

ARTICLE

# Volcanogenic Deposits of Non-ferrous Metals in the Lesser Caucasus and Eastern Pontides

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ABSTRACT

The paper presents brief characteristics of geological environments of ore deposit occurrences in Turkey, Georgia and Armenia. They can be attributed to Kuroko-type deposits, being distinguished by the character of ore accumulation. To the west, in Turkey, there are epigenetic and hydrothermal-sedimentary copper-zinc deposits that were formed in deep restricted basinal settings. An example of the latter is the Chayeli deposit. To the east, in the Caucasus, we have predominantly only epigenetic deposits. Besides, in the Bolnisi mining district (Georgia) there is the Madneuli deposit which represents an example of polyformational deposit. Here, within the restricted territory, have been concentrated: barite, barite-polymetallic, gold-bearing secondary quartzite, large-scale stockworks of copper ores. Judged by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, some volcanites which are spatially associated with ores, might have been products of the “differentiation” of undepleted mantle, or other magmas that were generated in the lower part of the earth crust.

In the Alaverdi ore district in Armenia, there are Jurassic volcano-depressions that host copper, copper-zinc and barite-sulfide ores. All the deposits of the Alaverdi district, porphyry copper including, contain economic reserves of ores.

On the basis of available literature material and our own data, there has been created a mental-logical geological-genetic model of volcanogenic deposits.

## 1. Introduction

Within the central part of the Alpine-Mediterranean-Himalayan mountain-fold belt there are fragments of ancient continental-margin structures – paleoisland arcs and backarc and interarc paleobasins. It is within these structures that economic volcanogenic deposits of non-ferrous metals have been concentrated. Among the most

important geological events that have conditioned the tectonic setting of this segment of the mountain-fold belt are: (1) the partition of the South Armenian-Iranian microplate from the north margin of Gondwana in Permian-Triassic time and its accretion to the active Pacific-type continental margin of the Eurasian continent<sup>[1-4]</sup>; (2) the opening of a rift in Late Triassic-Early Jurassic that was later trans-

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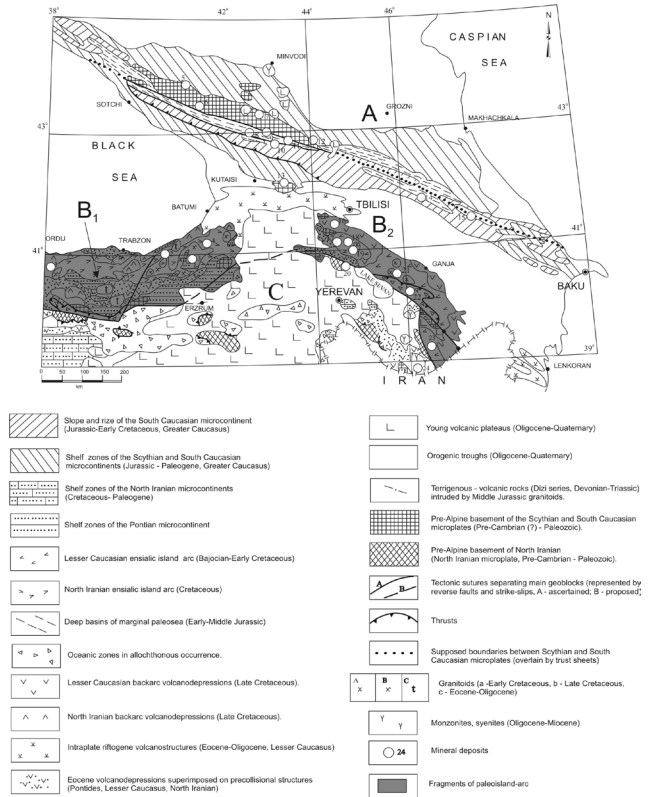
formed into a branch of the Neotethys; (3) the obduction of oceanic complexes in the Senonian that heralded the “death” of the Tethys ocean [2]. The further development of the region during the late Alpine cycle was conditioned by the interaction of the Scythian and South Caucasian-Pontian microplates (active paleomargin of the Eurasian continent) with the northernmost lithospheric blocks of Gondwana (Kirşehir, East Taurus, Daralagez and some others). At present, the boundaries between these mobile blocks of the earth’s crust (sometimes referred to as terrains) are represented by large fault zones commonly with evidence of significant dip-slip and strike-slip displacements and are marked by basitic and ultrabasic ophiolitic complexes and tectonic melange (Figure 1).

It should be noted that the above-mentioned geologic events of the Alpine cycle were accompanied by the following processes: (1) the divergency of microplates (crustal blocks) in Triassic-Early Bajocian and the activation of the processes of mantle diapirism; (2) the convergence of the microplates in late Bajocian-earliest late Cretaceous accompanied by specific island-arc volcanism revealed in both uplifted blocks (subaerial environments) and restricted deep basins that existed within the South Caucasian-Pontian province. The maximum activity of this islandarc volcanism occurred in the South Caucasus in the Bajocian-late Jurassic and in the Pontides – in the Turonian-Santonian. A. Yilmaz and his co-authors [5] pointed out that in the geodynamic evolution of the western and eastern parts of the islandarc system there are obvious distinctions. It was also shown that the start of the collision between South Caucasian and Daralagez blocks happened in the Coniacian whereas that between Pontides and Anatolides – in the Campanian [2,6].

During the convergent stage, within the active continental margin of the Eurasian plate appeared thermoanomalies whose location was generally controlled by tectonic factors; these anomalies commonly coincide spatially with areas experienced maximum tectonic deformations and are characterized by increased fracturing and faulting. It is these areas that reveal enhanced magmatic and volcanic activity and wide development of hydrothermal processes. The submarine environments that dominated in the region during the early Alpine cycle (middle Jurassic – late Cretaceous) were conducive to the formation and preservation of volcanic-hosted mineral deposits.

At first, in the Jurassic time, epigenetic volcanogenic copper and barite-polymetallic deposits were formed (Alaverdi, Shamlug, Kafan, Akhtala) which were followed in the early Cretaceous by the Tekhut-type porphyry copper deposits. All the above deposits are located within the Armenian part of the Lesser Caucasus. In the activated

deep restricted volcano-depressions epigenetic copper, gold-bearing and barite-polymetallic deposits of the Bolnisi-type (Georgia) were formed. To the west, in the Eastern Pontides, in the late Cretaceous intra-ark basins are developed volcanic- and sediment-hosted copper-zinc ores of the Chayeli-type as well as the large-scale epigenetic mineralization (Murgul and some others).



**Figure 1.** Distribution of main metal-bearing deposits within the geological structures of eastern Turkey and the Caucasus.

Main metal-bearing deposits of the Eurasian active paleomargin: 1. Aşıkoy (Cu); 2. Lachanos (Cu, Zn, Pb); 3. Chayeli – Madenkoy (Cu, Zn); 4. Murgul (Cu, Zn); 5. Urup (Cu); 6. Kti-Teberda (W); 7. Tirni-Auz (W); 8. Lukhra (Au); 9. Tsana (As, Au); 10. Luchumi(As); 11. Zopkhito (Au,Sb); 12. Sadon (Pb, Zn); 13. Chiatura (Mn); 14. Filizcay (Zn,Pb,Cu); 15. Kizil-Dere (Cu); 16. Madneuli (Cu,Zn, Pb, BaSO<sub>4</sub>); 17. Alaverdi (Cu); 18. Shamlug (Cu); 19. Tekhut (Cu); 20. Megradzor (Au); 21. Dashkesan (Fe, Co); 22. Zot (Au); 23. Kafan (Cu); 24. Kadjaran (Mo, Cu). Microplates: Eurasian paleocontinent: A – Scythian, B – Pontian – South Caucasian (B<sub>1</sub> – Eastern Pontides, B<sub>2</sub> – South Caucasus); Afro-Arabian paleocontinent: C- North Iranian

The deposits reveal distinct relationships with the specific lithogeodynamic complexes of paleoislandarc constructions. Some of them (for example, some deposits in Turkey) create integral spatial-temporal associations with

enclosing volcanites; the others were formed somewhat later than the enclosing rocks, but the time of their formation remained within the limits of the formation of volcanic-host complexes.

It is generally known that the majority of ore deposits are located within the uppermost 10 km-thick layer of the earth's crust, the highest position (0-1 km) being occupied by the deposits of non-ferrous and noble metals that are the subject of the present paper. As examples we consider some deposits in the eastern Pontides (Turkey), the Bolnisi (Georgia) and Alaverdi (Armenia) mining districts, and also a porphyry copper deposit of Tekhut (Armenia) located within an uplifted block adjacent to the Alaverdi group of volcanogenic deposits.

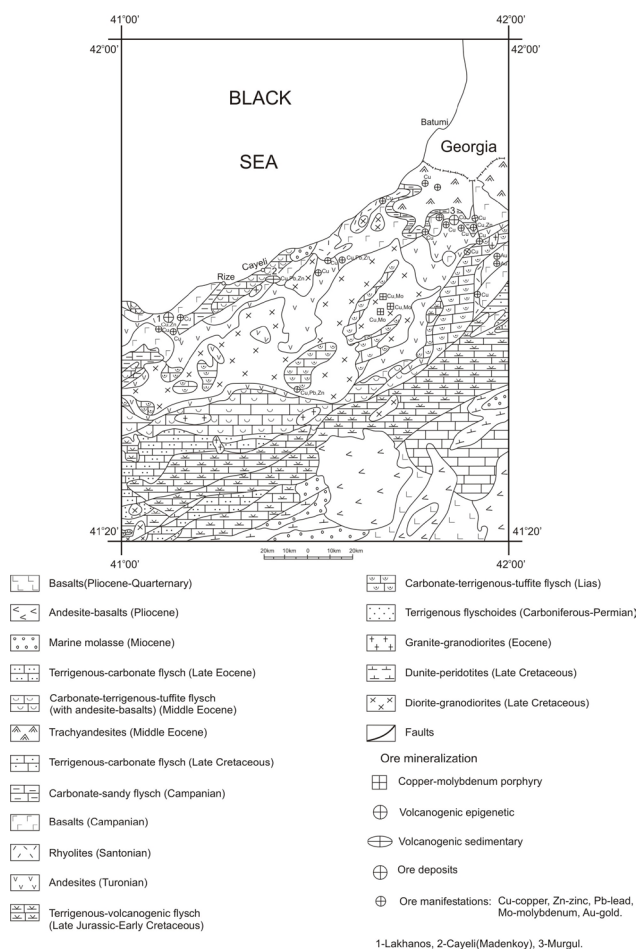
## 2. Ore Deposits of the Eastern Pontides (Turkey)

During the last decades it has been established that the volcano-plutonic activity in the Eastern Pontides (Turkey), which developed during the Alpine cycle as a typical island arc, resulted in the formation of significant volcanogenic and plutonic economic concentrations of non-ferrous metals. The volcanogenic deposits were formed within volcanodepressions which in Cenomanian-Campanian time represented parts of interarc marine basins, whereas the plutonic copper-molybdenporphyric deposits were related to the emplacement of granitoids into uplifted blocks. Important economic deposits here are Ashikoy, Lahanos, Chayeli, Kuttular, Murgul, Cerat Tepe and Guzeliayla (Cu, Mo) (Figure 2). It should be noted that the Eastern Pontides is the only region in the Pontian-South Caucasian paleoisland arc where hydrothermal-sedimentary deposits of non-ferrous ores, such as Chayeli and Ashikoy, have been discovered. The Chayeli deposit (Figure 3), known as a pearl of the Pontides, is distinguished by a very large accumulation of non-ferrous metals with estimated resources of 15.9 million tons of ore averaging 4.4% Cu, 6.1% Zn, 0.8 g/t Au and 4.4g/t Ag. Mining in the deposit commenced in 1994. Massive sulfide ore (VMS) form a body 920 m long along the strike; the body is traced at a depth of 650 m and is still open at depth and along strike. The maximum thickness of the ore-body attains 100m.

