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CHALCOPHANITE AND CORONADITE FROM AU-POLYMETALLIC MADJAROVO DEPOSIT, EASTERN RHODOPES

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ABSTRACT. Chalcophanite and coronadite are considered as quite rare minerals of mainly supergene origin. Reported findings of these minerals in our country are comparatively limited.

Chalcophanite and coronadite are determined during investigation of oxidised ore samples from Madjarovo deposit, Patronkaya sector, ore vein No 5 in association with quartz, hetaerolite, pyrolusite, goethite and other Fe and Mn oxides and hydroxides. Studies carried out include optical investigation in polarised reflected light, powder diffraction analyses, quantitative microprobe analyses and infrared spectroscopy.

Chemical composition of chalcophanite from Madjarovo deposit is very close to the theoretical one. No isomorphic presence of Fe, Mg, Ni, or other elements is established. Content of ZnO varies from 18.3 to 19.2 weight %. Infrared spectrum data registered confirm layered structure of the chalcophanite, as reported by other authors (Wadsley, 1955; Post and Appleman, 1988).

Content of PbO in the coronadite studied is from 26.6 to 28.8 weight %.

Chalcophanite and coronadite are observed in close association in the oxidised zone of Madjarovo deposit. As source of Pb and Zn for forming these minerals primary sphalerite and galena from sulphide ores could be accepted.

ХАЛКОФАНИТ И КОРОНАДИТ ОТ АU-ПОЛИМЕТАЛНОТО НАХОДИЩЕ МАДЖАРОВО, ИЗТОЧНИ РОДОПИ

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РЕЗЮМЕ. Халкофанитът и коронадитът се считат за твърде редки минерали с преобладаващо супергенен произход. Данните за находки на тези минерали в страната ни са сравнително ограничени.

При изследването на образци от окислени руди от находище Маджарово, участък Патронкая, рудна жила 5, халкофанит и коронадит са установени в тясна асоциация с кварц, хетеролит, пиролузит, гъотит и други Fe и Mn оксиди и хидроксиди. За изучаване на минералите са проведени микроскопски изследвания в отразена светлина, рентгеноструктурни анализи, количествени рентгеноспектрални микроанализи и инфрачервена спектроскопия.

Химизмът на халкофанита от находище Маджарово е близък до теоретичния състав на минерала. Не се установява наличие на изоморфни примеси от Fe, Mg, Ni или други елементи. Съдържанието на ZnO варира от 18.3 до 19.2 тегл.%. Регистрираният инфрачервен спектър потвърждава слоистата структура на халкофанита, описана в литературата от предишни изследователи (Wadsley, 1955; Post and Appleman, 1988).

В изследвания коронадит съдържанието на PbO е от 26.6 до 28.8 тегл.%.

Халкофанитът и коронадитът се наблюдават в тясна асоциация в окислителната зона на находище Маджарово. Като източници на Zn и Pb за образуването на минералите, са послужили сфалеритът и галенитът от първичните полиметални руди в находището.

Introduction

Chalcophanite and coronadite are considered as quite rare mineral phases. Findings of these minerals are reported in some Pb-Zn deposits in Central and Eastern Rhodopes and Kremikovtsi iron deposit. Chalcophanite is determined in Pb-Zn deposits Eniovtche, Kechikaya (data of N. Zidarov, after Kostov et al., 1964), Vurba (Kolkovski, 1966), Madjarovo (data of B. Kolkovski, after Kostov et al., 1964) and Kremikovtsi iron deposit (Atanasov et al., 1990). Coronadite is observed in deposits Vurba (Kolkovski, 1966), Madjarovo (Kolkovski et al., 1974) and Kremikovtsi (Radonova et al., 1964; Vassileva, 1986). Mineral phases are determined mainly using X-ray data, only chemical composition of chalcophanite from Kremikovtsi is studied (Atanasov et al., 1990).

