

Phase relations in the central portion of the Cu-Fe-Zn-S system between 800° and 500°C

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Abstract

Phase equilibrium in the central portion of the Cu-Fe-Zn-S system was studied by the evacuated silica glass tube method, and phase relations involving chalcopyrite, intermediate solid solution(iss), bornite, pyrrhotite and sphalerite have been determined between 800° and 500°C. Besides, compositional fields of each solid solution have been clarified. Chalcopyrite appearing only in experiments at 500°C has very limited solid solution field close to the stoichiometric CuFeS_2 , and dissolves small amounts of zinc less than 0.9 atm.%. However, iss having an extensive solid solution field dissolves considerable amounts of zinc from 12.7 atm.% at 800°C to 3.3 atm.% at 500°C, and these maximum solubilities of zinc are observed in more iron-rich iss than the cubanite composition at each temperature. Meanwhile, sphalerite solid solution also dissolves considerable amount of copper, and the CuS content in sphalerite increases with that of FeS in sphalerite above 600°C. The maximum observed CuS contents are 10.7 mole % at 800°C, 8.6 mole % at 700°C and 4.6 mole % at 600°C in sphalerite containing higher FeS than 40 mole %. Therefore, entry of copper into sphalerite is dependent upon both temperature and sulfur fugacity.

Introduction

In natural ores, chalcopyrite and sphalerite occur frequently as intimate intergrowths of skeletal sphalerite crystals (sphalerite stars) in chalcopyrite and chalcopyrite dots and blebs in sphalerite. How these characteristic intergrowths were formed has been an interesting subject of discussion on ore textures for many years, and they have been variously interpreted as the products of exsolution, replacement, epitaxial growth, and mechanical mixing. Among them, it is often believed that those are exsolution products, but experimental investigation on their implications has not been done fully.

In the present study, the phase relations in the central portion of the Cu-Fe-Zn-S system were determined over a wide temperature range to clarify the relationships between sphalerite and Cu-Fe-sulfides such as chalcopyrite and intermediate solid solution(iss), and compositional fields of all solid solutions appearing in the present system were also determined. As the first step, the authors report the experimental results between 800° and 500°C by the conventional dry method. Besides, sulfur

fugacities in some experimental runs were measured by the pyrrhotite indicator method at 800°, 700° and 600°C, and the relationships between sphalerite composition and sulfur fugacity were examined.

Previous studies

The work in the present system is built mainly upon the available information for the ternary systems Cu–Fe–S and Fe–Zn–S, in which numerous data have been provided.

Experimental investigations in the Cu–Fe–S system have been made since the first study of Merwin and Lombard (1937), and especially Yund and Kullerud (1966) determined the whole phase relations between 700° and 200°C. Afterward, Mukaiyama and Izawa (1970), Cabri (1973), Barton (1973), Sugaki *et al.* (1975), Ueno *et al.* (1980), Ueno (1981), and Sugaki *et al.* (1982) have further studied, clarifying the system in detail.

Phase relations in the Fe–Zn–S system have been also investigated since the first study of Kullerud (1953). Barton and Toulmin (1966) determined the phase relations in detail, and found out that sphalerite composition in the ternary system varies as a function of temperature and sulfur fugacity. The following studies have been carried out by Boorman (1967), Chernyshev and Anfilogov (1968), Chernyshev *et al.* (1968), Scott and Barnes (1971), Scott and Kissin (1973), Sorokin and Bezmen (1973), and Sorokin and Chichagov (1974). Among them, Boorman (1967) and Scott and Barnes (1971) determined the composition of sphalerite in equilibrium with pyrrhotite and pyrite experimentally.

Experimental investigations in the Cu–Fe–Zn–S system have been performed by many workers. Firstly, heating experiments for natural ores including chalcopyrite and sphalerite were conducted by Schwartz (1931), Buerger (1934), Borchert (1934), Nakano (1934, 1937 a, b), Sugaki and Yamae (1952), and Sugaki and Tashiro (1957), and most of them were focused on determining the mixing temperature. Synthetic experiments have been carried out to clarify phase relations in the system. Firstly, the pseudobinary join ZnS–CuFeS₂ was studied by Kullerud (1955), Donnay and Kullerud (1958), and Moh (1975). Czamanske (1974) determined sphalerite composition in the assemblage of chalcopyrite+pyrite+bornite+sphalerite under the hydrothermal condition. Recently, Wiggins and Craig (1980) and Shima *et al.* (1982) reported phase relationships in the Cu–Fe–Zn–S system, and gave chemical compositions of solid solutions at some univariant and divariant assemblages. Also Hutchison and Scott (1981) reported phase relations in the quaternary system and applied them to the sphalerite geobarometry over a wide range of temperature and pressure.

