A Phase Equilibrium Study of Cu-Fe Sulfides between 700℃ and 800℃

Laura Bilenker

Advisors: Dr. Philip A. Candela and Dr. Philip M. Piccoli with Brian Tattitch

GEOL 394

May 2, 2008

ABSTRACT: There are discrepancies regarding the presence of a liquid phase at 800℃ in the Cu-Fe-S system. This problem was explored through sealed silica tube experimentation in this study. Nine experiments were completed, with seven different temperature-composition combinations, and 20 runs total in which mixtures of sulfides, commonly found in volcanic rocks, were heated to 750℃ - 800℃ (Fig. 3). The run products were analyzed for the presence and composition of a melt, to determine the lowest temperature that sulfide liquid may exist in the Cu-Fe-S system. Methods of analysis included reflected light microscopy and use of an electron probe microanalyzer (EPMA). Compositions of the phases were plotted in Cu-Fe-S space.

First, an attempt was made to recreate the conditions and phase relations from Tsujimura and Kitakaze (2004) at 800℃ (Fig. 2B). Toward this end, a mixture of bornite (bn) and chalcopyrite (ccp) was used. Optical observations along with imaging and compositional analyses from the EPMA display evidence of melt at this temperature. The bulbous shape, dendritic patterns, and presence of vesicles indicated that a melt phase was present at 800℃.

Subsequent runs were held for 3 days near 900℃ before spending 3 days at run temperature. This conditioned the starting materials to increase the probability of homogeneous run products, which was lacking in the group 1 runs. Starting compositions of the runs included 60:40, 40:60, and 55:45 molar ratios of ccp to bn, respectively, as well as combinations of ccp, bn, and pyrrhotite (po). Run temperatures for these experiments were 800℃ to 750℃.

Evidence of a liquid phase was identified in charges of groups 1 and 2 which were run at 800℃ with a starting molar ratio of about 60:40 ccp to bn, and the resulting composition was between bn and ccp (Fig. 4). Many rounded vesicles and patterns of quenched liquid were seen. This is consistent with Tsujimura and Kitakaze's 2004 findings. No evidence of a quenched liquid phase was found in groups 3-9, which included starting compositions previously mentioned run between 800℃ and 750℃ (Fig. 5 and 6).

BACKGROUND:

- Hattori (1999) found that eruption products from Mt. Pinatubo show evidence of the existence of crystalline and molten sulfides.
- Previous studies (e.g. Kullerud et al. 1969) do not indicate melting below 900℃.

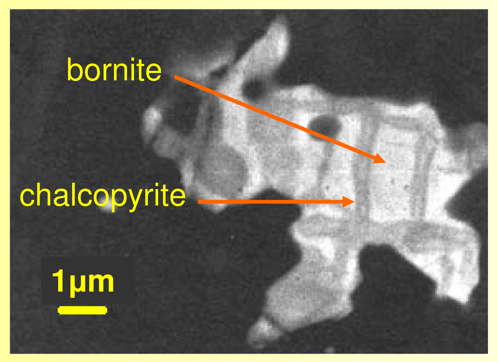

Fig. 1: Backscatter electron image showing exsolution of ccp from bn in a sulfide grain from Mt. Pinatubo eruption products (Hattori 1999).

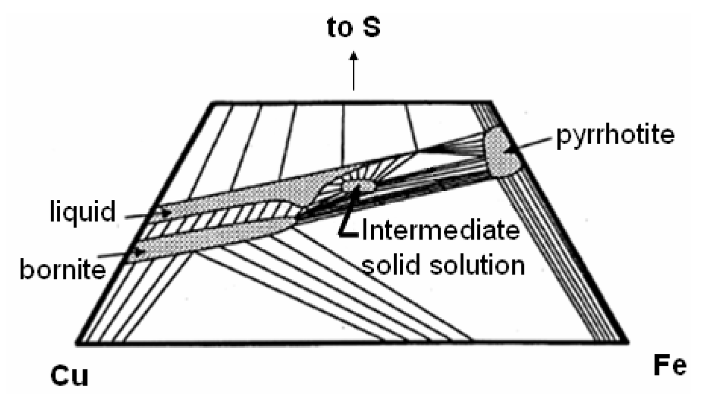

Fig. 2A: Cu-Fe-S system phase relations in atomic % by Kullerud et al. (1969) as redrawn by Tsujimura & Kitakaze (2004)

At 900℃:

- Three phase field with bn-iss-po
- Notice the location and size of the liquid field

