COPPER MINERALIZATIONS FROM BAIA DE ARAMĂ. HISTORICAL AND METALLOGENETIC DATA

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Abstract. The ancient historical sources (quoted by DENSUȘIANU, 1913) show that the copper deposits from Baia de Aramă were exploited even before the time of the Dacians. Specific details regarding the copper mining in this region are known from the time of the great rulers of the Romanian Country (Wallachia), especially Mircea cel Bătrân (1386-1418) and Matei Basarab (1632-1654). Although some data could be ambiguous, they can offer a coherent image of the Middle Ages mining in this region. Two important tectonic units of the western part of the South Carpathians emerge in the Baia de Aramă region: the Getic Nappe from the Bahna Outlier and the Severin Nappe, underlain by the Getic Nappe. The copper mineralizations (calcopyrite and pyrite) are located in the tuffogenic horizon of the Severin Nappe. The average copper content in the deposit is 0.24%. This paper presents data on mineralization in the sectors Boroaia-Măgura (0.27% Cu), Obârșia (0.41% Cu), Ponoare-Valea Cauna (0.40% Cu) and Creasta Gorunului-Dealul Ocnelor-Cracul Joiței (2.84% Cu). The analyses we have performed on two samples of slag from the dumps on the right side of the Valea Cujnița indicate copper contents of 0.54% and 0.14%, respectively. The technological possibility of processing the ancient slag to obtain a metallurgically usable concentrate was demonstrated in the 70s of the last century.

Keywords: copper, Baia de Aramă, history, metallogeny.

Rezumat. Mineralizațiile de cupru de la Baia de Aramă. Date istorice și metalogenetice. Sursele istorice antice (citate de DENSUȘIANU, 1913) arată că zăcămintele de cupru de la Baia de Aramă se exploatau încă înainte de vremea dacilor. Detalii concrete privind exploatarea cuprului în această regiune există din timpul marilor domnitori ai Țării Românești (Valahia), în special Mircea cel Bătrân (1386-1418) și Matei Basarab (1632-1654). Chiar dacă unele date pot fi ambigue, pe baza lor se poate contura o imagine coerentă a mineritului din această regiune în timpul Evului Mediu. Din punct de vedere geologic, în regiunea Baia de Aramă aflorează două unități tectonice importante ale Carpaților Meridionali de vest: Pânza Getică din Peticul de Bahna și Pânza de Severin, acoperită de Pânza Getică. Mineralizațiile de cupru (calcopirită și pirită) sunt localizate în orizontul tufogen al Pânzei de Severin. Valoarea medie a conținutului de cupru în zăcământ este de 0,24%. În această lucrare sunt prezentate date privind mineralizațiile din sectoarele Boroaia-Măgura (0, 27% Cu), Obârșia (0, 41% Cu), Ponoare-Valea Cauna (0, 40% Cu) și Culmea Gorunului-Dealul Ocnelor-Cracul Joiței (2, 84% Cu). Analizele făcute de noi pe două eșantioane de zgură din haldele din versantul drept al Văii Cujnița au dat conținuturi de cupru de 0, 54%, respectiv 0, 14%. Posibilitatea tehnologică a prelucrării zgurilor vechi pentru a obține un concentrat utilizabil metalurgic a fost demonstrată în anii '70 ai secolului trecut.

Cuvinte cheie: cupru, Baia de Aramă, istorie, metalogenie.

INTRODUCTION. HISTORICAL DATA

The copper mineralization in the Baia de Aramă area has been known for a very long time. Quoting ancient sources, DENSUȘIANU (1913) comes to the conclusion that the copper deposits at Baia de Aramă were exploited even before the time of the Dacians. During the time of Mircea cel Bătrân (1386-1418), the powerful ruler of Wallachia, in 1392, copper was mined at Bratilova on the Brebina Valley, the mine being concessioned to some Saxon miners. The 10% income (the tithe) that belonged to the ruler of the country was donated to the Tismana Monastery (PANAITESCU, 1943).

