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Experimental study of phase compositions in the region of chalcopyrite solid solution crystallization

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Compositions of chalcopyrite solid solution crystallization products have been studied to determine characteristics of formation of phase equilibria with chalcopyrite $CuFeS_2$, cubanite $CuFe_2S_3$, talnakhite $Cu_9Fe_8S_{16}$, mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$ in the process of the Cu-Fe sulfide melt crystallization. The determined Cu/Fe relations of tetragonal chalcopyrite (1.03–0.67), cubic fcc cubanite (0.61–0.39) and cubic pc haycockite (0.92–0.68) considerably differ from correspondent formula relations. Composition of mooihoekite with Cu/Fe = 1.04–0.93 corresponds to the bornite – mooihoekite - cubanite equilibrium line, which crosses chalcopyrite and haycockite phase associations regions.

Key words: Cu-Fe-S system, chalcopyrite solid solution, crystallization of the melt

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In respect of the composition the following minerals refer to the region of chalcopyrite solid solution crystallization: chalcopyrite $CuFeS_2$, talnakhite $Cu_9Fe_8S_{16}$, cubanite $CuFe_2S_3$, mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$. All of them are characterized by variable compositions but the limits of their compositions variation have not been established. This complicates determination of phase equilibrium formation characteristics during the Cu-Fe sulfide melt crystallization. Whereas in the given study the results of various experiments on the synthesis of phase associations of central part of the Cu-Fe-S system: 45–50 at.% S, Cu/Fe = 1.44–0.25 have been further studied and generalized [*Kravchenko, Nigmatulina, 2009; Kravchenko, 2009, 2011*]. The obtained results allowed to specify the compositions of synthesized chalcopyrite solid solution crystallization products and to supplement the phase relations scheme [*Kravchenko, 2011*] with talnakhite – mooihoekite and mooihoekite – haycockite equilibria lines (Fig.). The synthesis has been carried out in the evacuated quartz ampoules by cooling the melt from 1150–1100 °C to room temperature and its further annealing at 800, 600 and 400 °C. The synthesized samples have been studied using optical microscope, X-ray diffraction and microprobe analysis methods.

The results are shown in the figure and in table 1 below. The determined Cu/Fe relations of synthesized tetragonal chalcopyrite, isocubanite (cubic fcc cubanite), talnakhite, mooihoekite and cubic pc haycockite differ from the correspondent formula relations. The association isocubanite + pyrrhotite $Fe_{1-x}S$ (cb + po) with the same isocubanite composition as in the association isocubanite + haycockite + pyrrhotite (cb + hc + po) but with more sulfur pyrrhotite, and the association chalcopyrite + isocubanite + pyrrhotite (cp + cb + po) with stoichiometric isocubanite and chalcopyrite and enriched by sulfur pyrrhotite are not shown in the table 1.

Isocubanite, chalcopyrite, talnakhite. Isocubanite has been established in associations with all synthesized chalcopyrite solid solution crystallization products. The most high-melting isocubanite has been crystallized from melt the first, and its composition determines compositions of the equilibrium phases. The copper-enriched isocubanite (Cu/Fe = 0.61–0.52) is crystallized in associations with chalcopyrite or talnakhite depending on the cooling regime of the melt in interval of 1000–800 °C. By cooling melt with keeping at 850 °C isocubanite is crystallized with chalcopyrite (Cu/Fe = 0.99–0.67), whereas without keeping at 850 °C — with talnakhite (Cu/Fe = 1.16–1.09) and less iron-enriched but more copper-enriched chalcopyrite (Cu/Fe = 1.03–0.92). In case of the quick cooling of melt with Cu/Fe = 1–0.67 from 850 °C to room temperature in chalcopyrites with Cu/Fe = 0.99–0.82: 25–22.5 at.% Cu, 25–27.5 at.% Fe, the regions of exsolution textures with phase composition of maximal iron-enriched chalcopyrite (Cu/Fe = 0.67: 20 at.% Cu, 30 at.% Fe) are found. Thereby Cu/Fe of chalcopyrite is changed within 1.03–0.67. As the cooling melt speed increases and the sulfur composition decreases the region of iron-enriched chalcopyrite crystallization decreases.

