407
GEOME 2
Manuscript received: February 6, 2024
Accepted: May 7, 2024

Geologica Macedonica, Vol. **38**, No. 1, pp. 31–38 (2024)
On print ISSN 0352 – 1206
On line ISSN 1857 – 8586
UDC: 553.44:[550.42:549.3.086(497.115)
https://doi.org/10.46763/GEOL24381031d

Original scientific paper

SOME IMPORTANT CHARACTERISTICS OF POLYMETALLIC LEAD-ZINC ORE IN THE BADOVC MINERAL DEPOSIT, KOSOVO

Bedri Durmishaj, Sylejman Hyseni

University"Isa Boletini"in Mitrovicë, Faculty of Geosciences, Mitrovicë, Republic of Kosovo
sylejman.hyseni@umib.net

A b s t r a c t: In this paper, we have presented the scientific results of the chemical and mineralogical composition of sulphides mineralization at the Badovc mine. In the study, 20 samples were taken and the distribution of the metal content (Pb, Zn, Ag, Bi, Cd, Cu, As, and Sb) in the Badovc deposit was analyzed. Microscopic description of the smooth mineralogical section at the Badovc deposit has resulted in this mineral composition: sphalerite, pyrite, galena, magnetite, and non-metallic minerals. Statistical and correlative analyses, factor weights, and microscopic studies were performed. According to the correlative analysis, the results show the following geochemical relationships: Pb-Ag-Bi; Cu-Cd, while data for geochemical associations, according to another method known as factorial analysis, resulted in Pb-Ag-(Bi-Sb) and Cd-Cu. The Fe content of sphalerite ranges from 6 to 13%, or 0.16 Fe atoms in the crystal-chemical formula. In galena, apart from the very high content of Pb, the absence of Ag stands out among other elements. It contains more Sb than Bi. As a conclusion, in this study we can distinguish two generations, one with the predominance of "pyrite-sphalerite-magnetite-galena" and the other composed mainly of non-metallic minerals, "pyrite-marcasite" formed at low temperatures and acidic pH.

Key words: polymetallic sulphides; lead-zinc ore; geochemical association; Badovc mineral deposit

INTRODUCTION

The Kizhnica-Hajvalia-Badovc ore field (KHB) is located in central Kosovo, about 10 km SE of Prishtina. Pb-Zn-Ag deposits in the Badovc area are situated in the southern part of the Trepça Mineral Belt (TMB). The Badovc mine is 10 km away from Prishtina, just off the road to Gjilan. The main site is located near the Badovc dam and reservoir. The Badovc concentrator is 1 km away from the mine. The Pb-Zn-Ag deposit of Badovc is located in the south of the ore field, at the azimuth of strike NNW-SSE (Figures 1, 2), in the trending Vardar zone [9, 10].

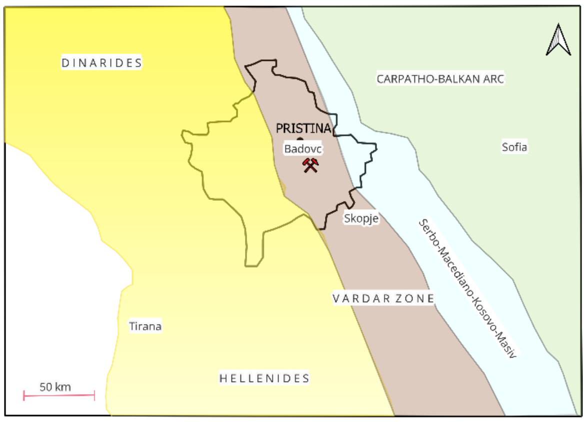


Fig. 1. The geographical position of the Badovc deposit [10]

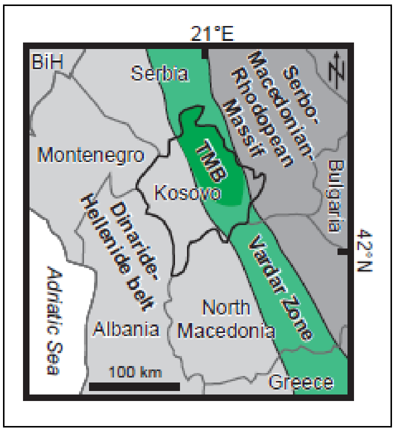


Fig. 2. Trepça mineral belt within the Vardar tectonic zone [9]

GEOLOGY OF THE BADOVC MINE

The oldest and most widespread rocks in the vicinity of the Badovc deposit belong to the Veles series of probable Paleozoic age although the upper part has been proven to be Triasic in age.

