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New phase relations in the Cu–Fe–S system at 800 °C; constraint of fractional crystallization of a sulfide liquid

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With 6 figures and 2 tables

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Abstract: Phase equilibrium in the Cu–Fe–S system has been investigated for over 100 samples by the sealed silica tube method at 800 °C. Bornite shows solid solutions ranging from $(Cu_{4.70}Fe_{1.30})_{6.00}S_{4.00}$ to $(Cu_{7.43}Fe_{0.00})_{7.43}S_{4.00}$, and those of pyrrhotite ranges from $(Cu_{0.04}Fe_{1.01})_{1.05}S_{1.00}$ to $(Cu_{0.00}Fe_{1.00})_{1.00}S_{1.00}$. The intermediate solid solution (iss) and the sulfide liquid exist in the central part of this system. The most important difference between the phase diagram obtained in this study with that reported by Kullerud et al. (1969) is that the sulfide liquid is between bornite and pyrrhotite, and that the tie-lines between bornite and iss and between bornite and pyrrhotite are unstable. The new phase diagram of this system at 800 °C is reported.

Key words: Cu–Fe–S, bornite, iss, pyrrhotite, sulfide liquid.

1. Introduction

Sulfide liquids separate from silicate liquids when silicate liquids saturate with sulfur. Ni, Cu and platinum group elements (PGE) in silicate liquids concentrate into the immiscible sulfide liquids strongly. Sulfides such as pentlandite and pyrrhotite crystallize from the immiscible sulfide liquids with decreasing temperature (e.g., Naldrett 1989), therefore the phase relation between these sulfides and the immiscible sulfide liquids has been considered to be important for the understanding of the magmatic sulfide ore genesis.

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From the investigations of field relations at Noril'sk (Siberia) and Sudbury (Ontario), the Cu-rich sulfide ores are formed from fractional crystallization of the initial sulfide liquids, and these ores are especially interesting because of their elevated PGE and gold contents (Li et al. 1992, Ebel & Naldrett 1996). In this case, the monosulfide solid solution (mss) will start to crystallize from the sulfide liquid upon cooling, and elements that are less compatible in mss than in liquid will become enriched in the residual liquid (Li & Naldrett 1994). From this background, the phase relations between the sulfides such as $(Fe, Ni, Cu)_{1-x}S$ (monosulfide solid solution, mss) and the Fe–Ni–Cu–S liquid have been investigated over 1000 °C (Ebel & Naldrett 1996).

The Cu-rich sulfides have been also found in the eruption products; Cu–Ni-bearing pyrrhotite in midoceanic ridge basalt (Mathez 1976), Cu-bearing pyrrhotite in dacite rocks from Satsuma-Iwojima, Southwest Kyushu, Japan (Ueda & Itaya 1981), Cu–Ni-bearing pyrrhotite and Cu–Fe sulfides in the 1959 Kilauea eruption (Stone & Fleet 1991) and Cu–Fe sulfides in the 1991 Pinatubo eruption (Hattori 1996). These sulfide globules in the eruption products indicate that the immiscible sulfide liquids are segregated from the parent silicate liquids. This mechanism is similar to that of magmatic sulfide deposits as described above. Therefore these Cu-rich sulfide globules in the products may form from fractional crystallization of sulfide liquids at the late stage (below 900 °C), and it is necessary to investigate the phase relation between the sulfide minerals and the sulfide liquids at low temperature.

A pioneering study of Kullerud et al. (1969) yielded the phase relations in the Cu–Fe–S system between 700 °C and 1100 °C. The re-calculated phase diagrams from weight % to atomic % in this system at 700 °C and 900 °C are shown in Fig. 1. At 700 °C, three phases, namely bornite, intermediate solid solution (iss) and pyrrhotite, were identified. In addition, the sulfide liquid was observed in the wide range of this system at 900 °C. The sulfur content of the sulfide liquid was higher than that of the bornite solid solution. However, the phase relations of this system at 800 °C, which temperature represents a late stage of fractional crystallization of sulfide liquids, have been still unclear.

In this paper, the phase relations in the Cu–Fe–S system at 800 °C were examined in more than 100 samples by the sealed silica tube method.