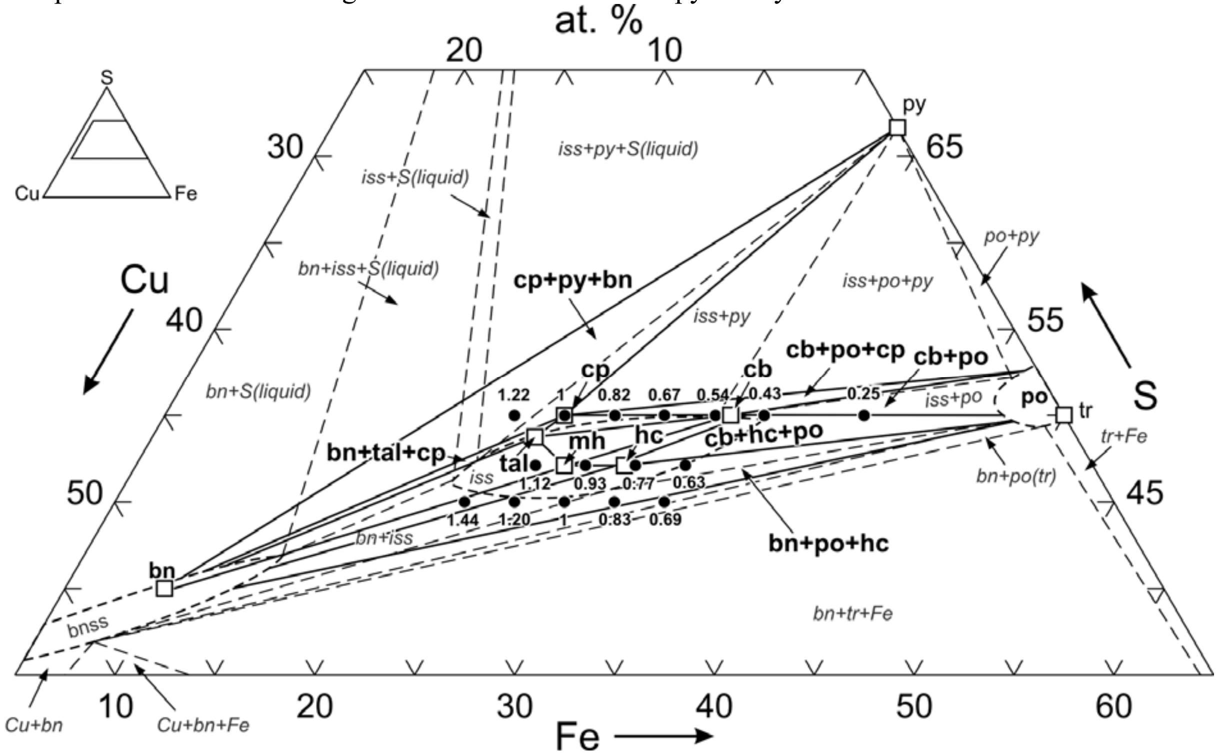

Fig. 1. The relations scheme of synthesized phases (solid lines) in the scheme of phase relationships of the central part of the Cu–Fe–S system at 600 °C (dashed lines, [*Cabri, 1973*]). • — the initial compositions of synthesized samples: 50 at.% S, Cu/Fe 1.22–0.25; 47 at.% S, Cu/Fe 1.12–0.63; 45 at.% S, Cu/Fe 1.44–0.69. The iss, bnss and po notations represent regions of chalcopyrite, bornite and pyrrhotite solid solutions correspondingly. The □ symbol shows stoichiometric compositions of the following minerals: $CuFeS_2$ (cp), bornite Cu_5FeS_4 (bn), pyrite FeS_2 (py), troilite FeS (tr) and chalcopyrite solid solution products: chalcopyrite $CuFeS_2$, talnakhite $Cu_9Fe_8S_{16}$ (tal), cubanite $CuFe_2S_3$ (cb), mooihoekite $Cu_9Fe_9S_{16}$ (mh) and haycockite $Cu_4Fe_5S_8$ (hc).

