Some Differences On Py-Sph-Ga Mineral Phases In Hajvali - Badovc - Kizhnica, And Artana Mine (Electronic Microprobe Analyses). Trepca Ore Belt, Kosovo

Bedri (Niman) Durmishaj, Sylejman (Hamit) Hyseni,

Department of Geology/Faculty of Geosciences/University of Mitrovica “Isa Boletini”, Mitrovica,
Trepça Industrial Park, 40000 Mitrovica, Republic of Kosovo
E-Mail: bdurmishaj@hotmail.com

ABSTRACT: In this paper we presented some differences on mineral mining phases: Hajvali Badovc Kizhnica, and Artana mine. From our study, the four mines have high values of iron (Fe) content in sfalerite: Badovc 9.43% Fe; Hajvali 10.24% Fe; Përroi i ngjyrosur (Artana) 10.61% Fe; and about 13% Fe for Kizhnica mine. Low content of bismuth in sphalerite: Hajvali (0.03% Bi), Përroi i ngjyrosur–Artana (0.04% Bi), Kizhnica (0.06% Bi), and Badovc deposit < 0.01% Bi. The silver (Ag) contents in sphalerite of these deposits are very low: Hajvali and Badovc mines 0.015% Ag respectively 0.01% Ag. In two other mines Ag-content in sphalerite is very-very low or almost absent in sfalerit. Pyrites of these deposits characterized by low arsenic (As) content, except Badovc where its value amounts to 1.3%. Whereas regarding the silver (Ag) content in pyrites: the higher its content are found in Përroi i ngjyrosur-Artana mine (0.03% Ag), then Kizhnica (0.02% Ag), Hajvali (0.01% Ag), and almost missing in mine Badovc. Galena of all the mining containing antimony (Sb), bismuth (Bi), and silver (Ag). Generally characterized by low values of Sb and Bi, although the Bi contents are higher compared to those of Sb, and with antimony leads them Artana mines (0.09% Sb). Galena of the Hajvalia mine contains more silver (> 100g/t Ag), than other mines (which are very poor with silver).

Keywords: Mineral phases, Hajvali, Badovc, Kizhnica, Artana mine, Trepça mineral Belt, Kosovo

1 INTRODUCTION

Field ores "Hajvali-Badovc-Kizhnicë" with three mines and several potential locations represents an important region in terms of the exploitation of lead and zinc mineralization. By its geographic position located in contact with boundary of the Kosovo Tertiary Basin, about 10 km southeast of the capital city of Kosovo, Prishtina. While, the region of Artana (farmer Novo Brdo) is located to the east of "Hajvali-Badovc-Kizhnica" ore field and Prishtina, (figure 1).

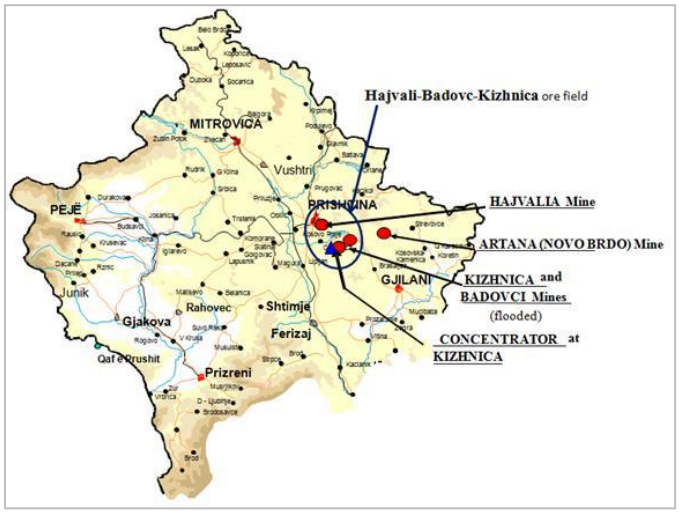

***Fig 1**. Map showing the location of “Hajvali-Badovc-Kizhnica” ore field and “Artana” mine*

2 GEOLOGICAL SETTING

The “Hajvali-Badovc-Kizhnica” ore field belongs to the Vardar zone [8], as in figure 2A, zone of Tertiary activity [4] and continental plate [5]. From the structural-tectonic point of view this area belongs to metallogenic region of Kopaonik [7] mineral Belt of Trepça respectively [6], figure 2B.

