

### **Case Report**

# Genetic Peculiarities, Gold-Containing Volcanogenic Deposits of the Non-Ferrous Metals of the Paleoisland-Arc Structures of the Lesser Caucasus and East Pontides according to Gas-Fluid Inclusions Data and Isotopic Investigations

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#### Abstract

The geological settings of deposits exploration in Turkey, Azerbaijan, Armenia and Georgia have been determined in the article. Most of them can be related to the Kuroko type and they are differed by ore accumulation nature: The copper-zinc deposits formed apparently in the conditions of the deep sea basin are known in Turkey but to the east - we have only epigenetic deposits examples. Moreover Madneuli deposit is developed in Bolnisi region. It is an example of polyformational deposit and therefore is unique. The barite deposits, barite-polymetallic veins, gold-bearing secondary quartzites and large-scale stockworks of copper ores are concentrated in a confined space (known as biclinal structure on large volcano slope).

Gadabey and Alaverdi ore districts are of interest because there are copper, copper-zinc and barite-sulphide ores in the Jurassic volcanic depressions but copper-porphyry deposits - Garadag and Tekhut are known in upstanding wedge-shaped blocks limiting volcanic depressions. All deposits of Gadabey and Alaverdi ore districts including copper-porphyry are commercially important.

The solutions from which the sulphides deposited were similar to seawater according to salinity and were weakly acidic; copper-containing sulphides were formed at maximum 410-390 °C temperatures but barite-sulphide ones - at ~ 280 °C. In all probability the fluid pressure didn't exceed 200 bar in the epigenetic deposits. The stable accumulation of hydrothermal-sedimentary deposits occurred at the bottom of the sea which depth reached 2-3 km.

Apparently the fluid boiling didn't occur and mineral zonation in deposits being similar to modern "ore hills" can be explained by redistribution of the ore-forming components as a result of "hills" destruction, their diffusion from the lower levels up to the upper ones in the process of ores "washout" by ore-bearing fluids.

#### **Keywords**

Pontic-Lesser Caucasus paleoarc, Gold-containing volcanogenic deposits, Gas-fluid inclusions, Isotopic ratio of sulfur and oxygen

### Introduction

The paleoisland-arc fragments and back-arc and intraarc marine paleobasins adjacent to its have been preserved in the central part of the Alpine-Himalayan mountain-fold belt (they displayed in black font in Figure 1). Commercial significant Alpine gold-containing volcanogenic deposits of the nonferrous metals have concentrated within these structures. The most representative gold-containing volcanogenic deposits are known in the strata composing fragments of the Pontic-South Caucasus paleoarc that functioned actively during Mesozoic time in the South Caucasus countries and Turkey. At this time oceanic crust subducted under arc which was marginal part of the Eurasian continent [1-6].

The individual arc segments were differed by their geodynamic development wherefore the heterogeneous

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volcanogenic deposits occurred. Apart from epigenetic deposits there are also known hydrothermal-sedimentary deposits in the west, within Pontids (Turkey). Chaeli deposit (Madenkoy) can be an example of the last ones [7,8].

The above-mentioned geological events are accompanied by: 1) microplates divergence (Triassic-Early Bajocian) and mantle diapirism activation; 2) convergence (Late Bajocian-Early period of Late Cretaceous) with typical island arc volcanism both in the upstanding blocks (islands) and in marine depressions located on South Caucasian-Pontic microplate [2,4,9-12]. During microplates convergence the epigenetic gold-containing volcanogenic deposits of copper and baritepolymetals (Gadabey Bitti-Bulag, Novo-Gorelovka, Gyulyatag, Janyatag, Kyapaz, Alaverdi, Shamlug, Kafan, Akhtala) were occurred firstly (Jurassic period) but copper-porphyry ones as Garadag, Damirli, Tekhut - in Early Cretaceous [13-15]. All of them were detected in Azerbaijan and Armenia. The epigenetic copper, gold, barite-polymetallic deposits such as Bolnisi (Georgia) [16,17], Dagkesaman (Azerbaijan) [15] and etc. formed at early collision stage in activated back-arc volcanic depressions. Volcanogenic-sedimentary copper-zinc ores (Chaeli and others, Turkey) were accumulated in intraarc sea basins (Late Cretaceous), in the west, in the Eastern Pontids and there were formed large-scale epigenetic ores -Murgul deposit and etc. [1,3,7,8,18,19].

1) Slope and uplift of the South Caucasus microcontinent (Jurassic-Early Cretaceous, the Greater Caucasus); 2) Shelf

zone of the Scythian and South-Caucasus microcontinents (Jurassic - Paleogene, the Greater Caucasus; 3) Shelf zone of Anatolian and Daralagez microcontinents (Cretaceous -Paleogene); 4) Shelf zone of Pontian microcontinent (Early Jurassic, Eastern Pontids); 5) Lesser Caucasus ensialic island arc (Bajocian-Early Cretaceous); 6) Pontian ensialic island arc (Cretaceous); 7) Deep water basins of the marginal paleosea (Early-Middle Jurassic); 8) Oceanic zones in allochtonous occurrence; 9) Lesser Caucasus back-arc volcanic depression (Late Cretaceous); 10) Pontian back-arc volcanic depression (Late Cretaceous); 11) Intraplate riftogenic volcanic structures (Eocene-Oligocene, Lesser Caucasus); 12) Eocene volcanic depressions superimposed on pre-collision structures (Pontids, Lesser Caucasus, Anatolids); 13) Young volcanic plateau (Oligocene-Quaternary); 14) Orogenic

