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Geochemical association of the sulfides of lead-zinc mineralization in Trepça mineral belt- Kizhnica mine, Kosovo

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Abstract: ***The mineral deposit of Kizhnica belongs to "Hajvali-Badovc-Kizhnica" ore field, and extends in the central part of it`s together with Badovc mine. Lead (Pb), zinc (Zn), and silver (Ag) are the major metals of economic priority for which the industrial ore reserves have been calculated in this paper presented the distribution of major metals (Pb, Zn, and Ag), and with special emphasis, we studied the main geochemical association of lead (Pb) and zinc (Zn) sulfides mineralization of the Kizhnica deposit. According to the factorial analysis, the result of these geochemical associations is as follows: Zn-Ag-As; Cd-Cu; and Pb-Sb. In 1% of the content of lead (Pb) has 10g/t silver (Ag). Variation coefficient for lead is*** VC^{Pb} ***= 85.67% and for zinc is*** VC^{Zn} ***= 103.95%.***

Keywords: geochemical association, lead-zinc mineralization, Trepça mineral belt, Kizhnica mine.

1. Introduction

The Kizhnica mineral deposit is located in the central part of the Hajvali-Badovc-Kizhnica ore field, about 9 km SE of Prishtina (figure 1). From the regionalization geotectonic aspect Kizhnica mineral deposit is located within tectonic Vardar zone [8], the metallogenic region of Kopaonik [6], the Trepça mineral Belt [5], Figure 1 and figure 2.

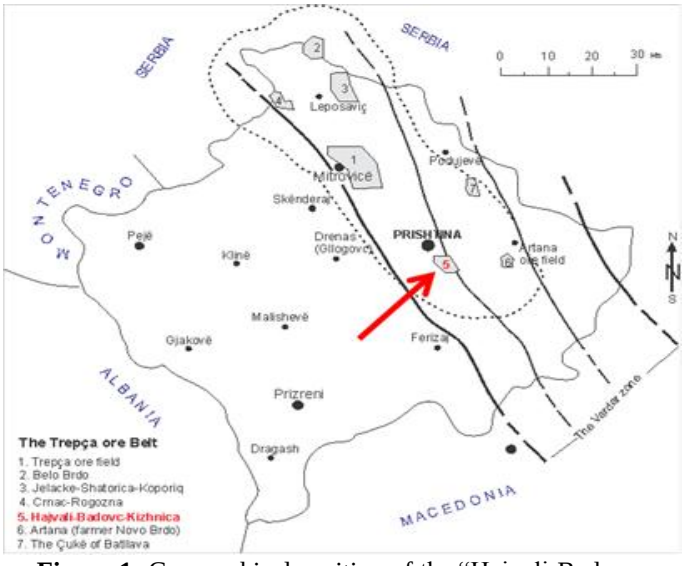

Figure 1: Geographical position of the "Hajvali-Badovc-Kizhnica" ore field (the Pb and Zn sulfide mineralization in the region of Kosovo)

The metalogenesis of which are genetically and timely is related to the andesitic magmatism of tertiary [1], [6].

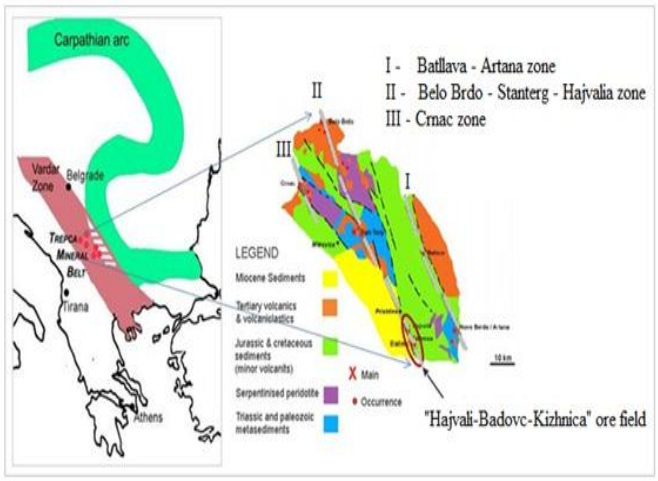

Figure 2: The Vardar zone and Trepça mineral Belt-Summary Geology

The general state of geological reserves in the Kizhnica mineral deposit was evaluated around 4 Mt ore reserves with average content of the main metals of 4.74% Pb, 1.02% Zn, and 64g/t Ag, [9], [7]). The main accompanying of metals in this deposit are: lead (Pb), zinc (Zn), 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 Kizhnica mineral deposit taken during the years of exploitation. The contents of main

