the issues of gold phase composition, modifications of carbon compounds and silica in the ores of major geologic-mining types of gold deposits in Russia, the Republic of Kazakhstan, Uzbekistan and Kyrgyzstan. The series of publications will be completed by a consolidated monograph on the results of the research provided with the account of the latest developments in this field. And finally, we expect to publish an Atlas of Standard Morphological Characteristics of Natural Gold, Carbonaceous Matter and Silica from the standpoint of "**morphogenetic method**" of assessment of the prospects of gold fields at the greenfield exploration stage.

Following the editors' request the article prepared for the publication due to its size was divided into two parts that will be published in separate issues of the magazine. Best regards,
V.N. Matvienko, Y. D. Kalashnikov and A.A. Goncharov

PART 1

In our opinion, the current state of knowledge of geology and composition of the majority of the known gold deposits, on the one hand, and the applied methods of ore processing, ore preparation and technology of extracting of precious metals, on the other hand, came to an apparent contradiction. A detailed study of the ores material composition in general, and the existing ore technology types, in particular, and application for the concentration of new cutting-edge methods of ore dressing and various modifications of the equipment, mainly, for gravity and flotation treatment, are not conducive to a marked increase recovery of useful components. Different researchers demonstrated that the use of new methods of ore crushing and abrasion (use of electric hydrocrushers, disintegrators and other equipment, excluding the use of ball mills, cone and jaw crushers, etc.) resulted in a maximum 15-20% increase of the precious metals recovery (for the account of nano-sized and submicroscopic forms thereof).

At the same time, currently there is hardly a method of efficient processing of complex (refractory, high sulphide-bearing, and carbon-bearing, etc.) ores where a metastable proportion of (ionic, colloidal, cluster, etc.) forms of noble metals predominate. There are no methods of the fullest extraction of fine dispersed and super microscopic native gold having, on the one hand, a distinct face-centered cubic structure, while on the other hand having unusual physicochemical properties [**10, 11**].

The study of natural colloidal and cluster forms of precious metal in ores is currently in its initial stage, despite the fact that the possibility of their participation in the natural processes was firstly identified over 25 years ago.

The authors attempted to study in detail the natural clusters and colloidal forms of noble metals in ores in order to use the results thereof to create a technology for extraction of nano- and cluster gold forms.

These works are based on a comprehensive study of the phase composition and typomorphism of gold ores at the macro -, micro - and nano-levels **[2, 10, 11, 12, 13]**, conducted at the Institute of Geological Sciences of the Academy of Sciences of the Republic of Kazakhstan from 1979 to 1989 by V.N. Matvienko and V.L. Levin under the supervision of A.A. Abdulin.

In addition, from 2001 through 2003, a detailed study of the natural cluster forms of precious metals in ores of various gold deposits in Kazakhstan and Russia was conducted, and new analytical methods of determination thereof were developed. From 2001 to 2011 Y. D. Kalashnikov, V. N. Matvienko, L. A. Nekhoroshev worked on creation and testing of operating modes of industrial ore processing disintegrators and concentrators. The following persons were also involved in the works: P.Ya. Kotelnikov, F. Kurmakaeva, E. Polkanova and T.A. Shabanova, as electronic engineers, and T. Zh. Netalieva, N.V. Ostapova, as analytical chemists.

The technology works were based on the idea of metallization of precious metals cluster forms by fundamentally new ways of ore preparation using centrifugal disintegrators that allowed to disperse flows of ore chips of 3-5 mm to meet each other at the sound speed using rotors. In this case, there was no ore overgrinding as well as no gold plating of the balls and waste rock particles as in ore grinding in ball mills or in electric hydrocrushers.

Special attention was paid to preparation of the pulp under strictly defined solid to liquid ratio (S/L). In parallel with the development of working modes of concentrators designed by the authors, the serial 1 t and 2 t concentrators manufactured in Narofominsk by Itamak and Gemini concentration tables were tested. The purpose of tests was to determine the most efficient concentrators, allowing to obtain concentrates with gold content of at least 1,000-2,500 g/t, including the processing of ores containing fine-grained and super-small gold (smaller than 5 microns).

Express control of the process at all stages was carried out with the author's analytical methods (including the method of "**direct cupellation**") enabling the extraction of the full range of precious metals to dore bead.

Development of the "**pyro-alkali analysis method**" and its modifications **[14]** allowed us both to specify the refined gold content in different types of ore in gold deposits and to evaluate its phase relations each time.

It was found that in the ores of black-shale gold-sulfide geological industrial type the cluster (colloidal) and ionic gold phase dominated, but the native gold phase is mostly presented by fine-dispersed gold. Thus, in some sampling pits of Bakyrchik field the content of fine native gold can be up to 100 g/t, and as a whole for the field only about 25-30% of ore types have mineable gold grade. The maximum number of native gold phase is discovered in often disseminated and massive pyrite-arsenopyrite ores of the field. However, most frequently high concentrations of native phases of fine-sized gold are identified in the early layered pyrite-arsenopyrite ores. Simultaneously, according to pyro-alkali analysis in the most ores samples
from Bakyrchik field studied the tens g/t of the ionic and cluster (colloidal) gold phase, were discovered, at that the latter was clearly predominant (**Table 1**).

No regularity in the ratio of colloidal and ionic gold phases in the ores of Bakyrchik field has been established. Depending on composition of the samples the cluster (colloid) or ion gold phase predominates, but as a whole the field is characterized by high contents of cluster gold, sometimes up to several tens or, in some cases, hundreds grams per tonne with the aggregate amount of gold (in all its phases) up to 188.58 g/t and 192.1 g/t (Samples 7 and 11, **Table 1, Part 1**) and even 746.1 g/t (Sample 285, **Table 1, Part 2**).

Having analyzed the data in Table 1 we can make a conclusion that in samples where the native phase of gold is found, it amounts mainly 5-10%, and in rare cases - up to 34-76% in the total balance of the metal in the ore. The average quantity of native phase in the overall balance of gold in the ores does not exceed 17%. Industrial native gold content in the analyzed samples (5-10 g/t and more) have been identified as 36% of the total amount. It is worth mentioning that previously it was considered that the native gold was hardly available in Bakyrchik field.

Table # 1. The content of the cluster (colloidal), ion and native phases of gold in different types of Bakyrchik ores

№	Sample weight, in g	Gold content in the sample, in g/t				Percentage of native phase in the total balance of Au
		Cluster (colloidal)	Ionic	Native	Total	
1.	75	1.13	3.13	2.70	6.96	38.79
2.	126	19.84	2.50	1.85	24.19	7.65
3.	175	29.14	1.91	103.00	134.05	76.83
4.	160	52.25	2.28	7.60	62.13	12.23
5.	136	5.29	10.80	-	16.09	-
6.	110	22.58	2.09	-	24.67	-
7.	135	166.60	13.33	12.20	192.13	5.83
8.	102	19.1	-	-	19.10	-
9.	100	49.40	-	-	49.40	-
10.	100	34.86	2.04	4.10	41.00	10.00
11.	100	121.18	2.40	65.00	188.58	34.47
Average		47.39	3.68	17.86	68.93	16.89

Significant quantities of fine native gold phase were identified by pyro-alkali analysis in individual grab samples at Kumtor field (Kyrgyzstan) amounting up to 412.5 g/t; Amantaitau field (Uzbekistan) equalling up to 45-50 g/t with the average amount in the ores 18.7 % and 23.15%, respectively.

