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GEOCHEMISTRY OF MICRO AND MACRO ELEMENTS IN PYRITE OF THE Pb - Zn ORE DEPOSIT KIZEVAK (Raska, Serbia)

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ABSTRACT. The paper treats the contents and distribution of characteristic micro and macro elements (Ni, Co, In, Ga, Tl, Au, As, Cu, Pb, Sb, Ag and Zn) in different generations and phases of pyrite formation as well as their geochemical characteristics.
The polymetallic hydrothermal Pb - Zn deposit Kizevak is located on the northwest slopes of the Kopaonik mountain, east of the town of Raska. Geotectonically it belongs to Serbo - Macedonian Mass (SMM), and metallogenic to the Serbo - Macedonian metallogenic Province (SMP).
The content of micro and macroelements in the monomineral pyrite was determined by a semi quantitative spectrohemical method. The pyrites are characterized with a low content of Ni up to 0.0045% and Co up to 0.0055%. The content of Tl in pyrite ranges from 0.0001 up to 0.031%. Gold is present up to 0.0019%, in younger generation of pyrite. Microelements (Co, Ni and Tl) are present in concentrations that are characteristic for low temperature Pb - Zn deposits, and reflect paragenetic intergrowth of ore minerals in the deposit.

ГЕОХИМИЯ НА МИКРО И МАКРО ЕЛЕМЕНТИТЕ В ПИРИТА В ОЛОВНО-ЦИНКОВО НАХОДИЩЕ КИШЕВАЦ (Раска, Сърбия)

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РЕЗЮМЕ. Докладът разглежда съдържанието и разпространението на характеристични микро- и макро елементи (Ni, Co, In, Ga, Tl, Au, As, Cu, Pb, Sb, Ag и Zn) в различните генерации и фази на образуване на пирита, както и техните геохимични характеристики.
Полиметалното хидротермално оловно-цинково находище Кишевац е разположено в северозападните склонове на планината Копаоник, на изток от град Раска. В геотектонско отношение находището принадлежи към Сърбо-македонския масив, а в металогенно отношение към Сърбо-македонската металогенна провинция.
Съдържанието на микро и макроелементи в мономинералния пирит е определено посредством полуколичествени спектрометрични методи. Piритът се характеризира с ниско съдържание на Ni – до 0.0045% и Co – до 0.0055%. Съдържанието на Tl в пирита варира от 0.0001 до 0.031%. Златото присъства в съдържание до 0.0019%, и то в по-късно отложените пиритни генерации. Микроелементите (Co, Ni и Tl) присъстват в концентрации, които са типични за ниско-температурни оловни-цинкови находища и показват парагенетично прорастване на минералите в находището.

Introduction

Monomineral assemblages of principal sulphides in the Kizevak polymetallic lead-zinc deposit were geochemically analyzed (Arsenijevic, 1987; Sudar 2001) during the complex geological works under long - term projects in the Sastavci - Kizevak area.

Pyrite is the third dominant mineral, afther sphalerite and galena, in sulphide parageneses, which also contains chalcopyrite, sulphosalts, subordinate pyrhotite and marcasite. Paragenetically, the mineral was formed in two phases, with three generations, but the proportion of either phase is difficult to estimate. Pyrite occurs in the form of crystals, often in coarse - grained aggregates, compact mass, and fine grains.

The earlier phase is characterized by crystals in form of pentagonal dodecahedron (210), in frequent associations of dark sphalerite, quartz and calcite. Later phase is associated with dark and yellow sphalerite and galena. Frequently it occurs in skin over dark sphalerite, and galena. In some cases pyrite is pressing back dark sphalerite to the substitute. Fine grains pyrite occurs in skin, vein, fine crystals mass, and impregnation. In some of pyrite the fissure is fill up with sulfosalts (bulangerite and tethaedrite).

Basic geology of the deposit

The polymetallic hydrothermal lead - zinc deposit of Kizevak is situated on northwestern slopes of Kopaonik Mt., east of the town of Raska on the right bank of Ibar river (Fig.1). Geotectonically, the deposit belongs to the Serbian-Macedonian Massif (SMM), and metallogenetically (Jankovic, 1967; Jankovic, Petkovic, 1974) to the Serbian-Macedonian metallogenic province (SMP). Classifiied by genetic features (Mudrinic, 1997), it is a volcanic hydrothermal deposit. The deposit and the surrounding area are made up of Mesozoic and Cenozoic rocks represented by peridotites, flysch sediments, and products of Tertiary magmatism.