metals of lead (Pb) and zinc (Zn) 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).

2. Geology settings of region

The central part as well as the immediate vicinity of the deposit are formed of serpentinites, representing a terrain base, than flysch of lower Cretaceous, gneiss and andesite. Jurassic serpentinites are placed between andesite, in test, while cretaceous flysch dominates in east part of the mineral deposit [9], [7]. The thickness of the serpentinites reduces with depth thus causing andesite to face flysch sedimente.

In the geological map (figure 3) are shown the structural zones:

1) Structure zone Hajvali-Badovc;
2) Structure zone of Kizhnica and
3) Structure zone of Okosnica, (figure 3).

Ore bodies are formed in the contact zone of andesites and flysch sedimente.

The structure of mineral deposit is characterized by a complex faults system with the general strike N-S and E-W.

The mine ore structure of the Kizhnica dislocation manifested by serpentinites discontinuity in the lying wall and Upper Cretaceous flysch in the overlying wall (the mine contact) as well as by the occurrence of andesite masses partly filling a contact space particularly in the southern part of structure.

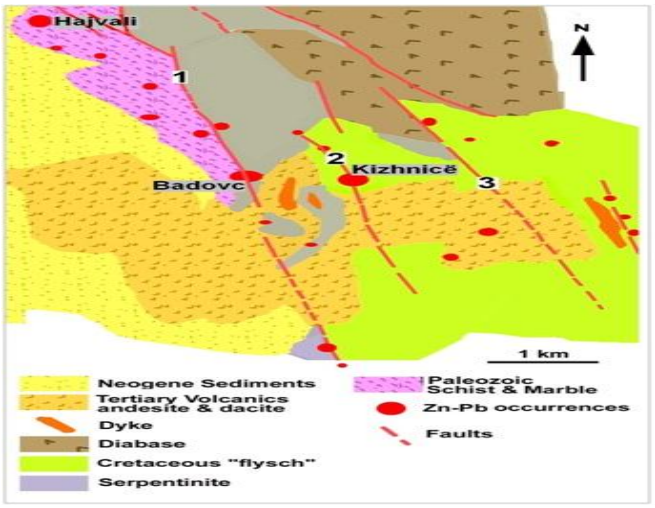

Figure 3: Geological map of "Hajvalia-Badovc-Kizhnica" ore field, simplified geology.

Economically most significant ore bodies are formed in serpentinite where flysch and gneiss partly have the role of screen.

Morphologically, three types of ore bodies are represented (compact ore bodies, vein like ore bodies, and stockwork-impregnation zones.

2.1 Mineralogy of the Kizhnica mineral deposit

Based on the studies conducted until now the poly-metallic sulphur mineralization of the ore deposits of Hajvali-Badovc-Kizhnica belongs to the sub-volcanic type of pneumatholite-hidrothermal phase of tertiary metalogenesis [10] & [11]. The main mineralogical paragenesis are lead-zinc sulphide paragenesis with sphalerite, galena, and pyrrhotite, characteristic for all ore deposits (Hajvali, Badovc, and Kizhnica). The Kizhnica mineral deposit is composed of the large number of metallic and non-metallic minerals. The metallic minerals are pyrrhotite, chalcopyrite, chalco-pyrrhotite, vallerite, cubanite, sphalerite, arsenopyrite, galena, krennerite, calaverite, pyrite, stannite, tetrahedrite, bournonite, jamesonite, boulangerite, marcasite, pyrargyrite, antimonite, falkmanite, melnicovite, lollingite. Between the non metallic minerals in this mineral deposit are present: quartz, siderite, rhodochrosite, Mn-calcite, aragonite, calcite, chalcedony and barite.

