

TRACE-ELEMENTS IN COLLOMORPH MARCASITE AND CHALCOPYRITE FROM SILVER-GOLD DEPOSIT SEDEFICHE, EASTERN RHODOPES

Georgi Lyutov

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

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 and trenches have been studied through optical microscopy, X-ray spectral micro-analyses and LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectroscopy) in order to determine trace elements (particularly rare and precious), their content and distribution in colomorph marcasite and chalcopyrite from deposit Sedefche.

The studies that were carried out, established that the presence of Au in marcasite is relatively low and unevenly distributed. Silver is more abundant, but its content and distribution are even more variable than those of Au. The studies established that Au and Ag contents increase somewhat towards the cores of colomorph marcasite aggregates. Brighter concentric circles in the colomorph marcasite are due to admixtures of Sb and As. Marcasite also hosts significant amounts of Tl. Chalcopyrite exhibits very low Au content and some Ag with very erratic distribution. The only other trace element with somewhat higher content in chalcopyrite is Ni.

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

ЕЛЕМЕНТИ-ПРИМЕСИ В КОЛОМОРФЕН МАРКАЗИТ И ХАЛКОПИРИТ ОТ СРЕБЪРНО-ЗЛАТНОТО НАХОДИЩЕ СЕДЕФЧЕ, ИЗТОЧНИ РОДОПИ

Георги Лютов

Минно-геоложки университет „Св. Иван Рилски“, 1700 София; georgi_lyutov@yahoo.com

РЕЗЮМЕ. Седефче е епитермално Ag-Au находище, често от Звездел-Пчелоядското рудно поле в Източните Родопи. Рудната минерализация е вметена 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 хидроксида, сулфати, карбонати и арсенати.

Проби от сондажни ядки и канали 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 коломорфен марказит и халкопирит от находище Седефче.

При проведените изследванията се установява, че присъствието на Au в марказита е относително ниско и неравномерно разпределено. Среброто е в по-голямо количество, но неговото разпределение е още по-неравномерно от това на Au. При изследванията се установява, че съдържанията на Au и Ag се повишават в известна степен към центъра на коломорфните марказитови агрегати. По-ярките концентрични кръгове в коломорфния марказит се дължат на примеси от Sb и As. Марказитът съдържа и значителни количества от Tl. Халкопиритът демонстрира много ниско съдържание на Au и малко Ag с много неравномерно разпределение. Единственият елемент-примес с по-високо съдържание в халкопирита е Ni.

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

Introduction

Deposit Sedefche is located in the Eastern Rhodopes, 25 km southeast of the town Momchilgrad, near the village Sedefche. Silver was mined from deposit Sedefche in The Early Middle Ages and possibly earlier. Ancient mining works, discovered during the modern geologic surveys confirm this presumption (Tzekova, 1965; Ciflijanov, 1995; Dragiev and Dragieva, 2006). Since 1963 the deposit has been subject of prospecting and surveying and it was initially classified as "ore occurrence" (Atanasov, 1965; Atanasov and Breskovska, 1964).

Geological setting

The deposit is considered to be part of the Zvezdel-Pcheloyad ore field in the area of Zvezdel paleo-volcano (Georgiev, 2012). The ore field belongs to Momchilgrad ore sub-region, which coincides spatially with Momchilgrad depression. The depression covers an area of 1500 km², south of the river Arda, around towns Dzebel, Momchilgrad and Krumovgrad. Two structural complexes outcrop in the area of deposit Sedefche (Dragiev and Dragieva, 2006; Georgiev, 2012) (Fig. 1):

Pre-tertiary metamorphic complex – it consists of metamorphic rocks, represented by biotite and dual-mica

gneiss, amphibolite-biotite gneiss (aPt1), marble (cPt1) and kyanite-garnet-biotite schists.

