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 authors consider the initial accumulation of the mined substance in lithgeochemical formations as metastable phases and protoclusters in sediments of sedimentagenous basins, enriched by the carbon-bearing substance and carbonates in the hydrosulphuric medium. The evolution model is provided for protocluster forms; their role as the main source of the mined substance in the course of the formation of gold ore fields is considered. As a result of evolutional processes of formation of ore-hosting rocks, exposed to the impact of PT-conditions of the epizone, mesozone and katazone, noble metals available as metalorganic protoclusters are transformed into native metals. Silicic acid gel and ore process stabilizing elements, including Te, Se, etc., with mandatory presence of plumbum, play an essential role in the formation of the ore-hosting matrix and in the conveyance of the mined substance by hydrothermal solutions. Formation of deposits of black-shale gold sulphide, gold-silver epithermal and gold sulphide-quarzitic types followed a consistent pattern, and they represent particular truncations of the same gold ore column (the subformation) on the present-day surface of denudation.

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PART 2

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Model of Evolution of Noble Metals Cluster (Colloidal) Forms in Ore Formation

Our model is based on the results of research in the following factors **[1, 2, 3]**:

1) sedimentagenous environment in the primary gold accumulation of which the processes of different nature (biogenic, chemogenic, adsorption, etc.) took part. These processes caused the initial enrichment with ore components and gold **mainly in metastable forms** (colloids, organometallic compounds, cluster formations, adsorbates with carbonaceous and clay matter, hydroxides of iron, manganese, etc., relics in freshly formed sediments (chloride, sulfide and hydrosulfide complexes) of ore-bearing rocks. As a result in size-specific facies areas (**lithogeochemical formations** as per V.N. Matvienko **[2, 3,4]**) on the local areas of the earth's crust ore fields were formed, which were the main sources of deposits forming ore substances **[5]**;

2) **mobilization mechanisms of gold metastable phases with the** subsequent processes (diagenesis, dynamometamorphism, magmatism), their transformations into native phase in different morphogenetic and natural forms (**gold process organization degree** as per V. N. Matvienko);

3) **evolutionary-directed formation of ore-hosting matrix** (quartz veins, zones of silicification, beresitization, etc.) and local areas that are favorable for the formation of mineralized areas and ore bodies by gradually reducing the role of metastable forms of gold in gold mining process with the formation of a stable native phase.

Based on the foregoing, the full range of geological, structural-tectonic, mineralogical, geochemical and other factors creates a dynamic unified paragenesis of metastable gold forms that is evolving in time and combined in space.

Originally enriched with ore matter deposits of sedimentagenous pools (under the influence of the processes occurring in the epizone and early mesozone) promote the formation of large concentrations of gold-sulfide mineralization (e.g. in black shale sequences), mainly in the form of clusters **[6, 7, 8, 9, 10]**.

As the dynamometamorphic processes develop in local areas of ore bearing rocks, particularly in areas of faults, plastic flow and high heterogeneity, together with pronounced change of lithified rock the primary metal organic clusters are destroyed to form metal-metal clusters of the second and higher orders. This is a period of maximum release of migration-capable ore material. In transportation of ore material the significant role is played by specific "additives" in hydrothermal systems (stabilizers), which consistently increase the possibility of migration of gold, contributing to formation of supersaturated solutions of gold, and serve as a powerful factor in separation of precious and non-ferrous metals in the ore-bearing system **[11]**.

It is important to note that metal-metal clusters of the second order form only in the areas of maximum influence of tectonic and metamorphic and physico-chemical factors of ore-forming environment. The areas located in the immediate vicinity of the routes of maximal migration of ore-generating solutions may contain significant amounts of ore material in cluster form, which did not participate in the ore process. Significant amounts of residual cluster forms of noble metals can remain in the rock of lithogeochemical formations of the gold column base, when the thermodynamic conditions of the ore-forming environment do not achieve the parameters under which metal-to-metal clusters of the second and higher orders are formed, and from which the maximum amount of free (native) gold is formed **[1, 4]**.