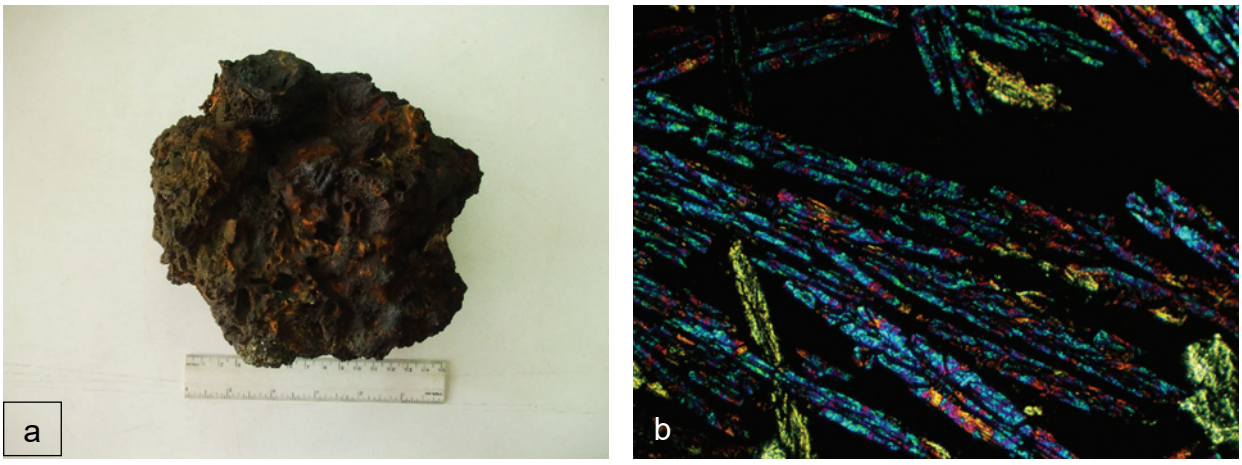

Figure 1. Ancient slag from the Baia de Aramă region: a) macroscopic appearance. b) Microscopic appearance with olivine rods (high birefringence) in a glassy mass impregnated with opaque minerals; photo width 1.4 mm.

In 1644, the Ruler Matei Basarab (1632-1654) transferred the exploitation of copper to the kingdom's account, modernizing the mining works with Serbian workers. From PAUL OF ALEPPO (1675) we find out that during Matei Basarab's time the annual production was 200,000 okas of copper (roughly 250 tons!), which is surely exaggerated in his own style. In reality, the annual production was 600 okas (RĂȚOI, 2013), about 760 kg. Important are the details regarding the exploitation technique that the indefatigable traveler gives. The ore from the deposit was crushed in mines (pits) by heating with wood fire and cooling with water. The pieces of ore were then brought to the surface and melted in furnaces several times for refining, with wood and coal fires. The final batch was poured into molds. Much of the copper production was exported to Turkey and Persia.

At the beginning of the 18th century, the temporary and unfortunate Austrian administration at the time reported that the deposits were almost exhausted. However, there is information that in the fourth decade of the 19th century there was an artisanal mining of chalcopyrite ore from Baia de Aramă (BERGRATH, 1838). At the end of the 19th century DENSUȘIANU (1913) visited the area and saw gallery mouths (salt mines), degraded surface mining works (aqueducts) and large deposits of slag (Fig. 1), partially covered by alluvium.

DRĂGHICEANU (1885), author of a monograph on the Mehedinți region, shows that mines were opened in the Ocnei Hill and Brebina Valley, where there were five galleries between 20 and 40 meters long, from which chalcopyrite was mined. In addition to the mineralization from Baia de Aramă, DRĂGHICEANU (1885) also mentions other copper and iron mineralization in the region, at Mărășești, Orzești Hill, Obârșia Cloșani and Podeni.

The author also cites four chemical analyses, two made in Romania, on ore samples from Cireșu, and two in France, on samples from the Orzești Hill, and Podeni, respectively. Copper contents vary from 5.18% to 12.67%, iron from 5.42% to 49.55%, and sulfur from 1.90% to 14.48%. Many data of Drăghiceanu, including the chemical analyses from Cireșu, are quoted by CRÉMER (1888) in a study on the mineral wealth of Romania. In his synthesis regarding the minerals from Romania, PONI (1900) also quotes the two chemical analyses on chalcopyrite from Cireșu, considering that one of them is erroneous, having too much iron content. In the author's opinion, the correct analysis indicates the following contents: Cu 5.18%; Fe 5.42%; S 8.84% and gangue 84.55%.

In the second half of the 20th century, the research of copper mineralizations in the Baia de Aramă region was carried out by geologists from the Geological Prospecting Enterprise and the Drilling and Special Geological Works Enterprise, assisted by researchers from the Geological Institute of Romania and teaching staff from Faculty of Geology of the University of Bucharest.

