

Cu-Fe-S-Zn (Copper-Iron-Sulfur-Zinc)

V. Raghavan

This quaternary system embraces many important sulfide minerals, which are primary sources for the extraction of copper and zinc. The phase relationships in the central part of the composition tetrahedron in the temperature range of 800-300 °C are reviewed. In addition, the pseudoternary system of Cu_2S -FeS-ZnS and the effect of the addition of about 5 at.% Fe on the liquid miscibility gap in the Cu-S-Zn system, at 1200 °C, are described.

Binary Systems

For brief descriptions of the Cu-Fe, Cu-S, and Fe-S systems, see the Cu-Fe-S update in this issue. The Fe-Zn phase diagram exhibits a γ loop, extensive solubility of Zn in body-centered-cubic (bcc) Fe (α), and four intermediate phases: $\text{Fe}_3\text{Zn}_{10}$ (Γ), $\text{Fe}_{11}\text{Zn}_{40}$ (Γ_1), FeZn_{10} (δ), and FeZn_{13} (ζ) [1982Kub]. See [Pearson3] for crystal structure data. The Zn-S phase diagram [1996Sha] exhibits a congruently melting compound ZnS, which exists in two allotropic forms. ZnS (wurtzite, *wz*) has the hexagonal *B4* structure and sphalerite, *sp* (also called zinc blende) has the cubic *B3* form. The high-temperature form is wurtzite, which transforms at 1020 °C to sphalerite.

Ternary Systems

The review of the Cu-Fe-S system by [1979Cha] presented a liquidus projection and five isothermal sections at 1100, 1000, 840, 600, and 350 °C. The crystal structure data on the ternary compounds of this system are listed in Table 1 under Cu-Fe-S in this issue. The Cu-Fe-Zn system reviewed by [1992Rag] includes two isothermal sections at

1000 and 701 °C and a schematic reaction scheme. The review of the Fe-S-Zn system by [1988Rag] includes a schematic liquidus projection, a reaction scheme, and four isothermal sections at 850, 700, 600, and 400 °C, with an additional section at 927 °C in [2004Rag]. The composition of sphalerite in equilibrium with other phases was given as a function of temperature and pressure. In the Cu-S-Zn system, [1973Cra] studied the phase relationships at 800 °C, employing differential thermal analysis, x-ray powder diffraction, and reflected light microscopy. They determined isothermal sections at 1000, 800, and 500 °C and at low temperatures (<100 °C). The isothermal sections at 800 and 500 °C are redrawn in Fig. 1 and 2. ZnS (sphalerite) forms tie-lines with all the Cu-S and Cu-Zn phases. Except for the Cu-Fe-S system, no ternary compounds are known in the other three ternary systems above.

Quaternary Phase Equilibria

With Fe, Cu, and S of purity of 99.9%+ purity, the binary sulfides FeS and Cu_2S were synthesized. Using pure metals, ZnS of purity of 99.99%, and synthesized sulfides, [1995Sur] melted about 20 ternary and quaternary compositions in evacuated quartz ampules, which were given a final anneal at 1200 °C for 4 h and quenched. The phase equilibria were studied by metallography and electron probe microanalysis. The pseudoternary section of FeS- Cu_2S -ZnS determined by [1995Sur] at 1200 °C is redrawn in Fig. 3. ZnS (wurtzite), with a congruent melting temperature of 1718 °C, is the only solid sulfide at 1200 °C. It dissolves up to 48 mol% FeS at 1200 °C. The liquid phase is present along the FeS- Cu_2S join, which is in equilibrium with the

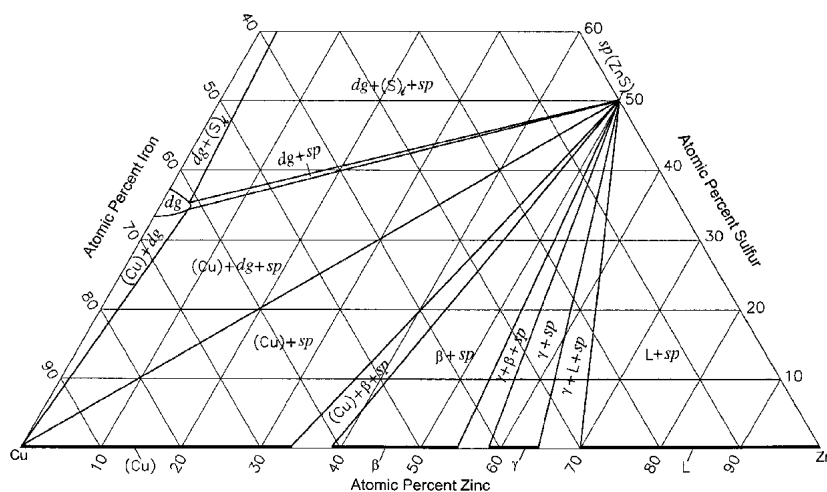


Fig. 1 Cu-S-Zn isothermal section at 800 °C [1973Cra]