Pyrrhotite has proved to be the most representative in this deposit, and is accompanied by sphalerite, galena, rarely chalcopyrite, pyrite, gold tellurides, native gold, Pb-Sb sulfosalts, tetrahedrites, and antimonites. A significant number of these minerals in mineral sukcesiji are represented in two or more generations [10] & [11]. So far, three major generations of mineralization are distinguished: katathermal, mesothermal, and epithermal zones. The zinc (Zn) is mainly related to the mezzo-epithermal phase and lead (Pb) by later phases (epithermal) [10] & [11].

3. Materials and Method

2.2 Chemistry and distribution of exploited main metals in the Kizhnica deposit

Based on the data of chemical analysis of the samples of mineralization in the polymetallic deposit of Kizhnica [2], it results that the polymetallic minerals have high content of useful components such as: lead (Pb), zinc (Zn), and silver (Ag). So, in the Kizhnica mineral deposit, the chemical composition of mineralization is averagely: 3.68 % Pb; 0.87 % Zn; 53g/t Ag; 0.02% Cd; 0.012 % Bi; 0.016 % Sn; 0.06 % Cu; 0.04% As; 0.021% Sb; 0.65g/t Au, (flotation samples taking, Kizhnica geological survey, Prishtina). As far as oxide components, results these average contents: 28.45% SiO_2; 1.85 % MgO; 1.06% MnO.

The distribution of main elements in the deposit is characterized with the following variation coefficient [4]: VC^{Pb}=85.67%, and VC^{Zn}=103.95%.

The main elements of economic importance are lead (Pb), zinc (Zn), and silver (Ag), for which are calculated the industrial reserves of the mineral deposit of Kizhnica.

Besides, the main metals during the technological process extradited other associated components such as gold (Au), cadmium (Cd), bismuth (Bi), etc. According [2], some of the platinum group elements (PGE) are present in the three main minerals (galena, sphalerite, and Pyrite) of Kizhnica mineral deposit. The average contents in galena mineral is 17ppm Ru, 37 ppm Pd; in sphalerite (618 ppm Os, 180 ppm Rh, 110 ppm Pd), and in Pyrite (17 ppm Os; 317 ppm Ir, 18 ppm Ru, 123 ppm Rh, 372 ppm Pt, 72 ppm Pd).

Based on 30 chemical analysis representative of the mineral deposit of Badovc [3], the result dates suggest a very strong correlation of Ag with Pb (figure 4), which could be related to the associated of pyrargyrite with galena as well as with isomorphic enrichment of galena with Ag. In 1% of the content of lead (Pb) has 10g/t silver (Ag).

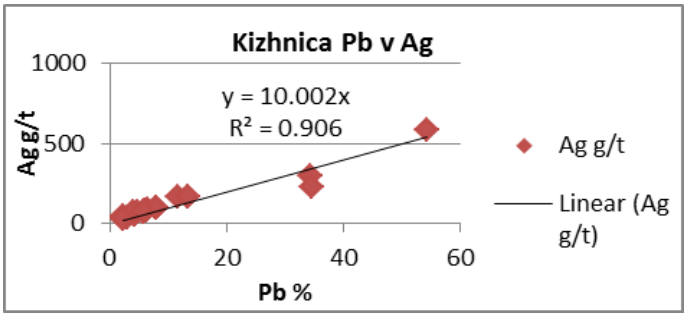

Figure 4: Contents and correlation between Pb v. Ag

2.3 Analysis of mineralization and results 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 26 samples [2]. Distribution of major chemical elements contents and the associated elements in the Kizhnica mineral deposit presented through the statistical parameters in Table 1.