In the ores of black shales field types **[11, 1, 15]** (except Muruntau) the carbonaceous material of lower levels of structures orderliness is well developed: amorphous, two-dimensional - and three-deminasional-ordered, anthraxolite, shungite and graphite with low-ordered structure. Such an assessment of the carbonaceous matter nature in ores and ore-bearing rocks allowed us to suggest and then prove the broad development in the fields of natural clusters, concentrating the main amount of the carbon contained in the rocks of gold and other noble metals (silver, palladium and platinum). In the ores of Muruntau the carbonaceous material of medium
and higher levels of structure ordering is well developed. Here native gold phase of various grain-sized classes (ranging from nano-sized to visible) predominates here.

We undertook the study of natural cluster formations using electronic microscopy and special chemical techniques. The results of such a research allowed us both to study and determine the content thereof, and to develop new original authors' analytical methods such as "pyro-alkali" and "direct cupellation" *). The latter allow us to metallize (**Fig. 1, 4**) various kinds of natural clusters (metallo-organic, metall-metall, monometallic, etc.) and to "capture" the noble metal contained therein by isolating them into the noble metal alloys (Au with Ag and platinum group if they available in the ore).

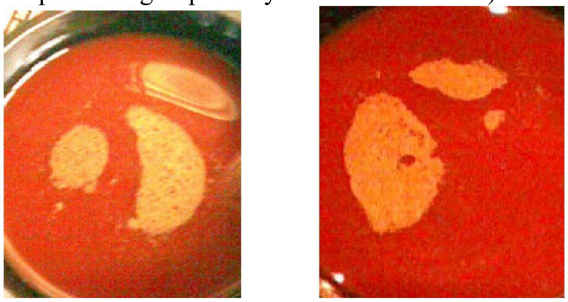


Fig. 1. Metallized films of cluster gold from pyrites of Zharkulak field on the surface of the melt in glass-carbon plates.

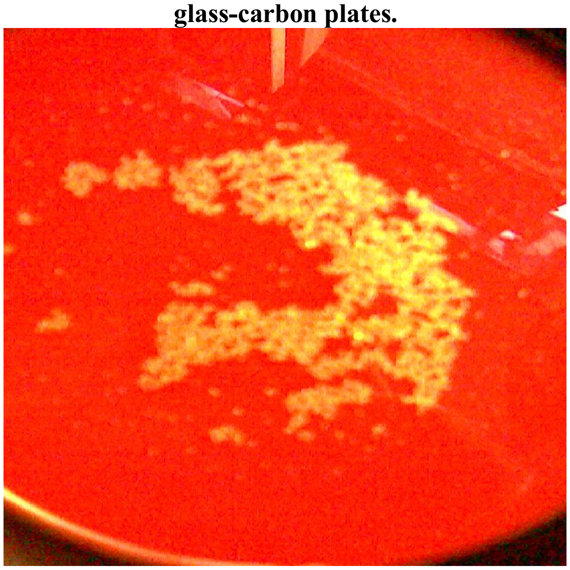


Fig. 2. Metallized cluster gold film from needle arsenopyrite of Bakyrchik field on the melt surface of a glass-carbon plate.

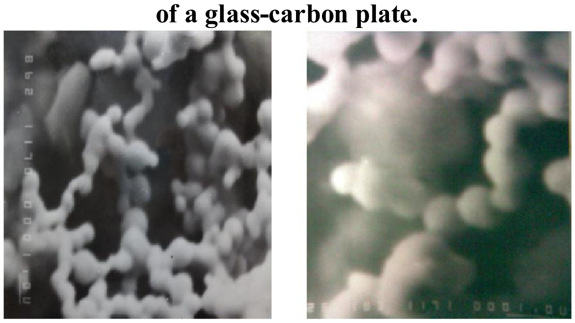


Fig. 3. Elongated chains of metallized gold clusters from quartz taken from Arkharly field (left, the size of a mark is 1 micron) and from gold-bearing pyrite from Zharkulak field (right, 18,000 times magnification). The globules are composed of 100% Au.

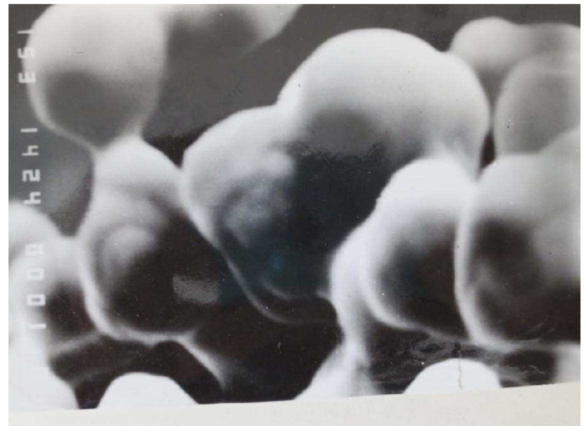


Fig. 4. The nature of globules of metallized gold clusters with embryonic crystalline forms extracted from gold-bearing arsenopyrite. Magnification is 15,000 times. The globules contain 100% Au. Bakyrchik field.

The content of cluster gold forms in pyrites and arsenopyrites depends not only (and maybe, not so much) on the field type, but also on the conditions of their formation. The studies in typomorphism of gold and gold bearing minerals as well as in the features of gold phase composition in ores and ore-bearing rocks revealed that gold mineralization in the in carbonaceous strata gold-sulfide fields, gold-sulfide quartz- and epithermal geological and industrial types was effected based upon following three scenarios:

1. In the gold-sulfide fields **in the black shale strata** the gold mineralization process took place under the scheme: **MATRIX** (host rocks) → **SULFIDES** + **CLUSTER (COLLOIDAL) GOLD**.
2. In the fields of **gold-sulfide-quartz type** the gold mineralization process took place under the scheme: **MATRIX** (mainly, quartz-vein) → **SULFIDES →NATIVE GOLD**. Thus, firstly, the ore-bearing matrix is formed, then sulfides overlap it (with a time break) and the mineralization process is completed by deposition of native gold with a time break again.
3. In the epithermal fields ore process took place under the scheme: **MATRIX** (silica gel) + **CLUSTER (COLLOIDAL) GOLD → SULFIDES**.

In this case, “matrix” means both quartz veins and zones of silicification, and the zones of beresitization, and other ore-hosting rocks that were prepared "especially" by pre-ore solutions. As the result a sponge-like frame resembling volcanic pumice is formed which is then filled with ore material under one of the above gold process schemes (**Fig. 5**). The concentration of the voids and cavities in the skeleton permits us to judge the potential of ore-bearing deposits in the specific, localized areas of the ore bodies. In addition, based upon the spatial orientation of ore-localizing cavities we can assess the movement direction of pre-ore and ore-bearing fluids. System selection of oriented samples of the ore bodies and their treatment using our method gave us an indication of the spatial position of the ore material source.

