EXPERIMENTAL STUDY OF CRYSTALLIZATION PRODUCTS OF CHALCOPYRITE SOLID SOLUTION

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In order to understand the conditions of formation of cubanite $CuFe_2S_3$, talnakhite $Cu_9Fe_8S_{16}$, mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$ in magmatic Cu-Fe ores of the Norilsk type the method of melt cooling from 1150 – 1100°C up to room temperature and subsequent annealing at 600 and 800°C phase associations of the central part of Cu-Fe-S system have been synthesized: 50 at.% of S, Cu/Fe = 1.22 – 0.25, 47 at.% S, Cu/Fe = 1.12 – 0.63 and 45 at.% S, Cu/Fe = 1.44 – 0.69. According to the received results, cubic cubanite enriched in copper (Cu/Fe ≥ 0.5) crystallizes in associations with tetragonal chalcopyrite $Cu_{1-x}Fe_{1+x}S_2$ and cubic talnakhite. The new data concerning steady phase equillibriums of mooihoekite with bornite Cu_5FeS_4 and cubic pc phase of the haycockite composition with cubic cubanite enriched in iron (Cu/Fe ≤ 0.5) bornite and pyrrhotite $Fe_{1-x}S$ are received.

1 figure, 1 table, 20 references.
Key words: Cu-Fe-S system, chalcopyrite solid solution, crystallization of melt.

Introduction

Cubic talnakhite $Cu_9Fe_8S_{16}$ (Bud`ko, Kulagov, 1963; Cabri, 1967), tetragonal mooihoekite $Cu_9Fe_9S_{16}$ (Cabri, Hall, 1972; Muraviova *et al.*, 1972), rhombic haycockite $Cu_4Fe_5S_8$(Cabri, Hall, 1972) and cubic cubanite $CuFe_2S_3$ (Cabri, 1973) are attributed to the products of crystallization of chalcopyrite (Yund, Kullerud, 1966) intermediate (Merwin, Lombard, 1937) solid solution established experimentally in the central part of the Cu-Fe-S system at 800 – 300°C. Together with chalcopyrite $CuFeS_2$ these minerals are the basic components of the magmatic Cu-Fe ores of the Norilsk type. Close of compositions and complex intergrowths with each other and other sulfides complicate diagnostics of natural minerals and do not allow to determine unambiguously their age relations and to connect features of their composition and structure with definite conditions of crystallization. The basic experimental researches of the Cu-Fe-S system (Yund, Kullerud, 1966; Kullerud *et al.*, 1969; Cabri, 1973; Barton, 1973; Likhachiov, 1973; Sugaki *et al.*, 1975; Vaughan, Craig, 1981; Vaughan, Craig, 1997; Tsujmura, Kitakaze, 2004) are connected with the sphere of existence of chalcopyrite solution at 800—300°C. Conceptions about phase equillibriums at low temperatures are not clear and inconsistent, because they are based on the results of investigation of natural phase associations and results of extrapolation of isolated experimental data in the sphere of low temperatures (Vaughan, Craig, 1981; Vaughan, Craig, 1997).

The purpose of the presented work is synthesis of steady at room temperature phase associations of the central part of the Cu-Fe-S system for determination of phase compositions and phase equillibriums in the sphere of chalcopyrite solid solution.

Methodics

Up to now the most complete experimental research of phases from the sphere of chalcopyrite solid solution is the work by L.J. Cabri (Cabri, 1973). The scheme of phase relations of the central part of the Cu-Fe-S system at 600°C constructed by Cabri agrees with the corresponding scheme of R.A. Jund and G. Kullerud at 700°C (Yund, Kullerud, 1966) and is an evident illustration of high-temperature and possible low-temperature phase associations in relation to the formation of tetragonal chalcopyrite (557°C, Yund, Kullerud, 1966). Hence, the scheme of Cabri (black hatch lines on the Fig.) has been used as a basis for a choice of initial compositions of samples synthesized in the presented work. As evident from the Figure, initial compositions of the synthesized samples correspond to compositions of possible phase associations with the listed above products of crystallization of the chalcopyrite solid solution (iss on the Figure).