Just as in other deposits of the Kuroko type, the Chayeli orebody is overlain by a thin (0.5 to 2 m) layer of jasper-like quartzite which is, in turn, overlain by a sequence of tuffites and basaltic flows. Overlying the basalts are green tuffs interbedded with dolomites that contain fragments of foraminifera fossils.

The orebody is divided, as is proposed by Turkish geologists, by a syn-ore fault into two parts forming two overlapping "lenses". The orebody itself consists of

massive sulfides, mainly brecciated, and of subordinate gangue minerals – barite, dolomite, quartz, sericite and kaolinite. Sulfides are represented by pyrite, chalcopyrite and sphalerite with lesser amounts of galena, bornite and tetrahedrite. As in other Kuroko-type deposits, massive sulfide ores are of two types – yellow ores enriched in pyrite and chalcopyrite and black ores enriched in sphalerite. Sphalerite content in the matrix of brecciated black ores exceeds 10%.



**Figure 2.** Schematic geological map of the uppermost eastern part of the Pontides (Turkey) showing mineralization. Materials used: 1) Geological map of Turkey on a 1:2 000000 scale (1989); 2) Geological map of Turkey on a 1:500 000 scale (2002).

Below the body of massive ores, veinlet-disseminated mineralization is developed. The hydrothermal-sedimentary system which preserved in Late Cretaceous volcanites in the form of orebody, underwent repeated process of brecciation under the influence of explosive (phreatic) activity associated with the functioning of hydrotherms. Clastic ores are dominant in the upper horizons of the deposit. Massive yellow ores and their powder varieties form the lower parts of the orebody and are most typical

of the thickest parts of the deposit. Massive ores overlie hyaloclastites that consist mainly of fragments of felsites and are intensely altered by the processes of pyritization and kaolinitization. Hyaloclastites are underlain by felsites with rare porphyric phenocrysts of quartz and feldspar. All the above rocks are superimposed by a quartz-pyrite-chalcocopyrite stockwork.

Another type of hydrothermal-sedimentary mineralization was found in the allochthone that was removed into the paleoislandarc structure from the marginal sea basin of the Paleotethys. Rocks that form the allochthone are known in literature under the term of “Kure complex”. The complex, aged as Triassic (?), is composed of ultrabasic tectonic slices, interbedded siliciclastic sediments and basaltic flows. According to reference [7] mineralization pattern and geological setting here are similar to those observed on the island of Cyprus – at the base of the section occur serpentinitic peridotites that are successively overlain by gabbro, a diabase dyke complex, and green-stone-altered basaltic pillow-lavas. The section is terminated with a sequence of clays and shales. Copper-bearing massive sulfide mineralization is concentrated in pillow-lavas overlapped by the shale sequence. These data are in accordance with the reference [8] who attributes pyritic deposits enriched with copper to the Cyprus-type volcanogenic massive sulfide (VMS) deposits. Other functioning ore deposits of the Pontides are characterized by epigenetic sphalerite-chalcocopyrite specialization.

In the works of Turkish and West European geologists there is information about the composition and structure of volcanogenic formations that host non-ferrous metal deposits of the Eastern Pontides [9]. The basement for Cretaceous rocks that contain ore deposits is composed of andesitic volcanic rocks and terrigenous complexes of Early-Middle Jurassic age [10], and also of Late Jurassic – Cretaceous formations with insignificant copper and gold mineralization (Figure 2). In the 1960-ies among Cretaceous volcanites 4 series were distinguished: upper dacitic, upper basaltic, lower dacitic, and lower basaltic. Later ore-bearing Upper Cretaceous sediments were grouped into two series [9]: upper, represented by basalts intercalated with red limestones and purple tuffs, and lower made up of dacitic tuff-breccias and sandy tuffites. The deposits were formed after the eruption of dacitic series or at the beginning of functioning of volcanoes that produced basic lavas (upper series). Structurally, the region of copper mineralization is represented by a system of horsts and grabens that are bounded by faults of NE and NW directions. The age of the dacitic series defined by microfaunal data is Senonian, while the age of large granite-granodiorite-diorite intrusions by the data of radiometric measure-

ments is about 30 mil. years (Late Oligocene-Miocene) [9]. Between the upper and lower series there is an unconformity registered by all investigators.

According to reference [9], basalts of the upper series are represented by plateau basalts sometimes showing pillow structure. Volcanic rocks of both series are deformed into folds whose axes trend into NE-SW and NW-SE directions, the first trend being older.

The rocks of dacitic series show widespread alterations of propylitization type; within the areas of development of quartz-sericite metasomatites the sulfide veinlet-dispersed mineralization type is also observed. Massive hydrothermal-sedimentary deposits are hosted in dacitic tuffs and tuffites and overlain by purple tuffs. In the lower levels of the basaltic series there are concordant lenses of massive ores of limited extension, and gypsum horizons. The marginal zones of the ore deposit of Chayeli are characterized by the presence of manganese minerals.

According to some researchers [11], bimodal volcanites which host VMS deposits are associated with large calderas and siliceous domes. VMS mineralization is developed at the ore deposits of Murgul, Cerattepe, Kutluler, Kotarakdere, Hrsit and Lahanos.

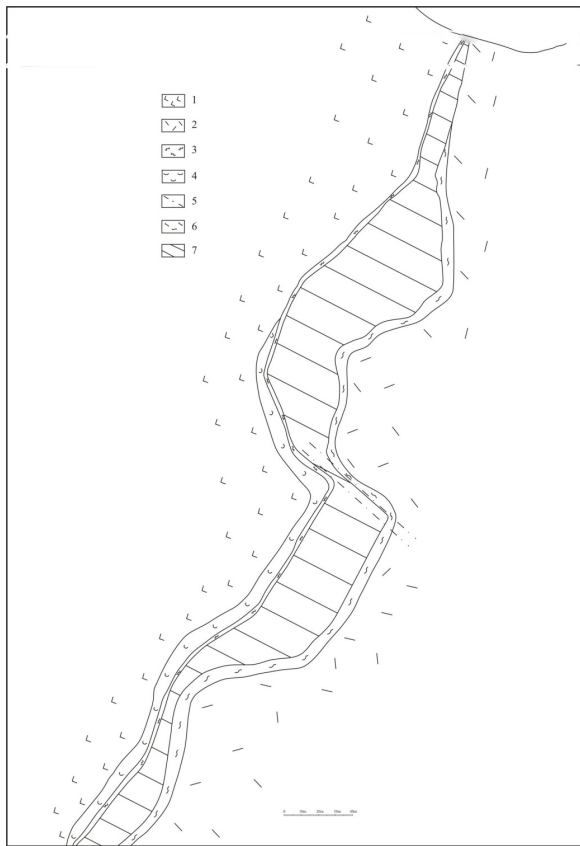
The study of published and unpublished (manuscript) materials shows that massive ores of non-ferrous metals in the Pontides were formed on the sea-floor of deep marine basins and, prior to diagenetic changes of sediments, ore deposits represented the so-called “ore hills”. The marine basins were, most likely, of intra-arc origin in Cretaceous that is confirmed by the composition of volcanites and the presence of basaltic dykes that cut both the ore deposit and upper basalts and purple tuffs. The rocks that cover the ore deposit of Chayeli are practically unaltered, not counting diagenetic changes.

The clastic ores of Chayeli are characterized by well-expressed bedding. The ores are represented by angular or semi-rounded fragments of sulfides–sphalerite, pyrite and chalcocopyrite. Most likely that the “clastic ores” formed as a result of the disintegration of “sedimentary” varieties and their re-deposition on the slope and the foot of the ore hill (like submarine colluvium).

At our disposal there are two analyses of sulfur isotopes (chalcocopyrite +3.1 and sphalerite +4.8) defined in laboratory of the U.S. Geological Survey (Denver, Colorado). We can propose that sulfur from sulfides was derived from a biogenic source. At the deposit of Chayeli quartz-sulfidic veins (Figure 3) that served as ways for ascending hydrothermal fluids are devoid of any appreciable amount of gaseous-fluidal inclusions. The fact probably indicates the considerable depths of the sea during the period of the ore-formation.



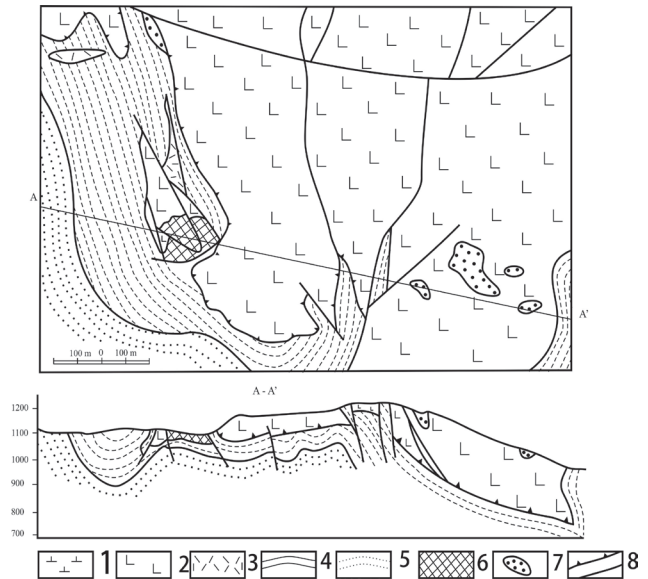
The massive ores are, as a rule, gold-bearing; gold is found in sulfides as grains measuring 200  $\mu$ . The ores often show not clearly-expressed vertical zonation (from top to bottom): sphalerite-galena-barite-pyrite-chalcopyrite; pyrite-chalcopyrite; pyrite-chalcopyrite-clays; pyrite-chalcopyrite-quartz. The size of pyrite crystals increases with depth. The thickness of clastic ores in Chayeli increases to the south where probably was located the paleoslope of the ore hill. Here stockworks are absent beneath the sedimentary ores, whereas to the north, beneath the yellow ores, occurs veinlet-dispersed mineralization which is of economic significance.