Experimental and analytical methods

Synthesis by the dry method

High purity elements were used as starting materials as follows: metallic copper (99.99%), metallic iron (99.9%), metallic zinc (99.999%) and crystalline sulfur (99.99%). Copper, iron and sulfur weighed exactly by the chemical balance were sealed in an evacuated pyrex glass tube for Cu-Fe-sulfides except chalcopyrite and pyrite, and heated first in electric furnaces for a few days at 550°C after keeping at 400°C for one day. Then, the products were taken out from the tube and resealed in an evacuated pyrex glass tube after grinding in an agate mortar under acetone to prevent oxidation. Subsequently they were reheated for some days at 550°C to produce homogeneous materials. Chalcopyrite was produced by reaction between such monosulfides CuS and FeS prepared through the above procedure, and pyrite also synthesized by reacting FeS with sulfur. Sphalerite (ZnS) was prepared by reaction between metallic zinc and sulfur sealed in an evacuated silica glass tube for one week at 800°–900°C after keeping for several days at 400°C to 700°C. The (Zn, Fe)S solid solution was prepared from carefully weighed portions of ZnS and FeS which were mixed by grinding in an agate mortar under acetone, and then sintered for 2 to 3 weeks at 800°–850°C. In the case of Fe-rich sphalerite solid solutions containing more than 40 mole % FeS, metallic iron as the buffer charge making low sulfur fugacity was sealed separately together with the mixtures of ZnS and FeS. For the experimental runs in the system these synthesized sulfides were used as starting materials and they were mixed in various proportions, and sealed in evacuated silica glass tubes. Then, they were heated in electric furnaces of which temperatures were controlled within $\pm 2^\circ\text{C}$ at 700°, 600° and 500°C, and $\pm 5^\circ\text{C}$ at 800°C. Heating periods were 10–22 days at 800°C, 20–135 days at 700°C, 30–148 days at 600°C, and 100–214 days at 500°C. After heating to equilibration, all samples were quenched in ice water.

Electron microprobe analysis

In determining chemical compositions of synthetic phases which often form solid solutions, electron microprobe analysis played a very important role. The analyses were performed by Shimadzu-ARL, EMX-2 type instrument in the conventional wavelength dispersive way under the conditions of 20 kV accelerating voltage, 0.02 μA specimen current on natural chalcopyrite. Radiation lines analyzed and curved crystals used for each element were as follows: $\text{CuK}\alpha$, $\text{FeK}\alpha$ and $\text{ZnK}\alpha$; LiF , and $\text{SK}\alpha$; ADP. Standards employed were: natural chalcopyrite for Cu, Fe and S, but in the case of bornite and pyrrotite, synthetic chalcocite for Cu and synthetic troilite for Fe respectively; synthetic pure sphalerite (ZnS) for Zn. Calculations for correction were made by a desktop computer (Yokogawa-Hewlett-Packard 9825S) connected to

the apparatus directly through an interface with the on-line system (Sugaki *et al.*, 1982). Using the input data, chemical composition was computed instantly by means of the Bence and Albee method (Bence and Albee, 1968; Sugaki *et al.*, 1974). Analytical value for each phase produced in the run was shown as the average of measurements in several grains, and chemical compositions of all phases except pyrite and covellite in each run were determined.

Measurement of sulfur fugacity

It has been frequently recognized that sulfur fugacity (f_{S_2}) performs an important role in sulfide phase relationship. Barton and Toulmin (1966) proved that sphalerite composition in the Fe–Zn–S system varies as a function of temperature and sulfur fugacity. Also, Barton (1973) determined the sulfur fugacity in equilibrium with iss at various metal/sulfur ratios for Cu=Fe in the Cu–Fe–S system. Afterward Ueno *et al.* (1980) determined sulfur fugacities for the univariant phase assemblages in the $CuFeS_2$ –FeS join.

In the present study, the pyrrhotite indicator method (Toulmin and Barton, 1964) was employed to determine the sulfur fugacity for assemblages including iss and sphalerite. Because thermochemical calculations of sulfur fugacity in quaternary system are very difficult, only experimentally measured sulfur fugacities were given in the present study.

The pyrrhotite indicator method is effectual to comparatively low sulfur fugacity region, and total error of this measurement was ± 0.35 in $\log f_{S_2}$. At the bottom of silica glass capsule a small amount of hexagonal pyrrhotite of known composition was placed, and a charge produced by the dry method was held in the middle of capsule separately from pyrrhotite. This capsule was evacuated and kept in an electric furnace at each temperature. After heating, the capsule was quenched in ice water. Heating periods were several days between 800° and 600°C. Then, the pyrrhotite composition after heating was determined by X-ray powder diffraction using Guinier-Hägg camera. On the basis of measured d_{102} value of pyrrhotite, pyrrhotite composition was estimated using the equation given in Sugaki *et al.* (1980). From the pyrrhotite composition, sulfur fugacity was determined by the equation given in Toulmin and Barton (1964).