Typical gold deposits formed under the influence of PT conditions of epizone and suture structures of the initial stages of mesozone development are Bakyrchik, Bolshevik, Amantaitau, Vyssokovoltnoye, Vassilyevskoe etc. These two successive processes are clearly reflected: sedimentogenesis and early diagenesis. During the first process the metastable forms of ore components (including gold and other precious metals) are accumulated in sludge-like environment that is rich in active organic matter and hydrogen sulphide. This stage is characterized by the extensive development of gold extracting microorganisms in the conditions of basin sedimentation and the formation of rhythmically-layered carbonaceous-clay and aleuropelitic increased deposits of high carbonate content and coarse-grained clastic rocks **[1, 3].**

In the sequential conversion of freshly formed sediments we identified three main stages: early-, late-diagenetic (including lithification) and postmagmatic. These latter two stages are developed under the condition of gradual rise of dynamometamorphous stress before their discharge as discontinuous forms of dislocation.

Transformations of geochemically-specific mass at the early-diagenetic stagelead to a practically complete cessation of biogenic extraction of ore-forming elements and the demonstration of the geochemical contradiction between the sediment and bottom water, which contributes at first to oxidative and then recovery minerogenesis. Such processes involve destruction of cluster forms, transformationof the colloidal formations, metal and other heavy metal complexes with fixing the latter by relatively stable framboidal and globular forms of iron disulfide containing non-ferrous metals (**Fig. 1**) and having complex composition and internal structure.

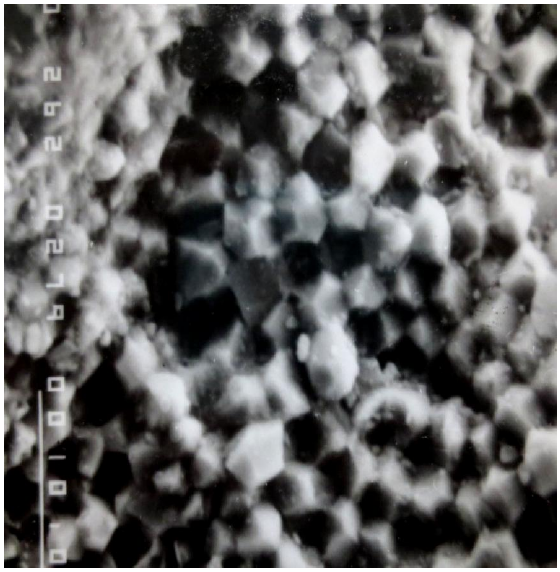
Framboidal forms of sulfides are always earlier forms in relation to their metacrysts and reflect a certain stage of tectonic-metamorphic conversion of precipitation generally, and organic and ore substances, in particular.

It should be noted that the specific nature of the mineral composition of epigenetic ore deposits, regardless of the geological and industrial types of gold deposits studied, is reflected in the features of internal structure of framboidal and globular forms of sulfides. Thus, in Bakyrchik field pyrite, arsenopyrite and less sphalerite are primarily recorded as a part of globules.

Late-diagenetic phase of transformation of sediments of lithogeochemical formation enriched by ore matter that is overlaped in space and time partially with the initial phases of local (suture) dynamometamorphizm of rocks corresponds to thermodynamic regime of mineral-formation that is close to conditions of epizone-top mesozone.

At this stage, the local large-scale redistribution of petro - and ore-genetic components followed by hydroplastic, flexural and rheological deformation of rocks took place with wide demonstration of injectables in local areas, which is most clearly manifested in the Bakyrchik field.

Kyzyl shear zone (Bakyrchik, Bolshevik, etc.), Akzhal-Bokonsky (Vassilyevskoe, etc.), and other viscous fractures are examples of such structures. Among these, against the background of epizone and lower tektono-facies of mesozone the degree of local deformation of rocks reaches high values (V-VIII). Here, under conditions of uneven triaxial compression, not only the collapse and foliation of rocks occur but also processes of differentiated hydroplastic extrusion and flowing of carbonaceous-pelitic layers, moving metallic and non-metallic substances in mineral form, as well asbudinageand lensing of rocks are widely developed **[7, 11]**.



