

SILVER-BEARING MINERALS FROM THE ORE BODY “NORTH” IN SEDEFICHE EPITHERMAL Au-Ag DEPOSIT (EASTERN RHODOPE)

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ABSTRACT. The paper discusses the features of the ore mineralisation of the ore body “North” of Au-Ag epithermal deposit Sedefche, Zvezdel-Pcheloiad ore field, Eastern Rhodopes. Special attention is drawn to the form of Ag presence and its behaviour during the experimental tests for mineral processing of ores. Pyrrargyrite and miargyrite are found as the main Ag-bearing minerals in ores, andorite and acantite are rarely observed, and preliminary data are obtained for plagiogonite (?) presence. Arsenian pyrite containing Ag as a trace element (0.15 wt. %) is established as well. Phase analyses of ore probe (75 kg) is performed and distribution of Ag during the hydrometallurgical processing and its extracting through flotation process has been done.

СРЕБРОСЪДЪРЖАЩИ МИНЕРАЛИ ОТ СЕВЕРНО РУДНО ТЯЛО НА Ag-Au ЕПИТЕРМАЛНО НАХОДИЩЕ СЕДЕФЧЕ (ИЗТОЧНИ РОДОПИ)

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РЕЗЮМЕ. Разгледани са особеностите на рудната минерализация в Северно рудно тяло на златно-сребърното епитермално находище Седефче, Звездел-Пчелоядско рудно поле в Източните Родопи, като е обърнато особено внимание на формата на присъствие и поведението на носителите на сребро по време на експериментални тестове за обогатимост на рудата. Като главни самостоятелни фази носители на сребро са установени минералите пираргирит, миаргирит, както и по-рядко срещаните се андорит и акантит. Получени са предварителни данни за наличието на плагиогонит (?). Установено е присъствие на арсенсъдържащ пирит (As до 7 тегл.%) с примеси от сребро (до 0.15 тегл.%). Направен е фазов анализ на проба (75 кг) от рудата и е установено фазовото разпределение на сребро в процесите на хидрометалургична обработка, както и извлекаемостта му по време на флотация в получения концентрат.

Introduction

Silver is one of the two main elements in the Sedefche epithermal Au-Ag deposit and investigations about its form of presence and behaviour during the mineral processing is very important for the economics of the deposit.

The recent study is focused on the ore body “North” – one of the three parts of the deposit, which is the most promising for future exploitation. Mineralogical studies are combined with pilot experimental tests of the ore to trace the future mineral processing operations for better extracting gold and silver from the economic mineralisation.

Geological setting

Sedefche is a typical representative of the epithermal low sulphidation Au-Ag deposits, which the last years are intensively explored at the Eastern Rhodopes (Dimitrov et al., 1996). The deposit is located in the SE part of the Pb-Zn Zvezdel-Pcheloiad ore field about 3 km east from the main polymetallic ore bodies and very close to the north-northwestern parts of the Sedefche village. The geological setting of the area of the deposit is determined by presence of two structural complexes – a basement, set up by metamorphic rocks and tertiary complex, including sedimentary, volcanogenic-sedimentary, volcanic and intrusive rocks lying discordantly over and crosscutting the basement.

