

LASER "RAMAN" SPECTROSCOPY AND LA-ICP-MS ANALYSIS OF COPPER-BEARING PYRITE AND SPHALERITE FROM GOLD-COPPER DEPOSIT CHELOPECH

Dimitar Petrov

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; dimitar@sitost.com

ABSTRACT. The presences of copper-bearing pyrite and sphalerite from the gold-copper deposit Chelopech are determined, by LA-ICP-MS analysis and μ -laser „Raman” spectroscopy. In polished sections of Western sector of the deposit, the quantitative LA-ICP-MS analysis are performed on zonal pyrite, which shows a varying contents of Cu, with values up to 37,000 ppm. Two types of zonal pyrite with idiomorphic octahedral and colloform texture are observed, in which the copper is a structurally bound and in the form of sub-microscopic inclusions of chalcopyrite. The studied sphalerite grain with a darker section also contains copper in the form of mineral inclusions of chalcopyrite.

Key words: „Raman” μ -spectroscopy, LA-ICP-MS analysis, element-impurities, ore minerals, Chelopech deposit

ЛАЗЕРНА „РАМАН” СПЕКТРОСКОПИЯ И LA-ICP-MS АНАЛИЗИ НА МЕД-СЪДЪРЖАЩИ ПИРИТ И СФАЛЕРИТ ОТ ЗЛАТНО-МЕДНО НАХОДИЩЕ ЧЕЛОПЕЧ

Димитър Петров

Минно-геоложки университет "Св. Иван Рилски", 1700 София, dimitar@sitost.com

РЕЗЮМЕ. Чрез използването на LA-ICP-MS анализ и μ -лазерна „Раман” спектроскопия е установено присъствието на мед-съдържащи пирит и сфалерит от златно-медно находище „Челопеч”. В полирани препарати от участък „Запад” на находището, са проведени количествени LA-ICP-MS анализи на зонален пирит, които показват различни съдържания на Cu със стойности до 37 000 ppm. Наблюдавани са два типа зонален пирит с идиоморфна октаедрична и коломорфна структура, в които медта е структурно свързана и под формата на субмикроскопични включения от халкопирит. Изучаваното сфалеритово зърно с по-тъмен участък, също съдържа мед под формата на минерални включения от халкопирит.

Ключови думи: „Раман” микро-спектроскопия, LA-ICP-MS анализ, елементи-включения, рудни минерали, находище Челопеч

Introduction

Pyrite is one of the main ore minerals in the main pyrite-chalcopyrite, enargite, and tennantite mineral associations in the gold-copper deposit Chelopech, which suppose relatively high correlation of Fe with the elements Cu, As, Sb, Au, Ag and Sn. Two types of zonal pyrite with idiomorphic octahedral and colloform texture in polished sections from the gold-copper deposit Chelopech are observed (Fig. 1).

The occasional presence of copper up to 10 wt. % in pyrite is reported by Frenzel and Ottemann (1967); Einaudi (1968); Pačevski et al. (2008) and Petrov et al. (2013). The authors are noted zoning, weak anisotropy, and variations in color and reflectivity in pyrite grains from epithermal Cu-Zn-Pb-Ag, Cu-Zn-Pb, Cu-Au-Ag-Zn-Pb and Au-Cu type of deposits.

Optically darker areas of sphalerite grains showed higher contents of Cu and Fe, analyzed by LA-ICP-MS. The presence of copper in sphalerite has been studied by several authors (Barton and Bethke, 1987; Kant et al., 2012), who reported for micron inclusions of chalcopyrite in the form of zones in Fe-bearing sphalerite.

The aim of the present study is to determine the form of presence of the Cu in pyrite and sphalerite in polished sections from the gold-copper deposit Chelopech - which originates from submicroscopic inclusions of Cu-minerals, and which is structurally bound copper. In addition to the microscopic and LA-ICP-MS analyses, for the implementation of the intended aim was conducted laser micro-Raman spectroscopy of the observed in polished sections two types of zonal pyrite and a copper-bearing sphalerite grains.

Materials and methods

Reflected light microscopy for establishing the optical and textural characteristics of ore minerals in 10 polished sections of ore bodies of block № 149 from sector "West" in the gold-copper deposit Chelopech is used.

In order to define the chemical composition and structural features of the most common minerals like pyrite and enargite, secondary chalcopyrite and sphalerite in the ore bodies of the recent study, LA-ICP-MS analysis and laser micro-Raman spectroscopy were applied.