Chalcophanite and coronadite in close association with quartz, goethite, hetaerolite, pyrolusite and other Mn and Fe

oxides and hydroxides are determined in oxidized ore from Madjarovo deposit (ore vein No 5). These two minerals are targets of recent study – determining their morphological and paragenetic peculiarities, optical properties, chemical composition, thermal behavior and IRS characteristic.

Gold – base metal deposit Madjarovo, related to the core of Oligocene volcano-plutonic structure is situated in the river Arda valley in the Eastern Rhodopes. Low-sulphidation epithermal veins are localized mainly along radial faults. Ore veins are quartz, quartz-barite and quartz-calcite in composition with different content of sulphide minerals. Oreforming processes are polyphase. Different authors describe various stages of mineralization (Radonova, 1960; Atanasov, 1962; Kolkovski, 1971 – after Breskovska et al., 1976; Breskovska, Gergelchev, 1988; Breskovska, Tarkian, 1993). Kolkovski et al. (1974) describe following hypogene stages: quartz-specularite, quartz-chalcopyrite, quartz-galenasphalerite, quartz-chalcedony-barite and calcite. In the oxidized zone of the deposit over 50 supergene mineral phases are determined – goethite, Mn oxides and hydroxides, phosphates, carbonates, sulphates and other.

Material and Methods

Reflected polarized light observations are made on microscopes NU-2 and Amplival-pol-U, photos taken by digital Panasonic CCD colour camera, fitted on NU-2. Quantitative microprobe analyses were accomplished using scanning electron microscope JEOL JSM 35 CF with Tracor Northern TN 2000 EDEX system in the laboratory of EUROTEST Plc., Sofia. Following standards were used: for Mn, Fe, Zn - pure metals, for Mg, Ca, Si - diopside, for K - biotite, for Al corundum, for Pb - PbTe. Oxygen and water are calculated as difference to 100 %. X-ray powder diffraction patterns are obtained on DRON-1 diffractometer (CuK α , Ni filter) and TUR-M-60 equipment (Ø 57.3 mm camera) in UMG "St Ivan Rilski" and Sofia University "St. Kliment Ohridski". DTA curves are registered on "Derivatograph" device. Infrared spectrum is registered on infrared spectrophotometer UR-20 (Karl Zeiss) within regionn 400-4000 cm⁻¹, using prisms of LiF (3000-4000 cm⁻¹), NaCl (700-1800 cm⁻¹) and KBr (400-700 cm⁻¹).

Results and Discussion

Chalcophanite

Mode of occurrence

Chalcophanite is determined in samples from oxidizing zone of quartz-sulphide veins (ore vein No 5) in close association with quartz, Fe and Mn oxides and hydroxides (goethite, coronadite, cryptomelane-coronadite, hetaerolite, pyrolusite), clay minerals and calcite. The mineral forms rosette-like, spherullitic, radiate-fibrous, bundle-like and fan-shaped aggregates of fine glittering black crystals. Crusts of cellular aggregates, formed by platy chalcophanite individuals, with basal pinacoids oriented transverse to the basement of Fe and Mn hydroxides (goethite, coronadite or hetaerolite) are also observed. In some cases on the surface of chalcophanite aggregates white or pale brown (coloured by Fe hydroxides) tarnish of clay minerals is observed. In some cases chalcophanite is facing as crustification vugs in oxidized ore.

Chalcophanite individuals are shortened along *c*-axes and represent platy $\{0001\}$ pseudohexagonal crystals with size up to 1 mm and thickness to $20 - 40 \ \mu$ m.

Observed in polarized reflected light the mineral is white, white-greyish to grey in colour, with very strong anisotropy and distinct bireflectance. Chalcophanite shows red internal reflexes. It is observed as flaky, fan-shaped and radial-fibrous aggregates, in some cases corroding quartz (Fig. 1 A, B). Platy and elongated prismatic grains (crosscuts parallel to the *c*-axes) in some cases with well expressed cleavage (Fig. 1 C, D), as well as lattice-like aggregates (cellular binded platy crystals in crosscuts parallel to the *c*-axes) also present (Fig. 1 E, F). Several generations of chalcophanite are established. Overgrowth of late radial-fibrous or bundle-like aggregates of chalcophanite on unraveled border of coarse platy (along {0001}) chalcophanite crystals is observed (Fig. 1 G), as well as fine-flaked and fan-shaped aggregates over coarse platy chalcophanite individuals (Fig. 1 H). The mineral is often

associated with coronadite and hetaerolite and in some cases with pyrolusite and is the latest formed mineral phase, compared with mentioned minerals.