Experimental results

Phase relations

Within the temperature range of this study five solid solutions are stably present in the present system; iss, chalcopyrite solid solution, bornite solid solution, pyrrhotite solid solution and sphalerite solid solution. Chalcopyrite is unstable above 557°C (Pankratz and King, 1970), so it appears only in experimental runs at 500°C. Addi-

TABLE 1. Chemical compositions for some univariant phase assemblages in the Cu-Fe-Zn-S system between 800° and 500°C.

T(°C)	Phase assemblages		Chemical compositions (atm.%)							
			This study				Wiggins and Craig (1980)			
			Cu	Fe	Zn	S	Cu	Fe	Zn	S
800	bn+iss+sp+S(l)	bn	41.6	14.5	1.8	42.1	41.5	14.2	1.5	42.8
		iss	32.1	18.2	4.1	45.8	32.4	18.2	3.1	46.3
		sp	2.0	5.4	42.9	49.8	1.4	4.4	43.7	50.5
	iss+po+sp+S(l)	iss	11.7	26.0	12.7	49.6	12.3	26.7	11.3	49.7
		po	3.5	43.1	0.2	53.2	2.1	44.5	0.0	53.4
		sp	3.8	16.0	30.7	49.6	3.1	14.0	33.1	49.8
700	bn+iss+sp+S(l)	bn	41.3	15.3	1.3	42.1	42.2	13.9	1.1	42.8
		iss	34.3	17.9	2.7	45.1	33.9	18.5	1.8	45.8
		sp	0.9	2.6	46.4	50.1	0.7	1.4	47.5	50.4
	iss+py+po+sp	iss	15.4	28.4	6.5	49.7	14.9	29.3	5.8	50.0
		po	2.1	43.9	0.2	53.8	1.9	44.1	0.0	54.0
		sp	1.2	10.7	38.2	49.8	1.0	10.4	38.2	50.4
600	bn+iss+sp+S(l)	bn	45.4	12.4	1.1	41.1	43.1	12.4	1.0	43.5
		iss	33.8	18.7	1.8	45.7	31.9	19.4	1.5	47.2
		sp	0.6	1.3	47.8	50.3	1.0	1.1	47.6	50.3
	iss+py+sp+S(l)	iss	24.8	23.3	3.1	48.8				
		sp	0.6	2.1	47.4	49.9				
		bn+iss+po+sp	bn	41.2	17.1	0.8	41.2			
		iss	22.1	28.5	3.4	46.0				
		po	1.9	47.6	0.2	50.4				
		sp	1.9	28.2	19.9	50.0				
	iss+py+po+sp	iss	15.4	30.5	4.5	49.6	15.3	31.3	3.4	50.0
		po	1.4	45.2	0.2	53.3	1.0	45.7	0.0	53.8
		sp	0.7	10.5	38.8	50.0	0.6	10.8	38.7	49.9
500	nk+bn+py+sp	nk	41.7	8.1	0.1	50.1				
		bn	51.3	8.6	0.6	39.5				
		sp	0.8	0.8	48.6	49.9				
	bn+cp+py+sp	bn	46.7	11.7	0.7	41.0				
		cp	24.6	24.7	0.7	50.0				
		sp	0.7	0.8	48.6	49.9				
	bn+iss+po+sp	bn	41.1	17.2	0.5	41.2				
		iss	18.1	32.6	2.5	46.8				
		po	1.8	48.1	0.2	49.9				
		sp	0.6	26.0	23.4	50.1				
	iss+py+po+sp	iss	15.8	31.9	2.5	49.9	15.8	32.5	2.4	49.3
		po	0.6	46.1	0.1	53.2	0.8	47.4	0.0	51.7
		sp	0.2	9.6	40.5	49.8	0.4	9.7	40.2	49.7

Abbreviation: bn—bornite, iss—intermediate solid solution, py—pyrite, po—pyrrhotite, cp—chalcopyrite, nk—nukundamite, sp—sphalerite, S(l)—Sulfur liquid.

tionally, nukundamite and covellite also appear as stable phases at 500°C. Sulfur liquid is present at each temperature.