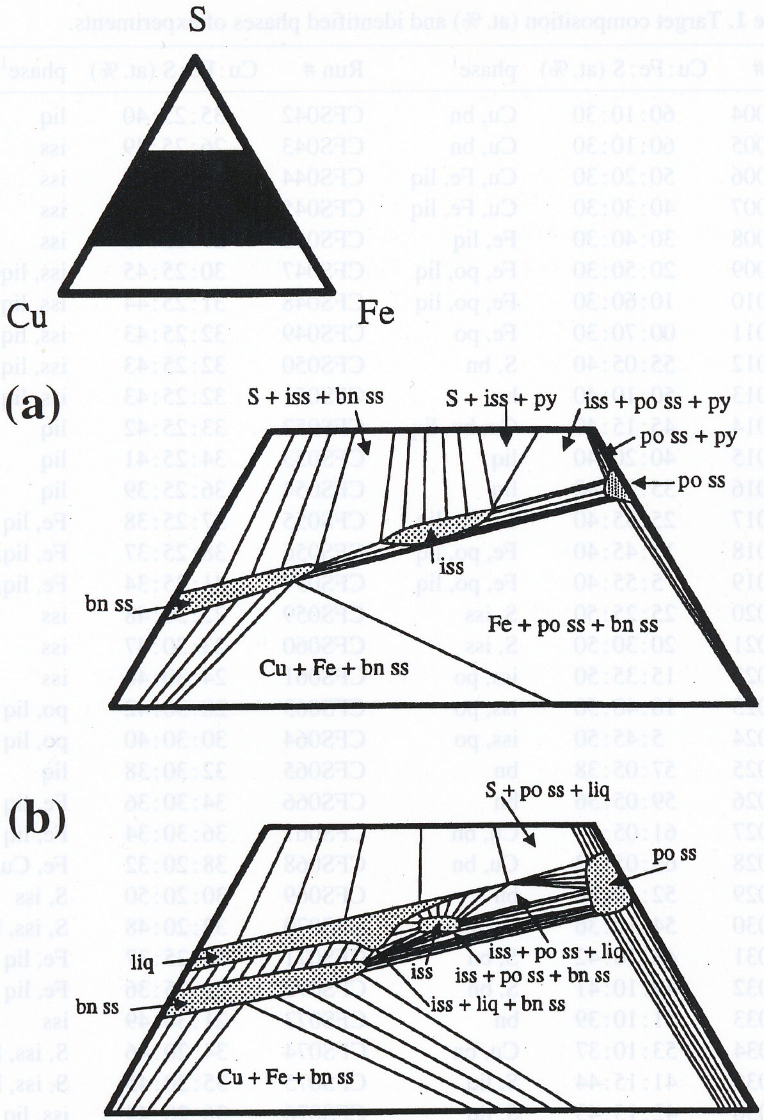

Fig. 1. (a) Phase relations in the Cu–Fe–S system at 700 °C (changed to atomic % from KULLERUD et al. 1969). (b) Phase relations in the Cu–Fe–S system at 900 °C (changed to atomic % from KULLERUD et al. 1969). All phases and phase assemblages coexist with vapor. bn = bornite; po = pyrrhotite; ss = solid solution; iss = intermediate solid solution; py = pyrite liq = sulfide liquid.

Table 1. Target composition (at. %) and identified phases of experiments.

