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GEOLOGICAL SETTINGS AND CONDITIONS OF GENESIS OF VOLCANOGENIC DEPOSITS OF NON-FERROUS METALS IN PALEOISLAND ARC ENVIRONMENTS

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Abstract: By the example of the Pontian-South Caucasian paleoisland arc actively functioning during the whole Mesozoic the authors consider the main peculiarities of spatial-temporal relationships between ores of non-ferrous metals and enclosing rocks, and discuss the conditions of the evolution of ore-magmatic systems. The authors' conclusions are substantiated by data on $^{87}Sr/^{86}Sr$ ratios, concentration of rare elements in enclosing volcanogenic rocks, isotopic ratio of sulfur and oxygen in ores, and results of thermobarogeochemical studies. The authors hold the opinion shared by many mining geologists that the main part of ore components in non-ferrous metal deposits was extracted from nearby magmatites enclosing and underlying mineralized zones. The solutions from which ores precipitated were, by their salinity, very close to sea water. The maximum temperature of ore formation at epigenetic deposits reached 400°C for copper ores and 280°C for barite-polymetallic ores, whereas the pressure did not exceed 200 bar. As for hydrothermal-sedimentary ores, they could most likely form at the sea bottom, at depths of 2-3km and maximum temperature no more than 300°C.

Keywords: the Pontides, the South Caucasus, Jurassic, Cretaceous, ore, non-ferrous metal

Within the Alpine-Himalayan mountain-fold belt there are known numerous fragments of paleoisland arcs and contiguous structures –back-arc and intra-arc basins. One of such paleoisland arcs is the Pontian-South Caucasian magmatic arc (fig.1). Volcanostructures situated within this arc host the largest and economically most important deposits of non-ferrous metals in the region. During the Alpine epoch, maximum volcanic activity in the eastern part of this belt (in Armenia and western Azerbaijan) occurred in Bajocian-Late Jurassic, whereas in the western part (Georgia and Pontides in Turkey) – in the Cretaceous time. Here, in areas that experienced the strongest tectonic stresses related to zones of large active faults, under the covergent interaction of lithospheric microplates (Pontian-South Caucasian and Iranian), intensive volcanism and hydrothermal activity took place accompanied by the appearance of considerable thermoanomalies in the earth crust (Biji-Duval et al., 1977; Monin and Zonenshain, 1987; Yilmaz et al., 1997).

During the convergence of above microplates, originally epigenetic volcanogenic and barite-polymetallic ores came into being (e.g.in Jurassic time in Armenia); later, in Late Cretaceous some copper, gold and barite-polymetallic deposits were formed in Georgia and the Pontides. The Pontides also host large-scale hydrothermal-sedimentary deposits, an example of which is the Çayeli deposit in eastern Turkey. At present, in the Eastern Pontides the following deposits are being exploited – Aşikoy (the Cyprus type of deposit), epigenetic deposits of Lahanos, Kutlular and Murgul, and the Kuroko-type Çayeli deposit. Estimated reserves of ores at the Çayeli deposit amount to 15.9 million tons averaging 4.4% copper, 6.1%zinc, 0.8g/t gold and 44g/t silver. All reserves of copper and zinc are concentrated within a single ore body that extends along the strike at a distance of 920m, maximum thickness being 100m (Altun, 1977). The ore-containing volcanostructure is made up of supra-ore basalts (pillow-lavas) alternating with limestones and "purple tuffs", and locally with propylitized dacites. This unit is overlain by massive sulfidic ores – sphalerite, chalcopyrite, pyrite. These ores are strongly brecciated and resemble