At 800°C five univariant phase assemblages are stably present as follows: bornite+iss+sphalerite+sulfur liquid, iss+pyrrhotite+sphalerite+sulfur liquid, bornite+pyrrhotite+metallic iron+sphalerite, bornite+metallic iron+metallic copper+sphalerite and bornite+iss+pyrrhotite+sphalerite. Among them the first four assemblages were recognized in the present experiment. Pyrite is stable at 700° and 600°, so that two univariant assemblages of iss+pyrite+sphalerite+sulfur liquid and iss+pyrite+pyrrhotite+sphalerite become stable. The former assemblage, however, was not confirmed at 700°C. Furthermore, the following two univariant assemblages appeared at 500°C: nukundamite+bornite+pyrite+sphalerite and bornite+chalcopyrite+pyrite+sphalerite. The appearances of covellite, nukundamite and chalcopyrite at 500°C should result in the additional univariant assemblages of covellite+bornite+sphalerite+sulfur liquid, nukundamite+bornite+sphalerite+sulfur liquid, nukundamite+pyrite+sphalerite+sulfur

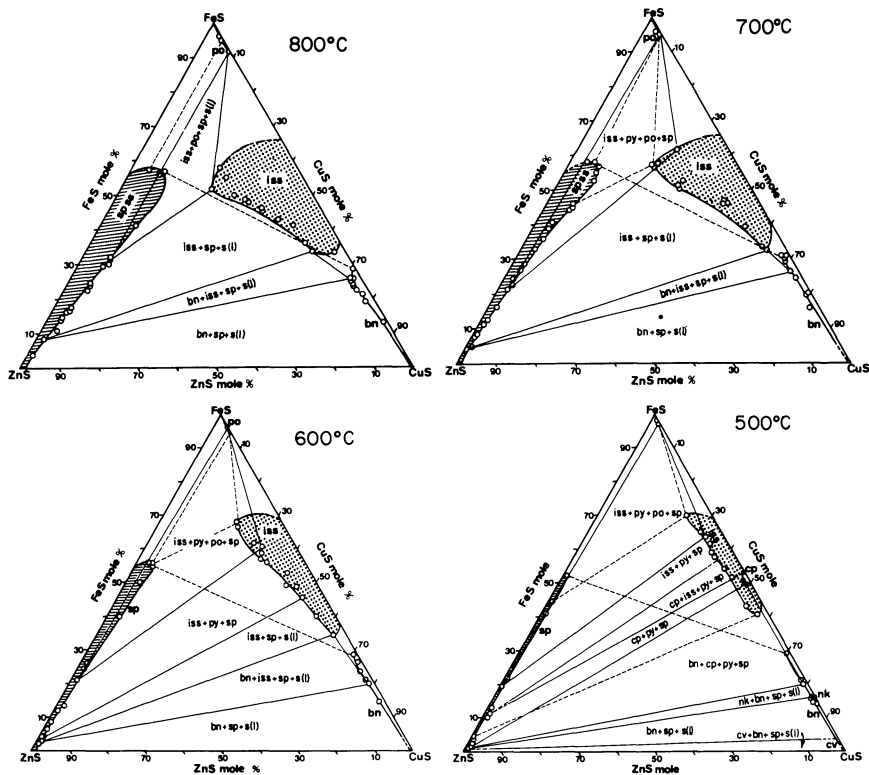


FIG. 1. Isothermal phase relations in the Cu-Fe-Zn-S system between 800° and 500°C shown by projection from the sulfur corner onto the CuS-FeS-ZnS plane.

liquid, bornite+chalcopyrite+iss+sphalerite and chalcopyrite+iss+pyrite+sphalerite. However, they were not found because reaction among phases was very slow at 500°C. The analyzed compositions for each phase of some univariant assemblages obtained in the present study are shown in Table 1 together with those from Wiggins and Craig (1980). They are nearly in good agreement. From these experimental results, phase relations at 800°, 700°, 600° and 500°C are shown together in Figs. 1 and 2. In those figures, comparatively sulfur-rich phase assemblages involving pyrite and sulfur liquid are summarized. Isothermal phase relations at each temperature are shown in Fig. 1 by projection from the sulfur corner onto the CuS-FeS-ZnS plane in the Cu-Fe-Zn-S tetrahedron, and schematic phase relations in this tetrahedron at 600°C also shown in Fig. 2. Stable solid solutions and phase appearing between 800° and 500°C are summarized as follows.

Iss: The *iss* phase has a sphalerite-type face centered cubic (fcc) structure, consisting of cubic close-packed sulfur atoms with variable amounts of copper and iron disordered over the tetrahedral sites (Cabri, 1973), and the behavior of *iss* with zinc in the