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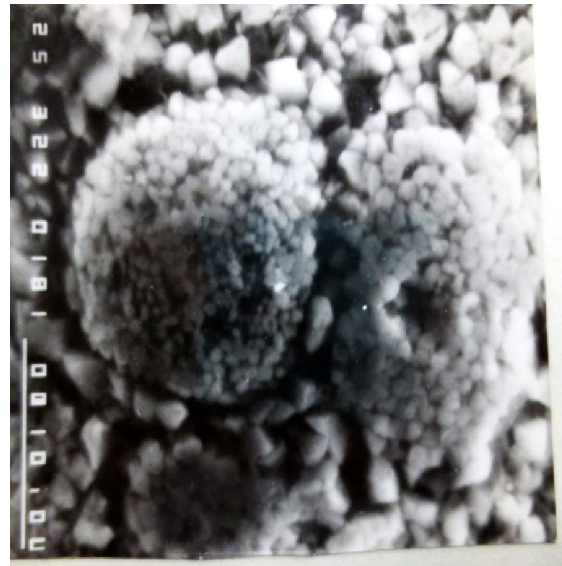

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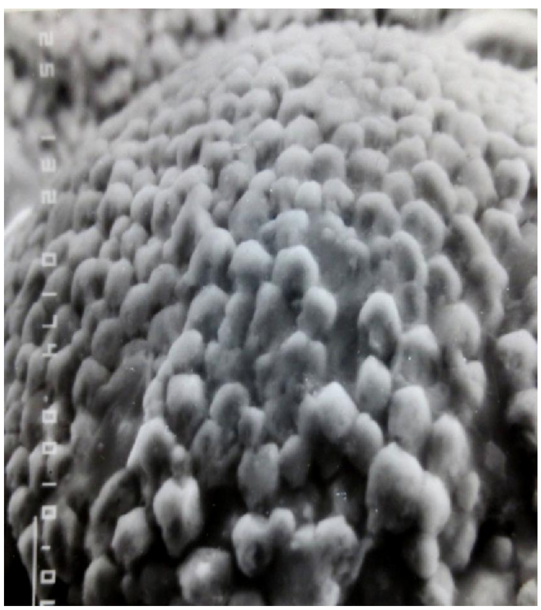

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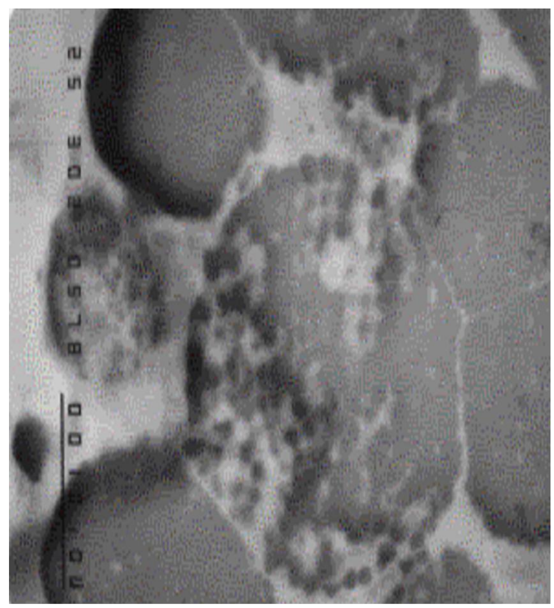

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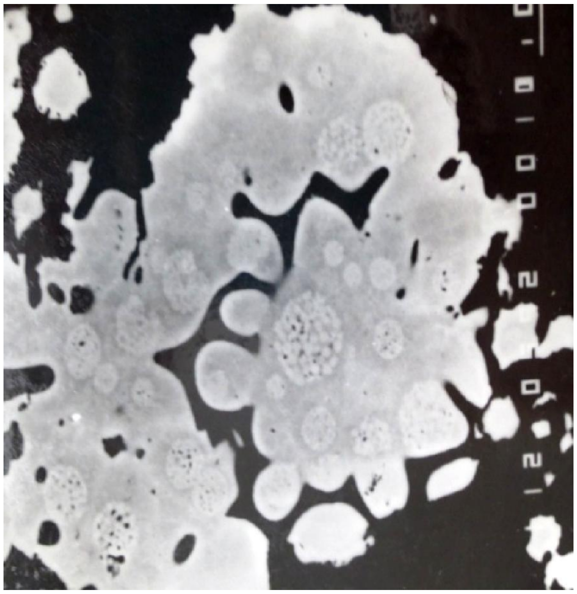
Fig. 1. Globular and framboidal forms of sulfides in the ores of the following deposits: 1 and 3 -Svetinskoye, 2 -Kvartsytovye Gorky, 4 -Bakyrchik.