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Accepted: November 23, 2022

Published online: November 25, 2022

**Citation:** Abdullayeva S, Baba-zadeh V, Kekeliya S, et al. (2022) Genetic Peculiarities, Gold-Containing Volcanogenic Deposits of the Non-Ferrous Metals of the Paleoisland-Arc Structures of the Lesser Caucasus and East Pontides according to Gas-Fluid Inclusions Data and Isotopic Investigations. Ann Earth Sci Geophys 1(1):13-21

troughs (Oligocene-Quaternary); 15) Terrigenous-volcanic rocks (Dizi series, Devonian - Triassic) intruded by Middle Jurassic granitoids; 16) Pre-Alpine basement of Scythian and South Caucasus microplates (Pre-Cambrian-Paleozoic); 17) Pre-Alpine basement of Anatolid and Daralageza (North Iran microplate, Pre-Cambrian-Paleozoic); 18) Tectonic wedges separating the main geoblocks (over faults and faults, A - determined, B - prospective); 19) Thrusts; 20) Prospective borderline between the Scythian and the South Caucasus microplates (overthrusted); 21) Granitoids (a - Early Cretaceous, b - Late Cretaceous, c - Eocene - Oligocene); 22) Monzonites, syenites (Oligocene - Miocene); 23) commercial minerals deposits; 24) Paleoisland arc fragments.

The most important ore deposits of the Eastern Pontids and the Caucasus: 1) Ashikoy (Cu); 2) Lakhanos (Cu, Zn, Pb); 3) Chaeli-Madenkoy (Cu, Zn); 4) Murgul (Cu, Zn); 5) Urup (Cu); 6) Kti-Teberda (W); 7) Tyrny-Auz (W); 8) Lukhra (Au); 9) Tsana (As, Au); 10) Lukhumi (As); 11) Zopkhito (Au, Sb); 12) Sadon (Pb, Zn); 13) Chiatura (Mn); 14) Filizchay (Zn, Pb, Cu); 15) Kizil-Dere (Cu); 16) Madneuli (Cu, Au, Zn, Pb); 17) Alaverdi (Cu); 18) Shamlug (Cu); 19) Tekhut (Cu); 20) Megradzor (Au); 21) Dashkesan (Fe, Co); 22) Zod (Au); 23) Kafan (Cu); 24) Kajaran (Cu, Mo); 25) - Chovdar (Au); 26) Gadabey (Cu); 27) Garadag (Cu). Microplates: Eurasian paleocontinent: A-Scythian, B-Pontian-South Caucasus (B<sub>1</sub>-East Pontids, B<sub>2</sub>-South Caucasus); Afro-Arabian paleocontinent: C - North Iran.

# Eastern Pontids (Turkey) and Their Ore Content

In the Eastern Pontids volcanogenic deposits were formed in volcanic depressions representing the intra-arc sea basins' parts in Cenomanian-Campanian but plutonogenic copper and molybdenum porphyry - in connection with granitoids formation in the upstanding blocks in relation to depressions. Ashikoy, Lakhanos, Kutlular, Chaeli, Murgul, Cherratepe and Guzeyyayla (Cu, Mo) are commercial deposits. The considerable reserves of non-ferrous metals (15.9 million tons of ore with content of copper - 4.4%, zinc - 6.1%, gold - 0.8 ppm and silver -44 ppm) have concentrated in Chaeli deposit that the geologists call "Pontids pearl". The massive sulphide ores (VMS) form deposit with 920 m length (along strike); it has been traced at 650m depth; its maximum capacity is 100 m. The deposit has been overlapped by low-power layer of jasperoid quartzites (up to 2m) on deposits such as Kuroko in Japan [20,21]. This layer is overlapped by thickness of the interbedded tuffites and basalts covers over which green tuffs with dolomites interlayers containing foraminifera fragments lie. Turkish geologists admit that the deposit has been divided by syn-ore fault in two parts. In this regard the body is composed of two mutually overlapped "lenses". The ore body consists of massive sulphides, the most part of which has been brecciated and a small amount of non-metallic minerals - barite, dolomite, quartz, sericite and kaolinite. Sulphides have been represented by pyrite, chalcopyrite, sphalerite, and in small amounts - by galenite, bornite, tetrahedrite. Yellow (enriched by chalcopyrite) and black (enriched by sphalerite) ores have been determined within the body as well as on deposits such as Kuroko. The sphalerite content in the matrix of brecciated black ores exceeds 10%. The stringerporphyry mineralization has manifested under massive ore's deposit. Hydro-thermal-sedimentary construction which was preserved in Late Cretaceous volcanites as ore deposit was subjected to repeated brecciation under the explosive phenomena influence during hydraulic system function. Clastic ores have been preferably located in the upper parts of the deposit. Massive yellow ores and their powdered differences build-up the lower parts of the body and they are characteristic for the thickest parts of the deposit. The hyaloclastites have been extensively changed: pyritized and kaolinized. There have manifested idiomorphic pyrite emissions and matrix consists of mica and clay minerals. The felsites with rare porphyry emissions of quartz and feldspar have been distributed under hyaloclastites. The quartz-pyritechalcopyrite stockwork superimposed on above-mentioned rocks.

