

## Experimental study of the phase equilibria in the crystallization region of the chalcopyrite solid solution

T. A. Kravchenko

V. S. Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the RAS, Novosibirsk  
[tanyuk@igm.nsc.ru](mailto:tanyuk@igm.nsc.ru), fax: 8 (383) 333 2792, tel.: 8 (383) 333 3026

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The Chalcopyrite (or intermediate) solid solution has been experimentally established in the center section of the Cu–Fe–S system at 300–800 °C [Merwin and Lombard, 1937; Yund and Kullerud, 1966; Cabri, 1973; Barton, 1973; Lihachev, 1973; Sugaki, et. al., 1975; Vaughan and Craig, 1978; 1997; Tsujmura and Kitakaze, 2004]. The phase equilibria concepts of the chalcopyrite solid solution crystallization products at low temperatures are not clear and contradictory, since they are based on the results of investigating the natural phase associations and the extrapolation of the separate experimental data to the low temperatures region [Vaughan and Craig, 1978; 1997].

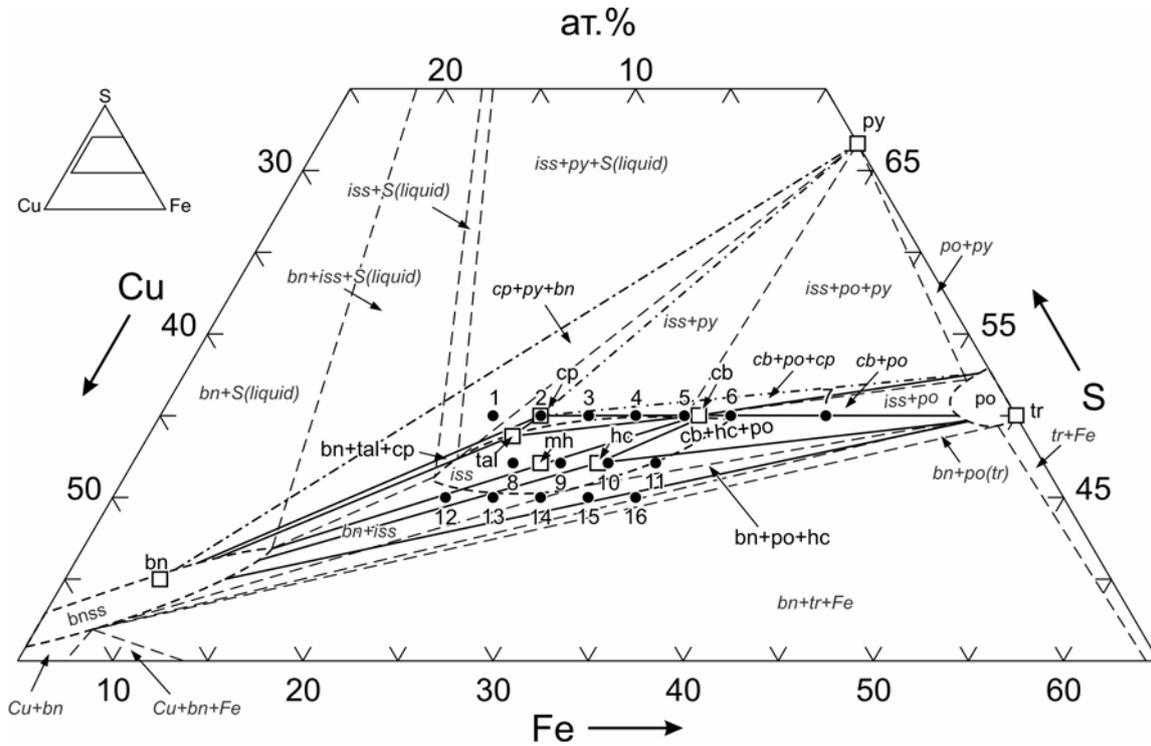
The phase associations of the center section of the system Cu–Fe–S: 50 at.% S, Cu/Fe = 1.22–0.25, 47 at.% S, Cu/Fe = 1.12–0.63 and 45 at.% S, Cu/Fe = 1.44–0.69 have been synthesized to determine the phase equilibria in the crystallization region of the chalcopyrite solid solution. The scheme of the phase relations in the central Cu–Fe–S system (marked with the dashed lines in the figure below) considering the results of the most complete experimental study of phases from the region of the chalcopyrite solid solution [Cabri, 1973] has been used as the basis for the selection of the initial compositions of the synthesized samples. The synthesis has been carried out in the vacuum quartz ampoules using the melt cooling method from 1150–1100 °C to the room temperature and the following annealing at 600 and 800 °C. The synthesized samples have been studied using the optical microscope and the X-ray diffraction methods. The obtained results are represented in the figure and in the table below.

