TRACE-ELEMENTS IN SPHALERITE, PYRARGYRITE, PYRITE AND ARSENOPYRITE FROM SILVER-GOLD DEPOSIT SEDEFCHE, EASTERN RHODOPES

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ABSTRACT. Sedefche is an epithermal type Ag-Au deposit, part of the Zvezdel-Pcheloyad ore field in the Eastern Rhodopes. The ore mineralization is hosted in volcanic tuffs, affected by intensive hydrothermal alteration. The deposit is located near the ground surface, hence its upper parts are subject to supergene changes. The primary ore minerals are sulfides and sulfosalts. The supergene minerals are typically hydroxides, sulfates, carbonates and arsenates.
Samples from drill cores have been studied through optical microscopy, X-ray spectral micro-analyses and LA-ICP-MS in order to determine trace elements (particularly rare and precious), their content and distribution in various sulfide and sulfosalt minerals from deposit Sedefche.
The analyses established that Au and Ag content in pyrite is somewhat higher than in marcasite. Analysis of arsenopyrite showed that its gold content is the highest among all studied minerals – about 100 times higher than Au content in pyrite. Sphalerite contains significant amounts of Cd and some admixtures of Ga, In and Ag. The distribution of Ag and In in sphalerite is very irregular, while the Ga content is much more consistent. The quantity of Au in sphalerite is low. Pyrargyrite contains some admixtures of Au and more significant amounts of Tl and Se.

Key words: *trace elements, silver-gold deposit, sulfide minerals, sulfosalts, deposit Sedefche*

ЕЛЕМЕНТИ-ПРИМЕСИ В СФАЛЕРИТ, ПИРАРГИРИТ, ПИРИТ И АРСЕНОПИРИТ ОТ СРЕБЪРНО-ЗЛАТНОТО НАХОДИЩЕ СЕДЕФЧЕ, ИЗТОЧНИ РОДОПИ

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РЕЗЮМЕ. Седефче е епитермално Ag-Au находище, част от Звездел-Пчелоядското рудно поле в Източните Родопи. Рудната минерализация е вместена във вулкански туфи, засегнати от силни хидротермални промени. Находището се намира близо до земната повърхност и така горните му части са подложени на хипергенни промени. Първичните рудни минерали са сулфиди и сулфосоли. Хипергенните минерали са предимно хидроксиди, сулфати, карбонати и арсенати.
Проби от сондажни ядки са изследвани с оптичен микроскоп, рентгено-спектрални микроанализи и LA-ICP-MS, за да се определят елементите-примеси (в частност редки и благородни), тяхното съдържание и разпределение в разнообразни сулфидни и сулфосолни минерали от находище Седефче.
Анализите установяват, че съдържанията на Au и Ag в пирита са малко по-високи от тези в марказита. Анализът на арсенопирит показва, че съдържанието на Au в него е най-високо в сравнение с всички останали изследвани минерали – около 100 пъти по-високо отколкото в пирита. Сфалеритът съдържа значителни количества Cd и малко примеси от Ga, In и Ag. Разпределението на Ag и In в сфалерита е много неравномерно, докато съдържанието на Ga е по-постоянно. Количеството на Au в сфалерита е малко. Пираргиритът съдържа малко примеси от Au и по-значителни количества Tl и Se.

Ключови думи: *елементи-примеси, сребърно-златно находище, сулфидни минерали, сулфосоли, находище Седефче*

Introduction

Deposit Sedefche is located in the Eastern Rhodopes, 25 kilometers southeast of the town Momchilgrad, near the village Sedefche. Since 1963 it has been subject of prospecting and surveying and it was initially classified as "ore occurrence" (Atanasov et al., 1964; Atanasov, 1965). Ancient mining works, discovered during the modern geologic surveys confirm the presumption that silver was mined from the deposit since Early Middle Ages and possibly earlier (Tzekova, 1965; Cjiflidjanov, 1995).

Geological setting

Sedefche deposit is located in the southeastern foothills of Strumni Rid Peak, between the towns of Momchilgrad and Krumovgrad, within Kardzhali district. The deposit is part of the Zvezdel-Pcheloyad ore field in vicinity of Zvezdel paleo-volcano (Georgiev, 2012). The ore field is part of Momchilgrad ore sub-region, which coincides spatially with Momchilgrad depression. The following two structural complexes outcrop in the area of Sedefche deposit.

