



THE MAIN GEOCHEMICAL ASSOCIATION OF THE SULFIDES OF LEAD-ZINC MINERALIZATION IN TREPÇA MINERAL BELT- HAJVALIA MINE, KOSOVO

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ABSTRACT

This paper presented the distribution of major metals (Pb, Zn, Ag and Au) and accompanying metals in Hajvalia mineral deposit. With special emphasis, we studied the main geochemical association of lead (Pb) and zinc (Zn) sulfides mineralization. The geochemical data suggest a very strong correlation of Ag with Pb, which could be related to the associated of pyrrargyrite with galena as well as with isomorphous enrichment of galena with Ag. From the available composite data (30 samples), average silver (Ag) for each 1% lead (Pb) is 14.75 g/t. According to the factorial analysis, the result of these geochemical associations is as follows: Pb-Zn-Ag-(Cd-Cu); Sb-(Cd); Bi- (Cu).

Keywords: lead-zinc mineralization, geochemical association, "Hajvalia" mineral deposit, Kosovo.

INTRODUCTION

The Hajvalia mine is located 12 km south-east from Prishtina, 2 km off the main highway from Prishtina to Gjilan, is part of "Hajvalia-Badovc-Kizhnica" ore field (Figure-1), and as a whole is located within tectonic zone of Vardar (Figure-2).

The metallogenesis of which are genetically and timely related to the andesitic magmatism of tertiary (Cissarc A., 1951; Jankoviq S., 1977; Jankoviq S., 1995). The Hajvali polymetallic mineral deposit is one of the richest with zinc component in Europe. Evaluated on 5Mt ore reserves with average content of main metals of 12.20% Zn, 6.50% Pb and 72 g/t Ag, (Radoslav P., *et al.*, 1989; Klisič M. 1995; Durmishaj B., 2002, 2007). The main associated of zinc (Zn) in this mineral deposit are lead (Pb) and silver (Ag), while other elements such as Cd, Bi, Au, etc., can be found in smaller quantities.

The study is based on the data of Hajvalia ore deposit taken during the years of exploitation. The contents of main metals of zinc (Zn) and lead (Pb) were analyzed in separate samples, whereas the content of Zn, Pb, Ag, Au, Cd, Bi etc., were analyzed only as composite samples (Kizhnica-chemical laboratory).

DEPOSIT GEOLOGY

The Hajvali mineral deposit is composed of rocks of various stratigraphies from Paleozoic to Tertiary in age and of various lithological types. The oldest and most widely represented rocks form part of the Paleozoic "metamorphic series" although the upper part is Triassic in age. These are the host units to the mineralization at Hajvalia mine. They consist predominantly of phyllite, sericite and quartz-sericite schists, while carbonate rocks, quartzite, meta-sandstones, chlorite and other schist.

Stratigraphically overlying the Paleozoic rocks in the Hajvali mineral deposit are Jurassic serpentinites, gabbro - diabases, sedimentary-volcanogenic series, diabase and spilite, fliish sediments of the upper Cretaceous; and quaternary sediments, (Radoslav P., *et al.*, 1989; Klisič M., 1995).



Figure-1. Map of Kosovo showing all major mines, concentrators and final processing facilities.

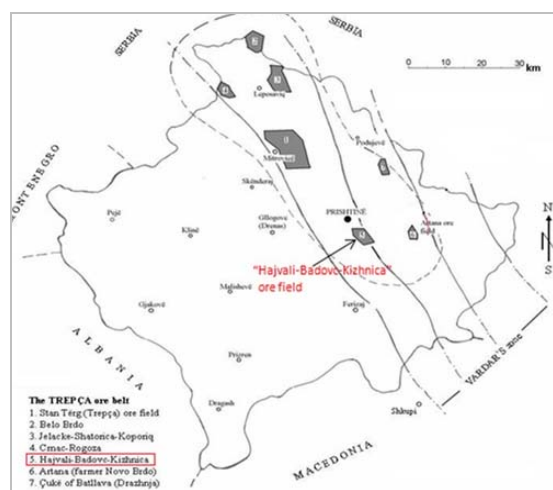


Figure-2. The leads and zinc sulfide mineralization in the region of Kosovo, geographical position of the "Hajvali-Badovc-Kizhnica" ore field.



It is important to note that in the Hajvali mineral deposit the rocks of metamorphic series have greater participation, which distinguishes this mineral deposit from two other deposits of the "Hajvali-Badovc-Kizhnica" ore field. Another characteristic is the fact that in this deposit, there is a lack of volcanic products (tertiary age), with which are thought to be related genetically mineral deposits of the ore field generally.