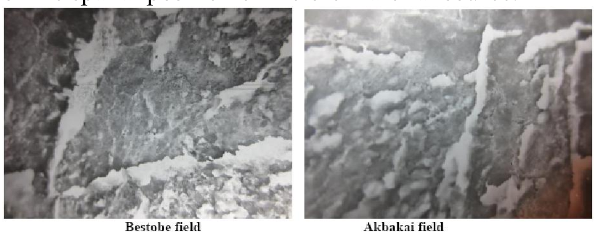


Fig. 5. The nature of the matrix of ore-hosting rocks after leaching of sulfides and gold. Light areas are etched "channels" and cavities where sulfides and gold were located. The direction of "channels" corresponds to the main fracture of ore-hosting rocks in the fields.

Thus, the ore-bearing matrix at all gold fields, regardless of their formation, age of host rocks and mineralization is primary in relation to gold process in cases 1 and 2, and is synchronous in case 3. Features of formation of the matrix and its pre-ore preparation under the first two schemes are largely different in terms of physical-chemical and thermodynamic parameters from the subsequent deposits of ore components and, in particular, gold and sulfides.

Migration capable silicic acid (H_4SiO_4) gel plays a major role in the formation of the matrix and transportation of the ore material in metastable forms under all three patterns. After separation from parent rocks during diagenesis, katagenesis and dynamo metamorphism (the movement of the gel begins during diagenesis of bottom sludge) processes H_4SiO_4 is transferred to the discharge areas located hypsometrically above. Here the gel fills the rock structural defects (e.g., crushing zones, dehydration vugs and cavities, fractured zones and others). In this case, there is a clear dependence of the number of mobile forms (colloidal, ionic and cluster) and native gold in ores on the degree of orderliness of the silica structure. While moving to the discharge zone the silicic acid gel also serves as a conveyor not only for ore components in the form of clusters, fullerenes, etc., but for larger particles. For example, in ores of Arkharly field we recorded the fragments of diatomic paleoalgae and paleobacteria (**Fig. 6-1 and 6-2**) in ore-bearing rocks, that are alien to the nature of their habitat (terrestrial volcanic rocks up to 650 m).

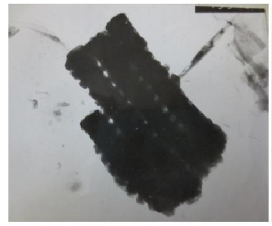


Fig. 6-1. Fragment of diatomic paleoalgae from amethyst quartz of Arkharly field.

Fig. 6-2. Paleobacteria from ore-quartz of Arkharly field.

In all fields the largest share of native gold is fixed in silica (quartz) possessing a distinct grain and numerous interstitial microscopic joints. The more granular quartz (not more crystallized but more granular), the larger the depositions of native gold are observed in this field and on this particular erosive cut of the ore body.

Firstly, further evolution of silicic acid gel leads to the formation of opal, and then with the development of epigenetic processes under the influence of temperature and pressure, its crystallization to chalcedony, quartzine and into quartz is provided. With solidification of silicic acid gel and its transformation into opal due to stripping of bound water the true solutions are formed from which druses and brushes of rock crystals (**Fig.7**) are developed in the residual lenticular cavities. These crystals "stratify" each pulse (rhythm) of income of silicic acid gel to the discharge areas permitting the establishment of their scope and boundaries. There are such 13 pulses in Arkharly.

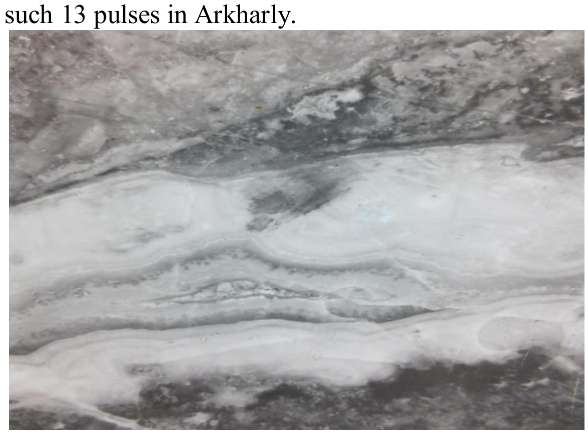


Fig. 7. Quartz-vein matrix with rock crystals in the center. Arkharly field.

Therefore, the sulfides from the gold-sulfide deposits primarily in black-shale formations are the most enriched with gold and other noble metals in cluster and colloidal forms. The smallest amount of these gold forms is noted in sulfides from gold-sulfide-quartz deposits. As to epithermal deposits (as compared with the gold-sulfide quartz fields) the maximum amount of cluster (colloidal) forms of noble metals is in the ore-bearing siliceous matrix rocks despite the fact that fine-grained and submicroscopic native gold was formed from a significant part of these rocks.

Characteristics of Noble Metals Natural Clusters and Possible Evolution thereof in the Ore Process

Some interesting data was obtained when processing the ores of Arkharly deposit in the course of enriching ores from a number of deposits using the concentrators designed by Y. D. Kalashnikov and L.A. Nekhoroshev (KS-K and N) and electric hydrocrusher (EGI-K), desintegrator (DI-KiN) in 2001. Such information did not fit into the existing ideas about the relationship of precious metals recovered in concentrates and remaining in the "tails" as defined by fire assay and atomic absorption methods.

Their essence is as follows. The content of gold in the original ore from vein No. 14 identified by assay analysis is 3.45 g/t. Following hydraulic breakage and disintegration, 5 concentrates were obtained with the gold content from 856 to 123 g/t and silver from 7,685 to 541 g/t and an overall recovery of precious metals 69.8%. At the same time, the content of gold in the "tails" according to pyro-alkali analysis method was identified to be 3.62 g/t. Moreover, when viewing the concentrator it was found out that the inside surface of the concentrator is anodized with gold layer having poor "adhesion" with the concentrator metal (**Fig.8**). The assessment of the amount of gold deposited on the walls of the concentrators has shown that the formation of the film took at least 40-50 g/t gold in terms of primary rock.

Thus the unknown "effect" was recorded. On the one hand this effect increased the gold content in the "tails", in comparison with the original ore, and on the other hand it resulted in metalization of gold that was not identified in ore by the existing analytical methods. In 2004, the authors of the first article named this effect after the researcher who was the first to find and analytically confirm it "**V.N.Matvienko's effect**". At that time, similar results were obtained from ores of vein No 30 of Arkharly field.

Later the revealed "effect" of increase of the contents of noble metals was observed in the processing of the gold recovery plant tailings of Baley field, ores of Nezhdaninsky, Bakyrchik, Zharkulakskiy and other fields. Moreover, during the experiments with concentrates of Nezhdaninskiy field, we obtained a 12 mm long spiral hollow tubular form of pure (undoped) gold with a 0.2 mm diameter, that represented more than 25 g/t gold in terms of concentrate. Similar 4-5 mm long spiral tubes with 0.1-0.15 mm diameter were obtained when analyzing the tails of Baley field containing from 1.1 to 1.56 g/t gold and not more than 5.5 g/t silver under the data of the known tests (including neutron activation). In this sample taken from Baley tails the total gold content was identified at 28.65 g/t with the silver content up to 136 g/t under the data of the tests we developed.