Chemical composition

Published crystallochemical formulas of chalcophanite show significant differences (Dana et al., 1946; Wadsley, 1955; Frenzel, 1980; Ostwald, 1985, 1987; Grice et al., 1994; Post, 1999 and others). Theoretical formula, according to Wadsley (1955) is ZnMn₃O₇.3H₂O, but most of the research-workers presume presence of Mn²⁺ cations replacing isomorphically Zn²⁺ in the chalcophanite crystal structure (Ostwald, 1985). Variation in composition of chalcophanite are mentioned by number of investigators (Radtke et al., 1967; Frenzel, 1980; Ostwald, 1981, 1984, 1985, 1987). In typical ("normal") chalcophanite content of ZnO is within 18 to 22 wt. % (Frenzel, 1980). Zn deficit varieties (ZnO up to 5.5 wt. %) are reported (Ostwald, 1984, 1985). Ostwald (1987) reported microinhomogeneity in mineral composition, observed in basal sections of chalcophanite monocrystals. The author described sectors with size tens of µm depleted in or lacking Zn among "normal" chalcophanite matrix. The heterogeneity observed most probably is due to non-equilibrium physical-chemical conditions during the crystal growth (Ostwald, 1987).

Findings of mineral phases with chalcophanite structure and high content of Ag, Mg and Ni are reported, such as Agbearing chalcophanite (aurorite) containing 7.5 wt. % Ag₂O and 1.3 wt/ % PbO (Radtke et al., 1967). Potter and Rossman (1979) announced unnamed mineral phase representing Maanalogue of chalcophanite, while Ellias et al., (1981) reported Ni-chalcophanite in lateritic Ni-Co deposits (Murrin Murrin) near Kalgoorlie, Western Australia. Later investigations proved two new mineral species, isostuctural with chalcophanite: jianshuiite – (Mg,Mn)Mn₃O₇.3H₂O (Jambor and Grew, 1994) and ernienickelite - NiMn₃O₇.3H₂O (Grice et al., 1994). Discovery of other new mineral species, isostuctural with chalcophanite is quite possible - position of Zn cations, situated in interlayers could be occupied by another cations with size close Zn ones (Potter and Rossman, 1979; Grice et al., 1994).

Quantitative microprobe analyses of single crystals of chalcophanite individuals and flaky aggregates are provided. Platy crystals (along {0001}), single prismatic crystals with well expressed basal cleavage, as well as slantwise cross-cuts were analysed. The results obtained (Table 1) are close to theoretical composition (Wadsley, 1953). ZnO content varies from 18.31 to 19.15 wt. %. Calculated formulas (Table 1) demonstrate some excess of Mn and deficit of Zn, probably due to presence of small quantity of Mn^{2+} , replacing Zn^{2+} . No isomorphic presence of Fe, Mg, Ni or other elements was determined. In two of analyses low concentrations of Pb (PbO -0.2 wt. %) and K (K₂O -0.09 wt. %) were established.

XRD, Thermal data and IRS

X-ray powder diffraction data for chalcophanite from Madjarovo deposit (Table 2) did not differ significantly from published ones (Grice et al., 1994). In some of the X-ray patterns registered an additional weakly expressed line with d-value 3.10 - 3.13 Å is observed, which is an evidence for coronadite admixture. In the samples studied chalcophanite is often close associating with coronadite.