This so-called "metamorphic series" represents the host rocks for mineralization and consists of phyllite and sericite schists with a central unit containing subordinated carbonate and calc-silicate layers. The metamorphic series is overlain by serpentinite, gabbros and diabase-hornfels of the Jurassic age, which together with flysch sediments of the upper cretaceous age cover large parts of the area [7]. Tertiary sediments occur as breccias, sandstone, clay, and marl. Volcanic rocks mainly andesite occur to the south of the mine (Figure 3) [12].

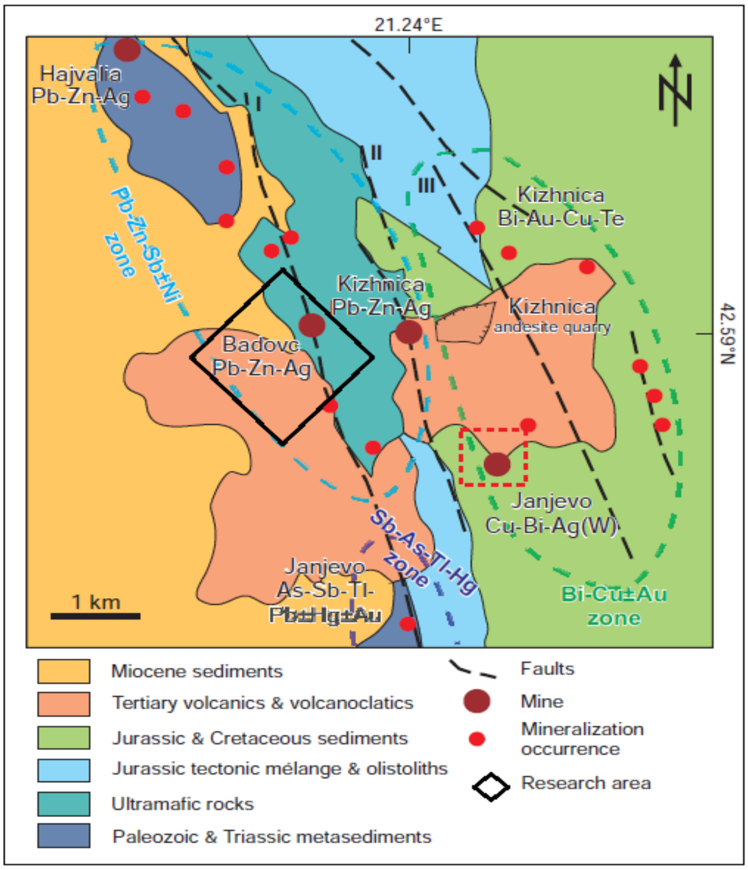


Fig. 3. Simplified geological map of the Kizhnica–Hajvalia–Badovc ore field.
Abbreviations: I = Hajvalia–Badovc tectonic zone; II = Kizhnica tectonic zone; III = Okosnica tectonic zone [2]

MATERIALS AND METHODS

From this deposit, two samples were analyzed, performing a total of 26 chemical analyses in different minerals. SX50 electron microprobe analyses were performed at the BRGM laboratory in Orleans, France. The working conditions for the quantitative determination of chemical elements were: the kosecande of the capture angles 1.556, the acceleration voltage 20 kV, the current 30 nA, and the counting time 10" [5].

Chemical composition and main geochemical associations in the Badovc mineral deposit

Regarding the chemical composition of the mineralizations in the deposit, we have used the analysis of the ore minerals deposited for processing in the Kizhnica factory/enrichment plant, as well as the analysis of the samples taken from the ore bodies in the Badovc deposit [1]. The distribution of the contents of the main chemical elements and accompanying chemical elements in the deposit is shown through statistical parameters in Table 1. Stojanović et al. (2018) [16] showed that in the Rudnik deposit (Serbia), according to microscopic observations and paragenetic analyses of Pb-Zn/Cu, Ag, Bi, and W, mineral associations have been identified: galena, chalcopyrite, pyrrhotite, colloform pyrite, siderite, and native bismuth. The average content varies widely: Pb (0.94–5.66 wt %), Zn (0.49–4.49 wt %), Cu (0.08–2.18 wt %), Ag (50–297 ppm), Bi (~100–150 ppm), and Cd (~100–150 ppm) [16].

Serafimovski et al. (2022) [17] found that in the Pb-Zn Toranica deposit (North Macedonia), the mineral associations determined by the chemical properties of the primary ore sulfides included quartz-pyrrhotite-galena-sphalerite, pyrite-chalcopyrite-sphalerite, quartz-epidote-sphalerite-galena, and quartz-calcite. Sphalerite was composed of Fe, Mn, Cd, and Cu, while galena displayed varying compositions of Bi, Ag, and Se [17].