Fig. 8. Gilt bowls of the concentrator after receiving the concentrate from ore Vein No 14 of Arkharly field (top and front views)

It was in 1985 that we first discovered nanotube forms of gold and silver during the study of typomorphism of precious metals from ores of Zholymbet and Arkharly fields, when separating the precious metals from ore-bearing rocks by the gentle pyro-alkali analysis method at temperatures up to 250-300 ^{0} (**Fig. 9 and 10**). Nanotube forms of gold are a 10-15 microns long cluster of the finest formations with a diameter not exceeding 0.01-0.2 microns that was elongated along the axis L_3. They were grouped in the cavities containing massive gold. The fineness of nanotubes is 1,000, and the fineness in the surrounding solid gold is 790-820. One hundred per cent. silver nanotubes from the ores of Arkharly field are tangled felt-like mass in the association with massive discharge of kustelite comprising 26-28% of gold and 74-72% of silver. Unfortunately, at that time there were no concepts of "nanogold" and "nanosilver", and they were not subject to detailed study except for observation of these interesting natural formations and determination of their composition with a microprobe.

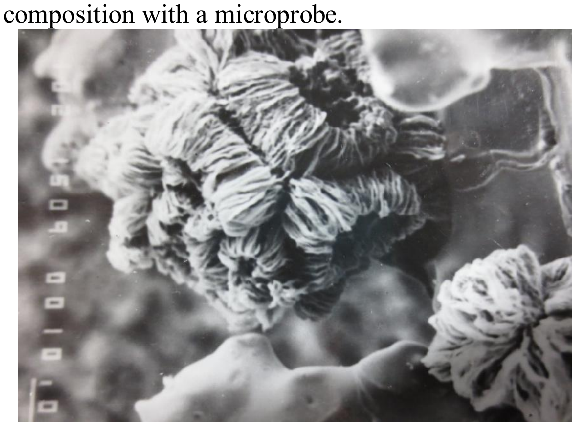
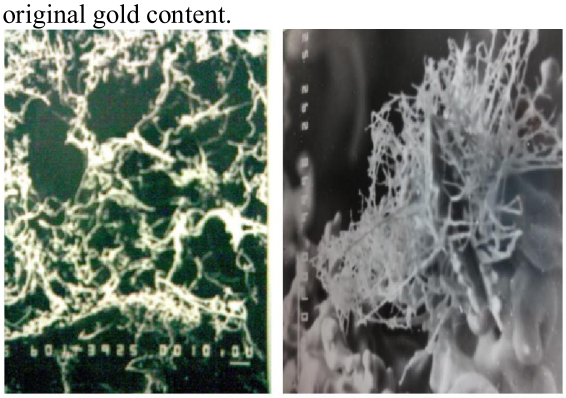


Fig. 9. The accumulation of gold nanotubes in association with massive gold in the ores of Zholymbet field. The tubes contain 100% Au.

In the subsequent years the more "inexplicable" phenomena from the classical technologies stand point were observed with respect to ores of Zharkulak field. Such phenomena essence is as follows. We managed to get a 3,560 kg concentrate containing 1,548.5 g/t gold with 87.5% recovery rate in the following procedure. We disintegrated 200 kg rich quartz ore from Zharkulak field with the gold content of 31.5g/t (average with respect to 5 samples) using concentrator KS-K and N with Matvienko V.N.'s modifications thereof and then prepared pulp with 1:0.9 S/L ratio. Tereafter we determined that the tail resulting from the ore processing using direct cupellation method contained 17.3 g/t of gold (average with respect to 5 samples), i.e., 54.9% of the original gold content.



1 2

Fig. 10. Accumulation of nanotubes (1) and needle-like nanocrystals (2) of 100% silver on the surface of kustelite in Arkharly field ores.

We got similar results in processing of several ordinary batches of ore from Zharkulak field. At that, the check of these analyses by other author's methods gave comparable results.

Equally amazing "phenomenon" was recorded in 15 days when the same "tails" were analyzed by the same methods. Such tails gold content did not exceed 1.5-2.0 g/t. In general, in the course of development of the best modes for concentrator performance it was identified that the maximum gold recovery from Zharkulak field ore into concentrates amounted 140-160% as compared to the results of the primary ore assay test.

It should be noted that **all of the author's analyses are based both on gold, platinum, palladium and silver content in the partings and microprobe studies of noble metals in dore beads**.

We obtained similar results in 2001 in the course of breaking, double wet disintegration and concentrating ore from Baley and Nezhdaninskoe fields. Gold content identified immediately in newly extracted tails was severalfold higher than in the same tails analyzed 7-10 days after ore processing.

Finally, it is worth describing the results of "metallization" of natural clusters of ore at Zharkulak field that we received from 2003 through 2008. The preparation of pulp from double disintegrated gold-sulfide quartz ore sieved through a sieve with 0.25 mm mesh was performed using mud pumps at a S/L ratio = 1:0.9 and stirring the pulp over 30 minutes. In such ore concentrates the dozens of gold and gold-silver beads with the size exceeding 0.25 mm (seldom up to 1.5-2.5 mm). Metallization and aggregation of noble metals clusters into spherical or other forms (**Fig. 11 and 11a**) occurs in the course of quartz vein ores fusion with alkali.

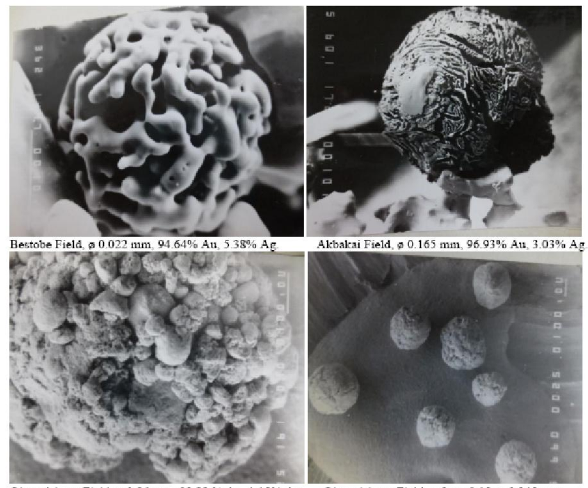
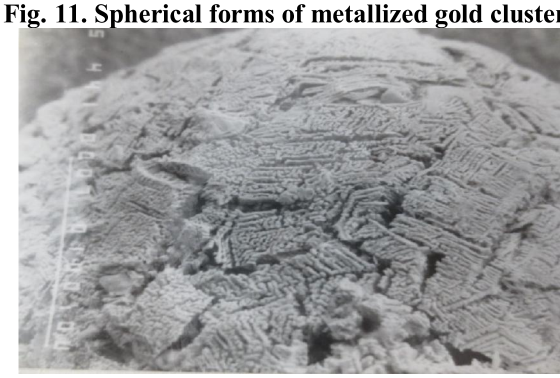


Fig. 11. Spherical forms of metallized gold clusters.



Olympiskoye Field, ø 0.425 mm, 100% Au

Fig. 11a. Spheres of dendritic metallized gold clusters.

Metallized lead clusters are roundish, flat and stretched particles of various size with the total weight up to 3.75 g. Copper clusters weigh 0.34 g. (**Fig.11b**). On the photo below please see flat and round Pb particles to be analyzed in microprobe. Please see the scale (in mm) at the photo bottom.