Section II: Phase Diagram Evaluations

Table 1 Composition of phases in univariant assemblages in the Cu-Fe-S-Zn system

Temperature, °C	Phase assemblages		Composition, at. %				
			Cu	Fe	Zn	S	
800	<i>bn + iss + sp + (S)₁</i>	<i>bn</i>	41.6	14.5	1.8	42.1	
		<i>iss</i>	32.1	18.2	4.1	45.8	
		<i>sp</i>	2.0	5.4	42.9	49.8	
	<i>iss + po + sp + (S)₁</i>	<i>iss</i>	11.7	26.0	12.7	49.6	
		<i>po</i>	3.5	43.1	0.2	53.2	
		<i>sp</i>	3.8	16.0	30.7	49.8	
700	<i>bn + iss + sp + (S)₁</i>	<i>bn</i>	41.3	15.3	1.3	42.1	
		<i>iss</i>	34.3	17.9	2.7	45.1	
		<i>sp</i>	0.9	2.6	46.4	50.1	
	<i>iss + py + po + sp</i>	<i>iss</i>	15.4	28.4	6.5	49.7	
		<i>po</i>	2.1	43.9	0.2	53.8	
		<i>sp</i>	1.2	10.7	38.2	49.8	
600	<i>bn + iss + sp + (S)₁</i>	<i>bn</i>	45.4	12.4	1.1	41.1	
		<i>iss</i>	33.8	18.7	1.8	45.7	
		<i>sp</i>	0.6	1.3	47.8	50.3	
	<i>iss + py + sp + (S)₁</i>	<i>iss</i>	24.8	23.3	3.1	48.8	
		<i>sp</i>	0.6	2.1	47.4	49.9	
		<i>bn</i>	41.2	17.1	0.8	41.2	
	<i>bn + iss + po + sp</i>	<i>iss</i>	22.1	28.5	3.4	46.0	
		<i>po</i>	1.9	47.6	0.2	50.4	
		<i>sp</i>	1.9	28.2	19.9	50.0	
		<i>iss + py + po + sp</i>	<i>iss</i>	15.4	30.5	4.5	49.6
			<i>po</i>	1.4	45.2	0.2	53.3
			<i>sp</i>	0.7	10.5	38.8	50.0
	500	<i>nk + bn + py + sp</i>	<i>nk</i>	41.7	8.1	0.1	50.1
			<i>bn</i>	51.3	8.6	0.6	39.5
			<i>sp</i>	0.8	0.8	48.6	49.9
		<i>bn + cp + py + sp</i>	<i>bn</i>	46.7	11.7	0.7	41.0
			<i>cp</i>	24.6	24.7	0.7	50.0
			<i>sp</i>	0.7	0.8	48.6	49.9
<i>bn + iss + po + sp</i>		<i>bn</i>	41.1	17.2	0.5	41.2	
		<i>iss</i>	18.1	32.6	2.5	46.8	
		<i>po</i>	1.8	48.1	0.2	49.9	
		<i>sp</i>	0.6	26.0	23.4	50.1	
		<i>iss + py + po + sp</i>	<i>iss</i>	15.8	31.9	2.5	49.9
			<i>po</i>	0.6	46.1	0.1	53.2
<i>sp</i>			0.2	9.6	40.5	49.8	
Pressure ≈ 500 kg/cm² (49 MPa)							
500		<i>iss + py + po + sp</i>	<i>iss</i>	15.9	30.7	3.3	50.2
			<i>po</i>	0.9	45.7	0.1	53.3
			<i>sp</i>	0.4	10.2	39.4	50.1
		<i>bn + cp + py + sp</i>	<i>bn</i>	50.4	10.1	0.3	39.2
	<i>cp</i>		25.1	24.2	0.7	50.0	
	<i>sp</i>		0.3	0.7	49.0	50.0	
	<i>nk + bn + py + sp</i>	<i>nk</i>	41.2	8.3	0.3	50.2	
		<i>bn</i>	55.6	5.9	0.2	38.3	
		<i>sp</i>	1.2	0.5	48.4	49.9	
400	<i>bn + cp + py + sp</i>	<i>bn</i>	50.7	9.7	0.2	39.4	
		<i>cp</i>	25.1	24.2	0.7	50.0	
		<i>sp</i>	0.3	0.5	49.1	50.1	
	<i>nk + bn + py + sp</i>	<i>nk</i>	41.8	8.2	0.3	49.6	
		<i>bn</i>	55.6	6.3	0.2	37.9	
		<i>sp</i>	0.3	0.4	49.2	50.0	
	<i>cv + bn + nk + sp</i>	<i>bn</i>	57.2	5.0	0.2	37.7	
		<i>nk</i>	42.0	8.0	0.4	49.7	
		<i>sp</i>	0.9	0.3	48.7	50.1	
300	<i>bn + cp + py + sp</i>	<i>bn</i>	52.2	8.8	0.4	38.6	
		<i>cp</i>	24.9	24.8	0.5	49.9	
		<i>sp</i>	0.7	0.6	48.8	49.9	
	<i>cp + py + po + sp</i>	<i>cp</i>	23.4	26.2	0.4	50.0	
		<i>po</i>	0.7	46.5	0.2	52.7	
		<i>sp</i>	0.9	10.3	38.7	50.1	