- Pre-Tertiary metamorphic complex – represented by biotite and two-mica gneiss, amphibolite-biotite gneiss, marble and kyanite-garnet-biotite schists.
- Tertiary volcanogenic-sedimentary cover consists of sedimentary, volcanogenic-sedimentary and volcanic rocks. They are spred uncomformly over the metamorphic rocks. Limestones and sandy-loam rocks are located above metamorhic rocks. Volcanic manifestations in Oligocene (*Pg_3*), formed acid to intermediate lava plains and dykes (rhyolite,

dacite, andesite). Geologic surveys outlined the following 3 ore bodies with not yet fully understood morphology.

- Northern ore body is located about 200 m north of Sedefche village. It is placed between silificated tuffs, tuff-breccia and andesite. The rocks are kaolinized, sericitized and pyritized. The North ore body is the most promising one for finding Au and Ag according to the results of geologic surveys.

- Southern ore body is located about 500 m west from Sedefche village. The South ore body consists of unevenly silificated limestones, which lie above sandy-loam sediments. Silification has affected the upper parts of the limestones with a thickness up to 6-7 m.

- Ralitza Dere is located in the ravine with the same name, about 300 m NNW from the North ore body. The largest outcrop of metamorphic rocks in the area is in that ravine. The ore body is emplaced within marble, which is heavily silificated. All volcanic rocks in the area, have undergone heavy hydrothermal alterations, such as, silification, sericitization, propylitization (Atanasov, 1965; Radonova, 1973).

Ore minerals

More than 20 ore minerals have been reported in Sedefche deposit (Mladenova, 1998; 1999; Strashimirov et al., 2005; Milev et al., 2007). The most widespread primary ore minerals in the deposit are:

- Sulphides – pyrite, arsenopyrite, sphalerite, acanthite, chalcopyrite and galena.

- Sulfosalts - tennantite-tetrahedrite, proustite, pyrargyrite, miargyrite and others.

The typical supergene ore minerals are: Fe-hydroxides, scorodite and jarosite.

Methods of study

Several polished sections have been prepared from drill core samples, taken from depth of 42 m (Sample 28). In the current study, analyses have been made in sections 28d, 28j and 28e (Fig. 1-6). These sections have been studied with optical reflected-light microscopes Meiji 9430 and Olympus BX60. Several areas and minerals have been designated for further studies by X-Ray microanalyses and LA-ICP-MS, in order to clarify the distribution and content of rare and trace elements and particularly gold.

X-Ray micro-analyses (*microprobe*), described in the current paper, have been carried out in Montanuniversitaet Leoben with the support by Prof. PhD Federica Zaccarini.LA-ICP-MS (*Laser Ablation – Inductively Coupled Plasma – Mass Spectroscopy*) studies have been carried out at the Geological Institute of the Bulgarian Academy of Sciences through device Perkin-Elmer SCIEX ELAN DRC-e and LA New Wave Research UP-193; λ=193 nm; laser Ar-F with the support by PhD Dimitrina Dimitrova.

Results of the study

Results from 33 microprobe analyses and 16 LA-ICP-MS analyses of primary sulfide and sulfosalt minerals are presented in this study. Microprobe studies include analyses of pyrite, arsenopyrite, sphalerite, pyrargyrite, miargyrite and stephanite. LA-ICP-MS include analyses of pyrite, sphalerite, arsenopyrite and pyrargyrite. Electron microscope photo-graphs show the location of microprobe point analyses (Fig. 1-6). LA-ICP-MS analyses correspond to the same points as these from microprobe. However, not all points of microprobe analyses have been subject to LA-ICP-MS analyses.

Sphalerite (ZnS): Microprobe analyses established that except the principal elements Zn and S in sphalerite, the mineral contains Fe too, which is not uncommon. Copper content is probably due to finely-dispersed chalcopyrite emulsion within sphalerite crystals, which was observed in some samples under reflected-light microscope. Cd is also present in the investigated sphalerite – its content according to microprobe analyses vary between 0.368 mass% (Table 2) and 0.462 mass % (Table 1). According to LA-ICP-MS analyses, the Cd content in sphalerite is about 2273.89 to 2779.28 ppm in samples 28d-5; p.6 (Table 8) and 28d-4; p.2 (Table 7).