Synthesis of samples is performed from the following elements: carbonyl iron A-2, copper B3 and ultrapure sulfur additionnally dehydrated by melting in vacuum. All samples have been synthesized in evacuated quartz ampoules by a method of melt cooling from 1150—1100°C up to room temperature. The temperature of melt (≈ 1070°C) is determined according to the results of the thermal analysis of the most infusible initial samples. The mode of cooling has been chosen experimentally in view of the data on temperatures of the iss crystallization. Cooling was

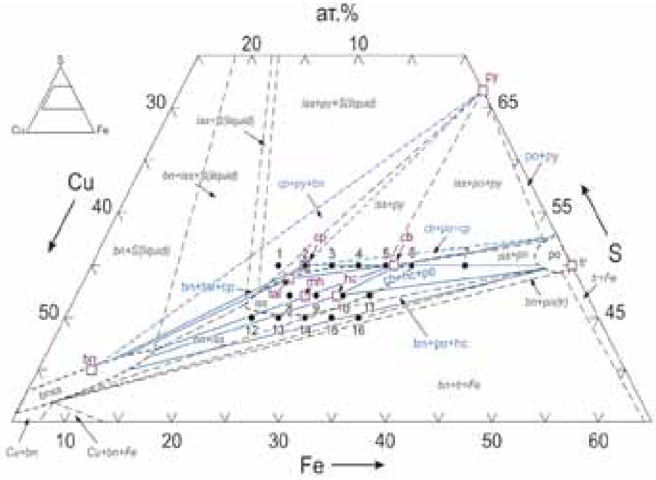

Fig. 1. The scheme of relationships of the phases synthesized in the presented work (continuous blue lines) on the scheme of phase relations of the central part of system Cu-Fe-S from Cabri (Cabri, 1973) at 600˚C (hatch black lines, Cabri, 1973). 1—16 — initial compositions of the synthesized samples. iss, bnss and po — areas chalcopyrite, bornite and pyrrhotite solid solutions. □ — stoichiometric compositions of minerals: tetragonal chalcopyrite $CuFeS_2$ (cp), bornite Cu_5FeS_4 (bn), pyrite FeS_2 (py), troilite FeS and products of crystallization of chalcopyrite solid solution (iss): talnakhite $Cu_9Fe_8S_{16}$ (tal), cubanite $CuFe_2S_3$ (cb), mooihoekite $Cu_9Fe_9S_{16}$ (mh) and haycockite $Cu_4Fe_5S_8$ (hc). On the Figure by hatch blue lines equillibriums with participation of phases present in insignificant quantities (designated by asterisk in the Table) are designated. These phases are formed after iss crystallization (Cabri, 1973).

carried out in two stages. The first stage — fast cooling (with a rate of 50° per hour) up to 1000, 900, 850 or 800°C and keeping at these temperatures from several hours up to 10 days. The second stage — slow cooling (with a rate of 60° per a day) up to 300°C, keeping at 300°C from several hours up to 3 months, further cooling up to room temperature with the switched off furnace. Fast cooling was performed for determination of the iss composition at temperatures of melt crystallization (1000— 850°C, Yund, Kullerud, 1966) in view of the data on the melt existence at 800°C (Tsujmura, Kitakaze, 2004). It is a mode I. Further representative parts of the synthesized samples annealed at 600°C within 1.5 months, and at 800°C — within 20 days with the subsequent cooling in cold water. It is a mode II.

Synthesized samples have been investigated by methods of optical microscopy and X-ray analysis. Polished sections are prepared from half of each sample (section along the center from top- down). The chemical composition of phases is determined by microprobe analysis with the help of microanalyzer "Camebax-Micro". Chalcopyrite $CuFeS_2$ is used as a standard. Accelerating voltage — 20 кV, current of absorbed electrons — 40 nA, angle of sampling — 40 °, time of account — 10 seconds on each analytical line, diameter of probe — 2—3 microns. Precision of determination of all components is within the limits of 2 relative %. Detection limit of elements C_{min} is calculated according to 2δ-criterion at a significance level of 99%. C_{min} is as follows (in weight %): Cu — 0.04; Fe — 0.03; S — 0.01. X-ray phase analysis was performed with the help of diffractometer DRON-3.

