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Zonation of porphyry copper mineralization and prediction criteria of blind mineralization in the Garadag ore field

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Abstract
Blind mineralization is an important resource for the Lesser Caucasus to increase base of non-ferrous and precious metal raw materials. In this regard, it is important to study the zonation of the copper and molybdenum-porphyry deposits of the Garadag ore field. The article deals with the regular occurrence of zonation in mineralization in space and time, zonation of wallrock metasomatites, mineralogical zonation and zonation of primary geochemical aureoles. The comparison between the distribution of copper in porphyry copper objects with different erosion sections, its zonation coefficient in basic mineralization and secondary scattering aureoles was investigated. It was stated that the zoning factor and including the secondary scattering halos can be successfully used to determine the erosional section of mineralization and to reveal ore localizing structures.
Key words: porphyry copper mineralization, zonation of wallrock metasomatites, Garadag ore field, Lesser Caucasus

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In terms of increasing the resources of non-ferrous and noble metal raw materials in the Lesser Caucasus, blind mineralization is considered a very important resource. For this reason, the determination of different types of zonation in porphyry copper deposits is of theoretical and applied importance. In general, the study of zoning has a great practical importance in the search, exploration and assessment of mineral deposits, as well as in the study of the genesis of the deposit, the discovery of the general regularities of formation and location of mineralization. Zoning is the regular location of rocks, ores, minerals and chemical elements that form the deposits in terms of time and space, is of great importance in the characterization of magmatic and ore formations, and therefore is widely used in the separation and systematization of formations [3]. As a result of the efforts of geologists who worked in the Garadag ore field for different years, different types of zoning were distinguished in the structure and location of porphyry copper deposits and it was determined that mineralization is directly related to multi-stage hydrothermal metasomatic alterations [1,2].

As a result of the analysis of the obtained actual material and available data [3,4] we will focus on the types of zoning observed in the Garadag ore field, their significance for the prediction and regular location of blind mineralization. Besides determining the zonation in the arrangement and formation of deposits (sulfur pyrite, copper pyrite, copper-arsenic, copper-zinc, copper-gold) along the lineament zone [4] in the central part of the Gadabay ore district, zoning is also observed in the Garadag ore field, which is a part of the ore district. So, porphyry copper mineralization, which is related to granodiorite-porphyry stocks in the central part of the system and is maximally enriched with copper, has developed.[2,8,9,10]

Zonation is more clearly reflected beyond the outer boundary of the ore field, in its southern and far eastern flanks. There are Maarif and Maskhit copper-polymetallic occurrences, Slavyanka sulfur pyrite, then Novo-Gorelovka and Siniy-Yar copper-zinc occurrences, Bitti-bulag copper-arsenic and Gadabay copper pyrite deposits on the southern side, beyond the boundary of the ore field. Dashbulag, Ahmedli and other polymetallic copper occurrences were observed on the northern flank of the ore field, outside its border (Fig. 1).

