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Galena-bearing myrmekitic intergrowths from the Radka deposit, Bulgaria: Origin and mechanisms of formation

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Abstract. Complex myrmekitic intergrowths involving galena, chalcocite and bornite from a betekhtinite-bearing assemblage in the Radka copper-gold epithermal deposit, Bulgaria, have been studied by means of electron microprobe, scanning electron microscopy and image analysis. Galena-bornite myrmekites correspond to textures formed by partial metasomatic replacement of bornite by galena during the formation of the betekhtinite assemblage. Galena-chalcocite composite crystals were formed by betekhtinite breakdown under increasing temperature (>150°C) following the reaction:

$Pb_{1.85}(Cu_{20.21}Fe_{0.92})S_{14.01} + 1.51Pb_{sol} \rightarrow 3.39Pb_{0.99}S_{1.00} + 10.31(Cu_{1.96}Fe_{0.01})S_{1.03} + 0.82Fe_{sol}$

The presence of betekhtinite derivate symplectite textures at Radka, formed at temperatures higher than the temperatures of original betekhtinite deposition, is an important argument supporting the idea of later, post-ore formation, reheating of the mineralised epithermal system at Radka by fluids probably derived from a deeply seated porphyry system.

Key words: myrmekites, galena, chalcocite, bornite, betekhtinite, Radka deposit
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Кузманов, К. 2004. Галенит-съдържащи мирмекитови структури от находище Радка, България: произход и механизми на образуване. *Геохим., минерал. и петрол.*, **41**, 17-30.

Резюме. Сложни мирмекитови структури, включващи галенит, халкоцит и борнит от бетехтинит-съдържаща парагенеза в епитермалното Cu-Au находище Радка, България, са изследвани с помощта на електронна микросонда, сканиращ електронен микроскоп и имидж анализ. Галенит-борнитовите мирмекити съответстват на структури, образувани при частично метасоматично заместване на борнит от галенит по време на отлагането на бетехтинитовата парагенеза. Галенит-халкоцитовите композиционни кристали са образувани при разпад на бетехтинит под въздействие на флуид с повишена температура (>150°C), следвайки реакцията:

$Pb_{1.85}(Cu_{20.21}Fe_{0.92})S_{14.01} + 1.51Pb_{sol} \rightarrow 3.39Pb_{0.99}S_{1.00} + 10.31(Cu_{1.96}Fe_{0.01})S_{1.03} + 0.82Fe_{sol}$

Наличието на мирмекитови структури, като продукти от разпад на бетехтинит, образувани при температури по-високи от температурата на отлагане и стабилност на бетехтинита, е важен аргумент в подкрепа на тезата за късно подгряване на системата в находище Радка от флуиди, вероятно свързани с по-дълбоко разположена порфирна система.

Introduction

Myrmekitic textures, called also “graphic”, “micrographic”, “pseudoeutectic”, “sub-graphic” or “symplectites”, are common feature for many ore minerals, especially Cu and Pb sulphides and sulphosalts. Ramdohr (1980) described them as “myrmekitic intergrowths”, summarising more than 110 different cases involving native elements, sulphides, sulphosalts, tellurides, oxides and tungstates. In ore mineralogy the term “myrmekite” has been adopted from the magmatic and metamorphic petrology, where it has been used to describe simultaneous deposition of several mineral phases, or different exsolution, oxidation, replacement and metamorphic corona textures. Myrmekites are mineral intergrowths produced by solid-state reaction (Sederholm, 1916), the grains being elongated and worm-like, perpendicular to the reaction front at which the product minerals grew from a single reactant mineral. The non-random, roughly periodic spacing of rods or lamellae should be explained in terms of reaction mechanism. Moëlo et al. (1988) described jamesonite-stibnite composite crystals, formed as epitaxial pseudomorphs after berthierite by partial replacement of the solid phase iron by lead in solution. Similar mechanism has been proposed by Wen et al. (1991) for bournonite-galena symplectites, replacing meneghinite, involving some diffusion replacement reaction in which Cu and S were added from the hydrothermal fluids. Wagner and Cook (1997) used isocon diagrams to reconstruct the reaction mechanisms of myrmekite formation affecting some complex Cu-Pb-Sb-Bi (±Zn-Fe) sulphides and sulphosalts.

In this paper we describe two types of galena-bearing myrmekitic intergrowths from the Radka Cu-Au deposit, Bulgaria (the term "symplectite" in the following is used as a synonym of "myrmekitic intergrowth"): galena-chalcocite and galena-bornite symplectites. Electron probe microanalysis (EPMA), scanning electron microscopy and image analysis (IA) have been used to study the textural relationship, mineral chemistry and distribution of the myrmekites. The proposed mechanism of formation for the galena-chalcocite symplectites corresponds to breakdown of former betekhtinite under increasing temperature during the late stage of ore-formation at Radka, probably, assisted by enriched in Pb higher-temperature hydrothermal fluids. In contrast, the galena-bornite symplectites were most probably formed by partial metasomatic replacement of bornite by galena during the deposition of the betekhtinite-bearing assemblage.

Geological setting

The Radka deposit is one of the largest epithermal Cu-Au deposits in the Panagyurishte ore province. The mine closed in 1995. During the period 1942-1995 the mine produced about 68000 t of copper and 78950 t of sulphur (Milev et al. 1996). Recently, Tsonev *et al.* (2000a) defined the deposit as a transitional epithermal system with an intermediate sulphidation style of mineralisation, closer to the high-sulphidation type. The complex hypogene mineralisation at Radka has been studied intensively during the last 40 years by Radonova (1962), Tzonev (1982), Kovalenker et al. (1986), Tsonev et al. (2000b), Kouzmanov (2001), Kouzmanov et al. (2004). Two types of ore exist at Radka: massive ores, with as much as 85-90% of sulphides, forming lenticular or stock-like bodies, and veins, veinlets or dissemination of pyrite, chalcopyrite and quartz at the periphery of massive bodies. Massive ores consist of pyrite, chalcopyrite, bornite, tennantite, enargite, sphalerite, galena and chalcocite in different proportions, as well as numerous subordinate and rare Ge-, Ga-, In-, Sn-, Bi- and Te-bearing minerals. Fig. 1 summarizes the distribution of the main ore minerals within the different mineralisation stages at Radka, as well as the corresponding intervals of measured temperatures of homogenisation and salinities in fluid inclusions. The studied galena-bearing symplectites have been found as isolated "inclusions" or patches within massive bornite and chalcocite ore, formed during the fifth Cu-Pb (± As, Ge, Au, Ag) stage of mineralisation (Fig. 1).