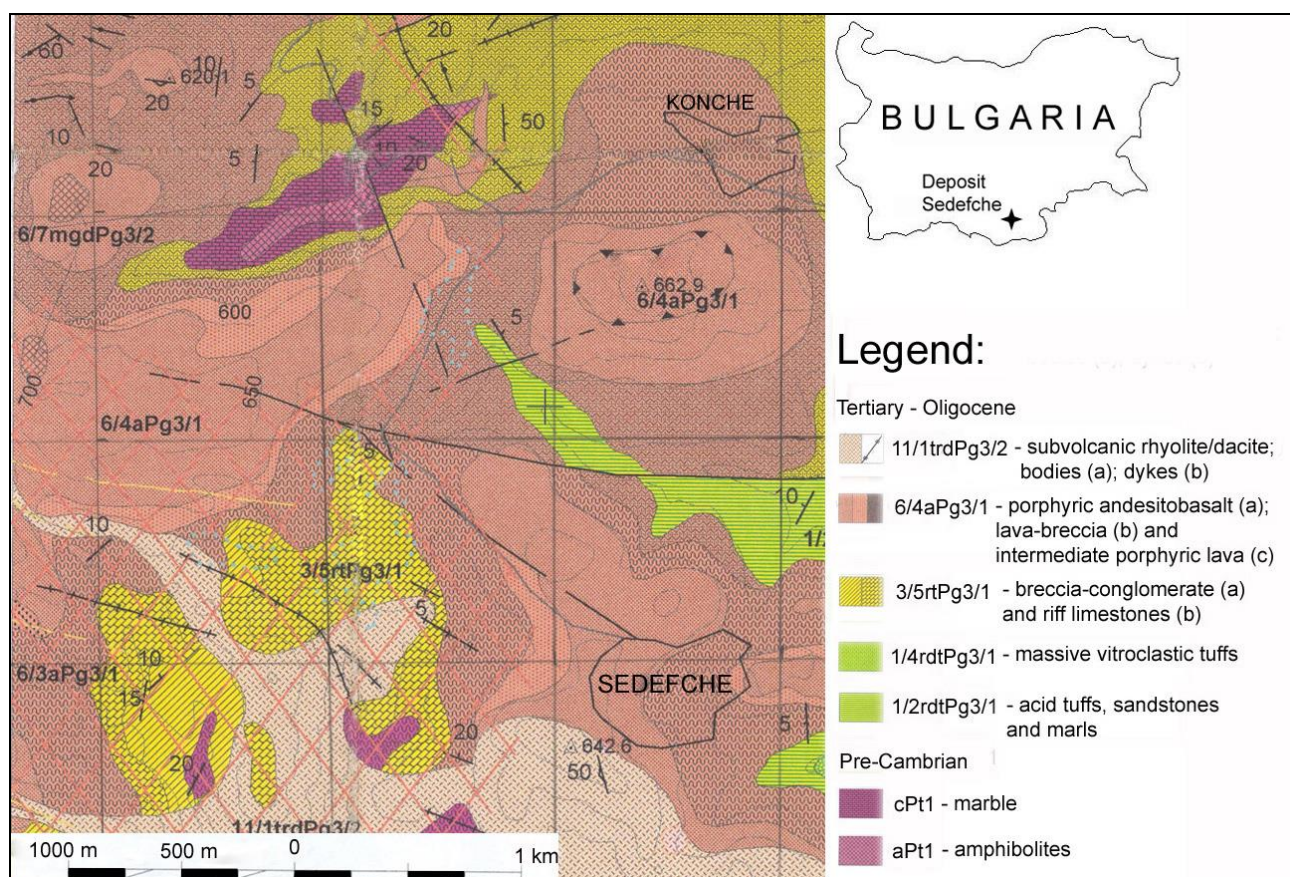


Fig. 1. Geologic map of deposit Sedefche and surrounding area (fragment, taken from Map Sheet K-35-88-B-a "Zvezdel"; Ministry of Environment and Waters; Scientific Investigations' Institute "Geology and Geophysics"; 1998).

Tertiary volcanogenic-sedimentary cover – it is represented by sedimentary, volcanogenic-sedimentary and volcanic rocks. Limestones (3/5rtPg3/1 - b) and sandy-loam rocks (3/5rtPg3/1 - a) cover unconformably the metamorphic rocks. In some areas, limestones have undergone silification, as a result of hydrothermal alterations. Volcanic manifestations in Oligocene (Pg₃), formed acid to intermediate lava plains and dykes of rhyolite, dacite and andesite (11/1trdPg3/2 a/b). Geologic surveys outlined 3 ore bodies in the deposit. Their morphology is defined by precious metal content and they do not have sharp boundaries: Northern ore body – it is located about 200 m to the north of the village Sedefche. It is placed between silificated tuffs, tuff-breccia and andesite (6/4aPg3/1 – a/b). The rocks are kaolinized, sericitized and pyritized. The contents of Au and Ag vary significantly. Evidence of ancient mining has been discovered in this area, which coincides with higher contents of Au and Ag. Southern ore body – it is located about 500 m westwards from the village Sedefche. The South ore body consists of unevenly silificated limestones (3/5rtPg3/1 - b), which lie above sandy-loam sediments (1/2rdtPg3/1). Silification has affected the upper parts of the limestones and is up to 6-7 m thick. Ralitz Dere is the third ore body, located in the ravine with the same name, about 300 m to the 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 (cPt1), which is heavily silificated. The North ore