**Figure 3.** Section through the ore body of the Chaeli deposit (Madenkoy, Turkey).

Late Cretaceous: 1-basalt lavas; 2- rhyodacites; 3-jasper quartzite; 4-tuffite; 5- synvolcanic faults; 6- hyaloclastites; 7 - ore body of chalcopyrite-pyrite-sphalerite composition (copper > 5%, zinc - 9%). (Graphics courtesy of Turkish geologists working at the Madenkoy mine.

It has been revealed that in the Kure region (North Turkey), at the Ashikoy deposit <sup>[12]</sup> (Figure 4), basalts of the ophiolitic complex should be attributed, by their chemical parameters, to volcanites of sea-floor spreading zones. It is assumed that in Early Jurassic the spreading axis was located in a back-arc basin.

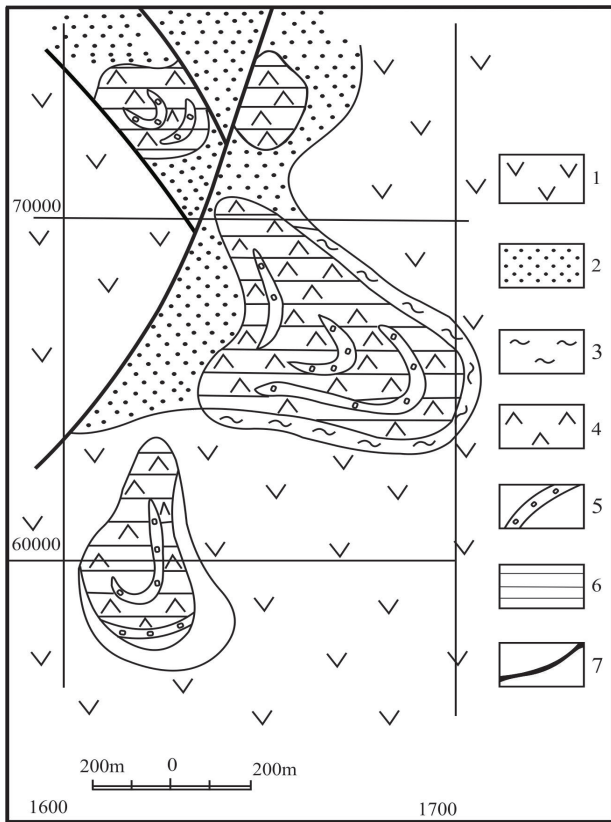


**Figure 4.** Diagram of the geological structure of the Ashikoy deposit (Turkey Geological Survey, 1966)

1. Ultrabasic rocks (in allochthonous occurrence); 2. greenstone altered basalt; 3. dacite; 4. shale; 5. intercalation of sandstones and shales; 6. massive fine-grained pyrite-chalcopyrite ores; 7. iron "hats"; 8. faults: a-thrusts, b-near-vertical.

The examples of stockwork-vein deposits within the Eastern Pontides that have strong similarities with copper ore deposits in Madneuli (Georgia) are Lahanos and Murgul hosted by Late Cretaceous volcanites (Figure 5). At Lahanos, the stockwork of sphalerite-pyrite-chalcopyrite composition occupies a dacitic stock. Here, the veinlet-disseminated mineralization is concentrated within the area of quartz-sericite-chlorite metasomatites. Similar geological conditions are observed in the Murgul deposit. Here, the stockwork of pyrite-chalcopyritic ores is limited from the top by quartz-ferruginous (jasperous) rocks on the level of which gypsum lenses were located. Ore-hosting dacitic lavas are eroded and overlain unconformably by Campanian-Maastrichtian volcanites. Not far from Murgul (Figure 5), at a site of Kizilkajia <sup>[13]</sup> occur hydrothermal-sedimentary deposits of "black" and "yellow" ores with characteristic banding and framboidal texture. Here also, ore-containing rocks are overlain unconformably by unaltered andesite-dacitic lava flows.

Finally, it should be noted that in the Eastern Pontides there are known gold prospects proper, for example Behcecik <sup>[14]</sup> and Maradit <sup>[10]</sup> associated with Late Cretaceous volcanites and Eocene quartz diorites. The economic significance of these prospects is still to be studied and evaluated.



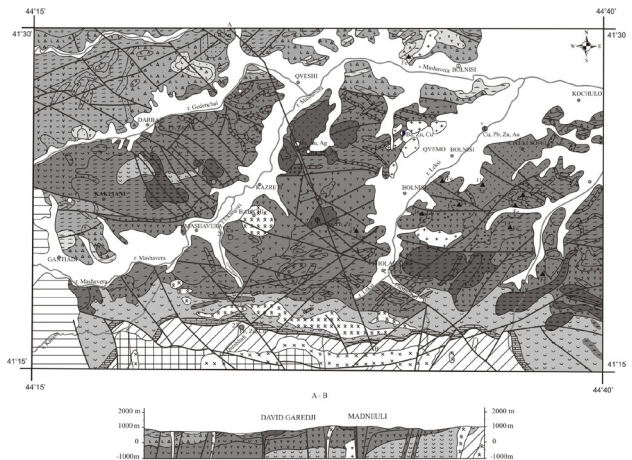
**Figure 5.** Schematic plan of the geological structure of the Murgul deposit (data of the Geological Survey of Turkey, Ankara, 1994).

Late Senonian (Campanian-Maastrichtian) rocks: 1. andesites and dacites; 2. mudstones, sandstones, tuffites, unconformably overlapping mineralized blocks; Early Senonian (Santonian) ore-bearing rocks: 3. siliceous-ferruginous sediments; 4. lavas of dacites and their pyroclastolites (within mineralized blocks brecciated and experienced quartz-sericite-chlorite alteration); 5. gypsum lenses; 6-stockwork-disseminated pyrite-chalcopyrite-sphalerite ores; 7. faults.

### 3. Ore Deposits of the Bolnisi Mining District (Georgia)

The Cretaceous volcano-tectonic depression of the Bolnisi ore district was formed in a back-arc residual sea basin environment at the end of the convergence phase, and took its final configuration at the beginning of the collision between the South Caucasus and Iranian lithospheric microplates. The depression is filled with Cretaceous volcanogenic-terrigeneous rocks within which we distinguish three complexes (Figure 6). The lower, pre-collisional (Early Cretaceous -Turonian), one is composed of submarine terrigenous-volcanogenic rocks, with rare andesitic flows and marly limestones at the bottom.

Within this complex there are necks of volcanoes (mainly of fissure-type) that host dioritic bodies. Majority of vents outpouring subaerial silicious volcanites were located at the intersections of earlier sublatitudinal faults with later NE – SW trending ones. The eruption of ignimbrites and felsic lavas was followed by the subsidence of the volcanic dome-shaped swellings formed as a result of squeezing of rhyodacitic extrusions on the slopes of large volcanic edifices. The areas of acidic and intermediate extrusive rocks are characterized by the development of volcanic cones (Figure 7 and 8), various collapse calderas (David Gareji), lava domes (Darbazi, Mushevani). Earlier works [15] suggest that ore-bearing volcanites on the FMA plot show two independent “differentiation” trends located within the calc-alkaline field. Some rocks are normal alkaline and aluminous andesites, others are rhyodacites. The latter are characterized by the increasing content of  $K_2O$  relatively to  $Na_2O$ , when passing from earlier differentiates to later ones.



Complexes	Facies				Zones of volcanic constructions
	Effusive	Pyroclastic (lava sheets)	Terrigenous (with volcanogenic)	Subvolcanic	
Andesitic-basaltic (Campanian)	Andesitic-basaltic sheets Igneous breccias of rhyolitic composition	Pyroclastic (lava sheets) Agglomerates of basaltic clasts; tuffa, lavas and breccias of basaltic and andesitic-basaltic composition	Agglomerate pyroclastic pyroclastic tuffites	Rhyolites Dacites Andesites Gabbro Diabases	Granoclastic porphyry a-belt and narrow b-slope and foot
Rhyodacitic (Turonian)	Rhyodacite Igneous breccia of rhyodacite composition	Agglomerate pyroclastic pyroclastic tuffites (often with rare siliceous breccias) Agglomerate pyroclastic pyroclastic tuffites (often with rare siliceous breccias)	Panamaite-pyroclastic tuffites Dacites	Rhyolites Dacites	Quartz dacites tholeiitic porphyries a-belt and narrow b-slope and foot
Terrigenous-volcanogenic (Turonian)		Andesitic- basaltic tuffa Pyroclastic tuffites (often with rare siliceous breccias of andesitic lavas)	Limestones and marls		Distant

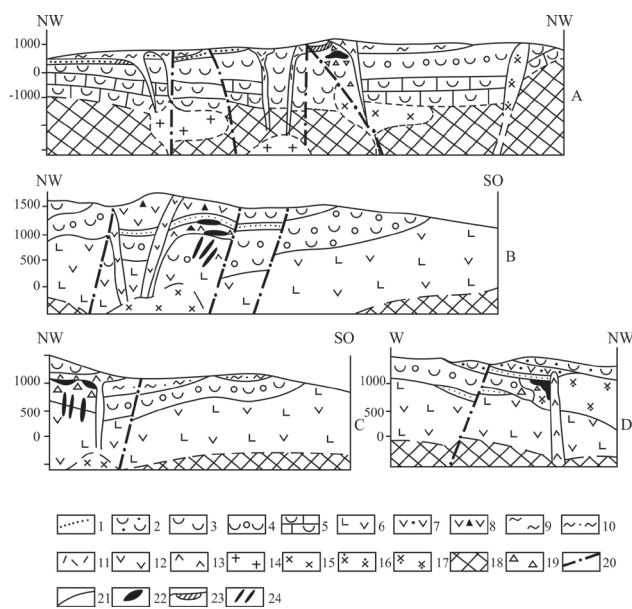
  

Ore mineralizations - Mineral types	
○	Ba ore
□	Ba ore-polymetallic
⊕	Chalcoprite-pyritic
⊗	Auriferous (gold in secondary quartzites)
△	Hematite
⊠	Example of the complex deposit of Madnuli
○/□	Size of mineralization: a-deposit, b-ore manifestation

**Figure 6.** Paleovolcanological map of the Bolnisi district with ore deposits.

List of deposits and ore manifestations: 1. Bektakari - Zn, Pb, Au ore manifestation; 2. Ratevani - Fe ore manifestation; 3. Musafriani - Ba ore manifestation; 4. Darbazi - Zn, Pb, Au,

Cu ore manifestation; 5. Kvemo-Bolnisi – Cu, Ba, Zn, Pb deposit; 6. Tsiteli Sofeli - Cu, Au deposit; 7. David Gareji - Ba, Zn, Pb, Ag, Au deposit; 8. Mushevani - Ba, Zn, Pb, Cu ore manifestation; 9. Abulmulk (Sakdrisi) - Au, Cu deposit; 10. Guzalchai - Fe ore manifestation; 11. Shulaveri - Fe ore manifestation; 12. Bolidari - Fe ore manifestation; 13. Kakliani - Ba, Zn, Pb, Cu ore manifestation; 14. Sarkineti - Fe ore manifestation; 15. Tashkesani - Fe ore manifestation; 16. Darklisi - Fe ore manifestation; 17. Madneuli - Cu, Au, Ba, Zn, Pb deposit; 18. Demursu - Fe ore manifestation; 19. Sangari - Fe ore manifestation; 20. Balichi - Cu, Zn ore manifestation; 21. Samtsverisi - Cu ore manifestation; 22. Kudroi - Fe ore manifestation; 23. Dambludi - Zn, Pb, Cu, Au deposit.