LA-ICP-MS analyses in sphalerite have shown the following contents of precious and rare metals:

The Au content is low – from below 0.29091 ppm (sample 28d-5; p.6; Table 8) to below 0.36363 ppm (sample 28d-4; p.2; Table 7).

The investigated sphalerite also contains Ag. Its content varies from 135.20 ppm (sample 28d-4; p.2; Table 7) to as high as 1583.53 ppm (sample 28d-5; p.6; Table 8). Indium has also been discovered as a trace element in sphalerite, which is not uncommon for this mineral. Indium content varies between 4.54 ppm (sample 28d-4; p.2; Table 7) and 49.92 ppm (sample 28d-5; p.6; Table 8). Its distribution seems to be very uneven. These analyses also show the presence of Ga. Its content in sphalerite varies between 132.8 ppm (sample 28d-4; p.2; Table 7) and 135.51 ppm (sample 28d-5; p.6; Table 8). These values are quite persistent, even though only 2 analyses have been made.

Pyrargyrite (Ag_3SbS_3): The greater part of Ag-bearing sulfosalt minerals from deposit Sedefche, belong to the Sb-rich varieties. Still, microprobe and LA-ICP-MS analyses show that they contain small amounts of As as well, which is not uncommon.

There are As-rich sulfosalt minerals in the deposit, forming standalone phases, but they are much less common. LA- ICP-MS analyses of pyrargyrite (6 analyses) show that the mineral contains significant admixtures of Se, from 218,73 ppm (sample 28j-3; p.2; Table 9) to 908,78 ppm (sample 28d-5; p.1; Table 8).

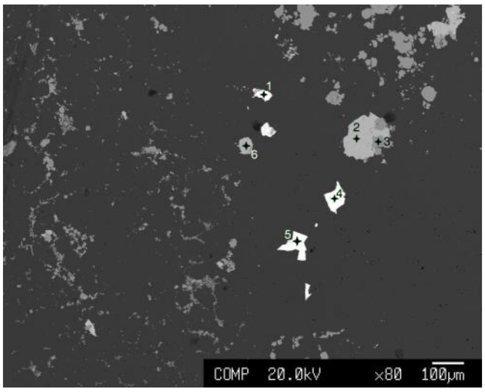

Fig. 1. Sample 28d, area 4. Electron microscope photograph and locations of microprobe point analyses. p.1 – pyrargyrite; p.2 – sphalerite; p.3 – pyrite; p.4-5 – myargyrite; p.6 – sphalerite

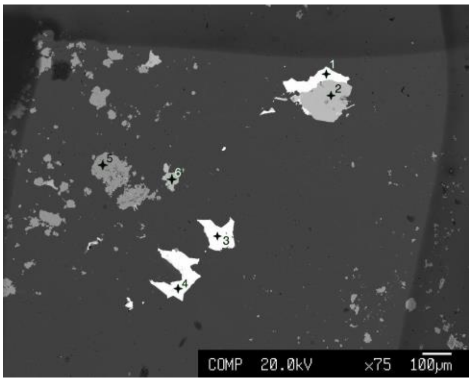

Fig. 2. Sample 28d, area 5. Electron microscope photograph and locations of microprobe point analyses. p.1 and p.4 – pyrargyrite; p.2 and p.6 – sphalerite; p.3 – myargyrite; p.5 – pyrite

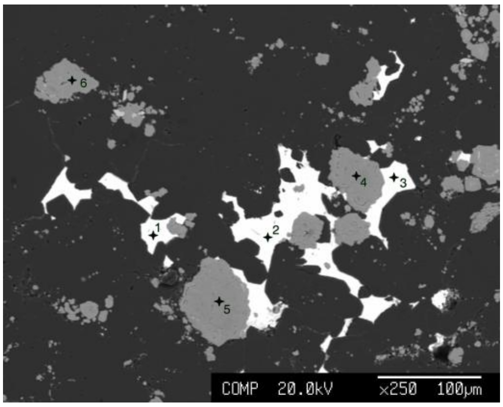

Fig. 3. Sample 28j, area 3. Electron microscope photograph and locations of microprobe point analyses. p.1-3 – pyrargyrite; p.3-6 – pyrite