These processes are clearly recorded in framboidal and globularforms of sulfides which are converted into a more stable crystalline form under the influence of metamorphic tectonic processes depending on the starting composition **(Fig 2)**.

Ore bodies are characterized by stratified occurrence with retaining the structural and textural features of the ore-bearing sedimentagenous formations. In the fields (Svetinskoe, Zholymbet, etc.), where the globular sulfides recrystallization processes are most clearly manifested in the local areas, the proportion of nanosizednative phase of gold **[7, 11]** (**Fig. 3**) increases dramatically to form visible grains up to 2-3 mm.



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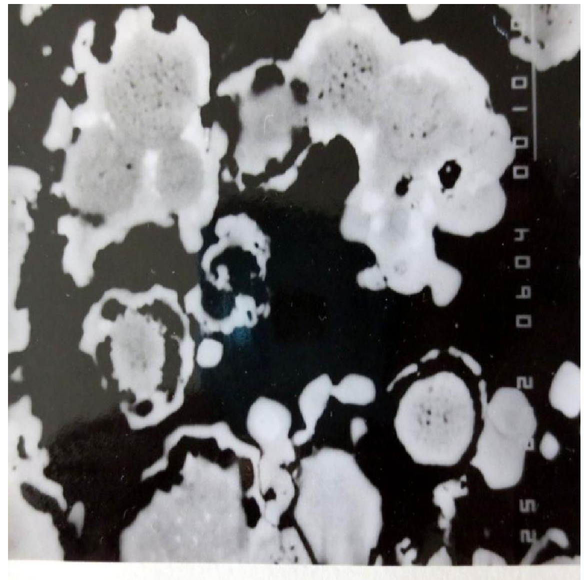

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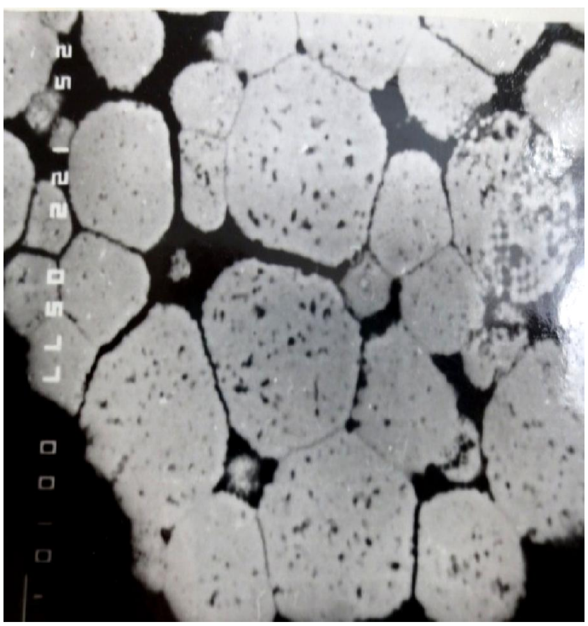

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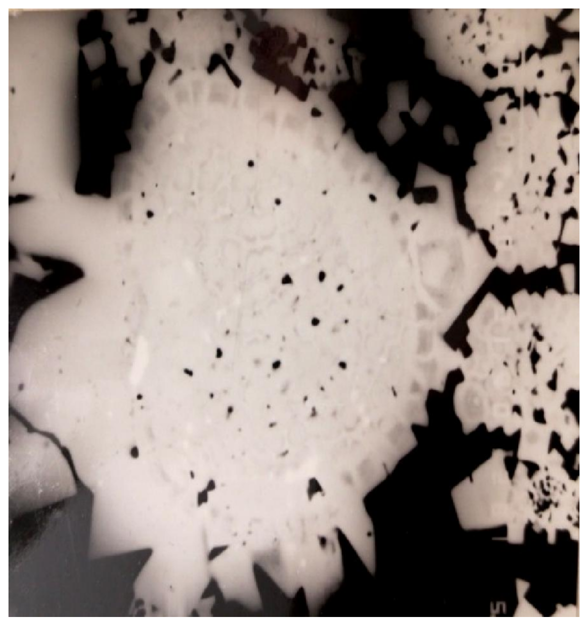

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Fig. 2. Crystallinity of framboidal forms of sulfidesintheores of the following deposits: 1 -Bakyrchik, 2 - Svetinskoye, 3–Zholymbet, 4 – Bestobe.

