NEW GEOCHEMICAL DATA AND MINERALOGICAL INTERPRETATION FOR CISMA ORE DEPOSIT, GUTÂI MOUNTAINS

Réka KOVÁCS[1,2]*, Călin G. TĂMAŞ[1]**

[1]Babeş-Bolyai University, Department of Geology, 1, Kogălniceanu str., 400084, Cluj Napoca, Romania;
[2]Victor Gorduza County Mineralogical Museum of Baia Mare, 8, Traian bld., 430212, Baia Mare, Romania.
* *kovacsreka056@gmail.com*; ***calin.tamas@ubbcluj.ro*.

Abstract: Geochemical analyses carried out for Cisma ore deposit allow to propose several correlations between the chemical composition and the mineralogy of the ore. The presence of precious metals was also confirmed, as well as the As dominant *vs*. Sb subordinate character of the Cu-rich ore. Additional studies are required for a complete clarification of the mineralogical composition of the ore from Cisma as suggested by the quantitative chemical data *i.e*. significant presence of Ag, Se, and Te.

Keywords: geochemistry, mineralogy, tetrahedrite-tennantite, enargite, Cisma ore deposit, Băiuţ, Baia Mare metallogenetic district, Gutâi Mountains

Geological setting

The Baia Mare Neogene metallogenetic district is situated along the southern edge of the Gutâi Mountains, from the north-western section of the Eastern Carpathian volcanic chain and hosts tens of Pb-Zn-Cu±Au-Ag and Au-Ag±Pb-Zn-Cu epithermal deposits. At the district scale Săndulescu (1984) pointed out the presence of three major structural units, *i.e*., *i*) the pre-Neogene basement (Paleogene sedimentary rocks/flysch-like deposits); *ii*) the Neogene sedimentary rocks cover; and *iii*) the Neogene volcanic rocks. The ore deposits from Baia Mare Neogene metallogenetic district are related to the intermediate calc-alkaline arc-type magmatism that started in Sarmatian (13.4 Ma; Edelstein et al., 1992). The age of the hydrothermal activity, which was genetically linked to the volcanic activity is Pannonian (11.5-7.9 Ma; Lang et al., 1994; Kovacs et al., 1997). From geographic and from the commodities points of view, the Baia Mare metallogenetic district was divided in three metallogenetic fields (from west to east), as follows: *i)* Ilba – Nistru (Pb-Zn-Cu ±Au, Ag); *ii)* Săsar – Dealul Crucii (Au, Ag); and *iii)* Herja – Băiuţ (Pb-Zn-Cu and Au-Ag) (Kovacs and Fülöp, 2010).

The ore deposits from the Baia Mare metallogenetic district are controlled by the Bogdan Vodă-Dragoş Vodă fault system with an overall west-east strike (Neubauer et al., 2005), situated on the southern slope of the Gutâi Mountains. This main metallogenetic structural control was interpreted by many authors (*e.g*. Csontos and Nagymarossy, 1998, Tischler et al., 2007) as the eastern prolongation of the so-called Mid-Hungarian Line that separates Alcapa and Tisia-Getia (Seghedi et al., 1998)/Tisza-Dacia (Csontos et al., 1992) microplates.

Representing the eastern extremity of Baia Mare Neogene metallogenetic district, the Băiuţ metallogenetic field is at its turn composed of the following three main ore deposits (Borcoş and Gheorghiţă, 1976), which from west to east are: *i*) Breiner – Băiuţ, *ii*) Văratec, and *iii*) Cisma-Poiana Botizei. The radiometric age of the ore deposits from the Herja-Băiuţ metallogenetic field (Lang et al., 1994; Kovacs et al., 1997) is 9.4-7.9 Ma and corresponds to Upper Pannonian.

The Cisma – Poiana Botizei (Cisma) ore deposit (Fig. 1) represents the easternmost ore occurrence within the Băiuţ metallogenetic field and the Baia Mare district as well. The ore deposit consists of several vein structures hosted in Paleogene flysch sequences that are pierced by Neogene quartz microdiorite and microgranodiorite subvolcanic bodies (Plotinskaya et al., 2012). The most important vein structures from Cisma ore deposits are Banduriţa, Cisma, Coasta Ursului, Olimpiu, and Prisăcele (Borcoş and Gheorghiţă, 1976; Istvan et al., 1995; Mariaş, 2005; Damian et al., 2016).