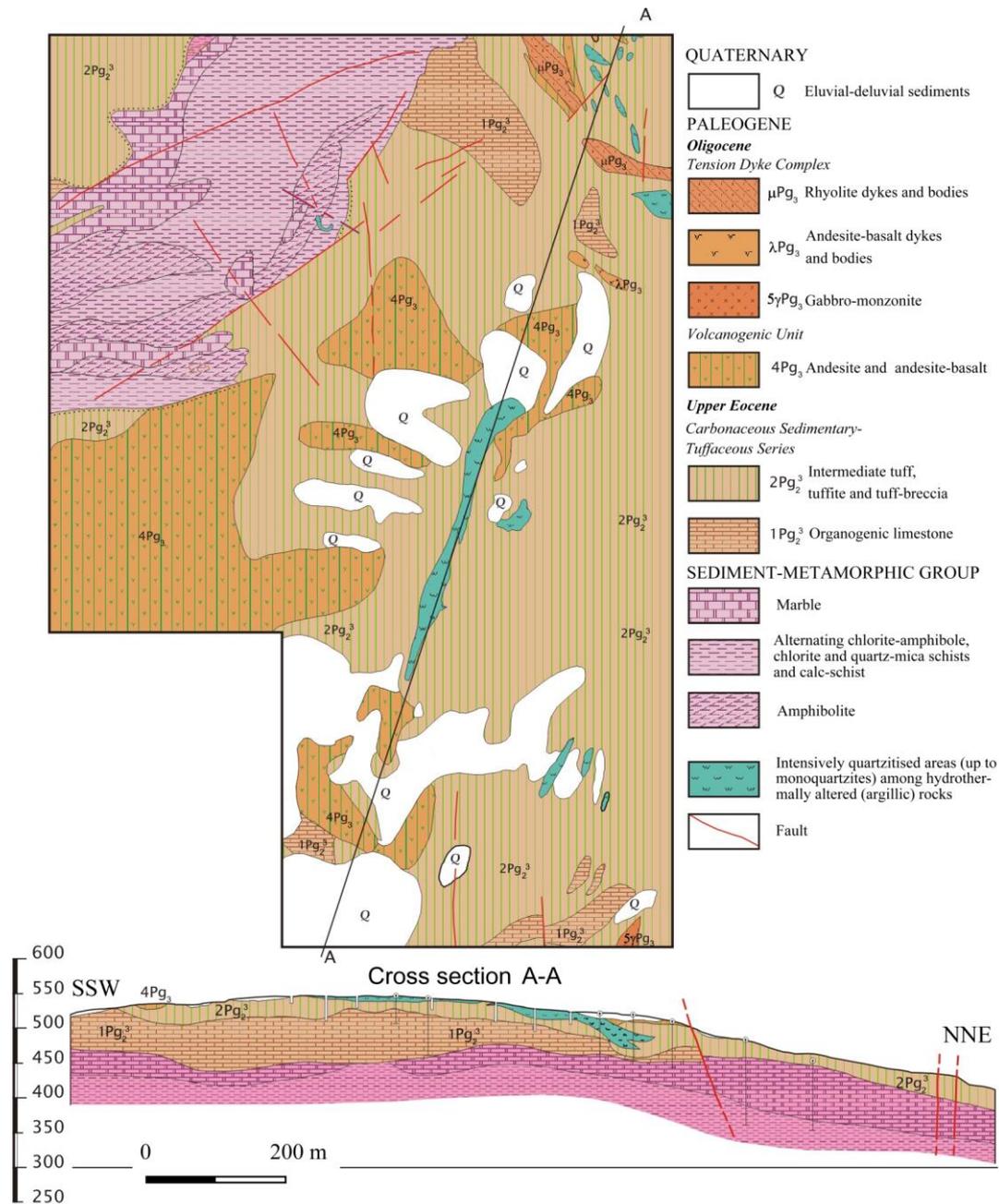


Fig. 1. Geological map of the Sedefche deposit (ore body "North")

The deposit includes two ore bodies – "North" and "South" and ore occurrence "Ralitza dere". The first ore body is located several hundred meters north from the village of Sedefche and it is developed as elongated in N-NE direction strip (400 x 60 m) in intensively hydrothermally altered (intensively quartzitised up to monoquartzites, sericitised, argilised and pyritised) pyroclastites and andesites. The basement includes marble, amphibolite, alternating chlorite, chlorite-amphibole and quartz-mica schists and calc-schist (Fig. 1). Paleogene rocks include carbonaceous-sedimentary-tuffaceous series of Upper Eocene age (organogenic limestones and intermediate tuff, tuffites and tuff-breccias). Oligocene tension dyke complex is presented by gabbro-monzonite, andesite-basalt bodies and rhyolite bodies and dykes covered by Quaternary eluvial-deluvial sediments.

The ore body "South" is located west from the village Sedefche and it is elongated in N-S direction. The mineralisation here is developed in the silica cap over limestones and

clay-sandy sediments. Ore occurrence "Ralitza dere" is found in the metamorphic basement (intensively quartzitised marbles) 300 m to the north from the "North" ore body.

Material and methods

Materials for the recent study are collected during the sampling of the pilot open pit developed at the central part of the ore body "North" close to the ancient mining works. Polished sections are prepared from 30 samples for ore mineralogy and fluid inclusion studies. One probe of 75 kg for experimental laboratory mineral processing of ore provides products, from which cemented briquettes were produced to determine the behaviour of ore minerals during the processes of beneficiation.