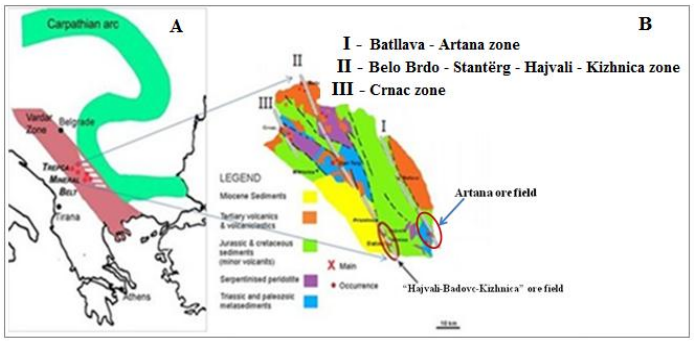

***Fig 2**. (A) Location of the Trepça ore belt in the tectonic Vardar zone; (B) the studied mineralization of “Hajvali-Badovc-Kizhnica”and “Artana” ore field*

The deep tectonic fracture II (Belo Brdo-Stantërg-Hajvali-Kizhnica zone), in region of the “Hajvali-Kizhnica” is divided into three structural-tectonic units of lowest order: the “Hajvali-Badovc” (1); “Kizhnica” (2); and “Okosnica” (3) fracture zones, that control the location of the lead-zinc mineralization, (figure 3).