Other type of hydrothermal-sedimentary mineralization was detected in allochthon apparently displaced in paleoisland structure from marginal sea basin of Paleotethys. Rocks forming allochthon are known in reference under the name of "Cure complex"; their age is Triassic (?), they consist of ultrabasic tectonic "plates", intermittent clay shales and basalts covers represented by island arc and oceanic tholeiites as well as by rocks of depleted mantle. According to Ustaömer, Robertson [10], geological pattern similar to Cyprus is observed in places of ore mineralization manifestation: Serpentinized peridotites have been known in the lower part of section over which gabbro, dyke doleritic complex and greenstone changed pillow-lavas of basaltes have been manifested. The lavas including doleritic dykes have been overlapped by clay shales. Copper-containing massive sulphide deposits are located especially under the last ones on the pillow-lavas. It should be agreed with M. Gyuner [3] who added sulphurfur-pyrite deposits "refined" by copper to the Cyprus type VMS.

Epigenetic sphalerite-chalcopyrite mineralization manifested on other producing Pontids deposits. Turkish and West European geologists' works include data on composition and structure of the volcanic strata enclosing the nonferrous metals' deposits of the Eastern Pontids [7] The basement for Late Cretaceous carriers-rocks of deposits are volcanites of andesite composition and terrigenes of Lower - Middle Jurassic age [22], and as well as Upper Jurassic- Cretaceous complex with small copper and gold manifestations.

Late Cretaceous ore-bearing sediments according to [7] were combined into two series: The upper part was represented by basalts alternating with red limestones and "purple tuffs" (probably tuffites); lower part - dacitic tuff breccia and sandy tuffites. The deposits were formed either at the end of the dacitic strata formation or at the beginning of the volcanoes activity whereof the basic lavas flowed out (upper series). Dacite series age according to microfauna has been determined as Cenonian but according to radiometric determination data the age of large granite-granodioritedioritic intrusions of the region corresponds to 30 Ma (Late Oligocene-Miocene) [7]. According to Altun [7] upper series basalts are blanket formations - pillow lavas. Both series

volcanites have crumpled into folds, their axes have NE-SW and NW-SE trending and the first ones are more ancient.

The widespread changes of propylitization type are observed in the dacitic series rocks and sulphide stringerporphyry mineralization - in places of quartz-sericitic metasomatites manifestation. Massive hydrothermalsedimentary deposits have been located on dacitic tuffs (probably, on tuffites) and they are overlapped by purple tuffs. The concordant lenses of massive ores with small sizes as well as gypsum horizons have been determined at basalt series bottom. Manganese minerals have characterized for the marginal parts of the ore deposit of Chaeli deposit.

According to data Akçay, Arar [8] the bimodal volcanites, where VMS are located, are associated with large calderas and siliceous domes. VMS were known in Murgul, Cherattepe, Kutlyuler, Kotarakdere, Khrzit and Lakhanos deposits.

The archival and published material shows that massive ores of the nonferrous metals of Pontids have formed on the seabed of deep-water basins and ore deposits have represented "ore hills" up to diagenetic transformations of sediments. The sea basins in all probability were intra-arc and their bottom was undergone rifting in Late Cretaceous, as evidenced by volcanites composition as well as basaltes dikes cutting both ore deposit and the upper basalts and purple tuffs. Rocks overlapping Chaeli ore deposit have not changed practically except for the diagenetic transformations.

It is noted Akçay, Arar [8] that well-defined bedding is characteristic for Chaeli clastic ores; the ores consist mainly of angular and subrounded sulphide's fragments (sphalerite, pyrite and chalcopyrite). The pyrite fragments have framboidal and colloformic structures. Most probably clastic ores are formed as a result of the destruction of "sedimentary" and redeposition of the last ones on the slope and at the ore hill foot (like submarine colluvium).

The massive ores of deposit are gold-bearing: Gold occurs in sphalerite as inclusions in size of 200  $\mu$ . Researchers can see indistinct vertical zonation (from top-downward) in the ore deposit: sphalerite-galenite-barite-chalcopyrite; pyritechalcopyrite-clays; pyrite-chalcopyrite-quartz. Pyrite crystals sizes are increased with depth. Clastic ores thickness increases in the southward where ore hill paleoslope has located apparently. There aren't stockworks under sedimentary ores while stringer-porphyry ones are located under the yellow ores in the north. Some of them have economic value.

It has been determined that according to chemical characteristics the ophiolite complex basalts relate to the spreading zones formation in the region of Cyure, in Ashikoy-Taykondu deposit [19]. It is assumed that the spreading zone has located in the back-arc basin in the Early Jurassic.

The examples of stockwork-vein deposits reminding of copper ores of Madneuli (Georgia) are Lakhanos and Murgul connected with Late Cretaceous volcanites in Pontids. Stockwork of sphalerite-pyrite-chalcopyrite composition has manifested in dacitic stock in Lakhanos. The stringer-porphyry mineralization has concentrated in the area of quartz-sericitechlorite metasomatites development. Murgul deposit is occupied a geological position similar to the Lakhanos. Here stockwork of pyrite-chalcopyrite ores has been bounded from above by quartz-ferruginous (jasperoid) formations where gypsum lenses have been located on their level.