Technological experimental tests for beneficiation of the ore include laboratory flotation and hydrometallurgical treatment. Additional processing of technological products are realised by extracting a "heavy fraction" from the flotation concentrate using bromoform (CHBr₃) and jigging the waste product to increase the quantity of ore minerals in it.

Analytical works include phase analysis, quantitative ICP-AAS analyses, quantitative and qualitative microprobe analyses, all of them realised in the laboratories of "Eurotest-Control" Plc., Sofia.

Mineral composition of the ore mineralisation

Mineral composition of the deposit as a part of the Zvezdel-Pcheloid ore field is discussed by Atanasov and Breskovska (1964), Breskovska et al. (1990) and Mladenova (1989). The first two papers cover mainly the features of sulphosalts found in the ore field while the last one includes detailed study of mineral composition and ore forming processes in it. Additional data for mineral composition of the deposit and the problem of gold presence and distribution in ore are provided by Mladenova (1998). According the last mentioned publication 17 ore minerals and mineral species are found in composition of pyrrhotite-arsenopyrite (pyrrhotite, arsenopyrite I), sulphide (pyrite I, marcasite I, sphalerite, galena, chalcopryrite, tetrahedrite and freibergite), sulphosalt (ramdorite, fizelyite,

owyheeite, freieslebenite, diaforite, myargirite, pyrrargirite, arsenopyrite II, pyrite II and marcasite II) and stibnite (stibnite and native As) parageneses.

The recent study of the ore body "North" establishes as the main minerals for this part of the deposit pyrite, arsenopyrite, marcasite and stibnite and rarely found sphalerite, chalcopryrite, galena and scorodite (?). Ag-bearing minerals include pyrrargirite, myargirite, andorite, acanthite and pligionite (?).

Pyrite is one of the most frequently found minerals in the samples. It is observed as irregular shaped aggregates usually intensively affected by marcasitisation (Fig. 2, Plate 1), as fine veinlets setup by semi-euhedral and xenomorphic grains also in association with marcasite (Fig. 2, Plate 2), or as a very fine (20 – 50 µm) dissemination of globular grains (Fig 2, Plates 3 and 4). During the observations in reflected light microscope it is found pyrite aggregates with anomalous optical properties manifesting lower reflectivity, light-grey to yellow colour and slight anisotropy (Fig. 2, Plate 5). Further quantitative microprobe analyses established that this variety is characterised with high (up to 6 – 7 wt. %) content of As (Table 1). According the classification of Chvileva et. al. (1988) this type of pyrite could be nominated as arsenian pyrite as the increasing of As over 3 wt. % caused increasing of the parameter a_0 of the unit cell up to 5.453 Å. This variety of pyrite is typical for the relatively low temperature mineral associations as it is in this case. Ag and Cu are also found in chemical composition of arsenian pyrite (Table 1).

Table 1. Chemical composition of minerals from the ore body "North", Sedefche deposit by microprobe analyses

Analysis No	Mineral	Elements [wt. %]									Total
		S	Ag	Sb	Fe	Cu	As	Zn	Pb	Te	
1	pyrrargirite	17.21	58.17	23.03	0.31	0.14	0.28	0.0	0.0	0.73	99.87
2	pyrrargirite	17.47	58.52	23.62		0.88					100.49
3	pyrrargirite	17.40	58.28	23.67		0.57					99.92
4	miargirite	34.37	20.96	43.29	0.24	0.69	0.23	0.0	0.0	0.0	99.78
5	miargirite	21.17	34.34	42.54		1.02	0.64				99.71
6	andorite	23.86	10.08	43.66	0.0	0.98	0.0	0.0	21.31	0.0	99.88
7	acanthite	12.19	87.40								99.59
8	acanthite	13.24	86.51								99.75
9	pligionite (?)	23.45	1.92	28.89		1.15			37.79		99.46
10	arsenian pyrite	49.59	0.15	0.0	42.87	0.71	6.82	0.0	0.0	0.0	100.14
11	arsenian pyrite	50.91			44.98	0.71	3.07				99.67
12	arsenian pyrite	52.00			46.67	0.46	0.93				100.06