body is the most promising one for finding Au and Ag according to the results of geologic surveys. Ore bodies in other deposits in the Zvezdel-Pcheloyad ore field, are vein-like, while these in the Sedefche deposit have layer-like, pseudo-conform shape (Georgiev, 2012). The volcanic rocks in the area, have been subjected to heavy hydrothermal alterations, such as, silification, sericitization, propylitization (Atanasov, 1965; Radonova, 1973). Silification is the most widespread – it affects limestones (3/5rtPg3/1 - b) in the Southern ore body, pyroclastic rocks, andesite (6/4aPg3/1 – a/b) in North ore body and marble (cPt1) in Ralitz Dere.

Ore minerals

More than 20 ore minerals have been reported in deposit Sedefche. The primary ore minerals are sulfides and sulfosalts. Supergene minerals are represented by oxides, hydroxydes, sulfates, carbonates and arsenates (Mladenova, 1998; 1999; Strashimirov et al., 2005; Milev et al., 2007). The most widespread primary ore minerals in the deposit are:

Pyrite – abundant ore mineral in the deposit, forming euhedral to semi-euhedral crystals. Later it has been partially turned into marcasite, which in turn exhibits anhedral and/or collomorphic structure.

Arsenopyrite – it is also very widespread ore mineral in the deposit, forming euhedral crystals with rhomboid or needle-like section.

Sphalerite – it is commonly encountered ore mineral in the deposit. It associates with other sulfides and exhibits semi-euhedral crystals.

Chalcopyrite – it has limited distribution and is encountered in isolated aggregates with other ore minerals. Sometimes it is seen as emulsion in sphalerite.

Galena – it is relatively rare mineral in the deposit – it appears as small isolated semi-euhedral crystals.

Tennantite-tetrahedrite – it has significant distribution in the deposit. Its composition is usually closer to the Sb-rich variety – tetrahedrite. It is silver-bearing and also contains admixtures of Fe and Zn.

Acanthite – it is one of the most important silver-bearing minerals in the deposit. It forms mostly isolated anhedral aggregates.

Ag-sulfosalts – (*proustite, pyrargyrite, miargyrite and others*) – many minerals of this group contribute to the overall silver content in the deposit.

The typical supergene ore minerals are the following:

Fe-hydroxides – goethite and lepidocrocite – they are widespread and common product of supergene alteration of Fe-rich sulfide minerals.

Scorodite – it is product of oxidation of arsenopyrite and As-rich sulfosalts.

Jarosite – it is common weathering product of iron sulfides and potassium-rich minerals in volcanic tuff host rocks.

Methods of study

Polished sections have been prepared from drill core samples, taken from depth of 42 m (Sample 28) and trenches (Sample 60). They have been studied with optical reflected-light microscopes Meiji 9430 and Olympus BX60. As a result, 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; $\lambda=193$ nm; laser Ar-F with the support by PhD Dimitrina Dimitrova.

Results of the study

Results from 18 microprobe analyses (Tables 1, 3, 5, 7) and 16 LA-ICP-MS analyses (Tables 2, 4, 6, 8) of marcasite and chalcopyrite are presented in this study. Electron microscope photographs show the location of microprobe point analyses. 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.

Marcasite (FeS₂): The collomorph marcasite aggregates have distinctive concentric-zonal structure, which is clearly visible on Fig 2 and Fig. 3.

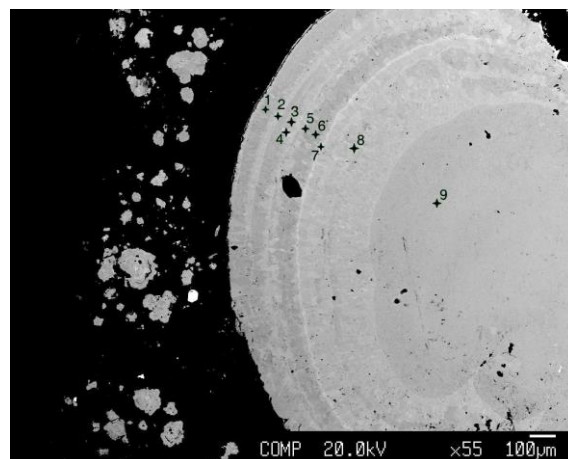


Fig. 2. Sample 28d, area 1. Electron microscope photograph and locations of microprobe point analyses in collomorph marcasite aggregate.

