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## Mineral associations in the geochemical halos of Milin Kamak ore deposit, Bulgaria

### Минерални асоциации в геохимичните ореоли на находище „Милин камък“, България

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**Abstract.** The focus of this study is the mineralogical interpretation of the determined geochemical associations in the Milin Kamak deposit. Based on the results of the factor analysis, an attempt was made for interpretation of the factor axes by mineralogical studies and EPMA analysis. Three factor associations are related to the hydrothermal ore-forming processes. The main factor axes related to Au is quartz-polymetallic stage and is represented by pyrite, marcasite, arsenopyrite, pyrrotite, sphalerite, galena and chalcopyrite.

**Keywords:** Milin Kamak deposit, geochemical associations, factor analysis, mineral associations, zonal distribution.

### Introduction

The Milin Kamak deposit is located near the town of Breznik. In tectonic position, the area belongs to Sofia tectonic unit which is part of the Srednogie Tectonic Zone. On the other hand, the tectonic area is part of the larger Apuseni-Banat-Timok-Srednogie Magmatic and Metallogenic Belt (ABTS) (Popov et al., 2002). Various volcanogenic-sedimentary succession are exposed around Milin Kamak deposit. They belong mainly to the Breznik paleovolcano, and they form up to 1400 m thick volcanic formations. Trachybasalts, shoshonites, ash, psephitic, lapilli and bomb tuffs as pyroclastic and epiclastic products predominate. Adjacent to the ore zones, the products of the Breznik paleovolcano are hydrothermally altered with intensive acid leaching and associated with argillic, advanced argillic, sericitic and propylitic rocks (Sabeva et al., 2012). The ore zones are localized in 8 veins, developed among lapilli tuffs and basalt dykes, which are affected by strong argillic and sericitic alteration. They are E-W trending, steeply dipping to the south and cut by ENE-WSW and NNW-SSE faults (Strahilov et al., 2022). The established mineral associa-

tions are formed during two stages – hydrothermal (including quartz-pyrite, quartz-polymetallic and carbonate-gold stages) and supergene (Sabeva et al., 2017). This gold-silver deposit is well-defined as intermediate sulphidation type in association with Pb, Zn and Cu (Sabeva et al., 2012). To estimate the spatial distribution of Au, Pb and Zn, Marinov et al. (2018) used RBF interpolation of structural data from exploration core drilling and mine decline and chemical analysis results.

### Materials and methods

To determine the spatial correlation and geochemical associations, the data obtained during the exploration drilling program conducted in the period 2016–2021 and provided by Trace Resources Ltd were used. The methodology to determine geochemical associations and developed by Popov (2016) is used to evaluate the spatial correlation of the elements and the 3D modeling. The statistical processing includes: preliminary data preparation and univariate statistical analysis → correlation and cluster analysis → factor analysis and 3D modeling of the geochemical associations. The mineralogical

study includes: the selection of representative samples, the prepared polished preparations, reflected plane polarized light observation, taking microphotographs with a digital camera with a digital reflex camera mounted on the trinocular of a microscope, electron microprobe analyzes of ore minerals with SEM EDS, crystallochemical formulas and analysis of the results.