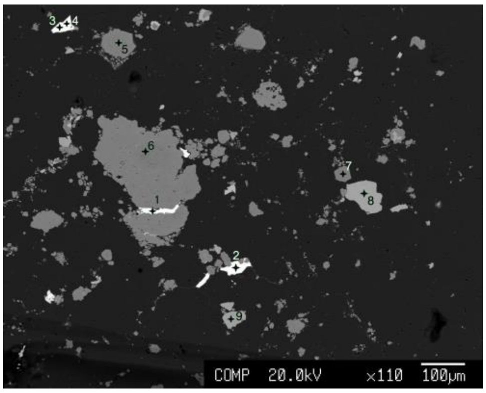

Fig. 4. Sample 28j, area 4. Electron microscope photograph and locations of microprobe point analyses. p.1, 2 and 4 – pyrargyrite; p.3 – stephanite; p.5 and 7 – pyrite; p.6 – marcasite; p.8 and 9 – sphalerite

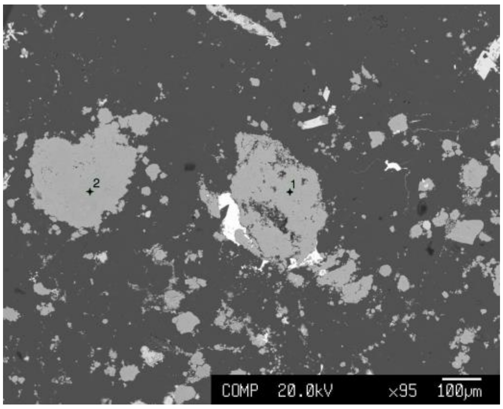

Fig. 5. Sample 28j, area 5. Electron microscope photograph and locations of microprobe point analyses. p. 1 and 2 – pyrite

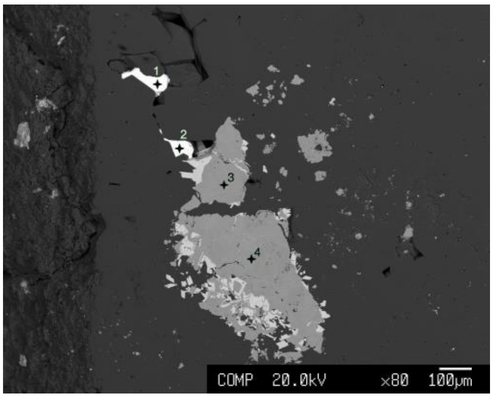

Fig. 6. Sample 28e, area 2. Electron microscope photograph and locations of microprobe point analyses. p. 1-2 – pyrargyrite; p. 3-4 – pyrite with intergrowths of arsenopyrite (brighter gray)

Table 1.
Results of microprobe point analyses in sample 28d, area 4

Sp. 28d-4	Composition in mass %									mineral
	As	S	Fe	Zn	Ag	Cu	Au	Cd	Sb	
P. 1	**0.348**	**17.756**	**0.015**	**0.025**	**64.391**	**0.013**	**0.048**	**-**	**21.154**	***pyrargyrite***
P. 2	**-**	**33.142**	**3.657**	**61.906**	**-**	**-**	**0.128**	**0.462**	**-**	***sphalerite***
P. 3	**0.632**	**53.281**	**46.384**	**0.624**	**0.105**	**0.028**	**0.042**	**0.007**	**0.037**	***pyrite***
P. 4	0.825	21.866	0.024	0.010	36.920	0.116	-	-	40.494	*miargyrite*
P. 5	0.549	21.764	0.029	-	38.832	0.032	-	-	38.523	*miargyrite*
P. 6	-	33.156	3.575	62.191	-	-	-	0.459	-	*sphalerite*

Table 2.
Results of microprobe point analyses in sample 28d, area 5

Sp. 28d-5	Composition in mass %									mineral
	As	S	Fe	Zn	Ag	Cu	Au	Cd	Sb	
P. 1	**0.332**	**17.906**	**0.022**	**0.126**	**61.326**	**0.114**	**-**	**0.013**	**21.719**	***pyrargyrite***
P. 2	0.064	32.757	3.933	60.963	0.064	0.283	-	0.408	0.475	*sphalerite*
P. 3	0.615	21.927	0.004	0.026	42.141	0.006	-	-	39.202	*miargyrite*
P. 4	2.870	17.380	0.001	-	65.558	0.264	-	-	16.730	*pyrargyrite*
P. 5	1.231	52.009	46.690	-	0.083	0.009	-	-	0.009	*pyrite*
P. 6	**0.021**	**32.534**	**3.370**	**61.926**	**-**	**0.024**	**0.059**	**0.368**	**0.040**	***sphalerite***