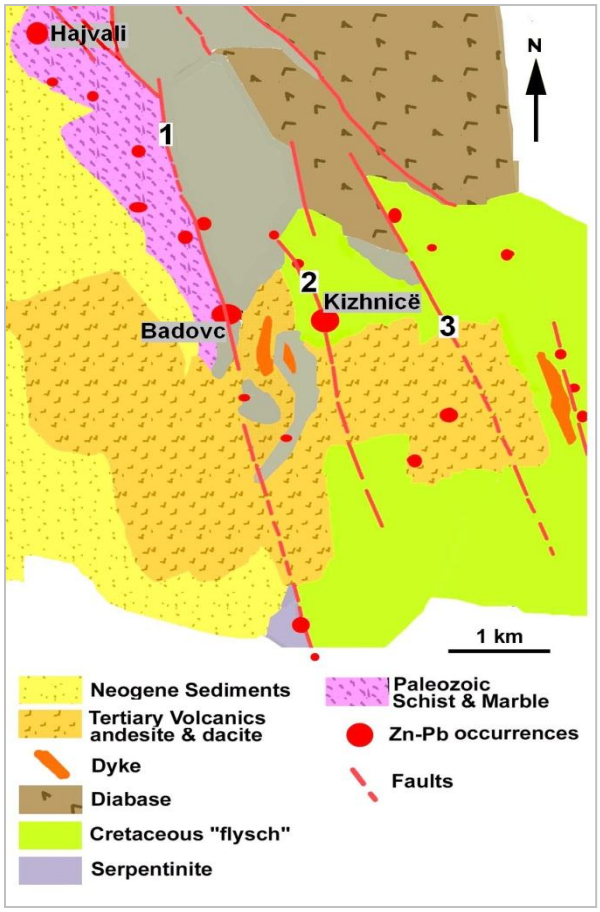

***Fig 3**. Geological map and three main fracture zones of the Hajvali, Badovc, and Kizhnica*

The main geologic subunits in the region of Hajvali-Kizhnica are: metamorphic series (Paleozoic); Jurassic sedimentary and magmatic formations; Cretaceous sedimentary depositions; Tertiary sedimentary-volcanic formation and Quaternary depositions (figure 3). Metamorphic series ((crystalline schists, carbonates (limestone, marbles, and crystalline dolomites), and quartz rocks)) present in the Hajvali and Badovc mineral deposits but not in the Kizhnica mine. The carbonates are the main ore bearing rocks in the Hajvali mineral deposit, but to a certain extent and for the Badovc deposit. The Jurassic sedimentary formation is composed of sedimentary-terrigenous rocks, whereas the magmatic rocks, mostly serpentinites are rare. The Cretaceous sediments (conglomerate, sandstones, clays, marls and limestone sub-layers) are found in all three mineral deposits but are more spread in the mine of Kizhnica, where scarce mineralization of lead (Pb) and zinc (Zn) are located in them. The tertiary formations represented by the sedimentary and volcanic rocks of paleogen and neogen age, are widely spread in the area of mineral deposits. The paleogen sediments (breccias, conglomerates, sandstones, marls and mostly clays) were formed before the volcanic activity. Neogen volcanic rocks (lava flows, and pyroclastic rocks) are present around the mines of Badovc and Kizhnica, but they are missing in the mineral deposit of Hajvali. In the region of Artana such rocks have a pronounced extension; great masses of them are found in the deep fracture that divides the series of Veles and Serbian-Kosovo-Macedonian massive. The first phase rocks are intensively pervaded by the hydrothermal alteration. The volcanic neogen rocks are believed to be the source of hydrothermal fluids that produced polymetallic mineralization in this region [11]

2.1 Ore bodies, location and morphological characteristics

Lead (Pb) and zinc (Zn) sulphur mineralisations are located in the different rock type [3], as well as carbonates, serpentinites, between serpentinites and andesites, shales or gneisses. Other the lithologic factor, the structural control is evident in all four mineral deposits. Three dislocation zones of the lowest order, “Hajvali-Badovc” (1); “Kizhnica” (2) and “Okosnica” (3) are control the hydrothermal mineralization in the Hajvali-Badovc-Kizhnica ore field and two others in the region Artana [12], [9], [10]. All these dislocation zones are accompanied by lower orders faults, which based on the direction of their extension, are longitudinal NW-SE with 60˚-70˚ dip towards NE; diagonal approximately meridian 350˚that decline in East, and transversal E-W. In the Hajvali mineral deposit a folded structure in the crystalline schists and in the cretaceous sediments controls the mineralization. Depending on the lithologic and tectonic factors, the complicated forms of the ore bodies are found such as along-lenticular, vein-lenticular, apophysis, etc., vein ore bodies with complicated entanglement.

2.2 Mineralogical composition

Based on the studies conducted until now [13]; [14]; the polymetallic sulphur mineralisations of the Hajvali, Badovc, Kizhnica, and Përroi i ngjyrosur deposit, belongs to the sub-volcanic type of pneumatholite-hydrothemal phase of tertiary metalogenesis. The main mineralogical paragenesis are: lead-zinc sulphide paragenesis with sphalerite, galena, and pyrrhotite characteristic for all deposits; carbonate paragenesis (iron, manganese oligonite ore bodies) with insignificant participation of lead-zinc sulphides characteristic for Hajvali and Badovc deposits. The siderite-smithsonite ore bodies are characteristic for Përroi i ngjyrosur ore deposit (Artana ore field) where are present also the paragenesis of Al-silicate minerals, group of kaoliniti (Halloysite), and paragenesis of oxide minerals like psilomelane. The main metallic minerals are: sphalerite, galena, pyrrhotite, cubanite, vallerite, stannite, chalcopyrite, arsenopyrite, tetrahedrite, calaverite, krennerite, primary gold, bournonite, lollingite, falcmanite, pyrargyrite, boulangerite, plumosite, bornite, covellite, and melnicovite associated with quartz, siderite, Mn-siderite, rhodochrosite, Mn-calcite, barite, and chalcedon. The main accumulation of zinc is related to the mesothermal phase, whereas that of lead is of later phase. After an evaluation [2] and [3], based on the average mine results the Zn content is higher in Hajvali and Përroi ngjyrosur deposits (respectively 14.4 and 5.5%) with a predomination over the Pb content (9.4 and 4.4 % respectively). In contrary, in Badovc and Kizhnica deposits the Pb content (5.5 and 6.9%) is higher than Zn content (2.6 and 1.5% respectively). The Ag content is higher in Përroi ngjyrosur deposit (125 ppm) and then in Hajvali, Badovc and Kizhnica deposits (108.83 and 74 ppm respectively). Ag is correlated with Pb in all deposits except Kizhnica deposit where a correlation with Zn and As is observed. Platinum group elements are found sporadically, but sometimes in high contents, in all three main minerals (galena, sphalerite and pyrite) of the mineral deposits of

Hajvali, Badovc, Kizhnica and Përroi i ngjyrosur-Artana ore field. The geochemical data [1], suggest a very strong correlation of Ag with Pb, which could be related to the associated of pyrargyrite with galenit as well as with isomorphic enrichment of galenit with Ag.