Ore-bearing lavas of dacites have been eroded and overlapped discordantly by Campanian-Maastrichtian volcanites. Hydrothermal-sedimentary deposits of "black" and "yellow" ores were known in Kyzylgaya region near Murgul [18] for which colloform banded and framboidal textures were characterized. Here the ore-hosting rocks with an angular discordance have overlapped by andesite-dacitic lavas.

In conclusion it should be noted that gold occurrences for example Bekhsesik [22] and Maradit [18] in the Late Cretaceous volcanites as well as in Eocene quartz diorites are known in the Eastern Pontids. The commercial value of gold occurrences has yet to be determined.

# Bolnisi Ore District (Georgia) and its Ore Content

Cretaceous volcano-tectonic depression of Bolnisi ore district was laid in the back-arc residual sea basin at the end of convergence and finally it took shape at the beginning of collision of the South Caucasus and Iran lithospheric microplates [1,2,4]. Depression is filled by Albian-Campanian volcanogenic-terrigenous deposits within which we have defined three complexes [16,17,23]. Lower precollision (Albian-Turonian) is composed of the submarine terrigenousvolcanogenic sediments with rare horizons of andesite lavas and at the base - marlaceous limestones. Volcanoes necks of fracture type being healed by diorite bodies are mapped out inside the lower complex. Magma- excurrent structures for ground siliceous volcanites were the junctions of earlier and later sub latitudinal disturbances of NE trending. Volcanic structure subsidence was occurred after the ignimbrites and felsic acid volcanites outflowing. Ore-bearing elements are synvolcanic dome-shaped "bulges" formed in places of radiodacite extrusions squeezing-out on major volcanic edifices slopes. Extrusive domes (Madneuli), mediumsize collapse caldera (David-Gareji), lava domes (Darbazi, Mushevani) are characterized for development fields of the acidic and medium-acidic effusives.

The average complex (Coniacian-Santonian) (preferably rhyodacite composition) is ore-bearing; it has been formed as a result of activation of five central type volcanoes at least in subaerial conditions and it consists of volcano-facies responding to vent-near vein zones (breccia ignimbrites, blocky tuffs, explosive breccia with ore mineralization, extrusions and lava domes) and zones of slope and foot (mainly different fragmental tuffs of dacite-rhyolite composition, tuffites, lahars, lavas of rhyolites and ignimbrites). A characteristic peculiarity of the complex is squeezed-out lava domes on the volcanoes slopes under which ore accumulations are observed.

The upper volcanic complex was formed most likely in Late Cretaceous. It is a contrast - basalt-andesite-rhyolite; relics of three central type volcanoes are defined within it.

The granodiorites and granodiorite-porphyries occupying the central part of the volcanic depression basement have been related to complex as comagmates. From our point of view they are "responsible" for formation of copper-gold mineralization of the region. Firstly only barite ores have been exhausted on the largest Madneuli deposit but today there are extracted copper and gold ores. From our point of view there are combined different age copper, barite-polymetallic and gold (in secondary quartzites) mineralization; on small Tsitelisopel deposit - copper and gold, on Sakdrisi deposit - gold and barite-polymetallic; on David-Garejin deposit barite, barite-polymetallic and gold-silver. On the example of Madneuli it can be seen that ore accumulation has been preceded by metasomatic column formation stage, its upper parts are occupied by monoquartzites-solfataric formations, lower parts - by quartz-sericite metasomatites, but flanks and deep horizons - by propylites. On Madneuli two ore levels are clearly distinguished under the lava domes screen: upper level - barite and barite-polymetallic, and lower - copper-sulphide. The gold-bearing quartzites "bodies" have manifested on upper and partly lower levels.

It is also noted that commercial volcanogenic deposits have been located in the upper parts of the effusive sedimentary rocks' blocks of Turonian-Santonian in Bolnisi region, in the places where last ones are complicated by extrusive and lava domes. The blocks are limited by faults of NW and NE trending which are magma- and ore excurrent. On the Madneuli deposit the extrusions and lava domes have been squeezed out according to destructions' systems which form "ring" structure as a whole. Under rhyodacites lavas spreads the explosive breccias transformed into secondary quartzites, quartz-hydromica metasomatites and propylites with chlorite were formed as a result of hydrothermal "collapse". It is important to emphasize that the tuffites untouched brecciation have been subjected to propylitization wherein one can be seen their primary bedding traces. On the open pit we can see (its eastern part, the horizon- 957m) tectonic contacts (the disturbances with clay gouge) of propylitized tuffites with intensely silicified and impregnated sulphides of the explosive breccia. Due to our field investigations it was confirmed that Madneuli volcano-domed structure was located on Dalidag paleovolcano slope formed besides pyroclastolites of andesite-dacites as well as by covers of ignimbrites and rhyodacites lavas. Near Madneuli it is known the following ore-bearing volcanic structures: 1) David-Gareji-barite-polymetallic caldera type where lacustrine sediments overlapped by ignimbrites are mineralized and 2) Sakdrisi gold-bearing defined by steep NE disturbance along which the effusives of rhyodacites and tuffites transformed into secondary quartzites. The commercial value of Sakdrisi deposit was proven by last year's research works (21t of gold at average gold grade - 2-3 ppm). Relatively poor copper stringer-porphyry ores are exhausted on Madneuli at present time.