GEOLOGY OF THE REGION

The Baia de Aramă region is located in the northeast of the Mehedinți Plateau, also in the northeast of the Mehedinți Mountains. On a small surface, two important tectonic units of the Western South Carpathians emerge here: the Getic Nappe from the Bahna Outlier and the Severin Nappe, underlain by the Getic Nappe. The Getic Crystalline from the Bahna Outlier consists of quartzo-feldspathic gneisses with sillimanite and cordierite, with intercalations of amphibolite rocks (BERCIA et al., 1977). Its metamorphic history is circumscribed to two regional metamorphism events, the first of medium pressure and medium temperature (M1-Cadomian), uniform over the entire area of the Getic Crystalline, and the second of low pressure and relatively high temperature (M2-Hercynic), circumscribed to the semi-window the Danubian Realm. The Severin Nappe is made up of Jurassic ophiolites and flysch formations of Upper Jurassic - Lower Cretaceous age (SĂNDULESCU, 1994).

Based on data from galleries and boreholes, SAVU et al. (1986) detailed the stratigraphy of the geological formations in the Severin Nappe, which they framed in an olistostrome in which they separated four horizons. From top to bottom, they are: a) the horizon of upper basalts in pillow-lava facies, with ophiolitic melange and olistoliths of ultramafic rocks; b) the pyroclastic (tuffogenic) horizon, with stratiform mineralizations of pyrite and chalcopyrite; c) a landmark horizon of black shists of Lower Jurassic age (Liassic); d) horizon of lower basalts, crossed by hydrothermal veins. The Jurassic matrix of the olistostroma, weakly metamorphosed, forms the lower horizon placed over a wildflysch formation of Upper Cretaceous age. Within the tuffogenic horizon, the copper mineralizations form two levels in the central area of the deposit, which towards the north merge into a single level.

In their study, SAVU et al. (1986) identify three types of mineralization: 1) a vein mineralization with pyrite, chalcopyrite, blende and galena parageneses, in quartz, calcium and epidote gangue; 2) a stratiform, massive mineralization of pyrite and chalcopyrite ± blende; 3) a pyrite ± chalcopyrite impregnation mineralization. The vein mineralization was formed in mesothermal conditions and the stratiform one in low temperature conditions. The average value of copper content in the deposit is 0.24%. The spatial distribution of copper shows an increase in contents in the NNE direction. According to the authors mentioned above, the deposit was formed by hydrothermal-sedimentary processes, from solutions springing up on the ocean floor on fractures along the rift zone.

THE COPPER MINERALIZATIONS

The researches from the years 1970-1990 highlighted the mineralized sectors of Băroaia-Măgura, Obârşia, Ponoare-Valea Cauna and Culmea Gorunului-Dealul Ocnelor-Cracul Joiței. On Valea Băroaia, the technological sample gave the following contents: Cu 0,27%; Pb 0,05%; Zn 0,06%; S 0,98%; Fe 8,30%; SiO2 48,50%; CaO 2,30%; Al2O3

14,70%; MgO 9,65%. By 0.27%; Pb 0.05%; Zn 0.06%; S 0.98%; Fe 8.30%; SiO2 48.50%; CaO 2.30%; Al2O3 14.70%; MgO 9.65%. Copper is found in the form of sulphides (chalcopyrite, chalcozine, coveline) and in the form of carbonates (malachite, azurite). Approximately 55% of the copper is bound to carbonates and the rest to sulphides. Blende and galena appear in much lower proportions than copper minerals. Fe sulphides (pyrite, marcasite, pyrrhotite) total less than 2%, and Fe oxides (magnetite, hematite, limonite) about 2% (POLICI et al., 1974a). The vein mineralizations on the Valea Măgura show fairly high contents, between 0.96% and 6.00% Cu, but the veins are small in size (CEAUȘU et al., 1986).

At Obârşia, the investigated mineralization is characterized by diffuse impregnation of pyrite and chalcopyrite, partially limonitized on the surface. The content in useful metals is: Cu 0.41%, Pb 0.01%, Zn 0.015%, and S 3.97%. 19% of Cu is found in the form of carbonates, oxides and copper sulphate (POPOVICI et al., 1979). From the Ponoare-Cauna sector, stratiform mineralization was exploited in the 80s, consisting mainly of pyrite and chalcopyrite, with contents of 0.40% Cu, cantonated in basic rocks (SAVU et al., 1987).