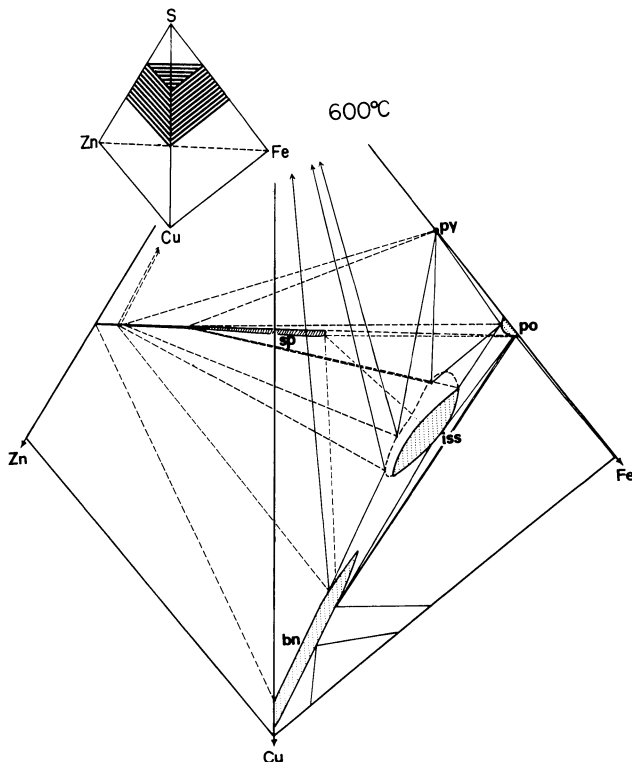


FIG. 2. Phase relations in the central portion of the Cu-Fe-Zn-S tetrahedron at 600°C.

TABLE 2. Chemical compositions of iss at the Cu-rich and Fe-rich extremities in the Cu-Fe-S and Cu-Fe-Zn-S systems between 800° and 500°C.

T(°C)	Chemical compositions									
	Atomic percent					Atomic percent				
	Cu	Fe	Zn	S	(Cu/Fe)	Cu	Fe	S	(Cu/Fe)	
800 a	32.7	17.8	4.3	45.3	(1.84)					
b	11.3	29.3	10.1	49.3	(0.39)					
700 a	34.3	17.9	2.7	45.1	(1.92)	31.5	23.3	45.2	(1.35)	(1)
b	10.5	28.5	11.1	49.9	(0.37)	16.7	33.3	50.0	(0.50)	(1)
600 a	33.8	18.7	1.8	45.7	(1.81)	33.0	21.0	46.0	(1.57)	(2)
b	10.0	34.0	6.5	49.5	(0.29)	15.5	35.0	49.5	(0.44)	(2)
500 a	30.1	21.6	1.6	46.8	(1.39)	28.8	23.8	47.4	(1.21)	(3)
b	11.6	35.1	3.3	49.9	(0.33)	15.8	35.0	49.2	(0.45)	(3)

References: (1) Yund and Kullerud (1966); (2) Cabri (1973); (3) Ueno (1981).

a; at the Cu-rich extremity

b; at the Fe-rich extremity

present system is closely similar to that in the zinc-free Cu-Fe-S system (Hutchison and Scott, 1981). Iss has an extensive solid solution field extending from near the stoichiometric cubanite composition toward the copper-rich composition as shown in Table 2, which gives measured compositions of iss at the Cu-rich and Fe-rich extremities in the present system together with those in the zinc-free Cu-Fe-S system. Also the table shows that zinc as an added component substitutes for both iron and copper in iss.

Iss produced at 800° and 700°C has generally very fine star-like sphalerite crystals even though it was quenched in ice water. Thus bulk composition of iss intergrown with fine sphalerite stars was obtained. Solubility of zinc in iss is considerably high, and the maximum observed solubilities of zinc are 12.7 atm.% at 800°C, 11.1 atm.% at 700°C, 6.5 atm.% at 600°C, and 3.3 atm.% at 500°C. Wiggins and Craig (1980), however, have reported much higher solubility of zinc in iss at 800°C. In Fig. 3, ZnS contents in iss at 700° and 600°C are shown by projection from the point ZnS onto the Cu-Fe-S plane in the quaternary tetrahedron. In these figures, iss fields in the zinc-free Cu-Fe-S system determined by Yund and Kullerud (1966), Cabri (1973) and Ueno (1981) are shown together by dashed lines. The diagrams indicate that the amount of ZnS in iss increases as iss composition is enriched in iron content, and that the maximum observed ZnS content is situated in more iron-rich iss than the cubanite composition.

As mentioned above, in iss coexisting with sphalerite, star-like sphalerite crystals are commonly observed as exsolved products under a reflecting microscope. They become larger when cooled slowly in air (Fig. 4).

