NEW DATA FOR THE MINERAL COMPOSITION OF ORES IN THE WESTERN SECTOR OF THE GOLD-COPPER DEPOSIT CHELOPECH

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ABSTRACT. Geological structure of gold-copper deposit Chelopech is shortly discussed and new data for mineral composition of Western sector in the newly found ore bodies in blocks 151 and 149. In polished sections from this sector are established two generations of pyrite, as well as enargite, phases from tennantite-tetrahedrite row, chalcopyrite, bornite, covellite, idaite, stanoidite and native gold. Their typical features and relationships are described. Quantitative microprobe analyses are performed for determination of their chemical composition. Zn-tennantite is found as dominating among tennantite-tetrahedrite phases in the samples. Chemical composition of the native gold is determined by relatively low silver and constant copper presence as trace elements. Based on data obtained comparison of the mineralogical features of newly found ore bodies and the type of the mineralisation in sectors Western and Central of the deposit is done. The analyses of the results obtained by present work will support clarification of the typical mineralogical and chemical zonality of this type of epithermal deposits.

НОВИ ДАННИ ЗА МИНЕРАЛНИЯ СЪСТАВ НА ОРУДЯВАНЕТО В УЧАСТЪК "ЗАПАДЕН" НА ЗЛАТНО-МЕДНОТО НАХОДИЩЕ ЧЕЛОПЕЧ

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РЕЗЮМЕ. В работата са разгледани накратко геоложия строеж на златно-медното находище Челопеч и се съобщават нови данни за минералния състав на участък "Западен", в новоустановените рудни тела на блок 149 и 151. В полирани препарати от участъка са наблюдавани две генерации пирит, както и енаргит, фази от редицата тенантит-тетраедрит, халкопирит, борнит, ковелин, идаит, станоидит и самородно злато. Описани са техни характерни особености и взаимоотношения. За определяне на химическият им състав са проведени редица рентгеноспектрални количествени анализи. Сред фазите с тенантит-тетраедритов състав е установено доминиращо присъствие на Zn-тенантит. Химическия състав на златото се отличава с относително ниско съдържание на сребро и постоянно присъствие на мед като елементи-примеси. Въз основа на получените резултати е направена съпоставка на минераложките особености на новоустановените рудни тела и характера на минерализацията в участъци "Западен" и "Централен" на находище Челопеч. Анализът на резултатите от настоящия труд ще спомогне за изясняване на типичната минерална и химична зоналност за този вид епитермални находища.

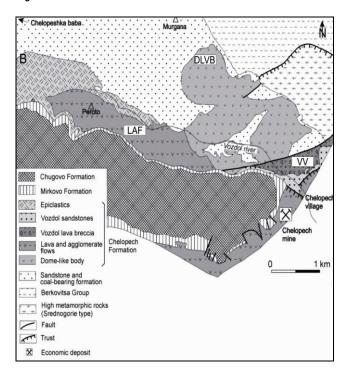
Geological features of the Chelopech deposit

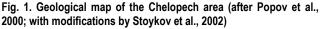
The Chelopech volcanic complex which hosted the deposit is located in the Central Srednogorie magmatic zone and hosts one of the largest Cu-Au deposits in Europe. Stoykov et al. (2004) distinguished three units of the volcanic complex: (I) dome-like bodies, (II) lava to agglomerate flows, and (III) the Vozdol lava breccias and volcanites. The volcanic rocks are porphyritic with plagioclase and amphibole phenocrysts, quartz and biotite are rare. The lava flows contain fully crystallised, fine-grained enclaves of more basic composition.

The geochemical evolution of the Chelopech volcanic complex developed from intermediate to basic lavas, but the evolution of the magmatism was more complex including magmatic differentiation, assimilation, mingling and mixing. The trace element distribution is typical for an active continental margin. The genesis of the Chelopech deposit, the major ore producing epithermal deposit in this area, is related to intermediate Late Cretaceous volcanism, which extruded in the northern part of the Central Srednogorie metallogenic zone.