Table 3.
Results of microprobe point analyses in sample 28j, area 3

Sp. 28j-3	Composition in mass %									mineral
	As	S	Ag	Fe	Zn	Pb	Cu	Au	Sb	
P.1	0.167	17.695	61.210	0.100	0.055	-	0.084	0.041	21.199	*pyrargyrite*
P.2	**0.502**	**17.993**	**60.700**	**0.157**	**-**	**0.004**	**0.011**	**0.116**	**21.227**	***pyrargyrite***
P.3	**0.267**	**17.488**	**62.198**	**0.211**	**0.068**	**0.099**	**0.026**	**-**	**21.704**	***pyrargyrite***
P.4	0.611	52.201	-	46.977	0.013	-	-	-	-	*pyrite*
P.5	**0.802**	**52.238**	**0.018**	**46.812**	**-**	**0.074**	**0.023**	**-**	**0.018**	***pyrite***
P.6	1.775	51.412	0.112	45.019	0.044	0.153	0.057	-	0.687	*pyrite*

Table 4.
Results of microprobe point analyses in sample 28j, area 4

Sp. 28j-4	Composition in mass %									mineral
	As	S	Ag	Fe	Zn	Co	Cu	Au	Sb	
P. 1	**0.509**	**17.759**	**60.768**	**0.180**	**0.131**	**0.004**	**0.039**	**0.075**	**21.587**	***pyrargyrite***
P. 2	**1.163**	**17.924**	**60.636**	**0.799**	**-**	**0.015**	**-**	**0.048**	**16.612**	***pyrargyrite***
P. 3	0.215	13.417	70.701	0.138	0.116	-	2.974	-	7.949	*stephanite?*
P. 4	0.320	17.235	63.605	0.130	0.073	0.010	0.671	-	18.153	*pyrargyrite*
P. 5	4.641	46.565	0.065	46.045	0.021	0.091	0.035	-	0.295	*pyrite*
P. 6	0.350	51.264	0.011	46.475	-	0.092	0.009	-	-	*marcasite*
P. 7	1.150	51.438	0.209	45.544	0.039	0.073	0.009	-	0.176	*pyrite*
P. 8	0.013	33.438	0.110	5.207	59.937	0.005	0.485	-	0.144	*sphalerite*
P. 9	-	33.864	-	3.530	63.120	0.009	0.159	-	0.034	*sphalerite*

Table 5.
Results of microprobe point analyses in sample 28j, area 5

Sp. 28j-5	Composition in mass %										mineral
	As	S	Ag	Fe	Pb	Co	Cu	Au	Cd	Sb	
P. 1	**1,460**	**51,585**	**0,069**	**45,942**	**0,018**	**0,052**	**0,017**	**0,083**	**-**	**0,199**	***pyrite***
P. 2	**0,681**	**51,782**	**0,024**	**46,578**	**-**	**0,070**	**0,011**	**-**	**0,016**	**-**	***pyrite***

Table 6.
Results of microprobe point analyses in sample 28e, area 2

Sp. 28e-2	Composition in mass %									mineral
	As	S	Ag	Fe	Zn	Co	Au	Cd	Sb	
P. 1	0.238	18.174	58.504	-	0.026	-	0.041	-	22.321	*pyrargyrite*
P. 2	0.230	18.202	59.699	0.103	0.027	-	-	-	23.606	*pyrargyrite*
P. 3	**0.730**	**51.162**	**0.009**	**46.651**	**0.031**	**0.063**	**0.041**	**0.002**	**0.286**	***pyrite***
P. 4	**0.295**	**52.843**	**-**	**47.556**	**-**	**0.070**	**0.062**	**0.040**	**-**	***pyrite***

Pyrargyrite contains Au from <0.9 ppm (sample 28j-4; p.1; Table 10) to 4.37 ppm (sample 28d-4; p.1; Table 7). Some analyses of pyrargyrite show increased Tl content – from 3.52 ppm (sample 28j-4; p.1; Table 10) to 64.52 (sample 28j-3; p.3; Table 9).