**Figure 7.** Fragments of the Lesser Caucasus ore-bearing volcano structures.

A - Late Cretaceous residual volcano-depression (Madneuli and David-Gareji deposits); B, C, D - Middle-Late Jurassic intrarc volcanic depression (B - Alaverdi, C - Shamlug, D - Kafan deposits).

1. Carbonate-sandy thin horizons; 2. Late Jurassic volcanogenic-terrigeneous flysch; 3. Late Cretaceous andesite-dacite lavas, psammo-psephitic tuffs and tuffites; 4. Late Cretaceous (a) and Middle Jurassic (b, c, d) agglomerate (to block) tuffs, tuffites and lavas of andesite-dacites; 5. Early Cretaceous tuffites, limestones, sandstones, lavas of andesite-dacites and andesite-basalts; 6. Early Bajocian lavas and lavobreccias of andesite-basalts and basalts, tuffites; 7-Middle Jurassic andesite lavas; 8-Bathonian lavas and lavas of andesite-basalts; 9.Late Cretaceous ignimbrites; 10. Middle Jurassic hyaloclastites; 11. Late Cretaceous rhyolites; 12. Middle Jurassic andesite-dac-

ites; 13. Dacites and rhyodacites; 14. Late Cretaceous potassium-sodium granodiorites and granites; 15. Sodium granodiorites; 16. Late Cretaceous quartz diorites; 17. Middle Jurassic quartz diorite porphyrites; 18. pre-Mesozoic foundation; 19. explosive breccias; 20. faults; 21. assumed boundaries of geological bodies; 22. copper ore bodies (stockworks and brecciated stock-like bodies); 23. barite deposits; 24. copper ore vein-like bodies.

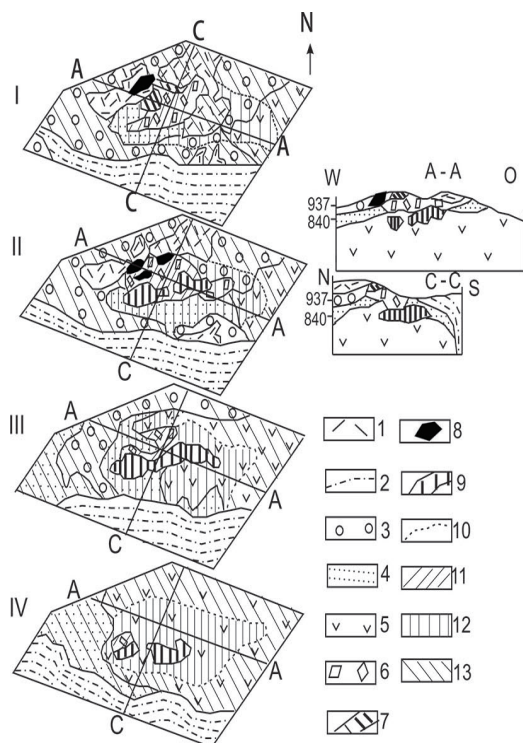
The middle (Coniacian-Santonian) complex is mainly of rhyo-dacitic composition and hosts mineralization; it was formed as a result of functioning, in subaerial conditions, of at least 5 volcanoes of central type. Lithologically it is composed of volcanogenous rocks characteristic of near-vent zones (breccia ignimbrites, coarse-grained tuffs, explosive breccias showing ore mineralization, extrusive and lava domes) and zones of volcanoes' slopes and basement (mainly dacite-rhyolite tuffs, lahars, ignimbrites, rhyolitic lavas). Characteristic features of this complex are parasitic lava domes squeezed on the slopes of some volcanoes, beneath which ore concentrations are often observed.

The uppermost volcanic complex was most likely formed at the end of the Cretaceous and is represented by contrast basalt-andesite-rhyolitic volcanites. Within this complex, relics of three central type volcanoes can be recognized. To this complex belong, as comagmates, granodiorites and granodiorite-porphyrries occupying the central part of the base of the volcanodepression and being responsible, in our opinion, for copper-gold mineralization in the region. In the largest Madneuli deposit (where originally were mined only baritic ores, and now copper and gold-bearing ores are being extracted as well) coexists copper, barite-polymetallic and gold (in secondary quartzites) mineralization of different age. The following ore specialization is observed within smaller deposits: copper and gold – in Tsitelsoveli, gold and barite-polymetallic – in Sakdrisi, and barite, barite-polymetallic and silver-gold – in David-Gareji. The example of the Madneuli deposit shows that the process of ore accumulation was preceded by the formation of a metasomatic column the upper part of which is enriched in monoquartzite-solfataric material, lower part – in quartz-cericite metasomatites, and the flanks and deepest horizons – in propylites. In Madneuli, beneath the screen produced by the lava domes, two distinct levels of mineralization are distinguished: the upper one – barite and barite-polymetallic, and the lower – copper pyrite. The upper and, partly, the lower horizon host bodies of auriferous quartzites.

In the deposits of the Bolnisi ore district, the Georgian geologists have fulfilled extensive thermobarogeochemical and isotope-geochemical investigations. Earlier studies



[16,15] indicate that two-phased gaseous-fluidal inclusions in quartz from copper pyrite ores become homogenous at the temperature of 320-370°C, in quartz from copper-zinc ores – at 280-300 °C, and in the barite from barite-polymetallic ores – at 120°C.



**Figure 8.** Distribution scheme of ores and metasomatites at different levels at the Madneuli deposit (Compiled by the authors, 1986).

1. Rhyodacites; 2. lava breccias and rhyolite lavas; 3. vitroclastic tuffs; 4. intercalation of mixed-clastic tuffites; 5. xenotuffs; 6. explosive breccia. Ore bodies: 7. barite; 8. barite-polymetallic; 9. copper; 10. boundaries of metasomatites; 11. secondary quartzite; 12. quartz-sericite-chlorite metasomatites; 13. propillites. I-Projection of the surface of the deposit before the opening of the quarry; II-projection of the open pit surface (as of 1.01.1985); III-cut 937m; IU-cut 840m.

The solutions were chloride-sulphate K-Na ones containing nitrogen and CO<sub>2</sub>. They contain also insignificant amount of heavy hydrocarbons and methane (less than 4% mol.)

The following data have been obtained concerning the sulphur isotope composition: the average figures of  $\delta^{34}\text{S}$  from sulphides only slightly deviate from standard meteoric values; in most cases values of  $\delta^{34}\text{S}$  range from +10 to +20%. The isotope composition data on carbon, oxygen and hydrogen are ambiguous and may be interpreted in favour of the participation in ore-forming process both meteoric and “magmatogenic” waters. The values of  $\delta^{13}\text{C}$

from calcite and fluidal inclusions are around  $-7.1\pm 2.1\%$  and  $+0.3\pm 1.6\%$ , respectively; the hydrogen isotope composition ( $\delta\text{D}$  of water) from present-day waters of the region – from  $-50$  to  $-70\%$ ;  $\delta^{18}\text{O}$  of quartz from copper ores ranges from  $+10.35$  to  $+9.25\%$ , whereas  $\delta^{18}\text{O}$  of barite from barite-polymetallic ores is within  $-1.07$  and  $-1.53\%$ .

It should be also noted that economically significant volcanogenic deposits in the Bolnisi district are located in the upper parts of blocks made up of effusive-sedimentary rocks of the Turonian-Santonian age where the latter are cut by extrusive and lava domes. The blocks are bounded by NW- and NE- trending faults that serve as magma and ore-channelways. Extrusions and lava domes within the Madneuli deposit were squeezed out along fault systems which collectively form a ring structure. As a result of the hydrothermal “collapse”, under the cover of rhyodacitic lavas there were formed explosive breccias which experienced transformation into “secondary” quartz-hydromica metasomatites and propylites. It is noteworthy that the process of propylitization also affected unaltered tuffites with distinctly expressed traces of their original bedding. Tectonic contacts between propylitically altered tuffites and explosive, intensively silicified and sulphide-impregnated, breccias are exposed in the eastern part of the quarry (horizon 957 m).

Our field works have confirmed that the Madneuli volcanic dome is located on the slope of the Dalidag paleovolcano composed of andesite-dacitic pyroclastolites, ignimbrites and rhyodacitic flows. In the vicinities of Madneuli some other ore-bearing volcanostructures are known: (1) David –Gareji caldera-type barite-polymetallic, within which mineralization is related to lacustrine sediments is overlain by ignimbrites, and (2) Sakdrisi gold-bearing, represented by a steeply-dipping NE-trending fault along which rhyodacites and tuffites are turned into secondary quartzites. Economic significance of the Sakdrisi deposit has been revealed lately as a result of prospecting works (21 tons of gold, with average gold content 2-3 g/t). At present, within the Madneuli deposit relatively poor veinlet-disseminated ores are exploited.

At our disposal there are data on the isotopic composition of strontium and concentration of rubidium and strontium in rocks occurring in the vicinities of volcanogenic ore deposits [17]. According to these data, basalts of the Bolnisi mining district ( $^{87}\text{Sr}/^{86}\text{Sr}$ -0.704910) might have been products of the differentiation of the undepleted mantle whereas rhyolites of Murgul (Turkey) might be derived from the bottom of the earth’s crust ( $^{87}\text{Sr}/^{86}\text{Sr}$ -0.707739) and rhyolites from the Madneuli deposit – from the upper part of the earth crust ( $^{87}\text{Sr}/^{86}\text{Sr}$ -0.7100269). The upper-crust source of magmas that produced rhyolites and



ignimbrites is also substantiated by the specific europium ratios  $Eu/Eu^*$  characteristic of these rocks (0.65 – 0.68 for rhyolites and 0.52 – 0.58 for ignimbrites), and also by their enrichment in light REE and large-ionic lithophilic elements (K, Rb, Ba, Sr) (Table 1) [18].

It seems relevant here to adduce geochemical data on ore-hosting at the Rapu-Rapu deposit in Philippines [19]. (Sherlock et al., 2003). Massive sulfide ores of the Rapu-Rapu deposit are spatially associated with dacites that underwent greenstone alterations. By its characteristics, this deposit can be attributed to Kuroko-type VMS deposit. The geological section of the Jurassic ore-hosting sequence contains, apart from ore-bearing dacites, mafic and quartz-feldspar sedimentary layers. The dacites by their geochemical parameters are similar to dacitic rocks developed in the back-arc Sumisu basin; the basic rocks are characterized by low concentrations of  $TiO_2$  ( $\leq 0.9\%$ ) and Zr (40-50ppm), low ratio Zr/Y (2.5-3.0) and slight enrichment in REE. These rocks are typical representatives of island arc tholeiites and can be compared with Miocene andesite-basalts of the Kuroko deposit and Oligocene basalts of the Fiji arc. Some authors [19] propose that volcanogenic rocks of the Rapu-Rapu deposit enriched in REE were formed at the stage of the active riftogenesis of an oceanic island arc or a Jurassic back-arc basin. It is noteworthy that in the Philippine Islands there is another deposit (Canatuan) that was formed within the immature arc environment that is evidenced by the abrupt decrease of REE concentrations in both acid and basic rocks. Our data (Table 1) show that values of Zr/Y are somewhat higher (9.5-11.2 for dacites, 2.7-6.2 for rhyolites and 3.7-4.1 for basalts) that are characteristic of more matured paleoisland arc.