The products of the Chelopech volcano are located in the Central Srednogorie volcanoplutonic area, which forms part of the Srednogorie tectonic zone (Dabovski et al., 2002). The basement of the volcanic rocks consists of high-grade metamorphic rocks (two-mica migmatites with thin intercalations of amphibolites, amphibole-biotite and biotite gneisses), and low metamorphic phyllites and diabases of the Berkovitsa group

(Early Paleozoic island-arc volcanic complex, Haydoutov, 2001). These units are in tectonic contact with each other. The base of the Chelopech volcanic rocks is partly exposed on the surface. although it has been intersected in the underground mine. The Late Cretaceous succession in the Chelopech region starts with conglomerates and coarsegrained sandstones intercalated with coal-bearing interbeds (coal-bearing formation, Moev, Antonov, 1978) covered by polymictic, argilleous and arkose sandstones to siltstones (sandstone formation). Collectively, these units have a thickness of less than 500 m. Pollen data suggests that both formations are Turonian (Stoykov and Pavlishina, 2003). The sedimentary rocks are cut by volcanic bodies and overlain by sedimentary and volcanic rocks of the Chelopech Formation (Moev, Antonov, 1978). It comprises the products of the Chelopech volcanic complex, epiclastics, as well as the Vozdol sandstones (Fig. 1 and 2). The Vozdol sandstones are paleontologically dated as Turonian in age (Stoykov, Pavlishina, 2003). These formations have been eroded and transgressively covered by sedimentary rocks of the Upper Cretaceous Mirkovo Formation (reddish limestones and marls), which are in turn overlain by flysch of the Chugovo Formation (Campanian-Maetrichtian in age, Moev, Antonov, 1978) (Fig. 1 and 2). Based on their structures, host rocks, cross-cutting relationships and alterations on the surface the products of the Chelopech volcanic complex is subdivided into 3 units by Stoykov et al. (2004): (I) dome-like volcanic bodies, (II) lava and agglomerate flows and (III) the Vozdol volcanic breccias and volcanites. Western and Central sectors of the Chelopech deposit where the new ore bodies are found are located in the Vozdol volcanic breccias and volcanites (Fig. 2). The location of the two sectors is shown on Fig. 3.





Material and methods

Studies are performed on 80 samples taken from ore blocks 149 and 151 in the Western sector of the deposit (Fig. 3). They are observed through stereomicrocsope Olympus SZ61 (magnification up to 45x) and after that 48 polished section are prepared from representative samples. Polished sections are observed through microscope for polarizing light Meiji 9430 supplied by photo camera Meidji DK 1000 (magnification up to 250x). Quantitative determination of minerals observed are done by electron microscope JEOL JSM 35 CF equipped by microprobe analyzer Tracor Northern TN 2000 EDEX in the laboratory of "Eurotest-Control" AD in Sofia.

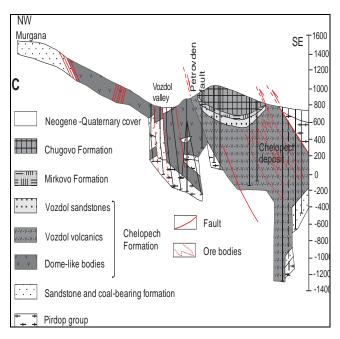


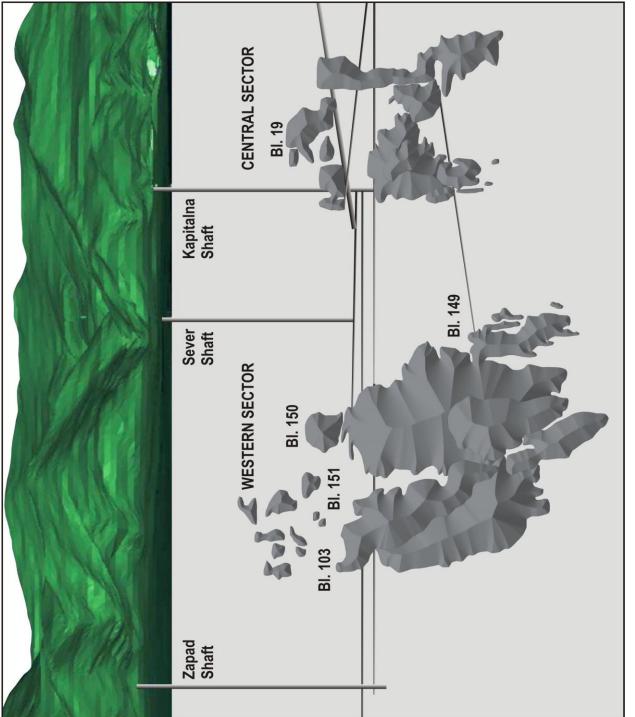
Fig. 2. Geological cross-section of the Chelopech area (after Stoykov et al., 2002)

Results

The recent study established mineral associations, which are relatively very similar in both ore blocks N149 and N151 located in the western part of the deposit (Table 1).