Analytical techniques

Electron-microprobe analyses were performed with a CAMECA SX 50 electron microprobe operated at an acceleration potential of 25 kV, a probe current of 30 nA and with a beam diameter of 1 μm. Counting times were 20 s for all elements. $K\alpha$ lines were used for Fe, Cu, S; $L\alpha$ line for Ag; $M\alpha$ lines for Pb and Bi. The standards used were pure metals for Cu, Ag and Bi; pyrite (for Fe, S) and galena (for Pb). Apparent concentrations were corrected for matrix effects with the PAP correction program (Pouchou, Pichoir, 1984).

Selected samples, after reflected light microscopy, were examined using a JEOL JSM

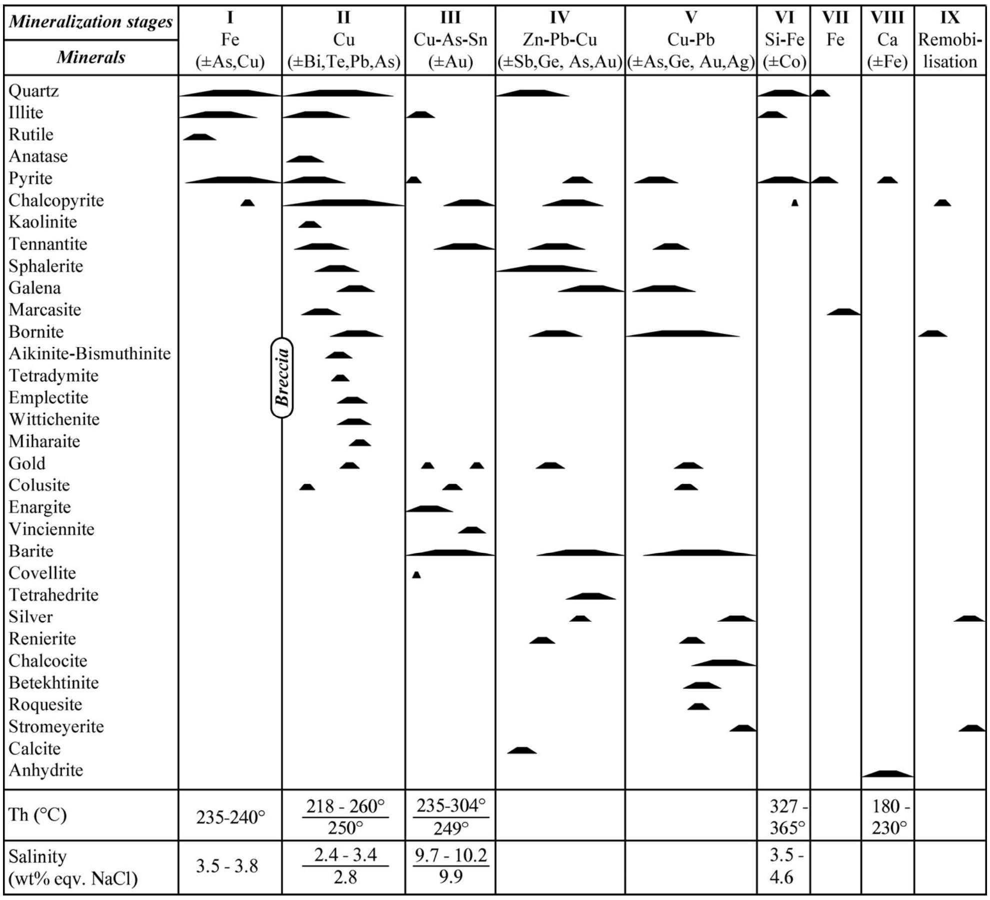

Fig. 1. Mineralisation stages in the Radka ore deposit. Temperatures of homogenisation (Th) and salinities, measured in fluid inclusions from different stages are indicated as well. Data are from Kouzmanov (2001) and Kouzmanov et al. (2002, 2004). Temperatures of homogenisation for the late Ca (±Fe) stage are from Strashimirov and Kovachev (1992)

Фиг. 1. Стадии на минерализация в находище Радка. Представени са също температурите на хомогенизация (Th) и соленостите, измерени във флуидни включения от различните стадии. Данните са от Kouzmanov (2001) и Kouzmanov et al. (2002, 2004). Температурите на хомогенизация за късния Ca (±Fe) стадий са от Страшимиров и Ковачев (1992)

6400 scanning electron microscope (SEM) equipped with a KEVEX Delta energy-dispersion spectrometer (EDS). Based on back-scattered electron (BSE) images, image analysis has been performed using the Scion software* in order to quantify mineral phase proportions of symplectites.

Mineralogy and textures

Two types of galena-bearing myrmekitic intergrowths (Fig. 2) were observed in coarse-grained copper ore comprising chalcopyrite, bornite, chalcocite, galena, tennantite, with minor sphalerite and roquesite: galena-

* Scion Image for Windows (http://www.scioncorp.com)