Structurally, the setting of the Hajvali-Badovc-Kizhnica ore field is an integral part of eastern zone of deep fracture of Kapaonik. This fracture in the region of the "Hajvali-Badovc-Kizhnica" ore field is divided into three smaller structural-tectonic units, which are: structure zone in Hajvali-Badovc (1); structure zone in Kizhnica (2) and structure zone in Okosnica (3), (Figure-3). Structural-tectonic zones are complex, and are associative with the structures of lower orders, which based on the direction of expansion are systemized (Figures 4 and 5).

In the Hajvali mineral deposit are found: The western reverse fault (the expansion direction is NW to SE, with a dip towards the NE of 60-70°) localized along the phyllite contacts in the deposit footwall; The eastern normal fault is located within "light" schist east of the central ore body (it also NW to SE direction, and dips to the NE at 30-40°); Fold structures represent an important factor in ore body distribution at the mineral deposit of Hajvali. As a result of anticlinal and synclinal folding the ore bodies can be split-this is evident on the IX working level, (Figure-5).

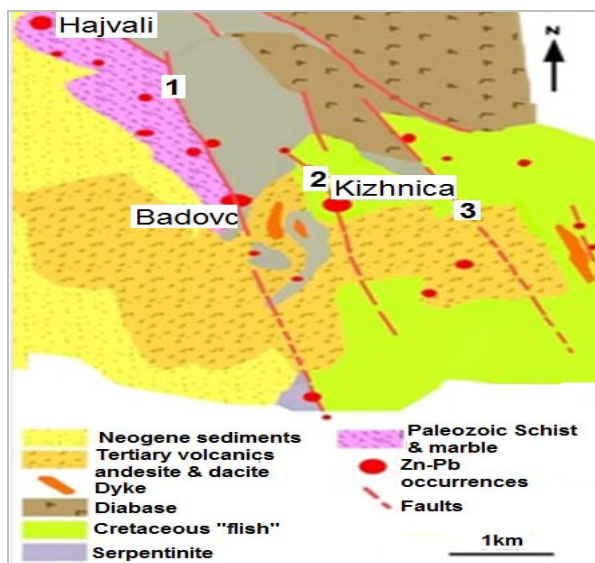


Figure-3. Geological map of "Hajvalia-Badovc-Kizhnica" ore field, simplified geology.

Contact metasomatic alteration occurs at Hajvali mineral deposit, related to Tertiary magmatism. This is most evident in the upper Cretaceous fish sediments. Hydrothermal alteration, which occurred mainly in the post-volcanic phase, is evident in all rocks of the ore field.

Spatial distribution of alteration depends on tectonic structure and is directly related to emplacement of Pb-Zn mineralization. Alteration seen within the ore host rocks includes: silification, sericitisation, kaolinitisation, chloritisation and pyritisation.

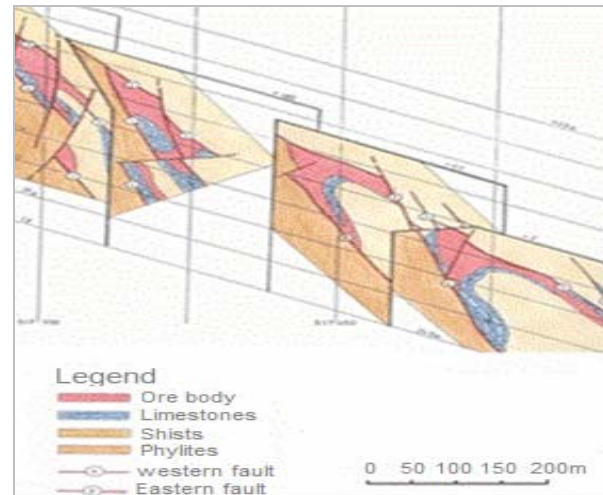


Figure-4. Block diagram of the Hajvali mineral deposit (5 to 9 level), geological survey of Kizhnica-Prishtina.