**Talnakhite**  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$  has been synthesized in samples 1 and 8: 50 at.% S, Cu/Fe = 1.22 and 47 at.% S, Cu/Fe = 1.12 in the association with chalcopyrite and bornite, whereas in sample 5a: 50 at.% S, Cu/Fe = 0.54 it has been synthesized in the association with cubanite.

**Cubanite**  $\text{CuFe}_2\text{S}$  (cubic fcc) has been synthesized in samples 3–7, which original compositions are located on the chalcopyrite-cubanite-pyrrhotite line (fig.). In samples 3–5a: 50 at.% S, Cu/Fe = 0.82–0.54 cubanite has been synthesized in the association with the tetragonal chalcopyrite, in sample 6: 50 at.% S, Cu/Fe = 0.43 — in the association with pyrrhotite and haycockite, and in sample 7: 50 at.% S, Cu/Fe = 0.25 — in the association with pyrrhotite. It has been established that cubanite  $\text{CuFe}_2\text{S}_3$  enriched by iron (Cu/Fe  $\leq$  0.5), is crystallized in the associations with haycockite and pyrrhotite, while being enriched by copper (Cu/Fe  $\geq$  0.5) it is crystallized in the associations with talnakhite or chalcopyrite (samples 5 and 5a), depending on the cooling regime.

**Mooihoekite**  $\text{Cu}_9\text{Fe}_9\text{S}_{16}$  has been synthesized in samples 9 and 12: 47 at.% S, Cu /Fe = 0.93 and 45 at.% S, Cu/Fe = 1.44 in the association with bornite, regardless of the synthesis regime. As opposed to cubanite and talnakhite, which are crystallized in the form of the exsolution texture with chalcopyrite, mooihoekite is the easily diagnosed homogeneous phase.

**Haycockite**  $\text{Cu}_4\text{Fe}_5\text{S}_8$  (phase of the haycockite composition with the cubic pc structure) has been synthesized in sample 10: 47 at.% S, Cu/Fe = 0.77 and 13: 45 at.% S, Cu/Fe = 1.20 in the association with bornite, in sample 11: 47 at.% S Of cu/Fe = 0.63 and 14–15: 45 at.% S, Cu/Fe = 1–0.83 in the association with bornite and pyrrhotine, and also in the above sample 6 in the association with pyrrhotite and cubanite enriched by iron. Same as mooihoekite, haycockite is diagnosed easily.



**Fig.** The relations of the phases synthesized in this work (solid lines) in the scheme of the phase relationships of the center section of system Cu–Fe–S at 600 °C (dashed lines, [Cabri, 1973]), 1–16 — initial compositions of the synthesized samples. The iss, bnss and po notations are the regions of the chalcopyrite, bornite and pyrrhotite solid solutions. The □ symbol represents the stoichiometric compositions of the following minerals: tetragonal chalcopyrite CuFeS<sub>2</sub> (cp), bornite Cu<sub>5</sub>FeS<sub>4</sub> (bn), pyrite FeS<sub>2</sub> (py), troilite FeS (tr) and the chalcopyrite solid solution products: talnakhite Cu<sub>9</sub>Fe<sub>8</sub>S<sub>16</sub> (tal), cubanite CuFe<sub>2</sub>S<sub>3</sub> (cb), mooihoekite Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub> (mh) and haycockite Cu<sub>4</sub>Fe<sub>5</sub>S<sub>8</sub> (hc). The dash-and-dot lines show the equilibria with the participation of a few phases (marked with the asterisk in the table), generated after the iss crystallization based on the data [Yund and Kullerud, 1966].