Ore minerals found	N149	N151
Main	pyrite, tennantite, enargite	pyrite, tennantite, enargite
Secondary	chalcopyrite, marcasute	chalcopyrite, marcasite
Rare	galena, sphalerite, covellite, bornite,	galena, sphalerite, covellite, bornite, native gold, idaite, stanoidite, famatinite

Table 1. Ore minerals in the western	part of Chelopech deposit
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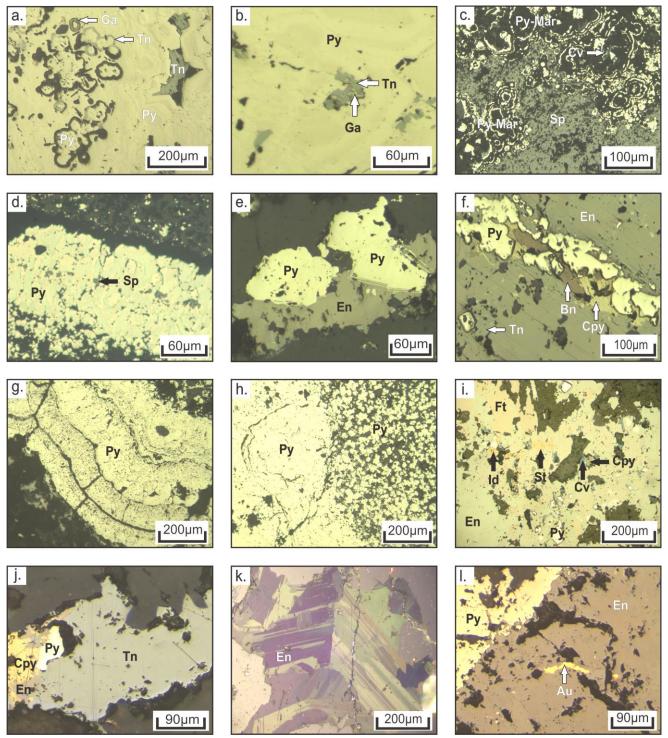


Fig. 4. Microphotos of ore minerals in polished sections from the Western sector of the gold-copper deposit "Chelopech" (reflected light): a – inclusions of tennantite (Tn) among zonal pyrite (Py); typical "atoll"-like pyrite (Py) in the left half of the observed field; gangue mineral (black) forming pyrite "atolls" probably was replaced later by tennantite (Tn) and galena (Ga); b – grains of tennantite (Tn) and galena (Ga) in zonal pyrite (Py); c – matrix of sphalerite (Sp) and pyrite-marcasite (Py-Mar) with the so-called "Bird's-eye" texture; fine grains of covellite (Cv) – a rare mineral in the studied sector; d – pyrite (Py) among the matrix of gangue minerals (black) and "droplets" of sphalerite (Sp); e – two mineral grains of pyrite (Py) in contact with enargite (En), surrounded by gangue minerals (black); observed zones of growing in pyrite (Py) filled with enargite (En); f – enargite (En) matrix crossed by a veinlet of pyrite (Py), chalcopyrite (Cpy) and bornite (Bn); bottom left – tennantite (Tn); g – colloform structure of pyrite (Py) with traces of "drying" among gangue minerals (black); h – two types of pyrite (Py) – a coarse-grained colloform (left) and a fine-grained (right); i – close sprout mineral grains of enargite (En) and famatinite (Ft) with inclusions of pyrite (Py), covellite (Cv), stanoidite (St) and idaite (Id); covellite is developed over chalcopyrite (Cpy); j – tennantite grain (Tn), among gangue matrix in association enargite (En), chalcopyrite (Cpy) and pyrite (Py) in the peripheral part; k – distinct lamellar structure of enargite (En) (cross nickols); I - elongated aggregate of native gold (Au) in enargite (En), left – pyrite (Py)