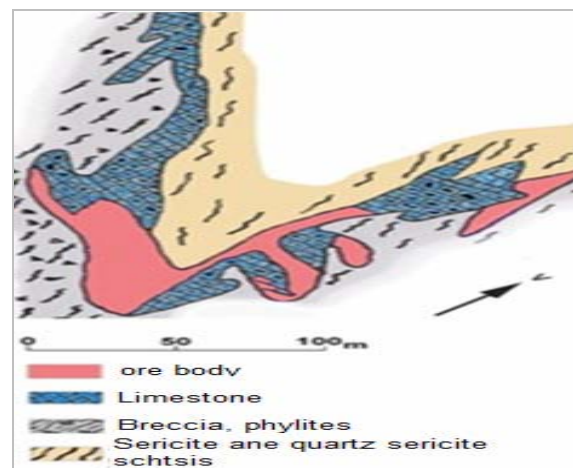


Figure-5. Ore body 1, detail from 9 level (245m) in Hajvalia mine.

CHEMICAL COMPOSITION AND DISTRIBUTION OF EXPLOITED MAIN METALS IN THE HAJVALI MINERAL DEPOSIT

Based on the data of chemical analysis of samples of mineralization in the polymetallic deposit of Hajvali, it results that the polymetallic minerals have high content of useful components such as Zn, Pb, and Ag.

So, in the Hajvali mineral deposit, the chemical composition of mineralization is averagely: 8.7 % Zn; 5.5 % Pb; 60g/t Ag; 14.35 % S; 0.09% Cd; 0.016 % Bi; 0.014 % Sn; 0.05 % Cu; 0.026% As; 0.5g/t Au, (flotation samples taking, Kizhnica geological survey). As far as oxide components, results these average contents: 24.60%



SiO₂; 0.87 % MgO; 5.18% MnO; 1.23% CaO and 7.40% Al₂O₃. The distribution of main elements in the deposit is characterized with the following variation coefficient (Durmishaj B., *et al.*, 1989):

$$K_v^{Pb} = 77.22 \% ; K_v^{Zn} = 62.52 \% ; K_v^{(Pb+Zn)} = 55.25 \%$$

Well, the main elements of economic importance are zinc, lead and silver, for which are calculated the industrial reserves of the mineral deposit. Besides, the main metals during the technological process extruded other associated components such as Au, Cd, Bi, etc. For gold (Au), results a strong connection with Zn, sphalerite mineral respectively.

The mineralogical data also ascertained the presence of native gold, mainly connected with quartz mass, but a good part of it is also present in the contact between pyrite and sphalerite of the third generation. With sphalerite are also connected compositions of some distributed elements. According (Jankovic S., 1995), results from the sphalerite analysis are as follows: Fe = 8.12%, Cd = 0.1%-0.3%, Mn = 0.2-1%, Ag = 10-20g/t, Sn = 30-50 g/t, Ga up to 3g/t.

Based on the thirty (30) representative samples from Hajvali ore deposit are analyzed separately for zinc (Zn), lead (Pb) and silver (Ag) in the laboratory of BRGM, France (ITT, 2000), the geochemical data suggest a very strong correlation of Ag with Pb, which could be related to the associated of pyrrhotite with galena as well as with isomorphous enrichment of galena with Ag. From the available composite data (30 samples), average silver (Ag) for each 1% lead (Pb) is 14.75 g/t.

MINERALOGICAL COMPOSITION

According to previous studies (Smejkal S., 1956 and 1960; Rakiq S, 1956), mineralogical composition of the Hajvali mineral deposit is as follows: Lead-zinc sulphide paragenesis with sphalerite, galena and pyrrhotite. Subordinate minerals include: chalcopyrite, pyrite, arsenopyrite, cubanite, tetrahedrite, bournonite, boulangerite, and jamesonite, with rare native gold. Carbonate paragenesis (Fe-Mn) with insignificant participation of lead and zinc sulphides (oligonite ore bodies).

Gangue minerals consist of quartz, siderite, Mn-siderite, Mn-Calcite, aragonite, calcite, calcedone, barite. Secondary minerals such as transformation of supergene products meet: cerussite, smithsonite, anglesite, melanterite, limonite, etc. Observed three main mineralogical generations, respectively hypo-meso-epithermal phases. The main and most important concentrations of zinc related with mesothermal phase, while those of lead by later phases. The high overall Zn: Pb ratio of the Hajvali ore body, averaging 2:1, is noteworthy as it is not typical of most of the Kosovo Pb-Zn deposits, which generally average 1:1.

ANALYSIS OF MINERALIZATION AND METHODS FOR DETERMINING THE GEOCHEMICAL ASSOCIATION

Study of ore mineral was made by representative samples of deposit during the evidence phase of exploitation. The results of chemical analysis were taken from Kizhnica chemical laboratory. For this study, we have exploited the chemical analysis result for united samples (composite), analyzed a total of 14 samples. Distribution of major chemical elements contents and the associated elements in the Hajvali mineral deposit presented through the statistical parameters in Table-1.