Table 1. Composition of synthesized phases

Phase association	Phases	Composition of phases, at. % wt. %			Cu/Fe
		Cu	Fe	S	
cb + cp	cb	17.34–19.32	31.75–33.13	48.93–49.53	0.61–0.52
		23.92–26.78	38.70–40.17	34.22–34.46	
	cp	20.31–25.54	25.81–30.47	48.65–49.81	0.99–0.67
		28.03–34.97	31.07–36.96	34.37–34.48	
cb + tal + cp	cp	24.22–25.43	24.71–26.42	49.36–49.86	1.03–0.92
tal + cp + bn		33.40–34.86	29.76–32.02	34.34–34.48	
cp + bn + py	tal	26.92–27.92	24.12–24.60	47.75–48.84	1.16–1.09
		36.64–37.68	28.75–29.13	32.74–33.42	
mh + bn	mh	25.64–27.38	26.37–27.52	46.25–47.15	1.04–0.93
		34.74–37.18	31.46–32.83	31.68–32.25	
po + cb+ hc	cb	14.04–16.80	34.06–35.90	49.13–50.06	0.49–0.39
		19.59–23.34	41.57–44.03	34.42–35.25	
	hc	21.01–25.35	28.17–31.05	45.97–47.94	0.90–0.68
		30.65–34.34	33.74–36.17	31.43–32.91	
po + hc + bn	hc	21.61–25.75	27.91–31.98	46.41–47.25	0.92–0.68
		29.46–34.71	33.06–38.32	31.93–32.74	

cb — isocubanite $CuFe_2S_3$ (Cu/Fe = 0.5), cp — chalcopyrite $CuFeS_2$, (Cu/Fe = 1),
tal — talnakhite Cu_9Fe_8S16 (Cu/Fe = 1.12), mh — mooihoekite $Cu_9Fe_9S_{16}$ (Cu/Fe = 1),

hc — haycockite $Cu_4Fe_5S_8$ (Cu/Fe = 0.8).

The phase relations typical for the exsolution textures of solid solution have been determined for chalcopyrite – containing phase associations only. The phase compositions and X-ray diffraction pictures of mixtures of chalcopyrite with talnakhite and isocubanite indicate that the studied exsolution textures talnakhite + chalcopyrite and isocubanite + chalcopyrite are caused by phase transition of

cubic fcc iss to tetragonal chalcopyrite. The obtained results confirm the experimental data [*Yund, Kullerud, 1966; Sugaki et. all, 1975 etc.*] demonstrating variability of chalcopyrite composition. Composition of maximal iron-enriched chalcopyrite synthesized in the given study corresponds to composition of maximal iron-enriched iss determined [*Tsujmura and Kitakaze, 2004*] in the 50 at.% S section of Cu-Fe-S system at 800 °C.

Mooihoekite. Composition of mooihoekite with Cu/Fe = 1.04 – 0.93 corresponds to the bornite (bn) – mooihoekite (mh) - cubanite (cb) equilibrium line, which crosses the chalcopyrite and haycockite phase associations regions.