Table 2. Results from microprobe (MP) analyses of minerals from blocks N149 and N151 (N1-28). Published data for stanoidite (N29-32); N29 – theoretical composition (Chvileva et al., 1988); N30 – St. Michael's Mount, Marazion, Cornwall, UK (Criddle, Stanley, 1993); N31 – Konjo mine, Okayama prefecture, Japan (Criddle, Stanley, 1993); N32 - Tada mine, Hyogo prefecture, Japan (Criddle, Stanley, 1993); N32 - Tada mine, Hyogo

Mineral				Pyri	ite					Gold			Galena		Spha	Sphalerite
Elements (wt.%)	١N	N2	N3	N4	N5	N6	N7	N8	6N	N10	N11	N12	N13	N14	N15	N16
		•	,	•					87,71	88,41	89,92	. 1	•	•	•	•
G	ı	•	0,47	1,97	0,74	0,10	0,07	06'0	7,93	4,29	2,89	2,27	0,57	1,72	1,13	0,43
	53,47	54,99	54,93	54,54	53,24	51,41	53,43	52,63	•	,	•	11,43	14,93	12,18	31,78	29,45
Fe	46,27	44,61	44,23	43,02	46,01	48,49	46,33	46,24	•	•	•	3,39	1,67	1,17	1,02	18'1
ප	0,11	0,14	0,12	0,12			00'0	0,15	•	,		0,25	1	1	ı	•
ïZ	0,04	0,05	0,04	0,06	•		0,05	0,08		,	•	0,36	•	•	•	•
Te	0,10	0,21	0,11	0,11	1			•	•	•		0,00	0,00	0,00	0,20	•
Zn	,	•	ł	1	1	1	·	ı	•	•		0,62	0,55	0,79	65,52	68,23
ß	•	•	0,10	0,18	00'0	0,00	0,00	00'0	F	F	-	00'0	0,00	. 0,00	00'00	00'0
Pb	1	1	•	8	0,00	0,00	0,00	00'0	•	•	•	81,67	82,26	84,12	0,00	00'0
Ag	•	•	•		0,00	0,00	0,12	00'0	4,57	7,45	4,82		0,00	0,00	0,00	0,00
Cd	-	•	•	E	0,00	0,00	•	•	•	•			1	•	0,34	00'0
Σ	66'66	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,21	100,15	97,63	66'66	99,98	99,98	66'66	99,92

Table 2. (continuation)

Mineral			Tenna	Tennantite				Enargite		ldaite			Stanoidite	oidite		
Elements (wt.%)	N17	N18	N19	N20	N21	N22	N23	N24	N25	N26	N27	N28	N29	N30	N31	N32
Cu	48,30	46,67	41,39	44,58	46,48	41,21	46,88	47,74	47,36	55,25	41,80	42,20	39,16	38,80	38,80	39,20
S	27,78	27,96	30,67	29,19	31,85	28,05	32,10	32,53	32,22	31,67	28,14	28,36	29,64	29,30	29,10	29,30
As	12,64	14,15	14,52	15,79	18,22	19,42	19,59	19,65	19,72	2,03	2,02	1,57	00 6 1	•		
Sb	1,43	0,24	00'0	0,00	3,11	2,53	0,69	1	1	•	0,81	0,30	> 0,00	•	•	•
Fe	0,70	2,10	4,98	1,67	0,09	0,40	0,56	•	•	11,49	11,62	11,63	12,91	10,30	11,70	9,20
Te	0,00	00'0	0,55	0,50	•	•	•	•	1	•	•	8	•		-	•
Zn	9,14	8,88	7,64	7,89	•	7,54	•	•	•	•	•	•	•	3,30	1,10	4,60
Ag			0,24	0,37	•	•	1		•	•	•	•	•		-	•
Sn		•	•		•	•	-	H	•	•	15,64	15,66	18,29	18,50	18,40	18,60
Σ	100,00	100,00	66'66	66'66	99,75	99,15	99,82	99,92	99,30	100,44	100,03	99,72	100,00	100,20	99,10	100,90