Results

For the phases synthesized in the presented work the following standard names of their natural analogues of stoichiometric composition and corresponding structure are used: cubic talnakhite $Cu_9Fe_8S_{16}$, tetragonal bornite Cu_5FeS_4, chalcopyrite $CuFeS_2$ and mooihoekite $Cu_9Fe_9S_{16}$, rhombic cubanite $CuFe_2S_3$ and haycockite $Cu_4Fe_5S_8$. Thus in the presented work, as well as in the work by Cabri (Cabri, 1973), for the synthesized phases with cubanite and haycockite compositions the cubic structure (fcc and pc, respectively) is established.

Results of synthesis of phase associations of the central part of the Cu-Fe-S system (samples with the following compositions: 50 at.% of S, Cu/Fe = 1.22—0.25; 47 at.% of S, Cu/Fe = 1.12—0.63 and 45 at.% of S, Cu/Fe = 1.44—0.69) containing the listed above products of iss crystallization are shown in the Table and on the Figure. For the samples synthesized by cooling of the melt from 1150°C up to room temperature (modes I), composition of all synthesized phases is presented. For the samples synthesized according to the mode I with subsequent annealing at

Table 1. **Results of synthesis of the samples belonging to the central part of system Cu-Fe-S**

N of sample	Synthesis according to modes I					Synthesis according to modes II			
Initial composition: S, Cu, Fe, at.%	Phases	Composition of phases, at.%, weight %			Total, weight %	Composition of phases, at.%, weight %			Total, weight %
Cu/Fe		Cu	Fe	S		Cu	Fe	S	
1	cp	25.28	24.86	49.86		25.29	24.98	49.73	
50, 27.5, 22.5		34.90	30.17	34.72	99.79	34.86	30.26	34.59	99.71
1.22	bn	47.90	10.79	41.31		*30.41*	*23.38*	*46.21*	
		60.78	12.04	26.46	99.28	*40.72*	*27.52*	*31.22*	*99.46*
	py*						bn, *bn*		
1a	tal	27.64	23.34	49.02		26.92	24.63	48.45	
50, 27.5, 22.5		38.00	28.19	33.99	99.79	36.64	29.45	33.27	99.36
1.22	iss	32.70	20.51	46.79		32.31	21.33	46.36	
		43.76	24.13	31.59	99.48	43.08	25.00	31.19	99.27
						29.62	*23.34*	*47.04*	
						39.80	*27.58*	*31.92*	*99.30*
							bn, *bn*		
5	tal + cb	25.54	25.81	48.65		27.72	24.53	47.75	
50, 17.5, 32.5		34.97	31.07	33.61	99.65	37.68	29.30	32.74	99.72
0.54									
8	tal	27.04	24.12	48.84		26.29	24.63	49.08	
47, 28, 25		36.68	28.75	33.42	98.85	35.80	29.48	33.52	98.80
1.12	cp	25.43	24.71	49.86			bn		
		34.86	29.76	34.48	99.10				
	bn	48.32	11.59	40.09					
		60.69	12.80	25.41	98.90				
2	cp	24.36	25.83	49.81		24.81	25.69	49.50	
50, 25, 25		33.43	31.15	34.48	99.06	33.94	30.90	34.16	99.00
1						*24.98*	*26.06*	*48.96*	
	bn*, py*					*33.99*	*31.16*	*33.61*	*98.76*
3	cp + cb	23.34	27.87	48.79		23.19	27.46	49.35	
50, 22.5, 27.5		32.16	33.74	33.90	99.80	31.74	33.02	34.07	98.83
0.82						*23.16*	*28.59*	*48.25*	
	py*					*31.79*	*34.49*	*33.41*	*99.69*
4	cp	22.72	27.67	49.61		19.82	30.14	50.04	
50, 20, 30		31.50	33.72	34.70	99.92	27.56	36.84	35.09	99.49
0.67	cb	17.64	33.08	49.28		*20.08*	*30.30*	*49.62*	
		24.54	40.44	34.59	99.57	*27.71*	*36.78*	*34.56*	*99.05*
5a	cp	22.08	28.28	49.64		20.93	29.29	49.78	
50, 17.5, 32.5		30.47	34.23	34.49	99.13	28.86	35.50	34.63	98.99
0.54	cb	18.15	32.48	49.37		17.34	33.13	49.53	
		25.20	39.62	34.58	99.40	23.92	40.17	34.46	98.55
	py*, po*					19.54	31.90	48.56	
	bn*					26.92	38.62	33.75	99.29
6	cb	16.33	34.07	49.60		16.56	34.06	49.38	
50, 15, 35		22.86	41.90	35.03	99.46	23.10	41.73	34.73	99.56
0.43	hc	22.41	30.65	46.94		23.66	30.46	45.88	
		30.38	36.52	32.10	99.51	31.78	35.95	31.07	98.80
	po	2.01	47.90	50.09		*19.86*	*32.00*	*48.14*	
		2.88	60.39	36.24	99.51	*27.34*	*38.72*	*33.43*	*99.49*
							po, *po*		

