



Minor and trace elements in pyrite from Chiprovtsi deposit: comparison between Gnili Dol and Lukina Padina sections

Елементи-примеси и следи в пирит от находище Чипровци: сравнение между участъците Гнили дол и Лукина падина

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Introduction

The Chiprovtsi deposit is hosted in Cambrian–Middle Ordovician low-grade metamorphic rocks (marbles and schists) of the Diabase-Phyllitoid Complex (Berkovitsa group). The Pb-Ag metasomatic mineralization, which is of stratabound type and is hosted in calcite-siderite marble bodies, is considered to be of Carboniferous age (model Pb-Pb age 340–320 Ma, Amov et al., 1981) with still controversial source of fluids (Atanasov, Pavlov, 1983; Dragov et al., 1991). The present LA-ICP-MS study reports 38 analyses of 24 minor and trace elements in pyrite from the Gnili Dol and Lukina Padina sections of the mine. Pyrite is selected as the object of this study because it is an important gold-concentrator in various genetic types of mineral deposits, but also incorporates toxic elements, such as As, Sb, Hg, and Tl, that could be a serious environmental pollutants.

Materials and methods

The samples were collected from the Gnili Dol (555 and 642 levels) and Lukina Padina (606 level) sections of the Chiprovtsi mine. All the studied pyrite grains are examined by reflected light microscopy prior LA-ICP-MS and electron microprobe analysis to avoid discrete sulfide inclusions.

Minor and trace elements in pyrite were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on polished sections at the Geological Institute (Bulgarian Academy of Sciences), Sofia, Bulgaria. The analyses were performed using a NW UP193-FX excimer laser ablation system combined with PE ELAN DRC-e

ICP-MS at the following operating conditions: 35 μm laser beam size with 6 Hz repetition rate and 3.4 J/cm² energy density on the sample. The NIST SRM 610 and MASS 1 sulfide standard were used as external standards and were measured recurrently during the course of the analyses. Data reduction was done using an internal standardization (Fe content measured by electron microprobe SEM JEOL JSM-6010 PLUS at MGU “St. I. Rilski”) by SILLS v.1.1.0 software (Guillong et al., 2008).

Results and discussion

The trace elements concentrations in pyrite from the Gnili Dol and Lukina Padina sections are summarized in Table 1. In addition to the results presented in Table 1, concentrations of Mo (X = 2.7 ppm), V (X = 1.1 ppm), Te (X = 1 ppm), Cd (X = 0.96 ppm) and Bi (X = 0.3) were determined in Gnili Dol; and Mo (X = 6.1 ppm) and Cd (0.95 ppm) in Lukina Padina. The following elements were found below detection limit: Gnili Dol – Ga, Se, Pt; and Lukina Padina – V, Ga, Te, Sn, Bi and Pt. Pyrite from Lukina Padina is significantly enriched with Sb, Hg, Tl, As, Se, Ag and Pb, whereas pyrite from Gnili Dol contains Mn, Co, Ni, V, Sn, Te and Bi. Gold, Ti, Cr, Cu, Mo, Zn, Cd and In are found in pyrite from both sections.

We consider the presence of trace elements in pyrite as: 1) mineral inclusions or crosscuttings in depth represented by irregular and sudden fluctuations of signal of most commonly measured element isotopes, excluding As, Hg and Cr, in Gnili Dol (Fig. 1a); 2) incorporation in crystal structure via substitution

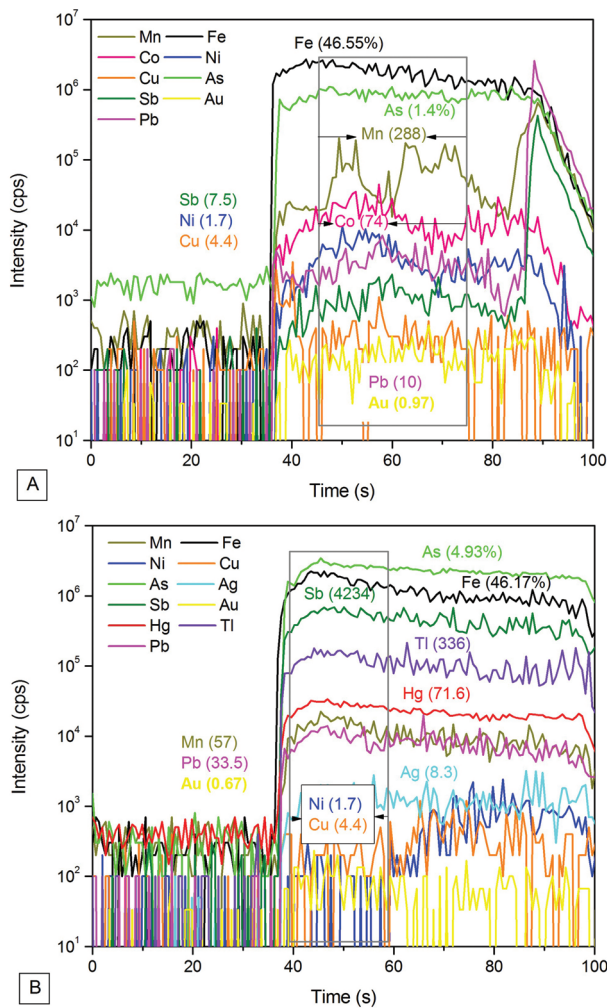


Fig. 1. Representative LA-ICP-MS depth spectra of pyrite from Gnili Dol (a) and Lukina Padina (b). Numbers in brackets are concentrations (in ppm, except otherwise cited)