The main ore body is found in volcanic rocks (andesite and quartz latite and their pyroclasts) which also build up most of the deposit. Products of the earlier magmatic stage underwent hydrothermal alteration, whereas quartz latite has been slightly hydrothermally altered.

Northward from the Kozja Glava peak, three ore fields are located in the deposit, about 500m apart one from the other. Vein or lenticular ore emplacement between the first and the second ore fields, designated as an interfield (Mz), is the ore - richest part of the deposit. Fractures of NE - SW or E - W general trend, transverse to the principal dislocations of the Vardar Zone, were the main channels for precipitation of hydrothermal solutions through a number of pulsation stages. In deposits of Tertiary magmatism, such as the Kizevak, the low - temperature hydrothermal parageneses are dominant. Minerals were formed in several magmatic events, that resulted in two, earlier and later, ore parageneses, each in two or three occurrences. Sphalerite - galena parageneses are dominant, with various proportions of pyrite and chalcopyrite, a marked presence of sulphoantimonide. Gangue minerals are quartz, siderite and rhodochrosite.

Fig.1. Sketch map of the position Ki`evak Pb -Zn deposit 1 : 200.000

Laboratory study methods

Different samples were collected mostly from uncaved - in and accessible adits at depths from 650 m to 830m (ore fields I and II) and from levels (ore field II and interfield). Monomineral fractions were separated chiefly manually from the ore samples. The extracted minerals were treated by electromagnetic separation and heavy fluids, optically controlled, and mechanical impurities were removed. Quantities of the contained elements were determined using spectrochemical analysis and atomic absorption spectrometry.

For spectrochemical analysis of micro and macro - elements a large - dispersion spectrograph HILGER - 478 was used with optical and quartz prisms, based on international geochemical standards (USGS, ZGI). Quantities of Au were chemically determined by the method of atomic absorption spectrometry (AAS). Samples were analyzed on plasma II emission spectrometer Perkin Elmer 306.

Results

For the statistical data processing, STATISTIKA computer programme packet was used to calculate minimum, maximum, and average (arithmetical mean) quantities (Tab.1), distribution over Xi^2 test (Tab.2), and correlations between pairs of elements (Tab.3).

The distribution of the micro and macroelements it closely connected with the paragenetic - genetic characteristics of the minerals in deposit. Because of this it is important to determine the contents and distributions of Cu, Zn, Pb, Sb, Ag, Ni, Co, As, In, Ga, Tl and Au. Phases are separated on the basis of micro and macro - paragenetic relations of pyrite, sphalerite and other minerals, and on distribution of Co and Ni in the pyrite.

Table1.
Statistical results of macro and microelements contents in pyrite (%, ppm)

element	N	min.	max.	mean X
Ni	33	0.0001	0.0045	0.001
Co	25	0.0001	0.0055	0.0011
Cu	61	0.0012	1.0	0.0619
As	60	0.03	0.8	0.2429
Pb	61	0.0018	1.0	0.586
Sb	34	0.012	0.45	0.0748
Ag	61	0.0001	0.035	0.0049
Zn	61	0.015	1.0	0.7421
In	18	0.0004	0.002	0.001
Ga	30	0.001	0.004	0.0022
Tl	15	0.001	0.031	0.008
Au ppm,%	27	0.005ppm	0.0019%	0.0006

N - analyzed element; min.- lowest concentration; max.- highest concentration; X - average proportion (arithmetical mean)

The content of copper in pyrite ranges from 0.0012 up to >1%, with a mean of 0.0619% (for 61 samples). High zinc of 1% or more is a characteristic result of paragenetic intergrowth of pyrite and sphalerite. Lead is present in contents ranging from 0.001 to 1%, or >1%, and average content of 0.586%. Antimony varies from 0.012 to 0.45%. Silver concentration ranges from 0.0001 to 0.035%, or the arithmetical mean of 0.0049%. Detected in each assay (61).