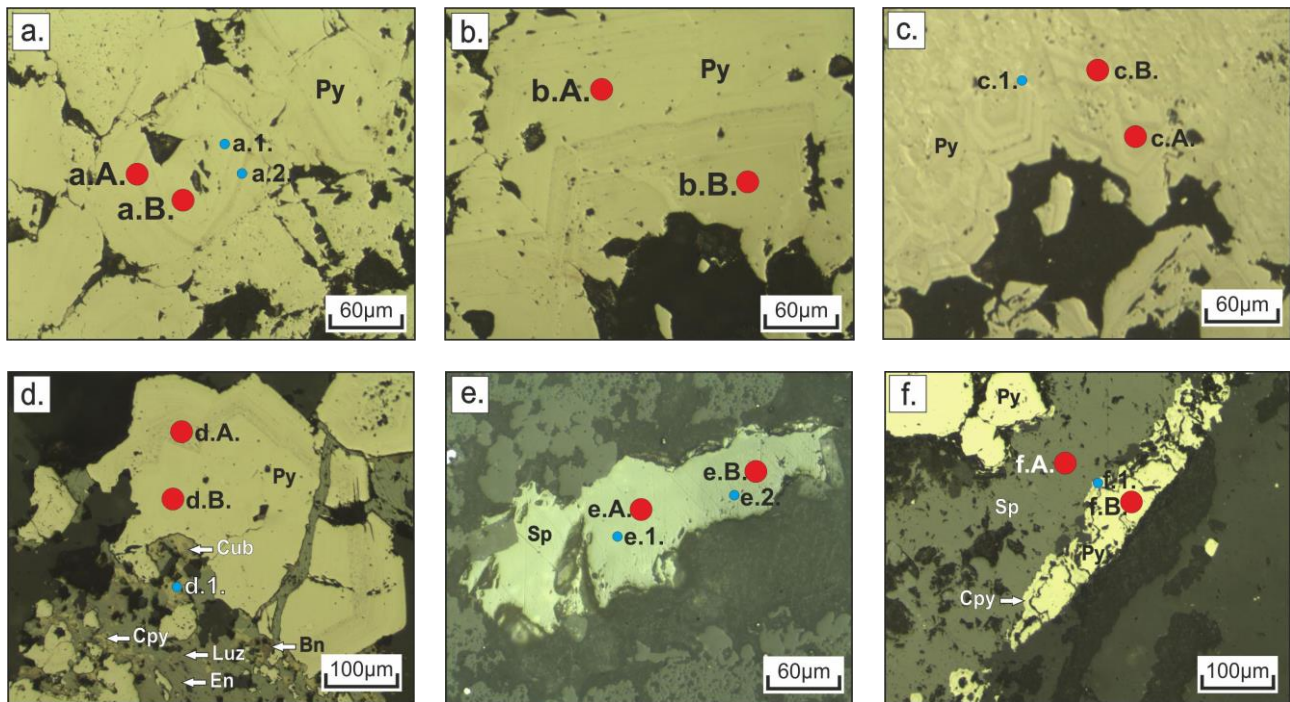


Fig. 1. Microphotos of ore minerals in polished sections from the Western sector of the gold-copper deposit Chelopech (reflected light):

a. - A zonal pyrite (Pyr) with narrow dark stripes and gangue minerals (black); b. - Massive pyrite, with alternating large dark and light areas, among gangue minerals (black); c. - A main mass of pyrite with octahedral dark and bright areas. Among the pyrite, brighter areas due to the admixing with chalcopyrite are observed; d. - Hypidiomorphic pyrite aggregate with alteration of dark and light areas of growth. The pyrite is cut by enargite (En). Nearby, a xenomorphic aggregates of chalcopyrite (Cpy), bornite (Bn), luzonite (Luz) and cubanite (Cub), among the main mass of enargite and single aggregates of pyrite are observed; e. - A sphalerite (Sp) mineral grain with a dark area, among gangue mineral mass; f. - A sphalerite among gangue matrix and a strip of colloform pyrite with darker bands of chalcopyrite.

Note: The positions of the LA-ICP-MS analyses are marked with a big point (for example – an. a.A. and a.B.), these of a micro-Raman analysis with a small point (for example – an. a.1. and a.2.).