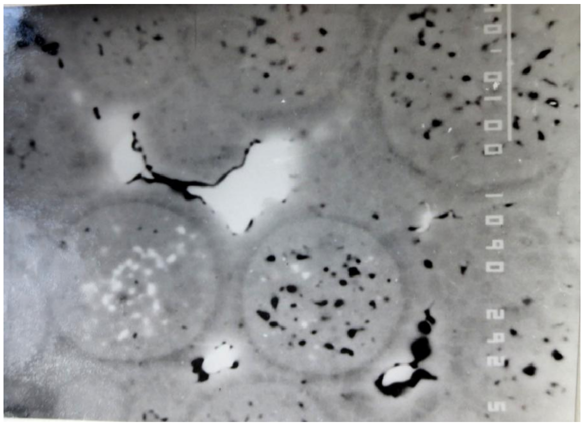

Fig. 3. Native gold (light 0.5-1.5 micron grains in pyrite) and galena (light spots among pyrite globular forms) formation in framboidal forms.

It is important to note that the formed ore deposits are characterized by different ratios of migration-capable (ionic, cluster and colloidal) and native gold **[12]** in the form with clearly dependent (not more than 10-15%) quantity of the latter (**Table 1, Fig. 4**).

Sequential change of thermodynamic conditions under which the gold deposits were formed, from the area of epizone to mesozone is characterized by an increase in activity of tectonic stress, manifestation of the magmatism, which enhances regeneration from the host rock of the ore material and its transportation to the zone of sediment as part of metamorphic and post-magmatic fluids [7].

In the initial periods of this stage quartz and quartz-carbon veins are formed due to intensive transfer of migration-capable forms of silica with alkaline solutions. The silica forms can be in equilibrium in a wide range of temperatures and pressures. After cleaving during the processes of diagenesis and increasing dynamometamorphism from the source rocks, silicic acid gel migrates into the zone of tectonic unloading filling the rock structural defects with variety on the morphology (such as cracks, brecciated areas, dehydration cavities and voids, contraction cracks, etc.).

Table № 1. The ratio of colloidal (cluster) and ionic (atomic) gold in ores of Bakyrchik deposit

Samples Nos	Results of pyro-alkali analysis [12]					Results of Assay test, in g/t	
	Quantity of gold in a sample, in g/t						
	1. Colloidal (cluster)	2. Atomic (ionic)	Total quantity	3. Native gold	% ∑1+2 over 3	Au	Ag
396.	11.52	3.9	15.42	1.90	811	1.85	weak
404.	1.00	1.9	2.9	2.66	109	2.2	weak
667.	0.96	2.0	2.96	1.57	188	2.8	weak
561.	2.88	2.4	5.28	0.92	574	2.8	weak
661	8.32	7.74	16.06	3.99	403	5.0	0.5
503.	0.9	2.3	3.2	2.91	110	2.9	0.5
291.	1.8	23.40	25.2	3.60	700	6.6	0.7
532.	4.42	4.7	9.12	3.80	240	6.5	0.6
393.	5.6	2.0	7.6	4.19	181	2.4	сл.
285.	741.06	5.06	746.12	98.69	756	6.5	0.6
524.	6.4	4.86	11.26	4.82	234	4.8	0.4
267.	14.4	4.2	18.6	4.80	387	4.8	сл.
520.	8.00	2.25	10.25	4.27	240	7.9	0.8
668.	10.88	21.84	32.72	5.00	654	5.0	0.5
286.	3.74	32.0	35.74	5.11	699	5.7	0.6
463.	2.70	3.60	6.30	5.29	119	5.3	0.6
655.	3.42	2.45	5.87	3.23	182	7.00	0.7
460.	0.9	6.24	7.14	5.41	132	5.4	0.6
640.	6.4	2.35	8.75	4.81	182	5.0	0.6
435	15.2	-	15.2	7.04	216	5.6	0.6
380.	8.8	3.3	12.1	6.95	174	5.7	0.6
633.	5.2	4.7	9.9	1.25	792	6.2	0.6
290.	18.6	28.16	46.76	6.38	733	6.0	0.6
643.	15.2	28.0	43.2	15.07	287	6.2	0.6
622.	7.28	10.8	18.08	9.67	187	6.3	0.6
453.	8.5	2.3	11.8	7.15	165	5.9	0.7
531.	9.12.	1.6	10.72	4.60	233	7.1	0.7
391.	12.6	1.95	14.11	2.89	488	6.6	0.7
588.	10.4	21.84	32.24	4.27	755	6.4	0.6
632.	18.24	13.22	31.46	5.28	596	5.4	0.5
666.	6.08	2.45	8.53	6.61	129	7.0	0.7
630.	1.00	21.84	22.84	3.96	577	6.2	0.6
627.	38.8	2.15	40.95	7.42	552	7.3	0.7
672.	8.36	17.34	25.71	10.37	248	7.4	0.7
337.	1.2	16.66	17.86	7.41	241	2.2	weak
528.	8.5	2.10	10.60	3.09	343	8.5	0.8