Analysis No	Mineral	Formula:
1	pyrrargirite	(Ag _{2.94} Cu _{0.01} Fe _{0.03}) _{2.98} (Sb _{1.03} As _{0.02}) _{1.05} (S _{2.93} Te _{0.03}) _{2.96}
2	pyrrargirite	(Ag _{2.91} Cu _{0.08}) _{2.99} Sb _{1.04} S _{2.97}
3	pyrrargirite	(Ag _{2.93} Cu _{0.05}) _{2.98} Sb _{1.05} S _{2.95}
4	miargirite	(Ag _{0.95} Cu _{0.03} Fe _{0.01}) _{0.99} (Sb _{1.06} As _{0.01}) _{1.07} S _{1.94}
5	miargirite	(Ag _{0.94} Cu _{0.05}) _{0.99} (Sb _{1.03} As _{0.03}) _{1.06} S _{1.95}
6	andorite	(Ag _{0.78} Cu _{0.13}) _{0.91} Pb _{0.86} Sb _{3.01} S _{6.23}
7	acanthite	Ag _{2.04} S _{0.97}
8	acanthite	Ag _{1.98} S _{1.02}
9	pligionite (?)	(Pb _{4.63} Ag _{0.95} Cu _{0.44}) _{6.02} (Sb _{5.72} As _{0.62}) _{6.34} S _{17.62}
10	arsenian pyrite	(Fe _{0.95} Cu _{0.01} Ag _{0.001}) _{0.96} (S _{1.92} As _{0.11}) _{2.03}
11	arsenian pyrite	(Fe _{0.99} Cu _{0.01}) _{1.00} (S _{1.95} As _{0.05}) _{2.00}
12	arsenian pyrite	(Fe _{1.01} Cu _{0.01}) _{1.02} (S _{1.96} As _{0.01}) _{1.97}

Marcasite is also well-presented mineral associating with pyrite and very often with arsenopyrite (Fig. 2, Plate 2), replacing intensively pyrite. Elongated veinlets with colloform texture (Fig. 2, Plate 3) are also very typical for this mineral. Marcasite usually takes the core parts of the aggregates and veinlets where it is observed (Fig. 2, Plate 1). Mladenova (1998) suggests that a part of marcasite was formed over pyrrhotite, which marks the initial stage of the ore-forming process, but in the samples from ore body “North” it is not often observed. It could be expected that probably on Fig. 2, Plate 5 the central part of the sulphide aggregate was formed by platy pyrrhotite aggregate later replaced by marcasite, but such relations are not often found.

Arsenopyrite forms well-shaped euhedral rhombic or elongated crystals and aggregates as single nests, or in association with other sulphide minerals. In this case it is usually developed as crown-like aggregates of euhedral crystals rimming pyrite-marcasite aggregates (Fig. 2, Plate 1), or around single sphalerite grains (Fig. 2, Plate 6). Qualitative microprobe analyses do not established any trace elements in it within the frame of detection of the device.

Stibnite is observed as needle-like elongated crystals or xenomorphic aggregates in association with marcasite and arsenopyrite (Fig. 2, Plate 2). It rarely intergrowths with Ag-Sb sulphosalts (Fig. 2, Plate 7), or with Pb-Sb-Ag sulphosalts cutting them (Fig. 2, Plate 8), which confirmed its later forming. Quantitative microprobe analyses established some deficit of sulphur at the expense of Cu (0.26 wt. %) and Fe (0.11 wt. %) but the calculated formula is very close to the theoretical one for this mineral.

Sphalerite has a minor distribution in the ore mineralisation usually as very fine (20 – 80 µm) irregular or slightly rounded grains. Some of the larger grains contain chalcopyrite emulsion.

Galena has also a very rare distribution in the ore mineralisation. It is observed as single quadrangle grains in quartz.

Chalcopyrite presents as fine emulsion in sphalerite or forms single grains of micron size.

A secondary mineral formed at the expense of arsenopyrite during the supergene alteration is observed as irregular or elongated aggregates around quartz. Its reflectivity is low, the

colour is light to darker grey similar to Fe-hydroxides (Fig. 2, Plate 9). Qualitative microprobe analyses established high content of Fe and As, but the quantitative analysis was not correct and it could be concluded that the mineral is probably hydroxide of Fe and As, the most possible – scorodite (?).