As the result of microprobe analysis (by V.L. Levin, analyst) no impurities were detected in gold, except for small amounts of silver and iron. Only gold was identified in silver. Less than 1% of Fe, Cl, Pb, and much Zn was observed in copper. Less than 1% of iron and silicon was tracked in lead.

Fig 11b. Metallized lean and copper clusters

1. Composition of gold balls+

samples No.	Fe	Ni	Cu	Rh	Ag	Te	Au	Hg	Pb	Σ %
12-3a	-	-	-	-	0.53	-	99.47	-	-	100
12-k-o-k	0.19	-	-	-	0.37	-	99.44	-	-	100
13-k	-	-	-	-	0.67	-	99.33	-	-	100
14-2	-	-	-	-	0.52	-	99.48	-	-	100
A-5	-	-	-	-	0.16		99.84	-	-	100
14-k-o-k-3-	-	-	-	-	-	-	100.0	-	-	100

+ Native gold maximum fineness does not exceed 910.

2. Composition of silver (with gold) balls ++

samples No.	Fe	Ni	Cu	Rh	Ag	Te	Au	Hg	Pb	Σ %
14-k-o-k-3	-	-	-	-	92.69	-	7.31	-	--	100
12-k-o-k-4	-	-	-	-	94.52	-	5.48	-	-	100
13-2	-	-	-	-	92.29	-	7.71		--	100

++ The table contains composition of balls with maximum quantity of silver and minimum quantity of gold.

3. Composition of copper disks

samples No.	Fe	Zn	Cu	Cl	Ag	Te	Au	Hg	Pb	Σ %
M-1	-	-	97.94	0.20	-	-	-	-	1.86	100
M-2	0.11	31.59	68.30	-	-	-	-	-	-	100
M-3	0.12	-	99.88	-	-	-	-	-	-	100
M-4	-	-	100.0	-	-	-	-	-	-	100

4. Composition of lead disks

samples No.	Fe	Si	Cu	Pb	Ag	Te	Au	Bi	Al	Σ %
S-1	0.43		-	99.57	-	-	-	-	-	100
S-2	0.35	0.71	-	98.94	-	-	-	-	-	100
S-3	0.37	-	-	99.63	-	-	-	-	-	100
S-4	0.24	1.28	-	98.48	-	-	-	-	-	100

Table 2. Composition of the metallized clusters

In fact, there exist various correlations of gold and silver in metallized clusters with the prevalence of the latter. However, in all analyzed newly formed gold balls the amount of impurities was below 1%, silver exclusive, and vice versa, in silver balls only gold was observed. In copper, only in one sample high zinc content was found. This may evidence that a copper and zinc intermetallide (having no analogue in nature with a high affinity). In lead just formed from clusters iron and silica are recorded.

Moreover, in the experiments with the combined carbon-containing concentrate of Nezhdaninskoye field dozens of diamond crystals (ranging in size from 0.5 to 2.5-3.0 mm with hardness of 10 on a Mohs scale) were generated from the clusters. Their total weight exceeded 2,500 carats per tonne based on the possible content. In the Moscow State University's laboratory these crystals were instrumentally diagnosed as "nitrogen-free diamonds of clean lines that are not found in nature". The "fate" of these diamonds is interesting. Repeated diagnosis in the same laboratory carried out a month later showed that they were "unknown in nature carbon-containing transparent minerals that crystallize according to the spinel law".

Thus, the discovered **feature** involving clusters consolidation to the gravity-recoverable size after double disintegration is not an exotic phenomenon. It is typical not only for clusters of noble metals, but also for zinc, lead, copper, carbon and other elements that have a natural native state. However, it is important to create the best conditions for enlargement thereof by chemical or mechanic means.

Previously, we continuously received concentrates, from the most complex and refractory ores of various deposits, which contained by 30-40% precious metals more as compared to the original sample identified by assay and atomic absorption analysis after processing by hydrocrusher and disintegrator. For example, at least 72.59 - 79.23% gold in the aggregate was recoverable into concentrates from the ores of Zharkulak field after their double dry treatment on a disintegrator. At the same time, 57.7 to 61.88% gold was found in the "tails" of the same samples by the author's analysis, compared to the original samples (fire assays were performed in Geoanalitika PIC LLP, Almaty). At that, concentrator inner surface plating with gold mixed with copper was constantly noted. It is worth mentioning that the ore samples weighing 100 - 150 kg each were used in the technology experiments.

Clarification of the nature of this phenomenon using electronic microscopic studies revealed many different shapes and sizes of predominantly spherical structures consisting of organometallic compounds containing detectable amounts of precious metals in ores of gold-sulfide and epithermal fields. These formations (a few tens of Angstroms) are generally covered by zonal covers that are clearly recorded on the electronic micrographs (**Fig. 12**).

Along with the numerous single forms these formations are also met as groups in a single zonal "shell" and less frequently in the form of aggregates consisting of groups of cloud spherical concretions united by a single "shell".

Extensive analysis of the electronic microscopic actual material (more than 700 observations as captured on photos) allowed us to conclude that the said spherical formations having outer zonal "shells" are **natural cluster forms** (organometallic clusters of first order) **participating** in the metals ore process.

At least the first-order organometallic clusters and ionical forms refer to the most probable original source, fixing and transportation of precious metals (gold, silver, platinum group metals) at gold fields in black shales (Bakyrchik, Kumtor, Muruntau, Nezhdannoye, Sukhoy Log, etc.) and near-surface epithermal deposits such as (Arkharly, etc.). In the stockwork ore deposits (Zharkulak, etc.) copper and lead are fixed in organometallic clusters forms (first-order clusters) in addition to specified noble metals.

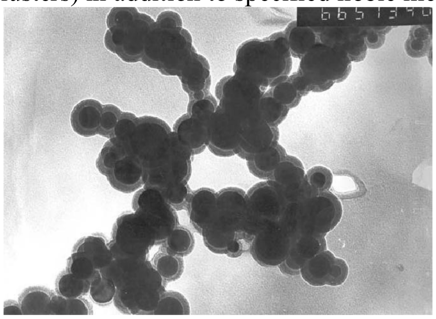


Fig 12. Spherical formations (spherules). Proto-clusters of primary forms of natural precious metals. Bakyrchik field. Magnification 66,500 thousand times

Analysis of the facts on the structure of clusters in the ores of Bakyrchik and Arkharly fields allowed us to separate among the significant diversity the following main forms: 1) isolated clusters of spherical, elliptical and slightly elongated forms, with a clear zonal shell (size of a few tens of nanometers (**Fig. 12**); 2) cluster groups united by a common shell with distinct spherical form (**Fig. 13**), consisting of the individual clusters (the size of first hundreds of nanometers); and 3) communities of cluster groups representing "cloud" contractions, ranging from hundreds to few thousand nanometers. The latter two groups are always covered by a single shell of a zonal structure (**Fig.14**).

After the special mechanical impact on the ores and metallization of clusters it was found that in the organometallic cluster form (cluster of the first order) in the ores of some deposits (Baley, Nezhdaninskoe, Arkharly, Bakyrchik, Zharkulak, etc.) platinum group metals (platinum, palladium and rhodium), lead and copper are also fixed significantly.