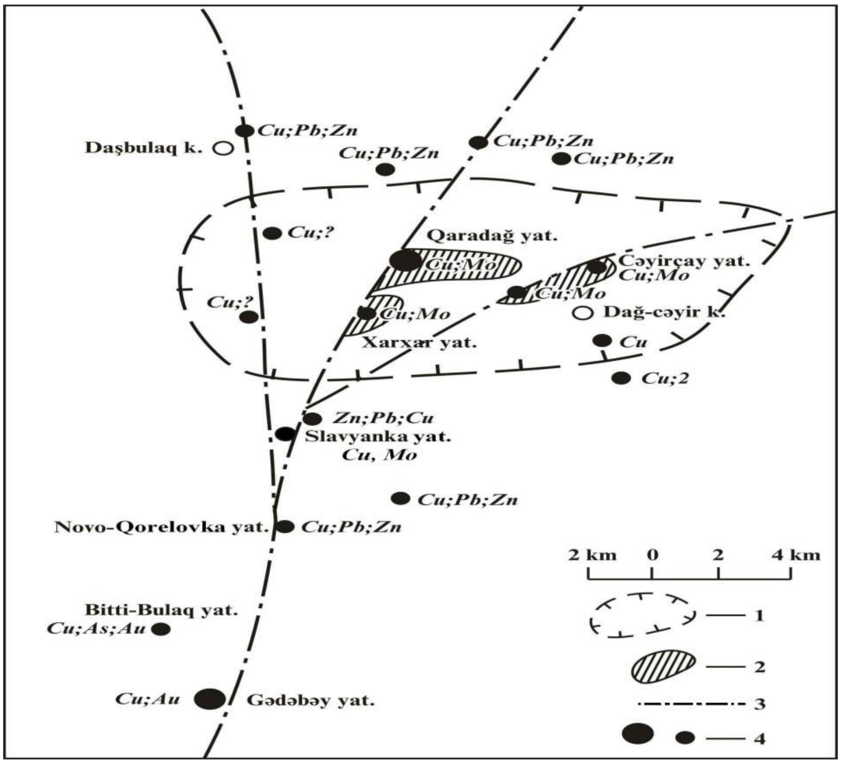

Figure 1. Scheme reflecting the ore zonation of porphyry copper system in the central part of the Gadabay ore district (according to V.M.Babazadeh, V.G.Ramazanov and A.M.Ismayilova, 1990): 1 - outer outline of the Garadag ore field; 2 - ore porphyry intrusive stocks; 3 - Gadabay depth fault and fractures spliting from it; 4 - deposits (a) and ore occurrences (b)

So, the zonation corresponds to the scheme Fe→Cu, (Mo)→(Fe), Cu, Mo→(Cu),Zn, Pb, As here.

Porphyry copper mineralization in the deposits of the Garadag ore field bears high amounts of gold. Gold is also observed in copper pyrite and copper-polymetallic ores outside the ore field. So, the following sequence can be distinguished in space and time for the considered group of deposits:

Fe→Cu, (Au)→Mo-Zn, Pb, Ac, Au, (Ag)

Zonation of wallrock metasomatites. There is no same mind on the general vertical and plan sequence of the metasomatic rock facies. Zonation is determined by the type of wallrocks and their spatial relationships. Amphibolitization, tourmalinization, hornblendization, etc. processes are connected with the plagiogranite massif, which plays the role of a framework, and their role in the formation of porphyry copper mineralization is not so great [9, 10, 11].

Table showing mineralization interactions with metasomatites

<table>
<tr><th>Vein minerals</th><th>Mineralization zones</th><th>Formation temperatures, T, °C</th><th colspan="2">Wallrock altered rocks</th></tr>
<tr><td rowspan="7">Anhydrite
Gypsum
Barite
Quartz
Pyrite</td><td rowspan="2">A barite occurrence bearing rare pockets of galena and sphalerite</td><td rowspan="2">85-100°</td><td colspan="2">Weak propylitization (quartz+chlorite+albite+calcite+ relic minerals)</td></tr>
<tr><td rowspan="4">Secondary quartzites</td><td>Monoquartzites, with barite, sometimes with jarosite, opal and chalcedony</td></tr>
<tr><td>Copper-zinc ores</td><td>255-265°</td><td>Quartz-sericite-aqueous micaceous rocks, with alunite, sometimes with alunite-jarosite or with jarosite</td></tr>
<tr><td>Copper-arsenic ores</td><td>260-275°</td><td>Quartz-sericite rocks, with alunite, pyrophyllite and chlorite</td></tr>
<tr><td>Copper pyrite ores</td><td>270-290°</td><td>Quartz-sericite, quartz-sericite-chlorite, quartz-chlorite</td></tr>
<tr><td>Sulfur pyrite ores</td><td>320-350°</td><td colspan="2">Propylites (pyrite+epidote+chlorite+albite+ anhydrite)</td></tr>
<tr><td>Copper-porphyry ores</td><td>335-370°</td><td colspan="2">Monoquartzite and quartz-sericite type secondary quartzites</td></tr>
</table>