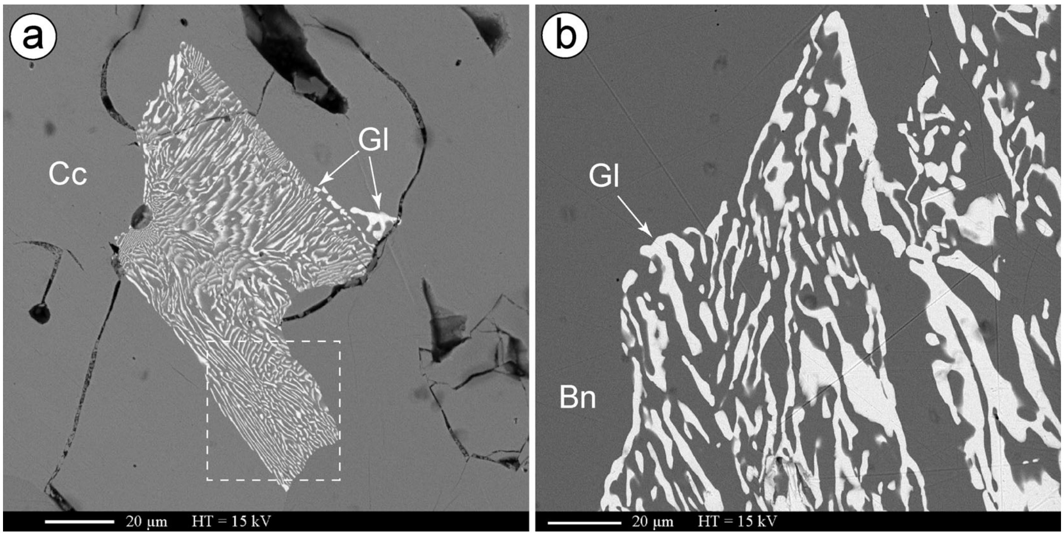

Fig. 2. Back-scattered electron (BSE) images of galena-bearing symplectites from the Radka deposit: a) Galena-chalcocite symplectite in chalcocite matrix. The small rectangle shows the area used for image analysis, as shown on Fig. 3; b) Galena-bornite symplectite in bornite matrix. *Abbreviations*: Gl – galena, Cc – chalcocite, Bn – bornite

Фиг. 2. BSE изображения на галенит-съдържащи симплектити от находище Радка: а) Галенит-халкоцитов симплектит в халкоцитова основна маса. Малкият правоъгълник отговаря на областта използвана за имидж анализ, както е показано на фиг. 3; b) Галенит-борнитов симплектит в борнитова основна маса. *Съкращения:* Gl – галенит, Cc – халкоцит, Bn –борнит

chalcocite and galena-bornite intergrowths. Betekhtinite (Tsonev et al. 1970) is also a very common mineral in this assemblage, but it has never been observed in sections where galena-bearing symplectites are present.

Galena-chalcocite intergrowths (Fig. 2a) occur as very well defined symplectitic grains within a chalcocite matrix. Their size varies between 50 and 200 μm in diameter. The two-component symplectites have very sharp contacts with the ambient chalcocite and show typical graphic texture. Galena lamellae (1-2 μm thick) are commonly perpendicular to the symplectite border and develop a typical rounded "fingering" (Ramdohr, 1980) – rounded finger-like endings of the galena rods. In cross polarized reflected light the chalcocite symplectite matrix shows the same extinction in all parts of the structure, thus indicating the presence of a single chalcocite crystal. Its orientation regarding the host chalcocite is different.

Galena-bornite intergrowths (Fig. 2b) form more irregular in shape patches embedded in a bornite matrix, or at the contact between bornite and tennantite, as well as partial rims embaying galena. They are much larger than the galena-chalcocite symplectites and may reach up to 500 μm in diameter. The galena lamellae are also much thicker, up to 10-20 μm, and their distribution within the symplectites is much more irregular.

Image analysis

In order to quantify the phase proportion and composition of the symplectitic galena-chalcocite and galena-bornite grains, image analysis has been performed on selected areas with well defined phase contrast on the BSE images (Fig. 3a). The first step consists of selecting and extracting of the external matrix from the initial image (Fig. 3b). Then, the

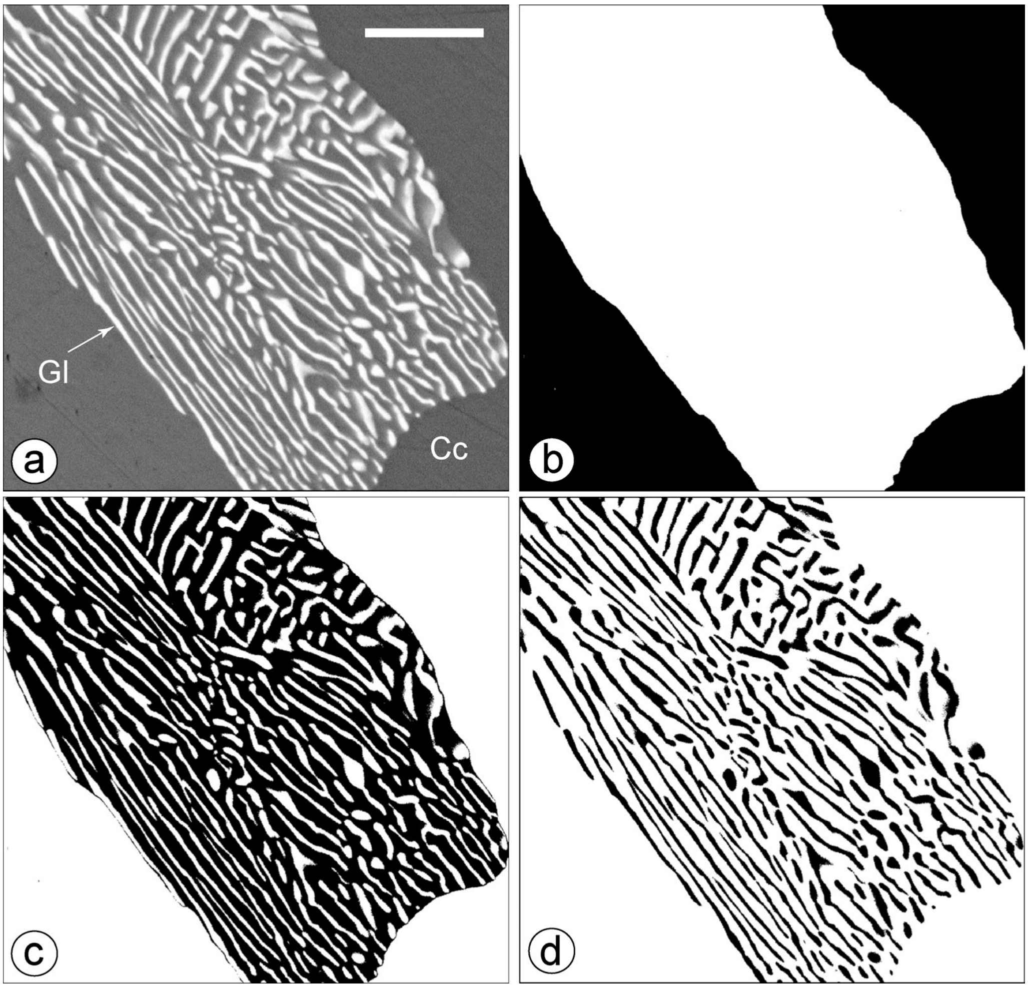

Fig. 3. Image analysis on galena-chalcocite symplectite. Selected area is shown on Fig. 2a: a) BSE image (1 007 616 pixels). Scale bar = 10 µm; b) Subtraction of the symplectitic grain (686 400 pixels) from the chalcocite matrix; c) Chalcocite matrix of the symplectitic grain (468 397 pixels); d) Galena lamellae of the symplectitic grain (218 003 pixels). *Abbreviations*: as in Fig. 2