Run #	Cu : Fe : S (at. %)	phase[1]	Run #	Cu : Fe : S (at. %)	phase[1]
CFS004	60 : 10 : 30	Cu, bn	CFS042	35 : 25 : 40	liq
CFS005	60 : 10 : 30	Cu, bn	CFS043	26 : 25 : 49	iss
CFS006	50 : 20 : 30	Cu, Fe, liq	CFS044	27 : 25 : 48	iss
CFS007	40 : 30 : 30	Cu, Fe, liq	CFS045	28 : 25 : 47	iss
CFS008	30 : 40 : 30	Fe, liq	CFS046	29 : 25 : 46	iss
CFS009	20 : 50 : 30	Fe, po, liq	CFS047	30 : 25 : 45	iss, liq
CFS010	10 : 60 : 30	Fe, po, liq	CFS048	31 : 25 : 44	iss, liq
CFS011	00 : 70 : 30	Fe, po	CFS049	32 : 25 : 43	iss, liq
CFS012	55 : 05 : 40	S, bn	CFS050	32 : 25 : 43	iss, liq
CFS013	50 : 10 : 40	bn	CFS051	32 : 25 : 43	iss, liq
CFS014	45 : 15 : 40	Cu, bu, liq	CFS052	33 : 25 : 42	liq
CFS015	40 : 20 : 40	liq	CFS053	34 : 25 : 41	liq
CFS016	35 : 25 : 40	liq	CFS054	36 : 25 : 39	liq
CFS017	25 : 35 : 40	Fe, po, liq	CFS055	37 : 25 : 38	Fe, liq
CFS018	15 : 45 : 40	Fe, po, liq	CFS056	38 : 25 : 37	Fe, liq, Cu
CFS019	5 : 55 : 40	Fe, po, liq	CFS057	41 : 25 : 34	Fe, liq, Cu
CFS020	25 : 25 : 50	S, iss	CFS059	22 : 30 : 48	iss
CFS021	20 : 30 : 50	S, iss	CFS060	23 : 30 : 47	iss
CFS022	15 : 35 : 50	iss, po	CFS061	24 : 30 : 46	iss
CFS023	10 : 40 : 50	iss, po	CFS063	28 : 30 : 42	po, liq
CFS024	5 : 45 : 50	iss, po	CFS064	30 : 30 : 40	po, liq
CFS025	57 : 05 : 38	bn	CFS065	32 : 30 : 38	liq
CFS026	59 : 05 : 36	bn	CFS066	34 : 30 : 36	Fe, liq
CFS027	61 : 05 : 34	Cu, bn	CFS067	36 : 30 : 34	Fe, liq
CFS028	63 : 05 : 32	Cu, bn	CFS068	38 : 20 : 32	Fe, Cu, liq
CFS029	52 : 10 : 38	bn	CFS069	30 : 20 : 50	S, iss
CFS030	54 : 10 : 36	Cu, bn	CFS070	32 : 20 : 48	S, iss, liq
CFS031	48 : 10 : 42	S, bn	CFS071	38 : 25 : 37	Fe, liq
CFS032	49 : 10 : 41	S, bn	CFS072	39 : 25 : 36	Fe, liq
CFS033	51 : 10 : 39	bn	CFS073	21 : 30 : 49	iss
CFS034	53 : 10 : 37	Cu, bn	CFS074	34 : 20 : 46	S, iss, liq
CFS035	41 : 15 : 44	S, liq	CFS075	35 : 20 : 45	S, iss, liq
CFS036	42 : 15 : 43	S, liq	CFS076	36 : 20 : 44	iss, liq
CFS037	43 : 15 : 42	liq	CFS077	38 : 20 : 42	liq
CFS038	44 : 15 : 41	bn, liq	CFS078	41 : 20 : 39	liq
CFS039	46 : 15 : 39	Cu, bn, liq	CFS079	42 : 20 : 38	liq
CFS040	47 : 15 : 38	Cu, bn, liq	CFS080	43 : 20 : 37	Cu, Fe, liq
CFS041	40 : 20 : 40	liq	CFS081	44 : 20 : 36	Cu, Fe, liq

Table 1. Continued.

Run #	Cu : Fe : S (at. %)	phase[1]	Run #	Cu : Fe : S (at. %)	phase[1]
CFS082	45 : 20 : 35	Cu, Fe, liq	CFS119	10 : 42 : 48	po, liq
CFS083	47 : 20 : 33	Cu, Fe, liq	CFS120	10 : 41 : 49	iss, po
CFS084	45 : 11 : 46	S, bn	CFS121	10 : 39 : 51	iss, po
CFS086	46 : 12 : 42	bn, liq	CFS122	10 : 38 : 52	iss, po
CFS089	43 : 13 : 44	S, liq	CFS123	10 : 37 : 53	S, po, iss
CFS090	45 : 13 : 42	bn, liq	CFS124	33 : 23 : 44	iss, liq
CFS091	47 : 13 : 40	bn	CFS125	28 : 28 : 44	iss, liq
CFS093	27 : 30 : 43	po, liq	CFS126	56 : 05 : 39	S, bn
CFS094	27 : 23 : 50	S, iss	CFS127	58 : 05 : 37	bn
CFS098	26 : 25 : 49	iss	CFS128	9 : 08 : 16	iss
CFS104	27 : 27 : 46	iss	CFS129	9 : 09 : 16	iss
CFS113	22 : 32 : 46	iss, po, liq	CFS130	4 : 05 : 08	iss
CFS114	65 : 00 : 35	bn	CFS131	46 : 12 : 42	bn, liq
CFS115	70 : 00 : 30	Cu, bn	CFS132	38 : 20 : 42	liq
CFS116	60 : 00 : 40	S, bn	CFS133	20 : 34 : 46	po, iss, liq
CFS117	10 : 45 : 45	Fe, po, liq	CFS134	15 : 33 : 52	S, po, liq
CFS118	10 : 44 : 46	Fe, po, liq			