## Results and discussion

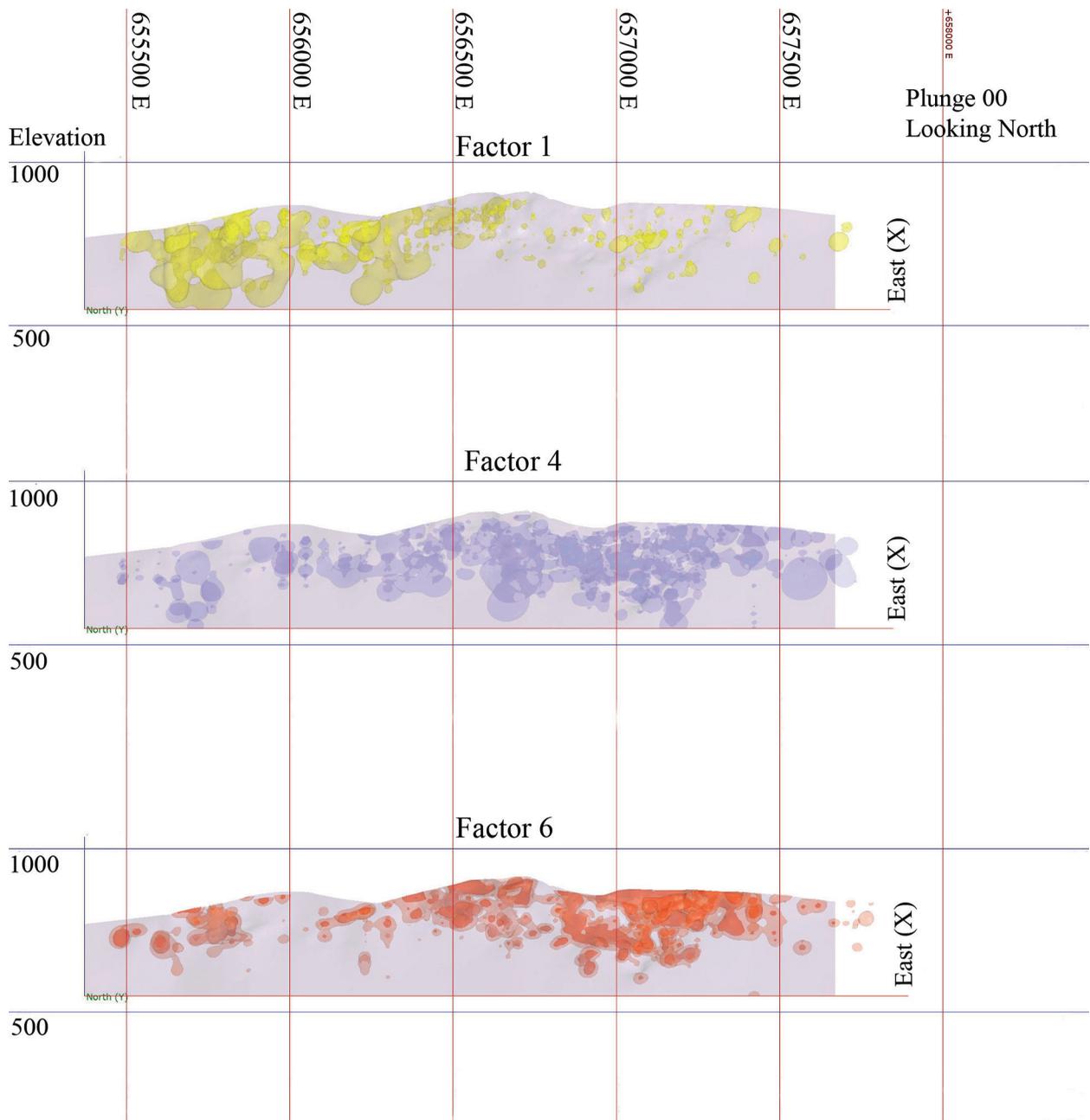
Based on similar element's spatial distributions, six groups of factors were obtained in the Milin Kamak deposit as a result of the applied multivariate factor analysis (Marinov et al., 2019). On the basis of the results of the factor analysis for 22 elements (Ag, Bi, Cu, Sb, Cd, Zn, Pb, As, Au, Mn, Mo, Ba, Be, Cr, Ni, W, Co, Fe, Ti, V, Ca, Mg) the factors are distributed into 6 axes. The results of the factor scores make it possible to clarify the geochemical associations and spatial distribution of groups of elements characterized by a certain similarity. Only three axes are related to the hydrothermal ore-forming processes and represent the ore bodies. These are: factor 6 ([As] Au) Mn, factor 4 ([Cu, Sb] Bi)+Ag, Pb±As, Fe, Au, Ba, Zn and factor 1 [Cd, Zn, Pb].

According to this research, the represented by factor 6 geochemical association ([As] Au) Mn is characterized by a negative correlation with Ca, Mg (Pearson correlation: Au:As is 0.535; Au:Mn is 0.273). It represents the main ore body coinciding with the positions with the highest Au contents (Fig. 1). The distribution of this factor is along the entire ore zone 1 as well as zone 2. Along zone 1, factor scores are most manifested in the eastern parts. From a mineralogical point of view (Sabeva et al., 2012; Nikolova et al., 2019), Au is finely dispersed in pyrite from the quartz-polymetallic stages. In pyrite, the gold is in the form of microinclusions of native gold or Au-bearing mineral phases. It is often connected isomorphically. According to Simon et al. (1999) an indication of this is the presence of elements such as As, Te, Se and Sb, which replace sulfur and deform the lattice and help the pass of gold. This is also possible with Au-HS complexes, which are more characteristic of Au transport in lower temperature conditions in place of Fe or in the empty cation. The strong positive Au-As relationship also suggests substitution of the type  $\text{Au}^{3+} + \text{As}^+ \Rightarrow 2\text{Fe}^{2+}$  (Arehart et al., 1993) and/or adsorption or chemisorption of Au on As-rich growth surfaces in pyrite probably due to a semiconductor effect (Mironov et al., 1981).