3 MATERIALS AND METHODS

The analyses of the composition of mineral phases have been made by electronic microprobe of type CAMECA-SX50, BRGM, France. In total, are made 211 analysis (Appendix, Table 8-2, Dissertation [3], UP- FGM, Tirana, Albania).

3.1 Results and discussion

By the result of electronic microprobe analyses, notice several differences in the content of some elements in the same mineral for different mineral deposits (diagram 1-13). Sphalerite -ZnS, (Zn, Fe)S, in the all deposits observed highest value of iron (Fe) contents in sphalerite (9% - 13% Fe average value). The highest average value of iron (Fe) in sphalerite is characteristic for Kizhnica deposit (about 13% Fe), leaving behind three other deposits with 9 -11% Fe, (figure 4).

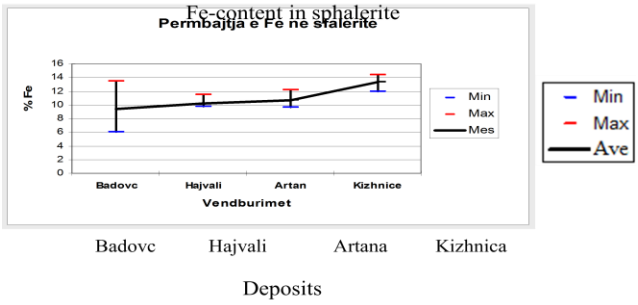

***Fig 4**. Iron (Fe) content in sphalerite for Badovc, Hajvali, "Përroi i ngjyrosur"-Artana and Kizhnica ore deposits.*

From practice is known that the iron (Fe) content in sphalerite depend on the forming temperature, and in some cases can be used as geothermometer. In our case we can use the approximate diagram shown in figure 5.

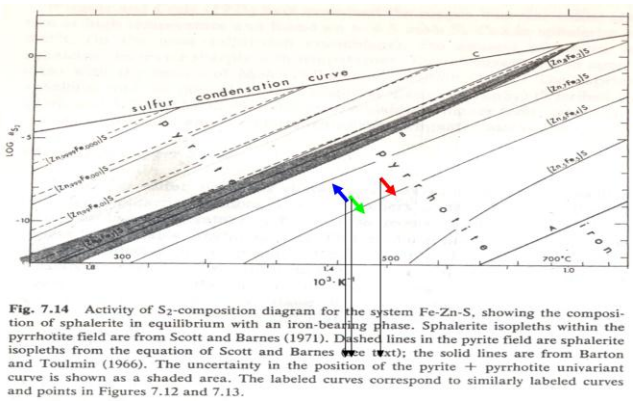

***Fig 5**. Activity of S_2-composition for the system Fe-Zn-S, showing the composition of sphalerite in equilibrium with an iron-bearing phase. The uncertainty in the position of the pyrite + pyrrhotite univariant curve is shown as a shaded area (H. Ll. Barnes, 1979, pp 363). In the figure, arrows indicate the composition of sfaleritit for deposits: in Badovc (blue), Hajvali and Artana (green), and Kizhnica (red), [3].*

From diagram (Figure 5) shows that the sphalerite of the all deposits are formed in temperature approximately from 450˚ C to 500˚C for all our deposits. Besides iron (Fe), sfalerite of these deposits also contain bismuth (Bi) and silver (Ag). Bismuth contents are generally low (figure 6), although we observe an increase in Kizhnica deposit (0.06% Bi). Its lower content has resulted in Badovc deposit, although in diagram (figure 6) according to the results of electronic microprobe bismuth (Bi) has a maximum value of the content about 0.2%. It does not present any significant importance because it would be a single sample analyzed that provided this high content compared with the other deposits. While in the Hajvali and Përroi i ngjyrosur-Artana deposits bismuth has approximately equal content (0.004% Bi) in sphalerite.