[1] Phases: po = pyrrhotite, bn = bornite, iss = intermediate solid solution, liq = quenched sulfide liquid.

Some samples, such as CFS004 and CFS005, have same composition because the experimental reproduction was checked.

2. Experimental procedure

Fe (99.99 %), Cu (99.99 %) and S (99.99 %) from Kanto Chemical Co., Ltd., were used as starting materials. The metals and S were precisely weighted in the proportion to the ideal compositions. The weight accuracy was within 0.1 mg. The materials were sealed in the silica tube under vacuum of 1.33×10^{-1} Pa (10^{-3} Torr). The sealed tubes with the charge were preheating at 400 °C for at least 3 days. Free space in the tubes should be less than 50 % of the internal volume. The product was homogenized by grinding, resealed in an evacuated silica tube and reheated at 800 °C for at least 7 days. The chromel-alumel thermocouple was used. The tube was then cooled rapidly in water. We checked achievement of equilibrium. The target compositions of this experiment are summarized in Table 1.

The final products were polished and examined under the reflected-light microscope and analyzed by the JEOL XMA-8800 electron microprobe microanalyser at Tohoku University. Copper, iron and sulfur in sulfides were analyzed using a PET crystal, 20 kV accelerating voltage and probe diameter of 1 ~ 10 μm. The analytical uncertain is within 0.1 at. % as derived from repeated analysis at each spot.

3. Results and discussion

In this system, three phases of bornite, pyrrhotite and iss were observed under the reflected-light microscope (Table 1). Bornite has the solid solution areas ranging from $(Cu_{4.70}Fe_{1.30})_{6.00}S_{4.00}$ to $(Cu_{7.43}Fe_{0.00})_{7.43}S_{4.00}$, and pyrrhotite has from $(Cu_{0.04}Fe_{1.01})_{1.05}S_{1.00}$ to $(Cu_{0.00}Fe_{1.00})_{1.00}S_{1.00}$.

In the central portion of this system, a fine assemblage of sulfides was also observed. This texture was very similar to the quenched sulfide liquids of Fe–Ni–S reported by SUGAKI & KITAKAZA (1998). The boundary between the fine assemblage and the sulfides was very sharp and visible through the tube wall. In addition, the heterogeneity was observed in the sealed silica tube. In CFS049, for example, the fine sulfide aggregate was observed in the top of the charge, whereas the massive iss and small amounts of the fine sulfide aggregate were observed in the bottom of the charge (Fig. 2). This can be interpreted that the iss precipitated through the sulfide liquids at high temperature. Similar observation was reported in the case of $(Fe, Ni, Cu)_{1-x}S$ (monosulfide solid solution, mss) and the sulfide liquid of the Fe–Ni–Cu–S system (EBEL & NALDRETT 1996). Therefore, we considered that this fine texture was formed as breakdown of the sulfide liquid. The phase identifications under the reflected-microscope are summarized in Table 1 and Fig. 3.

The analytical results with the electron microprobe are shown in Table 2. Using these results, the phase diagram in the Cu–Fe–S system at 800 °C is illustrated in Fig. 4. This phase diagram shows that iss in this study is slightly higher sulfur content than that at 700 °C reported by KULLERUD et al. (1969), and that of the sulfide liquid in this study are lower than that at 900 °C by them. This difference of the portion of the sulfide liquid can not be explained by the difference of temperature.