#### 4. Ore Deposits of the Alaverdi Mining District (Armenia)

In the Alaverdi district (Figure 9), copper-bearing stockwork ore bodies are concentrated in Upper Bajocian aleuolite-sandstone horizons, and vertically-dipping vein-shaped bodies – in rhyodacitic hyaloclastites and andesite-basaltic effusions of Early Bajocian age. Vein bodies are marked by narrow zones of quartz-sericite-chlorite metasomatites. Besides the Alaverdi volcanogenic ore deposits (Figure 10 and 11), the authors also examined the nearby Tekhut copper-porphyry deposit. The Tekhut deposit is located within a Shnokh-Kokhb tonalite intrusion whose age is defined as Late Jurassic-Early Cretaceous. Within the Somkhito-Karabakh zone, besides the Shnokh-Kokhb intrusion, there are a number of smaller intrusive bodies (Tsakhkashat, Dashkesan, Kedabek, Tsav) associated with magmatic porphyric bodies and insignificant porphyry copper bodies. K-Ar dating of the phaneritic intrusions gives a Neocomian age of  $133 \pm 8$  m.y. [20]. Phaneritic magmatic rocks as well as porphyric bodies show essentially sodic and high-aluminous character that attributes them to the group of tonalities [15]. V. Jaroshevich who studied gaseous-fluidal inclusions [21] suggests that fluids from which the precipitation of ore material took place were high-salinity chloride-sodic-potassic (50-20 wt % NaCl equivalent). According to this author, the formation of minerals occurred at temperatures of 400-220°C and pressure perhaps more than 100 bars. Sulfidic sulfur from the Tekhut deposit is characterized by the insignificant dispersion of  $\delta^{34}S$  and approach the meteoric standard. The isotopic composition of oxygen from water ranges between +3.0 and -4.1‰ that may indicate some dilution

**Table 1.** Chemical analyses of magmatic rocks of Bolnisi ore district ( $TiO_2$  - wt %, rare elements - ppm)

Sample №	1-99	2-99	12-99	32-99	7-99	8-99	14-99	15-99	18-99	22-99
Rock	Rhyolites				Basalts		Andesite-basalts		Dacites	
TiO <sub>2</sub>	0.63	0.53	0.44	0.40	1.13	0.99	1.00	1.01	0.23	0.22
Y	44	49	52	58	36	34	141	145	35	33
Zr	224	190	226	222	90	82	388	383	56	57
La	17.97	14.12	19.11	26.71	18.50	19.04	43.42	46.54	8.72	8.59
Ce	38.45	31.20	39.79	57.25	40.06	39.34	88.68	92.61	15.47	15.29
Pr	4.54	4.03	5.19	7.01	5.30	5.04	10.01	11.02	1.80	1.89
Nd	17.86	11.75	18.61	28.31	18.63	14.87	37.19	40.65	5.91	6.79
Sm	4.19	3.46	4.97	5.58	4.34	4.05	8.20	7.00	1.42	1.55
Eu	1.01	0.87	1.32	1.35	1.43	1.39	1.62	1.74	0.42	0.41
Gd	3.64	3.99	5.39	4.66	4.14	3.96	5.72	6.32	1.01	1.06
Dy	3.57	4.12	6.24	3.96	3.63	3.52	4.81	5.02	0.92	0.98
Er	2.47	2.52	4.19	4.39	2.02	2.11	2.91	2.95	0.62	0.56
Yb	2.33	2.19	4.40	2.31	1.71	1.59	2.32	2.38	0.41	0.42
Lu	0.37	0.34	0.66	0.36	0.28	0.24	0.35	0.36	0.07	0.08
La <sub>n</sub> /Yb <sub>n</sub>	5.2	4.6	2.9	7.8	7.5	7.6	12.7	13.6	14	13.5
La <sub>n</sub> /Sm <sub>n</sub>	2.7	2.5	2.3	2.9	2.7	2.9	3.3	4.1	3.5	3.3
Zr/Y	5	4.3	3.8	2.7	4.1	3.7	10.7	10.9	11.2	9.5

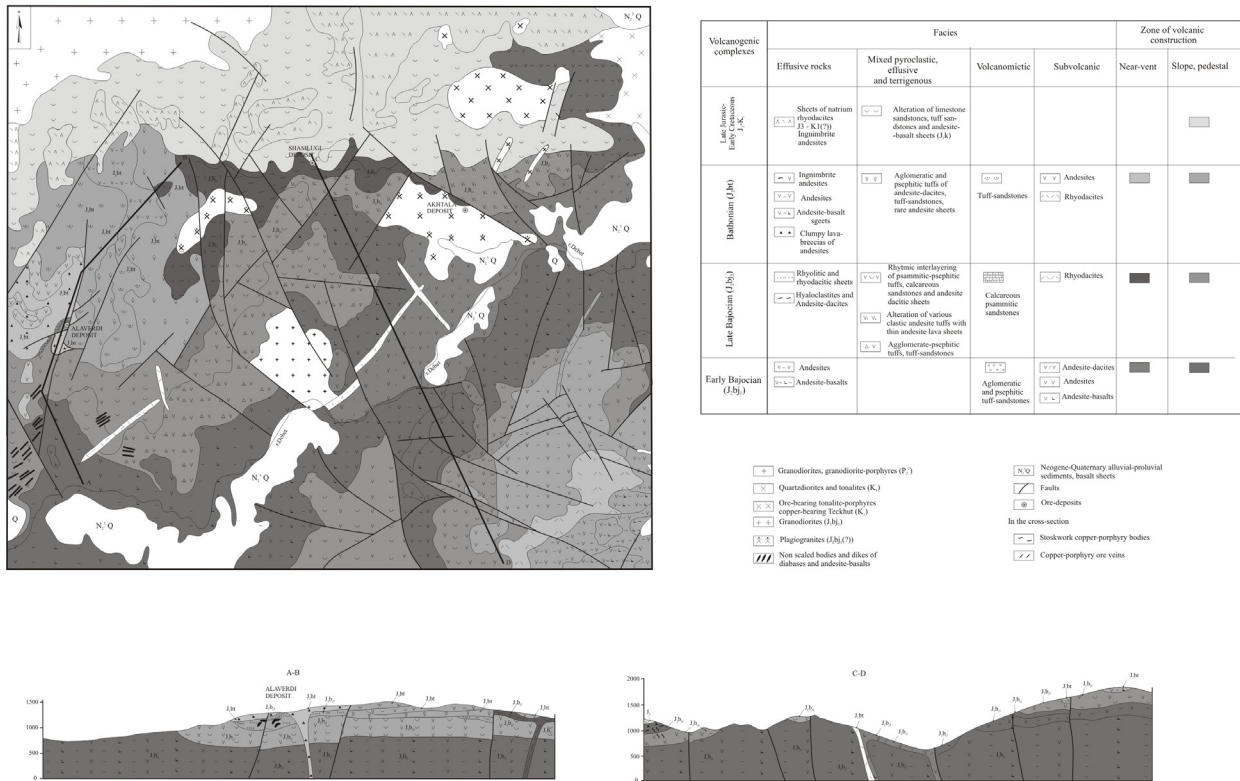


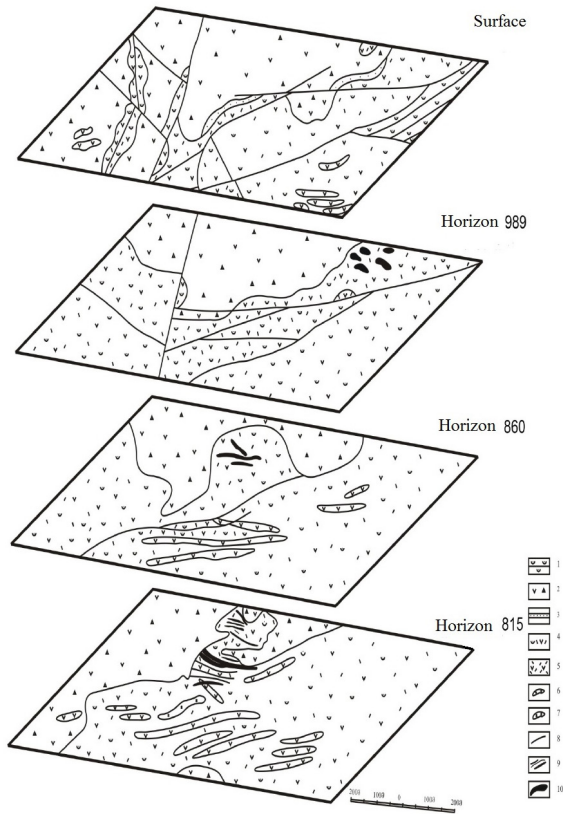
Figure 9. Paleovolcanological map with ore deposits of the Alaverdi district (Armenia).

of magmatic fluids by meteoric waters. The copper porphyry mineralization here is associated with stockworks and dykes of quartz-dioritic porphyries that are developed in the south-western apical part of the Shnokh-Kokhb massif. The contacts of porphyry bodies with the intrusive massif underwent intensive metasomatic reworking – the monoquartz “core” is replaced by quartz-feldspathic metasomatites and quartz-sericite-anhydrite metasomatites.

The Alaverdi ore-bearing region occupying the south-westernmost part of the Somkhito-Kafan tectonic unit – a fragment of a paleoislandarc structure – is composed, in its central part, mainly of Bajocian-Bathonian and Upper Jurassic-Lower Cretaceous volcanic complexes. The paleovolcanological map on a 1:25 000 scale, compiled by the authors shows that the Alaverdi volcanostructure was formed as a result of at least three strong phases of volcanic activity (Figure 7B). At first, in early Bajocian, volcanoes of fissure type were functioning, outpouring lavas of andesite-basaltic and, to somewhat lesser degree, basaltic composition. In our opinion, these lavas are pre-subduction formations generated during the divergent stage between the South Caucasian and North Iranian lithospheric microplates. In late Bajocian, within the areas of previous outpouring, two volcanodepressions formed which were subsequently filled with andesite-dacitic lavas, their pyroclasts and breccias and, at the later stage of functioning

of volcanoes of central type, with rhyodacites and their pyroclasts and hyaloclastites. In the most eroded parts of the volcanic necks there are outcrops of the Akhpata plagiogranitic and Akhtala granodiorite-porphyrific intrusions. The latest phase of Middle Jurassic volcanism occurred, most likely, in the Bathonian. In the western part of the Alaverdi ore field are developed volcanites characteristic of the neck and proximal volcanic facies of a local volcano represented by very coarse breccias and agglomerates of andesite-basalts. As the volcano rose, these volcanites experienced intensive erosion, that resulted in the appearance of the stratified colluviums on its eastern slope. It is noteworthy that on the AFM diagram [15] the trend of “differentiation” of the Upper Bajocian volcanites occupies the transitional zone between the tholeiitic field and calc-alkaline strip, while the trends of later Middle Jurassic volcanites are localized within the calc-alkaline strip. In the study region four groups of endogenic deposits are identified according to general geological considerations. It is thought that the earliest of them are barite-polymetallic ores located in the apical part of the Akhtala intrusion. The Alaverdi and Shamlug copper deposits (Figure 10 and 11) was formed, most likely, in Late Bajocian-Bathonian, while the Shamlug deposit – in Late Jurassic, because here massive porphyry copper stocks are overlapped by Upper Jurassic rhyodacites. The latest mineralization of the

subduction stage of the development of the paleoislandarc system is the above-mentioned Tekhut porphyry copper deposit which reveals the paragenetic relationship with the Lower Cretaceous tholeiitic complex.