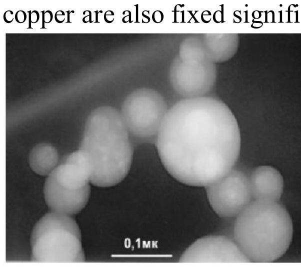


Fig. 13. Single clusters with globular internal structure in a zonal shell. Bakyrchik field.

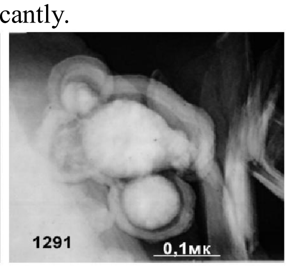


Fig. 14. Group of clusters in a single zonal shell. Arkharly Field.

Under the influence of a focused electron beam these cloud formations "burst", breaking up into small spherical particles that are diagnosed as gold by electronic microscopy, and lamellar crystallites of hexagonal habit, that are diagnosed as graphite (**Fig. 15**).

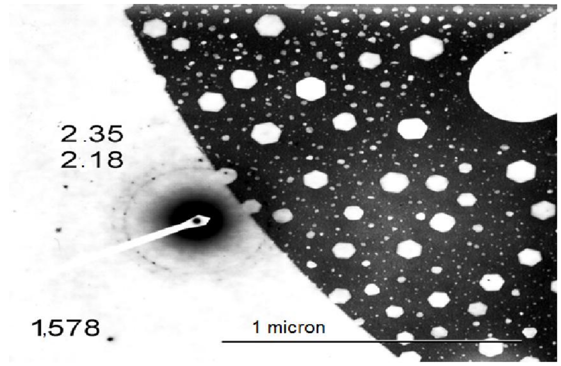


Fig. 15. Spherical (gold) and hexagonal (graphite) fallout products of cloud concretions of cluster groups under the influence of the electron beam. Bakyrchik field. Similar fallout products are detected in ores of Arkharly.

Silver and gold were reliably recorded along with the carbonaceous material in the course of electronic and microscopic studies in groups of clusters and in communities of clusters groups (by F. Kurmakaeva and T. Shabanova, analysts).

Thus, **a controlled way of destruction of shells of primary organometallic clusters has been found. The possibility of their transformation into mono-, bi-, tri-, etc. metal clusters (clusters of the second, third and higher order) was identified. The most important was that we were able to enlarge the metal clusters mechanically and chemically (see Table. 2) to the size, which makes it possible not only to determine the amount of noble metals fixed in them but also to extract (yet partially) them by the concentrators developed and tested by their authors on an industrial scale using the original methods of ore preparation**.

Based on the results of electronic-microscopic study of the discovered gold-organic cluster forms of the first order (more than 750 photos), the possible structure of single proto-clusters and data on their degradation under the electron beam exposure is shown in **Fig. 16 and 17.**

The proposed model of the metalized natural noble metals clusters (and possibly some non-ferrous metals) that are in nature in native state, such as lead, copper, zinc and others, explains their great resistance not only to natural, but also to artificial influences. This model also explains why modern analytical methods (assay and atomic absorption) cannot identify the actual content of noble metals fixed in noble metals clusters. The clusters have high volatility under the influence of high temperatures and they do not decompose under the influence of acids at low temperatures.

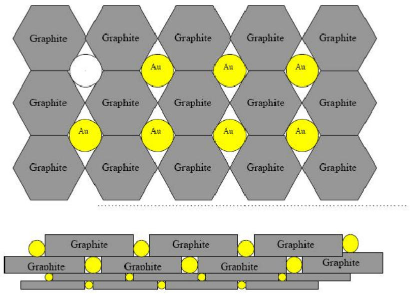


Figure 16. Layout and sectional view of crystallites (graphene) shells from the center to the periphery with increasing crystallite packet thickness and sizes of spherical Au precipitates.

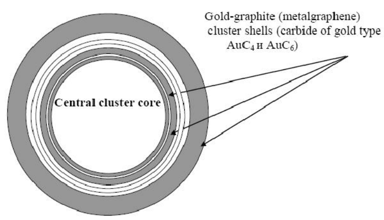


Fig. 17. Structural diagram of a proto-cluster. Central core is an accumulation of metal atoms in an organic substance in the "tar-like" state. Light rings are noble metals of larger sizes in graphite microcrystalline or in the metalgraphene structure. Dark rings are graphite, carbides of Au (possible Ag ,Pd, Pt) of AuC_n. type

We can assume with great probability that primary natural clusters are unit cells, groups or conglomerates of cells of some parts of metal-extracting paleo-bacteria **(Fig. 18 and 19)**. Perhaps, the latter used noble metals atoms not only for their normal life support but also for protection in the process of their vital activity, e.g., silver was used to "protect ill cells shells", gold and platinum metals were used to ensure normal functional activity of cells and effective life support of bacteria. When metal-extracting paleo-bacteria died they destructed with release of cluster forms of noble metals. This can be confirmed by the results of experiments for cultivation of bacteria that are "fed" with gold chlorides in Australia. Further fullerens and other forms of metal fixation evolve from the cells of similar paleo-bacteria.

In the areas of intensive development of metal extracting bacteria (along with other factors of chemogenic sorbtion, geochemical barriers and others promoting initial accumulation of noble and heavy metals) the lithogeochemical formations (bases of the unified gold column **[15]**) were formed that, in our understanding, were the main source **[16, 17]** of ore elements when forming the deposits. We recorded a lot of metal extracting paleo-bacteria **(Fig. 20, 21)** previously by electronic microscopic study of ores and ore-containing rocks of gold fields (Bakyrchik, Arkharly, Amantaitau, Kumtor and others) **[10, 16].**

We identified experimentally that artificial colloidal (cluster) forms of Ag begin to sublimate at 70^0 C (1.71% of their weight). The results of these experiments are shown in **Tables 3 and 4.**

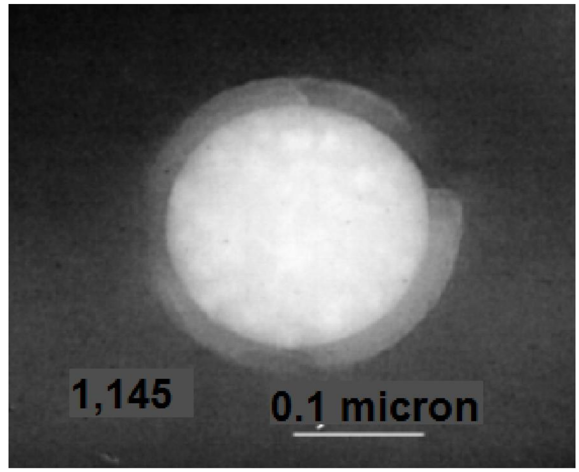
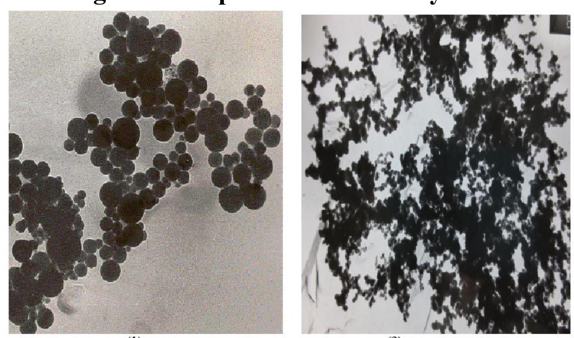


Fig. 18. Single protocluster with "spotty" internal structure due to heavy metals and with partially damaged zonal spherical shell. Bakyrchik field.