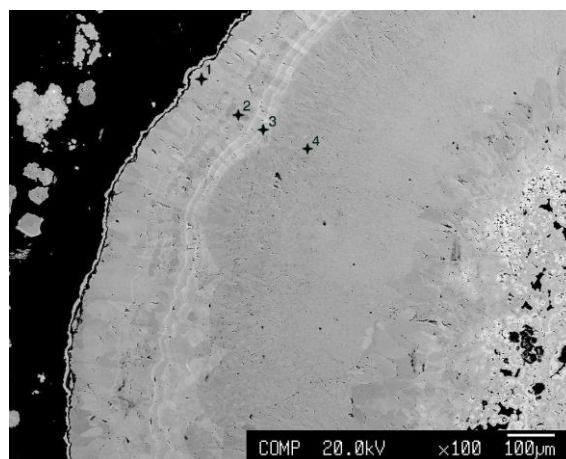


Fig. 3. Sample 28d, area 2. Electron microscope photograph and locations of microprobe point analyses in collomorph marcasite aggregate.

Microprobe analyses of marcasite show that the composition varies little from the mineral's stoichiometry. Nevertheless, admixtures of some other elements have been discovered in small quantities, around the detection limit of the microprobe (Tables 1 and 3), hence they are not very accurate. LA-ICP-MS analyses in the same areas have given more accurate results about these trace elements and their content (Tables 2 and 4). Rare and precious metals are of particular interest, such as Au and Ag. According the LA-ICP-MS analyses, Au content in marcasite varies from less than 0.092031 ppm (Sample 28d-2; p.1; Table 4) to 0.19 ppm (Sample 28d-2; p.2; Table 4).

Table 1.

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

Sp. 28d-1	Composition in mass %										mineral
	As	S	Fe	Zn	Ag	Co	Cu	Au	Cd	Sb	
P. 1	0.325	53.486	47.325	0.025	0.031	0.062	-	-	-	-	marcasite
P. 2	0.813	52.086	46.997	-	0.052	0.042	0.022	0.068	-	0.162	marcasite
P. 3	0.373	53.482	47.568	-	-	0.068	-	-	-	0.044	marcasite
P. 4	0.383	53.295	47.440	-	-	0.072	-	-	0.032	0.018	marcasite
P. 5	0.860	52.529	47.248	0.001	-	0.072	0.022	0.014	0.011	0.117	marcasite
P. 6	0.078	52.241	47.844	0.002	-	0.081	0.002	0.014	-	-	marcasite
P. 7	0.639	53.112	47.025	0.025	0.020	0.067	0.005	0.062	0.048	0.703	marcasite
P. 8	0.383	53.368	47.500	0.024	-	0.083	-	-	0.024	0.045	marcasite
P. 9	0.240	53.390	47.697	0.036	0.011	0.071	0.019	0.007	-	0.046	marcasite

Table 2.

Results of LA-ICP-MS point analyses in sample 28d, area 1

Element [ppm]	28d-1; p.1; (marcasite)	28d-1; p.2; (marcasite)	28d-1; p.6; (marcasite)	28d-1; p.7; (marcasite)	28d-1; p.8; (marcasite)	28d-1; p.9; (marcasite)
Cr	41.92	46.45	52.33	46.60	48.44	51.59
Mn	174.11	193.40	411.02	75.72	86.58	289.34
Fe ¹	473250.00	469970.00	478440.00	470250.00	475000.00	476970.00
Co	0.75	0.65	<0.29079	20.33	0.27	<0.2925
Cu	33.11	62.36	5.88	15.65	26.29	41.99
Zn	47.03	98.33	18.47	70.70	91.83	80.18
As	4487.03	5038.97	983.36	6746.74	4067.45	1713.93
Mo	58.84	66.16	4.63	65.29	55.85	30.56
Ag	29.40	43.29	16.34	12.92	33.16	64.17
Sb	602.46	791.02	67.79	4799.97	698.24	164.21
Au	<0.13055	<0.15955	0.14	<0.12389	<0.13584	<0.15838
Tl	146.82	158.09	8.14	49.94	13.38	11.66

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

Table 3.