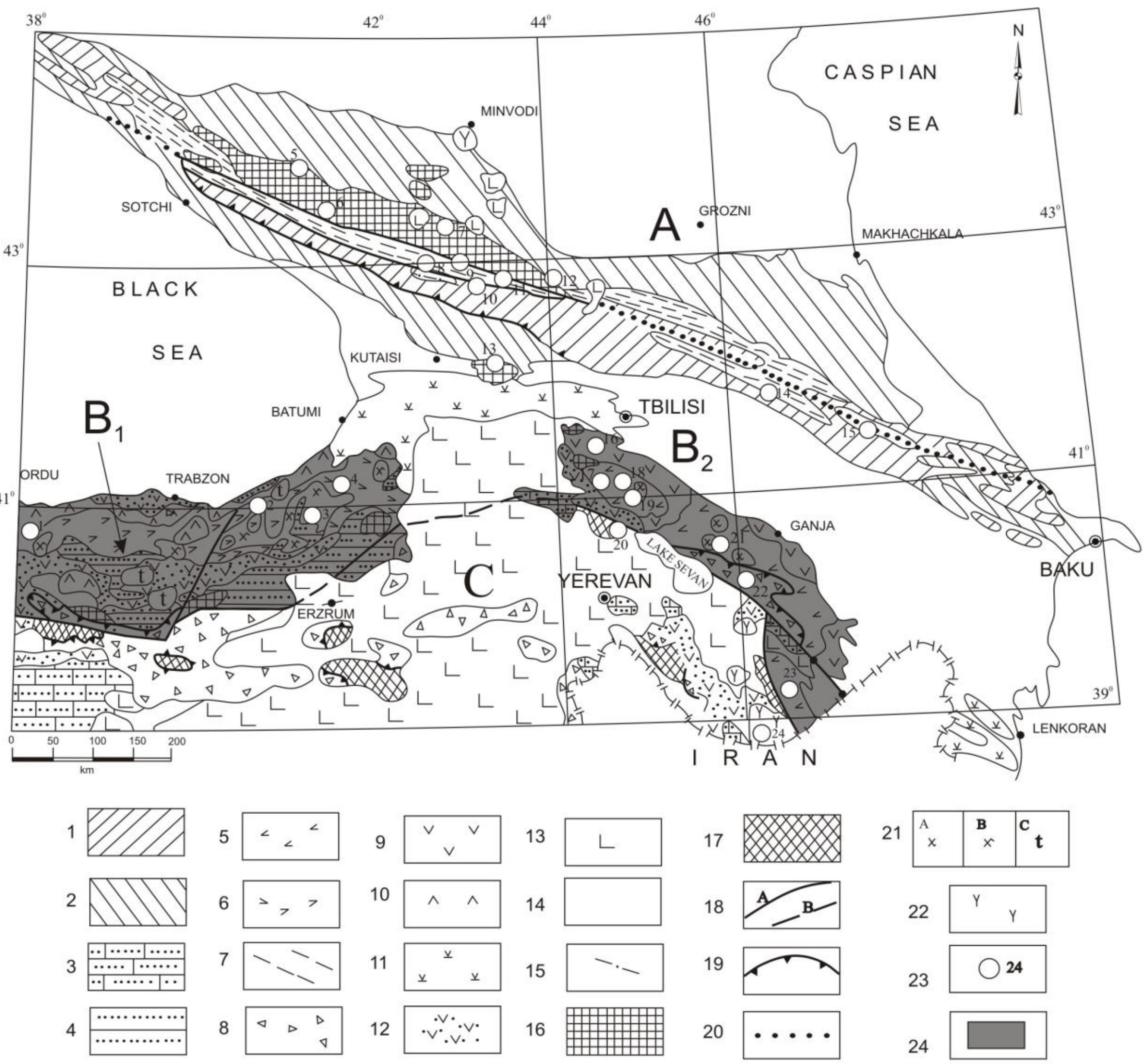

Fig. 1. Distribution of main metal-bearing deposits within the geological structures of eastern Turkey and the Caucasus. 1- Slope and rize of the South Caucasian microcontinent (Jurassic-Early Cretaceous, Greater Caucasus); 2- Shelf zones of the Scythian and South Caucasian microcontinents (Jurassic - Paleogene, Greater Caucasus); 3- Shelf zones of the North Iranian microcontinents (Cretaceous- Paleogene); 4- Shelf zones of the Pontian microcontinent (Early Jurassic, Eastern Pontides); 5- Lesser Caucasian ensialic island arc (Bajocian-Early Cretaceous); 6- Pontian ensialic island arc (Cretaceous); 7- Deep basins of marginal paleosea (Early-Middle Jurassic); 8- Oceanic zones in allochthonous occurrence. 9- Lesser Caucasian backarc volcanodepressions (Late Cretaceous); 10- Pontian backarc volcanodepressions (Late Cretaceous); 11- Intraplate riftogene volcanostructures (Eocene-Oligocene, Lesser Caucasus); 12- Eocene volcanodepressions superimposed on precollisional structures (Pontides, Lesser Caucasus, N. Iranian); 13- Young volcanic plateaus (Oligocene-Quaternary); 14- Orogenic troughs (Oligocene-Quaternary); 15- Terrigenous - volcanic rocks (Dizi series, Devonian-Triassic) intruded by Middle Jurassic granitoids; 16- Pre-Alpine basement of the Scythian and South Caucasian microplates (Pre-Cambrian (?) - Paleozoic); 17- Pre-Alpine basement of North Iran (North Iranian microplate, Pre-Cambrian - Paleozoic); 18- Tectonic sutures separating main geoblocks (represented by reverse faults and strike-slips, A - ascertained; B - proposed); 19- Thrusts; 20- Supposed boundaries between Scythian and South Caucasian microplates (overlain by thrust sheets); 21- Granitoids (a -Early Cretaceous, b - Late Cretaceous, c - Eocene-Oligocene); 22- Monzonites, syenites (Oligocene-Miocene); 23- Mineral deposits; 24- Fragments of paleoisland-arc. Main metal-bearing deposits of the Eurasian active paleomargin: 1 - Asikoy (Cu), 2- Lahanos (Cu, Zn, Pb), 3- Çayeli –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- Lukhumi (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, $BaSO_4$), 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_1 – Eastern Pontides, B_2 – South Caucasus); Afro-Arabian paleocontinent: C- North Iranian.