The most important difference of the phase diagram in this study with that reported by KULLERUD et al. (1969) is that the sulfide liquid is between bornite and pyrrhotite, and both of the tie-line between bornite and iss and

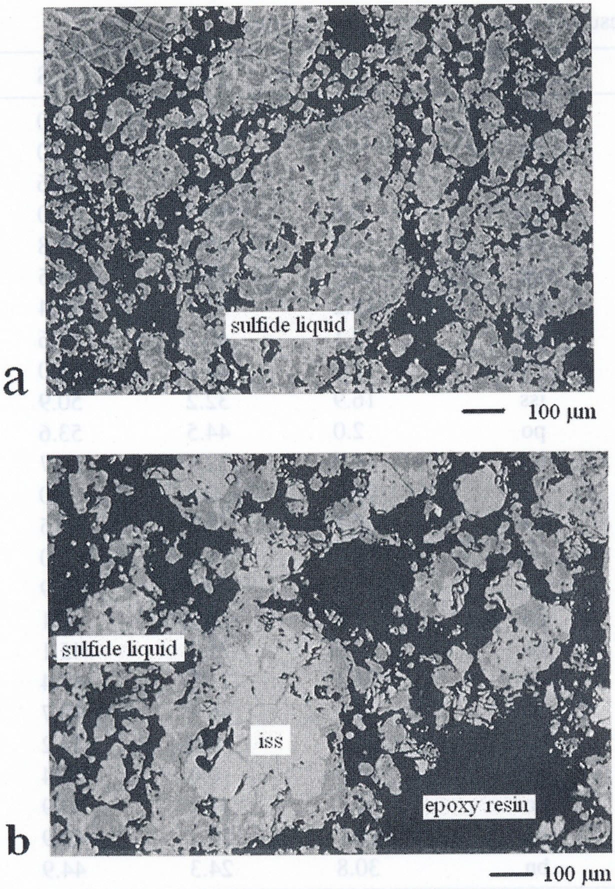

Fig. 2. Photomicrograph of quenched run products (Run # = CFS049). Dark area is an epoxy resin (a) Quenched products of upper part of sealed silica tube. (b) Quenched products of lower part of sealed silica tube. A fine assemblage of sulfides is considered to be a quenched sulfide liquid.

that between bornite and pyrrhotite are unstable. The reason of the difference has been unclear, however, the difficulty of identification of the quenched sulfide liquids may cause the difference between our phase diagram and Kullerud et al. (1969) s'.

The composition of the sulfide liquid in this study is considered to be that at the late stage of fractional crystallization of a sulfide liquid. The re-

Table 2. Result of electron mocroprobe analysis.

Run #	phase[1]	Cu	Fe	S	total
CFS007	Cu	97.0	2.8	0.0	99.8
	Fe	1.3	98.7	0.0	100.0
CFS012	bn	55.4	4.9	39.6	99.9
CFS018	Fe	0.6	99.3	0.0	99.9
	po	1.9	49.4	48.8	100.1
CFS020	iss	25.7	24.8	49.5	100.0
CFS022	iss	18.2	32.4	49.4	100.0
	po	2.1	46.2	51.6	99.9
CFS023	po	1.7	44.3	54.0	100.0
	iss	16.9	32.2	50.9	100.0
CFS024	po	2.0	44.5	53.6	100.1
	iss	16.8	32.5	50.7	100.0
CFS028	Cu	99.6	0.3	0.0	99.9
	bn	58.3	5.2	36.5	100.0
CFS040	Cu	98.0	1.9	0.0	99.9
	bn	46.1	14.0	39.9	100.0
CFS048	iss	28.8	25.1	46.1	100.0
CFS049	iss	29.6	25.3	45.1	100.0
CFS069	iss	31.4	21.3	47.4	100.1
CFS093	po	2.9	46.4	50.7	100.0
CFS115	bn	66.8	0.0	33.2	100.0
CFS116	bn	63.6	0.0	36.4	100.0
CFS123	po	4.1	41.9	53.9	99.9
	iss	19.9	30.2	49.9	100.0
CFS124	bn	30.8	24.3	44.9	100.0

[1] Phases: po = pyrrhotite, bn = bornite, iss = intermediate solid solution. Analytical error is within 0.1 %.