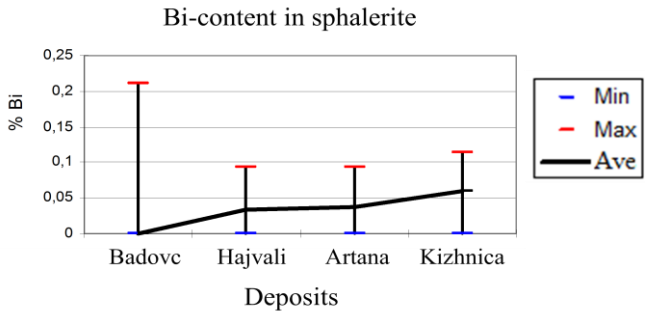

***Fig 6**. The bismuth (Bi) content in sphalerite of the Badovc, Hajvali, Përroi i ngjyrosur-Artana and Kizhnica mineral deposits*

In diagram (Figure 7) the silver (Ag) contents in sfalerite are very low if not absent, characteristic for Kizhnica and Artana deposits. Different from these, the sphalerite of Hajvali and Badovc deposits containing more silver (Ag) and a certain rise in Hajvali deposit.

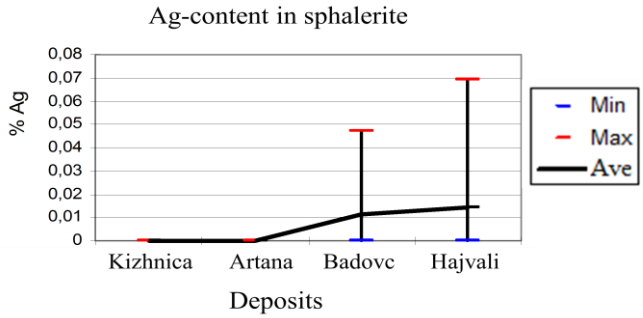

***Fig 7**. The silver (Ag) content in sphalerite of the Kizhnica, Përroi i ngjyrosur-Artana, Badovc and Hajvali mineral deposit.*

In the diagram (Figure 8) is shown the Ni/Co ratio in pyrite of the Badovc, Hajvali, Artana and Kizhnica deposits. The report is different for different deposits. The low values of content of this report resulting in pyrite of the Badovc, Hajvali, and Artana deposits, while there is an increase in Artana deposit. On the contrary, in pyrite of the Kizhnica deposit this ratio is the higher (≈3.5 average value).

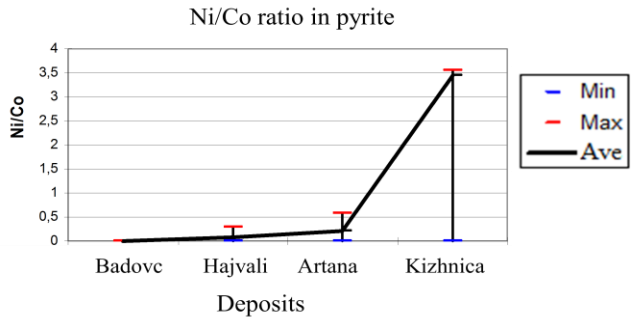

Fig 8. *The Ni/Co ratio in sphalerite of the Badovc, Hajvali, Artana and Kizhnica deposit*

Pyrite-FeS_2, in pyrite there are differences between ore deposits to the content of elements (As, Ag, and Sb). The contents of these elements in pyrite are different for different deposits. Arsenic (As) in pyrites of the studied deposits (Figure 9), there are with higher its contents of Badovc deposit (1.3% As average value). While, in pyrite of the Hajvali, Kizhnicë, and Artana deposits have the low content of As, although Artana leadeth them from these last with a very small increase.