Kuroko-type ores in Japan. Çayeli ores are also close to "ore hills" of modern mid-oceanic ridges (MOR) and rifting zones of marginal basins, by their textural-structural characteristics and mineralogical zonality. In the course of the formation of the Çayeli ore body, simultaneously took place its destruction as a result of hydrothermal explosions. As a result, there were formed breccias of "black" (sphaleritic) ores that were healed, in most cases, by quartz-chalcopyritic substance ("yellow" ores). The ore body is overlain by a thin horizon of hematitous tuffites containing manganese minerals which, in turn, are overlain by andesite-basalts. Most of the scientists consider Çayeli ores to be hydrothermal-sedimentary products being an analogue of modern ores of MOR. At the same time, some authors assume that there is no complete similarity between ancient and modern ores (e.g. Ohmoto and Skinner, 1983). It is quite naturally since ancient ores during the long geological time experience deep structural and mineralogical transformations together with enclosing volcanogenic and sedimentary sequences.

Another type of hydrothermal-sedimentary mineralization in the Pontides is represented by the Aşikoy massive sulfide deposit, 2km west-northwest of Küre in northern Turkey. Here, ores are hosted by an allochthonous slab of volcanogenic and sedimentary rocks known in literature as"the Kure complex" (Guner, 1980; Ustaomer and Robertson, 1993; Çakir, 1995). It is generally accepted that the allochthone was transported onto the paleoisland arc structure from the marginal sea basin of the Paleothethys. Mineralization pattern and geological setting here are similar to those observed on the island of Cyprus – at the base of the section occur serpentinous peridotites that are successively overlain by gabbro, a diabase dyke complex and greenstone-altered basaltic pillowlavas. Above the latter there are coper-bearing massive sulfidic ores.