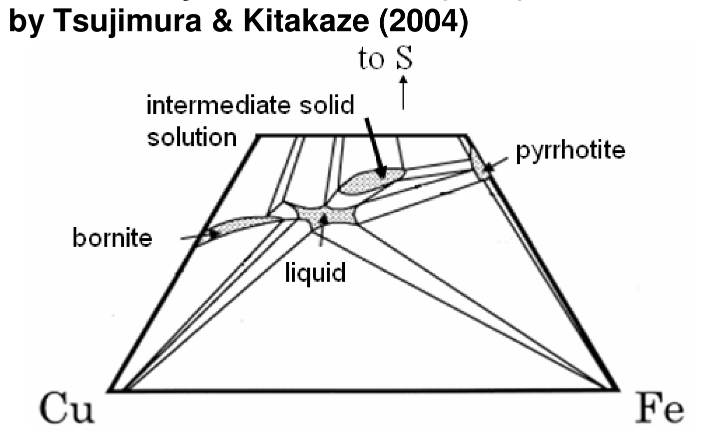

Fig. 2B: Cu-Fe-S phase relations by Tsujimura & Kitakaze (2004)

At 800℃:

- Bn is cut off from iss and po
- The liquid phase is in a different location--this liquid phase may or may not be related to that of 900℃

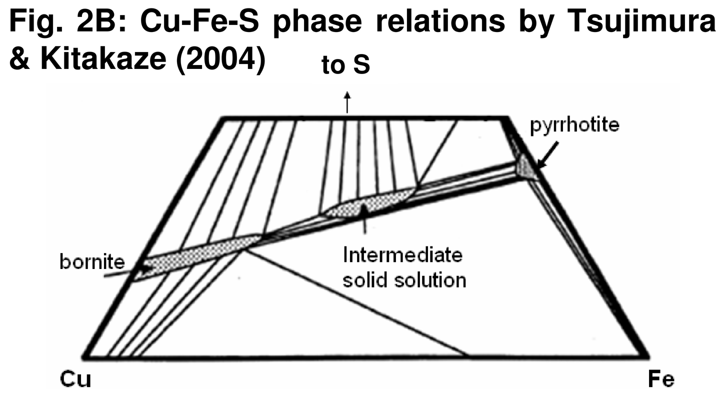

Fig. 2C: Cu-Fe-S system phase relations in atomic % by Kullerud et al. (1969) as redrawn by Tsujimura & Kitakaze (2004)

At 700℃:

- There is no liquid field
- There is a 3 phase field between bn, iss, and po.

HYPOTHESES:

Between 800℃ and 700℃:

1.) With decreasing temperature, liquid remains stable and a bn-iss tie-line is established.

2.) Liquid remains stable and the bn-po tie-line is established.

3.) The 3 phase assemblage bn-iss-po is established and the liquid phase disappears, or becomes an interior phase.

IMPLICATIONS:

The presence of small amounts of sulfide liquids in arc magmas has petrologic implications and applications for mineral exploration. Given that ore metals such as Ag or Au can partition into sulfide phases, small amounts of magmatic sulfides may "poison" ore formation. With the separation of sulfides, the silicate melt becomes depleted in ore metals, and the probability of the formation of a hydrothermal ore deposit decreases. Sulfide melts, including potential Cu-Fe-S melts, may extract a greater proportion of ore metals from a melt.

METHODS:

- Sealed silica tubes containing mixes of common sulfides
- Began with binary mix of bornite + chalcopyrite, then added pyrrhotite
- Preconditioning for 3 days near 900℃ (except group 1)
- Run temperature between 700℃ and 800℃ for 3 additional days
- Quench in water bath
- Analyzed using reflected light microscopy & EPMA

Run	Run Temperature (°C)	Run Time	Composition (molar ratio)	Furnace/Quench	Before Run Temperature…
1A	803	3 days	60cp:40bn	H/7 seconds	No preconditioning
1B	803	3 days	60cp:40bn	H/7 seconds	No preconditioning
1C	803	3 days	60cp:40bn	H/7 seconds	No preconditioning
1D	803	3 days	60cp:40bn	H/7 seconds	No preconditioning
2A	800	3 days	60cp:40bn	H/6 seconds	900 for 3 days
2B	800	3 days	60cp:40bn	H/6 seconds	900 for 3 days
3A	800	3 days	40cp:60bn	H/6 seconds	900 for 3 days
3B	800	3 days	40cp:60bn	H/6 seconds	900 for 3 days
4A	750	3 days	60cp:40bn	H/5 seconds	900 for 3 days
4B	750	3 days	60cp:40bn	H/5 seconds	900 for 3 days
5A	750	3 days	40cp:60bn	H/5 seconds	900 for 3 days
5B*	750	3 days	40cp:60bn	H/5 seconds	900 for 3 days
6A	800	3 days	55cp:45bn	V/rapid	913 for 3 days
6B	800	3 days	55cp:45bn	V/rapid	913 for 3 days
7A	800	3 days	37.5cp:25bn:37.5po	V/rapid	913 for 3 days
7B	800	3 days	37.5cp:25bn:37.5po	V/rapid	913 for 3 days
8A	752	3 days	60cp:40bn	V/rapid	903 for 3 days
8B	752	3 days	60cp:40bn	V/rapid	903 for 3 days
9A	752	3 days	1/3 po of group 7	V/rapid	903 for 3 days
9B	752	3 days	1/3 po of group 7	V/rapid	903 for 3 days