Ag-bearing minerals found in the ore body “North” of the deposit include pyrargyrite, miargyrite, andorite, acanthite and plagiogite (?).

Pyrargyrite is the most often found among Ag-bearing minerals in the ore body. It is observed as fine slightly rounded, triangle or irregular shaped grains near the contacts of marcasitised pyrite (Fig. 2, Plate 10). The size of the grains is usually about or less than 100 µm. It demonstrates typical for this mineral optical properties such as light grey colour, sphalerite-like reflection, distinct anisotropy and specific red internal reflections. Quantitative microprobe analyses established as trace elements in it Te, Cu and As in minor quantities (Table 1), which is normal for this mineral.

Miargyrite closely associates with pyrargyrite, but it is rarely observed. It has also grey colour, but a little bit lighter than pyrargyrite. The differentiation between both minerals is done on the basis of quantitative microprobe analyses (Table 1). Minor quantity of Fe and As present in miargyrite as trace elements. In several cases this mineral is observed as fine intergrowths with stibnite (Fig. 2, Plate 7). Both minerals are also very similar by their optical properties, but miargyrite has specific beige-brownish-grey shade, while stibnite demonstrates variations of grey colour due to the different orientation of single grains. Miargyrite is also observed as intergrowth with a mineral with slightly light grey colour (Fig. 2, Plate 7). In the optical microscope this difference is very difficult to be mentioned, but it is clearly visible during observations in backscattered electrons in Scanning electron microscope (Fig. 2, Plate 12). The analyses of the second phase established much complicated composition including elements like Pb, Sb and S as main elements and minor quantities of Ag and Cu. Several attempts to calculate the possible formula of the mineral are performed. The results established formula (Table 1) much closer to the theoretical composition of plagiogite (calculated as $Pb_5Sb_8S_7$). It is known

Table 2. Distribution of Au, Ag and As in ore and different flotation products

Product	Production [%]	Content			Extraction		
		Au [g/t]	Ag [g/t]	As [%]	Au [%]	Ag (%)	As (%)
Concentrate (1 st and 2 nd main flotation)	9.9	11.7	430	1.49	44.62	61.03	16.32
Concentrate (control flotation)	4.4	5.4	92	1.02	9.15	5.80	4.97
Waste	85.7	1.4	27	0.83	46.23	33.17	78.71
Ore	100.0	2.6	69.8	0.90	100.0	100.0	100.0

Table 3. Distribution of Ag in different products from hydrometallurgical test

Phase	Class -0.08 mm			
	Content g/t for 85%	Content g/t for 95%	Distribution % for 85%	Distribution % for 95%
free	-	-	-	-
cyanidable	47	46	67.14	65.71
in oxide envelope	13	5	18.57	7.14
in sulphides	9	18	12.86	25.71
in insoluble residium	1	1	1.43	1.44
in the initial probe	70	70	100.0	100.0