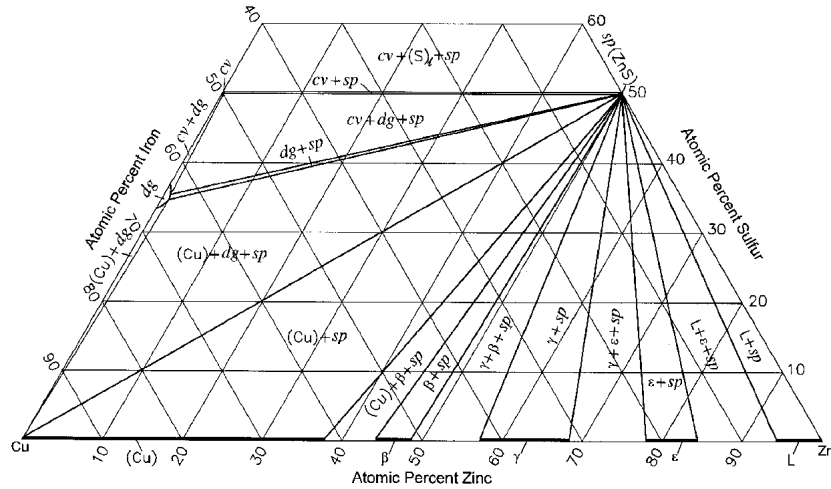


Fig. 2 Cu-S-Zn isothermal section at 500 °C [1973Cra]