Examples of stokwork-veinlet deposits in the Pontides are Lahanos and Murgul whose mineralization pattern is very close to that observed in Madneuli, South Georgia.

The Georgian deposit Madneuli situated in the Bolnisi mining district in South Georgia represents a rather rare type of ore deposits in which gold, barite-sulfidic and copper ores belonging to temporally different stages are spatially clustered within a limited area. A volcano-tectonic depression (Bolnisi Cretaceous structure) that hosts the deposit represented a part of a back-arc basin. The volcanostructure is made up of three complexes that are the products of functioning during the Albian-Campanian time a number of various volcanoes (at first fissure-type and later composite stratavolcanoes) (Kekelia et al., 1993). The uppermost contrast basalt-andesite-rhyodacitic complex terminates volcanic activity in the Bolnisi Cretaceous structure. Most likely, that the comagmatites of this complex are granodiorites and granodiorite-porphyries discovered by drilling in the central part of the volcanodepression beneath the Madneuli quarry. Here productive are cupola-shaped rises squeezed on the slopes of large volcanic structures and consisting of rhyodacitic extrusions of the middle "rhyodacitic complex". The complex also contains ignimbrites and lavas and extrusions of rhyolites. The lower complex is made up of volcanogenic-sedimentary rocks with the predominance of intermediate (andesitic) volcanites.

Available data on the isotopic composition of strontium and concentrations of rubidium and strontium in mineralized rocks (Kekelia et al., 2004) indicate that basalts of the Bolnisi district (87Sr/86Sr=0.704910) were, most likely, products of undepleted mantle, rhyolites of Madneuli might have been the melt of the upper part of the crust ($^{87}Sr/^{86}Sr=0.707739$), whereas the rhyodacites of the Murgul deposit (Eastern Turkey) – products of the bottom of the earth crust ($^{87}Sr/^{86}Sr=0.710269$). Original data on various types of rocks, including rocks characteristic of the undepleted mantle are summarized by Abramovich et al., (1989).

In Armenia, some epigenetic copper and barite-polymetallic deposits hosted by Middle Jurassic volcanites have been exploited for a long time. These are Alaverdi, Shamlug, Akhtala and Kafan deposits. At the Alaverdi district, the geological section of Middle Jurassic productive series is represented by (from bottom to top): andesite and dacite lavas, tephroidal turbidites, piles of submarine colluvium, hyaloclastites, and a thin unit of chemogenic-sedimentary rocks. This ore-bearing sequence is overlapped by a Late Jurassic volcanogenic complex (Kekelia et al., 1993).

Copper veinlet-dispersed mineralization is characteristic of the Bolnisi, Alaverdi and Kafan deposits. At Madneuli, gold mineralization was found in secondary quartzites. Barite-sulfidic mineralization in Madneuli is developed in form of veins, veinlets and gently-dipping ore bodies. At the Alaverdi deposit, veinlet and veinlet-dispersed ore bodies are located within narrow zones of quartz-sericite-chlorite metasomatites which are developed among widespread propylites.

Differences in ore characteristics from various parts of the paleoisland arc show strong dependence on the geodynamic regimes of specific metallogenic episodes. Below we propose a genetic model of the evolution of ore-generating systems of volcanogenic deposits of non-ferrous metals. The proposed model should be considered as a some abstraction that takes into account not the formal resemblance of individuals (ore bodies, ore deposits) but the standard course of processes proceeding in the system.

Isotopic-geochemical data (Franklin et al., 1984; Sinyakov, 1986; Kekelia et al., 1993) indicate the participation of a considerable amount of sea waters in the hydrosystems of volcanogenic deposits. Experimental studies (Hodgson and Lyndon, 1977; Grichuk et al., 1984) on the extraction of elements from rocks under PT-conditions corresponding to fluid functioning, assume it possible to regard both magmatic and sedimentary rocks as a source of metals for volcanogenic deposits.