Pyrite (FeS_2): Seven LA-ICP-MS analyses have been performed for pyrite. The Au content in pyrite, measured with LA-ICP-MS is highly variable - from 0.19 ppm (Sample 28e-2; p.4a; Table 12) to 4.54 ppm (28j-3; p.5; Table 9). Ag content in pyrite is between 38.87 ppm (Sample 28e-2; p.3; Table 12) and 902.83 ppm (Sample 28j-5; p.1; Table 11). The measured Tl content in pyrite is bewtween 6.9 (Sample 28e-2; p.4; Table 12) and 366.99 ppm (28j-5; p.1; Table 11).

Arsenopyrite (FeAsS): Only one LA-ICP-MS analysis of arsenopyrite was made, even though it is widespread mineral in deposit Sedefche.

Table 7.
Results of LA-ICP-MS point analyses in sample 28d, area 4

Element [ppm]	28d-4; p.1; (*pyrargyrite*)	28d-4; p.2; (*sphalerite*)	28d-4; p.3; (*pyrite*)
Cr	209.22	<24.8633	82.80
Mn	<5.5652	2916.89	1710.18
Fe	<429.5351	41052.38	*463840*[1]
Co	3.49	0.69	16.57
Cu	154.28	816.84	213.02
Zn	261.59	*619060*[2]	8475.86
Ga	<4.5144	**132.80**	<1.9762
As	9915.60	64.73	13362.54
Se	**745.17**	<27.8726	<35.9161
Ag	*643910.00*[2]	**135.20**	**576.90**
Cd	109.70	**2779.28**	22.18
In	<0.41117	**4.54**	0.33
Sn	<5.5317	231.95	9.04
Sb	337564.14	152.09	1096.86
Au	**4.37**	**<0.36363**	**0.99**
Tl	**18.57**	<0.49036	**110.80**
Pb	78.37	11.39	355.28
Bi	41.90	<0.24285	<0.44584

[1] - Internal standard of Fe content, according to data from X-ray spectral microanalysis.
[2] - Internal standard of Zn content, according to data from X-ray spectral microanalysis.

Table 8.
Results of LA-ICP-MS point analyses in sample 28d, area 5

Element [ppm]	28d-5; p.1; (*pyrargyrite*)	28d-5; p.6; (*sphalerite*)
Mn	<3.7807	2242.92
Fe	<381.2932	35047.97
Cu	406.43	2852.08
Zn	<90.8891	*619260*[1]
Ga	<3.6998	**135.51**
As	3412.76	507.59
Se	**908.78**	<28.1115
Ag	*613260*[2]	**1583.53**
Cd	<5.4247	**2273.89**
In	<0.32139	**49.92**
Sn	<3.9536	677.52
Sb	299083.58	2293.40
Au	**2.89**	**<0.29091**
Hg	3.89	41.92
Pb	<1.5207	85.74

[1] - Internal standard of Zn content, according to data from X-ray spectral microanalysys.
[2] - Internal standard of Ag content, according to data from X-ray spectral microanalysys.

The analysis show Au content of 308.43ppm and Ag content of 218.95 ppm (Sample 28e-2; p.3a; Table 12). No other trace elements of potential economic interest have been found in arsenopyrite.

Table 9.
Results of LA-ICP-MS point analyses in sample 28j, area 3

Element [ppm]	28j-3; p.2 (*pyrargyrite*)	28j-3; p.3 (*pyrargyrite + pyrite*)	28j-3; p.5 (*pyrite*)
Cr	232.91	305.37	78.14
Fe	<802.4041	31751.71	*468120*[1]
Cu	244.34	299.19	464.67
Zn	81.61	<99.9308	31.00
As	68649.11	93629.88	26697.93
Se	**218.73**	**710.09**	21.19
Ag	***607000.00***[2]	***621980.00***[2]	**612.44**
Sn	7.84	<15.1236	<1.4529
Sb	237486.68	245740.24	2001.50
Au	**<1.3605**	**<2.1636**	**4.54**
Tl	**7.85**	**64.52**	**202.55**
Pb	42.61	149.59	948.86

[1] - Internal standard of Fe content, according to data from X-ray spectral microanalysis.
[2] - Internal standard of Ag content, according to data from X-ray spectral microanalysis.