The ([Cu, Sb] Bi)+Ag, Pb±As, Fe, Au, Ba, Zn association explained by factor 4 has a similar spatial distribution with the factor 6 anomalies along

ore zones 1 and 2 (Pearson correlation: Cu:Sb is 0.577; Bi:Cu is 0.317). In the other ore zones, geochemical anomalies are not so well represented. This factor is more manifested in the central parts of zone 1 and is deeper than factor 6 (Fig. 1). This geochemical association clearly marks the distribution of minerals represented by the quartz-sulfosaltpyrite-galena-sphalerite association. Cook et al. (2009) studied trace elements in sphalerite and define it a common trace element is Cu, which may enter its structure isomorphically. More recent research (George et al., 2018) shows that the role of isomorphous impurity should not be underestimated, as monovalent silver quite readily replaces  $\text{Cu}^+$  in tetrahedral coordination. According to our studies, the higher Cu (around 40 wt %) concentrations are due to tennantite-tetrahedrite microinclusions given the positive correlations of Cu with Sb, As and Ag. Furthermore, the positive Cu-Ag correlations also point to an isomorphism scheme of the type  $\text{Ag}^+ + \text{Cu}^+ + \text{Sn}^{4+} \Rightarrow 3\text{Zn}^{2+}$ . Also, the As and Sb may isomorphically substitute for sulfur in some sulfosal minerals with a possible zonal distribution. In most cases, there are microinclusions in tennantite-tetrahedrite mineral phases, given the positive As-Ag-Cu-Sb correlations. They point to the presence of microinclusions of As-containing mineral phases in tennantite-tetrahedrites proven by microprobe analyses, where As together with Ag or Cu can replace Fe (Nikolova et al., 2019). The Sb for its part, is also possible to go in isomorphically in the structure of sphalerite (combination isomorphism with Ag and Cu given the positive correlations between them), as well as in the form of microinclusions of Sb-containing mineral phases such as tennantite-tetrahedrite. Silver in tetrahedrites is a characteristic element. It is probably associated with microinclusions of Sb and/or Bi-containing galena, which in this case is evidenced by the positive Ag-Pb-Sb-Bi correlations.

The association of factor 1 [Cd, Zn, Pb] is mainly developed in the most western part of the ore zones 1 and 2 (Pearson correlation: Cd:Zn is 0.966; Cd:Pb is 0.756). In the other parts of zone 1, as well as in the other zones, factor anomalies are poorly manifested. The distribution of this geochemical association is usually in places, where factor associations 4 and 6 are the least prevalent (Fig. 1). From a mineralogical point of view, the group clearly marks the distribution of minerals from the quartz-galena-sphalerite association. The strong correlation of Cd and Zn is unique as all other trace element pairs show little or no correlation. In general, higher Zn concentrations in chalcopyrite are associated with higher Cd concentrations (George, 2018). Any distinct difference in the Cd:Zn ratios in the two minerals or a non-continuous Cd:Zn ratio in chalcopyrite



**Fig. 1.** Distribution of the geochemical associations (after Marinov et al., 2019, with modifications): Factor 1, cross section of [Cd, Zn, Pb] association; Factor 4, cross section of ([Cu, Sb] Bi)+Ag, Pb±As, Fe, Au, Ba, Zn association; Factor 6, cross section of ([As] Au) Mn±Fe, –([Mg] Ca)±Fe association

may be an indication of different physicochemical conditions during crystallization (George et al., 2018). Under constant physicochemical conditions, the Cd:Zn ratios in the simultaneous crystallization of chalcopyrite and sphalerite are usually approximately the same. Cd is a common trace element in sphalerite. Pb from galena easy pass in the pyrite lattice, sphalerite and chalcopyrite in low concentrations. This regularity explains the high correlation between the items in a factor 1.

## Conclusions

The results of the factor analysis are tied to the mineral associations. The factors represent the spreading of chemical elements and mineral composition. Three groups of factors with a similar spatial distribution are distinguished, which are related to the zonal distribution of minerals.

Factor 6 is characterized by the spread of the quartz-polymetallic stage and is represented by: py-

rite, marcasite, arsenopyrite, pyrrhotite, sphalerite, galena, chalcopyrite. Tennantite-tetrahedrite and seligmanite-burtonite series minerals are almost always found. Rare minerals as enargite, yordanite, robinsonite and gratonite are also observed. Factor 1 follows the distribution of quartz-galena-sphalerite association. Factor 4 clearly marks the quartz-sulfosalt-pyrite-galena-sphalerite association with a significant increase in tennantite-tetrahedrite.

3D modeling of the similarity in the spatial distribution of the elements clearly shows that the elements in factors 1, 4 and 6 are related to hydrothermal ore-forming processes and represent the ore bodies.

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