Crystallochemical formulas of minerals in Table 2

Crystano	chemical formulas of minerals in Table 2
Pyrite	N1 (Fe 0,994 Co 0,002 Ni 0,001 Te 0,001) 0,998 S 2,002
Pyrite	N2 (Fe 0,951 Co 0,003 Ni 0,001 Te 0,002) 0,957 S 2,043
Pyrite	N3 (Fe 0,944 Cu 0,009 Co 0,002 Ni 0,001 Sb 0,001 T 0,001)0,958S2,042
Pyrite	N4 (Fe 0,922 Cu 0,037 Co 0,002 Sb 0,002 Ni 0,001 Te0,001)0,965S2,035
Pyrite	N5 (Fe 0,990 Cu 0,014) 1,004 S 1,996
Pyrite	N6 (Fe 1,053 Cu 0,002) 1,055 S 1,945
Pyrite	N7 (Fe _{0,996} Ag _{0,002} Cu _{0,001} Ni _{0,001}) _{1,000} S _{2,000}
Pyrite	N8 (Fe 0,998 Cu 0,017 Co 0,003 Ni 0,002)1,020 S 1,980
Pyrite	N8 (Fe 0,998 Cu 0,017 Co 0,003 Ni 0,002) 1,020 S 1,980
Gold	N9 (Au 0,727 Ag 0,069 Cu 0,204) 1,000
Gold	N10 (Au 0,767 Ag 0,118 Cu 0,115) 1,000
Gold	N11 (Au 0,835 Ag 0,082 Cu 0,083) 1,000
Galena	N12 (Pb 0,909 Fe 0,140 Cu 0,082 Zn 0,022 Ni 0,014 Co 0,010)1,177S0,823
Galena	N13 (Pb 0,873 Fe 0,066 Cu 0,020 Zn 0,018) 0,977 S 1,023
Galena	N14 (Pb 0,960 Fe 0,050 Cu 0,064 Zn 0,028) 1,102 S 0,898
Sphalerite	e N15 (Zn 0,985 Fe 0,018 Cu 0,017 Cd 0,003 Te 0,002) 1,025 S 0,975
	e N16 (Zn 1,043 Fe 0,032 Cu 0,007) 1,082 S 0,918
	e N17 (Cu 11,831 Zn 0,686 Fe 0,185) 12,703 (As 2,627 Sb 0,183) 2,810 S 13,487
	e N18 (Cu 11,355 Zn 0,663 Fe 0,552) 12,570 (As 2,919 Sb 0,030) 2,949 S 13,481
Tennantite	e N19 (Cu _{9,769} Fe _{1,267} Zn _{0,553}) _{11,589} (As _{2,907} Te _{0,126} Ag _{0,033}) _{3,066} S _{14,345}
	e N20 (Cu10,707Zn0,581Fe0,432)11,720 (As3,217Te0,117Ag0,052)3,386S13,894
	e N21 (Cu 10,632 Fe 0,023) 10,655 (As 3,535 Sb 0,371) 3,906 S 14,439
Zn-tennar	ntite N22 (Cu9,765 Zn1,737 Fe 0,108)11,610 (As 3,903 Sb 0,313)4,216 S13,173
Enargite	N23 (Cu 2,927 Fe 0,041) 2,968 (As 1,037 Sb 0,022) 1,059 S 3,972
Enargite	N24 Cu 2,960 As 1,045 S 3,994
Enargite	N25 Cu 2,961 As 1,046 S 3,993
Idaite	N26 Cu 4,992 Fe 1,181 (S 5,671 As 0,156) 5,827
Stanoidite	N27 Cu 8,615 (Fe 2,725 As 0,353 Sb 0,087) 3,165 Sn 1,726 S 11,494
	N28 Cu 8,682 (Fe 2,723 As 0,274 Sb 0,032) 3,029 Sn 1,725 S 11,564
Stanoidite	N29 Cu 8,000 (Fe, Zn, As, Sb) 3,000 Sn 2,000 S 12,000
	• N30 Cu _{7,971} (Fe _{2,408} Zn _{0,658}) _{3,066} Sn _{2,034} S _{11,929}
	N31 Cu 8,036 (Fe 2,758 Zn 0,221) 2,979 Sn 2,040 S 11,945
Stanoidite	N32 Cu _{8,022} (Fe _{2,142} Zn _{0,915}) _{3,057} Sn _{2,038} S _{11,883}