Table 2.
Distribution over Xi^2 test

Element	Distribution		Element	Distribution	
	Xi^2	Xk^2		Xi^2	Xk^2
Ni	0.722	**5.55**	Ag	8.074	7.81
Co	3.876	**3.84**	Zn	31.38	4.88
Cu	39.1	5.99	In	-	-
As	1.531	**11.07**	Ga	4.03	**5.99**
Pb	13.5	11.07	Tl	-	-
Sb	-	-	Au	0.247	**3.84**

Xi^2 - square calculated value; Xk^2 - square (critical) value

Nickel and cobalt have a normal distribution in pyrite.(Tab. 2). Nical is contained within a range from 0.001 to 0.0045% (33 samples), or its arithmetical mean 0.001%. Cobalt is contained within a range from 0.0001 to 0.0055% (25 samples). Although these elements had normal distribution, participation of them are slightly. Arsenic also has a normal distribution. Arsenic is result of the arsenopyrite growth with pyrite, and detected in 60 samples, from 0.03 to 0.8%.

Indium, gallium and thallium are detected in some of samples. Thallium is contained within a range from 0.0001 to 0.031%, or average 0.008%. These pyrites have a relatively high content of Tl, and accompanies content of Ni. Such a dependence is result of association of these elements in low temperature phase formed pyrite. We can say that this pyrites are thallium-bearing phase. Gold is detected in each of the assayed samples within the range from 0.005ppm to 0.0019%, with an average value of 0.0006%. These pyrites have a relatively high content of Au, also. Gallium and gold have a normal distribution in deposit.

For geochemical relationships, pairs of the detected elements are correlated by the phases and summarily (phase I and II).The correlation between As, Cu, Pb, Ag, Zn and Sb is the result of paragenetic relationships in the deposit.

The very important correlation between Co and Ni (r_i 0.33; r_k 0.33 - 0.38) in total pyrite is positive, and he is reflection of pyrite later (II) phase. Following relation between Co and Ni by levels (Tab. 3), we can conclude that pyrites are formed on "higher" temperature (except levels 690m). However, the main mass of pyrites in earlier (I) phase is low temperature, particularly in later phase. Also, this relationship is not real, because of decreases content of Co and Ni.

Table 3.
Relationships of Co/Ni ratio by levels of pyrite

hor. (m)	N	Co/Ni	rk_i	rk_k
650	1	0.8		
670	5	0.13 - 2.0	0.27	0.75
690	17	0.3 - 13.0	**0.60**	0.45
700	3	0.21 - 1.7	-0.19	0.88
750	5	0.68 - 2.5	0.62	0.75

N - analyzed elements; Co/Ni - ratioCo/Ni; rk_i - calculated value; rk_k - critical value

Distribution by levels

The distribution of the content for the most important macro and microelements of pyrites is presented with their average content (X) in wt.%, and in the form of diagrams (Fig. 2, 3) for all levels (650 - 830m) in the deposit. On the basis of such a presentation it is possible to accompanies the content oscillation for the characteristic elements and their mutual relationship in a horizontal and vertical direction. The spatial distribution is closely connected with the content of different generations in different levels of the deposit.

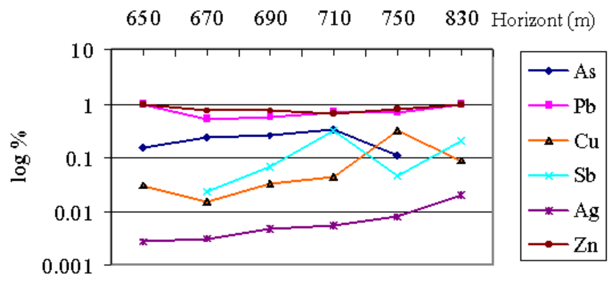

Fig. 2. Distribution of average As, Pb, Cu, Sb, Ag and Zn concentrations in pyrite by deposit levels

The best investigated are level 670 and 690 m, until results of level 650 and 830m are more informative. The content of elements (Fig.2) are result of paragenetic relationships on deposit. Silver, copper and antimony displays a decrease in concentration with depth, with the deviation on the highest levels. Lead and zink can be followed in levels of the deposit. For geochemistry of pyrites most important are contents of Ni, Co and Tl (Fig.3). The content of Ni decreases with depth and accompanies Co and Ga - except level 690m. The content of Tl have deviation in level 690m, with a maximum concentration in deposit.