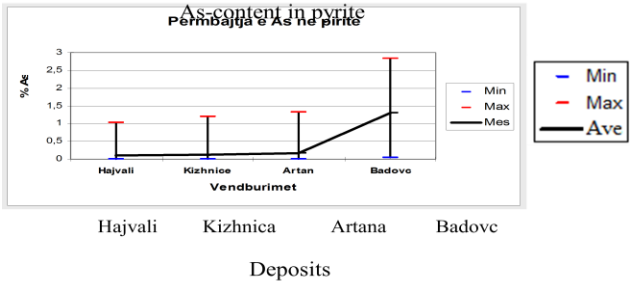

Fig 9*.The arsenic (As) content in pyrite of the Hajvali, Kizhnica, Përroi i ngjyrosur-Artana and Badovc mineral deposits*

From the diagram (Figure 10) pyrite of Artana deposit it results with high content of silver (about 0.03% Ag average value) compared to other deposits, although pyrite of the Kizhnica deposit after Artana is very rich in silver.

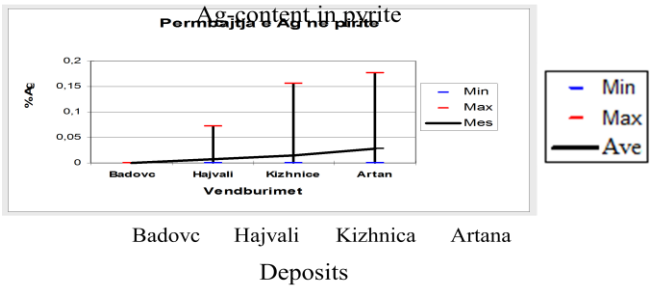

Fig 10*.The silver (Ag) content in pyrite of the Badovc, Hajvali, Kizhnica, and Përroi i ngjyrosur Artana mineral deposits*

Galena – PbS, The average content of antimony in galena of all deposits it results approximately equal. The lower average its value results in the Kizhnica deposit.

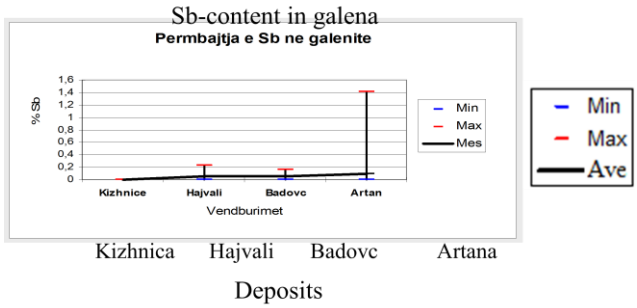

Fig 11*. The antimony (Sb) content in galena from Kizhnica, Hajvali, Badovc, and Përroi i ngjyrosur-Artana ore deposits*

From the result of electronic microprobe analyses galena results with very low content Bi (Badovc, Kizhnicë, and Hajvali). Otherwise, galena of Artana mine is the richest in Bi (1.3% average value).

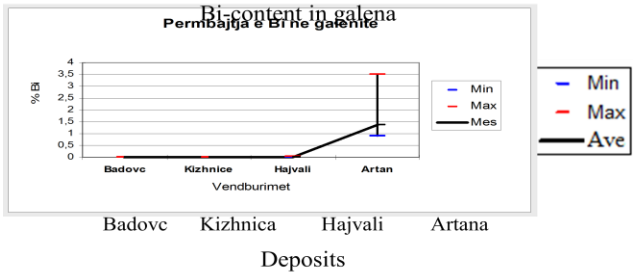

Fig 12. *The bismuth (Bi) content in galena from Badovc, Kizhnica, Hajvali, and Përroi i ngjyrosur -Artana ore deposits*

Galena of the Hajvalia mine contains more silver (> 100g/t Ag), than other mines (which are very poor with silver), Figure 13.

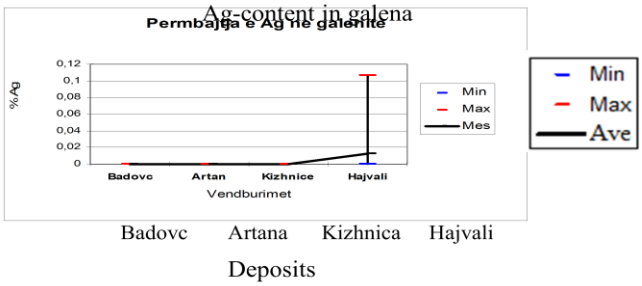

Fig 13. *The silver (Ag) content in galena for Badovc, Përroi i ngjyrosur -Artana, Kizhnica and Hajvali ore deposits*