Ore mineralisation in the Chelopech deposit is characterized by a rich geochemical variety, typical for the high-sulphidation Au-Cu deposits. The main economic elements Cu, Au and Ag have a strong correlation relationship with higher contents of As due to the large presence of sulphosalts such as tennantite, enargite, luzonite and famatinite as well as high content of S which main carrier is pyrite. The most common minerals in the ore blocks N149 and N151, which are the objects of the recent study, are pyrite, tennantite and enargite, while chalcopyrite is in less quantity and bornite, covellite, galena, sphalerite, famatinite, idaite, stanoidite and native gold are rarely found (Table 1). The last four minerals are found only in ore block N151 till now. Ore minerals in both ore blocks are accompained mainly by quartz and baryte, and rarely by dickite as gangue minerals.

Pyrite in the ore blocks studied is observed as two generations that differ in their structures and relationships to the other minerals. The first generation pyrite (I) often forms colloform aggregates with concentric-zonal, typical "bird's eyes, or "atoll-like" structures (Fig. 4, c, g) including marcasite as well. They are accompanied by fine semi-euhedral to xenomorphic fine pyrite grains located nearby the larger pyrite-marcasite aggregates (Fig. 4, h). These aggregates are representatives of pyrite-marcasite association formed probably at hydrothermal-sedimentary conditions before deposition of the main economic associations in the deposit. Comparison with pyrite-marcasite aggregates and

other sulphide associations reported in the massive-sulphide mineralisation found nearby "black smoker chimneys" near contemporary submarine volcanoes such as Brothers volcano, Kermadec Arc, Pacific Ocean (Berkenbosch et al., 2012) established high similarity in structures and mineral composition.

The second generation (II) of pyrite forms larger aggregates. In some of them it is clearly seen the zones of growth marked by lighter and darker strips (Fig. 4, a). Pyrite II forms also fine veinlets that cut enargite (Fig. 4, f). Microprobe analyses established often Cu, Co, Ni, Te and sporadically Sb and Ag (Table 2, N1-8) as trace elements in pyrite. Different zones of growth in pyrite (Fig. 4, a) are marked by higher content of Cu (up to 1.97 wt. %) in darker strips. Fine size of the strips do not allow precise determination of trace elements by microprobe analyses, but no doubt, the differences in optical properties in strips are due to different chemical composition.

Enargite is one of the most common minerals in both ore blocks. It forms coarser-grained aggregates in association with pyrite, chalcopyrite, bornite (Fig. 4, e, f) and tennantite or single crystals among baryte mass. Distinct lamellar structure observed in cross nickols is typical for it (Fig. 4, k) Relationships between enargite and pyrite II, chalcopyrite and bornite suggest earlier formation of enargite (Fig. 4, f). In some cases part of pyrite II is formed before enargite, because some zones of growth in it are replaced by enargite (Fig. 4, e).

Famatinite is relatively rare mineral in the western sector. It associates with enargite (Fig. 4, i) as fine grains up to 100-200 μ m. In some cases it is difficult to separate from luzonite only by its optical properties.

Minerals from tennantite-tetrahedrite row in Chelopech deposit are presented mainly by phases closer to tennantite member of the row. It the western part of the deposit, tennantite is one of the largest spread mineral, associating with pyrite, enargite and chalcopyrite (Fig. 4, j) Several microprobe analyses established tennantite members with very low content of Sb in phases from both blocks (within 0 up to 3.11 wt.%). Typical feature for tennantite studied is a constant and high presence of Zn in it (within 7.54 to 9.14 wt.%, Table 2), so it could be nominated as Zn-tennantite according classification of Chvileva et al. (1988). Based on suggestions of Mozgova and Tzepin (1983) as Zntennantite should be nominated only those tennantites which contain ≥1 atomic units. Among samples studied as Zntennantite could be accepted only one (Table 2, # 22) in which Zn is 7.54 wt.%. Previous studies of tennantite established mainly low content of Zn in tennantite (up to 0.41 wt.%, Tokmakchieva, 1994). Some analyses with higher Zn content are reported by Kovachev et al. (1988). Silver is found in two of analyses in low content (up to 0.37 wt.%).