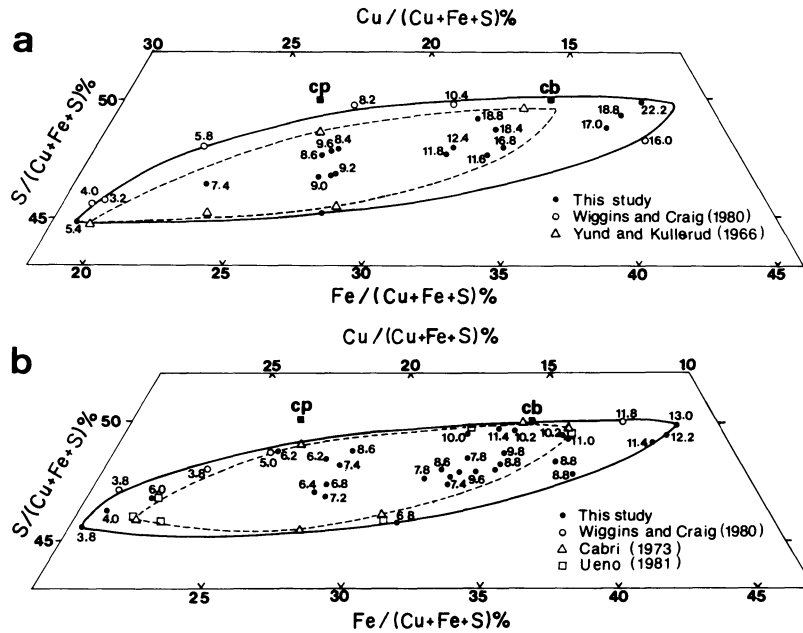


FIG. 3. ZnS content of iss at 700°C (a) and 600°C (b) shown by projection from the point ZnS onto the Cu-Fe-S plane in the Cu-Fe-Zn-S system. Figures show ZnS mole % in iss. Dashed lines show the iss field in the Cu-Fe-S system determined by (a): Yund and Kullerud (1966) and (b): Cabri (1973) and Ueno (1981). Solid squares represent the stoichiometric compositions of chalcopyrite (cp) and cubanite (cb).

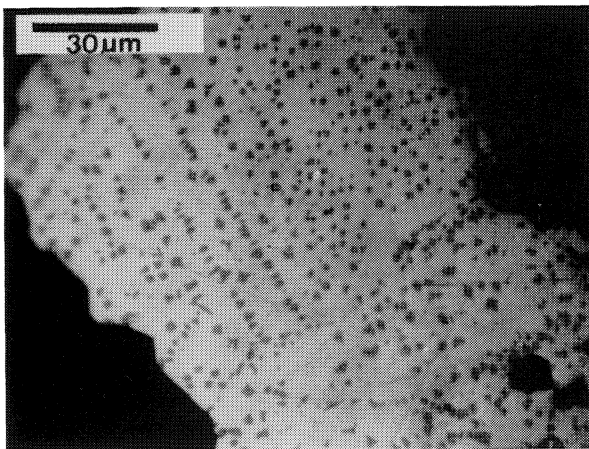


FIG. 4. Photomicrograph of exsolved sphalerite crystals in iss cooled slowly in air from 800°C.

Chalcopyrite: Chalcopyrite appearing in experimental runs at 500°C has a small solid solution field extending from nearly stoichiometric CuFeS_2 to the slightly iron-rich side, keeping the metal to sulfur ratio of approximately one (Sugaki *et al.*, 1975). In the present system, the measured composition of chalcopyrite at the Fe-rich extremity is $\text{Cu}_{0.94}(\text{Fe}_{1.02} \cdot \text{Zn}_{0.04})\text{S}_{2.00}$ ($\text{Cu}_{23.5}\text{Fe}_{25.5}\text{Zn}_{0.9}\text{S}_{50.0}$). The observed solubilities of zinc in chalcopyrite are generally low, and are no more than 0.9 atm.%

Bornite, nukundamite and pyrrhotite: Bornite has an extensive solid solution field especially in its copper and iron ratio. The solubility of zinc in bornite solid solution is much lower than that in iss, and the maximum zinc contents are 2.0 atm.% at 800°C and 0.9 atm.% at 500°C.

Nukundamite appearing as a stable phase at 500°C coexists with bornite, pyrite, sphalerite and sulfur liquid. Chemical compositions of nukundamite obtained in this study are nearly as constant as those determined by previous workers. Its zinc content is less than 0.4 atm.%

Pyrrhotite solid solution of the hexagonal type dissolves significant amount of copper from 3.5 atm.% at 800°C to 1.8 atm.% at 500°C. However, the solubilities of zinc in pyrrhotite are no more than 0.3 atm.% at each temperature.