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

Sp. 28d-2	Composition in mass %										mineral
	As	S	Fe	Zn	Ag	Co	Cu	Au	Cd	Sb	
P. 1	0.547	52.961	47.662	0.035	0.036	0.073	0.016	0.068	-	0.017	marcasite
P. 2	0.237	53.033	47.915	0.012	-	0.072	-	0.007	0.019	-	marcasite
P. 3	0.991	52.738	46.700	-	0.029	0.124	-	-	-	0.742	marcasite
P. 4	0.239	53.116	47.705	0.013	0.016	0.042	0.002	-	0.014	-	marcasite

Table 4.

Results of LA-ICP-MS point analyses in sample 28d, area 2

Element [ppm]	28d-2; p.1; (marcasite)	28d-2; p.2; (marcasite)	28d-2; p.3; (marcasite)	28d-2; p.4; (marcasite)
Ti	15.44	16.01	15.08	16.56
Cr	53.58	46.32	48.55	44.78
Mn	236.73	184.51	204.85	127.00
Fe ²	476620.00	479150.00	467000.00	477050.00
Cu	15.40	53.98	26.58	71.66
Zn	106.96	85.87	90.53	96.84
As	6642.91	6034.56	1658.92	2618.32
Mo	76.45	47.16	22.61	61.59
Ag	11.59	72.63	48.56	118.87
Sb	827.70	2466.19	133.35	202.77
Au	<0.092031	0.19	<0.14191	<0.12209
Tl	138.45	17.60	7.22	16.35

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

Silver content in marcasite varies from 11.59 ppm (Sample 28d-2; p.1; Table 4) to 118.87 ppm (Sample 28d-2; p.4; Table 4). The presence of TI in marcasite is also noteworthy. Its content varies from 7.22 ppm (Sample 28d-2; p.3; Table 4) to 158.09 ppm (Sample 28d-1; p.2; Table 2). It appears that Au and Ag contents in marcasite increase somewhat towards the cores of collomorph aggregates, but this may be just a coincidence. The microprobe and LA-ICP-MS analyses have discovered that the brighter rings in marcasite have increased content of Sb and As.

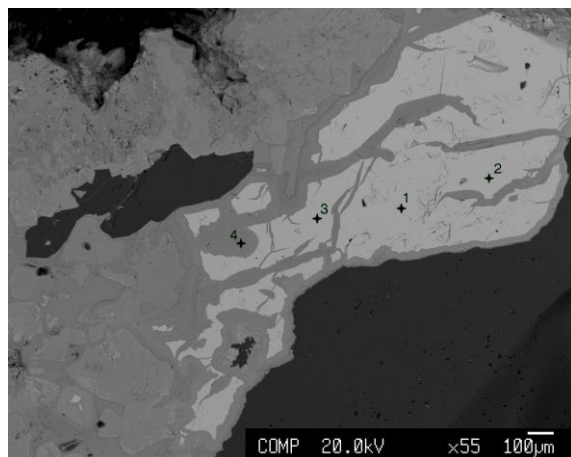


Fig. 4. Sample 60a, area 1. Electron microscope photograph and locations of microprobe point analyses. p.1-3 chalcopyrite; p.4 – supergene halo of Fe-hydroxides and malachite.

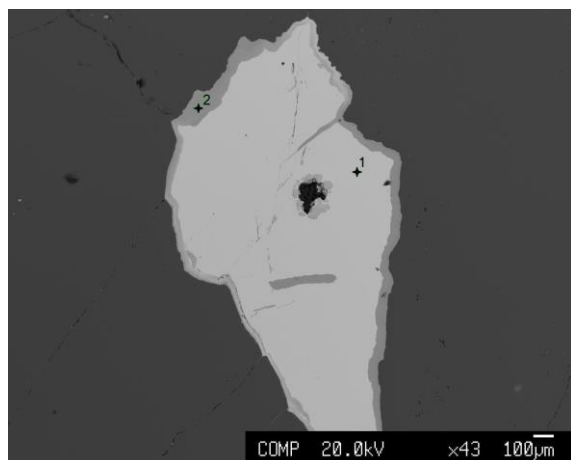


Fig. 5. Sample 60a, area 2. Electron microscope photograph and locations of microprobe point analyses. p.1 chalcopyrite; p.2 – supergene halo of Fe-hydroxides and malachite.

The analyses show that Au content in chalcopyrite is very low – from <0.129 to <0.165 ppm (Tables 6 and 8), which is near the lower detection limit of LA-ICP-MS device. Investigated chalcopyrite has some Ag content, with erratic distribution – from 0.54 to 107.09 ppm (Tables 6 and 8). The only other trace element with somewhat higher content in chalcopyrite is Ni – from 186.62 to 209.8 ppm.