According to Wadsley (1955) chalcophanite is pseudotrigonal of triclinic symmetry, $P \bar{i}$ space group and theoretical compo-

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sition corresponding to formulae ZnMn₃O₇.3H₂O. Mineral has layered crystal structure, based on layers of edge-shared [MnO₆] octahedra, alternating with layers of Zn cations and water molecules in the stacking sequence: Mn - O - Zn - H₂O - Zn - O - Mn. Detail investigations of single chalcophanite crystals (also including chalcophanite from classic Sterling Hill deposit, New Jersey, USA) carried out by Post and Appleman

(1988) and later by Grice at al. (1994) proved trigonal symmetry of chalcophanite, space group **R** 3, or **R** $\overline{3}$. Standard powder X-ray data for chalcophanite (JCPDS 15-807) are made more precise and re-indexed by Grice et al. (1994). X-ray data obtained are compared with those of Grice et al. (1994) in Table 2.



Fig. 1. Microphotographs, showing morphology of chalcophanite and coronadite from Madjarovo deposit. Reflected polarized light, parallel Nicols. A – Flaky chalcophanite aggregates; B – Quartz individuals (dark grey) corroded by flaky chalcophanite; C – Penetration of platy along {0001} chalcophanite crystal into transverse oriented chalcophanite individuals (crosscuts parallel to the c-axes); D – Aggregates of elongated chalcophanite individuals, in places with well expressed basal cleavage. Bireflectance is well observed. Twinning is visible (right, bottom); E – Lattice-like chalcophanite aggregates (cellular-binded chalcophanite crystals in crosscuts parallel to the c-axes); F – Lattice-like chalcophanite aggregates (crosscut of cellularbinded platy chalcophanite crystals). Bireflectance is well observed. G – Overgrown of late radiate-fibrous and bundle-like chalcophanite aggregates on unraveled edges of platy along {0001} chalcophanite crystal; H – Overgrown of fan-shaped fine-flaked chalcophanite aggregates on platy to flaky chalcophanite crystal, which on its turn had overgrown on goethite aggregate; I – Coronadite, fine-grained aggregate with desiccation cracks; J – Finegrained coronadite aggregate with banded structure among goethite (light bands are from coronadite, darker – from cryptomelane); K – Succession of mineral deposition: goethite \rightarrow coronadite \rightarrow chalcophanite (radiate-fibrous, bundle-like and flaky aggregates); L – Coronadite (light thin rim) formed over pyrolusite and fine prismatic chalcophanite individuals. On coronadite rim coloform aggregates of late hetaerolite and chalcophanite are overgrown

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DTA curve of chalcophanite from Madjarovo deposit studied is characterized by quite intensive deep endothermal effect at 200° C and weak endoeffect at 540° C. Thermogramm obtained is quite similar to the thermal data for crystal chalcophanite from Sterling Hill (Dasgupta, 1974 - after Frenzel, 1980). The only difference is absence of low temperature endoeffect at about 100° C. In DTA curve registered the first endoeffect (200° C) corresponds to dehydratation of mineral phase and formation of ZnMn₃O₇, according to Frenzel (1980), while the second endoeffect (540° C) is a result of transition to hataerolite (Zn,Mn)Mn₂O₄.

Table 1.

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No	Oxides (wt. %)							
INU	MnO ₂	ZnO	PbO	K ₂ O	H ₂ O	Σ		
1	65.83	20.54	-	-	13.63	100.00		
2	67.41	19.15	-	-	13.44	100.00		
3	67.65	18.48	-	-	13.87	100.00		
4	68.75	17.67	-	-	13.58	100.00		
5	67.37	18.58	-	0.09	13.96	100.00		
6	68.68	17.56	0.20	-	13.56	100.00		
7	68.34	18.31	-	-	13.35	100.00		
8	67.72	18.37	-	-	13.91	100.00		

H₂O is calculated as difference to 100 %

1. Chalcophanite ZnMn₃O₇.3H₂O after Wadsley (1953), cited according to Minerals - Handbook (1967).

2-8. Chalcophanite from Madjarovo deposit.