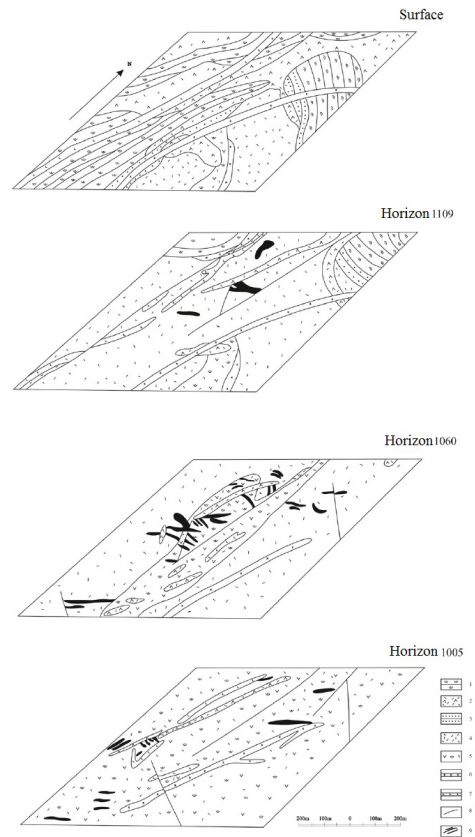


**Figure 10.** Horizontal sections of the Alaverdi deposit.

GPS Coordinates: 44 ° 65 'E, 41 ° 13' N. 1. Tuff sandstone (Bahtonian); 2. andesite tuffs and andesite-basalts (Bahtonian); 3. calcareous tuffaceous sandstones (Bajocian); 4. rough rhythmic interbedding of calcareous tuffaceous sandstones, tuffs and nappes of andesite-dacites and dacites (Bajocian); 5. dacite stocks; 6. andesites; 7. plagioclase porphyry; 8. faults; 9. ore-bearing veins (quartz-pyrite-chalcopyrite); 10. ore-bearing stocks (massive and stockwork ores of pyrite-chalcopyrite composition).

The available data (the temperature of homogeneity of gaseous-fluidal inclusions in ore-containing quartz) [15,16] indicate that the Alaverdi deposit was formed at the temperatures 205-280°C, the Shamlug deposit – at 185-270 °C, and the Akhtala deposit – at 170±20°C. The gases that have been identified in inclusions are represented by N<sub>2</sub>, CO<sub>2</sub> and minor amount of H<sub>2</sub>O. The water extractions from gaseous-fluidal inclusions in ores of the Kafan deposit (which is an analog with the Alaverdi deposit) contain high concentrations of SO<sub>4</sub><sup>2-</sup>, Ca and Na. Besides, the water extractions also contain, along with common

cations (K, Na, Ca, Mg), considerable concentrations of heavy metals. In the deposits of the Alaverdi ore district, isotopic composition of oxygen in quartz from copper deposits proved to be equal to +10,3±0.5‰. Hydrogen of the water from fluidal inclusions (the Alaverdi deposit) is characterized by values of δD equal to -75±0.5‰.



**Figure 11.** Horizontal sections of the Shamlug deposit.

1. Calcareous tuffaceous sandstones (Callovian); 2. rhyodacites and rhyolites (Callovian); 3. calcareous tuffaceous sandstones (upper Bajocian); 4. dacites and rhyodacites (Bajocian); 5. calcareous tuffaceous sandstone, andesite-dacite (Bajocian); 6. granodiorite-porphyry (Lower Jurassic); 7. diabase (Lower Jurassic (?)); 8. tectonic faults; 9. Ore bodies (quartz-pyrite-chalcopyrite composition).

The authors possess new figures on the isotopic ratios of sulfur from sulfides and oxygen from quartz of the rocks of the Bolnisi and Alaverdi mining districts (see Table 2 and 3) (analyses were carried out by our co-author at the USGS laboratory in Denver).

In the laboratory of USGS were also determined the temperatures of homogenization of gaseous-fluidal inclusions in quartz from epigenetic deposits of the Lesser Caucasus. These temperature proved to be: for the Madneuli copper ores – 315-325°C, for the polysulfidic de-



posit of Akhtala (Armenia) – 245-250°C, and for the porphyry copper deposit of Tekhut (Armenia) - 325-330°C. The isotopic ratios of oxygen in quartz from copper ores of Madneuli, Tekhut and Shaumian (see Table 3) may evidence in favour of the participation of magmatic waters in the process of ore-formation<sup>[22]</sup>. At the epigenetic deposits of the Lesser Caucasian paleoisland arc, isotopic ratios of sulfur from sulfides are somewhat ambiguous but the authors assume that majority of sulfur had a magmatic source. It should be noted that these data are generally in compliance with the results of thermobarogeochemical investigations carried out earlier in the Caucasian institute of Mineral Resources (the results are given above).

**Table 2.** Isotopic ratios of sulfur from sulfides

№	Sample description	$\delta^{34S}$ ‰
1	Madneuli 9, PY	3.3
2	Madneuli 9, PY	3.6
3	Madneuli 32, PY	-1.2
4	Madneuli 32, PY	-1.3
5	Madneuli 33, CPY	-1.4
6	Madneuli 35, CPY	2.5
7	Madneuli 40, PY	2.2
8	Madneuli 40, PY	3.3
9	Madneuli 41, PY	2.7
10	Alaverdi 1, CPY	2.6
11	Shamlug 2, CPY	0.9
12	Shamlug 3, CPY	0.3
13	Tekhut 9, CPY	1.4

**Table 3.** Isotopic ratios of oxygen from quartz

№	Sample description	$\delta^{18O}$ ‰
1	Madneuli- 32, copper-pyrite-chalcopyritic ore	9.1
2	Madneuli- 33, copper-pyrite-chalcopyritic ore	8.1
3	Madneuli- 34, copper-pyrite-chalcopyritic ore	9.0
4	Madneuli- 35, copper-pyrite-chalcopyritic ore	9.2
5	Madneuli- 33, copper-pyrite-chalcopyritic ore	11.4
6	Tekhut – 9, copper-porphyry ore	10.05

## 5. Geological-genetic Model of Volcanogenic Deposits of Non-ferrous Metals of Paleoisland Arc Systems

Volcanogenic deposits are concentrated largely within complexes that were formed in the process of interaction of oceanic and continental lithospheric plates. Commonly, this interaction occurs along the active continental margins (subduction zones) where the oceanic crust plunges beneath the continental plate. Active continental margins at various stages of their geologic history underwent dis-

integration and now represent “pilings” of microplates and blocks. As far back as in the 1980s, some authors<sup>[23-26]</sup>, distinguished blocks of the earth’s crust that corresponded to fragments of both active and passive continental margins. Amongst these fragments there are complexes hosting various kinds of ore mineralization. In our case, we deal with Alpine fragments of the Pontian-Lesser Caucasian paleoisland arc which is distinguished by the presence of both volcanogenic-sedimentary and epithermal (epigenetic) ore deposits known in literature as the Kuroko-type deposits<sup>[27]</sup>.

The ore-forming process is identified with the evolution of a high-energy geological system practically open for its moveable components<sup>[28]</sup>. As macroelements of the dissipative fluidal systems may be present: (1) areas of the formation of fluids (this point is however disputable<sup>[29]</sup>); (2) ways of fluid migration; (3) areas of discharge with structural (physical) and geochemical barriers where ore accumulation takes place. In the present work, we propose a mental-logical model of the evolution of ore-generating systems and, in the first place, that part of the latter that is responsible for the precipitation and preservation of ore material. In the model we distinguish those signs and factors that are necessary and sufficient for the functioning of ore-generating processes. For substantiating proposed inferences, besides general geological data, we have presented results of thermobarogeochemical studies and data on isotopic correlations of main ore-forming elements. It is noteworthy that the genetic model should be regarded as a certain abstraction in which the main significance is attached not to the outer resemblance between individuals (ore deposits, ore bodies) but to the standardization of processes proceeding within a system.

It should be noted once more that data on isotopic ratios of strontium and concentrations of rubidium indicate that basalts and dacites developed near the volcanogenic deposits represent products of the “differentiation” of undepleted mantle whereas magmas giving birth to rhyolites of the Madneuli and Murgul deposits had most likely their source in the base of the earth’s crust.

According to geophysical data<sup>[30]</sup>, the roots of magmatic bodies beneath island arcs with mature sialic crust are usually located at depths of 60 km. Since these depths correspond to the very bottom of the crust, many authors<sup>[30-32]</sup> assume the relationship between the magmas of orogenic series and the partial melting of amphibolites.

Usually, beneath (Madneuli) or above (Chayeli) volcanic domes there are evidences of intensive activity of heated fluids – hydrothermally-altered rocks and various kinds of ore accumulations. The idea about the magmatic source of fluids of volcanogenic deposits has lost,

during the last two decades, its attractiveness because of the difficulties related to the necessity of explanation of participation of very large volumes of water in the hydrothermal process. The mechanism of separation of fluids is considered a relatively short-term process. Its “traces” in magmatic bodies are expressed by autometamorphic alterations, and uniform distribution of submicroscopic particles of oxides and sulfides in the crystals of silicates or in the groundmass of rock-forming minerals. Results of isotopic-geochemical studies of volcanogenic deposits give evidence of a significant role of meteoric waters in hydrosystems<sup>[33]</sup>. Experimental works also indicate the insignificant amount of magmatic waters in the hydrosystems, not exceeding 0.0005% of the total mass of water<sup>[34]</sup>.