Table 1.

7	cb	14.74	35.07	50.19		15.31	35.62	49.07	
50, 10, 40		20.72	45.34	35.61	99.67	21.31	43.58	34.46	99.35
0.25	po	1.08	48.50	50.42		*17.37*	*33.75*	*48.88*	
		1.55	61.30	36.58	99.43	*24.00*	*41.00*	*34.08*	*99.08*
						21.28	*31.53*	*47.19*	
						38.94	*37.68*	*32.37*	*98.99*
							po, *po*		
9	mh	25.64	27.21	47.15		25.81	27.52	46.67	
47, 25.5, 27.5		34.74	32.34	32.25	99.33	35.03	32.83	31.97	99.83
0.93	bn	45.37	13.68	40.95			bn		
		58.10	15.40	26.46	99.96				
12	mh	25.82	27.17	47.01		25.95	27.19	46.86	
45, 32.5, 22.5		34.91	32.29	32.07	99.27	35.11	32.33	31.98	99.42
1.44	bn	46.19	12.92	40.89		31.75	23.46	44.79	
		59.04	14.51	26.37	99.92	42.06	27.31	29.93	99.30
								bn	
10	hc	23.29	29.19	47.52		22.79	29.37	47.84	
47, 23, 30		31.73	34.96	32.68	99.36	30.94	35.05	32.77	98.76
0.77		49.40	11.05	39.55			bn		
	bn	62.37	12.26	25.19	99.82				
13	hc	23.71	29.40	46.89		24.53	28.22	47.25	
45, 30, 25		32.09	34.97	32.02	99.08	33.16	33.54	31.80	98.93
1.20	bn	47.52	12.86	39.62		*24.65*	*29.17*	*46.18*	
		60.24	14.34	25.35	99.93	*33.34*	*34.69*	*31.52*	*99.55*
							bn, *bn*		
11	hc	22.56	30.12	47.32		22.66	29.68	47.66	
47, 20.5, 32.5		30.75	36.09	32.55	99.81	31.00	35.69	32.91	99.60
0.63	bn	49.20	10.85	39.95			bn, po		
		62.87	12.18	25.75	100.80				
	po	1.65	47.85	50.50					
		2.37	60.46	36.62	99.46				
14	hc	23.09	30.05	46.86		22.83	30.39	46.78	
27.5 ,27.5, 45		31.63	36.18	32.38	100.19	31.09	36.36	32.13	99.58
1	bn	46.33	13.67	40.00			bn, po		
		58.76	15.24	25.60	99.60				
	po	1.27	48.46	50.27					
		1.81	60.85	36.24	98.90				
15	hc	22.56	30.45	46.99		23.54	29.84	46.62	
25, 30, 45		30.60	36.30	32.16	99.06	31.94	35.58	31.90	99.42
0.83	bn	44.52	14.90	40.58		*23.65*	*29.94*	*46.41*	
		56.50	16.62	25.99	99.11	*32.22*	*35.85*	*31.90*	*99.97*
	po	1.17	48.76	50.07			bn, po		
		1.68	61.88	36.47	100.03		*bn, po*		
16	bn	54.50	6.90	38.60			bn, po		
45, 22.5, 32.5		67.73	7.54	24.20	99.47		*bn ,po*		
0.69	po	1.86	48.08	50.06					
		2.67	60.68	36.36	99.97				