We carried out a large volume of thermobarogeochemical investigations on Bolnisi region's deposits. According to previous research data [17,24] two-phase gas-fluid inclusions homogenized at 320-370 °C (maxima - 350-420 °C) in quartz

of copper-sulphide ores; in quartz of copper-zinc ores - at 280-300 °C; in barites of barite-polymetallic ores - at 260-270 °C, and in barites of barite ores - at 120 °C (Table 1).

According to cryometric investigations of fluid inclusions the salinity of solutions that deposited copper and polymetallic ores, was low and equal to ~ 40 gram equivalent of NaCl per liter of solution. The solutions were chloride-sulphate, potassium-sodium and contained nitrogen and  $CO_2$ . There were also determined heavy hydrocarbons and methane, their total concentration didn't exceed 4 mol.%.

Data on isotopic composition of sulfur are the following:  $\delta^{34}$ S values are slightly deviated from meteoritic standard in sulphates;  $\delta^{34}$ S values range from + 10 to + 20‰ in most sulphates (Table 2). Data on isotopes of carbon, hydrogen and oxygen are varied and can be interpreted in favor of the participation of both meteoric and magmatogene water in ore formation process. So, the values of  $\delta^{13}$ C are grouped around values of -7.1 ± 2.1‰ and +0.3 ± 1.6‰ in calcite and fluid inclusions; the isotopic composition of fluids hydrogen ( $\delta$ D water) varies within -70 -90‰, and recent region water from -50 to -70‰;  $\delta^{18}$ O ranges from +10.35 to + 9.25‰ (Table 3) in quartz of copper ores and it ranges from -1.07 to -1.53‰ in barite of barite-polymetallic ores.

The authors have data on the isotopic composition of strontium and concentrations of rubidium and strontium in rocks located near the volcanogenic deposits. It emerged that the basalts of Bolnisi region ( $^{87}Sr/^{86}Sr = 0.704910$ ) could be products of the undepleted mantle differentiation but the rhyodacites could arise in the lower parts of crust on Murgul deposit (Turkey) ( $^{87}Sr/^{86}Sr = 0.707739$ ); rhyolites of Madneuli deposit - in the lower parts of the upper crust ( $^{87}Sr/^{86}Sr = 0.710269$ ). Europium ratios (for rhyolites - Eu/Eu\* = 0.65-0.68, ignimbrites - 0.52-0.58) determined in them, as well as rocks enrichment by light REE and large ionic lithophylic elements indicate crustal source of rhyolites and ignimbrites magmas [25]. Higher Zr/Y ratios in these rocks indicate that (for dacites, - 9.5-11.2; for rhyolites - 2.7; for basalts - 3.7-4.1) probably we have dealing with more mature paleoarc [14].

# Gadabey Ore District (Azerbaijan) and its Ore Content

Gadabey ore district as one of the largest regions in the Caucasus with a long history of gold-copper-producing industry, with its gold-copper-sulphide and gold-copperporphyry mineralization is the most typical for the development of Upper Bajocian volcanogenic complexes [13-15].

It is located in the axial line of large Shamkir horst-uplift complicated by the Upper Jurassic-Lower Cretaceous Ajikend-Dashkesan superimposed trough. Its disjunctive framework consists of two systems of faults: Early, northwest and later, the north-east. Main Gadabey fault zone tracing in the southwest region belongs to the first of them.

A special place in the ore district structure is given to its central part where well-known Gadabey gold-coppersulphide ore field controlled by volcano-dome structure and

Table 1: Thermometric analysis results.						
No	Samples numbers	Freezing temperature of gas-fluid inclusions	Temperature of gas-fluid inclusions homogenization			
1	Madneuli 1	-0.9	320			
2	" 2	-1	318			
3	" 3	-1.3	325			
4	" 4	-1.2	320			
5	" 5	-1	322			
6	" 6	-1.6	325			
7	"7	-1.2	320			
8	" 8	-0.8	315			
9	" 9	-0.9	318			
10	" 10	-2.1	328			
11	" 11	-1.9	325			
12	" 12	-0.9	315			
13	" 13	-1.2	320			
14	" 14	-0.9	325			
15	" 15	-0.9	325			
16	" 16	-1 2	325			
17	" 17	_1	215			
17	" 17	-1 2	215			
10	" 10	-1.2	219			
19	Lo Cadaboy Azori 4E 1	-1.2	200			
20	Gauadey - Azeri 45-1	-1.0	200			
21	2 " 2	-1.2	202			
20	3	-0.9	302			
21	4	-0.9	300			
22	" 5 " C	-1.1	305			
23	" b	-0.8	298			
24	" / " 2	-0.8	295			
25		-1	302			
26	" 9	-1.2	305			
27	" 10	-0.8	300			
28	Garadag - Azeri 38-1	-1.5	310			
29	" 2	-1.2	305			
32	" 3	-1.4	305			
33	" 4	-0.9	305			
34	" 5	-0.7	300			
35	" 6	-1.3	310			
36	"7	-1.4	345			
37	Kyapaz-Azeri-Kap 3 -1	-0.7	300			
38	" 2	-1	320			
39	" 3	-1.1	315			
40	" 4	-1	315			
41	" 5	-0.9	310			
42	Akhtala 1	-1.7	248			
43	" 2	-1.6	245			
44	" 3	-1.5	245			