Metasomatites formed at a relatively later stage and directly related to the hydrothermal activity of porphyry intrusives are of greater interest. Metasomatites of monoquartzite, quartz-sericite, argillite and propylite facies have been developed in the ore area. The horizontal zonation from the outer zone to the granodiorite-porphyry stock is as following (wall and frame rocks – andesites, quartz plagioporphyries, rhyolite porphyries, plagiogranites): chlorite-sericite-quartz, sericite-quartz, monoquartzite. Mineralization is mainly associated with quartz-sericite and monoquartzite metasomatites. The alteration of rocks in the acid regime is predominant among the quartz-sericite metasomatites - argillization - epidote-chlorite propylites, which correspond to the ore-magmatic section. The geochemical fields of the concentrations of the complex of elements coincide directly with such metasomatites, and the concentration of copper, molybdenum, bismuth, silver, zinc, and lead is five or more times compared to the background, which created the anomalies covering the entire Garadag ore field.[11,12]

The outer zone extends deeper than the inner zone. As we mentioned above, the outline of industrial type ores corresponds to chlorite-sericite-quartz zones.

Metasomatic formations of porphyry copper deposits in the Garadag ore field are represented by successively occurred potassium spar, greisen, propylitic, secondary quartzite and argillite formations [3, 4]. It is very characteristic for them that later metasomatic formations occur on top of early formed metasomatites. This is directly related to the directed evolution of ore solutions, which is related to the change of their acidity-alkalinity, partial pressure and temperature. Secondary quartzites are closely related to porphyry copper ores in Garadag, Kharkhar, Jayirchai and other places, are spatial and widespread. As mentioned above, these new formations are more inclined to the apical parts of the small porphyry intrusives that cut through the Atabey-Slavyanka plagiogranite massif.

The evolution of their formation can be observed based on the analysis of the spatial arrangement of hydrothermal vents: regional propylitization-greenstone formations with wide-area development, metasomatites of later processes that are superimposed on them and are considered to be the product of pre-mineralization processes. Metasomatites of later processes are distinguished from primary regional propylitization by their small scale and clearly marked adaptation to splitting faults.

The ore mineralization (porphyry copper) was formed directly in this section of the hydrothermal process resulting in the occurrence of polyfacies secondary quartzites (including ore-locating quartz-sericite metasomatites). In general, the
evolution of hydrothermally altered rocks leads to the zonal structure of metasomatites (Fig. 2) [7,10,11,12,].

The presented scheme is quite conventional, however, in our opinion, it clearly reflects the ore-metasomatic zonation of copper- and molybdenum-porphyry deposits. The ore mineralization is observed in minor amounts of solfatara argillites in near-surface conditions. However, the ore-bearing quartz-sericite metasomatites are already in the middle horizons, and mineralization also developed in quartz facies rocks in the zone of primary ores. The contours of metasomatic aureoles decrease gradually towards depth. The metasomatites are sometimes also bordered by broad aureoles of pyritization that extend beyond the intrusives.