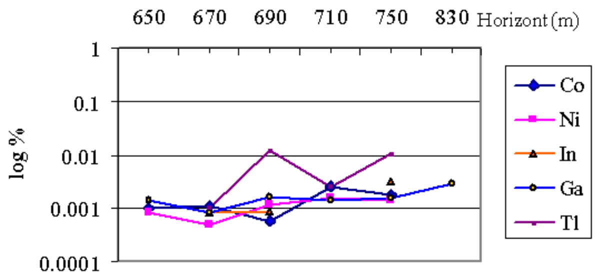

Fig. 3. Distribution of average Co, Ni, In, Ga and Tl concentrations in pyrite by deposit levels

Discussion

The following association of macro and microelements for pyrites is characteristic: Cu, As, Co, Ni and Au. These microelements are absorbed in the crystal lattice of pyrites. Other elements: Zn, Pb, Sb, etc. constitute mechanical impurities of mineral origin.

Besides the microelement concentrations, important data for the geochemistry of pyrite are the derivation of iron and sulphur - the principal elements in the mineral.

Hydrothermal fluids with iron circulated through the deposit, but the biggest amount of Fe was set apart at the same time, or before dark sphalerite was formed, when the earlier generation of sphalerite have crystallized. The third - younger generation of pyrites implicates that the low temperatures in some parts of deposit made impossible the formation of bigger amounts of brown and dark sphalerite. The reaming Fe was used to form younger pyrites. Arsenopyrite occurs on lowest level on the deposit. An isotope δS^{34} study in pyrite on level 670 and 690m (Dangic, Sudar et al., 1998) led to the conclusion that sulphur originated from continental crust (+6.02 +7.038‰). The variation interval (1.18‰) suggests the prevalence of homogeneous physical and chemical conditions with slight deviations within the tested levels.

The presence of arsenic in crystal lattice of pyrite is influenced by coalescence of arsenopyrite and pyrite. The high abundances of As are on the levels 670 and 710m. In earlier phase As had lower abundances than in the later, when it associates with Tl, In and Ga. At the later phases it is associated with Zn, Pb and Sb. Characteristic correlations of As with Co at some levels, suggest the higher temperature of formation. Cobalt and nickel are the very important elements for geochemistry of pyrite and are the best temperature indicators. Nickel (Ni^{2+}) and cobalt (Co^{2+}) have perfect diadochy replacement of Fe^{2+} in pyrite, because of their similar ionic radius and the same charge. Hydrothermal fluids were depleted of Co and Ni, because of their deficit in serpentinites, so the concentration of these elements was not possible.

Two phases of pyrite are distinguished by the ratio Co/Ni: high temperature, with predominant Co, and low temperature, in which the quantities of Ni are higher then in earlier phase. It can be possible to conclude that pyrites on the Pb - Zn deposit Kizevak have crystallized at "higher" temperature, except on the level 690m. Low content or deficit of Ni and Co, present all of them like low-temperature pyrites.

Studied pyrites are characterized by higher quantities of Au and Tl. We can say that these pyrites are gold-bearing, particularly at level 690m, at characteristically low-temperature condition. Thallium is also connected for low-temperature pyrites, respectively to later Ni-bearing phase. It is indicated by good Tl : Ni correlation.

Conclusions

Pyrite is the third dominant mineral after sphalerite and galena in the Kizevak lead-zinc deposit. It occurs in the form of crystals-pentagonal dodecahedron, coarse-grained aggregates, compact mass and fine grains, commonly in paragenesis with sphalerite, galena, chalcopyrite, sulphosalts and gangue minerals.

A high abundance of Tl, Au, extremely low abundances and proportions of Ni and Co characterize the analysed pyrites. On the basis of the micro and macro - paragenetic relationships, and the abundance of Co and Ni, two phases of pyrites are distinguished:

- Earlier phase (I), in which the proportions of As, Cu, Pb, Ag, Zn and Ga are under the average content for pyrite in general. The content of In at an average, content of Tl, Ni and Co are above the average.
- Later phase (II), in which the proportions of As, Pb, Co, In and Tl are under the average content. The highest content has Cu, Ag, Zn, Ni and Ga. This phase is characterized by maximum Tl content (0.031%). Also, correlation between Co and Ni is more expressed than at earlier phase.

The described geochemical relation in the deposit allows tracing the pattern of distribution between Co, Ni and Tl. The elements (Pb, Zn and Ag) had homogenous abundance, but Sb and Cu in higher level point to a deviation. The best accompanied Pb and Zn.

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