In Table 2 we present the geochemical associations using correlative analysis, and in Table 3 we present geochemical associations through factorial analysis. According to the correlative analysis, the results show these geochemical associations: Pb-Ag-Bi; and Cu-Cd. Whereas data on geochemical associations according to another method known as factorial analysis [14], result in Pb-Ag- (Bi-Sb); Cd-Cu. Graphic representation of factor weights in the Badovc deposit is given in Figure 4.

T a b l e 1

Statistical parameters of the distribution of metal content in the Badovc deposit [6]

Parameters	Elements							
	Pb%	Zn%	Ag g/t	Bi %	Cd %	Cu %	As %	Sb %
Average	5.51	2.57	83.15	0.03	0.03	0.07	0.09	0.07
Median	5.00	2.44	64.50	0.02	0.02	0.05	0.05	0.04
Standard deviation	3.24	1.73	64.33	0.02	0.02	0.06	0.08	0.06
Minimum	1.45	0.37	25.00	0.01	0.01	0.02	0.01	0.02
Maximum	14.06	6.13	265.00	0.06	0.09	0.19	0.26	0.18
No. of samples	20	20	20	20	20	20	20	20

T a b l e 2

Correlation matrix, Badovc deposit. Correlation coefficients are significant for $\rho < 0.05$, when they have a value of > 0.41. Number of samples =20 [6]

Elements	Pb %	Zn %	Ag g/t	Bi %	Cd %	Cu %	As %	Sb %
Pb %	1.000							
Zn %	0.183	1.000						
Ag g/t	**0.649**	0.242	1.000					
Bi %	0.419	–0.093	0.317	1.000				
Cd %	0.228	–0.272	–0.234	0.118	1.000			
Cu %	0.257	–0.320	0.080	0.079	**0.734**	1.000		
As %	0.363	–0.115	0.225	0.091	–0.030	–0.091	1.000	
Sb %	0.246	0.191	0.311	0.224	–0.161	–0.099	0.275	1.000

T a b l e 3

Weights of factors
(Method of principal components, normalized Varimax)

Elements	Factors		
	F1	F2	F3
Pb %	**0.870245**	0.236144	0.004436
Zn %	0.317157	–0.425097	–0.685874
Ag g/t	**0.832436**	–0.114704	–0.132544
Bi %	0.563094	0.177981	0.156768
Cd %	0.006821	**0.897576**	0.069218
Cu %	0.138699	**0.895070**	–0.010600
As %	0.391624	–0.187423	0.746405
Sb %	0.532278	–0.315838	0.213648
Expl.Var	2.323913	2.022979	1.120257

Significant values greater than 0.7 are emphasized in bold numbers [6]

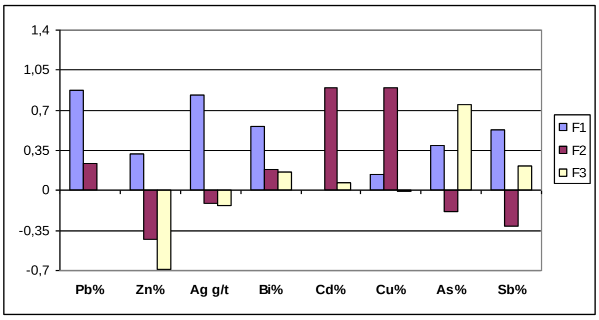


Fig. 4. Graphic representation of factor weights in the Badovc deposit

Microscopic study and the results of chemical analysis of the main minerals in the Badovc deposit, Kosovo

From the microscopic description of the polished section (BD2 and BD3) that results in this mineralogical composition:

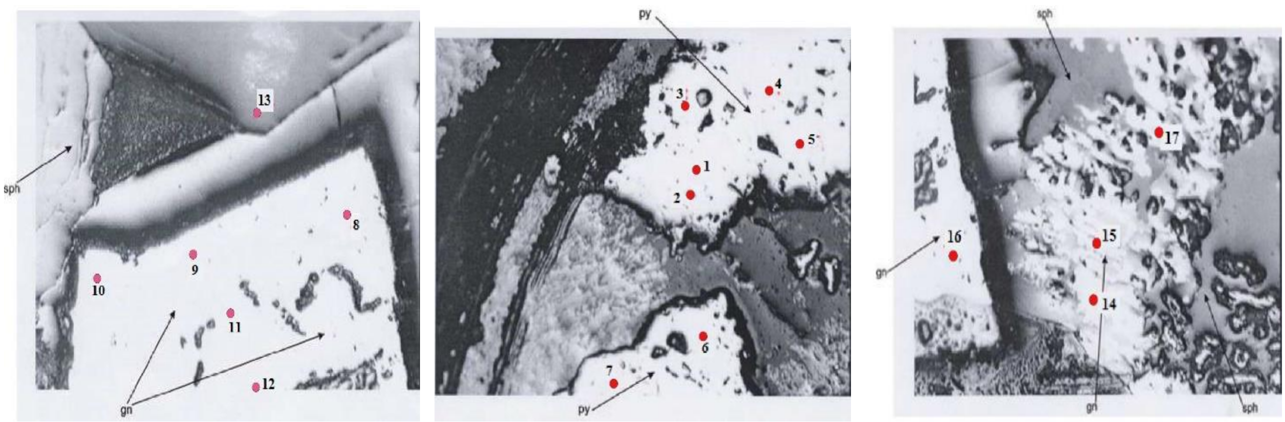
The **BD2-**polished section consists of the following minerals: 5% sphalerite. 10% magnetite. 15% pyrite. and traces of galena as well as non-metallic minerals (Microphoto 1).

Sphalerite is found in the form of granular aggregates with dimensions of several millimeters, as well as in a certain form of isolated grains with dimensions of 0.5 mm. The aggregates may also consist of grains with dimensions of several tenths of a millimeter. Sphalerite is surrounded by non-metallic minerals that also present a regular boundary. In general, non-metallic minerals surround sphalerite crystals. which results in the latter being an earlier form than non-metallic ones.

Inclusions of magnetite are observed in the middle of the sphalerite. However. most of the magnetite is associated with the non-metals that have replaced the others [6].

It seems that initially there will be a "sphalerite-magnetite" association judging by the dark-colored color (macroscopically. and from sphalerite analyses in other Badovc samples). It seems that we have an iron sphalerite but firstly we had a mineralization rich in Fe and Zn probably formed at relatively high temperature.

Pyrite – consists of relatively fine crystalline aggregates. with crystal sizes of about 0.1 mm. Pyrite is mainly associated with magnetite. In some places, needle aggregates of pyrite and marcasite are also found, which is associated with non-metallic minerals that have replaced magnetite. This indicates that the second generation of minerals (mainly non-metallic) that have replaced magnetite formed at a low pH and T. In some places. we observe co-growth of "pyrite-magnetite" where the latter forms elongated shapes oriented in the middle of the pyrite [6].

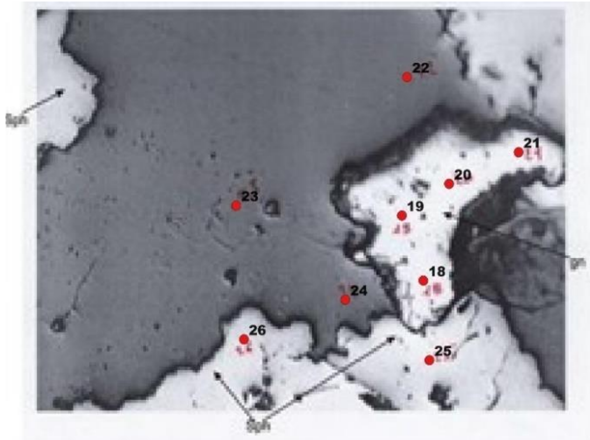


Microphoto 1. Mineral composition of BD2-polished section. Badovc deposit, Kosovo [6]

Galena appears from a cube with 0.8 mm edges in a regular shape. This mineral appears to have formed together with coarse-grained sphalerite during the first generation [6]. Sphalerite, which is present in the galena mineral, is accompanied by some microcrystals of pyrite in its peripheral parts. This fine crystalline pyrite of 0.05 mm size is also associated with a mineral with a double pronounced reflection which varies the same as sphalerite up to 4–5% less. with a pronounced anisotropy and internal red reflex (probably iron hydroxide). In conclusion, in this polished section we can single out two generations, one with the predominance of "pyrite-sphalerite-magnetite-galena" and the other mainly composed of non-metallic minerals "pyrite-marcasite" formed at low temperatures and acidic pH.

BD3-polished section consists of 5% galena, 15% sphalerite, and traces of pyrite (Microphoto 2).

Sphalerite has a zonal construction that is distinguished by internal reflections and confirmed by microprobe analysis. There are fine micro-inclusions of galena [6]. This mineral forms crystals of 0.1 mm in size in regular shape and is surrounded by non-metallic minerals. Galena forms xenomorphic crystals it sometimes also has inclusions of nonmetallic minerals. It seems that galena was formed at the same paragenetic time as sphalerite. Pyrite is found in very low concentrations in grains with a size of a few hundredths of a millimeter and it is mainly found with non-metallic minerals.