Table 10.
Results of LA-ICP-MS point analyses in sample 28j, area 4

Element [ppm]	28j-4; p.1; (*pyrargyrite*)	28j-4; p.2; (*pyrargyrite + pyrite*)
Fe	<536.1793	235604.39
Cu	323.91	656.93
As	1394.44	5387.49
Se	**748.25**	**551.13**
Ag[1]	*607680*	*606360*
Sb	329915.93	307424.45
Au	**<0.90426**	**3.30**
Tl	**3.52**	**33.42**
Pb	9.73	107.60
Bi	6.72	4.98

[1] - Internal standard of Ag content, according to data from X-ray specral microanalysis.

Table 11.
Results of LA-ICP-MS point analyses in sample 28j, area 5

Element [ppm]	28j-5; p.1; (*pyrite*)	28j-5; p.2; (*pyrite*)
Cr	55.34	51.27
Mn	214.09	1237.84
Fe[1]	*459420*	*465780*
Co	35.44	7.47
Ni	21.02	2.59
Cu	548.10	198.96
Zn	45.30	30.65
As	21118.03	11050.92
Mo	32.94	34.29
Ag	**902.83**	**327.58**
Sb	1649.10	720.67
Au	**4.47**	**2.10**
Tl	**366.99**	**334.44**
Pb	728.01	246.98

[1] - Internal standard of Fe content, according to data from X-ray spectral microanalysis.

Table 12.
Results of LA-ICP-MS point analyses in sample 28e, area 2

Element [ppm]	28e-2; p.3; (*pyrite*)	28e-2; p.3a; (*arsenopyrite*)	28e-2; p.4; (*pyrite*)	28e-2; p.4a; (*pyrite*)
Cr	46.80	42.60	46.61	46.25
Mn	79.47	45.76	103.98	102.44
Fe[8]	*466510*	*343000*	*475560*	*466510*
Cu	24.51	593.85	29.63	67.17
Zn	30.71	<32.0019	30.74	65.30
As	8682.11	423105.60	7754.23	8761.97
Se	<17.1133	68.93	<12.6481	<15.5031
Mo	64.46	<7.1774	40.24	44.71
Ag	**38.87**	**218.95**	**41.01**	**94.42**
Sb	3073.80	2899.36	1447.94	5893.80
Au	**0.24**	**308.43**	**0.37**	**0.19**
Tl	16.38	10.84	6.90	82.52
Pb	39.47	261.26	55.51	30.32

[8] - Internal standard of Fe content, according to data from X-ray spectral microanalysis.

Conclusions

The measured contents of precious metals (Au and Ag) in pyrite are somewhat higher than these in marcasite (Lyutov, 2016).

The single LA-ICP-MS analysis of arsenopyrite showed that it contains Ag and Au. The measured Au content in arsenopyrite (308.43 ppm) is about 100 times higher than these values in pyrite. Single analysis of arsenopyrite is not enough to establish a trustworthy model of Au distribution, but opens a new field for further studies. According to Fleet et al. (1997), high Au content (up to 3 wt%) in arsenopyrite, corresponds to excess of As and deficiency of Fe in the mineral's formula. Arsenopyrite analyzed in the current study does not exhibit such traits.

Except Cd, sphalerite contains admixtures of Ag, In and Ga. The distributions of Ag and In in sphalerite are very irregular, while the distribution of Ga is much more consistent. The measured Au content in sphalerite is low.

The gold content in pyrargyrite, measured in the current study (0.09-4.37 ppm) is about the same as Au content in pyrite. Pyrargyrite also hosts significant amounts of Se and Tl.

Acknowledgements. I would like to express my gratitude and highest esteem towards my advisor Prof. PhD Strashimir Strashimirov for the guidance he provided during preparation of my studies.
I would like to thank Prof. PhD Federica Zaccarini for her help and support for X-ray spectral microanalyses completed in Montanuniversity Leoben.

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The article is reviewed by Assoc. Prof. Stanislav Stoykov and recommended for publication by the Department "Geology and Exploration of Mineral Resources".