Key: orange: chalcopyrite-rich starting mixture
blue: bornite-rich starting mixture
green: pyrrhotite included in starting materials
5B*: dropped to the bottom of the furnace (~1 inch lower) at the start of run
H: horizontal furnace/slow quench
V: vertical furnace/instantaneous quench

Fig. 3: Table summarizing run information of all experiments.

EVIDENCE OF LIQUID IN GROUPS 1 & 2:

- 3 days at 800℃ (group 2: 3 days at 900℃ first)
- Starting molar ratio of 60:40 ccp:bn
- Methodological uncertainty: how to tell if there is liquid present?

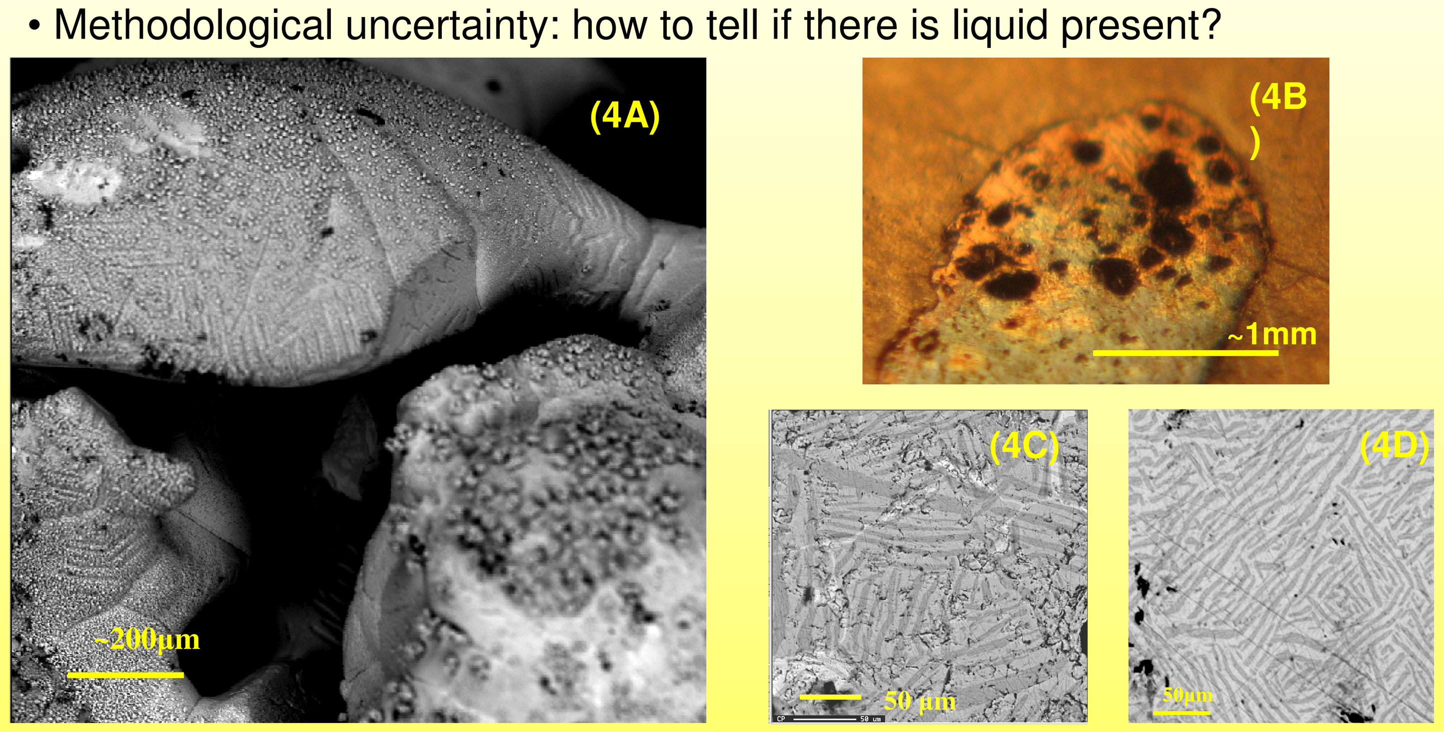

Fig. 4: Evidence of liquid seen in run products from groups 1 & 2 which were run at 800℃ with a 60:40 molar ratio of ccp to bn, respectively. (A) Run 1C: bulbous shape, vesicles, and parallel structures interpreted to be the surface manifestation of dendritic structures grown