Microphoto 2. Mineral composition of BD3-polished section. Badovc deposit, Kosovo [6]

The chemistry of sphalerite is distinguished by a fairly high Fe content ranging from 6–13%. The lowest Fe contents are found in the peripheral parts of the sphalerite, while the highest is in its central parts. It seems that during sphalerite crystallization there was a progressive reduction of Fe activity. Significant Pb contents of approximately 0.25% may have been dictated by the presence of very fine micro-inclusions that are difficult to distinguish. In general, these contents of Pb are also accompanied by contents of As, which makes you think about the presence of sulfo-salts.

Following are the calculations of the crystallochemical formulas from the results of the electron microprobe analyses (Table 4).

T a b l e 4

Crystallochemical formulas of major minerals according to electron microprobe analyses. Ore bodies of the Badovc deposit, Kosovo [6]

No.	Polished section	
	Crystallochemical formulas	Mineral
BD3	(Zn 0.836, Fe 0.163, Pb 0.001, As 0.001) 1.001S 0.999	Sphalerite
BD2	(Pb 0.985, Fe 0.003, Sb 0.001, Zn 0.001) 0.990S 1.010	Galena
BD2	(Fe 1.008, Co 0.001, Pb 0.001) 1.010 (S 1.969, As 0.021) 1.990	Pyrite

In galena, in addition to very high contents of lead (Pb). the absence of silver (Ag) stands out among other elements. It contains more antimony (Sb) than bismuth (Bi). Considering the excess in cations, the presence of metalloids should again be attributed to the substitution $3Pb^{2+} \rightarrow 2Sb^{3+}$. Characteristic is the presence of tellurium (Te), although in low content, in isomorphism with sulfur (S). Sphalerite is again characterized by a high content of iron (Fe). In contrast to galenite, silver (Ag) content is found in some cases and tellurium (Te) is absent. The contents of arsenic (As) should be related to the heterovalent isomorphism $2As^{3+} \rightarrow 3Zn^{2+}$, while those of lead (Pb), to the presence of galena micro-inclusions [4]. In the analyzed pyrites, the content of arsenic (As) and mercury (Hg) stands out. Arsenic (As) is located apparently in isomorphism with sulfur (S^{2-}), while the contents, although sporadic, of mercury (Hg) must constitute point defects "interstitial insertion".

In Figures 5 and 5a it is clearly observed that the presence of As is related to the filling of vacancies created by the absence of S. The predominance of Co over Ni, as well as Bi over Sb, is noted.

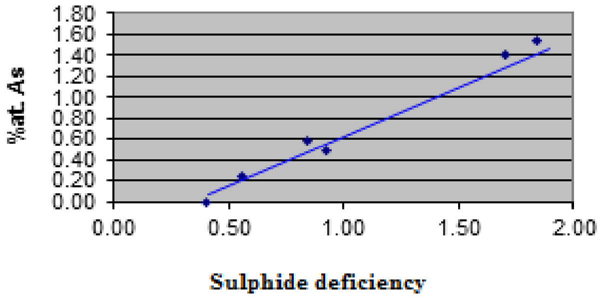


Fig. 5. Diagram of sulphur (S) deficiency in pyrite, Badovc deposit

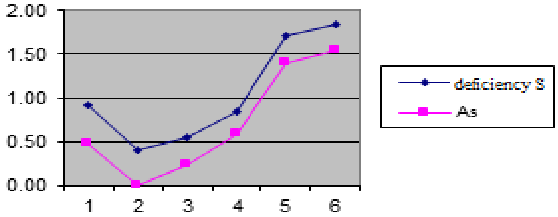


Fig. 5a. Diagram of sulphur (S) deficiency in pyrite, Badovc deposit

In Figure 6, we observe some different distributions of arsenic (As) contents in pyrites of sample BD2. Its high values are above 2% and its low values are below 0.5%.

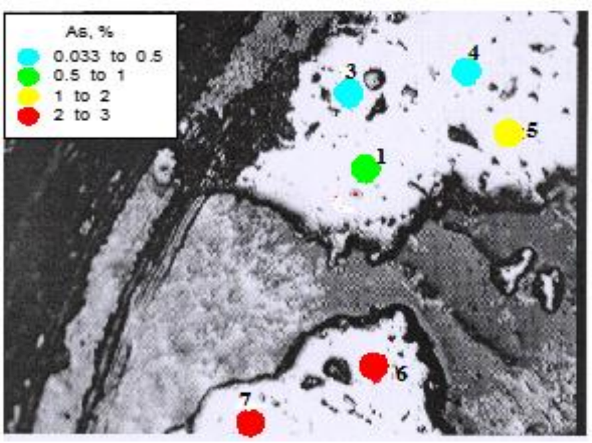


Fig. 6. Contents of As. BD2-polished section [6]

In Figure 7, the Hg content in the pyrites of sample BD2 is characteristic. In those analyzed points where there is less As, we find a high content of Hg above 0.05% (Table 5). while where there is more As, we find a low content of Hg (0.015%).