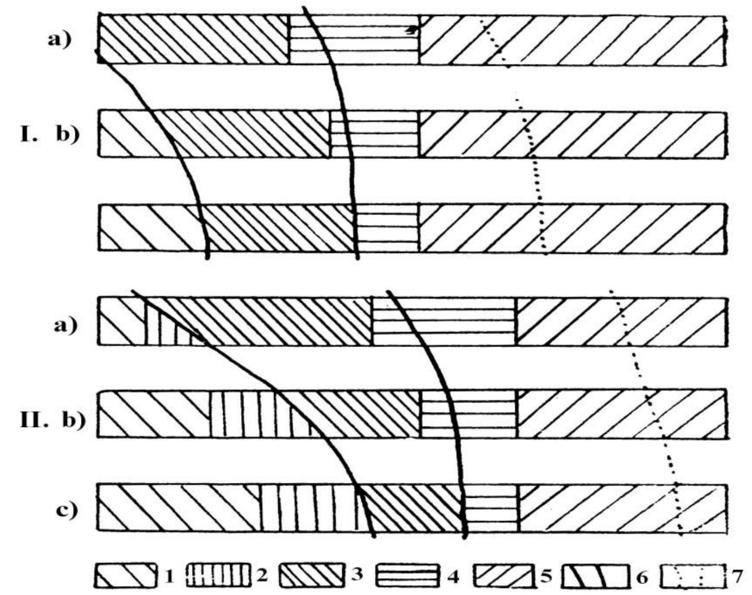

Figure 2. Ore-metasomatic zonation in porphyry copper deposits of Azerbaijan (I - Somkhit-Karabagh zone; II - Miskhana-Zangazur zone) (according to V.M.Babazadeh, V.G.Ramazanov and A.M.Ismayilova, 1990): Zones: 1-quartz; 2-potassium spar; 3-quartz-sericite; 4-argillite; 5-propylite; 6-distribution outline of porphyry copper ores; 7-boundaries of pyritization aureoles

According to the data obtained from the borehole drilling in the Garadag field, the ore zonation within the deposit boundary was studied. The depth of the deepest well is 540 meters here. The analysis of the tests taken from the well allowed to determine the average amount of ore elements on separate horizons, as well as the

zoning indicator. For the Garadag field, the following zoning order was obtained vertically (from bottom to top):

$$Mo \rightarrow Cu \rightarrow Co \rightarrow Ni \rightarrow Cr \rightarrow Ag \rightarrow Pb \rightarrow Zn$$

The vertically arrangement of the elements is clearly visible in Figure 4 according to the zonation indicator. According to the depth of the well, it is divided into 6 horizons; Zn, Pb, Ag and Cu are located in the first and second horizons where quartz-sericite-kaolinite metasomatites are developed. Ni and Co correspond to the third horizon. Cu reaches its maximum value in the fourth and fifth horizons, and Mo reaches its maximum value in the sixth horizon. [7,8,9]