from liquid. (B) Run 2A: rounded vesicles. (C) and (D) Lamellae in Runs 1D and 2A, respectively, indicating a quenched liquid.

- Rounded vesicles
- Dendritic patterns/parallel lines on surface (4A)
- Lamellae are evident (4C, 4D)
- Bulbous shape (4A) in runs that approached 800℃ from lower temperature
- The combination of these features supports the presence of a melt phase

EVIDENCE OF EQUILIBRIUM & ABSENCE OF LIQUID IN GROUPS 3 - 9:

- Preconditioned for 3 days at ~900℃ then 3 days at 750℃ to 800℃
- 60:40, 40:60, and 55:45 molar ratios of ccp to bn, as well as combinations of ccp, bn, and po (Fig. 3)

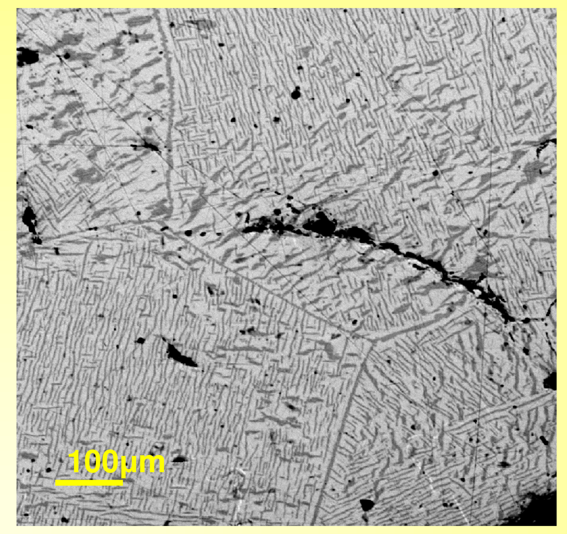

Fig. 5: Run 6A triple junctions

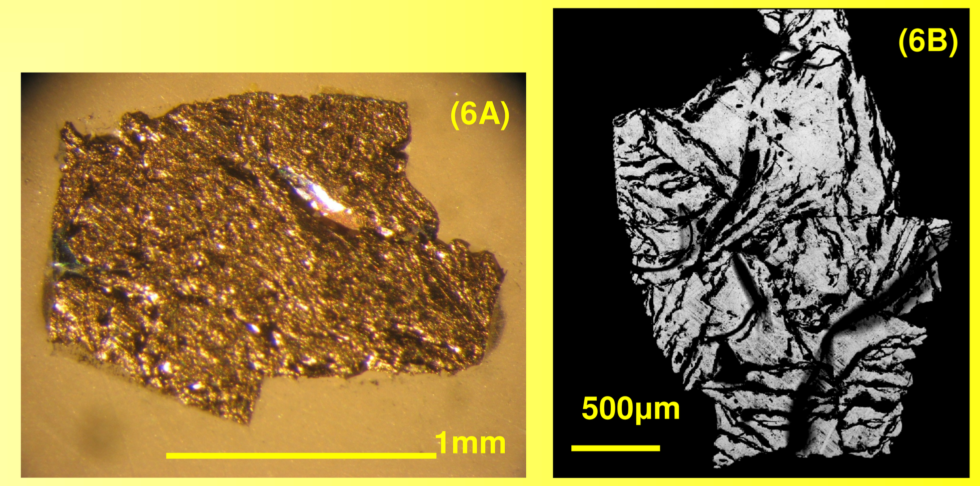

Fig. 6: Run 3A deep, faceted cracks. (A) is an image through a reflected light microscope and (B) is a backscatter electron image.