Further evolution of silicic acid gel firstly results in formation of opal, and then as the thermodynamic level of epigenetic processes rises, in its gradual recrystallization to chalcedony and then to quartz.

In the presence of source rock carbonate material it is transferred in the form of true solutions together with silicic acid gel. However, the stability of carbonates compared with silica taking into account their different forms of migration (true solutions for the first and colloids for the second) results in the fact that carbonates are transported to short distances from the source rock and settle out in conjunction with silica in the form of quartz-carbonate veinlets. The analysis of development of such veinlets in various gold deposits indicates that the area of their distribution is limited by the source rocks.

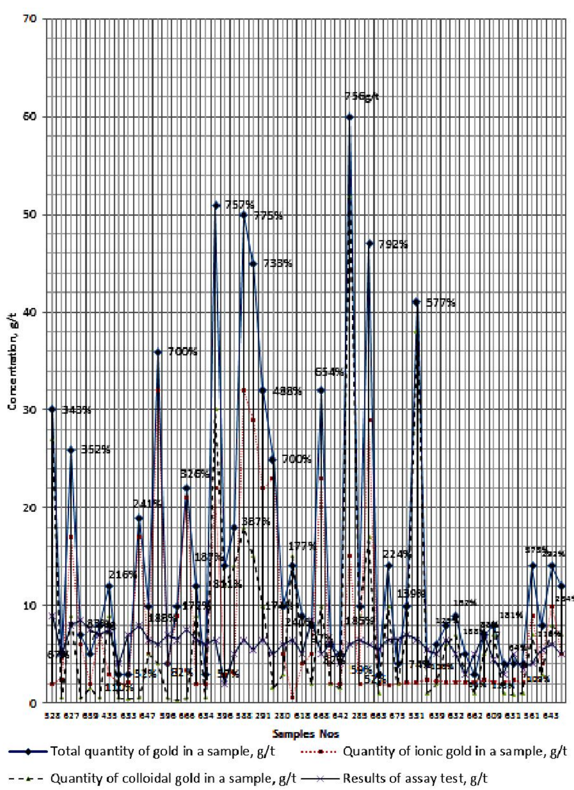

Fig. 4. The ratio of colloidal (cluster) and ion (atomic) gold in the ore of Bakyrchik field [12]

Less frequently quartz-carbonate veins are found among ore bodies of gold deposits of gold-sulfide-quartz geological and industrial type. There properly carbonate veins may be developed with well-formed crystals of calcite formed.

With increase of thermodynamic parameters of progressively developing processes that are characteristic for mesozone, the ore deposits are depleted gradually by migration-capable (ionic, cluster, colloid, etc.) gold with increase in the proportion of gold native phase (**Table # 2** and **Fig. 22 in Part 1**).