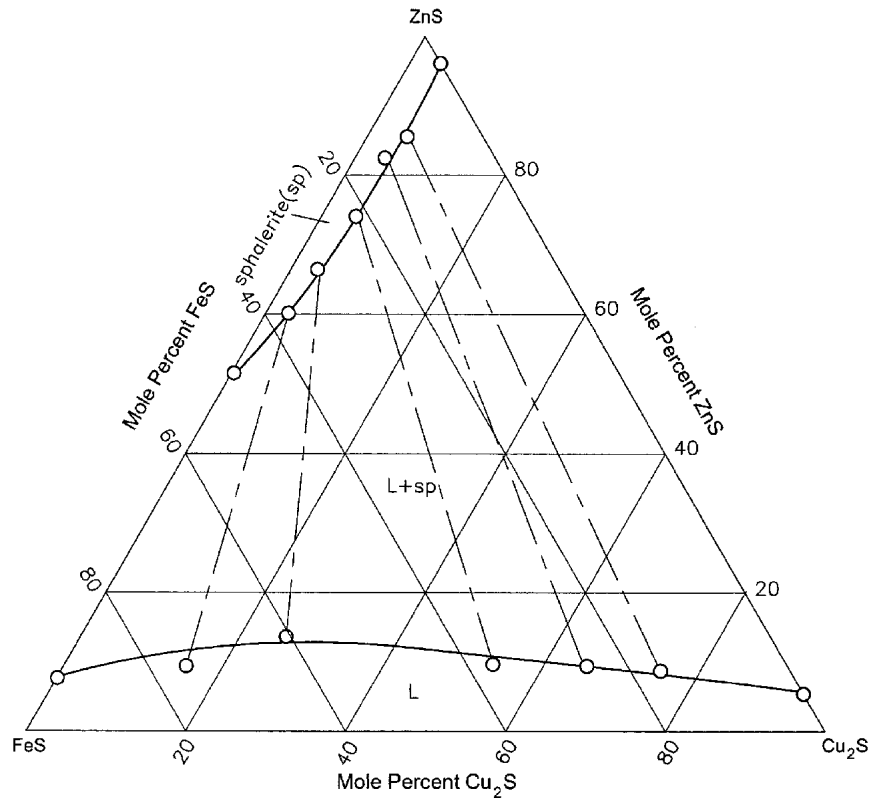


Fig. 3 Cu-Fe-S-Zn pseudoternary section Cu_2S -FeS-ZnS at 1200 °C [1995Sur]

above solid solution. [1975Kop] studied the liquidus surface of the $\text{Cu}_{1.8}\text{S}$ -FeS-ZnS pseudoternary system and found that the final solidification occurs close to the eutectic point of the $\text{Cu}_{1.8}\text{S}$ -FeS join.

The liquid miscibility gap determined by [1995Sur] for the Cu-S-Zn system and the Cu-Fe-S-Zn system at 5.5 at.% Fe are redrawn in Fig. 4. The presence of Fe increases significantly the width of the liquid miscibility gap. The

distribution ratio (wt.% Fe in sulfide liquid)/(wt.% Fe in alloy) is about 6 at 1200 °C and is constant for the Zn range of 5-20 wt.%. The ratio decreases slightly with the increase in the overall Fe content from 3.4-5.5 at.%.

The low-temperature equilibria in this quaternary system has been studied extensively. In this update, the more recent reports of [1980Wig], [1981Hut], [1984Koj], and [1985Koj] are reviewed. For a brief summary of the earlier

Section II: Phase Diagram Evaluations

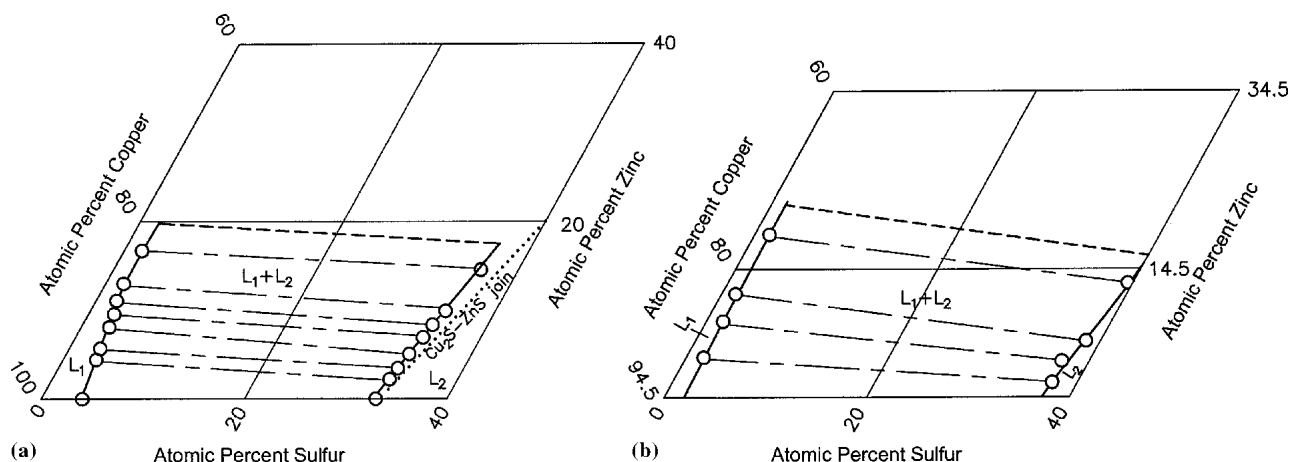


Fig. 4 Cu-Fe-S-Zn liquid miscibility gap near the Cu corner at 1200 °C (a) 0% Fe and (b) 5.5 at.% Fe [1995Sur]