*Note: modes: I — cooling of samples from 1150°C with different speed in the interval 1000–850°C and further cooling up to room temperature, II — annealing of the samples synthesized according to the mode I at 600°C (usual font) and 800°C (italics) with cooling up to room temperature in cold water. For annealed samples (mode II) compositions of crystallization products of solid solution iss are shown. Composition of other phases (specified by badges) was not determined. Phases: cp — chalcopyrite, bn — bornite solid solution, py — pyrite, cb — cubanite, po — pyrrhotite, tal — talnakhite, mh — mooihoekite, hc — haycockite. * — Phases present in insignificant quantities on the surface or in cavities within the synthesized samples.*

600 and 800°C (modes II) — only composition of corresponding products of iss crystallization is presented. Influence of the cooling mode on phase composition of the investigated products of the melt crystallization has been established for samples of compositions No 1 and 5 and is discussed below. The scheme of relations of the synthesized phases is constructed according to the results of the modes I synthesis (blue lines on the Figure). Equillibriums with participation of the phases present in insignificant amount (they are designated by an asterisk in the Table) are shown by blue hatch lines on the Fig. 1.

Talnakhite $Cu_9Fe_8S_{16}$ it is synthesized in the samples No 1 and 1a, having the following composition: 50 at.% of S, Cu/Fe = 1.22, and in the sample No 8 with sulfur content — 47 at.% and Cu/Fe = 1.12. Talnakhite in it is in association with chalcopyrite and bornite. In the sample No 5 (50 at.% of S, Cu/Fe = 0.54) it is in the association with cubanite. In the sample No 1 cooled quickly up to 1000 or 900°C, talnakhite and chalcopyrite form very thin disinyegration structure. Only composition of chalcopyrite from this structure is determined. In the sample No 1a with the same composition as the sample No 1, but cooled quickly up to 800°C, talnakhite and iss are established. The composition of iss is located on the line talnakhite — bornite and corresponds to the extreme iss, enriched in copper, established at 600°C. The composition of the sample No 5 cooled quickly up to 1000°C corresponds to the composition of the mix of cubanite with talnakhite, and after the annealing at 600°C it is close to the talnakhite composition and to the initial composition of the sample No 8. In the sample No 8 which has been quickly cooled up to 850°C and kept at this temperature for 4 days, segregations of chalcopyrite and talnakhite, forming a disintegration structure larger than in the sample No 1. Both phases in this structure are easily determined. Except for the characteristic for talnakhite reflex 7.50, the X-ray diffraction pattern of the mix of talnakhite with chalcopyrite differs from the X-ray diffraction pattern of chalcopyrite by the bifurcation of the reflex 3.04, inverse ratio of intensities tetragonal doublets 1.870—1.856; 1.592—1.575 and displacement of reflexes 1.870 —1.856 towards big angles according to the reduction of interplanar spacing which is connected with an increase of the Cu/Fe ratio. Bifurcation of the reflex 3.04 on the X-ray diffraction pattern confirms the presence of two phases, and inverse ratio of intensities of tetragonal doublets 1.870—1.856; 1.592—1.575 corresponds to the greater content of cubic talnakhite in comparison with tetragonal chalcopyrite. Thus, talnakhite is synthesized during the cooling of the melt of the composition: 47—50 at.% of S, Cu/Fe = 1.12—1.22 in association with chalcopyrite and bornite, and also from the melt of the composition 50 at.% of S, Cu/Fe = 0.54 in association with cubanite.