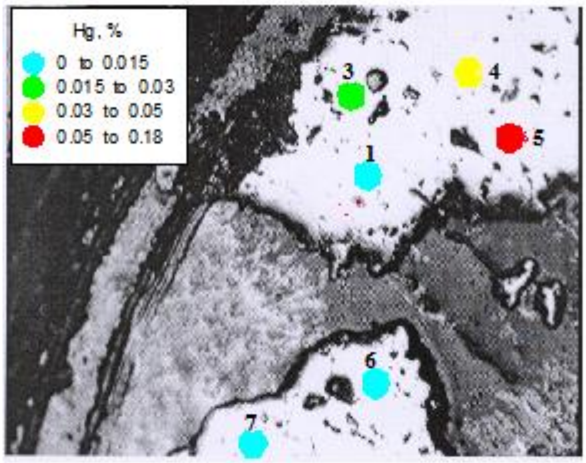


Fig 7. Contents of Hg. BD2-polished section [6]

In addition to As and Hg, the distribution of Pd contents in the pyrites of sample BD2 is also characteristic. In Figure 8 its contents range from 0.08% to 0.11% (Table 5).

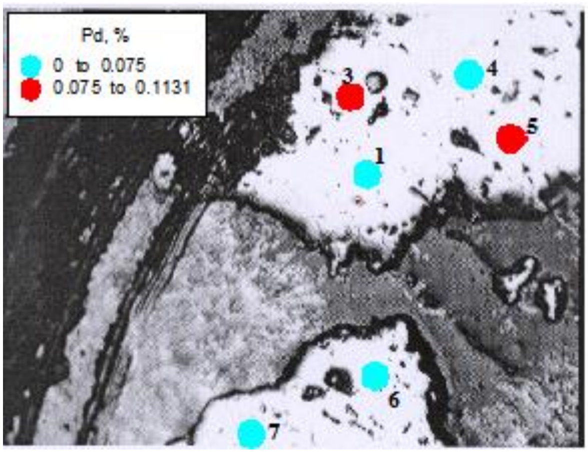


Fig 8. Contents of Pd. BD2-polished section [6]

In Figure 9 we observe different distributions of Fe content in sphalerite of sample BD3. In the mentioned figure we observe analyzed points with high content of Fe above 12% and low content of 6% (Table 5). As for silver (Ag), in the sphalerite of sample BD3 (Figure 10) we observe the same distribution, and increasingly low content (<0.0001%) except at some point where sometimes we find values somewhat higher than it.

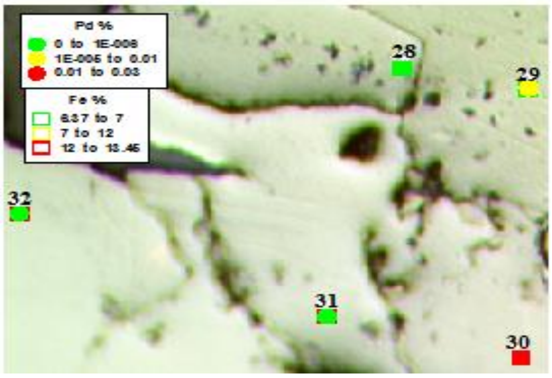


Fig. 9. Contents of Fe and Pd. BD3-polished section [6]

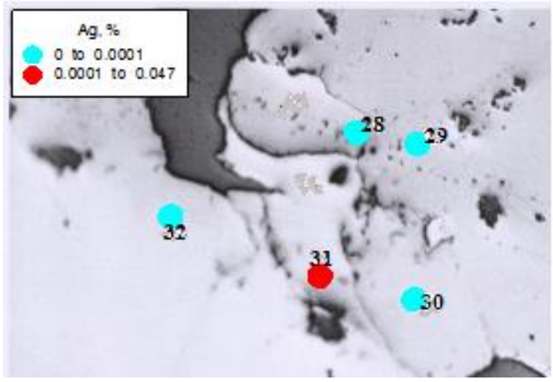


Fig. 10. Contents of Ag. BD3-polished section [6]