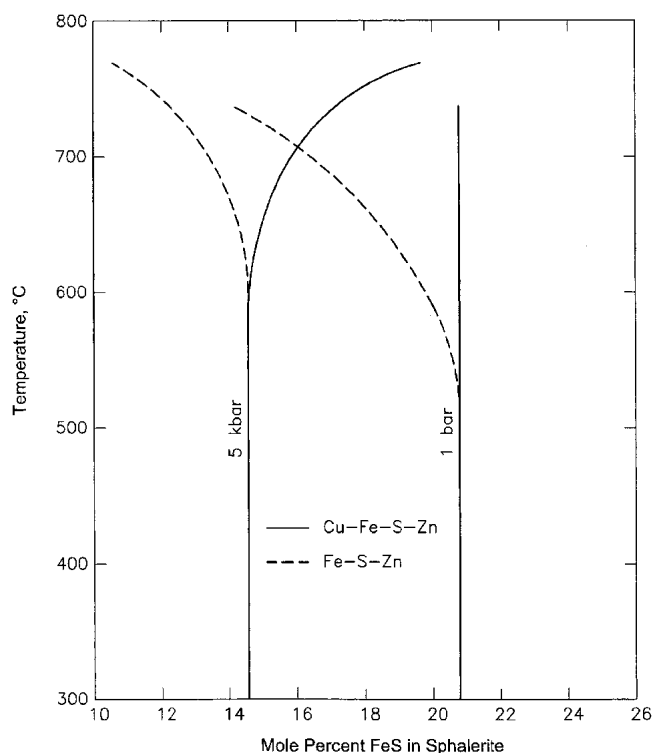


Fig. 5 Cu-Fe-S-Zn composition of sphalerite as a function of temperature and pressure [1981Hut]

investigations, see [1980Wig] and [1984Koj]. [1980Wig] measured the Cu content of sphalerite in this quaternary system between 800 and 500 °C and found that sphalerite dissolves 5 wt.% Cu, when it coexists with pyrrhotite and *iss* and 7 wt.% when it coexists with bornite. In contrast, naturally occurring sphalerites contain less than 0.5 wt.% Cu. This is attributed, at least partially, to the precipitation from the high-temperature solution during cooling, as evidenced by the presence of inclusions of chalcopyrite in sphalerite. [1981Hut] measured the composition of sphalerite as a function of pressure and temperature. They found

that in a certain temperature range, the FeS content of Cu-bearing sphalerite is a function only of the pressure and is given by the equation: $P \text{ (kb)} = 42.30 - 32.10 \log (\text{mol}\% \text{ FeS})$. The temperature-independent range is illustrated in Fig. 5. The deviation from this range is seen above 600 °C at 5 kb. The dotted lines show this deviation in Cu-free sphalerites at pressures of 1 b and 5 kb.

[1984Koj] investigated the phase relations in the central part of the Cu-Fe-S-Zn tetrahedron at 800, 700, 600, and 500 °C. Using starting materials of purity of 99.99% Cu, 99.9% Fe, 99.99% S and 99.999% Zn, [1984Koj] prepared quaternary compositions by heating mixtures in evacuated tubes in several stages. The final anneal was done for 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. The compositions of the coexisting phases were determined by electron probe microanalysis. S fugacity measurements were also made by employing the pyrrhotite technique. The measured compositions at the above temperatures are listed for the univariant (four-phase) assemblages in Table 1. As an example, the projection of the phase equilibria on the FeS-Cu₂S-ZnS plane from the S corner at 600 °C is illustrated in Fig. 6. A perspective view of the composition tetrahedron depicting two tie-tetrahedra at 600 °C is shown in Fig. 7. At 800 °C, five four-phase assemblages are stable: *bn* + *iss* + *sp* + (S)₁, *iss* + *po* + *sp* + (S)₁, *bn* + *po* + *sp* + (Fe), *bn* + *sp* + (Fe) + (Cu), and *bn* + *iss* + *po* + *sp*. As pyrite (*py*) temperature becomes stable below 743 °C, the univariant equilibria of *iss* + *py* + *sp* + (S)₁ and *iss* + *py* + *po* + *sp* become stable at 700 and 600 °C. At 500 °C, covellite (*cv*), nukundamite (*nk*), and chalcopyrite (*cp*) become stable and several additional univariant equilibria occur. The compositions of only those four-phase assemblages, which were found experimentally by [1984Koj], are listed in Table 1. The composition of *py* and *cv* is approximated to the stoichiometric value; (S)₁ is taken to be ~100% S.