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

Parameters/Elements	Pb %	Zn %	Ag gr/t	Bi %	Cd %	Cu %	As %	Sb %
Average	6,92	1,53	74,38	0,01	0,02	0,07	1,19	0,02
Median	6,39	1,35	70,00	0,01	0,02	0,06	1,06	0,02
St.Dev.	4,77	1,31	36,99	0,00	0,01	0,04	0,48	0,01
Min	2,50	0,10	20,00	0,01	0,01	0,01	0,70	0,01
Max	18,77	6,08	195,00	0,02	0,03	0,15	2,40	0,03
No. of samples	26	26	26	26	26	26	26	26

Based on the correlation analysis for the Kizhnica mineral deposit in Table 2, indicating these geochemical association:

1. Pb-Zn-Ag, dhe
2. Zn in antagonism with Cu

Table 2: Correlation matrix for the Kizhnica mineral deposit "Hajvali-Badovc-Kizhnica" ore field. The correlation coefficients are significant for p <0.05, when have a value greater than 0.42. No. of samples = 26.

Elements	Pb %	Zn %	Ag gr/t	Bi %	Cd %	Cu %	As %	Sb %
Pb %	**1,00**							
Zn %	**0,42**	**1,00**						
Ag gr/t	**0,64**	0,19	1,00					
Bi %	0,20	0,33	0,01	1,00				
Cd %	-0,06	0,11	-0,02	-0,19	1,00			
Cu %	-0,36	-0,42	-0,24	0,07	0,16	1,00		
As %	-0,05	-0,09	0,14	-0,03	-0,13	0,02	1,00	
Sb %	-0,20	-0,04	-0,10	0,22	0,20	0,14	-0,26	1,00

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

1. Zn-Ag-As,
2. Cd-(Cu), dhe
3. Pb-Sb

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	F4
Zn%	**0.951168**	0.152292	0.063456	0.079965
Ag gr/t	**0.945497**	0.113765	0.012309	-0.010600
Bi%	0.076564	-0.069134	0.074658	0.927788
Cd%	-0.124891	**0.822334**	0.140091	-0.223420
Cu%	0.325287	**0.676613**	-0.176192	0.433142
As%	**0.874773**	-0.203614	-0.082158	0.131260
Sb%	0.209633	0.176604	**-0.825075**	-0.205407
Pb%	-0.242133	-0.288091	**-0.760461**	0.149177
Expl.Var	2.793760	1.330597	1.326220	1.186502

However, exact data on geochemical association except correlation analysis taken by factorial analysis presented in Table 3 and then in the Figure 5.

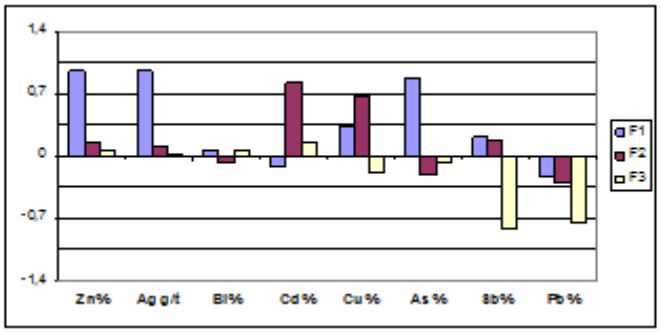

Figure 5: Graphic factors weights, the Badovc mineral deposit, "Hajvali-Badovc-Kizhnica" ore field

4. Conclusion

The mineral deposit of Kizhnica belongs to "Hajvali-Badovc-Kizhnica" ore field, and extends in the central part of it`s together with Badovc mine. Lead (Pb), zinc (Zn), and silver (Ag) are the major metals of economic priority for which the industrial ore reserves have been calculated. In this mineral deposit estimated at about 4 Mt geological reserves with average content of the main metals of 4.74% Pb%, 1.02% Zn, and 64g/t Ag. As a conclusion, based on factorial analysis resulting these geochemical association that show the strongest link of zinc (Zn) with silver(Ag) and arsenic (As), while less with copper (Cu). On the contrary, lead (Pb) shows strong link with antimony (Sb). While the cadmium (Cd) shows strong link with copper (Cu).

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