In the Culmea Gorunului-Dealul Ocnelor-Cracul Joiţei sector, indices of mineralization appear on the surface through numerous blocks of different sizes, made up of iron hydroxides, predominantly limonite, with different textures (crustiform, pseudoscoriate). Low copper and sulphur contents were determined on the limonite samples, around 0.1% (CEAUȘU et al., 1986). The blocks mainly come from the old exploitation works, less from the outcrops, the area being generally covered with a thick blanket of soil, sometimes coloured red. The drillings executed in this sector intercepted tuffogenic rocks with impregnations of pyrite and sporadically chalcopyrite, the copper content determined in these rocks being 2.84% (CEAUȘU et al., 1986).

The possibility of ancient slag utilization. The attempt to recover some useful elements contained in metallurgical slags was the subject of research in the 70s in Romania (POLICI et al., 1974b.). The fragments of copper slag from the dumps in Valea Brebina are 2-10 cm in size, rarely 20-30 cm, brown in colour, and brown-black in fresh breach, high hardness, a finely granular to microcrystalline structure and an uneven scoriaceous texture. Macroscopically, the constituent minerals could not be identified, but iron hydroxide powders and copper carbonate films (malachite, azurite) could be observed on some surfaces. The slag fragments are made up of a microcrystalline mass of silicates (fayalite) concrescent with magnetite in which copper sulphides, native copper and Fe sulphides are finely dispersed.

The useful elements in the slag, interesting for their contents, are copper (0.68%) and iron (47.70%). Preparation research for copper recovery from the slag has led to the separation of copper concentrates of acceptable quality, but with low recoveries. Regarding the recovery of magnetite, the experiments led to the separation of a quantitatively reduced concentrate (12%) with a high copper content (0.96%). The study carried out demonstrated the technological possibility of ancient slag processing to obtain a metallurgically usable concentrate.

On the occasion of this study, we also performed XRF analyses on two samples of ancient slag collected from the dumps in the right side of the Valea Cujniţa (Table 1). The analyses were performed with a Brukerenergy dispersive XRF spectrometer, type SI Titan 600. The GeoMining application was used with an exposure time of 90 seconds in three stages of 30 seconds each, with kilovoltages of: 30, 50, 15. The results presented are the average of 5 measurements of the same sample. Obviously, the copper contents (0.54% and 0.14%) are much lower than the iron ones (40.82% and 23.49%, respectively) but they are comparable to the contents obtained on copper mineralizations. This last fact is due to the copper extraction procedures, scarcely refined at that time.

Table 1. XRF analysis of two samples of ancient slags collected from the dumps from Valea Cujniţa.

Sample	Element/Compound (%)														
	MgO	Al_2O_3	SiO_2	P	S	Cl	K_2O	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ba
S 1	1.50	7.66	25.63	0.06	1.29	0.08	1.42	2.09	0.19	0.02	0.11	40.82	0.54	0.12	-
S 2	2.00	12.61	48.21	0.07	0.72	-	2.93	2.09	0.35	0.02	0.11	23.49	0.14	0.18	0.22

DISCUSSIONS AND CONCLUSIONS

From the historical data presented in the paper, it follows that the copper mineralization from the Baia de Aramă region has been exploited, with some interruptions, for more than 2000 years. It seems that between the 14th and 17th centuries the deposits were much richer and the large production of copper brought substantial income to the rulers of Wallachia. If the data are correct, during the reign of Matei Basarab this production was quite large, most of it being exported to the Ottoman Empire, the suzerain authority of the country. Very likely, the intensive mining during this period led to the deposits' depletion, reported by the temporary Austrian occupation of Oltenia (1718-1739) from the beginning of the 18th century.

Towards the end of the 19th century, a few years after gaining state independence, there is an increased interest of Romanian and foreign researchers in the knowledge and popularization in Europe of Romania's mineral wealth. Just now the monographic works on the Mehedinți region (DRĂGHICEANU, 1885), the mineral wealth of Romania (CRÉMER, 1888) and the minerals of Romania (PONI, 1900) appear.

In the second half of the 20th century, the Baia de Aramă region was intensively researched and new mineralizations were highlighted in the sectors of Băroaia-Măgura, from the basin of Valea Brebina, (0, 27% Cu), Obârşia (0, 41% Cu), Ponoare-Valea Cauna (0, 40% Cu) and Culmea Gorunului-Dealul Ocnelor (2, 84% Cu). An interesting conclusion of our study is the one regarding the ancient slags, which have interesting copper contents and are easy to mine. The technological possibility of slag processing to obtain a metallurgically usable concentrate was already demonstrated in the 70s. More analysis on such slags could provide surprising results.

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