It is widely known that there is a correlation between ore components and their concentration in ore-containing rocks<sup>[35,36]</sup>. Moreover, the hydrothermally-altered rocks are characterized by the deficiency of metals in the direct closeness to ore accumulations. Experimental works on the extraction of elements from rocks<sup>[34,37]</sup> under the P-T-conditions corresponding to the functioning of fluids also confirm the supposition that ore-containing magmatic and sedimentary sequences may be regarded as a possible source of metals. Hydrothermal solutions with ore elements are similar by their salinity to sea water, but at the same time, they are enriched, at several orders, with Fe, Ag, Pb, Cu and Zn in comparison with the sea water<sup>[38]</sup>. The initial redistribution and exsolution of ore components are related to the conditions of crystallization of magmatic rocks characterized by a certain component composition. Some authors<sup>[39]</sup> identified, in the basalts of mid-oceanic ridges and, earlier, in the siliceous rocks, spherical aggregates of oxidic-ore material of liquid nature. In ore-bearing subalkaline effusive rocks of rift valleys of midoceanic ridges were also found sulfides impregnated in form of small “drops” in clinopyroxene and feldspar<sup>[40]</sup>. In these ore liquates were identified nickel pyrrhotite, sphalerite, chalcopyrite, silver, albite and potassium feldspar.

The further way of migration of ore elements in volcanic environments is conditioned by the involvement of sea and ground (meteoric) waters in the convective flow, in connection with the decreasing of their density due to the heat produced by cooling intrusions<sup>[41]</sup>. The resulting aggressive heated waters acquire properties and composition characteristic of ore-bearing fluids interacting with surrounding intrusive rocks and volcanites.

According to vast material collected on the base of studying the world ocean<sup>[42-44]</sup>, the large-scale ore-genesis is successively realized in the process of: (1) crystallization of magmas; (2) interaction between “aggressive” me-

teoric waters and surrounding volcanites; (3) stable functioning of physical-chemical barriers in areas of discharge of hydrotherms (whether it be the sea floor or the ground surface).

Volcanogenic deposits of non-ferrous metals are characterized by the following features: (1) Both sedimentary-hydrothermal and veinlet-impregnated deposits are related to volcanodepressions. The former are usually located in the axial zones of the depressions whereas the latter occur in their peripheral parts being controlled by extrusive domes.

(2) The component composition of ores reveals dependence on petrochemical peculiarities of ore-bearing volcanites and their comagmatites. Potassium-sodic rhyodacites are usually associated with barite-polymetallic mineralization, whereas andesite-basalts and sodic rhyolites are largely accompanied by the copper-zinc mineralization<sup>[45]</sup>.

(3) The scope of economic mineralization depends on the capacity of ore-bearing depressions (and the volume of volcanites filling them) and on the content of metals in the volcanites<sup>[15]</sup>.

(4) Within the ore knots, ways of migration of fluids are marked by the traces of hydrothermal alterations. Zones of down-going flows are distinguished by argillization of rocks (the presence of hydromica-montmorillonitic and chlorite-montmorillonitic neomineralization minerals); above-intrusion and flank parts of the depressions are intensely propylitized. At barite-sulfidic near-surface and shallow deposits the up-going branches of therms (the discharge zones) are marked by explosive breccias in which hydrothermal alterations are represented by secondary quartzites and quartz-adular-sericite (hydromica) metasomatites. The host rocks of veinlet-impregnated copper and copper-zinc ores, as well as the volcanites underlying hydrothermal-sedimentary mineralization are transformed, by the up-going branches, into quartz-chlorite (with sericite) metasomatites often containing anhydrite and gypsum.

Recently experimental works (5-29 days of duration) reconstructed conditions under which the formation of hydrothermally-altered rocks occurred as a result of interaction of sea waters with felsic magmatites<sup>[46]</sup>. The latter lost their K and Na and instead became enriched in Mg and Ca. The process leads to the formation of smectites, and from the hydrotherms enriched in rock components emanate barite, anhydrite and gypsum.

(5) Barite-sulfidic ores usually hosted in secondary quartzites (Madneuli) are characterized by a not-very-distinct zonality of minerals: barite-sulfidic and baritic (in vein zones) associations are replaced downwards by sphalerite-galena-chalcopyritic ones. It is noteworthy that the veinlet-impregnated bodies are confined from the top

by a screen (effusives, subvolcanic gently-dipping bodies), and from the bottom – by gypsum zones and jaspery quartzites, and small bodies of fine-grained pyrite and, less frequently, chalcopyrite<sup>[15]</sup>. Stockworks of copper-pyritic and zinc ores contain, in their upper parts, schlieren infilled with druses of quartz, pyrite, chalcopyrite, and also, probably hypergene bornite and covellite. Above the copper mineralization, besides gypsum-anhydritic lenses, there are also, not unfrequently, quartz-hematite concentrations. The described pattern of copper-zinc veinlet-impregnated mineralization is also valid for hydrothermal-sedimentary mineralization of the Kuroko-type (e. g., Chayeli in Turkey). This circumstance was underlined by T. Matsukama and E. Khorikosi<sup>[47]</sup> as far back as 1973.

(6) Fluids responsible for volcanogenic deposits were subacid chloro-sodic low-salinity solutions<sup>[27,33,48]</sup>. Our data indicate solution salinity equal to 1.5-3.5 wt% NaCl equiv., taking into account the melting of frozen gaseous-fluidal inclusions<sup>[49]</sup>. Low-salinity fluids are also characteristic of the recent accumulation of sulfides in the world ocean<sup>[50,51]</sup>. However, in some sites of sulfide formation, brines with salinity up to 30 wt.% NaCl eq. (at temperatures 200-400°C) have been discovered<sup>[51]</sup>. Data obtained from the Lesser Caucasian deposits do not contradict these figures<sup>[15,52]</sup>.

B.W.D. Yardley<sup>[53]</sup> summarized information on crustal fluids pointing out that temperature was one of the main factors influencing on the concentration of metals in solution. Such metals as Fe, Mn, Zn and Pb are in solutions, most likely, in form of chloridic complexes. For example, in case of Zn, this metal is represented chiefly by  $ZnCl_3^-$  and  $ZnCl_4^{2-}$ <sup>[54]</sup>. The concentration of above metals also increases with increased content of chlorides. Metals, most probably, are concentrated in brines of evaporitic sequences where Pb-Zn deposits of the Missisipi-type have been formed.

Maximum temperatures of ore-accumulation seem to be comparable with temperature of boiling up the solutions<sup>[27]</sup>. Within the areas of recent volcanic activity, the lower boundary of boiling the solution with generation of water steam, under the temperature more than 270°C, lies at depths of 300-400 m<sup>[33]</sup>. The material from the Lesser Caucasus shows that maximum temperatures of homogenization of fluidal inclusions at copper deposits are 410-390°C, and at barite-sulfidic deposits ~280°C<sup>[21]</sup>. According to our data (Table 4) maximum pressure of fluids in epigenetic deposits reached 150-200 bars, and the formation of minerals took place at depths of 400-600 m from the surface. In case of trapping gaseous-fluidal inclusions under temperature of 320°C minimum pressure may be perhaps about 80 bars; however, under greater temper-

ature about 350°C pressures could reach 500 bars (but no higher). (Figures obtained from the water-NaCl system liquid-vapor curve on the P-T plot)<sup>[49]</sup>.

(7) Available data on isotopic composition of hydrogen and oxygen of fluidal inclusions in quartz, barite and calcite from barite-polymetallic ores were earlier interpreted in favour of the significant participation of meteoric waters in the ore-generating process. As for copper ores<sup>[27,21,45]</sup>, here meteoric waters might have played an inferior role as compared with magmatic waters. Our new results on oxygen isotopy, obtained, as was mentioned above in the laboratory of USGS in Denver, also do not contradict to these data.

(8) Data on the isotopic composition of sulfur in sulfides and sulfates are, as was mentioned above, somewhat ambiguous: S in sulfides is close to meteoritic standards whereas sulfur in sulfates is increased in density at  $14\pm 3\%$ <sup>[21]</sup>. As an example of hydrothermal-sedimentary barite-sulfide deposit where sulfur in sulfides is characterized by lesser density ( $\delta^{34}S = -2\div -11\%$ , unpublished data by V. Buadze) it may be adduced the deposit of Wed Al Kebir in Algeria.

(9) At the majority of hydrothermal-sedimentary deposits, the boiling up of fluids did not take place at all, or might happen possibly before thermae's outflow on the sea floor thus favouring the formation of ore-conveying systems. The most conducive conditions for the stable accumulation of hydrothermal-sedimentary ores were on the sea bottom, at depths of 2-3 km<sup>[55,56]</sup>. Lesser depths are not completely forbidding, taking into consideration physical-chemical peculiarities of ore-forming minerals, but they are not altogether conducive to stable proceeding of ore-forming processes because of the upwelling and high-energy conditions characteristic of shelf and transitional zones.

We assume that the onset of functioning of hydrosystems within the volcanic complexes was preceded by the following succession of events: deposition of terrigenous-volcanogenic sediments in the local depressions of sea basins (backarc or/and intraarc); intensification of volcanic activity giving rise to the formation of andesite-dacitic and rhyolitic complexes; final stage of volcanism with outflow of andesite-basalts and subordinate sodic rhyolites. After some attenuation of volcanic activity (that was reflected by partial washout of previously formed volcanites and deposition of tuffites) there was an emplacement of intrusions that cooled and crystallized at depths of about 2 km from day-surface, perhaps even deeper. It should be noted that hydrothermal-sedimentary ores were formed after the accumulation of andesite-dacite-rhyolitic complexes (ore-concentrations at the Kuroko-



type deposits are usually localized on rhyodacitic domes). Mineral zonality observed in hydrothermal-sedimentary deposits may be explained by the re-distribution of ore-forming components as a result of the destruction of “hills” and their diffusion from lower levels to upper ones in the process of leaching of ores by fluids <sup>[57,58]</sup>. An example of this may serve a recent ore-bearing structure in the Pacific ocean, on the Explorer ridge, where high-temperature sulfides underlie beds of relatively low-temperature sulfides of Fe and Mn, barites and silica. According to <sup>[59]</sup> who proposed a thermodynamic model, the anhydrite-pyritic mineralization is in due course replaced by a later silica-sulfidic substance. The emergence of anhydrite in “ore hills” is explained by the involvement of sea waters in the discharge zones. The sea waters are heated and as a result anhydrite is precipitated from them <sup>[60]</sup>.

Unfortunately, as was mentioned above, we did not succeed in studying of gaseous-fluidal inclusions at the Chayeli deposit. For that reason, we use published data on deposits that are typical representatives of the Kuroko-type one of which is a hydrothermal-sedimentary deposit in the Kermadec island arc <sup>[61]</sup>. Thermobarogeochemical investigations of gaseous-fluidal inclusions showed that the salinity of hydrothermal solutions ranged between 1.75-3.9 wt % NaCl-equiv., and temperatures of homogenization – between 175-322°C. Two-phased inclusions are predominant, although rare monophased aqueous inclusions are also found. The average salinity is approaching the standard salinity of sea water (3.2wt % NaCl equiv.). Here, there are no any signs of boiling, such as the co-existence of inclusions enriched in gas and in liquid under the equal values of  $T_h$ . It should be also noted that the method of gaseous chromatography allowed identifying in massive sulfides the following volatiles: H<sub>2</sub>O (99.8-99.98 mol %), CO<sub>2</sub> (0.03-0.17 mol %), N<sub>2</sub> (0.004-0.023 mol %) and CH<sub>4</sub> (0.002-0.026 mol %). It is assumed <sup>[61]</sup> that part of methane might be of abiogenic origin. Thus, numerous examples of deposits, both hydrothermal and epigenetic types, confirm an earlier idea <sup>[48]</sup> about the standard pattern of PT – conditions of ore accumulation at volcanogenic deposits.