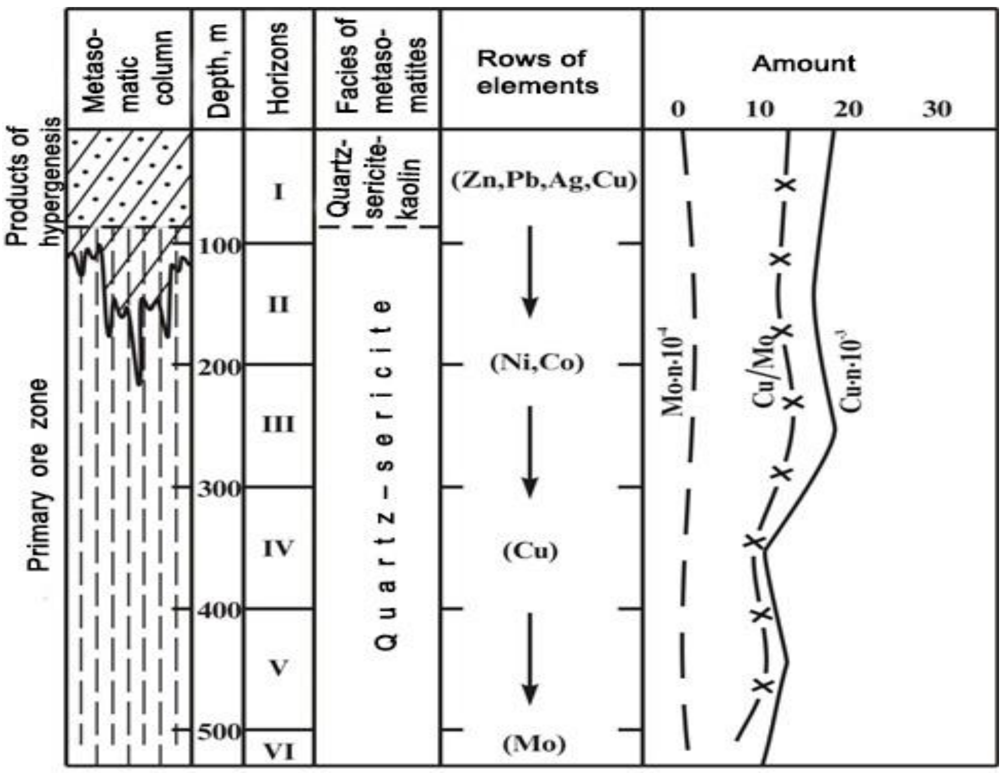

Figure 3. Ore zonation in a vertical section (Garadagh deposit) (according to V.M. Babazadeh, V.G. Ramazanov and A.M. Ismayilova, 1990)

Zonation is characterized by the predominance of the following morphological types of mineralization from bottom to top: impregnated, veinlet- impregnated, veinlet impregnated-vein, veinlet-vein and vein. Zonation of horizontal and vertical arrangement of quartz-chalcopyrite vein mineralization around copper and molybdenum-porphyry deposits is noticeable. In this respect, the

deposits of the Garadag ore field are similar to the deposits of the Ordubad ore district, Gacharan and Agharag in Armenia, Kalmakir in Uzbekistan and Chatyrkul in Kazakhstan.

Mineralogical zonation. The occurrence frequency of ore and nonmetallic minerals in ore masses at different depths of the ore field was studied based on the histogram. For this purpose, testing was carried out at intervals of every 20m in boreholes. As a result, the generalized vertical zonation of occurrence frequency of minerals was as following (from bottom to top): anhydrite, molybdenite, chalcopyrite, magnetite, carbonates (calcite, ankerite, dolomite), polysulfide paragenesis (brown ores, galena, sphalerite, chalcopyrite) with gold and silver, hematite, zeolites, barite. The correlations of the occurrence frequency of minerals show that the amount of chalcopyrite and anhydrite increases compared to pyrite, and molybdenite and anhydrite compared to chalcopyrite increases as moving from the surface to the depth.[7,8]

So, the dominant zones alternate vertically from bottom to top in the following order: molybdenite; chalcopyrite, gold; pyrite; gold-polysulfide paragenesis. Horizontal zonation is characterized by the formation of wide pyrite aureoles around industrial-type porphyry copper sites.

Geochemical zonation. Geochemical zonation in the ore field is observed as following: a) in the main ore components within the ore contour, b) in chemical elements in aureoles outside the ore masses, and c) in the distribution of mixed elements in ore and vein minerals. The results of the statistical development of the sample concentrations and isolines taken from different horizons show that three elements rouse interest for direct porphyry copper mineralization in the Garadag field along the lateral: copper, molybdenum and indirectly – silver. The vertical distribution of elements is as following: molybdenum, sulfur sulfate-copper-sulfur sulfide-gold-silver.

The distribution of components in ores is highly dependent on the type of wallrocks. The apical and outer parts of the stocks were subjected to mineralization in granodiorite-porphyries. The average indicators of gold relative to molybdenum increase regularly with the decrease of the depth of the erosion section of copper relative to molybdenum in the deposits. The absolute amount indicators of copper

and molybdenum increase with depth, while those of gold, on the contrary, decrease. This feature is probably related to the depth of formation of ore masses.