Rare minerals bornite, luzonite and cubanite are also identified by reflected light microscopy and laser micro-Raman spectroscopy. Ore minerals in the observed polished sections are accompanied mainly by quartz, barite and kaolinite, rarely by dickite and apatite as gangue minerals.

Twelve LA-ICP-MS analyses in geochemical laboratory "Geochemistry and Petrology" at the Geological Institute of the Bulgarian Academy of Sciences are performed. The laboratory facilities include ELAN@DRC-e of Perkin Elmer with dynamic reaction cell-(DRC) and 193 nm excimer laser of New Wave Research UP193FX, at a frequency of pulsing of the laser beam of 10 Hz. External standards on glass SRM-610 from NIST is used. To transform data in absolute terms is used internal standard.

The content of the 29 elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ta, W, Re, Pt, Au, Hg, Pb and Bi) is analyzed in minerals pyrite (9 analyzes) and sphalerite (3 analyzes). Copper-bearing pyrite and sphalerite grains are selected, on which is carried out a μ -laser "Raman" spectroscopy at room temperature in the Laboratory of fluid inclusions of the University of Leoben (Austria). Raman spectra were obtained with a laser "Raman" micro-spectrometer Horiba Jobin-Yvon, laser with a nominal power of 100 mW and a wavelength of 532 nm. The "Raman" device includes a microscope Olympus BX60, camera CCD CV-252, connected to a monitor for direct observation, computer system and specialized software LabSpec. The data acquisition was performed by 5x5 seconds exposure and

added various filters (from D0.6 to D2), as spectra were recorded with a spectral resolution within 2 cm^{-1} .

Results and discussion

The presence of copper-bearing pyrite (up to 37 000 ppm) and sphalerite (up to 20 317 ppm) from the gold-copper deposit Chelopech, using LA-ICP-MS analysis are established (Table 1.).

Two types of pyrite can be distinguished - *type I*, with the idiomorphic octahedral texture, in which is clearly observed symmetrically alternating darker and brighter zones, measuring up to several tens of μm each, and *type II*, with a colloform shape, in which thin (about 1-2 μm) gray stripes, alternate with brighter zones of mineral grains (Fig. 1). The very small size of the stripes in pyrite of *type II* do not allow precise determination of trace elements by chemical analyses like microprobe and LA-ICP-MS analysis, but using a μ -laser "Raman" spectrometry would prove, that the differences in optical properties in stripes are due to different chemical composition. These differences are marked with the characteristic peaks of the Raman spectral waves, presented in Table 2 and Figure 2. It is assumed that the peaks at 341, 377 and 428 cm^{-1} mark the group of Fe-S, and that at 470 cm^{-1} of the Cu-S in the wavelength range of darker zones of pyrite *type I* (Fig. 1 a, an. Nea.2). The brighter zones of the same mineral grain show typical "Raman" spectra of „clear“ pyrite from the Chelopech deposit (Fig. 2, Table 2, an. Nea.1).

Table 1.
Contents of 29 elements in pyrite and sphalerite from the gold-copper deposit Chelopech, determined by LA-ICP-MS analysis (in ppm).