For the deposits of the Madneuli type which were formed after the squeezing of rhyodacitic domes (baritic and barite-polymetallic bodies) and later, as a result of the emplacement of porphyry granodiorites (stockwork dissemination copper mineralization), the way of their generation was somewhat different. Before the beginning of intensive volcanic activity that gave rise to processes of ore-formation, there existed vast territories with subaerial conditions, and within the volcanodepressions artesian basins with buried sea waters were developed. The pale-

odepressions were bounded by blocks of hydrogeological massifs.

As a result of the emplacement of rhyodacites and eruption of felsic lavas and ignimbrites, the meteoric ground waters became overheated and saturated with volatile magma components that finally led to catastrophic blasts and explosions and formation of explosive breccias beneath the impermeable screen. Two hydrochemical zones were formed within the depressions: the upper one – sulfate-ammonium and the lower one – chloride-sodic <sup>[15]</sup>. The boundary between these zones is marked by gypsum-anhydrite concentrations, jasper-like quartzites and iron sulfides. In our opinion, the presence of hydrochemical zonality was promoted: (1) at first, by the boiling up of the solution at a temperature more than 350°C <sup>[62]</sup> and at shallow depths, with the differentiation into fluidal and gaseous phases (with separation of sulfides, quartz, carbonate and, locally, adular); (2) later, by the efflux of volatiles (H<sub>2</sub>S, SO<sub>2</sub>, HCl, CO<sub>2</sub>, NH<sub>4</sub>, etc.) into the near-surface zone and their oxidation; (3) by the boiling up of the solution retaining part of soluble acidic components, hydrogen sulfide in the first place.

It should be noted that the destabilization of the solution in the sea-bottom conditions related to the drop of temperature and its oxidation may be a cause for the mass precipitation of ore matter. Since “black smokers” are commonly made up of pyrite, pyrrhotite and sphalerite suspensions, it is very likely that copper- and zinc-containing solutions might have transported metals in form of hydrosulfidic complexes. The enrichment of hydrotherms within the volcanodepressions was probably realized in the process of degasation of a shallow-occurring magmatic body (intrusions that are often observed beneath ore bodies). According to experimental works <sup>[48]</sup>, among gases at temperatures below 600°C a dominant one is hydrogen sulfide, and at higher temperatures – sulfurous gas. The latter in mixture with a fluid at temperature 500-600°C is capable of producing hydrogen sulfide and sulfuric acid.

Levels of mineral generation in epigenetic deposits are generally compared with zones of “black smokers” whose bordering anomalous physical-chemical parameters cause a synchronous crystallization of anhydrite and iron sulfides. These conditions correspond to zones of hydrotherms with minimum activity of PO<sub>2</sub> coinciding with the lower boundary of the field of barite stability under equal activities of H<sub>2</sub>S-SO<sub>4</sub><sup>2-</sup> <sup>[27]</sup>.

At the barite-sulfidic deposits, the zonal distribution of metals is conditioned by the following factors: (1) different stability of complex compounds <sup>[27,48]</sup>; (2) greater dependence of the solubility of copper minerals on temperature as compared with that of sphalerite and galena

<sup>[27]</sup>; (3) dependence of precipitation of metals on the concentration of  $S^{2-}$ . Under the equal concentrations of metals in solution, precipitation of copper and zinc demands higher concentrations of  $H_2S$  than it needs for lead <sup>[63]</sup>; (4) functioning of a  $H_2S$  – barrier efficiency of which is determined by low concentrations of  $S^{2-}$  <sup>[64]</sup>.

It can be supposed that in the zones of discharge of fluids,  $\Sigma S$  proves to be sufficient for the precipitation of copper, whereas lead, zinc and silver reveal a trend of passing through the hydrogen sulfide barrier. The excessive ion-settler plays a role of a solvent-complexgenerator.

It seems possible that in polyformational deposits of the Madneuli-type, the origin of quartz veinlets coincides in time with that of the explosive breccias and the arising of the above-mentioned hydrochemical zonality within volcanostructures. Precipitation of gold, quartz and sulfides can be regarded as an one-act process related to the destabilization of magmatic fluids. This process proceeded within the medium characterized by high oxidizing potential, corresponding to the level of formation of secondary quartzites.

Basing on physical-chemical studies <sup>[65]</sup> points out that low-salinity magmatic waters are capable of transporting gold under high temperature regime. One of the main requirements is the presence of a sufficient quantity of  $H_2S$  that plays the role of a bisulfide complex. Under high pressure, vaporized magmatic fluids pass into liquid form, without heterogenous phase transition. These fluids are responsible for significant potassium and propylitic alterations of rocks hosting epithermal mineralization. In his paper, Ch. Heinrich considers Au-Cu porphyry deposits; however, in our opinion, the results of this work may be used for gold-bearing deposits of the Madneuli-type as well. In spite of the fact that fluids producing low-sulfide Au-bearing epithermal deposits contain considerable portion of meteoric water, their gold “reserves” have been formed, mainly, at the expense of metal dissolved in an insignificant part of vapor-condensed fluids of magmatic origin.

In conclusion, it should be once more underlined that hydrothermal-sedimentary deposits of “ore-hill” type obtain their zonality in the process of recrystallization, solution and redeposition of ore material. Usually, the stifling of the sulfide-forming process takes place where the therms reach zones with high partial oxygen pressure – outside depressions and above ore-concentrations where precipitation of oxides of Fe and Mn and formation of Jasper in supra-ore horizons occurs.

Some authors <sup>[45]</sup> explain the formation of large mass of sulfide deposits by better, providing of hydrotherms with water in submarine environments as compared with epige-

netic deposits. We think that the mechanism of ore-formation on the sea floor – frequently-repeated supply of ore matter – was decisive under the generation of volcanogenic massive sulfide deposits (VMS).

## 6. Conclusions

The above material allows to draw a conclusion that most ore deposits in paleoisland arc environments, and in the Pontian-Lesser Caucasian arc in particular, can be expected within and around volcanic vents or on the slopes of large volcanoes located in volcanodepressions and, also, in silicious parts of volcanogenic-sedimentary sequences or directly above the latter (as in case of hydrothermal-sedimentary deposits). As a rule, ore accumulations are overlain by basic volcanites, but there may be exceptions, e.g. the Madneuli deposit. In the flank zones of ore bodies and, often, in their hanging walls, concentrations of gypsum are commonly found. Mineral composition of ores is practically identical in all copper deposits, also with the exception of Madneuli, where one volcanostructure hosts an association of gold, barite-sulfidic and copper ores belonging to various stages of the ore-formation.

Of a particular interest is the composition of ore-containing sequences in the region: a) in the Alaverdi district ore-containing Middle Jurassic unit is represented by thin chemogenic-sedimentary rocks, hyaloclastites, accumulations of submarine colluviums, tephroidal turbidites, andesitic and dacitic lavas; the ore-containing sequence is overlain by the Upper Jurassic complex represented by andesite-basaltic flows alternating with carbonate clastic tuffites; b) in the Bolnisi district, the ore-containing stratified sequences (tuffites with rare dacitic flows, and crater-lacustrine deposits) are overlain by subaerial ignimbrites and rhyodacitic lavas; c) the Chayeli volcanostructure containing hydrothermal-sedimentary ores is composed of supra-ore basalts (pillow lavas) alternating with limestones and “purple” tuffs, and also with propylitized dacites. The latter are overlain by massive sulfidic ores (VMS) in the lower part of which quartz-chlorite-hydromicaceous metasomatites host veinlet-impregnated copper ores. According to Turkish geologist, the volcanostructure represents a large caldera located on the floor of a deep-marine basin.

The Lesser Caucasian deposits by their genesis are undoubtedly epigenetic: in the Alaverdi district, veinlet-impregnated and vein mineralization is superimposed on hyaloclastites and tuffites; in Bolnisi, mainly veinlet-impregnated copper mineralization is developed in silicified tuffites; besides, gold and barite-sulfide mineralization in veins and shallow-dipping sills is present in second-

ary quartzites. In Chayeli, ores show similarity with “ore hills” in the present-day middle-oceanic ridges and rift zones of marginal seas.

It should be noted that ore bodies in the Alaverdi district are located in narrow zones of quartz-sericite-chlorite metasomatites; in the Bolnisi district, the vertical metasomatic “column” contains in its upper part secondary quartzites (near-surface solfataric alterations), while the lower part shows more high-temperature silicification (quartz-chlorite-sulfidic metasomatites with little sericite). Here ore metasomatites are surrounded by propylites. At the Chayeli-type deposits (Madenkoy), the dacite unit that underlies the hydrothermal-sedimentary mineralization contains, at the background of regional propylitization, veinlet-impregnated “yellow” ores. The latter mark ways of migration of hydrothermal solutions to the paleo-sea floor.

In the Alaverdi district small stocks and thin veins containing copper ores, are predominant; in the Bolnisi district main ore bodies are large copper stockworks; in the Eastern Pontides both stockworks and thick lens-shaped bodies of massive sulfidic ores (VMS) consisting mainly of pyrite, chalcopyrite and sphalerite are present.

Most likely, that these differences are caused chiefly by different geodynamic regimes dominating in various blocks of the earth crust of the study region. Thermobarogeochemical studies indicate that the principal copper deposits, in spite of the existing differences in the mechanism of ore accumulation, were formed in similar PTX-conditions and, therefore, can be attributed to the same genetical class of volcanogenic ore deposits.

It has been established that depending on the stage of geological investigation, it is necessary to know main parameters characterizing both an ore-magmatic system on the whole and its individual components. The search for hydrothermal-sedimentary ores of non-ferrous metals within the Georgian and Armenian part of the Lesser Caucasian paleoislandarc is condemned to failure due to the absence of “geodynamic basis” for their accumulation. Previously proposed prospecting model had been created for the certain area – the Bolnisi ore district in Georgia. In the proposed model, the main consideration was given to the relationship between the basic parameters of mineralization and dimensions of a volcanodepression<sup>[15]</sup>. When planning large scale (1:50,000) mapping at the stage of the prognostication works, it is necessary to take into account the results of geophysical and geochemical investigations. Thus, in the Bolnisi district, it has been delimited areas corresponding to source zones (overlying magmatic bodies and defining mineralized blocks). In the gravity field, these areas are expressed as low intensity minimums. As

for the geochemical data, they show the aureoles of titanium, zircon, arsenic, zinc, molybdenum, bismuth, copper, manganese, iodine around the copper bodies, Gold-bearing quartzites are marked by aureoles of silver, gold, arsenic, bismuth and iodine.

It is noteworthy, that the prognosis of ore concentrations should be made with due regard for the standard object: morphostructural peculiarities of the upper parts of ore-magmatic paleosystems; degree of differentiation of rhyodaitic magmas; relation between size and structure of ore bodies and dimensions of local volcanostructures; character of pre-ore and syn-ore re-working of rocks; component composition of aureoles.

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