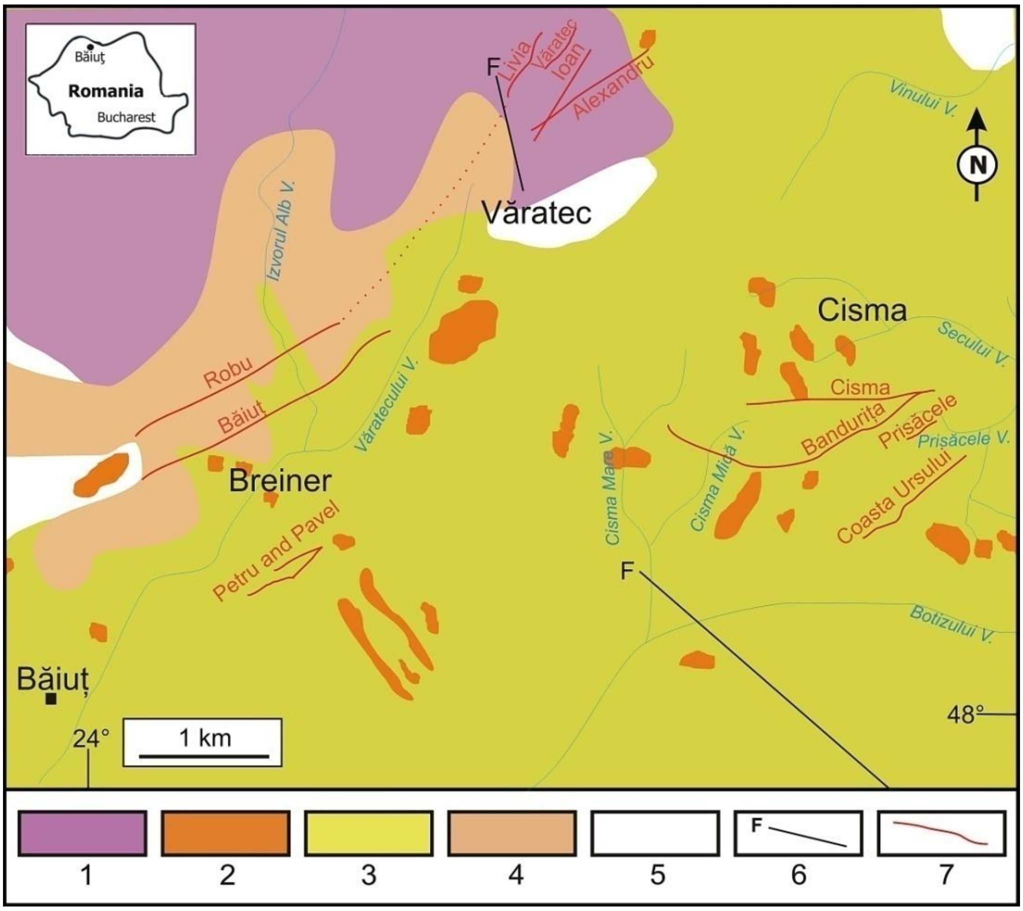

Fig. 1. Simplified geological map (modified after Borcoş and Gheorghiţă, 1976; András, 2017) of the Băiuţ metallogenetic field, showing the location of the main veins from the Breiner (W), Văratec (N) and Cisma (E) fields. 1-Pontian pyroxene andesites; 2-Pontian pyroxene andesites±biotite; 3-Paleogene sedimentary rocks; 4-Neogene volcanic rocks; 5-Quaternary sedimentary rocks; 6-Faults; 7-Veins.

Materials and methods

The studied sample represents an ore fragment of the former ore stock pile from Cisma ore deposit, in the neighborhood of the Băiuţ processing plant. According to a previous mineralogical study (András, 2017, unpubl.) the following minerals were identified by optical microscopy from similar samples: galena, chalcopyrite, tetrahedrite, sphalerite, hematite, covellite and enargite; the X-ray diffraction data by the same author confirmed the presence of kaolinite, as main alteration mineral.

Multi-elemental geochemical analyses have been carried out on the sample BT5089 from Cisma ore deposit, by ALS Romania, Roşia Montană. Macroscopically, the sample is dominated by the presence of pyrite and chalcopyrite (Fig. 2). The geochemical analyses included the grade measurement for 49 elements, including Ag, As, Au, Bi, Cd, Cu, Mn, Pb, Sb, Se, Te, Zn. The Au was measured by fire assay, with the detection limit ranging between 0.001 and 10 ppm. The Ag grade was measured by acid digestion (HF-HNO_3-$HClO_4$ with HCl leach) and ICP-AES finish, with the detection limit ranging from 1 to 1500 ppm. The remaining chemical elements were measured by four acid digestion and ICP-AES finish. The detection intervals for the chemical elements presented in Table 1 is (in ppm), As 0.2-10000; Bi 0.01-10000; Cd 0.02-1000; Cu 0.2-10000; Mn 5-100000; Pb 0.5-10,000; Sb 0.05-10,000; Se 1-1000; Te 0.05-500; and Zn 2-10000 ppm. Due to the over-limit Cu grade by the above-mentioned method, Cu was additionally measured by aqua regia digestion with ICP-AES finish with the detection interval 10 ppm – 40 %.