Analysis Elem./Min.	a.A. Pyrite	a.B. Pyrite	b.A. Pyrite	b.B. Pyrite	c.A. Pyrite	c.B. Pyrite	d.A. Pyrite	d.B. Pyrite	e.A. Sphalerite	e.B. Sphalerite	f.A. Sphalerite	f.B. Pyrite
Ti	14,25	17,14	795,32	4039,21	<12,19	19,25	<12,38	16,90	<6,25	17,78	9,37	50,03
V	<1,74	1,18	5,88	23,36	<2,08	<0,43361	16,03	2,31	1,30	<0,79	<0,61	6,09
Cr	63,37	56,15	47,04	49,38	63,33	42,35	47,03	56,85	<7,86	<6,69	<8,58	47,88
Mn	60,91	111,69	116,51	96,98	60,02	52,47	3738,05	305,17	11,18	1712,58	2,06	80,86
Fe	441600,00	441600,00	459900,00	459900,00	429500,00	429500,00	442700,00	442700,00	255,02	17106,65	183,99	465500,00
Co	10,41	2,18	205,28	305,75	3,72	15,91	0,60	2,05	<0,25	<0,28	<0,19	29,79
Ni	16,72	7,78	9,33	15,12	16,34	37,49	14,34	6,02	<1,89	10,30	<2,20	4,61
Cu	18762,05	3611,93	1150,39	11356,34	23248,21	37080,28	19197,72	8045,23	1723,13	20317,57	245,14	413,77
Zn	57,03	515,64	77,82	7,28	38,56	151,04	500,37	25,63	655200,00	655200,00	640600,00	334,12
Ga	<1,55	8,73	<1,54	1,62	<1,95	<0,43	6,90	3,83	17,38	74,61	15,51	2,25
Ge	49,32	46,36	56,02	54,29	59,96	51,06	52,11	58,66	388,08	22,93	5,15	62,17
As	299,22	1145,82	127,93	218,83	203,35	69,92	1071,87	302,85	868,66	<2,98	29,31	144,01
Se	129,92	135,15	178,99	70,83	98,98	428,54	56,14	128,00	9,87	9,69	23,77	<16,08
Mo	<2,02	<0,53	6,97	3,03	<1,79	<0,45	2,99	7,14	<1,10	<0,85	5,37	4,29
Pd	0,61	<0,14	<0,28	<0,14	<0,46	0,89	<0,41	<0,59	<0,18	0,47	<0,25	<0,24
Ag	21,15	27,94	4,48	4,09	7,98	37,94	36,42	6,46	36,83	14,35	14,48	10,74
Cd	<5,17	4,42	<3,97	<1,57	<6,61	<1,54	<4,98	<7,69	1945,45	3132,90	3619,84	<4,31
In	0,19	1,42	0,23	<0,07	0,54	0,61	2,39	<0,28561	27,77	1,95	<0,07	0,89
Sn	22,60	<0,59	<1,44	1,29	42,89	1,92	10,27	<1,75	5,45	15,90	2,00	6,08
Sb	42,90	2,52	7,31	7,51	47,47	5,32	73,84	6,93	3,34	1,30	33,94	2,93
Te	62,08	149,78	14,39	22,46	167,15	189,98	943,85	151,36	<7,00	<3,66	<3,05	29,53
Ta	<0,17	<0,05	<0,07	0,07	<0,14	<0,02	<0,11	<0,09	<0,10	<0,04	<0,038	<0,07
W	0,54	4,89	0,47	2,01	<0,86	0,30	0,81	<0,40	<0,26	<0,399	<0,17	<0,53
Re	<0,50	<0,18	<0,28	<0,11	<0,51	<0,07	<0,33	<0,47	<0,30	<0,15	<0,12	<0,21
Pt	<0,56	<0,21	<0,35	<0,14	<0,30	<0,13	0,41	<0,62	<0,28	<0,17	<0,18	<0,26
Au	0,59	1,55	0,76	1,35	0,57	0,90	2,25	0,68	2,42	<0,05	<0,04	<0,18
Hg	1,46	0,97	0,82	1,57	<0,75	0,37	<0,82	<1,19	71,91	63,32	108,93	<1,09
Pb	6484,39	11426,44	618,88	5192,87	1457,30	1018,25	3879,76	807,57	2229,48	84,38	58,90	614,99
Bi	64,74	36,56	70,74	78,28	46,30	82,21	47,67	20,96	<0,20	<0,15	<0,18	0,69

The results obtained below the detection limit of the particular element of a given analysis are marked with a sign "<".