(1) (2)

Fig. 19. "Colonies" of individual spherical gold-organic proto-clusters from ores of the following fields: (1) Bakyrchik; (2) Arkharly.

Fig. 19. "Colonies" of individual spherical gold-organic proto-clusters from ores of the following fields: (1) Bakyrchik; (2) Arkharly.

The cluster forms of noble metals (mainly silver) extracted from ores of **Arkharly** field after being processed with electric hydrocrusher and subsequent disintegration allowed us to follow their evolution with the native silver formation under influence of air oxygen using microprobe Superprob-733 (by V. L. Levin, analyst) and make photos of such processes.

Cluster metallization apparently proceeds under intensive oxidation of the internal organic component after mechanical (or thermochemical) destruction of resistant outer shells. At the beginning of the metallization process dendritic needle crystals are formed. Then from these crystals the teardrop-shaped and spherical concretions of native silver are formed. From the spherical concretions skeletal and frame clusters evolve first, and then massive native silver crystals are formed at the last stage of oxidation of the primary clusters. At that, the cluster metallization runs at 25^0C and the pressure of 1 atm.

The clusters fixing gold and platinum group metals behave similarly.

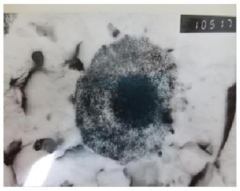


Fig. 20. Gold-bearing paleo-bacteria from Bakyrchik field. Magnification is 105,000 times.

Fig. 21 Paleo-bacteria substituted by iron sulphides from Arkharly field ores. Magnification is 55,000 times.

Type of clusters	Initial weight, in gram	Heating temperature in ^{0}C					
		+ 70	+ 150	+ 250	+ 300	+ 350	+ 400
		Weight of cuvette at the presented temperature, gram					
Black *	23.75915	23.75598	23.7530	23.75041	23.74336	23.73665	23.73232
Weight difference, gram		-0.00326	-0.00607	-0.00874	-0.01579	-0.0225	- 0.26830
%% total weight loss		**1.71**	**3.18**	**4.57**	**8.26**	**11.77**	**14.04**
Chocolate	23.90447	23.9031	23.9009	23.89897	23.89568	23.88915 0	23.88780
Weight difference, in gram		-0.00137	-0.00351	-0.00550	-0.00879	-0.01532	-0.01667
Brown	24.44967	24.44887	24.44774	24.44617	24.44548	24.4412	24.43922
Weight difference, in gram		-0.00080	-0.00220	-0.00350	-0.00419	-0.00845	-0.01045

Continuation of Table #3

Type of clusters	Initial weight, in gram	Heating temperature in ^{0}C					
		+ 450	+ 500	+ 550	+ 600	+750	+ 950
		Weight of cuvette at the presented temperature, gram					
Black *	23.7590	23.7254	23.70903	23.6523	23.51384	x	22.2841
Weight difference, in gram		-0.03374	-0.05012	-0.10676	-0.24531	x	1.47505
%% total weight loss		**17.66**	**26.23**	**55.87**	from 600^0 – intensive oxidation of cuvette and weight loss		
Chocolate	23.90447	23.8858	23.87775	23.8465	23.76460	x	22.78913
Weight difference, in gram		- 0.1868	-0.05012	- 0.5794	-0.139870	x	1.11534
Brown	24.44967	24.4349	24.41501	24.3603	24.24678	x	22.99702
Weight difference, in gram		-0.01474	-0.03466	-0.08929	-0.20289	x	1.45265

Table 3. Data on volatility of artificial silver clusters

Total weight of black clusters = 0.19109 g. It was noted that at 450-5000 C silver cluster metallization commences. At 5500 C intensive silver cluster metallization is noted. Silver melting temperature is 9620 C.

Furnace holding time at the following temperature: from 70 to 6000 C – 30 min: from 650 to 9500 C – 15 min.

From these experimental results the following conclusions can be made:

Metallization of silver clusters is observed at t = 200^{0}C. At 250^0 C metallization increases slightly, and at 300^0 C well-defined circular, elliptical, etc. isometric isolation of native silver is observed. At 500^0 C silver clusters metallize as "vapor" at the bottom of the cuvette. In the cuvette with "black" clusters the individual spots of silver are recorded, their number is maximum with the "chocolate" spots and it is minimum with the "brown" spots. At 550^0 C the intensive silver clusters metallization is noted, when the bottom of the cuvette is covered with native silver almost completely. At 300^0 C the surface of the particles of non-metallic minerals in the sample with clusters is covered with numerous micro-cracks (like "takyr"), which indicates the beginning of the degassing of non-metallic minerals (their fallout).

Type of clusters	Initial weight of cuvette + sample	Initial weight of clusters	Heating temperature in ^{0}C				
			+ 70	+ 150	+ 250	+ 300	+ 350
			Weight of cuvette at the presented temperature, in gram				
Black *	24.03393	0.15427	24.01782	24.0298	24.02397	24.01846	24.01414
Weight difference, in gram			- 0.00215	- 0.0413	-0.00996	-0.01547	-0.01979
%% total weight loss			**- 1.39 %**	**-2.68 %**	**- 6.46 %**	**-10.03%**	**-12.83%**
Chocolate	24.2429	0.13931	24.24248	24.24029	24.23569	24.22953	24.22614
Weight difference, in gram			- 0.0044	-0.00263	-0.00723	0.01339	-0.01678
%% total weight loss			**- 0.32 %**	**-1.89 %**	**- 5.19 %**	**- 9.61 %**	**-12.05%**
Brown	23.72936	0.16104	23.72910	23.72823	23.72846	23.72364	23.71978
Weight difference, in gram			- 0.00026	-0.00113	-0.00090	-0.00572	-0.00958
			- 0.16 %	**- 0.70%**	**- 0.56 %**	**- 3.55 %**	**- 5.95 %**

Continuation of Table #4

Type of clusters	Initial weight of cuvette + sample	Initial weight of clusters	Heating temperature in ^{0}C					Button weight Ag in grams
			+ 400	+ 450	+ 500	+ 550	+ 650	
			Weight of cuvette at the presented temperature,					
Black *	24.03393	0.15427	24.00915	24.00120	23.96053	23.89619	x	0.03979
Weight difference, in gram			- 0.02478	- 0.03273	-0.07340	-0.13774	x	
%% total weight loss			**- 16.06 %**	**- 21.22%**	**-47.58%**	**89.29%**	x	
Chocolate	24.24292	0.13931	24.21615	24.19058	2405101	23.87061	x	0.03863
Weight difference, in gram			- 0.02677	- 0.05234	-0.19191	-0.37231	x	
%% total weight loss			**- 19.22 %**	**- 37.57%**	**137.76%**	**257.15%**	x	
Brown	23.72936	0.16104	23.71178	23.69003	23.61999	23.51108	x	0.02734
Weight difference, in gram			- 0.01758	- 0.03939	-0.10937	-0.21828	x	
%% total weight loss			**- 10.92 %**	**- 24.42%**	**- 67.91%**	**135.54%**	x	

Table 4. Data on volatility of artificial silver clusters

The degree of clusters "plating" decreases from "black" to "brown", despite the fact that the maximum number of "brown" clusters were used in the experiment. In their turn "black" and "chocolate" clusters behave similarly, and the behavior of the "brown" ones significantly differs from the first ones.