Table № 2. The ratio of native gold in the ores of Akbakai, a gold-sulfide-quartz deposit [12]

Nos	Quantity of gold in a sample, in g/t				
	Atomic (ionic)proto-cluster	Colloidal (cluster)	Native gold	Total	%% of native phase in the total amount of AuAu
1	2	3	4	5	6
1.	1.04	6.49	0.45	7.98	5.64
2.	1.34	0.80	2.60	4.74	54.85
3.	2.56	9.36	2.10	14.02	14.98
4.	1.0	0.50	1.70	3.20	31.25
5.	1.0	14.90	4.75	20.65	23.00
6.	1.5	3.02	7.20	11.72	61.43
7.	1.79	10.08	-	11.87	-
8.	1.60	27.36	-	28.96	-
9.	1.00	4.86	12.30	18.16	67.70
10.	1.42	3.52	9.60	14.28	67.20
11.	1.16	2.56	2.80	6.52	42.90
12.	1.08	3.52	5.91	10.51	56.32
13.	0.38	14.08	11.20	25.66	43.60
14.	0.37	15.26	-	15.63	-
15.	1.54	11.86	6.40	19.80	32.30
16.	2.32	6.85	27.30	36.48	74.80
17.	0.96	27.20	-	36.48	-
18.	1.10	10.42	6.90	18.42	37.50
19.	3.20	10.88	18.50	32.58	56.80
20.	0.90	21.40	6.30	28.60	22.00

Among the most important elements, i.e., stabilizers that contribute to the formation of ore bodies on gold deposits with a widely manifested native phase, Te and Se **[2]** deserve special attention. Cd, Bi, Sb, etc. may play the same role, but it should be clarified by laboratory experiments. For the various fields of the type described only certain elements (or groups) listed above would have the stabilizing value, however, heir influence on the process of gold formation would be identical.

Role of stabilizers of the ore process with an example of tellurium was explained by us through laboratory experiments that showed that with presence of small quantities thereof in ore solutions there appear a transfer of gold and silver in the form of simple or complex compounds **with the mandatory presence of lead.**

With the passage of such fluids through the zone of influence of the anionic group elements (such as sulfur) the sulfate complexes are destroyed with formation of galena and native gold settling out, containing a strictly specific amount of silver. Thus, it is not accidental that in all the studied deposits of gold-sulfide-quartz geological and industrial type the constant ratio of gold to silver is observed in native gold **[5]**.In other words, every gold deposit is characterized by a specific average fineness of gold.

The only difference is in the cation environment where gold and other noble metals would be transported by hydrothermal ore-bearing solutions. The presence of a particular stabilizer in ore-bearing fluids would influence the complexity of mineral composition of the ore deposits.

Systematization of the results of our research on gold deposits subject to:

1. - extensive development of globular and framboidal forms of sulfides consisting of a specific set of ore components in the ore-bearing strata and ore deposits in the fields of gold-sulfide and gold-sulfide-quartz formations;
2. - unifiedevolution of silica under the scheme: silicic acid gel → opal → chalcedony → quartz in formation of the quartz-vein matrix, as well as zones of quartz, stockworks, cementation, brecciation, etc., regardless of different geological commercial types such objects belong to;
1. - monotonous nature of the carbonaceous material in the ore, the identification of microorganisms, including diatoms in opal-chalcedony atgold-sulfide quartz and epithermal deposits, and finally;
2. - extensive development of the cluster forms of the initial fixation of the ore material - **convinces us that**the **gold objects of the geological industrial types under consideration were formed based upon a single scheme** (**Fig. 19 of Part 1**) **with the formation of a single gold ore column (a unified gold ore subformation)** (**Fig. 5**) **[1, 2, 3, 6]**.

Moreover, cluster forms primarily fixated in rocks play animportant role as a source of the noble metals in the ore process. Upon reaching the thermodynamic parameters of the environment of ore deposition of certain levels the clusters are destroyed and the precious metals contained in clusters are released into the migration-capable state.

The evolution of noble metals forms is completed by building "second", "third", and higher orders (metal-metal) clusters out of these forms **[13, 14, 15, 16]**. In our understanding, such clusters are four and eight nuclear formations of noble metals around an atom of lead in the central part and in the presence of atoms of tellurium, selenium, bismuth, and, possibly, cadmium (when being transported to the unloading zone along with gold and silver, and also metals of the platinum group). This noble metals clusters form is the most likely one to fix such elements and transport them during formation of compact high-grade ores of gold-sulfide - quartz type with maximum development of the native phase (the highest degree of organization of gold mining process).