Galena and sphalerite are rarely found in the western sector of the deposit. They are observed as fine grains (Fig. 4, a, d) and in some cases sphalerite is found as larger aggregates (Fig. 4, c). On Fig. 4, a, it is observed one unusual pseudomorph in which galena and tennantite replaced earlier formed atoll-like nearby located pyrite aggregates. Trace elements found in galena such as Co, Ni and Fe (Table 2, N12-14) are not typical for this mineral and probably they are due to influence on MP analyses from the pyrite matrix in which fine galena grains are analyzed. Sphalerite, which forms larger aggregates, compared to the galena includes low content of Fe (up to 1.81 wt.%), and traces of Cd and Te (Table 2, # 5-16). Galena and sphalerite are found the most often in ores along the marginal parts of ore blocks N149 and N151 which is typical appearance for this mineral association in the Central sector, as well.

Native gold is observed in microscope only in samples from block N151 till now. Chemical analyses of samples from block 149 established content of gold, which is comparatively close to the content in block N151, so the form of Au presence should be expected to be the same in both blocks from the western part of the deposit. Native gold is found as fine (10-50 μ m) inclusions among enargite (Fig. 4, I) or it associates with pyrite and baryte. The shape of gold inclusions is irregular or elongated along the micro fractures in matrix from enargite or baryte. Coarse-grained gold (avarage 2 mm), which is presented in the central part of the deposit (Kovachev et. al., 1988) is not established in the western part.

Chemical composition of the native gold shows low content of Ag (up to 7.45 wt.%) and sustainable content of copper within 2.89 to 7.93 wt.%. Gold from both parts of the deposit is characterised with relatively low silver content. Previos studies of chemical composition of gold established relatively low silver content up to 3.5 wt.% for the gold from tennantite association. Higher silver content (up to 19 wt.%) is reported for the gold in galena-sphalerite association (Kovachev et al., 2007) but at the western part it is not found as well.

Two relatively rare minerals – idaite and stanoidite are found in block N151. They present as irregular shaped fine grains up to 30-50 µm in enargite. The association also includes pyrite, chalcopyrite and famatinite. Idaite and stanoidite are diagnosed by quantitative microprobe analyses. Idaite contains As as trace element in it (Table 2, N26) and stanoidite is characterized by some deficit of Sn and increasing content of Cu (Table 2, N27-28). Such variations in chemical composition for stanoidite are not an exception for this mineral as it could be seen by comparison (Table 2, N29-32) to some analyses of this mineral provided by Chvileva et al. (1983) and Creedle, Stanley (1993). Fine sizes of the grains do not allow extraction of X-ray pattern for much precise diagnostic of them, but based on their optical properties and quantitative microprobe analyses they could be accepted as presented in the ores from the western part.

Conclusions

Based on data obtained from the initial stage of exploration of ore bodies 149 and 151 from the western part it could be suggested that there are not significant differences in general features of mineralisation studied in the central part of the deposit. The most common paragenesis including minerals of the main economic Cu-As-Au association here is wide spread. Gold is presented as fine inclusions of native gold in enargite, pyrite and baryte. Electrum which is rarely found in the central part and the coarser-grained gold found at the same part, here are not established. Minerals representatives of Cu-Pb-Bi-S-Se, Pb-Bi-Hg-Te-Se and Cu-Au-Ag-Te geochemical associations, typical for the upper central levels of the deposit, are not found in the western part, as well. It should be mentioned that the number of samples included in this study is relatively less compared with all polished sections from the central part of the deposit studied in the past.

Tennantite found in the western part of the deposit is close to its chemical composition to this typical for the central part, where phases with relatively low content of Zn are described. In some cases Zn could reach up to 5.19 wt. % in samples from central part. The general regularity of distribution of galena-sphalerite association along the marginal part of ore bodies is also observed in the western sector of the deposit.

Acknowledgements. The authors should like to thank Chelopech Mining AD and personaly to Eng. Plamen Doychev for their support during the realisation of this study. Part of the studies is done under a project financied by Chelopech Mining AD. We also like to thank to SEG Student Chapter for a grant that supported studies done by Magdalena Karakusheva in this work.

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