sult of this study, which shows that the tie-lines between bornite and iss and that between bornite and pyrrhotite are unstable, indicates that one-phase of bornite can not form by the fractional crystallization of sulfide liquids. In fact, bornite was little found in the natural sulfide globules from the eruption products. For example, the compositions of the Fe–Ni–Cu–S sulfides in the 1959 Kilauea eruption (STONE & FLEET 1991) and those of the Cu–Fe–S sulfides in the 1991 Pinatubo eruption (HATTORI 1996) are plotted on the obtained Cu–Fe–S phase diagram of this study (Figs. 5 and 6). The

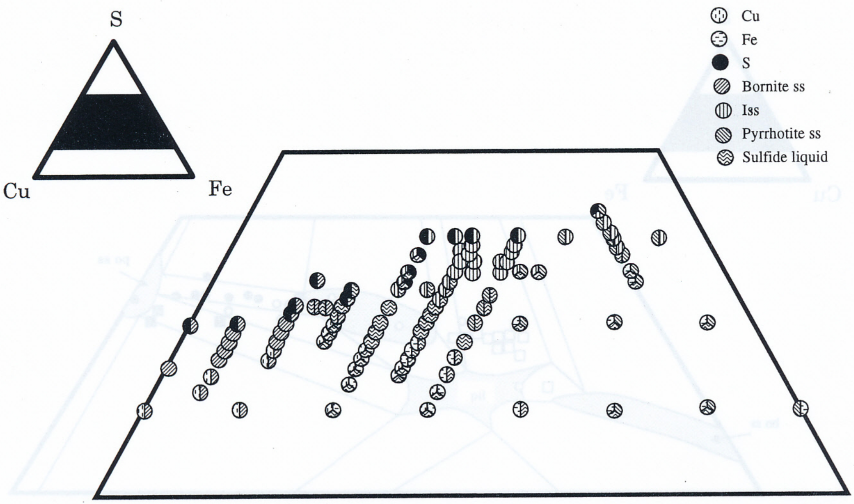

Fig. 3. Summary of phase identification with reflected-light microscope.

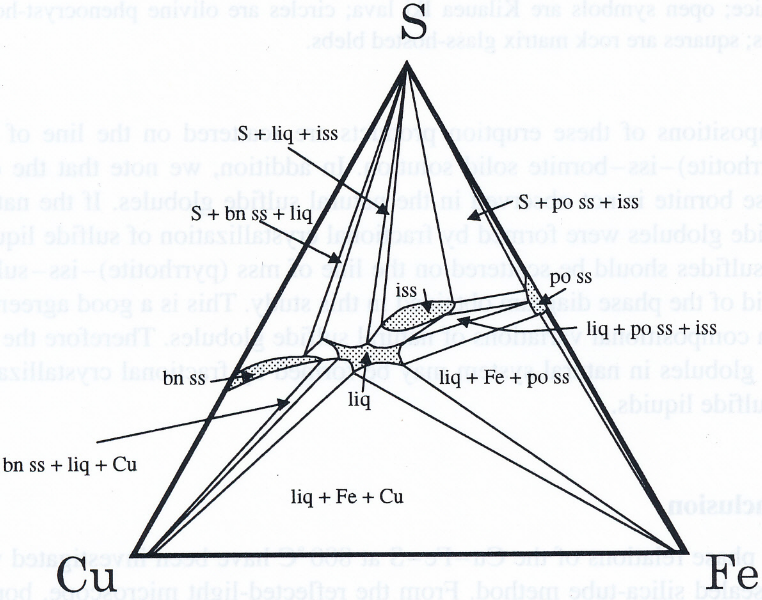

Fig. 4. Phase relations in the Cu–Fe–S system at 800 °C of this study. All phases and phase assemblages coexist with vapor. bn = bornite; iss = intermediate solid solution; po = pyrrhotite; liq = sulfide liquid; ss = solid solution.