Фиг. 3. Image анализ на галенит-халкоцитов симплектит. Използваната за изчисленията област е показана на фиг. 2a: a) BSE изображение (1 007 616 pixels). Мащаб = 10 µm; b) Отделяне на симплектитовото зърно (686 400 pixels) от халкоцитовата основа маса; c) Халкоцитова основа маса на симплектитовата структура (468 397 pixels); d) Галенитови ламели от симплектитовата структура (218 003 pixels). *Съкращения:* както на фиг. 2

symplectitic grain is decomposed using different intervals of greyscale onto symplectite matrix (Fig. 3c) and symplectite lamellae (Fig. 3d). For both, the surface (in number of pixels) has been calculated, assuming the total surface of the symplectite as 100%. Table 1 summarizes the image analysis results on the two types of myrmekitic intergrowths at Radka. In the case of galena-chalcocite symplectite galena lamellae constitute 31.76% of the grain, against 68.24% of chalcocite matrix. In the galena-bornite symplectite the proportion is slightly different: 38.99% against 61.01%, respectively.

Table 1. *Results of the image analysis of galena-chalcocite and galena-bornite myrmekitic intergrowths (in number of pixels). Phase proportions (in %) between galena and chalcocite, and galena and bornite, respectively, are indicated as well*

Таблица 1. *Резултати от имидж анализ на галенит-халкоцитова и галенит-борнитова мирмекитова структура (в брой пиксели). Фазовите отношения (в %) между галенит/халкоцит и галенит/борнит също са отбелязани*

Galena-chalcocite myrmekite	Image	External matrix	Myrmekitic grain	Phases	
				Galena	Chalcocite
	1 007 616	312 216	686 400	218 003	468 397
			100%	31.76%	68.24%

Galena-bornite myrmekite	Image	External matrix	Myrmekitic grain	Phases	
				Galena	Bornite
	1 007 616	326 999	680 617	265 362	415 255
			100%	38.99%	61.01%

Betekhtinite – textures and mineral assemblage

Betekhtinite in the Radka deposit formed mainly as a product of metasomatic replacement of bornite. It forms irregular grains and veinlets in massive patchy textures (Figs. 4a and 4b) and rarely – idiomorphic crystals (Fig. 4c). Its mineral association consists of bornite, tennantite, chalcocite, galena, roquesite and abundant barite. Rarely, it coexists also with sphalerite, colusite and renierite. Betekhtinite formed after bornite and galena, and is corroded by the chalcocite, which is the latest mineral of the assemblage (Figs. 1 and 4a). Bornite relicts observed in the betekhtinite (Fig. 4b) give a textural evidence of replacement of bornite by betekhtinite by solid-state reaction. In all studied samples betekhtinite is intimately associated to roquesite which forms usually idiomorphic single crystals or twins as inclusions in the later (Fig. 4a). Roquesite is also corroded by the later chalcocite (Fig. 4c).

The galena-bearing composite crystals occur in the same mineral assemblage as betekhtinite, but they do not coexist. If symplectites are present in the studied samples, betekhtinite is absent and *vice-versa*.

Mineral compositions

Table 2 summarizes results from electron microprobe analyses of chalcocite, bornite and galena from the studied samples. Chalcocite systematically shows trace amounts of Fe (0.17-0.63 wt.%) and Ag (0.07-0.24 wt.%). Bornite sporadically shows presence of Ag, Pb and Bi as trace elements. Galena is completely depleted in trace elements. Just one analysis of galena lamella from a galena-bornite myrmekite (n° 26; Table 2) shows high Cu content (2.6 wt.%), which is probably due to the small size of the analyzed grain and in this case - to unavoidable matrix effect.

Betekhtinite has also been systematically analyzed on the electron microprobe (Table 3). Its composition is homogeneous, sometimes with Ag (up to 0.27 wt.%) or Bi (up to 0.24 wt.%) as trace elements. The average composition of betekhtinite from Radka shows small excess of Cu and slightly lower Pb and S content, compared to the theoretical one (Table 3). Despite this small variations, the composition of betekhtinite from Radka fits well to the theoretical formula: $Pb_2(Cu,Fe)_{21}S_{15}$, proposed by Dornberger-Schiff and Höhne (1957).