In the temperature range below 500 °C, reaction among the refractory sulfides such as chalcopyrite is extremely sluggish, so that dry annealing in sealed tubes does not result in equilibrium. Under such conditions, the thermal gradient transport method or the isothermal recrystallization

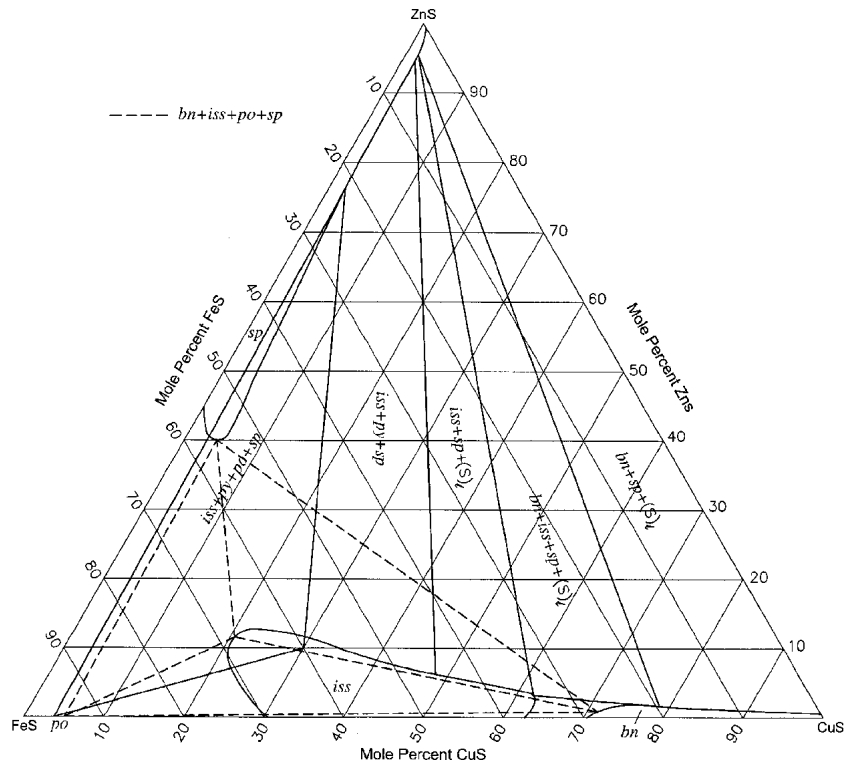


Fig. 6 Cu-Fe-S-Zn phase relationships at 600 °C projected on the FeS-CuS-ZnS plane from the S corner [1984Koj]

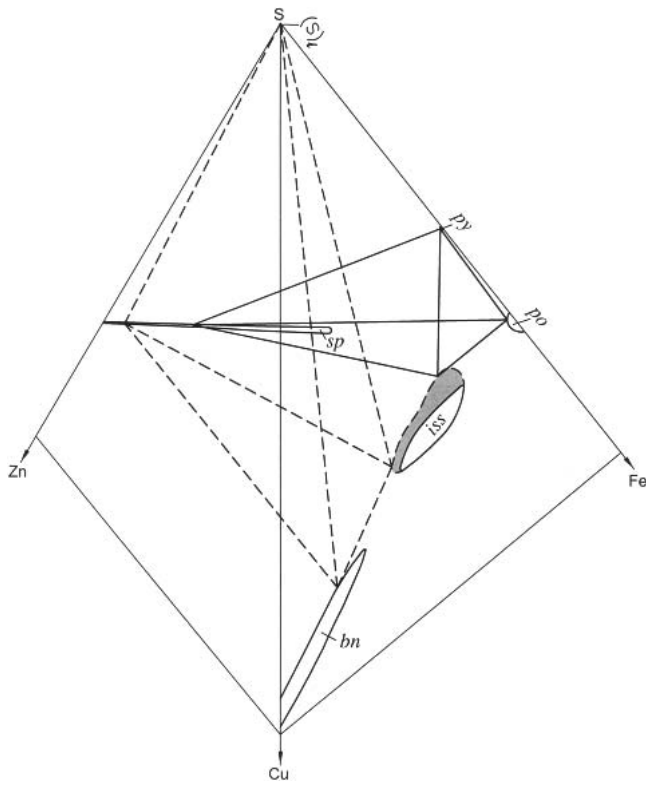


Fig. 7 Cu-Fe-S-Zn perspective view depicting the $[bn + sp + iss + (S)]$ and $[iss + py + po + sp]$ tie-tetrahedra at 600 °C [1984Koj]