Cubanite $CuFe_2S_3$ is synthesized in the samples NN 3—7 which initial compositions are located on the line chalcopyrite — cubanite — pyrrhotite (Fig.). In the samples NN 3—5a (50 at.% of S, Cu/Fe = 0.82— 0.54) cubanite is in the association with tetragonal chalcopyrite, in the sample No 6 (50 at.% of S, Cu/Fe = 0.43) — with pyrrhotite and haycockite, and in the sample No 7 (50 at.% of S, Cu/Fe = 0.25) — with pyrrhotite. During the change of the samples composition from chalcopyrite to cubanite, the quantity of cubanite increases in it. Phases form the disintegration structure that is often not seen during the microprobe analysis that complicates determination of their composition and quantitative ratios. It was appeared possible separate determination of composition of chalcopyrite and cubanite only in the samples No 4 and 5a that have been quickly cooled up to 900— 850°C and are maintained at 850°C during 4—10 day. In the sample No 5a, cooled quickly up to 800°C, only cubanite was synthesized which composition is close to the initial composition of the sample and corresponds to the composition of cubanite, synthesized in the sample No 5a annealed at 600°C (Cu 17.34, Fe 33.13, S 49.53). X-ray diffraction patterns of the mix of chalcopyrite and cubanite correspond to the X-ray diffraction pattern of the tetragonal chalcopyrite with shift of reflexes 1.870 and 1.856 towards smaller angles according to the increase in interplanar spacings during the reduction of the Cu/Fe relation. Besides, X-ray diffraction pattern of the mix of cubanite and chalcopyrite of the sample No 5a with the prevailing content of cubanite, as well as X-ray diffraction pattern of the mix of talnakhite and chalcopyrite of the sample No 8, differs from the X-ray diffraction pattern of chalcopyrite by bifurcation of the reflex 3.04 and an inverse ratio of intensities of tetragonal doublets: 1.870—1.856; 1.592—1.575. In the sample No 6 cubanite is synthesized in the association with haycockite and pyrrhotite. In the sample No 7 synthesized according to the mode I the composition of cubanite corresponds to the initial composition of the sample No 6 and to the composotion of the extreme member, enriched in iron iss at 600°C. In the same sample, annealed at 800°C, cubanite of the stoichiometric composition is synthesized in the association with pyrrhotite and iss which composition lies on the line haycockite — pyrrhotite and corresponds to the initial composition of the sample No 11. As it could be seen from the Table and Figure, the composition of cubanite of the sample No 5a is close to the composition of the stoichiometric cubanite from the chalcopyrite side, and sample No 6 — from the side of pyrrhotite. Thus, enriched in copper (Cu/Fe ≥ 0.5) cubanite $CuFe_2S_3$ crystallizes in association with chalcopyrite or talnakhite (sample No 5) depending on the mode of cooling, and enriched in iron (Cu/Fe ≤ 0.5) — with haycockite and pyrrhotite.

Mooihoekite $Cu_9Fe_9S_{16}$ is synthesized in the samples No 9 (47 at.% of S, Cu/Fe = 0.93) and No 12 (45 at.% of S, Cu/Fe = 1.44) in association with bornite regardless of the mode of synthesis. As it could be seen from the Fig. 1 and Table, the initial composition of the sample No 9 is close to the composition of mooihoekite, and the sample No 12 — lies on the line bornite — mooihoekite, and corresponds to the iss composition after the annealing at 800°C. Unlike cubanite and talnakhite that crystallize in the form of a disintegration structure with chalcopyrite, mooihoekite is a homogeneous phase and can easily be detrmined.

Haycockite $Cu_4Fe_5S_8$ (a phase of the haycockite composition with cubic pc structure) is synthesized in the sample No 10 (47 at.% of S, Cu/Fe = 0.77) and No 13 (45 at.% of S, Cu/Fe = 1.20) in association with bornite, in samples NN 11 (47 at.% of S Cu/Fe = 0.63) and 14—15 (45 at.% of S, Cu/Fe = 1—0.83) in association with bornite and pyrrhotite, and also in the described above sample No 6 in association with the enriched in iron cubanite and pyrrhotite. Haycockite, as well as mooihoekite, is easily determined.

Thus, phase associations of the central part of the Cu-Fe-S system are synthesized by the method of melt cooling, and compositions of phases and phase equillibriums are determined in the field of crystallization of the chalcopyrite solid solution.

As it could be seen from the Figure, the constructed scheme of mutual relations of synthesized phases agrees with experimental researches of the Cu-Fe-S system at 600°C (Cabri, 1973). Investigation results of phase composition of the samples annealed at 800°C do not conform to T. Tsudzhimura and A. Kitakaze's data (Tsujmura, Kitakaze, 2004) on the instability of the equillibriums bn-iss, bn-po and existence of melt at 800°C. According to the results of the thermal analysis of initial samples, crystallization of melt in the investigated area of the system is finished at the temperature ≈ 854°C. It conforms to the data of Yund and Kullerud (Yund, Kullerud, 1966). Compositions and phase mutual relations of the products of iss crystallization synthesized in the present ed work correspond to the literature data on their natural analogues (Bud`ko, Kulagov, 1963; Cabri, 1967; Cabri, Hall, 1972; Muraviova *et al.*, 1972; Fiulimonova *et al.*, 1974; Genkin *et al.*, 1981; Distler *et al.*, 1996).