### Table 2: Sulphur isotopes ratio in sulphides.

No	Deposits, N° samples, minerals	δ <sup>34</sup> S, ‰
1	Madneuli, 9, pyrite	3.3
2	Madneuli, 9, pyrite	3.6
3	Madneuli 32, pyrite	-1.2
4	Madneuli 32, pyrite	-1.3
5	Madneuli, 33, chalcopyrite	-1.4
6	Madneuli, 35, chalcopyrite	2.5
7	Madneuli, 40, pyrite	2.2
8	Madneuli, 40, pyrite	3.3
9	Madneuli, 41, pyrite	2.7
10	Gadabey, Az KS 3 PY, pyrite	1.5
11	Gadabey, Az 51 PY, chalcopyrite	2.6
12	Garadag, Az 1008a PY, pyrite	2.0
13	Bitti-Bulag, Az A 12 2PY, pyrite	-2.3
14	Bitti-Bulag, Az A 12 enargite	-4.0
15	Gadabey, Az E 413, sphalerite	4.2
16	Novogorelovka, AzF 431, sphalerite	4.8
17	Gyulyatag, Az 63 1PY, pyrite	-1.4
18	Damirli, Az62 1 PY, pyrite	-1.0
19	Paragachay, Az 85 3PY, pyrite	0.9
20	Gadabey, Az 731 PY, pyrite	1.2
21	Garadag, Az 1008b PY, chalcopyrite	2.5
22	Gadabey, BMFR 1, sphalerite	7.2
23	Alaverdi, 1, chalcopyrite	2.6
24	Shamlug, 2, chalcopyrite	0.9
25	Shamlug, 3, chalcopyrite	0.3
26	Tekhut, 9, chalcopyrite	1.4

Table 3: Oxygen isotopes ratio in ores quartz.

No	Samples description	δ¹8Ο, ‰
1	Madneuli- 32, pyrite-chalcopyrite ores	9.1
2	Madneuli- 33, pyrite-chalcopyrite ores	8.1
3	Madneuli- 34, pyrite-chalcopyrite ores	9
4	Madneuli- 35, pyrite-chalcopyrite ores	9.2
5	Madneuli- 33, pyrite-chalcopyrite ores	11.4
6	Garadag - Azer 1008-v, copper-porphyry ores	10.2
7	Garadag - Azer 1008-B, copper-porphyry ores	11.3
8	Garadag - Azer 1008-e, copper-porphyry ores	11.1
9	Bitti-Bulag, Azer A13-3, pyrite-enargite ores	9.4
10	Damirli - Azer 62-2, copper-porphyry ores	12.8
11	Paragachay, Azer 53-3, copper-molybdenum ores	9.7
12	Gyulyatag - Azer 63-3, pyrite-chalcopyrite ores	12.8
13	Janyatag - Azer 611, pyrite-chalcopyrite ores	6.9
14	Gadabey - Azer Vb-1-pyrite-chalcopyrite ores	8.9
15	Tekhut-9, copper-porphyry ores	10.05

complicated by radial faults. There are located Bitti-Bulag, Ertepe (Novo- Gorelovskoe), Maskhit and other deposits and ore manifestations of gold-copper-sulphide, gold-copperarsenic, gold-copper-polymetallic ores representing Gadabey ore-magmatic system in total.

The ore bodies have been confined to the upper strata horizons of rhyolites and rhyodacites; they have turned generally into secondary quartzites. Ore bodies' part has concentrated in main volcanites of Early Bajocian. These strata were intruded by dikes connected with the establishing andesite-basalt-plagiorhyolitic and basalt-andesite-daciterhyolitic formations and also by comagmated with them Mesozoic plagiogranites (Atabek-Slavyan intrusion) and gabbro-diorites, quartz-diorites and etc. (Gadabey intrusion). They can be joined in a volcano-plutonic association according to all features complex.

The main ore bodies of Gadabey deposit (Karl-stock, Fedorov-stock) have been confined to the most uplifted blocks parts at the intersection node of half-ring fault with submeridional disturbance stretching along the central part of the deposit. In the post-ore stage during renewed tectonic motions the formed deposit blocks were removed with respect to each other and there were thrown down a part of Fedorov-stock.

General morphology and structural peculiarities of the Garadag ore field as the central part of Gadabey ore district determine Maarif-Garadag ore-controlling (boundary) fault of northwest (submeridional) trending and also the diagonal ore supplying faults to which crushing and shearing zones, small zones of eruptive breccias, subvolcanic and hydrothermal formations have been confined. Zones of increased fracturing, adjacent to these faults were place of Late Jurassic (Early Cretaceous?) stork-works of gold-bearing Cu-Mo porphyry mineralization. Due to dynamic stresses the space between the ore-controlling faults represents highly-fractured block where the fractures are located perpendicular to oresupplying (Garadag) fault. Their direction is sublatitudinal or northeast. These fractures network contains subvolcanic dikes suites of quartz-diorite porphyrites and veinlet-vein mineralized zones.