Vast geological material collected under the study of the world ocean (Zonenshain and Kovalev, 1974; Rona, 1986; Grinberg et al., 1990; Elianova and Mirlin, 1990; Elianova, 1999) gives all reason to suppose that the large-scale ore-formation has been realized in case of proceeding some successive processes: (1) magma crystallization; (2) interaction between “aggressive” heated sea waters and magmatites, heat source being igneous rocks emplaced into volcanogenic-sedimentary complex; (3) stable functioning of a physical-chemical barrier in the area of hydrotherms discharge (depressions on the seafloor or closed structures in upper horizons of the earth crust).

Thus, volcanogenic deposits in island arc environments are distinguished by the following peculiarities:

1. Ore composition strongly depends on petrochemical features of rocks. For example, copper-zinc mineralization is usually associated with andesite-basalts and/or sodic rhyolites (Krivtsov, 1989). It has been noted that ore-bearing rocks of the mid-oceanic ridges often contain spherical oxidized-ore aggregates (Prokoptsev and Prokoptsev, 1990). Subalkaline lavas developed in rift valleys of MOR also contain sulfides as impregnation in clinopyroxene and feldspar phenocrysts (Akimtsev and Sharapov 1993). All these facts indicate that some magmatites were primarily productive.
2. Within the limits of ore-knots, ways of hydrotherm migration are marked by alterations in mineral composition of rocks. In down-going zones rocks are predominantly argillized, while upper and flank zones undergo strong propylitization.
3. Barite-sulfidic ores in secondary quartzites display vertical zonality (e.g. Madenuli). Stockworks of copper and copper-zinc ores are often overlapped by gypsum-anhydrite lenses. Similar picture is also characteristic of hydrothermal-sedimentary Kuroko-type deposits that was noted by Matsukama and Khorikosi (1973).
4. By their salinity hydrothermal solutions are close to sea water but in comparison with latter they are enriched in Fe, Ag, Pb, Cu and Zn (Mottl et al., 1979). Low salinity is a characteristic feature of fluids in zones of recent ore-formation (Bortnikov et al., 2004; Bortnikov and Vikentiev, 2005). Data on the Lesser Caucasian deposits (Kekelia et al., 1991; Kekelia et al., 1993) also confirm these observations. In the Lesser Caucasian deposits, the maximum temperature of mineral formation was established by the method of homogenization and was 410-390°C for copper and 280°C for barite-polymetallic deposits (Yaroshevich, 1985); pressure was equal to 150-200 bar (we used diagrams published by Shepherd et al., 1985). According to Arevadze et al. (1983) and Yaroshevich (1985), salinity of fluids in Madneuli from which copper and barite-zinc-lead ors were deposited, did not exceed 40g/l NaCl eq. The solutions were chloride-sulfatic potassium-sodic by composition. These data are confirmed by the results of chemical analyses of aqueous extracts from quartz, sulfides and barite.
5. The most favourable conditions for the stable accumulation of hydrothermal-sedimentary ores existed on the seafloor, at depths of 2-3km (Stackelberg, 1985; Gablina et al., 2000).
6. Data on the isotopic composition of hydrogen and oxygen in fluidal inclusions in quartz, barite and calcite from volcanogenic barite-polymetallic ores are interpreted in favor of the participation of both sea and meteoric waters in the ore-forming process, with the predominance of the former (Franklin et al., 1984; Yaroshevich, 1985; Krivtsov et al., 1987).

7. Data on isotopic composition of sulfides and sulfates are ambiguous and cannot be used for the identification of a sulfur source.