Table 2. Composition of phases synthesized in this study and natural chalcopyrite solid solution crystallization products

Phases	Composition of phases, wt. %			Source
	Cu	Fe	S	
Isocubanite (cb)	23.92–26.78	38.70–40.17	34.22–34.46	This study, with cp,
	19.59–23.34	41.57–44.03	34.42–35.25	with hc.
	22.23	41.98	35.79	*Missack et. al., 1989*
	19.25–23.40	37.60–43.80	34.30–37.52	*Mozgova et. al., 1995, 2002*
	18.10–24,94	34.46–41.73	34.20–36.70	*Distler et. al., 1996*
Chalcopyrite (cp)	28.03–34.97	31.07–36.96	4.37–34.38	This study, with cb,
	33.40–34.86	29.76–32.03	34.34–34.38	With cb and with tal.
	30.2–32.0	33.2–34.9	33.8–35.7	*Karpenkov, 1974*
	26.54–31.37	31.98–36.56	33.74–35.66	*Distler et. al., 1996*
	31.23–34.17	27.87–32.36	35.06–36.03	*Phardust et. al., 2005*. Lamele
	32.63–33.21	31.42–31.85	34.98–35.64	from exsolution textures
Isochalcopyrite	33.1–35.3	31.4–32.4	33.2–34.1	Philimonova et. al., 1974
	34.04	32.20	33.87	*Missack et. al., 1989*
	31.69	34.51	33.85	*Phardust et. al., 2005*. Lamele
	33.08	32.81	33.88	from exsolution textures
Talnakhite (tal)	36.64–37.68	28.75–29.13	32.74–33.42	This study.
	36.5– 8.6	29.5–32.0	31.0–32.0	*Budko, Kulagov, 1963*
	36.86–37.36	28.79–29.47	33.06–33.84	*Cabri, Hall, 1972*
	36.8	29.8	34.0	*Philimonova et. al., 1974*
Mooihoekite (mh)	34.74–37.18	31.46–32.83	31.68–32.25	This study.
	34.87–36.71	31.38–32.40	31.93–33.29	*Cabri, Hall, 1972*
	35.3–36.2	31.4–31.9	32.1–32.9	*Philimonova et. al., 1974*
Haycockite (hc)	30.65–34.71	33.06–38.32	31.43–32.91	This study.
	31.83–32.55	34.64–35.46	31.94–32.86	*Cabri, Hall 1972*

Thereby formation of the phase relations in the central part of the Cu-Fe-S system is determined by the initial composition and cooling regime of the melt. Pyrrhotite + iron-enriched isocubanite (Cu/Fe = 0.49–39), stoichiometric isocubanite (Cu/Fe = 0.52–49) and copper-enriched isocubanite (Cu/Fe = 0.61–0.52) + chalcopyrite (Cu/Fe = 0.99–0.67) are crystallized from the melt with 50 at.% S. When decreasing the sulphur content the composition of the following phase associations is changed: pyrrhotite + isocubanite → pyrrhotite + isocubanite + haycockite (Cu/Fe = 0.90–0.68) → pyrrhotite + haycockite (Cu/Fe =0.92–0.68) + bornite, isocubanite → isocubanite + mooihoekite (Cu/Fe = 1.04–0.93) + bornite, isocubanite + chalcopyrite → isocubanite + talnakhite (Cu/Fe = 1.16–1.09) + chalcopyrite (Cu/Fe = 1.03–0.92).

Cubic pc haycockite. The iron-enriched isocubanite is crystallized in associations with pyrrhotite and haycockite. As opposed to natural rhombic haycockite, synthetic phase of haycockite composition is characterized by cubic pc structure [*Cabri, 1973*]. Cubic pc structure has been determined for phases of 46–48 at.% S, Cu/Fe = 1–0.68 synthesized in the given study. Cubic pc haycockite (Cu/Fe = 0.92–0.68) is crystallized in the associations: pyrrhotite + iron-enriched isocubanite (Cu/Fe = 0.49–0.39) and pyrrhotite + bornite. As shown in the table 1 the similar total range of the Cu/Fe value for mooihoekite and haycockite (1.04–0.68) and for chalcopyrite (1.03–0.67) has been determined.

The compositions of synthesized phases correspond to published data about compositions of the appropriate minerals (table 2).

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