Maarif and Maskhit ore fields with analogous deposits of Garadag mineralization group are determined within Maarif-Garadag ore-controlling fault. The development of copperporphyry ores is also assumed at deep horizons of copperarsenic deposit of Bitti-Bulag.

Gadabey deposit was formed at temperatures of 295-305 °C according to the temperature data of gas-fluid inclusions homogenization (Table 1).

## Alaverdi Ore District (Armenia) and its Ore Content

In Alaverdi region the copper-containing stock-like ore bodies concentrated in Late Bajocian horizons of aleurolites and sandstones but the vertical vein-like - in rhyodacite hyaloclastites and effusives of andesite-basalts of Early Bajocian age. The vein bodies were marked by narrow bands of quartz-sericite-chlorite metasomatites. Moreover the article's authors have investigated Tekhut copper-porphyry deposit located near Alaverdi that is situated in Shnokh-Kokhb tonalite intrusion of Early Cretaceous age.

According to K-Ar method data, phaneric intrusions' age is Neocomian ( $133 \pm 8$  Myr/million years). "Background" (phaneric) igneous rocks as well as porphyry bodies are appreciably sodium and high-aluminous and relate to tonalites group [23].

According to the data of Yaroshevich [9], who investigated the gas-fluid inclusions and fluids whereof ore material falling out occurred, they were chloride-sodium-potassium highly concentrated (50-20 wt% or 30-40 g/kg on NaCl base); mineral formation occurred in the interval of 400-220 °C, the pressure could exceed 100 kbar; sulphide sulfur was characterized by low dispersion of  $\delta^{34}$ S values on Tekhut deposit and approached to meteoric standard; sulfate sulfur weighted at 13.5‰ (anhydrite) with respect to the sulphide. Oxygen isotopic composition of water inclusions ranges from +3.0 to -4.1‰ that can indicate magmatic water dilution (fluids) by meteoric ones.

Alaverdi ore district covering the extreme south-western part of the Lok-Garabag tectonic zone - paleoisland-arc structure fragment is mainly composed of Bajocian-Bathonian and Late Jurassic-Early Cretaceous volcanic complexes in its central part.

Alaverdi volcanic structure was formed at least as a result of three powerful phases of volcanic activity. The fracturetype volcanoes functioned and lavas of andesite-basalts and in lesser degree - basalts flowed out on the surface at the beginning (Early Bajocian). In our opinion these formations are pre-subducted, formed during divergence of the South Caucasus and North Iran lithosphere microplates. There were formed two volcanic depressions filled with lavas of andesitedacites, their breccias and pyroclastolites on the wide lava fields of previous out-flows as well as filled with rhyodacites, their pyroclastolites and hyaloclastites at later phase of the central type volcanoes activation in Late Bajocian. Akhpat plagiogranite and Akhtal granodiorite-porphyry intrusions exposed in the most eroded parts of the volcanic necks. The latest phase of the Middle Jurassic volcanism manifested apparently in Bathonian. For example, vent and near vent facies of local volcano represented by blocky and agglomerate breccias of andesite-basalts are mapped in the western part of Alaverdi ore field. These facies eroded intensively while volcano grew. This led to the shelves' formation of stratified Colluvium on its eastern slope.

According to common geological data there are four groups of endogenous deposits of non-ferrous metals in the region. It is assumed that barite-polymetallic ores confined to the apical part of Akhtal intrusion are the earliest ones. Alaverdi copper deposit was formed apparently in Late Bajocian-Bathonian but Shamlug - in Late Jurassic as massive copper-sulphide stocks were screened by Late Jurassic rhyodacites here. The above-mentioned copper-porphyry Tekhut deposit showing paragenous connection with the Early Cretaceous tholeitic complex is the youngest mineralization of subduction stage of paleoisland-arc structure development. Due to available data (temperature of gas-fluid inclusions homogenization in ores quartz [17,24] Alaverdi deposit was formed at temperatures of 205-280 °C, Shamlug - at 185-210 °C and Akhtal - at 170-200 °C. There were determined N<sub>2</sub>, CO<sub>2</sub> and a small amount of water taken from gases in inclusions. The high concentrations of SO<sup>2-</sup>, Ca, Na have been determined in water extracts from the gas-fluid ores inclusions of Gafan deposit that is an analogue of Alaverdi. Moreover the considerable concentrations of heavy metals together with ordinary cations (K, Na, Ca, Mg) were revealed in water extracts. The isotopic composition of sulphides sulfur is practically similar to meteoritic sulfur composition in deposits of Gadabey and Alaverdi regions. Pyrites of early quartz-pyrite stage of mineral formation are characterized by  $\delta^{34}$  S = 4.9‰ value but at chalcopyrite-pyrite-sphalerite stage -1.2-1.5‰ that can be explained by sulphides sulfur lightening due to <sup>34</sup>S accumulation in barite and anhydrite. The isotopic composition of chalcopyrite sulfur - 2.6‰ and sphalerite - 4.2 and 7.2‰ shows stage ore formation of Gadabey deposit (Table 3). The isotopic composition of oxygen in quartz taken from copper deposits of Gadabey ore district was equal: +8.9 - 11.3‰, Mekhman ore district (Azerbaijan) +6.9 – 12.8‰, Paragachay copper-molybdenum deposit (Daralagez block, Azerbaijan) - + 9.7‰, Alaverdi ore district + 1.3 ± 0.5‰ (Table 3). Water hydrogen from fluid inclusions (Alaverdi deposit) is characterized by  $\delta D$  values being equal to -75 ± 0.5‰. To this must be added the new data on isotope ratios of sulphides sulfur and oxygen taken from quartz on Bolnisi, Gadabey and Alaverdi regions deposits (see Table 2 and Table 3). The analyses were carried out in USGS laboratory (Denver, USA). The temperatures of gas-fluid inclusions homogenization in quartz taken from epigenetic deposits of the Lesser Caucasus were determined in this laboratory. The temperatures of fluid inclusions homogenization taken from copper ores on Madneuli were equal to 315-325 °C, on Gadabey gold-coppersulphide deposit - to 295-305 °C, on Kyapaz gold-sulphide