Fig.2. The studied ore sample BT5089 from Cisma, used for geochemical analyses, dominated by pyrite and chalcopyrite.

Results and Discussions

The geochemical analyses obtained on the BT5089 sample from Cisma ore deposit are presented in Table 1. These results highlight the Cu-extremely rich character of the ore (8.67 %) and the presence of precious metals (Au and Ag at 1.74 and 105 ppm respectively).

Table 1. The geochemistry results (selection) for the sample BT5089, Cisma ore deposit, Băiuţ metallogenetic district.

Element	Ag ppm	As ppm	Au ppm	Bi ppm	Cd ppm	Cu %	Mn ppm	Pb ppm	Sb ppm	Se ppm	Te ppm	Zn ppm
Grade	105	1280	1.74	1.41	14.45	8.67	263	1470	100.5	16	1.73	1980

According to Damian and Damian (2004) and Damian et al. (2016) the ore from Cisma consists mainly of common sulfides (pyrite, chalcopyrite, galena, sphalerite) and Cu-sulfosalts (tetrahedrite and tennantite), associated to Pb-sulfosalts (semseyite, boulangerite, and jamesonite), Fe-sulfides (pyrrhotite, marcasite) and hematite, Sb- and As-sulfides (stibnite, realgar, and orpiment), Bi-minerals (lillianite-gustavite, and native Bi), wolframite and native gold.

Recent reflected light ore microscopy study and semi-quantitative SEM-EDS investigations carried out on Cisma ore samples (Kovács and Tămaş, 2017), confirmed the presence of hematite, galena, chalcopyrite, sphalerite, pyrite, tetrahedrite-tennantite, and enargite.

The high Cu content of the analyzed ore sample from Cisma is related to the abundance of chalcopyrite and the presence of Cu-sulfosalts (tetrahedrite-tennantite mineral compositions). Significant Au grade is certainly given by the presence of native gold, as this mineral was previously mentioned from Cisma by Damian and Damian (2004). With the exception of Ag-bearing tetrahedrite-tennantite mineral compositions pointed out by SEM-EDS semi-quantitative measurements by Kovács and Tămaş (2017) no other Ag-bearing minerals were mentioned previously from Cisma. Taking into account the relative low Au grade as compared to Ag grade (1.74 *vs*. 105 ppm respectively) it seems unlikely that the native gold could be considered as a major Ag-bearing mineral within the ore. It is more likely that some other Ag-bearing minerals apart tetrahedrite-tennantite could be also present in the ore, but these minerals are not yet identified.

The As to Sb ratio (Table 1) 1280/100.5 (in ppm) reflects accurately the predominance of tennantite versus tetrahedrite within the ore. Moreover, it also reflects the input of enargite in the bulk As-content of the analyzed ore sample.

The Zn and Pb grades mirror the presence of sphalerite and galena respectively. Taking into account the capacity of sphalerite to accommodate over 15 wt % impurities (Udubaşa et al., 1974; Cook et al., 2009), it seems that Cd, Mn and probably at least part of Se represent impurities hosted by sphalerite.

The presence of Bi-minerals (Damian and Damian, 2004) correlates well to the Bi grade within the analyzed ore sample, while for Te and Se it is possible to infer traces of Te- and Se-bearing minerals or minerals that may accommodate these chemical elements as impurities (*e.g*. sphalerite?).

Conclusion

The geochemical analyses carried out correlate well to the overall known mineralogical composition of the ore from Cisma ore deposit. However, the new geochemical results suggest the precious metals character of the ore and the possible occurrence of Te-Se bearing mineral(s) or the presence of these elements as impurities hosted most likely by sphalerite.

References

András K. (2017) Mineralogical study of the ore deposits from the Băiuţ district (Maramureş county), focusing on the Văratec, Cisma, Coasta Ursului, Johan Hell, Breiner and Poiana Botizei deposits (in Romanian). Unpublished MSc Thesis, Babeş-Bolyai University Cluj Napoca, Romania.

Borcoş M., Gheorghiţă I. (1976) Neogene hydrothermal ore deposits in the volcanic Gutâi Mountains. IV. Băiuţ-Văratec-Botiza metallogenetic field. Revue Roumaine de Géologie, Géophysique et Géographie, Série de Géologie, 20, 2, p. 197-209.