- Long run times and thermal conditioning at a minimum temperature of 900℃ helped to ensure equilibrium at run temperature.
- The following suggest equilibrium without a melt phase present:
  - Many runs (e.g. 6A, Fig. 5) exhibit an exsolution pattern and well defined grain boundaries, known as triple junctions (Walte et al. 2007)
  - Junctions meet at approximately equal 120° angles
  - Deep, faceted cracks (Fig. 6) are evidence of a solid phase, as opposed to the rounded vesicles seen in groups 1 & 2

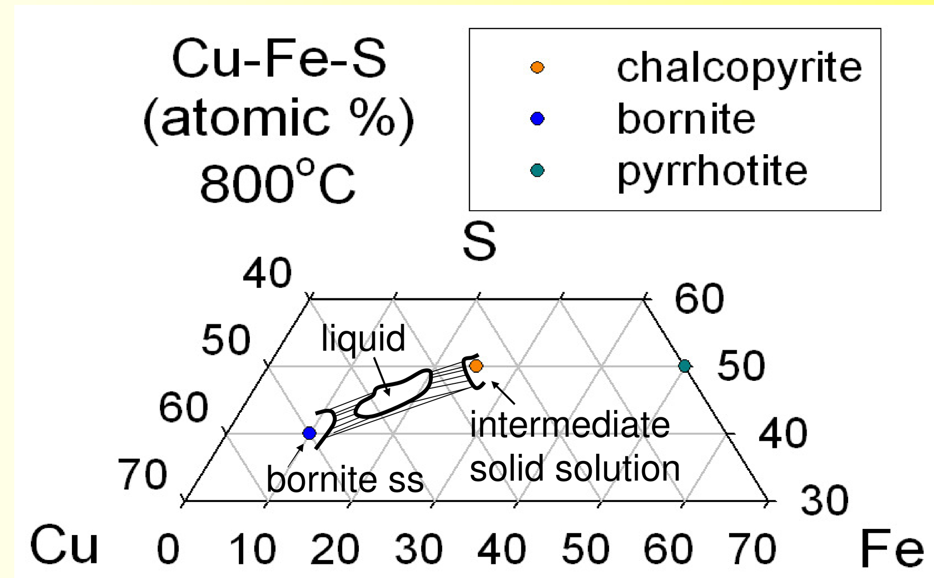

Fig. 7: Approximation of phase relations based on the presence or absence of liquid in experiments performed for project.

Run	Bornite	Intermediate Solid solution	Pyrrhotite	melt	T (°C)
1A	√	√	-	√	803
1B	√	√	-	√	803
1C	√	√	-	√	803
1D	√	√	-	√	803
2A	√	√	-	√	800
2B	√	√	-	√	800
3A	√	√	-	-	800
3B	√	√	-	-	800
4A	√	√	-	-	750
4B	√	√	-	-	750
5A	√	√	-	-	750
5B	√	√	-	-	750
6A	√	√	-	-	800
6B	√	√	-	-	800
7A	√	√	√	-	800
7B	√	√	√	-	800
8A	√	√	-	-	752
8B	√	√	-	-	752
9A	√	√	√	-	752
9B	√	√	√	-	752

Fig. 8: Check marks denote the presence of a phase while dashes indicate the absence of that phase for the indicated temperature for every run.

CONCLUSIONS:

- **Hypotheses #1 and #2, that the liquid remains stable as temperature drops from 800℃ to 750℃, does not seem to hold based on these experiments. I did not see evidence that there is a substantial liquid field at 750℃, but Tsujimura and Kitakaze's speculation that a sulfide melt exists at 800℃ was confirmed (Fig. 7); however, my results suggest that bn + iss + melt is a stable assemblage at 800℃.**
- **Hypothesis #3 holds because the three phase assemblage, bornite-intermediate solid solution-pyrrhotite was reestablished and no evidence of liquid was found in experiments with run temperatures around 750℃.**
- **Mixtures of bornite and chalcopyrite, which are found in volcanic and plutonic igneous rocks, may, therefore, reflect the presence of melt, depending upon their composition, down to 800℃. These melts, if segregated, may affect the concentration of Ag, Au and other ore metals, in arc magmatic systems.**

REFERENCES CITED::

Hattori, K. (1996): Occurrence and origin of sulfide and sulfate in the 1991 Mount Pinatubo eruption products. http://pubs.usgs.gov/pinatubo/hattori/.
Kullerud et al. (1969): Phase relations in the Cu-Fe-S, Cu-Ni-S, and Fe-Ni-S systems. Economic Geology Monograph 4: 323-343.
Tsujimura, T. & Kitakaze, A. (2004): new phase relations in the Cu-Fe-S system at 800℃; constraint of fractional crystallization of a sulfide liquid. –N. Jb. Miner. Mh. 2004 (10): 433-444; Stuttgart.
Walte et al. (2007): Liquid-distribution and attainment of textural equilibrium in a partially-molten crystalline system with a high-dihedral-angle liquid phase, Earth and Planetary Science Letters, v. 262, p. 517-532.