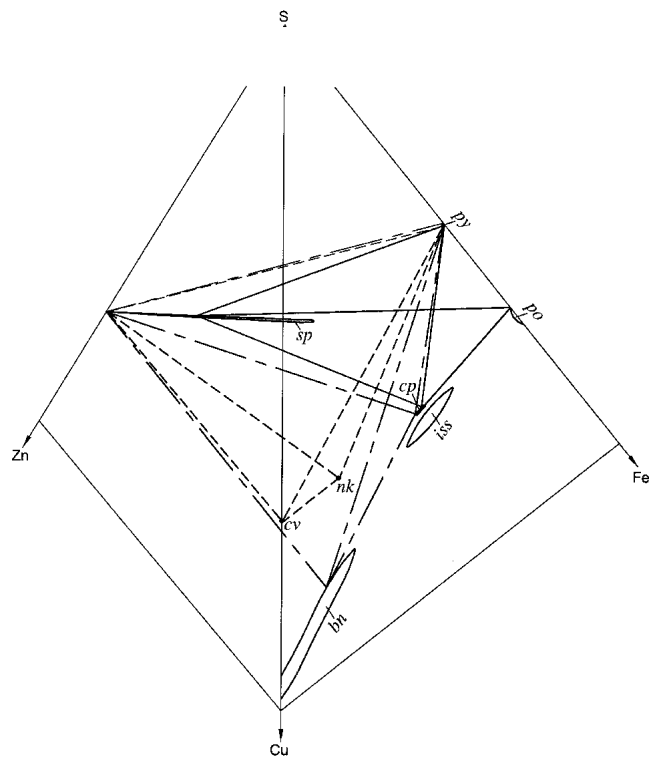


Fig. 8 Cu-Fe-S-Zn perspective view of the location of three of the tie-tetrahedra at 300 °C [1984Koj]

Section II: Phase Diagram Evaluations

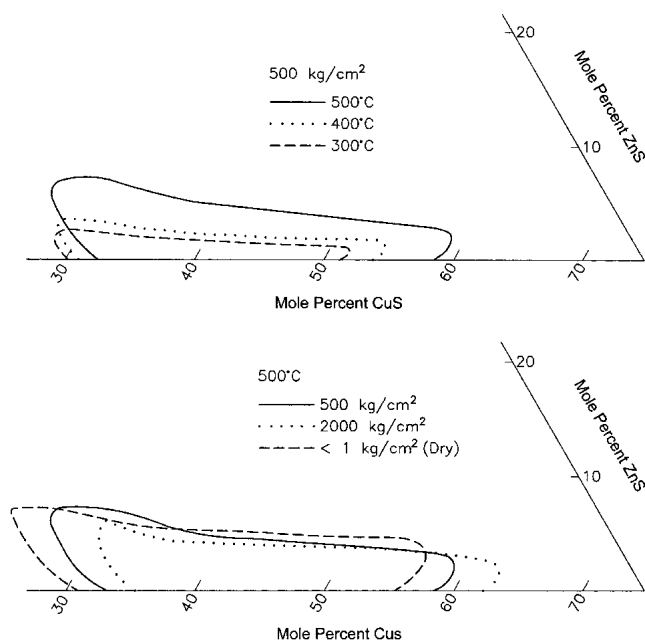


Fig. 9 Cu-Fe-S-Zn homogeneity range of *iss* projected on the FeS-CuS-ZnS plane from the S corner [1985Koj]

method under hydrothermal conditions is commonly adopted in mineral studies. This former method comprises the dissolution in an aqueous medium of the sulfide mixtures at the hot end of a reaction tube, transport by convection under a thermal gradient, and precipitation as intergrown crystals at the cool end of the reaction tube. [1985Koj] adopted mainly this method and measured the phase assemblages under a confining pressure of ~ 500 kg/cm² (= 49 MPa) or ~ 2000 kg/cm² (= 196 MPa). The stable univariant four-phase equilibria at 500 and 400 °C in the central part of the composition tetrahedron are: (*cv* + *nk* + *py* + *sp*), (*cv* + *bn* + *nk* + *sp*), (*bn* + *nk* + *py* + *sp*), (*bn* + *cp* + *py* + *sp*), (*bn* + *cp* + *iss* + *sp*), (*cp* + *iss* + *py* + *sp*), and (*iss* + *py* + *po* + *sp*). At 300 °C, the assemblages (*cp* + *py* + *po* + *sp*) and (*cp* + *iss* + *po* + *sp*) appear in place of the last two assemblages at 500 and 400 °C listed above. Chalcopyrite (*cp*) dissolves less than 0.9 at.% Zn at all three temperatures. The extensive solid solution field of *iss* dissolves up to 3.3, 1.7, and 1.2 at.% Zn at 500, 400, and 300 °C, respectively. Sphalerite (*sp*) dissolves up to ~ 2.4 mol% of CuS at the three temperatures, which is indepen-