The analysis of prospecting profiles shows that they have almost the same structure. The widest and most intense aureoles are formed by the copper and molybdenum. No integrity is observed in the structure of copper aureoles on the Earth's surface. The aureole that is formed by silver on the surface and at the level of the ore mass also rouses interest. It forms relatively large at the level of the tin ore mass, and single isolated anomalous points on the Earth's surface. It creates narrow, linearly elongated aureoles of low intensity at the level of lead, nickel, cobalt ore

mass, which is not very large. Zinc, tungsten, antimony, bismuth and arsenic form anomalous fields in the form of single isolated points that do not follow any regularity in space. Barium does not create aureoles. The fact that this element, as well as arsenic, antimony, lead and zinc do not form aureoles on the surface shows probably that the Garadag deposit is subject to deep erosion.[9,10]

In order to determine and quantitatively assess the zonation order of the aureole-forming elements, the quantitative indicators of the zonation of the elements were calculated for each prospecting profile according to the methodology proposed by IMGRE (Russia) [5]. Indicators reflect the quantitatively relative concentration of the element in the studied horizon. According to the mineralization maximum in the Garadag field, 5 intervals are conditionally separated: upper ore; ore top; medium ore and sub ore. Intervals are characterized by a gradual decrease of the zonation coefficient (K_3). However, the practical use of this standard has certain difficulties. First, 2-stage geochemical testing of the object is required: first, contouring of secondary scattering aureoles is carried out, its dimensions and shape are determined, and then the average value of the zonality coefficient is calculated. Second, whether or not there are surface mining. The proposed method allows to eliminate these difficulties to predict blind porphyry copper mineralization within the deposit.The study of the geochemical peculiarities of the primary mineralization and related secondary scattering aureoles is based on a great amount of actual analytical material collected as a result of geological exploration in the Garadag ore field (spectral analyzes of bedrock, alluvial-delluvial sediments, etc.).

The value distribution of zonation indicators within ore mass was studied in vertical and horizontal sections. The value of the zonality indicator reflects quite the main regularities, in other words:

1) the highest value indicators of the zoning coefficient are in the upper ore and ore top horizons and the smallest coefficient - in the lower ore and sub-ore intervals;

2) the value indicator of the zonation coefficient in the linear elongated ore localizing structures differs from the main aureole area in the same section.

Analysis of the actual material has limits of zonation indicators of elements for each interval. According to the assessment, the following order of the zoning indicator of the elements can be established (from top to bottom):

$$(Au, Mo, Sn) \rightarrow Cu \rightarrow W \rightarrow (Zn, Co, Ni) \rightarrow (Pb, Bi)$$

Elements with unclear interrelationships are shown in parentheses, because the maximum amounts of their zonation indicators were determined in the same horizon of aureoles. In order to determine the arrangement of elements in such a zoning order, in accordance with paragraph 26 of the manual on "Geochemical methods of searching for ore deposits", the gradient of zoning indicators was calculated, and as a result, the following zoning orders were obtained for the profiles (from top to bottom):

Profile I-I: Sn-Mo-Ag-Cu-W-Zn-Ni-Co-Pb-Bi

Profile III-III: Pb-Sn-Mo-Ag-Ni-Cu-Co-W-Bi

Profile V-V: Mo-Ag-Cu-Sn-Pb-Co-W-Ni-Bi-Zn

Profile VII-VII: Ag-Bi-Zn-Cu-Ni-Mo-W-Co-Pb-Sn

The study of primary aureoles and zonation sequences on separate profiles in the Garadag field shows that there is no noticeable regularity in the zonal structure of aureoles of indicator elements in porphyry copper deposits. In turn, this does not allow to build a generalized vertical zonation sequence, and the data obtained are not consistent with classical models of porphyry copper deposit. As you know, porphyry copper deposits are represented in the following order along the axis zonation:

Ba-Ag-Sb – (Ag, Pb, Zn) – Au-Bi – (Cu, Mo) – (Sn, Co, W, Be)

For this reason, the obtained data do not allow to determine the aureoles of indicator elements of zonation in the Garadag field. Accordingly, it becomes difficult to determine the prospect of mineralization in the lower horizons from geochemical anomalies and to assess the criterion of the level of erosion section.