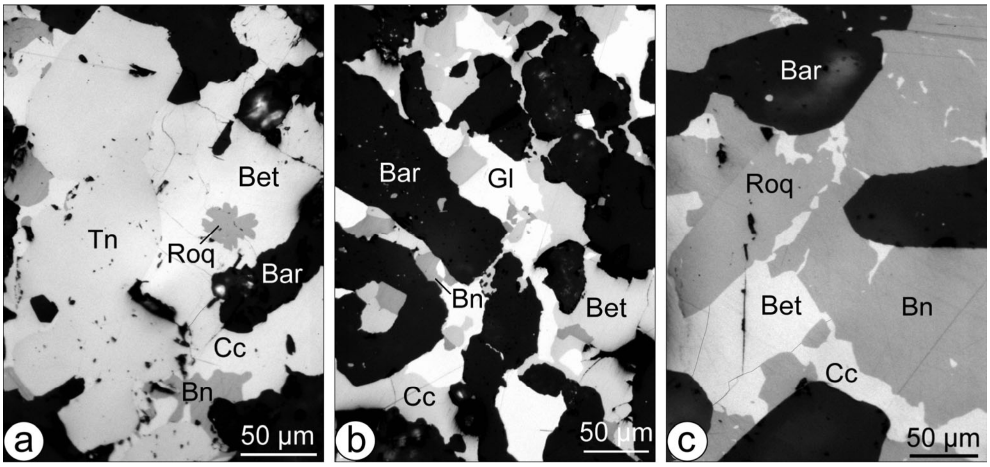

Fig. 4. Mineral association of betekhtinite in massive chalcocite-bornite ore from the Radka deposit. Microphotographs in reflected light: a) Tennantite, chalcocite and bornite associated with betekhtinite, hosting roquesite inclusions; b) Betekhtinite with bornite relicts associated with chalcocite and galena in a gangue of barite; c) Idiomorphic roquesite and betekhtinite crystals in bornite matrix, corroded by chalcocite. *Abbreviations*: Bar – barite, Bet – betekhtinite, Bn – bornite, Cc – chalcocite, Gl – galena, Roq – roquesite, Tn – tennantite

Фиг. 4. Минерална асоциация на бетехтинит от масивни халкоцит-борнитови руди от находище Радка. Микрофотографии в отразена светлина: a) Тенантит, халкоцит и борнит в асоциация с бетехтинит, съдържащ рокезитови включения; b) Бетехтинит с реликти от борнит, в асоциация с халкоцит и галенит, сред баритова нерудна маса; c) Идиоморфни рокезитови и бетехтинитови кристали сред борнитова маса, кородирана от халкоцит. *Съкращения:* Bar – барит, Bet – бетехтинит, Bn – борнит, Cc – халкоцит, Gl – галенит, Roq – рокезит, Tn – тенантит

Two analyses of galena-chalcocite symplectite have been done with unfocused beam, scanning a square surface of 20 × 20 µm (analyses n° 20-21; Table 3). The average symplectite composition determined by this method corresponds to: Cu (50.09 wt.%), Pb (30.49 wt.%), Fe (0.31 wt.%), Ag (0.17 wt.%), Bi (0.18 wt.%) and S (19.04 wt.%).

Discussion

Origin of the galena-bearing myrmekites and their relation with betekhtinite

Betekhtinite was first described by Schüller and Wolhmann (1955) from the Mahnsfeld Kupferschiefer, Germany and was subsequently reported from some other localities including Djeskasgan deposit, Kazakhstan, former USSR (Satpaeva, 1959; Mukanov et al., 1960); Mt. Lyell, Tasmania (Markham, Ottemann, 1968); Urup deposit, former USSR (Kachalovskaya, Khromova, 1970); Furutobe mine, Japan (Matsukuma, 1970); La Leona deposit, Argentina (Honnorez-Guerstein, 1971). In all these occurrences betekhtinite-bearing assemblage consists of bornite, chalcocite, galena, with minor amount of tennantite and digenite, and quartz and/or carbonates as gangue minerals. In some localities galena-chalcocite and/or galena-bornite symplectitic intergrowths have been also described.

Tsonev et al. (1970) reported for the first time the presence of betekhtinite in massive ores from the Radka deposit, Bulgaria. They described the mineral association of betekhtinite, performed detailed X-ray diffraction analysis and determined its physical properties, such as grain size distribution, optical properties, reflectance spectrum, and micro-indentation hardness. Tsonev et al. (1970) mentioned the presence of Ag, Bi and As as trace elements, in addition to the major

Table 2. *Representative compositions of chalcocite, bornite and galena from the betekhtinite-bearing assemblage in the Radka deposit, Bulgaria*
Таблица 2. *Представителни състави на халкоцит, борнит и галенит от бетехтинит-съдържащата парагенеза в находище Радка*

Mineral	Chalcocite							Bornite					
Analysis n°	1	2	3	4	5	6	7	8	9	10	11	12	13
Cu, wt.%	79.53	79.37	78.70	77.98	78.51	78.36	78.92	63.57	63.21	63.29	62.73	62.03	62.20
Pb	--	--	--	0.10	--	--	--	--	--	--	--	0.11	--
Fe	0.63	0.52	0.17	0.24	0.55	0.31	0.24	10.54	10.58	10.82	10.92	11.29	10.97
Ag	0.07	0.11	0.24	0.17	0.09	0.08	0.12	--	0.12	0.15	--	--	--
Bi	--	--	--	--	--	--	--	0.10	--	0.09	--	--	--
S	20.94	20.97	20.94	20.92	21.34	20.62	21.03	25.59	25.65	25.64	26.05	25.64	26.07
Total	101.17	100.98	100.05	99.40	100.50	99.38	100.31	99.80	99.56	99.99	99.70	99.07	99.24
	Σ atoms = 3							Σ atoms = 10					
Cu, *apfu*	1.959	1.958	1.959	1.952	1.939	1.965	1.958	5.032	5.011	5.002	4.948	4.933	4.923
Pb				0.001								0.003	
Fe	0.018	0.015	0.005	0.007	0.015	0.009	0.007	0.950	0.954	0.973	0.980	1.022	0.988
Ag	0.001	0.002	0.004	0.002	0.001	0.001	0.002		0.006	0.007			
Bi								0.002		0.002			
S	1.022	1.026	1.033	1.038	1.045	1.025	1.034	4.016	4.030	4.017	4.072	4.042	4.090
Total	3	3	3	3	3	3	3	10	10	10	10	10	10

Mineral	Bornite				Galena								
Analysis n°	14	15	16	17	18	19	20	21	22	23	24	25	26
Cu, wt.%	61.84	61.61	62.04	62.74	--	--	--	--	--	--	--	--	2.60
Pb	--	0.11	--	0.06	86.71	86.97	87.56	86.67	85.77	86.70	86.79	86.36	85.25
Fe	11.87	11.16	10.94	10.80	--	--	--	--	--	--	--	--	--
Ag	--	--	0.09	--	--	--	--	--	--	--	--	--	--
Bi	--	--	--	0.08	--	--	--	--	--	--	--	--	0.13
S	26.17	25.94	25.43	26.02	13.83	13.80	13.50	13.80	13.73	13.77	13.58	13.67	13.72
Total	99.87	98.81	98.49	99.70	100.54	100.76	101.06	100.47	99.50	100.47	100.37	100.03	101.71
	Σ atoms = 10				Σ atoms = 2								
Cu, *apfu*	4.861	4.900	4.965	4.954	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.093
Pb		0.003		0.001	0.985	0.987	1.002	0.986	0.983	0.987	0.994	0.989	0.934
Fe	1.062	1.009	0.997	0.971									
Ag			0.004										
Bi				0.002									0.001
S	4.077	4.088	4.034	4.072	1.015	1.013	0.998	1.014	1.017	1.013	1.006	1.011	0.972
Total	10	10	10	10	2	2	2	2	2	2	2	2	2