Behavior and properties of the same clusters in contact with air for 10-15 hours (1st experiment) and within 72-96 hours (2nd experiment) differ greatly, that may be associated with either enhanced "metallization" of the latter (?) or with a hydroxide film on their surface. Dwell time in the furnace with the samples in cuvettes at a temperature from 70 to 550^0 C was 60 minutes, and at 600 to 950^0 C it was 30 minutes.

Discovery of precious metals in form of clusters helps to explain the likely source of the majority of gold, silver, palladium, platinum, and others in ore deposits; the difference in the gold fineness in endogenous ores; the possible presence both of gold and silver, and also platinum and other metals in the ores of many gold deposits. In particular, from the above explanation of the cluster nature we have identified palladium, platinum and rhodium in ores of Bakyrchik and Zharkulak fields, and palladium and rhodium in ores of Arkharly field; and platinum in ores of Enbekshi field ores.

At the initial stages of diagenesis and lithification of deposits the destruction of noble metals cluster forms results in the formation of various forms of movable metastable forms of fixation: chlorides, sulfates, thiosulfates, etc. The most important among them are gold chlorides, particularly, tetravalent. More stable forms of gold ore in the initial stages of the process are likely presented by gold hydroxides of type $Au_n(OH)_m$ where n = 1, m = from 1 to 4. An important role in transport of gold in ore solutions can be played by H_2S, CO, CO2 and other gases that are constantly present in the gas-liquid inclusions in quartz, carbonates and sulfides (**Fig. 22**). Thus, together with chlorides of two- or four-valent gold of type $[AuCl_2]$, $[AuCl_4]$, Au can be (for a long time) in a state when it is capable to migrate in ore solution as a complex Au (HS-), $[Au\ (HS)_2]$ or complex $[Au\ (HS)_2S]^2$ in presence of lead ions with tellurium. With the temperature increase, firstly, white colloidal (cluster) gold $[Au\ (OH)_4]$ is formed in natural objects; then this gold transforms to violet ($Au\ (OH)_3$-$Au\ (OH)_2$), and after that to black ($Au\ (OH)_2$, brown Au (OH) and finally to metallic Au °.

$AuCl_4 + 4KOH = Au\ (OH)_4$ (white colloidal Au)+ 4 KCl
$Au\ (OH)_4 + H^+ + e^- = Au\ (OH)_3$ (violet colloidal Au)+ H_2O
$Au\ (OH)_3 + H^+ + e^- = Au\ (OH)_2$ (violet colloidal Au)+ H_2O
$Au\ (OH)_2 + H^+ + e^- = Au\ (OH)$ (black colloidal Au)+ H_2O

The resulting colloidal gold is transported to the zones of ore deposition with silicic acid gel, where due to recrystallization of the gel it is metallized gradually to form monometal and metal-metal clusters first. The latter under the influence of thermodynamic conditions of ore deposition in favorable physical and chemical conditions are grouped into fine super-microscopic formation of native gold phase described above, according to the scheme:

$Au\ (OH)_2 + Au\ (OH) \rightarrow Au_2\ (OH)_3 \rightarrow Au_n\ (OH)_m \rightarrow$ Au black
$Au\ (OH) + H^+ + e^- = Au^0$. Where n>m=black; with $m=0 \rightarrow Au^0$.

The scheme of the above process of evolutionarily directed transformation of natural proto-cluster forms of noble metals and formation of ores of gold deposits is shown in **Fig. 22.**

In this scheme, the authors suggested a general reflection of the entire gold-ore process of accumulation of ore material from erosion zones in sedimentation zones in the form of the ionic, cluster and organometallic compounds in conditions of early mesozone through multiple metastable compounds of noble metals in the form of chlorides, sulfates and thiosulfates of noble metals in conditions of transient thermodynamic parameters of epizone and mesozone into more stable forms as tellurides, selenides, etc. Here in the local areas of the ore bodies the nuggets of precious metals begin to form with their metastable state dominance.

Based upon the foregoing, the authors believe that in order to develop effective ways of extraction of cluster, supersmall, fine-grained forms of precious metals, that exceed severalfold the amount of visible native phases in the overall balance of Au, Ag, Pt, and Pd in ore (**and this an established fact!**) it is not enough to create highly efficient analytical methods. It is also necessary to commence a large-scale systematic study of precious metals in the above referred forms together with carbonaceous material and silica in all their natural forms in ores and ore-hosting rocks using electron microscopy and microprobe, etc.

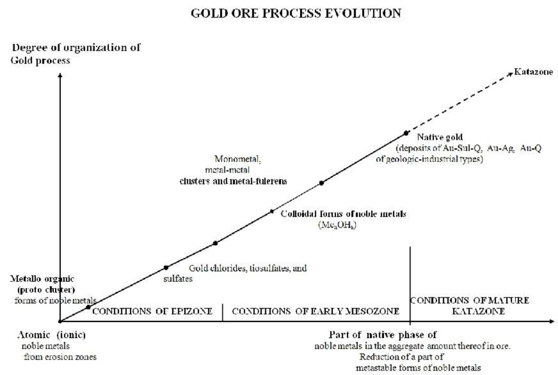


Fig. 22. GOLD ORE PROCESS EVOLUTION

The following are the most crucial objectives of electron-microscopic study of ores and ore-bearing rocks at gold deposits:

1) clarification of the evolutionary recrystallization of silica in the scheme: opal-chalcedony-quartz and ore material deposits to prove the unity of these processes, regardless of the genetic and formational deposits types;

2) search for paleo-bacteria (or colonies thereof) substituted with ore matter and corresponding precious metals cluster forms;

3) identification of natural colloidal forms of noble metals fixation in ores;

4) control of experiments for natural clusters metallization.

Attaining certain above objectives will promote the development of new instructional techniques both in the sphere of precious metals analysis, in the methods of ore enrichment and in creation of the cluster as well as nanotechnology extraction of gold, silver and platinum metals group.

We have already obtained first promising results on these issues in subcommercial scale as described above and will be described in the works scheduled for publication and dealing with these issues.

Transformation of noble metals metastable forms in the thermodynamic conditions of mature mesozone results in more stable compounds of noble metals hydroxide forms. Here the proportion of native noble metals discharge gradually increases with the prevalence of metastable compounds thereof.

Under conditions of mature katazone all (or almost all) metastable compounds of noble metals decompose to form the native phase in the form of nano-, micro-sized, fine and larger allocations up to the formation of large nuggets. Here, the size of native gold precipitates is conditioned on the composition and nature of the ore-hosting matrix and the size of cavities formed therein in pre-ore and inter-ore periods.

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1/9/2014