Sphalerite: Sphalerite has a considerably wide solid solution field in its FeS content, and it has already been known that the maximum FeS content of sphalerite increases from 52 mole % at 580°C to 56 mole % at 850°C in the Fe–Zn–S system (Barton and Toulmin, 1966). In the present system, however, sphalerite solid solution dissolves more FeS molecules than that in the Cu-free system; the maximum FeS content of sphalerite is 57.5 mole % with 4.6 mole % CuS at 800°C. Above 600°C sphalerite also dissolves significant amount of CuS, and the maximum CuS contents are 10.7 mole % at 800°C, 8.6 mole % at 700°C and 4.6 mole % at 600°C in sphalerite

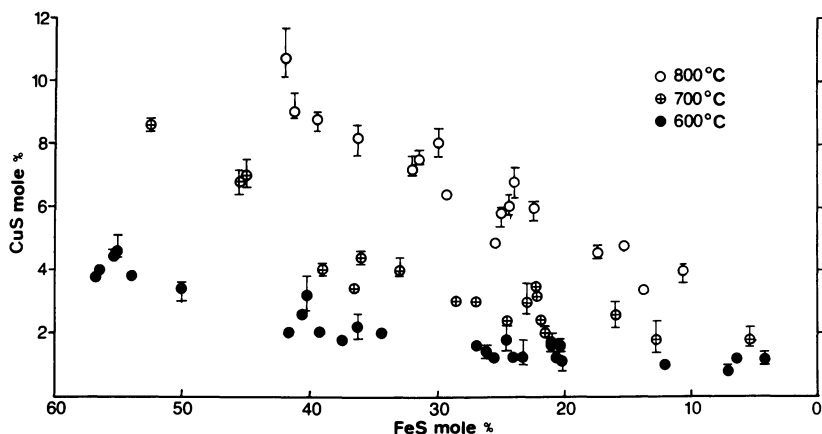


FIG. 5. Correlative relation between CuS and FeS contents in sphalerite coexisting with iss between 800° and 600°C.

containing higher FeS than 40 mole %. The correlative relationship between CuS and FeS contents in sphalerite solid solution coexisting with *iss* is shown in Fig. 5. The figure indicates that entry of copper into sphalerite is facilitated as FeS content of sphalerite increases, and that CuS/FeS value becomes smaller as the temperature decreases. At 500°C the CuS content of sphalerite solid solution is less than 1.8 mole %.

According to Table 1, at 700°C sphalerite in the univariant assemblage of *iss*+pyrite+pyrrhotite+sphalerite contains about 21 mole % FeS, that is nearly equal to the FeS content in sphalerite coexisting with pyrite and hexagonal pyrrhotite in the Cu-free system at lower temperatures than about 550°C. In the Fe–Zn–S system the FeS content of sphalerite equilibrated with pyrite and hexagonal pyrrhotite remains constant up to about 550°C (Boorman, 1967), but it is clearly shown that the constant FeS content of sphalerite is kept up to 700°C in the Cu-saturated system as reported by Hutchison and Scott (1981).

TABLE 3. Sulfur fugacities for the assemblage involving *iss* and sphalerite determined by the pyrrhotite indicator method between 800° and 600°C.

$T(^{\circ}\text{C})$	Bulk composition(atm.%)				Sp (mole %)		Pyrrhotite		$\log f_{\text{S}_2}$ (atm.)
	Cu	Fe	Zn	S	CuS	FeS	d(102) (A)	NFeS	
800	4.2	8.4	37.9	49.8	3.4	13.7	2.0632	0.9415	-1.5
	5.8	11.6	32.9	49.7	4.6	17.3	2.0601	0.9361	-1.2
	6.6	14.1	30.0	49.3	6.8	23.9	2.0668	0.9478	-2.0
	11.8	17.4	22.1	48.7	5.8	24.9	2.0679	0.9498	-2.1
	5.8	18.2	26.3	49.7	7.2	31.9	2.0713	0.9561	-2.7
	11.8	22.7	18.8	48.7	8.2	36.2	2.0765	0.9659	-3.6
	4.6	21.1	24.8	49.5	9.0	41.4	2.0792	0.9711	-4.1
	6.6	21.6	22.5	49.3	10.7	41.9	2.0779	0.9686	-3.9
700	4.6	12.9	33.1	49.5	2.0	21.6	2.0692	0.9522	-3.5
	6.6	14.1	30.0	49.3	2.4	21.7	2.0684	0.9507	-3.3
	11.8	17.4	22.1	48.7	3.2	22.3	2.0691	0.9520	-3.5
	8.5	15.3	27.2	49.1	3.0	22.9	2.0699	0.9535	-3.6
	11.8	22.7	18.8	48.7	4.0	32.9	2.0746	0.9623	-4.4
	6.6	21.6	22.5	49.3	4.4	36.1	2.0757	0.9644	-4.7
	5.8	24.8	19.7	49.7	7.1	45.1	2.0765	0.9659	-4.8
	4.2	23.4	22.6	49.8	6.8	46.0	2.0769	0.9668	-4.9
	4.6	27.7	18.2	49.5	8.6	52.6	2.0882	0.9893	-6.9
600	6.6	14.1	30.0	49.3	1.0	20.0	2.0635	0.9420	-3.8
	4.2	15.9	30.1	49.8	1.8	24.4	2.0707	0.9549	-5.1
	6.6	21.6	22.5	49.3	2.2	36.1	2.0748	0.9626	-5.9
	4.2	23.4	22.6	49.8	2.6	40.4	2.0769	0.9667	-6.4
	4.6	27.7	18.2	49.5	3.8	53.8	2.0863	0.9854	-8.9
	5.8	30.0	14.5	49.7	4.6	54.8	2.0812	0.9751	-7.4
	4.1	29.5	16.5	49.8	4.4	55.1	2.0840	0.9807	-8.2
	2.3	28.8	19.1	49.9	4.0	56.2	2.0883	0.9895	-9.7