Alluvial genetic "C" horizon is considered to be the most reliable soil horizon in mountainous landscape conditions, where mainly residual, open secondary aureoles are developed. Its depth is between 0.2-0.5 m depending on the microrelief of the surface. In other words, all the properties of scattering aureoles belong to this genetic horizon. [7,8] It was determined that the distribution peculiarities of zonation coefficient indicators in rooty ores are completely inherited to the secondary aureoles related with them. The Garadagh deposit is occurred only in the form of anomalies of copper and molybdenum, and in small amounts of silver in lithochemical flows. In general, large flows of copper - 0.015-0.1%, silver - 0.00004-0.00016%, zinc 0.008-0.015% and local flows of molybdenum and lead are separated in the Garadag deposit. The largest and most contrasting flow belongs to silver and copper, followed by zinc, and the smallest and contrasting flow belongs to molybdenum and lead.

As a result of the work carried out on the initial aureoles in the field of Jeyirchai deposit, several lithochemical flows of gold were separated on the left bank. These flows are also accompanied by lithochemical flows of copper, lead and zinc. The maximum lithochemical flows of gold coincide with the most intense flows of silver in space. According to prospecting materials, the amount of gold in lithochemical flows was 0.01-0.15 g/t, in two tests - 0.8 g/t, in one test - 2 g/t. Interestingly, lithochemical flows of gold are accompanied by mechanical flows of pyrite. A significant amount of pyrite crystals of pentagonal dodecahedron and octahedron form dominate in thin section. The analysis of lithochemical and thin section-mineralogical analyzes shows that porphyry copper mineralization in Jeyirchai is accompanied by gold aureoles, unlike the Garadag deposit. This fact increases the perspective of the object greatly.[4,5,6]

Mono and polyelement anomalous areas are distinguished in Jeyirchai, which is considered promising for the search for ore masses, as in Garadag. A regular lateral zonation is observed in the structure of anomalies here: copper, molybdenum and barium from the center to the edges; they are surrounded by anomalies of silver, on the eastern side - of zinc. The amount of anomalies, geochemical parameters, element composition (Cu, Mo, Ba, Pb, Zn) and finally, their position in the highest part of the porphyry copper ore column show that if the porphyry copper mineralization in the Garadag deposit was formed at a shallow depth, the gold-bearing ores were formed at medium and large depths in Jeyirchai. The indicated situation is probably related to splitting faults before mineralization and shows the block-shaped nature of the Garadag ore field as a whole. Geophysical studies also show that the Garadag ore field has a block structure. At the same time, according to the geochemical parameters, we should say that the Garadag porphyry copper deposit is significantly eroded, while Jeyirchai is eroded very little; in the latter, the ore column is almost completely preserved in some places. This fact increases the perspective of Jajirchai. The average value of copper endogenous anomalies on the surface in Jeyirchai is $14.23 \cdot 10^{-3}$%, in the Garadag deposit – $13.02 \cdot 10^{-3}$%. However, the comparison of the indicated values, as well as visual observations show that intensive impoverishment of copper anomalies with this element, i.e. weathering processes did not bypass the field of Jeyirchai deposit. Nevertheless, if we take into account the almost complete preservation of the porphyry copper ore column under the complex of Bajocian sediments, we can conclude that the Jeyirchai deposit has a great industrial importance.[6,8]

So, the abovementioned vertical and horizontal types of zonation in the Garadag ore field reveal new possibilities for predicting gold-bearing blind porphyry copper mineralization at depth.

Conclusion:

As a result of the efforts of geologists working in the Garadagh ore field in different years, different types of zoning were identified in the structure and location of porphyry copper deposits and it was determined that mineralization is directly related to multi-stage hydrothermal metasomatic alterations. Porphyry copper mineralization in deposits of the ore field contains large amounts of gold. Gold is also observed in copper pyrite and copper-polymetallic ores outside the ore field.

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