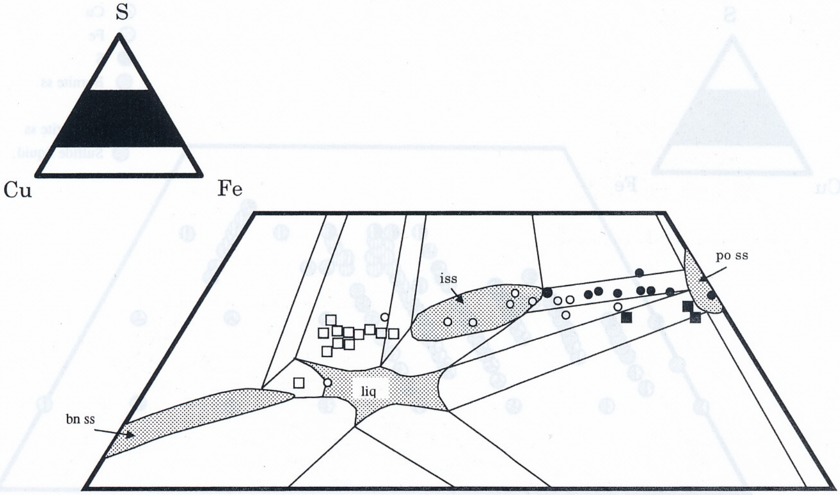

Fig. 5. The composition of sulfides from the 1959 Kilauea eruption products (STONE & FLEET 1991) on the obtained Cu–Fe–S phase diagram. Full symbols are eruption pumice; open symbols are Kilauea Iki lava; circles are olivine phenocryst-hosted blebs; squares are rock matrix glass-hosted blebs.

compositions of these eruption products are scattered on the line of mss (pyrrhotite)–iss–bornite solid solution. In addition, we note that the one-phase bornite is not observed in the natural sulfide globules. If the natural sulfide globules were formed by fractional crystallization of sulfide liquids, the sulfides should be scattered on the line of mss (pyrrhotite)–iss–sulfide liquid of the phase diagram obtained in this study. This is a good agreement with compositional variations of natural sulfide globules. Therefore the sulfide globules in natural system may be formed by fractional crystallization of sulfide liquids.

Conclusion

The phase relations of the Cu–Fe–S at 800 °C have been investigated with the sealed silica-tube method. From the reflected-light microscope, bornite solid solution, pyrrhotite solid solution, intermediate solid solution and the fine assemblage of small sulfides, which was formed as breakdown of the sulfide liquid, were identified. The important difference of the phase dia-

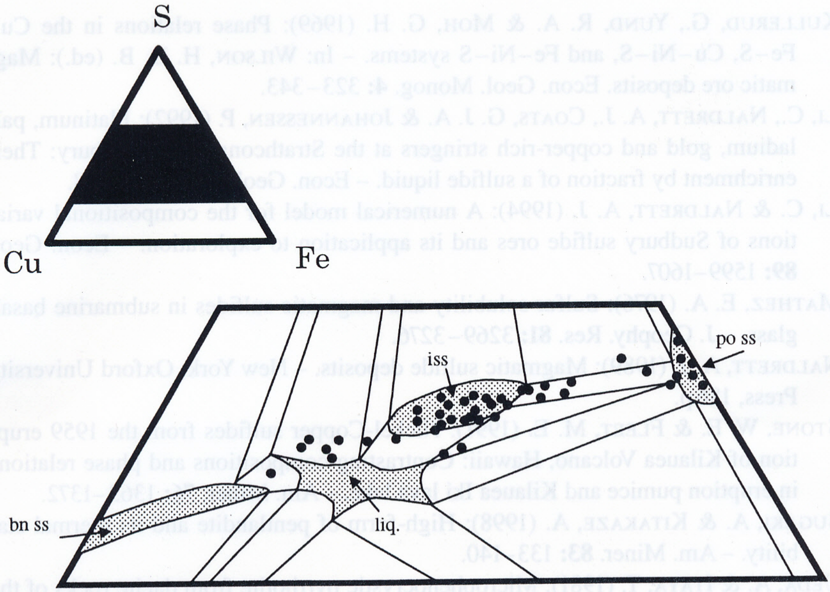

Fig. 6. The composition of sulfides from the 1991 Pinatubo eruption products (Hattori 1996) on the obtained Cu–Fe–S phase diagram.

gram with that of Kullerud et al., (1969) is that the sulfide liquid is between bornite and iss, and both of the tie-line between bornite and iss and that between bornite and pyrrhotite are unstable in this study.

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