Chalcopyrite (CuFeS_2): Six LA-ICP-MS analyses of chalcopyrite have been performed as part of the current study. Chalcopyrite is among the less abundant minerals in deposit Sedefche. The samples used in the current study are taken from trenches in Ralitz Dere, near the ground surface. They are affected by partial supergene alteration and chalcopyrite aggregates have noticeable rim of secondary minerals (Fig. 4 and Fig. 5).

Conclusions

The results for the Au content in marcasite, show that its distribution is relatively uneven (values vary by factor of about 2). This is probably caused by its presence as miniature nanoparticles (inclusions), within the crystal lattice of marcasite. The distribution of Ag is even more variable (values vary by factor of about 10). Fleet et al. (1997), conclude that invisible gold in marcasite represents Au removed from ore fluids by chemical absorption at As-rich, Fe-deficient surfaces and incorporated in the solids in metastable solid solution.

It is possible that Au and Ag contents increase towards the cores of collomorph marcasite aggregates, but the low number of measurements are not enough to be conclusive. The Au content in marcasite is low – near the lower detection limit of the LA-ICP-MS device. Still the Ag content in marcasite is notably higher in the very cores of the investigated marcasite aggregates. The distribution of TI follows pattern opposite of that of Ag – TI content is higher near the rim and lower in the cores of collomorph marcasite (Tables 2 and 4). Chalcopyrite exhibits very low Au content and somewhat increased content of Ag and Ni.

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Table 5.

Results of microprobe point analyses in sample 60a, area 1

Sp. 60a-1	Composition in mass %									mineral
	As	S	Ag	Fe	Zn	Co	Cu	Au	Sb	
P. 1	0.018	34.394	0.035	30.933	0.009	0.023	34.507	0.085	0.015	chalcopyrite
P. 2	0.043	34.263	-	31.143	0.029	0.049	34.535	0.023	-	chalcopyrite
P. 3	0.057	34.186	0.100	31.137	0.014	0.046	34.648	0.062	-	chalcopyrite

Table 6.
Results of LA-ICP-MS point analyses in sample 60a-1, area 1

Element [ppm]	60a-1; p.1; (chalcopyrite)	60a-1; p.2; (chalcopyrite)	60a-1; p.3; (chalcopyrite)
Ti	20.31	18.72	24.10
Cr	37.87	29.54	34.71
Mn	36.59	34.90	37.42
Fe	301577.92	302022.27	305272.40
Ni	186.62	203.65	192.40

Element [ppm]	60a-1; p.1; (chalcopyrite)	60a-1; p.2; (chalcopyrite)	60a-1; p.3; (chalcopyrite)
Cu ³	345070	345350	346480
Zn	835.36	887.99	62.97
Ga	3.92	4.58	3.23
Ag	0.54	1.93	0.89
Cd	4.59	4.32	<2.0833
Au	<0.12981	<0.16554	<0.15209

³ - Internal standard of Cu content, according to data from X-ray spectral microanalysis.

Table 7.
Results of microprobe point analyses in sample 60a, area 2

Sp. 60a-2	Composition in mass %									mineral
	As	S	Ag	Fe	Zn	Co	Cu	Au	Cd	
P. 1	-	34.568	-	31.130	0.057	0.047	34.587	0.054	0.032	chalcopyrite
P. 2	0.069	0.100	0.029	37.321	3.131	0.044	10.750	-	0.038	Fe-hydroxides and malachite

Table 8.
Results of LA-ICP-MS point analyses in sample 60a-1, area 2

Element [ppm]	60a-2; p.1; (chalcopyrite)	60a-2; p.1a; (chalcopyrite)	60a-2; p.1b; (chalcopyrite)
Ti	21.53	20.23	24.07
Cr	26.71	24.43	30.61
Mn	35.18	35.09	34.69
Fe	292499.17	291886.34	291152.16
Ni	209.80	200.17	188.18
Cu ⁴	345870	345870	345870
Zn	1132.41	672.40	1157.58
Ga	2.84	1.60	1.53
Ag	107.09	69.73	111.64
Sn	1.43	1.11	<1.2843
Sb	0.43	<0.53605	<0.52461
Au	<0.14869	<0.15882	<0.15004

⁴ - Internal standard of Cu content, according to data from X-ray spectral microanalysis.

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