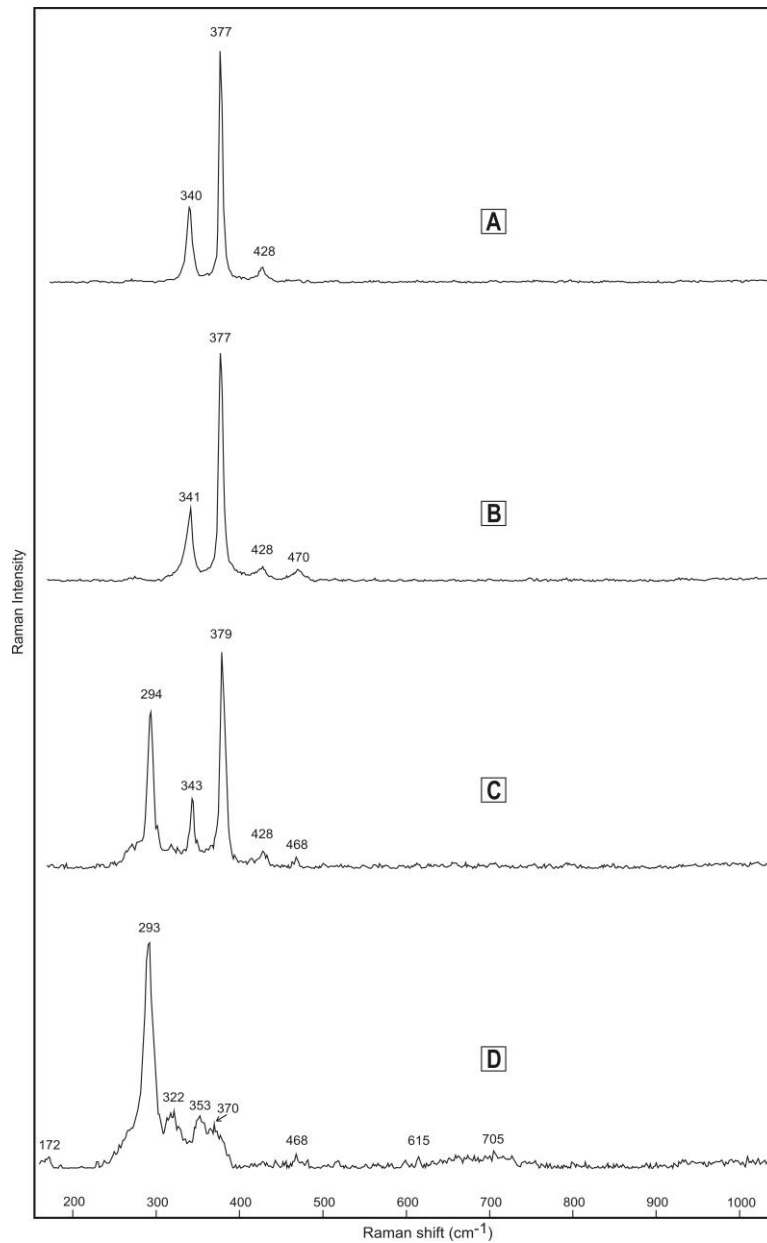


Fig. 2. "Raman" spectra of pyrite and chalcopyrite from the Chelopech deposit at 532 nm wave length (A. - pyrite, analysis №a.1; B. - pyrite, analysis №a.2; C. - pyrite + chalcopyrite, analysis №c.1; D. - chalcopyrite, analysis №d.1.). The locations of the analyzes are shown in Fig. 1.

Table 2.
"Raman" spectral wave's peaks of pyrite and chalcopyrite (cm⁻¹)

Pyrite (an. a.1.)	Pyrite (an. a.2.)	Pyrite+Chalcopyrite (an. c.1.)	Chalcopyrite (an. d.1.)
			172
		294	293
			322
340	341	343	353
377	377	379	370
428	428	428	
	470	468	468
			615
			705