for Fe and S or adsorption to growing crystal surfaces, evidenced by relatively flat LA-ICP-MS profiles for As, Sb, Tl, Hg, Mn, Pb, Cr, Se and rarely for Ag (Fig. 1b) in Lukina Padina. The Co and Ni intensity profiles in pyrites from both deposits suggest either change in chemical composition of the hydrothermal solution or presence of Co-Ni-bearing minerals. Predominant irregular signals for Cu and Au (Fig. 1a, b), as well as positive correlations Cu vs. Ag vs. Sb, Ag vs. Pb vs. Sb and Au vs. Ag suggest the presence of chalcopyrite, Cu-Ag-Sb- and Ag-Pb-Sb-bearing minerals, Ag-bearing galena and native gold inclusions. The incorporation of ‘invisible gold’ in solid solution is not excluded because of the positive correlation Au vs. As in Gnili Dol (with Pearson coefficient $R=0.57$) and negative correlations Fe vs. As vs. Au that support the couple substitution of type $2\text{Fe}^{2+} \leftrightarrow \text{Au}^+ + \text{As}^{3+}$ (Deditius et al., 2008) and/or adsorption.

Table 1. Statistic parameters of trace-element concentration in pyrite from Gnili Dol and Lukina Padina sections, Chiprovtsi Deposit

		Gnili Dol	Lukina Padina
Mn	N (W%)	24 (100)	14 (100)
	min-max	55.1–488	54.5–70.4
	X (V%)	102 (97)	61.5 (8)
Ti	N (W%)	24 (100)	14 (100)
	min-max	11.5–37.5	11.5–335 (incl.)
	X (V%)	23.7 (23)	49.1 (111)
Cr	N (W%)	24 (100)	14 (100)
	min-max	44.7–75.9	38.3–57.9
	X (V%)	53.5 (13)	46.6 (12)
As	N (W%)	24 (100)	14 (100)
	min-max	5503–18983	8521–65130
	X (V%)	11248 (32)	50134 (28)
Pb	N (W%)	24 (100)	14 (100)
	min-max	0.2–705 (incl.)	17.8–485
	X (V%)	56 (265)	200 (93)
Co	N (W%)	24 (96)	14 (79)
	min-max	1.4–177	0.6–35.2
	X (V%)	42.4 (112)	7.2 (143)
Ni	N (W%)	24 (92)	14 (86)
	min-max	2.2–302 (incl.)	1.5–46.4
	X (V%)	44.7 (149)	13.2 (113)
Sb	N (W%)	24 (83)	14 (100)
	min-max	0.7–17.2	224–10891
	X (V%)	6.5 (66)	5227 (55)
Cu	N (W%)	24 (79)	14 (100)
	min-max	2.3–25.7	2.6–67
	X (V%)	10.1 (67)	27.2 (92)
Ag	N (W%)	24 (79)	14 (100)
	min-max	0.1–2.9	0.4–336
	X (V%)	1.0 (93)	71.3 (141)
Au	N (W%)	24 (96)	14 (57)
	min-max	0.1–3.7 (incl.)	0.4–2.9 (incl.)
	X (V%)	1.4 (81)	1.3 (79)
Hg	N (W%)	24 (50)	14 (100)
	min-max	0.2–1.0	17.1–317
	X (V%)	0.4 (70)	134 (76)
In	N (W%)	24 (25)	14 (86)
	min-max	0.03–0.06	0.03–0.09
	X (V%)	0.05 (18)	0.05 (33)
Zn	N (W%)	24 (21)	14 (93)
	min-max	2.8–7.6	3.3–12.5
	X (V%)	4.9 (37)	7.5 (37)
Tl	N (W%)	24 (8)	14 (100)
	min-max	0.05–0.24	16.1–1169
	X (V%)	0.14 (92)	516 (73)
Se	N (W%)	24	14 (57)
	min-max	bdl	5.9–18.7
	X (V%)		13 (36)
Sn	N (W%)	24 (21)	14
	min-max	0.5–6.9	bdl
	X (V%)	2.3 (118)	

Note: N, analysis number; W, frequency of occurrence (in %); min-max, minimum and maximum values (in ppm); X, mean concentration (in ppm); V, coefficient of variation (in %); incl., inclusion; bdl, below detected limit

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