N <sub>o</sub>	Initial composition at. %			Phase association
	S	Cu	Fe	
1	50.0	27.5	22.5	Tal + bnss + cp (py*)
5		17.5	32.5	Cb + tal
8	47.0	28.0	25.0	tal + bnss + cp
2		25.0	25.0	cp (bn*, py*), cp + cb (py*)
3	50.0	22.5	27.5	cp + cb (py*)
4		20.0	30.0	cp + cb
5a		17.5	32.5	(py*, po*, bn*)
6		15.0	35.0	cb + hc + po
7		10.0	40.0	cb + po
9	47.0	25.5	27.5	mh + bnss
12	45.0	32.5	22.5	
10	47.0	23.0	30.0	hc + bnss
13	45.0	30.5	25.0	
11	47.0	20.5	32.5	hc + bnss + po
14	45.0	27.5	27.5	
15		25.0	30.0	
16		22.5	32.5	bnss + po

The synthesized phase associations can be divided in two groups based on their composition and the crystallization type. The first group represents the associations of talnakhite with chalcopyrite and bornite (samples 1, 5, 8), and also associations of the cubanite enriched by copper with chalcopyrite and talnakhite (samples 3–5a). This group is characterized by the complex exsolution textures and the sensitivity to the cooling regime. The second group is characterized by the equilibria of haycockite with cubanite enriched by iron, pyrrhotite and bornite (samples 6, 10, 11, 13–15). As shown in the figure, the above mentioned groups of phase associations are divided by the bornite-mooihoekite-cubanite equilibrium line. The crystallization region of the phase associations of the first group is shown above the line, and one of the second groups is shown below the line. In accordance with the experimental data [Yund and Kullerud, 1966; Cabri, 1973] the phase associations of the first group correspond to the sulfur enriched iss and iss + bn regions, and the second group corresponds to the region of iss with pyrrhotite and bornite. Thereby after the iss crystallization the cooling of the first group phase associations occurs in the presence of free sulfur, which specifies the dependence of their phase composition on the cooling regime. The iss crystallization and cooling in the second group of phase associations occurs under the conditions of the invariant equilibrium, which probably causes the haycockite crystallization in the cubic (pc), and not in the rhombic [Hall, 1975] form. The different cooling conditions after crystallization of iss of different compositions are confirmed by different behavior of gold, silver, platinum and palladium during the melts crystallization of the mentioned phase associations groups [Kravchenko and Nigmatulina, 2009; Kravchenko, 2009].

Thus the phase associations talnakhite + chalcopyrite + bornite, chalcopyrite + cubanite, cubanite + talnakhite, cubanite + pyrrhotite, cubanite + pyrrhotite + haycockite, mooihoekite + bornite, haycockite + bornite, haycockite + bornite + pyrrhotite, bornite + pyrrhotite are stable products of the melts crystallization of the center section of the system Cu–Fe–S: 50 at.% 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 at room temperature. In this case in the associations with chalcopyrite or talnakhite the cubic fcc cubanite  $\text{CuFe}_2\text{S}_3$  enriched by copper ( $\text{Cu/Fe} \geq 0.5$ ) is crystallized, while in the associations with haycockite and pyrrhotite the cubic fcc cubanite  $\text{CuFe}_2\text{S}_3$  enriched by iron ( $\text{Cu/Fe} \leq 0.5$ ) is crystallized.

As shown in the figure, the scheme of the synthesized phase relations conforms to the experimental study of the Cu–Fe–S system at 600 °C [Cabri, 1973]. The research results of the phase composition of samples annealed at 800 °C do not conform to the data showing the instability of the bn-iss and bn-po equilibria and the presence of melt in the examined part of the system at 800 °C [Tsujimura and Kitakaze, 2004]. According to the results of the thermal analysis of original samples the melt crystallization in the examined system's region is completed at  $\approx 854$  °C, and this conforms to the results of the most complete experimental study of the Cu–Fe–S system [Yund and Kullerud, 1966].

The compositions of the synthesized products of the solid solution crystallization correspond to the published data about their natural analogs in the magmatic Cu–Ni ores [Bud'ko and Kulagov, 1963; Cabri, 1967; Cabri and Hall, 1972; Philimonova, et al., 1974; Distler, et al., 1996]. The stated equilibria lines: bornite–talnakhite–chalcopyrite, talnakhite–chalcopyrite–cubanite and mooihoekite–cubanite have been previously assumed by Cabri and Hall based on the investigation results of the natural mineral associations and the Cu–Fe–S system [Cabri, 1967; 1973; Cabri and Hall, 1972]. The mentioned authors have assumed the existence of the mooihoekite–talnakhite, mooihoekite–haycockite–troilite and mooihoekite–haycockite–copper equilibria. However, the cubanite–haycockite equilibrium stated in the given work contradicts to the mooihoekite–haycockite–troilite equilibrium, while the bornite–haycockite–pyrrhotite equilibrium contradicts to the mooihoekite–haycockite–copper one. The more detailed research of the synthesized and natural mineral equilibria is required to understand the reason of the existing contradictions.

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