Crystallochemical formulas:

1 . ZnMn ₃ O ₇ .3H ₂ O	2 . Zn _{0.94} Mn _{3.09} O ₇ .2.97H ₂ O
3. Zn _{0.89} Mn _{3.07} O ₇ .3.04H ₂ O	4. Zn _{0.86} Mn _{3.14} O ₇ .3.00H ₂ O
5. Zn _{0.90} Mn _{3.05} O ₇ .3.05H ₂ O	6. Zn _{0.86} Mn _{3.14} O ₇ .3.00H ₂ O
7. Zno mMn3 14O7.2.96H2O	8. Zno 89Mn 3 07O7.3.04H2O.

Infrared spectrum (IRS) of chalcophanite from Madjarovo deposit (Fig. 2) is quite similar to spectrum of chalcophanite from oxidizing zone of Pb-Zn deposits in Tarnowskie Gory, Silezia, Poland, reported by Kulig (1973). It also corresponds to published standard spectrums of mineral (Potter and Rossman, 1979 a, b; Ostwald, 1984, 1985). In IRS obtained four intense absorption bands in region 400 – 550 cm⁻¹ are observed, with maximums at 445, 475, 502 and 535 cm⁻¹, which, according to Potter and Rossman (1979 a, b) are diagnostic for chalcophanite. Other well expressed absorption bands are also established at 1625 cm⁻¹ (OH – deformations), 3320 and 3400 cm⁻¹ (OH - valency vibrations), indicating presence of water molecules in the crystal structure of mineral. Low intensity absorption bands at 1120 and 1150 cm⁻¹, most probably are in a result of impurities in the sample analysed.

Potter and Rossman (1979 a, b) emphasized, that IRS data confirm layered structure of chalcophanite, as described by other researchers (Wadsley, 1955; Post, Appleman, 1988).

The former authors suggest possibility for discovery of new natural mineral species of chalcophanite group, determined by cation types in interlayers - at positions of Zn²⁺ cations. Confirmation of these prognoses is the discovery of 2 new mineral phases isostructural with chalcophanite - its Ni and Mg analogues respectively, as mentioned above (Grice et al., 1994; Jambor and Grew, 1994).

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(RD data of chalcophanite								
Chalcophanite			Chalcophanite, Madjarovo					
(Gric	e et al.	, 1994)	Samp	le 1	Sample 2			
d(Å)	I/I₁	hkl	d(Å)	I/I₁	d(Å)	I/I ₁		
6.96	10	003	6.91	10	6.90	10		
6.23	1	101	6.27	2	6.21	3		
4.08	5	104	4.10	6	4.08	7		
			3.78	<1	3.82	0.5		
3.50	6	015	3.50	7	3.47	8		
3.32	1	113	3.34	1	3.36	1		
3.23	<1	021	3.13*	4				
2.77	2	024	2.78	3	2.77	3		
2.71	<1	107	2.71	1				
2.57	4	205	2.57	5	2.57	6		
2.46	2	211	2.46	4	2.47	3		
2.41	2	122	2.42	3	2.42	2		
2.24	5	214	2.24	7	2.24	7		
2.13	2	125	2.13	2	2.13	2		
1.986	<1	10 [.] 10	1.984	1	1.981	1		
1.900	3	217	1.907	4	1.910	5		
1.849	1	306	1.851	2	1.850	2		
1.795	2	128, 312	1.796	<1	1.799	4		
1.750	<1	02 [.] 10			1.733	1		
1.715	<1	134	1.718	1				
1.668	1	315	1.665	2	1.669	2		
1.597	4	21.10	1.594	6	1.599	7		
1.563	<1	404	1.557	1	1.560	1		
1.507	1	12 [.] 11	1.504	4	1.505	4		
1.431	3	410	1.431	5	1.434	5		
1.402	<1	413	1.401	2				
1.324	<1	416						
1.308	<1	051						
1.279	1	054						

* - coronadite line

Coronadite

Mode of occurrence

Macroscopically it is observed as dense, massive, black to black-brown aggregates in oxidized ore samples, associating closely with guartz, goethite, hetaerolite, pyrolusite and other Fe and Mn oxides and hydroxides.