deposit - to 300-320 °C, on Akhtala polysulphide deposit - to 245-250 °C, on Tekhut copper-porphyry deposit - to 325-330 °C, on Garadag - to 340-345 °C, (Table 2).

Isotopic ratios of oxygen taken from copper and coppermolybdenum ores' quartz on Madneuli, Gadabey, Bitti-Bulag, Gyulyatag, Janyatag, Damirli, Garadag, Paragachay and Tekhut deposits (Table 3) can testify in favor of the magmatogenic water participation in ore formation process [26]. The ratios of sulfur isotopes taken from sulphides are various on epigenetic deposits of Lesser Caucasus Island paleoarc. This work authors consider that a big part of sulfur had a magmatogenic source.

### Conclusion

From the above-mentioned one can be inferred that the ore deposits of paleoisland-arc structures in particularly the Pontic-Lesser Caucasus arc it should to be expected in the following geological conditions: in the craters and on paleovolcanoes slopes located in volcanic depressions; ore bodies in the siliceous parts of volcanogenic-sedimentary strata or above them (in the case of hydrothermalsedimentary deposits); generally the ores are overlapped by main volcanites but there may be exceptions - for example Madneuli deposit; we often observe gypsum accumulations on the flanks of ore bodies and in their hanging wall; mineral composition is practically identical on all copper deposits. Madneuli deposit of Georgia is an exception where different stage gold, barite-sulphide and copper ores spatially bring together in one volcano-structure. Pay attention to the orebearing strata composition: a) Thin chemogenic-sedimentary deposits are changed from top to bottom by hyaloclastites, accumulations of underwater Colluvium, tephritic turbidites, lavas of dacites and andesites in Gadabey and Alaverdi ore districts in the section of Middle Jurassic stratum; ore-bearing stratum is overlapped by Late Jurassic complex representing alternation of andesite-basalt sheets with different fragmental carbonate-containing tuffites; b) In the Bolnisi region - ore-bearing stratified sediments (tuffites with rare dacites sheets or crater-lacustrine sediments) overthrusted by ignimbrites (ground formations) and rhyodacites lavas; c) Chaeli volcanic structure that includes hydrothermalsedimentary ores is composed of supraore basalts (pillowlavas) alternating with limestones and "purple" tuffs as well as with propylitized dacites. Massive sulphide ores occur on the last ones under which the stringer-porphyry copper ores have been manifested in quartz-chlorite-hydromicaceous metasomatites. Volcanic structure represents a large caldera that has located at the bottom of the deep water basin.

The ores of Lesser Caucasus deposits are clearly epigenetic: stringer-porphyry and vein mineralization has been superimposed on hyaloclastites and tuffites in Gadabey and Alaverdi ore districts; the stringer-porphyry copper mineralization has been manifested in silicified tuffites in Bolnisi as well as the disseminated gold and barite-sulphide mineralization as veins and flat deposits - in secondary quartzites. The Chaeli deposits' ores are similar to "ore hills" of modern mid-ocean ridges and rifting zones of the marginal seas.

The ore bodies have been located in cover of narrow bands of quartz-serite-chlorite metasomatites in Gadabey and Alaverdi ore districts; vertical metasomatic column has manifested in Bolnisi region: At the upper part - secondary quartzites (subsurface solfataric changes), and at the lower part - higher-temperature silicification (quartz-chloritesulphide metasomatites with small quantity of sericite). Ore metasomatites have been surrounded by propylites cover. On Chaeli (Madenkoy) type deposits under hydrothermalsedimentary deposits the stringer-porphyry "yellow" ores have been surrounded by quartz-hydromica metasomatites in dacites underlying them against the background of regional propylites. The last ones mark the advance ways of hydrothermal solutions to the sea paleo-floor.

The stocks and narrow veins-lenses (northern lenses group in Gadabey) of copper ores have revealed in Gadabey and Alaverdi ore districts; the high-volume copper stockworks have preferably manifested in Bolnisi region; thick deposits of lenticular massive sulphide ores consisting mainly of pyrite, chalcopyrite and sphalerite together with stockworks have revealed in Eastern Pontids.

In our opinion these differences have been determined by different geodynamic regimes of individual crustal blocks of paleoisland-arc structures.

Thermobarogeochemical investigations have shown that the main copper and gold deposits as one of the major associate ores components were formed in the similar RFF (Reserve Fuel Facility) conditions despite the difference in ore deposition mechanism and therefore they refer to single genetic volcanogenic deposits class.

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