Results of f_{S_2} measurement

For products synthesized by the dry method, sulfur fugacities for assemblage involving iss and sphalerite were measured between 800° and 600°C by the pyrrhotite indicator method, and a part of experimental results are summarized in Table 3. According to the table, the CuS content of sphalerite at higher temperatures above 600°C increases with decreasing sulfur fugacity. Besides, the solubility ranges of copper in sphalerite are shown in the diagram of $\log f_{S_2}$ vs $1000/T$ as Fig. 6, where univariant curves in the Fe–Zn–S system are depicted together. The univariant curves in the diagram are quoted from Toulmin and Barton (1964), Barton and Toulmin (1966) and Barton and Skinner (1979). From the diagram, it is clearly shown the CuS content of sphalerite is dependent upon both temperature and sulfur fugacity (or activity of FeS in sphalerite) and that entry of copper into sphalerite is facilitated with increasing temperature and decreasing sulfur fugacity.

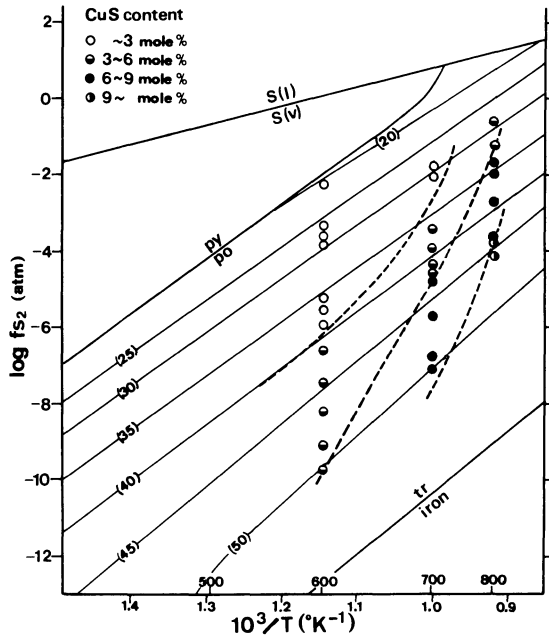


FIG. 6. Solubility ranges of copper in sphalerite coexisting with iss in $\log f_{S_2}$ vs $1000/T$ diagram. Copper content is represented as mole % CuS. Bracketed figures show the FeS isopleths of sphalerite associated with hexagonal pyrrhotite in the Fe–Zn–S system. The univariant curves are quoted from Toulmin and Barton (1964), Barton and Toulmin (1966) and Barton and Skinner (1979).

Summary and remarks

According to the experimental and analytical results, iss and sphalerite dissolve considerable amounts of zinc and copper respectively, and solubilities of zinc in iss and copper in sphalerite increase as bulk chemical composition in the system is enriched in iron.

The maximum zinc contents in iss are 12.7 atm.% at 800°C, 11.1 atm.% at 700°C, 6.5 atm.% at 600°C and 3.3 atm.% at 500°C, which are observed in more iron-rich iss than cubanite composition. However, the solubility of zinc in chalcopyrite is much lower than that in iss, and is no more than 0.9 atm.% at 500°C. On the other hand, in sphalerite containing higher FeS than 40 mole % the maximum CuS contents are 10.7 mole % at 800°C, 8.6 atm.% at 700°C and 4.6 mole % at 600°C. Entry of copper into sphalerite is facilitated with increasing iron content of sphalerite, and is dependent upon temperature and sulfur fugacity above 600°C.

Considerable amounts of CuS and FeS enough to be exsolved as chalcopyrite at lower temperatures are dissolved in sphalerite solid solution above 600°C. In the present study, however, solubility relation and textural features between sphalerite and Cu-Fe-sulfides such as chalcopyrite and iss at geologically significant temperatures and pressures are not given. The present authors are now doing studies on these problems at lower temperatures under hydrothermal conditions, and the results will be discussed elsewhere.

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