4 Conclusion

From our study, the four mines have high values of iron (Fe) content in sfalerite**:** Badovc 9.43% Fe, Hajvali 10.24 % Fe, Përroi i ngjyrosur (Artana) 10.61 % Fe, and about 13 % Fe for Kizhnica mine; low content of bismuth in sphalerite: Hajvali (0.03 % Bi), Përroi i ngjyrosur - Artana (0.04 % Bi), Kizhnica (0.06 % Bi), whereas the sphalerite of Badovc deposit oppositely from them contains very little bismuth under 0,01% Bi . The silver (Ag) contents in sphalerite of these deposits are very low, sphalerite of Hajvali and Badovc mines contain more silver 0.015 % Ag respectively 0.01 % Ag. In two other mines Ag-content in sphalerite is very-very low or almost absent in sfalerit. Pyrites of these deposits characterized by low contents of arsenic (As), except Badovc where its value

amounts to 1.3%. Whereas regarding the silver (Ag) content, pyrites of these deposits are characterized with different Ag-content. So, the higher its content are found in Përroi i ngjyrosur-Artana mine (0.03% Ag), Kizhnica (0.02% Ag), and Hajvali (0.01% Ag), and almost missing in mine Badovc. Galena of all the mining containing antimony (Sb), bismuth (Bi), and silver (Ag). Generally characterized by low values of Sb and Bi, although the Bi contents are higher compared to those of Sb, and with 0.09% Sb leads them Artana mines. Galena of the Hajvalia mine contains more silver (> 100g/t Ag), than other mines (which are very poor with silver).

REFERENCES

[1] Bedri Durmishaj, “The situation and perspective of the deposit of Hajvalia”, MSc Thesis (Faculty of Mining and Metallurgy), Mitrovica-Kosovo, 2002.

[2] Durmishaj B, Tashko A, & Hyseni S, “Distribution of Zn and Pb in polymetallic ore deposit Hajvalia”, Bul. Shk. Gjeol. Vol.1/2003, pp. 62-71, 2003.

[3] Durmishaj B., “Perspective and potential of the Hajvali-Badovc-Kizhnica ore field based in geological-geochemical study”, (PhD, Thesis). Faculty Geology and Mining in Tirana- Albania, 2007.

[4] Grubič A., Jankovič A., “Metallogeny and concepts of the geotectonics development of former Yugoslavia”, Belgrade, 1974.

[5] Grubič A., Dimtrijevič M., “Model of geotectonic development of the northeastern Mediterranean”. FGM-Belgrade, 1977.

[6] Hyseni S and Large D., “The Trepça lead-zinc Mineral Belt, Kosovo-Geological Overview and Interpretation”, 7th Biennial SGA Meeting on Mineral Exploration and sustainable development Poster, No. 120, Athens-Greece. pp. 1-2, 2003.

[7] Jankovič S., “The principal metallogenic features of the Kopaonik district”, SGM-Kapaonik Beograd. pp. 79-101, 1995.

[8] Kossmat et al., “Geologie der zentralen Balkan halbinsel”, Berlin, 1924.

[9] Klisič M., “Synthesis of geological exploration in the region Hajvali-Kizhnica”, Mines flotation in Kizhnica and Novo Brdo, Prishtina, 1990.

[10] Klisič M., “Mineral deposit lead and zinc in the Hajvali-Kizhnica ore field”, Meeting Geology and Metallogeny Kopaonik, Belgrade, 1995.

[11] Miletič G., “The control structures volcanic apparatus and accompanying of lead and zinc mineralization”, Kopaonik metallogenic district (Symposium IRL), Beograd, 1977.

[12] Radoslav P., et al., “Geology of Hajvali-Badovc-Kizhnica ore field”, Mines flotation in “Kizhnica and Novo Brdo”-Prishtina, 1989.

[13] Smejkal S. and Rakič S., “Mineral paragenesis of lead and zinc ore field Hajvalia, Prlina and Kišnica”, Profess. Doc. Fond. Geozavod Beograd, 1956.

[14] Smejkal S., “Structure, mineralization, mineral paragenesis and genesis of Kopaonik district lead-zinc deposits”, (PhD) MGFU-Belgrade. pp. 58-63, 1960.