The mineral is white in reflected light, with clear strong anisotropy. It forms fine-grained masses in some places with desiccation cracks (Fig. 1 I), fine-fibrous or filiform aggregates. Occasionally the mineral is manifesting zonal structure, marked by alternation of light, almost white bands with high content of Pb (PbO - 30 wt. %) and darker bands of cryptomelane-coronadite (K₂O - 3.4 wt. %) - Fig. 1 J. Thickness of separate strips in zonal coronadite aggregates is up to 70-80 µm. Such a zonality and rhythmic texture of coronadite is described in Bou Tazzoult deposit, Imini, Morocco (Frenzel, 1980). Most often coronadite associates with quartz, goethite and chalcophanite. The mineral is filling vugs and forms overgrowth on goethite, in some places coloform, convergence-zonal aggregates are observed - with fine-banded structure and rhythmic alternation of mentioned above two phases. Often transverse or slantwise oriented fan-shaped, bundle-like and flaky aggregates of chalcophanite form overgrowth on fine-grained or finefibrous coronadite (Fig. 1 K). In some cases coronadite is in close association with pyrolusite and hetaerolite (Fig. 1 L). Coexistence of coronadite and Mn oxide and hydroxides, containing manganese as high valence Mn⁴⁺ cations (pyrolusite), as well as lower valence Mn³⁺ cations (hetaerolite) is an evidence of significant variations in composition of solutions and physical and chemical conditions while forming of supergene mineralization.



Fig. 2. Infrared spectrum of chalcophanite from Madjarovo deposit

Chemical composition

Coronadite belongs to hollandite mineral group, which composition could be summarized with universal formulae Roa _{1.5}Mn⁴⁺Mn³⁺₈O₁₆, where R = Ba, Pb, K, Na (Post, 1999). Isostructural minerals of hollandite group (hollandite, coronadite, cryptomelane, manjiroite) are characterized by tunnel-type structure, based on double chains of edge-shared [MnO₆] octahedra (Turner and Buseck, 1979; Potter and Rossman, 1979; Post and Bisch, 1989; Chukhrov et al., 1989; Post, 1999). The type of prevailing cations with relatively large size, situated in structural tunnels, determines separate mineral species: cryptomelane (K), hollandite (Ba), manjiroite (Na), coronadite (Pb). Natural end-members of this isomorphic group are quite rare, phases studied are with non-persistent composition, due to variation of cations, situated in structural tunnels. It is accepted that in discussed mineral phases manganese is mainly as Mn4+, but some quantity of low valence Mn cations is also present. Recent investigations indicate that low valence Mn cations are of Mn³⁺ type (Post and Bisch, 1989; Post, 1999), not Mn²⁺, as it was assumed by previous researchers. Discussion also occurs on the form of water presence - water molecules or/and hydroxyl group (OH).

Tabl	e 3.
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Micro	probe	anal	yses	of	coronadite	
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Ovidos	Samples (wt. %)						
Oxides	1	2	3	4	5		
MnO ₂	59.38	67.25	68.11	69.72	70.66		
MnO	12.85	-	-	-	-		
PbO	26.88	29.12	28.82	28.72	26.63		
ZnO	-	-	2.88	1.66	1.71		
CuO	-	0.26	-	-	-		
Fe ₂ O ₃	-	0.31	0.19	-	-		
Al_2O_3	-	2.77	-	-	-		
K ₂ O	-	0.01	-	-	0.10		
BaO	-	0.04	-	-	-		
SiO ₂	-	0.20	-	-	-		
Σ	99.11	99.96	100.00	100.10	99.10		
Cations	Formula coefficients						

Mn ⁴⁺	6.55	7.00	7.22	7.32	7.36
Mn ²⁺	1.74	-	-	-	-
Fe³⁺	-	0.03	0.02	-	-
Cu ²⁺	-	0.03	-	-	-
Zn ²⁺	-	-	0.33	0.19	0.19
Al ³⁺	-	0.49	-	-	-
Σ	8.29	7.55	7.57	7.51	7.55
Pb ²⁺	1.16	1.18	1.19	1.17	1.08
K⁺	-	-	-	-	0.02
Σ	1.16	1.18	1.19	1.17	1.10

1. Coronadite, Maiskoe deposit, Central Kazakhstan (Minerals –

Handbook, 1967); 2. Coronadite, Imini, Morocco (Perseil, Giovanoli, 1988);

3-5. Coronadite, Madjarovo deposit.