dent of the FeS content of *sp*. The compositions of the phases in four-phase univariant equilibrium determined by [1985Koj] using the electron probe microanalysis at 500, 400, and 300 °C and at a pressure of ~ 500 kg/cm², are listed in Table 1. Figure 8 is a perspective view of the composition tetrahedron depicting three of the univariant equilibria (tie-tetrahedra) at 300 °C. Figure 9 depicts the effect of pressure and temperature on the homogeneity range of the intermediate solid solution *iss*, as projected on the FeS-CuS-ZnS plane.

References

- 1973Cra:** J.R. Craig and G. Kullerud, The Cu-Zn-S System, *Mineral Deposita*, Vol 8, 1973, p 81-91
- 1975Kop:** N.I. Kopylov and M.Z. Toguzov, The Cu_{1.8}S-FeS-ZnS System, *Zhur. Neorg. Khim.*, Vol 20 (No. 9), 1975, p 2562-2565 (in Russian); TR: *Russ. J. Inorg. Chem.*, Vol 20 (No. 9), 1975, p 1420-1422
- 1979Cha:** Y.A. Chang, J.P. Neumann, and U.V. Choudary, Phase Diagrams and Thermodynamic Properties of Copper-Sulfur-Metal Systems, *INCRA Monograph VII*, The International Copper Research Association, 1979, p 58-88
- 1980Wig:** L.B. Wiggins and J.R. Craig, Reconnaissance of the Cu-Fe-Zn-S System: Sphalerite Phase Relationships, *Econ. Geol.*, Vol 75, 1980, p 742-751
- 1981Hut:** M.N. Hutchison and S.D. Scott, Sphalerite Geobarometry in the Cu-Fe-Zn-S System, *Econ. Geol.*, Vol 76, 1981, p 143-153
- 1982Kub:** O. Kubaschewski, Iron-Zinc, *Iron—Binary Phase Diagrams*, Springer-Verlag, Berlin, 1982, p 172-175
- 1984Koj:** S. Kojima and A. Sugaki, Phase Relations in the Central Portion of the Cu-Fe-Zn-S System Between 800 and 500 °C, *Mineral. J.*, Vol 12 (No. 1), 1984, p 15-28
- 1985Koj:** S. Kojima and A. Sugaki, Phase Relations in the Cu-Fe-Zn-S System Between 500 and 300 °C Under Hydrothermal Conditions, *Econ. Geol.*, 1985, Vol 80, p 158-171
- 1988Rag:** V. Raghavan, The Fe-S-Zn (Iron-Sulfur-Zinc) System, *Phase Diagrams of Ternary Iron Alloys. Part 2*, Ind. Inst. Metals, Calcutta, 1988, p 335-349
- 1992Rag:** V. Raghavan, The Cu-Fe-Zn (Copper-Iron-Zinc) System, *Phase Diagrams of Iron Ternary Alloys. Part 6*, Ind. Inst. Metals, Calcutta, 1992, p 781-785
- 1995Sur:** S. Surapunt, C.M. Nyamai, M. Hino, and K. Itagaki, Phase Relations and Distribution of Minor Elements in the Cu-Zn-S, Cu-Zn-Fe-S and Cu-Zn-Pb-S Systems at 1473 K, *Metall. Review MMIJ*, 1995, Vol 12 (No. 2) p 84-97
- 1996Sha:** R.C. Sharma and Y.A. Chang, The S-Zn (Sulfur-Zinc) System, *J. Phase Equilibria*, Vol 17 (No. 3), 1996, p 261-266
- 2004Rag:** V. Raghavan, Iron-Sulfur-Zinc, *J. Phase Equilibria Diffusion*, Vol 25 (No. 4), 2004, p 380-381