Table 5

The contents of As, Hg and Pd in pyrite, as well as Pd and Fe in sphalerite in the Badovc deposit [6]

	Pyrite (% wt.) Analyzed points	Content (%) As	Hg	Pd		Sphalerite (% wt.) Analyzed points	Content (%) Fe	Pd
BD2 -polished section	1	0.89	0.00	0.00	**BD3**-polished section	28	6.39	0.00
	3	0.03	0.02	0.11		29	6.37	0.01
	4	0.44	0.04	0.00		30	12.43	0.03
	5	1.09	0.18	0.08		31	13.44	0.00
	6	2.57	0.01	0.00		32	12.22	0.00
	7	2.84	0.00	0.00				

CONCLUSIONS

The Badovc deposit holds an evaluated 8 Mt ore reserves with average content: 5.20 % Pb, 3.13 % Zn, and 71 g/t Ag.

According to the correlative analysis, the results show these geochemical associations: Pb-Ag-Bi and Cu-Cd, whereas data on geochemical associations according to another method known as factorial analysis, result in: Pb-Ag-(Bi-Sb); Cd-Cu.

The microscopic description of the mineralogical polished section in the Badovc deposit resulted in this mineral composition: sphalerite, pyrite, traces of galena, magnetite, and non-metallic minerals. As a conclusion in this study, we can single out two generations, one with the predominance of "pyrite-sphalerite-magnetite-galena" and the other mainly composed of non-metallic minerals, "pyrite-marcasite" formed at low temperatures and acid pH.

The Fe content in the sphalerite varies from 6 to 13%, or 0.16 Fe atoms in the crystallochemical formula. In galena, in addition to very high contents of Pb, the absence of Ag stands out among other elements. It contains more Sb than Bi. Characteristic is the presence of Te, although in low content, in isomorphism with S. In contrast to galenite, Ag content is found in some cases and Te is absent. In the analyzed pyrites, the contents of As and Hg stand out. Arsenic is located; apparently in isomorphism with S^{2-}, while the contents, although sporadic, of Hg must constitute point defects "interstitial insertion". We observe some different distributions of arsenic (As) contents in pyrites of sample BD2. Its high values are above 2% and its low values are below 0.5%.

It is characteristic that where we have less arsenic, we find high mercury contents and vice versa. In addition to arsenic and mercury,. the distribution of palladium contents (0.08% – 0.11%) in the pyrite of the Badovc deposit is also characteristic.

REFERENCES

[1] Durmishaj, B., Hyseni, S., Hyseni, A. (2023): Some important characteristics of polymetallic lead-zinc ore in Hajvalia mine. Kosovo. *Geologica Macedonica* **37** (1), pp. 5–14. https://doi.org/10.46763/GEOL23371005d

[2] Borojević Šoštarić, S. B., Cvetković, V., Neubauer, F., Palinkaš, L. A., Bernroider, M., Genser, J. (2012): Oligocene shoshonitic rocks of the Rogozna Mts. (Central Balkan Peninsula): Evidence of petrogenetic links to the formation of Pb–Zn–Ag ore deposits. *Lithos* **148**, 176–195.

[3] Durmishaj, B. (2002): *The situation and perspective of the deposit of Hajvalia.* Unpubl. Master thesis (in Albanian), University of Prishtina, Faculty of Mining and Metallurgy, Mitrovica, Kosovo. 68 p.

[4] Durmishaj, B., Tashko, A., Hyseni, S. (2003): Distribution of Zn and Pb in polymetallic ore deposit Hajvalia. *Bul. Shk. Gjeol*. Vol. **1**, pp. 62–71.

[5] Durmishaj, B., Tashko, A., Sinojmeri, A., Neziraj, A. (2006): On the chemical composition of the mineral phases of the Hajvali, Badovc and Kizhnica deposits, Kosovo (in Albanian). *Bulletin of Geological Sciences* **2**, 91–100.

[6] Durmishaj. B. (2007): *Perspective and potential of the Hajvali-Badovc-Kizhnica ore field based in geological-geochemical study*. Unpubl. PhD thesis (in Albanian). University of Tirana, Faculty of Geology and Mining,164 p.

[7] Durmishaj, B., Hyseni, S., Tashko, A. (2010): Pb-Zn sulphide mineralisation of Hajvali-Badovc-Kizhnica and Artana ore field, Kosovo: Geology and sulphur isotopic composition. *Journal of International Environment Application & Science*. Vol. **5** (4), 514–522.

[8] Hyseni, S. (2000): *Metallogenic characteristic of polymetallic mineralization ore field Hajvali-Badovc-Kizhnica* (in Albabian). Unpubl. PhD thesis, University of Tirana, Faculty of Geology and Mining. 87 p.