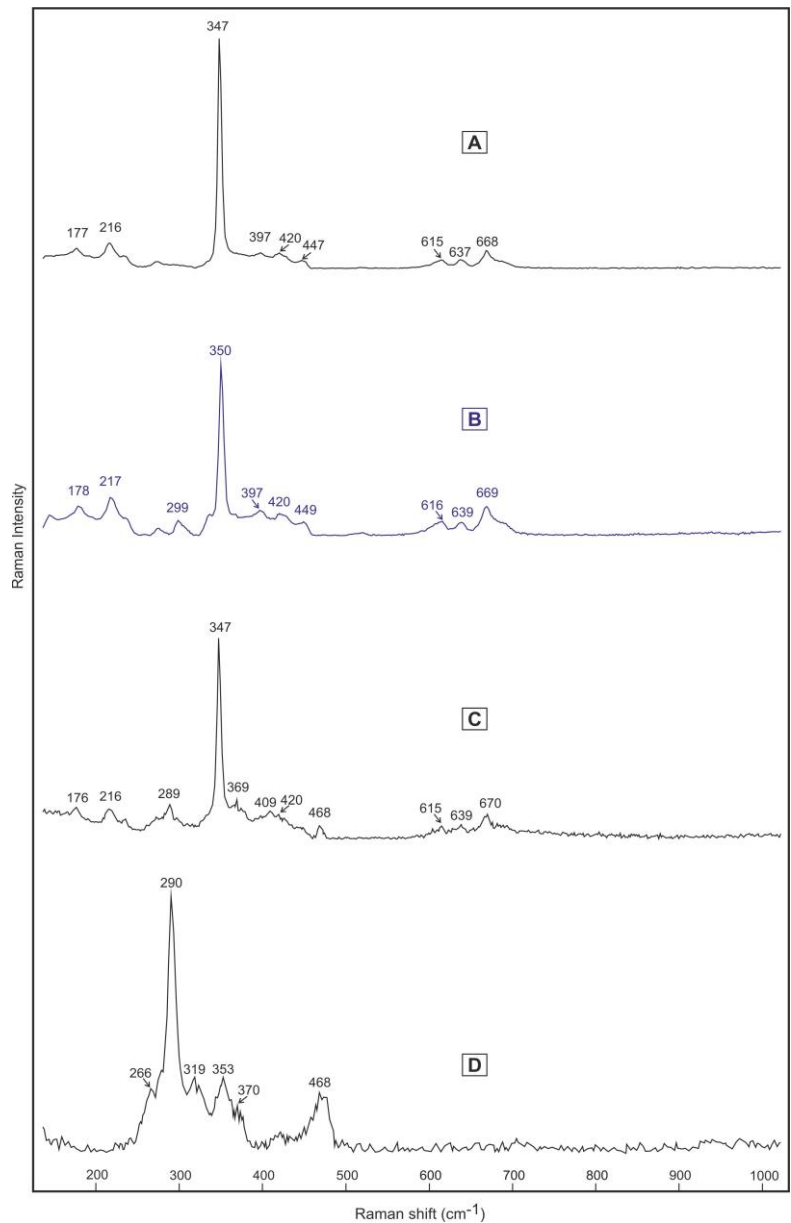


Fig. 3. "Raman" spectra of sphalerite and chalcopyrite from Chelopech deposit at 532 nm wave length (A. - sphalerite, the analysis №e.1.; B. - sphalerite, database RRUFF №050005, Taolin deposit, China; C. - sphalerite + chalcopyrite, analysis №e.2; D. - chalcopyrite, analysis № f.1).

Table 3.

"Raman" spectral waves peaks of sphalerite and chalcopyrite (cm^{-1})

Sphalerite (an. e.1.)	Sphalerite, RRUFF № R050005	Sphalerite+Chalcopyrite (an. e.2.)	Chalcopyrite (an. f.1.)
177	178	176	171
216	217	216	266
		289	290
	299		319
347	350	347	353
		369	370
397	397	409	
420	420	420	
		468	468
615	616	615	
637	639	639	
668	669	670	

The successful chemical and structural characteristics of samples in sizes less than 1 μm in diameter is possible by using μ -laser "Raman" spectrometry, which is the big advantage of spectroscopic methods, as well as the fast, easily and proper identification of minerals and ores. The comparison of Raman spectra of the colloform pyrite of *type II* and optically proved chalcopyrite (Fig. 1) indicate an accretion of chalcopyrite in the form of very thin grey stripes with the pyrite. The accretion of these two minerals is well marked by the peaks at 343 and 379 cm^{-1} - typical for pyrite and 294 and 468 cm^{-1} , for chalcopyrite (as submicroscopic inclusions) in the plotted "Raman" spectra, presented on Figure 2 and Table 2 (an. N \acute{e} c.1).

The conducted analyzes from the present studies and previous work (Petrov et al., 2013) indicate, that the zonal structure of the pyrite of *type I* has chemical nature and it is related to variations in the content of elements-impurities, presented mainly by Cu and in some cases of As, Te and Au. The presence of "invisible" gold in pyrite has been the subject of research of a number of authors (Cook and Chryssoulis, 1990; Fleet et al., 1993, Michel et al., 1994; Simon et al., 1999), according to which the gold spatially associate with enrichment of arsenic in pyrite and deficit of Fe. A straight correlation between As and Au is reported by Zacharias et al. (2004) in the study of As-bearing pyrite from the deposit "Rudni", Bohemian Massif.

LA-ICP-MS analysis of sphalerite shows presence of Cu in the range from 245 ppm to 20 317 ppm, as the higher content of Cu is related with higher quantity of Fe (up to 17 106 ppm) (Table 1, an. N \acute{e} c. B). The microscopic studies and the μ -laser "Raman" analysis shows intergrowth texture of sphalerite with an unoriented inclusions of chalcopyrite (the so-called "chalcopyrite disease"). Mineral inclusions of chalcopyrite have been widely recognized in sphalerite from most sulfide deposits, using ore microscopy (Barton and Bethke, 1987). The origin of these micro inclusions of chalcopyrite in sphalerite is not very clear. They have been attributed to exsolution or result of replacement of Fe-bearing sphalerite by an aggregate of chalcopyrite. Craig and Vaughan (1994) suggest that the temperature-dependent exsolution is not the means by which these intergrowths are formed.