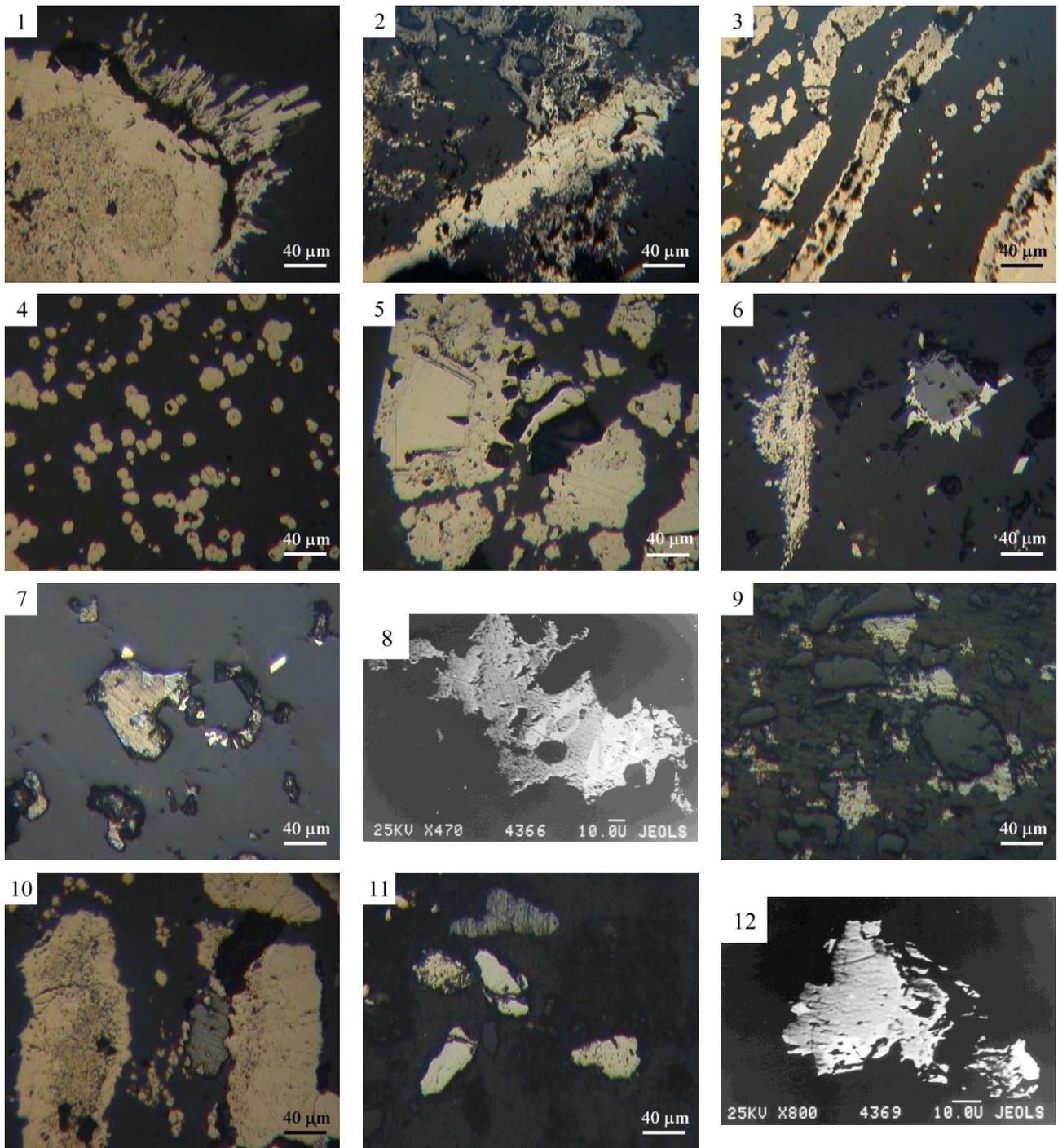


Fig. 2. Microphotographs (Reflected light, parallel Nicols, if not especially noticed)

Plate 1. Zonal aggregate including elongated arsenopyrite crystals in the periphery, pyrite in the between (white) and marcasite (greyish), replacing pyrite in the core; **Plate 2.** Irregular aggregate of fine intergrowths between stibnite (grey), marcasite (light grey) and arsenopyrite (white), crosscut by later formed veinlet of pyrite and marcasite (white to whitish); **Plate 3.** Elongated colloform textured veinlets of pyrite and marcasite (greyish and white) among quartz (dark grey). At the right – fine globular grains of pyrite; **Plate 4.** Fine inclusions of globular pyrite in quartz (dark grey); **Plate 5.** Aggregate of platy marcasite crystal (white in the centre) and arsenian pyrite (whitish) crosscut and corroded by later formed quartz (dark grey). It is possible marcasite to replace early formed pyrrotite; **Plate 6.** Crown-like texture of euhedral arsenopyrite crystals (white) rimming sphalerite grain (light grey). At the left – an aggregate of marcasite, pyrite and arsenopyrite; **Plate 7.** Slightly rounded aggregate of miargyrite (light grey) and stibnite (whitish) among quartz (dark grey). Two single grains of miargyrite present at the bottom and fine euhedral arsenopyrite crystals (white) are observed in the centre and at the right; **Plate 8.** Aggregate of andorite (grey) and stibnite (white) grown up over slightly rounded quartz crystals. – SEM, Backscattered electron image, COMPO regime. Marker – 10 µm; **Plate 9.** Scorodite (?) particles (grey) in association with quartz (dark grey, with high relief) among resin in the waste product from flotation; **Plate 10.** Slightly elongated and rounded grain of pyrargyrite (grey) on the contact with marcasite-pyrite aggregate (white and whitish) among quartz; **Plate 11.** Elongated grain of acanthite (grey), associating with pyrite (white) and marcasite (whitish) particles; **Plate 12.** Intergrowth between miargyrite (grey) and plagiogite (?) in quartz (dark grey). – SEM, Backscattered electron image, COMPO regime; Marker – 10 µm.