Table 3. *Representative compositions of betekhtinite from the Radka deposit, Bulgaria. Analyses n° 20-21 are of galena-chalcocite myrmekitic intergrowths (beam "spot" 20 × 20 µm)*

Таблица 3. *Представителни състави на бетехтинит от находище Радка, България. Анализи n° 20-21 са на галенит-халкоцитова мирмекитова структура (размер на електронния лъч 20 × 20 µm)*

Analysis n°	1	2	3	4	5	6	7	8	9	10	11	12
Cu, wt.%	59.24	58.93	59.49	59.48	59.51	59.48	59.26	59.23	59.16	59.14	59.11	59.11
Pb	17.62	17.59	17.22	17.86	17.54	16.99	17.43	17.13	17.63	17.63	17.62	17.65
Fe	2.29	2.20	2.31	2.21	2.22	2.22	2.25	2.22	2.41	2.44	2.46	2.42
Ag	0.27	0.18	0.26	0.16	0.11	0.14	0.13	0.18	--	--	--	--
Bi	--	0.16	0.11	0.13	0.24	--	--	--	--	--	--	--
S	20.23	20.13	20.39	19.91	20.37	20.56	20.36	20.36	21.09	20.88	21.02	20.83
Total	99.65	99.19	99.77	99.74	99.99	99.39	99.42	99.11	100.29	100.10	100.20	100.01
					Σ metals = 23							
Cu, *apfu*	20.213	20.233	20.246	20.238	20.261	20.328	20.270	20.298	20.215	20.202	20.199	20.208
Pb	1.844	1.852	1.797	1.864	1.831	1.781	1.829	1.800	1.848	1.847	1.846	1.850
Fe	0.889	0.861	0.894	0.854	0.861	0.862	0.874	0.867	0.938	0.949	0.955	0.942
Ag	0.054	0.037	0.052	0.031	0.021	0.029	0.027	0.035				
Bi		0.017	0.011	0.013	0.025							
S	13.681	13.697	13.754	13.428	13.745	13.925	13.801	13.834	14.281	14.138	14.239	14.117
Me/S	1.681	1.679	1.672	1.713	1.673	1.652	1.666	1.663	1.610	1.627	1.615	1.629

Analysis n°	13	14	15	16	17	18	19	Ave.	Theor.	20	21	Ave.
Cu, wt.%	58.73	58.65	58.86	58.26	58.20	58.53	58.28	58.98	57.20	49.71	52.27	50.09
Pb	17.77	17.74	17.72	17.68	17.71	17.87	17.75	17.59	18.65	31.13	29.84	30.49
Fe	2.74	2.56	2.55	2.43	2.42	2.48	2.29	2.35	2.51	0.07	0.54	0.31
Ag	--	--	--	--	--	--	--	0.08		0.16	0.18	0.17
Bi	--	--	--	--	--	--	--	0.03		0.12	0.24	0.18
S	21.08	20.77	20.79	20.97	20.71	20.72	20.79	20.63	21.64	19.03	19.05	19.04
Total	100.32	99.72	99.91	99.34	99.04	99.60	99.10	99.66	100.00	100.23	102.12	101.17
					Σ metals = 23							
Cu, *apfu*	20.070	20.131	20.147	20.166	20.165	20.141	20.210	20.215	20.0			
Pb	1.863	1.868	1.860	1.877	1.882	1.886	1.888	1.849	2.0			
Fe	1.067	1.001	0.993	0.957	0.953	0.972	0.902	0.918	1.0			
Ag								0.015				
Bi								0.004				
S	14.279	14.130	14.103	14.390	14.224	14.134	14.289	14.014	15.0			
Me/S	1.611	1.628	1.631	1.598	1.617	1.627	1.610	1.641	1.533			

Cu, Pb, Fe and S, determined by electron microprobe analysis. The authors presented textural evidence for the formation of betekhtinite at Radka as a product of diffusion-like replacement of bornite with partial heritage of its structure, as well as for later replacement of betekhtinite by chalcocite.

Slavskaya et al. (1963) studied the thermal properties of betekhtinite and found out that after heating at temperatures higher than 150°C the mineral undertook irreversible decomposition onto galena-digenite mixture. Their conclusion that betekhtinite is stable just at low temperatures (<150°C) has been confirmed later on by Craig and Kullerud (1968) who were not able to produce phase analogous to pure betekhtinite during mineral synthesis experiments at temperatures between 200° and 600°C in the system Cu-Pb-Fe-S. Based on their results Craig and Kullerud (1968) concluded that betekhtinite is not stable in the Cu-Pb-S system above 200°C. To explain the presence of composite galena-chalcocite and galena-bornite crystals in some of the Djeskasgan ores, Slavskaya et al. (1963) proposed the hypothesis of local reheating of the system (at temperature >150°C) provoking the thermal decomposition of the betekhtinite and its transformation to composite galena-chalcocite and galena-bornite symplectites.