Discussion

Synthesized phase associations can be subdivided onto two groups according to the composition and character of crystallization. The first group — association of talnakhite with chalcopyrite and bornite (samples NN 1, 1a, 5, and 8) and enriched in copper cubanite with talnakhite and chalcopyrite (samples NN 3—5a) — is characterized by complex structures of disintegration and sensitivity to the mode of cooling. The second group is characterized by equillibriums of haycockite with enriched in iron cubanite, pyrrhotite (sample No 6), haycockite with bornite (sample No 10), haycockite with bornite and pyrrhotite (samples NN 11, 13—15). As it could be seen from the Figure, the mentionned groups of phase associations are divided by the line of the equillibrium bornite-mooihoekite-cubanite. Above this line lies the area of crystallization of phase associations of the first group, and lower — of the second. According to agreeed data of Yund, Kullerud and Cabri (Yund, Kullerud, 1966; Cabri, 1973), phase associations of the first group are in agreement with enriched in sulfur area iss and iss + bn, and phase associations of the second group are in agreement with the area iss with pyrrhotite and bornite (dashed lines without a line py-iss on the Fig. 1). Thus, after the crystallization of iss, cooling of phase associations of the first group occurs in the presence of free sulfur and it causes dependence of their phase composition on the mode of cooling. Crystallization and cooling of iss in the second group of phase associations occurs in conditions of invariant equillibrium and it is, probably, a principal cause of haycockite crystallization in cubic (pc) form instead of rhombic (Hall, 1975). Different conditions of cooling after iss crystallization of different composition are proved by various behaviour of gold, silver, platinum and palladium during crystallization of melts of the mentioned groups of phase associations (Kravchenko, 2009; Kravchenko, Nigmatulina, 2009). In the presented work we are not discussing phase associations bornite + pyrite + chalcopyrite and chalcopyrite + cubanite + pyrrhotite (blue hatch lines on the Figure) which are present at insignificant quantities and, according to the data of Yund and Kullerud, are formed after the melt crystallization (Yund, Kullerud, 1966).

Conclusions

1. Phase associations: talnakhite + chalcopyrite, chalcopyrite + cubanite, cubanite + talnakhite, cubanite + pyrrhotite, cubanite + pyrrhotite + haycockite, mooihoekite + bornite, haycockite + bornite, haycockite + bornite + pyrrhotite, bornite + pyrrhotite are steady at room temperature products of crystallization of melts of the central part of the Cu-Fe-S system (50 at.% of S, Cu/Fe = 1.22 —0.25; 47 at.% of S, Cu/Fe = 1.12 —0.63 and 45 at.% of S, Cu/Fe = 1.44—0.69). At the same time in associations with chalcopyrite or talnakhite cubic fcc cubanite $CuFe_2S_3$ enriched in copper (Cu/Fe $\geq$ 0.5), crystallize, and in associations with haycockite and pyrrhotite – cubanite enriched in iron (Cu/Fe $\leq$ 0.5) crystallize.

2. Established in work phase equillibriums: bornite – talnakhite – chalcopyrite, talnakhite – chalcopyrite – cubanite and mooihoekite – cubanite have been previuosly predicted by L.J. Cabri and S. Hall according to the results of investigations of natural associations and Cu-Fe-S system (Cabri, 1967, 1973; Cabri, Hall, 1972). The same authors have assumed the existence of the following equillibriums: mooihoekite – talnakhite, mooihoekite – haycockite – troilite and mooihoekite – haycockite – copper. However, the equillibrium established in the presented work (cubanite – haycockite) contradicts with the equillibrium mooihoekite – haycockite – troilite, and the equillibrium bornite – haycockite – pyrrhotite contradicts with the equillibrium mooihoekite – haycockite – copper. For understanding of the reasons of the existing contradictions further more detailed investigation of the synthesized samples and corresponding natural mineral associations is necessary.

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