that the diagnostic of the minerals from the group of sulphantimonides is much complicated and it has been an object of discussion in mineralogy for a long time. The very close parameters in chemical composition and optical

properties leads to the fact that in some cases minerals is impossible to be exactly determined. Anyway, in this case presence of plagiogite is also expected on the base that this

mineral is usually common for deposits with low content of galena, such as recent one studied.

Andorite is found in intergrowth with stibnite as irregular shaped aggregate developed over slightly rounded quartz crystals. In reflected light there is no difference between both minerals, but in observation through SEM in backscattered electrons this difference is distinct (Fig. 2, Plate 8). Quantitative microprobe analyses of andorite established chemical composition similar to andorite IV from the Oruro deposit (Bolivia) described by Chvileva et al. (1988). The other variety mentioned by the same authors as andorite VI contains more silver in its composition. Microprobe analyses established as well copper as trace element which is typical for both varieties.

Acanthite is found as fine slightly elongated grains in the concentrate from the experimental flotation of the ore in association with pyrite and intergrowth between fine needle-like arsenopyrite in quartz (Fig. 2, Plate 11). The size of the acanthite grains along the long axis is about 100 µm. The colour is light grey, anisotropy of the mineral is not distinct due to the poor polishing of the mineral in the cemented briquette. The final diagnostic of the mineral is performed by quantitative microprobe analysis (Table 1) and calculated formula is very similar to the theoretical for this mineral. No trace elements are found in it.

The quantitative chemical analyses of the products from experimental tests for ore flotation established that extracting of silver in concentrates is higher compared with gold (Table 2), which could be explained with greater part of silver including in silver's own minerals. The most of this amount is related to mineral phases that are successfully liberated during the ore crushing and milling. Phase analyses performed on products from hydrometallurgical test for class -0.08 mm established that for 95 % of ore milled to this size about 25.71 % of silver is related to sulphide form and only 1.44 % is in the insoluble residuum (Table 3). Over 65 % presents in a form that could be successfully extracted through cyanidisation. Another 7.14 % are related to the oxide envelope of the mineral grains, probably pyrite altered into Fe-oxides.

Discussion and conclusions

The recent study of silver distribution in the mineralisation of ore body "North", Sedefche deposit and the products of the experimental mineral processing tests could be discussed as following.

Silver bearing minerals here are presented mainly by pyrargyrite, miargyrite, andorite, acanthite and as trace element silver presents in pligionite (?) and very rarely in arsenian pyrite. Some of the previously reported silver minerals in the deposit were not found now due to the relatively limited number of samples studied. Two of the minerals (andorite and acanthite) are reported for the first time for this deposit.

The largest part of the silver minerals could be successfully liberated during the process of ore crushing and milling as they are observed without any intergrowth with quartz or main sulphide minerals in the concentrate obtained.

Two varieties of pyrite are found one of them could be nominated as arsenian pyrite carrying As between 3 and 7 wt. %. Both of them are successfully beneficiated and the content of intergrowths of pyrite with other minerals in the concentrate obtained is very low.

Pieces of quartz with inclusions of globular pyrite that could not be liberated due to their minor size are observed in the tailings.

The main carrier of As in the mineralisation is arsenopyrite and probably in the oxidising zone Fe arsenates such as scorodite. The content of As in waste from the flotation experiment is relatively high, which could be explained with the large amount of very fine arsenopyrite crystals in quartz.

The microprobe analyses of pyrite and arsenopyrite do not register gold in both minerals within the frame of the device detection limit. Gold is reported as trace element in them by Mladenova (1998), discussing the problem of "invisible" gold in this deposit. Additional study for this problem is necessary not only for the gold distribution which is the main element for the deposit but also for the possibility of presence of silver together with gold as electrum in fine-dispersed colloidal particles with size below 1 µm. This will support the proper treatment and extraction of the largest quantity of both elements from the ore.

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