To test this hypothesis for the galena-bearing symplectites at Radka, we combined the results of electron microprobe and image analyses. Perfect linear correlation exists between galena-chalcocite symplectite composition determined by EPMA and the one, estimated on the basis of image analysis of mineral phase proportions between galena and chalcocite and their average chemical compositions (Fig. 5). The obtained result shows that the IA is a method that could be successfully used for quantitative study of the chemical composition of complex myrmekitic-like textures, in combination with EPMA data for the different mineral phases present. Thus the estimated mineral compositions of galena-chalcocite and galena-bornite myrmekitic intergrowths (Table 1) have been used to quantify the chemical composition of the

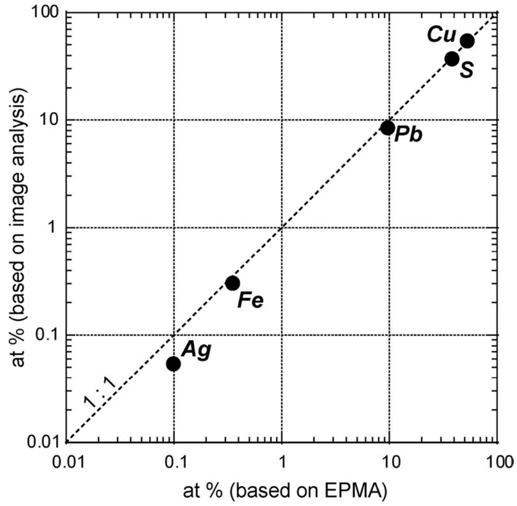

Fig. 5. Copper, lead, sulphur, iron and silver content of the galena-chalcocite symplectite measured on the electron microprobe versus composition estimated on the basis of image analysis. For the calculations average compositions of chalcocite and galena from the betekhtinite-bearing assemblage in the Radka deposits (Table 2) have been used

Фиг. 5. Съдържания на мед, олово, сяра, желязо и сребро в галенит- халкоцитов симплектит, измерени с електронно-микросондов анализ, спрямо съдържанията на същите елементи, изчислени въз основа на image анализ. За изчисленията са използвани средните състави на халкоцит и галенит от бетехтинит-съдържащата парагенеза в находище Радка (табл. 2)

studied composite grains, based on the average mineral compositions of chalcocite, bornite and galena from the studied assemblage at Radka (Table 2).

The calculated compositions of galena-bearing symplectites were plotted versus the average composition of betekhtinite from Radka (Fig. 6). Almost perfect correlation exists between the galena-chalcocite myrmekite and the betekhtinite compositions (Fig. 6a). Copper and sulphur remain constant; lead is slightly enriched in the symplectite, while iron is slightly enriched in the betekhtinite. Such an element distribution is in favour of the hypothesis of the galena-chalcocite symplectite formation as a derivate of betekhtinite breakdown, with addition of small amount of

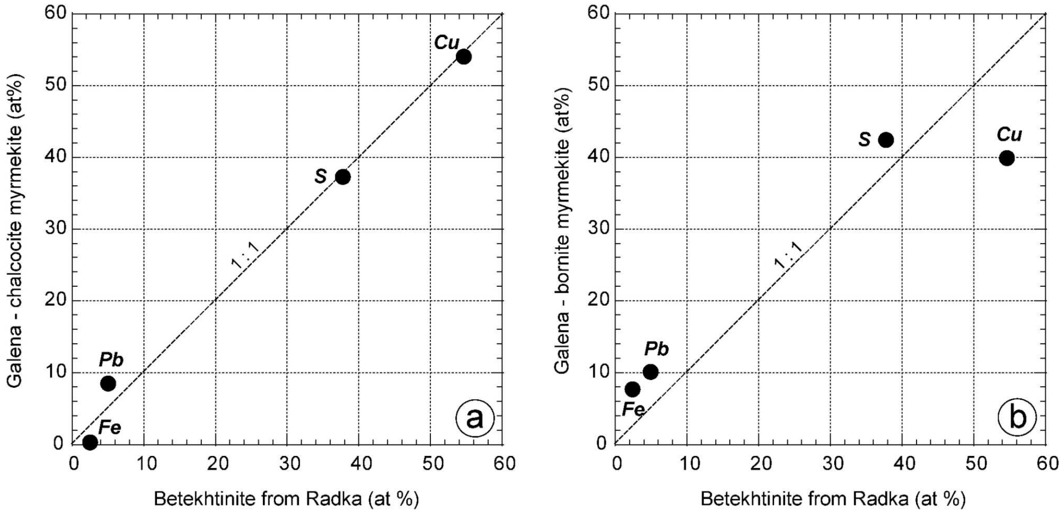

Fig. 6. Projection of the betekhtinite composition from Radka versus composition of symplectites (at.%). Concentrations are based on image analysis results, taking in account the average compositions of galena, chalcocite and bornite from Radka (Table 2). Betekhtinite composition is based on electron microprobe analyses (Table 3): a) Galena-chalcocite symplectite; b) Galena-bornite symplectite

Фиг. 6. Проекция на състава на бетехтинит от Радка спрямо състава на изследваните симплектити (в ат.%). Съдържанията са изчислени въз основа на резултатите от image анализ, вземайки предвид средните състави на галенит, халкоцит и борнит от находище Радка (табл. 2). Съставът на бетехтинита е определен с електронно-микросондов анализ (табл. 3): а) Галенит-халкоцитов симплектит; b) Галенит-борнитов симплектит

Pb by the hydrothermal fluid. Compositional relations represented on Fig. 7, where compositions of the galena-bearing symplectite from Radka are projected onto the PbS-Cu_2S-FeS diagram, together with galena, chalcocite, bornite and betekhtinite compositions, strongly support such an interpretation. Similar mechanisms of formation were proposed for jamesonite-stibnite (Moëlo et al., 1988) and bournonite-galena (Wen et al., 1991) symplectites.

Brodin (1960, 1963) gave a detailed description of galena-chalcocite myrmekites from the Ken-Shanik (former USSR) and Vrancic (Check Republic) deposits, which are very similar texturally to those, observed at Radka. The author interpreted these textures, mainly based on petrographic observations, as formed by crystallographically oriented diffusion replacement of chalcocite by galena. Such a mechanism is not acceptable for the galena-chalcocite symplectites in Radka, because of the very sharp contacts of their composite grains (Fig. 2a), but is a plausible explanation for the observed galena-bornite myrmekitic aggregates, where the variations in composition are much more pronounced, compared to the galena-chalcocite myrmekite (Figs. 6b and 7). This composite structure is enriched in S, Pb and Fe, and depleted in Cu, regarding the betekhtinite composition. No one element is lying onto the 1:1 line on Fig. 6b. Such a configuration is difficult to be explained by simple decomposition of betekhtinite, without a very important mobility of all elements involved in the reaction. As Wen et al. (1991) mentioned, in a replacement process, there is transport on a scale larger than the reacting system, but some more local effect is necessary to produce a symplectitic texture. The later can be attributed to diffusion control if at least two constituents are approximately conserved, defining an isocon, which is not the case of the galena-bornite symplectite from Radka.