[9] Hyseni, S., Hoxha, G., Large, D. (2003): 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, 1–2.

[10] Hyseni, S., Durmishaj, B., Fetaha, B., Shala, F., Berisha, A., Large, D. (2010): Trepça ore belt and stan terg mine – Geological overview and interpretation, Kosovo. *Geologija* **53** (1), 87–92, Ljubljana. www.geo-zs.si

[11] Hyseni, A., Muzaqi, E., Durmishaj, B., Hyseni, S. (2022): Metal losses at the enrichment process. *MMD*. **16** (4), 132–137. https://doi.org/10.33271/mining16.04.132

[12] Klisić, M. (1995): Mineral deposit lead and zinc in the Hajvali-Kizhnica ore field. *Meeting Geology and Metallogeny, Kopaonik*. Belgrade. 305–313.

[13] Kołodziejczyk, J., Pršek, J., Voudouris, P., Melfos, V., Asllani, B. (2016): Sn-bearing minerals and associated sphalerite from lead-zinc deposits, Kosovo: An electron microprobe and LA-ICP-MS study. *Minerals* **6**, 42. https://doi.org/10.3390/min6020042

[14] Mederski, S., Wojsław, M., Pršek, J., Majzlan, J., Kiefer, S., Asllani, B. (2021): A geochemical study of gersdorffite from the Trepça mineral belt, Vardar zone, Kosovo. *Journal of Geosciences* **66** (2), 97–115.

[15] Mederski, S., Pršek, J., Kołodziejczyk, J., Kluza, K., Melfos, V., Adamek, K., Dimitrova, D. (2023). Mineralogical and geochemical studies of Cu–Bi–Ag±W ores from Janjevo (Kosovo): Insights into the Bi sulfosalt mineralogy and the distribution of bismuth in base metal sulfides. *Journal of Geosciences* **68** (2), 139–162. DOI: http://doi.org/10.3190/jgeosci.371

[16] Stojanović, J. N., Radosavljević, S. A., Tošović, R. D., Pačevski, A. M., Radosavljević-Mihajlović, A. S., Kašić. V. D., Vuković, N. S. (2018): A review of the Pb-Zn-Cu-Ag-Bi-W polymetallic ore from the Rudnik orefield. Central Serbia. *Geološki anali Balkanskoga poluostrva* **79** (1), 47–69.

[17] Serafimovski, T., Tasev, G., Stafilov, T. (2022): General features of some pollymetalic ore deposits in the Republic North Macedonia. *Geologia Croatica* **75** (special issue), 349–364.

Р е з и м е

НЕКОИ ВАЖНИ КАРАКТЕРИСТИКИ НА ПОЛИМЕТАЛНАТА ОЛОВНОЦИНКОВА РУДА ВО РУДНОТО НАОЃАЛИШТЕ БАДОВЦ, КОСОВО

Бедри Дурмишај, Силејман Хисени

Универзитет „Иса Болетини“, Факултет за геонауки, Митровица, Република Косово
sylejman.hyseni@*umib*.net

Клучни зборови: полиметални сулфиди; оловноцинкова руда; геохемиска асоцијација; минерално наоѓалиште Бадовц

Во овој текст ги презентираме научните резултати за хемискиот и минералошкиот состав на минерализацијата на сулфидите во рудникот Бадовц. Во студијата беа земени 20 примероци и беше анализирана распределбата на содржината на металите (Pb, Zn, Ag, Bi, Cd, Cu, As и Sb) во наоѓалиштето Бадовц. Микроскопскиот опис на мазниот минералошки дел на наоѓалиштето Бадовц резултира со овој минерален состав: сфалерит, пирит, галена, магнетит и неметални минерали. Направени беа статистички и споредбени анализи, тежински фактори и микроскопски проучувања. Според корелативната анализа, резултатите ги покажаа следните геохемиски врски: Pb-Ag-Bi и Cu-Cd, додека податоците за геохемиските состави, според друг метод познат како факторна анализа, резултираа со Pb-Ag-(Bi-Sb) и Cd-Cu. Содржината на Fe во сфалеритот се движи од 6 до 13%, или 0.16 атоми на Fe во кристално-хемиската формула. Во галенитот, покрај многу високата содржина на Pb, меѓу другите елементи се издвојува отсуството на Ag, а содржи повеќе Sb отколку Bi. Како заклучок, во оваа студија можеме да разликуваме две генерации, едната со доминација на „пирит-сфалерит-магнетит-галенит“ и другата составена главно од неметални минерали, „пирит-марказит“, формирана на ниски температури и кисела pH-вредност.