Composition of coronadite from Madjarovo deposit is given in Table 3. Content of PbO varies from 26.63 to 28.82 wt. %. Isomorphic admixtures of Zn^{2+} (ZnO – 1.66 to 2.88 wt. %), Fe^{3+} (Fe_2O_3 - 0.19 wt. %) and K⁺ (K₂O - 0.10 wt. %) are determined.

XRD data

Because of absence of suitable for analyses monocrystals and impossibility of separating of homogenous material for X-ray powder diffraction analyses, often in XRD patterns obtained lines of admixture components present (chalcophanite, goethite and quartz). Diagnostic for coronadite intense standard reflexes (Frenzel, 1980; JCPDS 41-596; JCPDS 7-361) with d-values (Å) 3.48-3.49; 3.12-3.13; 2.40 and 2.22 are observed, as well as weak, but also characteristic reflexes with following d-values (Å): 2.16; 1.833-1.835; 1.698; 1.642-1.649; 1.552; 1.543; 1.431; 1.370-1.375; 1.365; 1.299 and 1.237.

Conclusions

Chalcophanite and coronadite are observed in close association in the oxidised zone of Madjarovo deposit. Sources of Pb and Zn for forming these minerals are primary sphalerite

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and galena from sulphide ores in the deposit. Chalcophanite most often is later formed, than coronadite, due to the higher migration ability of Zn, compared with that of Pb within the oxidizing zone.

References

- Atanasov, V., M. Vassileva, L. Andreeva. 1990. Chalcophanite from Kremikovtsi deposit. – Ann. Higher Inst. of Mining and Geol., 36, 1. Geol., 49-54 (in Bulgarian).
- Breskovska, V., Z. Iliev, B. Mavroudchiev, I. Vapzarov, I. Velinov, P. Nozharov.1976. The Madjarovo ore field. *Geochem., Mineral. and Petrol., 5*; 23-57 (in Bulgarian).
- Breskovska, V., V. Gergelchev. 1988. The Madjarovo ore field. – In: *The lead-zinc deposits in Bulgaria*, Technika, Sofia, 114-127 (in Bulgarian).
- Breskovska, V., M. Tarkian. 1993. Mineralogy and fluid inclusion study of polymetallic veins in the Madjarovo ore field, Eastern Rhodopes, Bulgaria. – *Mineral. and Petrol.*, 49, 103-118.
- Chukhrov, F. V., A. I. Gorshkov, V. A. Drits. 1989. Supergene manganese oxides. – Nauka, Moskow, 208 p. (in Russian).
- Dana, J. D., E. S. Dana, C. Palache, H. Berman, C. Frondel. 1946. THE SYSTEM OF MINERALOGY of James Dwight Dana and Edward Salisbury Dana - Yale University 1837-1892 – Volume 1. New York, J. Wiley and Sons, 834 p.
- Elias, M., M. J. Donaldson, N. Giorgetta. 1981. Geology, mineralogy and chemistry of lateritic nickel-cobalt deposits near Kalgoorlie, Western Australia. – *Econ. Geol.*, 76, 1775-1783.
- Frenzel, G. 1980. The manganese ore minerals. In: *Geology and Geochemistry of Manganese*. (Eds. Varentsov, I. M. and G. Grasselly), Akademiai Kiado, Budapest, I, 25-157.
- Grice, J. D., B. Gartrell, R. A. Gault, J. Van Velthuizen. 1994. Ernienickelite, NiMn₃O₇.3H₂O, a new mineral species from the Siberia complex, Western Australia: Comments on the crystallography of the chalcophanite group. – *Canad. Mineral.*, *32*, 333-337
- Jambor, J. L., E. S. Grew. 1994. New mineral names. Jianshuiite. – Amer. Mineral., 79, 185-189.
- Kolkovski, B. 1966. Secondary zonality in the Vurba lead-zinc deposit (Madan ore area) – *Trav. géol. Bulgarie, Sér.* géochim., mineral. et petrogr., 6; 293-313 (in Bulgarian).
- Kolkovski, B., B. Mavroudchiev, Z. Iliev, V. Gergelchev. 1974. The Madjarovo polymetallic deposit. – In: *Twelve ore deposits of Bulgaria*. (Eds. Dragov, P. and B. Kolkovski), 4th IAGOD Symposium, Varna, Guidebook. Publ. House of Sofia Univ. "St. Kliment Ohridski", Sofia, 192-215.