On the basis of the established unified geodynamic model of noble metals deposits formation of three main geological and industrial types **[2, 6, 7]**, **where a proto-cluster (colloidal forms) of stratiform type is the main source of ore material, we concluded that the gold-ore process evolution is unified, regardless of the deposits formational type, and discovered a fundamentally important metallogenic regularity of gold.**

Such regularity comes down to the fact that gold deposits, being a product of interconnected geological and ore-generating processes, are rather anomalous structural and real field of the Earth crust, than a general pattern.

Deposits formation may be summarizedin a two-step process. Firstly, the relatively poor ore accumulation of stratiform type with varying degrees of concentration is formed mainly in cluster form on the confined area (usually in the presence of submarine fluids) **[6].**

BASIC DIADRAM OF UNIFIED GOLD ORE COLUMN

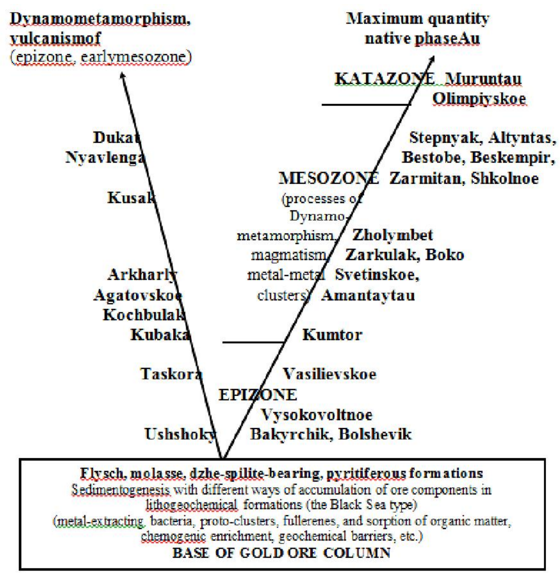

Fig. 4. Basic diagram of the unified gold column (single gold-bearing formation) with the ranking of the major studied gold-ore fields

Then, based upon the first step and due to mechanical and thermal, i.e. dislocation and metamorphic (tectonic and metamorphic) effects, ore material remobilizes, it is transported to favorable structural defects in the earth crust with silicic acid gel in the form of chloride, hydrate, oxide, thiosulfate etc. complexes, is concentrated with the help of process stabilizers (Te, Bi, Se, etc.) and only in some exceptional cases the deposits are formed. Based upon the proposed model we justified the unity of the gold deposit formation processes.

Based upon the proposed model we justified the unity of the gold deposit formation processes. This resulted in a conclusion that numerous geological industrial types (in modern understanding) represent different erosion sections of the abstract unified "gold column" on the modern denudation surface **[17]**.

We purposefully presented our understanding of gold deposits formation in the main geological and industrial types from the standpoint of "cluster" estimate of the ore material source in a schematic form.

This resulted in a conclusion that numerous geological industrial types (in modern understanding) represent different erosion sections of the abstract unified "gold column" on the modern denudation surface. In this case, of course, there are some (that are significant in in some cases) differences of individual gold-ore fields in terms of their structural features, material composition of ores, the nature of metasomatic transformation of ores and ore-bearing rocks, etc. This is due to the geochemical specialization of source and ore-bearing rocks, geology structure of gold fields and deposits, and the specific manifestation of magmatism and metasomatism, etc.

Due to the size of this article we purposefully presented our understanding of gold deposits formation in the main geological and industrial types from the standpoint of "cluster" estimate of the ore material source in a schematic form.

Perhaps, some of the provisions of this Article are surprising, but, in our opinion, it is much easier to measure the expected results and to plan the development of analytical methods for determining the number of cluster and nanoforms of noble metals and technology of their extraction, knowing in advance the increased concentration of noble metals in certain fields and ore-hosting rocks and the reasons there of.

In this context gold-sulfide fields in black shale sequences **(Bakyrchik – Muruntau – Negdaninskiytype)**, epithermal (Arkharly type) deposits and as a whole the areas of the black shale rocks, similar to the Kyzyl and Zhalair-Naiman crumple zones in the East and South Kazakhstan, respectively, are the most promising **[18]**.

In order to resolve these problems it would be necessary to fully decipher the natural processes resulting in the formation of metastable forms of gold, silver and platinum groups of metals (organometallic, cluster, fullerenes with precious metals, etc.) to the native stable phase of all known granulometric classes (from nano-particles to big nuggets).

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