Cook N.J., Ciobanu C.L., Pring A., Skinner W., Shimizu M., Danyushevsky L., Saini-Eidukat B., Melchner F. (2009) Trace and minor elements in sphalerite: LA-ICPMS study. Geochimica and Cosmochimica Acta, 73, p. 4761-4791.

Csontos L., Nagymarosy A., Horváth F., Kovacs M. (1992) Tertiary evolution of the Intra-Carpathian area: a model. Tectonophysics, 208/1-3, p. 221-241.

Csontos L., Nagymarosy A. (1998) The Mid-Hungarian Line: a zone of repeated tectonic inversions. Tectonophysics, 297/1-4, p. 51-71.

Damian F., Damian Gh. (2004) Mineral parageneses of the hydrothermal ore deposits from Baia Mare area, Romania. Mining explorations, preparation of non-ferous metallurgy, geology and environmental engineering, Series D, vol. XVIII, p. 155-172.

Damian G., Damian F., Konecny P., Kollárová V. (2016) A new occurence of wolframite-ferberite in Romania. Romanian Journal of Mineral Deposits, 89/1-2, p. 49-54.

Edelstein O., Iştvan D., Kovacs M., Bernad A., Stan D., Iştvan E., Gabor M., Bálint B., Haranth G., Vârşescu I. (1992) Preliminary data regarding the K-Ar of some eruptive rocks from Baia Mare Neogene volcanic zone. Revue Roumaine de Géologie, 36, 45-60.

Iştvan D., Vârşescu I., Halga S., Grancea L. (1995) Gold-silver epithermal levels and association of the eastern area of the Gutâi Mts. and in the Văratec Mts. (Firiza-Botiza area), East Carpathians, Romania. Studia Universitatis Babeş-Bolyai Cluj Napoca, Geology, XL, 1, p. 195-210.

Kovacs M., Edelstein O., Gabor M., Bonhomme M., Pécskay Z. (1997) Neogene magmatism and metallogeny in Oaş-Gutâi-Ţibleş Mts.; a new approach based on radiometric datings. Romanian Journal of Mineral Deposits, 78, p. 38-45.

Kovacs M., Fülöp A. (2010) Baia Mare metallogenetic district. In: Iancu G., Kovacs M. (2010) Ore deposits and other classic localities in the Eastern Carpathians: From metamorphics to volcanics. Acta Mineralogica-Petrographica, Field Guide Series, 19, p. 5-13.

Kovács R., Tămaş C. (2017) Cu-sulfosalts in Băiuţ metallogenetic field, Baia Mare district, Gutâi Mountains – Preliminary Scanning Electron Microscopy Data. "Ion Popescu Voiteşti" Yearly Scientific Session, Babeş-Bolyai University Cluj Napoca, Geology Department, 15th December 2017, p. 24-30.

Lang B., Edelstein O., Steinitz G., Kovacs M., Halga S. (1994) Ar-Ar dating of adularia – A tool in understanding genetic relation between volcanism and mineralization: Baia Mare area (Gutâi Mountains), Northwestern Romania. Economic Geology, 89, p. 174-180.

Mariaş Z.F. (2005) Metallogeny of the Baia Mare mining district. An approach based on the Cavnic hydrothermal system, comparison with other epithermal systems in the world (in Romanian). Cornelius Publishing House, 450 pp., Cluj Napoca, Neubauer F., Lips A., Kouzmanov K., Lexa J., Ivăşcanu P. (2005) Subduction, slab detachment and mineralization: The Neogene in the Apuseni Mountains and Carpathians. Ore Geology Reviews, 27, p. 13-44.

Plotinskaya O.Y., Prokofiev V.Y., Damian Gh., Damian F., Lehmann B. (2012) The Cisma deposit, Băiuţ district, Eastern Carpathians, Romania: sphalerite composition and formation conditions. Carpathian Journal of Earth and Environmental Sciences, 7/2, p. 265-273.

Săndulescu M. (1984) Geotectonics of Romania (in Romanian). Tehnică Publishing House, 336 pp., Bucureşti.

Seghedi I., Balintoni I., Szakács A. (1998) Interplay of tectonics and Neogene post-collisional magmatism in the Intracarpathian area. Lithos, 465, p. 483-499.

Tischler M., Gröger H.R., Fügenschuh B., Schmid S.M. (2007) Miocene tectonics of the Maramureş area (Northern Romania): implications for the Mid-Hungarian fault zone. International Journal of Earth Sciences, Geologische Rundschau, 96, p. 473-496.

Udubaşa G., Medesan A., Ottemann J. (1974) On geochemistry and influence of Fe, Mn, Cd and Cu of lattice constant of natural sphalerite (in German). Neues Jahrbuch für Mineralogie Abhandlungen, 121, p. 229-251.