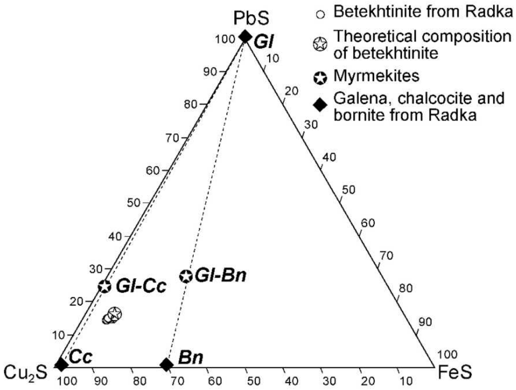

Fig. 7. Compositional relations represented in the system PbS-Cu_2S-FeS. Compositions of betekhtinite, galena, chalcocite and bornite from Radka are plotted, together with the two types of galena-bearing symplectites. Dashed lines indicate the two symplectite trends. *Abbreviations*: as in Fig. 2

Фиг. 7. Минерални взаимоотношения в системата PbS-Cu_2S-FeS. Проектирани са съставите на бетехтинит, галенит, халкоцит и борнит от находище Радка, както и съставите на галенит-съдържащите симплектити. Двата симплектитови тренда са показани с пресечени линии. *Съкращения:* както на фиг. 2

Another possible explanation consists of partial metasomatic replacement of bornite by galena, in the sense of Brodin (1963), giving rise to the observed myrmekitic texture (Ramdohr, 1980). The more diffuse nature of the borders of galena-bornite symplectite (Fig. 2b), compared to the galena-chalcocite one, supports such an idea. Because mutual crystal orientation between galena lamellae and bornite matrix has not been observed in the myrmekites from Radka (galena lamellae have more oval-shaped character), it is difficult to suggest a topotaxial replacement mechanism *sensu stricto*. However, this idea could not be completely rejected because at low-temperature conditions (<170°C) bornite, having *Fm3m* symmetry with *a* 5.50 Å, turns into a pseudotetragonal orthorhombic structure *Pbca* with *a* 10.95Å, *b* 21.862 Å, and *c* 10.95 Å (Kanazawa et al. 1978), thus having *a* and *c* parameters corresponding to the ~2*a* parameter of galena (*a* 5.93 Å; Kostov, Minčeva-Stefanova, 1981).

Mechanism of formation, involving betekhtinite breakdown

Based on X-ray study on betekhtinite after heating experiments at temperatures >150°C, Slavskaya et al. (1963) proposed the following mechanism of betekhtinite breakdown to a mixture of galena and digenite: $2Pb_2Cu_{21}S_{15} \rightarrow 4PbS + 4.66Cu_9S_5$. Our results on Radka samples indicate that such a breakdown of the betekhtinite structure produced galena-chalcocite symplectites, instead of galena-digenite ones. In addition, the isocon diagram of this reaction (Fig. 6a) explicitly demonstrates that two of the major elements remain immobile during this reaction (Cu and S), but the two others (Pb and Fe) show different behaviour – Pb was transported by the fluids and "added" to the reaction, and Fe was leached partially during the replacement. According to this model and using the real mineral compositions of betekhtinite, galena and chalcocite from Radka, we can tentatively propose the following reaction to describe the betekhtinite transformation to galena-chalcocite symplectites:

$Pb_{1.85}(Cu_{20.21}Fe_{0.92})S_{14.01} + 1.51Pb_{sol} \rightarrow$
$3.39Pb_{0.99}S_{1.00} + 10.31(Cu_{1.96}Fe_{0.01})S_{1.03} +$
$0.82Fe_{sol}$

Experimental results of Slavskaya et al. (1963) and Craig and Kullerud (1968) determining betekhtinite stability just at low temperatures (generally <150°C) define the betekhtinite-bearing assemblage at Radka as a relatively late low-temperature paragenesis. Kouzmanov et al. (2004) determined a temperature range of ore-formation at Radka between 210 and 270°C for the main economic stages (all of them are pre-betekhtinite), based on fluid inclusion microthermometry (Fig. 1). However, the presence of symplectite structures, formed from betekhtinite breakdown indicates some local reheating of the system after the deposition of the betekhtinite-bearing assemblage. Another argument in favour of this hypothesis is the formation of late high-temperature quartz-pyrite veins at Radka at temperatures as high as 365°C (Kouzmanov et al., 2002), crosscutting the massive copper ore bodies and interpreted as an analogue of a deeply seated porphyry system. If such a high-temperature hydrothermal event took place after the deposition of the betekhtinite-bearing assemblage, it could be at the origin of the local thermal overprint affecting some parts of the massive ore bodies at Radka.

Conclusions

The two types of galena-bearing myrmekitic intergrowths from the Radka deposit, Bulgaria, are products of two different processes, separated also in time. Galena-bornite myrmekites were most probably formed by partial metasomatic replacement of massive bornite by galena during the deposition of the betekhtinite-bearing assemblage. A decomposition or breakdown of a former mineral phase is not a plausible hypothesis in this case, because all elements present show extremely high mobility, which is not typical for diffusion processes, where at least two of the major components should remain immobile during the replacement. Galena-chalcocite composite crystals show all characteristics of derivates of a breakdown of former betekhtinite crystals under increasing temperature during the late stage of ore-formation at Radka, probably, assisted by enriched in Pb higher-temperature hydrothermal fluids. Phase proportions and symplectite composition indicate that more mobile Pb and Fe were transported through the growing symplectite probably by grain-boundary diffusion, while Cu and S showed relative immobility during the replacement of betekhtinite.

The presence of betekhtinite derivate symplectite textures at Radka, formed at temperatures higher than the temperatures of original betekhtinite deposition, is another argument supporting the idea of later, probably post-ore formation, reheating of the mineralised epithermal system at Radka by fluids derived from a deeper porphyry system (Kouzmanov et al., 2002).

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