The evolution and functioning of hydrosystems in volcanic complexes can be conceived as follows: firstly, accumulation, in local depressions of back-arc and intra-arc basins, of volcanogenic-sedimentary, predominantly calc-alkaline sequences; then, after the decrease in volcanic activity (the stage of volcanostructure inversion), emplacement of intrusives took place whose crystallization occurred at a depth of about 2 km from the surface or 1 km – from the seafloor. Hydrothermal sedimentary ores by their mineral composition and structure have similarity with modern extint "black smokers". Mineral zonality in them can be explained by the re-distribution of ore-forming components as a result of destruction of "ore hills" and their subsequent diffusion from deeper to shallower levels (Hanington et al., 1986; Elianova, 1989).

In the Keramdec island arc (the south-west Pacific), volcanites host hydrothermal-sedimentary Kuroko type deposits (de Ronde et al., 2003). According to thermobarogeochemical studies, salinity of hydrothermal solutions here ranged from 2.2 to 3.9wt % NaCl eq. and the temperature of homogenization was 175-322°C. We adduce this example in order to demonstrate the uniformity of physical-chemical conditions of ore-forming processes, irrespective of the way of their deposition - epigenetic of hydrothermal-sedimentary.

At the seafloor conditions, destabilization of fluids occurs in connection with the temperature drop and oxidation of fluids. Taking into account the composition of suspended matter emanated by "black smokers" (pyrite, sphalerite, pyrrhotite), we may suppose that metals were transported in form of hydro-sulfidic complexes. Levels of ore-formation in epigenetic deposits are generally comparable with pipe zones of "black smokers" whose boundary anomalous physical-chemical parameters stipulated synchronous crystallization of anhydrite and iron sulfides. Such conditions are observed in zones of hydrosystems with minimum activity of oxygen coinciding with the lower boundary of barite stability, under equal activity of H_2S-SO_4^{2-} (Franklin et al., 1984); Tvalchrelidze, 1987; Kekelia et al., 2004). At barite-sulfidic deposits, the zonal distribution of metals is conditioned by a number of factors: (1) greater dependence of the solubility of copper minerals on temperature as compared with that of sphalerite and galena (Franklin et al., 1984); (2) different stability of complex compounds (Franklin et al. 1984; Ovchinikov 1988); (3) dependence of precipitation of metals on the concentration of S^{2-}; under equal concentrations of metals in solution, precipitation of copper and zinc demands higher content of H_2S than it needs for lead (Ganeev, 1989); (4) functioning of a H_2S- barrier whose efficiency is determined by low content of S^{2-} (Kraynov et al., 1988).

Under the conditions of hydrothermal-sedimentary ore accumulation when mineral zonality of "ore-hills" is a result of the recrystallization, solution and redeposition of ore matter, the stifling of the sulfide-forming process takes place where the therms reach zones with high partial oxygen pressure; in this case occurs the precipitation of oxides of Fe and Mn and formation of jasper rocks in the upper horizons of the deposit. It should be noted that the mechanism of ore accumulation on the seafloor – frequently-repeated deposition of ore matter – was decisive under the formation of volcanogenic massive sulfide deposits.

Several words about formation of gold-beraing quartz veins and veinlets at Madneuli. We assume that they were fromed simultaneously with the formation of explosive breccias (Kekelia et al., 1991; Kekelia et al., 1993). Precipitation of gold, quartz and minor sulfides in the secondary quartzites occurred during the destabilization of magmatogenic fluids. Heinrich (2005) studying Cu-Au porphyry deposits pointed out that the low-salinity magmatic waters are capable of transporting gold under high temperature regime. One of the main requirements for this, according to Heinrich, is the presence of a sufficient quantity of H_2S. Magmatic fluids under high pressure pass into liquid form, without heterogenous phase transition, and their influence on the surroundings is expressed by significant potassium and propylitic alterations.

In the long-functioning hydrothermal systems, gold-beraing low-sulfidic epithermal deposits are distinguished by a large proportion of meteoric waters. Gold could have penetrated into hydrosystems together with magmatic steamy-condensed fluids.

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