Concluding remarks

The comparison of the results, obtained from the μ -Raman spectra and LA-ICP-MS analyses is indicated that the copper is a structurally bound in darker zones of the zonal pyrite with an octahedral habit, while a submicroscopic inclusions of chalcopyrite form the gray stripes in the colloform pyrite. The existence of mineral inclusions of chalcopyrite in the sphalerite, but not the presence of Cu as an element-impurity, is proved by the characteristic peaks at 289, 369 and 468 cm^{-1} of the wavelength spectrum of analysis N \acute{e} c.2. (Figure 3, Table 3).

The increased content of Cu in the sphalerite from the central parts of the ore bodies, the most probably is due to the "chalcopyrite disease", typical for the ore sectors with a high

degree of hydrothermal alteration in such type of epithermal deposits.

Acknowledgements. The author would like to thank to the Geological Department of "Dundee Precious Metals Chelopech" EAD for their support during the realization of this study. Special thanks to the Head of the Department of Mineral Resources at the University of Leoben Prof. Dr. Frank Melcher, and the Head of the Laboratory of fluid inclusions Prof. Dr. Ronald Bakker for comprehensive assistance during the research, related to this work.

References

- Barton, P., P. Bethke. Chalcopyrite disease in sphalerite: pathology and epidemiology. *Am. Mineral.*, 72, 1987. – 451-467.
- Cook, N., S. Chryssoulis. Concentrations of "invisible gold" in the common sulphides. *Canad. Mineral.*, 28, 1990. – 1-26.
- Craig, J., D. Vaughan. Ore Microscopy and Ore Petrography, (2nd Ed.). *John Wiley and Sons, New York*, 1994. – 434.
- Einaudi, M. Copper zoning in pyrite from Cerro de Pasco, Peru. *Am. Mineral.* 53, 1968. – 1748-1752.
- Fleet, M., S. Chryssoulis, J. MacLean, R. Davidson, C. Weisener. Arsenian pyrite from gold deposits: Au and As distribution 43 investigated by SIMS and EMP, and color staining and surface oxidation by XPS and LIMS. *Canad. Mineral.*, 31, 1993. – 1-17.
- Frenzel, G., J. Ottemann. Eine Sulfidparagenese mit kupferhaltigem Zonarpyrit von Nukundamu/Fiji. *Mineral. Deposita*, 1, 1967. – 307-316.
- Kant, W., W. Warmada, A. Idrus, L. Setijadji, K. Watanabe. Ore mineralogy and mineral chemistry of pyrite, galena, and sphalerite at Soripesa prospect area, Sumbawa Island, Indonesia. *J. SE Asian Appl. Geol.*, 4, 1, 2012. – 1-14.
- Michel, D., G. Giuliani, G. Olivo, O. Marini. As growth banding and the presence of Au in pyrites from the Santa Rita gold vein deposit hosted in Proterozoic metasediments, Goias state, Brazil. *Econ. Geol.*, 89, 1994. – 193-200.
- Pacevski A., E. Libowitzky, P. Zivkovic, R. Dimitrijevic, L. Cvetkovic. Copper-bearing pyrite from the Čoka Marin polymetallic deposit, Serbia; mineral inclusions or true solid-solution?. *Canad. Mineral.*, 46, 1, 2008. – 249-261.
- Petrov, D., S. Strashimirov, S. Stoykov, M. Karakusheva. New data for the mineral composition of ores in the western sector of the gold-copper Chelopech. *Ann. Univ. Min. Geol. "St. Iv. Rilski"*, 56, 1, 2013. 39-46.
- Simon, G., H. Huang, J. Penner-Hahn, S. Kesler, L-S. Kao. Oxidation state of gold and arsenic in gold-bearing arsenian pyrite. *Am. Mineral.*, 84, 1999. – 1071-1079.
- Zacharias, J., J. Fryda, B. Paterova, M. Mihaljevic. Arsenopyrite and As-bearing pyrite from Roudny deposit, Bohemian Massif. *Mineral. Mag.*, 68, 2004. – 31-46.

The article is reviewed by Assist. Prof. Sergey Dobrev and recommended for publication by the Department "Geology and Exploration of Mineral Resources".