- Kostov, I., V. Breskovska, J. Minceva-Stefanova, G. N. Kirov. 1964. *The Minerals of Bulgaria*. Publ. House Bulg. Acad. Sci. Sofia; 540 p. (in Bulgarian).
- Kulig, M. 1973. Chalcophanite from the Silesian-Cracovian Zn-Pb deposits. – *Mineralogia Polonica, 4,* 23-36.
- Minerals (*Complex oxides, titanates, niobates, tantalates, antimonates*). *Handbook.* 1967. Nauka, Moskow, 2, 3, 676. (in Russian).
- Ostwald, J. 1981. Some observations on the mineralogy and genesis of chalcophanite. *Mineral. Mag., 44,* 109-111.
- Ostwald, J. 1984. A low zinc chalcophanite from Norseman, Western Australia. – *Mineral. Mag.*, *48*, 556-558.
- Ostwald, J. 1985. Some observations on the chemical composition of chalcophanite *Mineral. Mag.*, 49, 752-755.
- Ostwald, J. 1987. Chemical variation in a single crystal of chalcophanite. *Mineral. Mag.*, *51*, 321-325.
- Perseil, E. A., R. Giovanoli. 1988. Sur la variation de la composition ponctuelle des termes de la série isostructural: Cryptomélane-Hollandite-Coronadite et les conditions de gisement. – Schweiz. Mineral. Petrogr. Mitt., 68; 113-123.
- Post, J., D. E. Appleman. 1988. Chalcophanite, ZnMn₃O₇.3H₂O: New crystal-structure determinations. – *Amer. Mineral.*, 73, 1401-1404.
- Post, J., D. L. Bish. 1989. Rietveld refinement of the coronadite structure. Amer. Mineral., 74, 913-917.
- Post, J. 1999. Manganese oxide minerals: Crystal structures and economic and environmental significance. – *Proc. Natl. Acad. Sci. USA*, *96*, 3447-3454.
- Potter, R. M., G. R. Rossman. 1979 a. The tetravalent manganese oxides: Identification, hydration, and structural relationships by infrared spectroscopy. *Amer. Mineral.*, 64, 1199-1218.
- Potter, R. M, G. R. Rossman. 1979 b. A magnesium analogue of chalcophanite in manganese-rich concretions from Baja California. – *Amer. Mineral.,* 64, 1227-1229.
- Radonova, T. G., Y. Daskalova, L. Pounev. 1967. Rancieite, coronadite and baidellite – new minerals for the Kremikovtsi iron deposit. – *Bull. Geol. Inst., Geochem., Mineral. and Petrogr., 16*; 127-133. (in Bulgarian).
- Radtke, A. S., C. M. Taylor, D. F. Hewett. 1967. Aurorite, argentian todorokite, and hydrous silver-bearing lead manganese oxide. – *Econ. Geol., 62,* 186-206.
- Turner, S., P. R. Buseck. 1979. Manganese oxide structures and their intergrowths. – *Science*, 203, 1024-1027.
- Vassileva, M. 1986. New data about secondary manganese minerals from the Kremikovtsi mineral deposit. – Ann. Higher Inst. of Mining and Geol., 32, 2; 137-147. (in Bulgarian).
- Wadsley, A. D. 1955. The crystal structure of chalcophanite, ZnMn₃O₇.3H₂O. – *Acta Crystallogr., 8,* 165-172.

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