Table-1. Statistical parameters of the distribution of metals contents in the Hajvali mineral deposit, "Hajvali-Badovc-Kizhnica" ore field.

Parameters/Elements	Pb %	Zn %	Ag gr/t	Bi %	Cd %	Cu %	As %	Sb %
Average	9,35	14,41	107,90	0,02	0,05	0,06	0,09	0,15
Median	10,25	14,02	78,00	0,02	0,05	0,06	0,06	0,13
Standard Deviation	5,48	4,84	64,01	0,01	0,02	0,01	0,06	0,08
Minimum	4,68	5,38	24,00	0,01	0,02	0,05	0,03	0,05
Maximum	24,34	21,06	204,00	0,06	0,10	0,10	0,21	0,29
No. of samples	14	14	14	14	14	14	14	11

Based on the correlation analysis for the Hajvali mineral deposit, Table-2, indicating these geochemical associations:

1. Pb-Zn-Ag
2. Zn-Ag-Cd, dhe
3. Sb-Bi



Table-2. Correlation matrix for the Hajvali mineral deposit “Hajvali-Badovc-Kizhnica” ore field. The correlation coefficients are significant for $p < 0.05$, when have a value greater than 0.52. No. of samples = 14.

Elements	Pb %	Zn %	Ag gr/t	Bi %	Cd %	Cu %	As %	Sb %
Pb %	1							
Zn %	0,653215	1						
Ag gr/t	0,671419	0,659889	1					
Bi %	0,060286	-0,24774	-0,08904	1				
Cd %	0,448503	0,598125	0,407301	-0,03885	1			
Cu %	0,192734	0,33962	0,405992	0,347134	-0,18641	1		
As %	-0,27762	-0,34705	-0,19854	-0,15269	-0,30433	-0,12497	1	
Sb %	-0,37315	-0,1202	-0,28466	0,526416	0,196047	0,278879	0,042862	1

From Table-3 as follows, results of these geochemical associations are:

1. Pb-Zn-Ag-(Cd-Cu);
2. Sb-(Cd); and
3. Bi-(Cu)

Table-3. The weights of the factors (Vary max normalized). The method of main components. Bold values are about the 0.7 and biggest that so

Elements	Factors		
	F1	F2	F3
Pb %	0,817058	0,065103	0,09369
Zn %	0,924607	-0,05719	-0,1262
Ag gr/t	0,844945	0,005692	0,088278
Bi %	-0,14305	0,132794	0,902195
Cd %	0,622247	0,554685	-0,16552
Cu %	0,377635	-0,59013	0,616399
As %	-0,4043	-0,31668	-0,34351
Sb %	0,035485	0,809868	0,168302
Expl.Var	2,951394	1,437278	1,400119

However, exact data on geochemical association except correlation analysis taken by factorial analysis presented in Table-3 and then in the Figure-6.

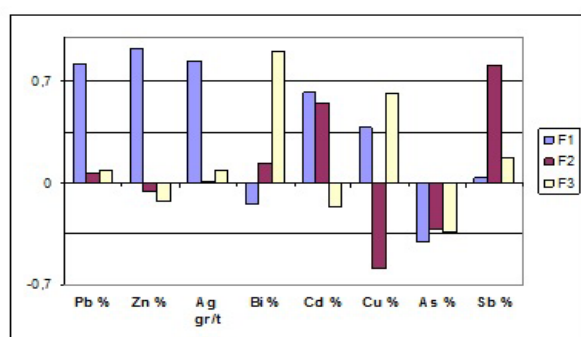


Figure-6. Graphic factors weights, the Hajvali mineral deposit, “Hajvali-Badovc-Kizhnica” ore field.

CONCLUSIONS

The Hajvali zinc-lead polymetallic mineral deposit is one of the richest with zinc component in Europe are evaluated on 5Mt ore reserves with average content of main metals of 12.20% Zn, 6.50% Pb and 72 g/t Ag. The main associated of zinc (Zn) in this mineral deposit are lead (Pb) and silver (Ag), while other elements such as Cd, Bi, Au, etc., can be found in smaller quantities.

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These geochemical associations show the strong links to lead (Pb) with zinc (Zn) and silver (Ag), and weak links with cadmium (Cd), and very weak links with copper (Cu). Has an association of antimony (Sb) with cadmium (Cd) in antagonism with copper (Cu). There is also another geochemical association of copper (Cu) with bismuth (Bi) but in antagonism with arsenic (As).

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