

A thermodynamic prediction on the stability of the nukundamite + chalcopyrite and bornite + pyrite assemblages

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Abstract

A thermodynamic prediction of the Gibbs free energy of formation (ΔG_f°) of nukundamite (empirical composition $\text{Cu}_{5.5}\text{FeS}_{6.5}$) was made in order to specify whether the nukundamite + chalcopyrite or the bornite + pyrite assemblage is stable in the Cu–Fe–S system. The results of calculations using previously reported data of ΔG_f° values of some Cu–Fe–sulphide minerals in equilibrium with nukundamite indicate that the total free energy of the nukundamite + chalcopyrite assemblage is appreciably higher than that of the bornite + pyrite assemblage in the temperature range 250–400°C. This means that nukundamite + chalcopyrite is a metastable assemblage under common ore-forming conditions.

The occurrence of nukundamite is not uncommon in the Fijian kuroko deposits in contrast to the Japanese kuroko deposits. A thermochemical treatment for this phenomenon leads to the interpretation that the black ore containing nukundamite in the Fijian deposit was formed under relatively high-sulphidation and low-pH conditions. This suggestion is in good agreement with the present experimental result that the bornite + pyrite assemblage was produced in the temperature range 350–250°C by using near-neutral hydrothermal solutions.

KEYWORDS: nukundamite, chalcopyrite, bornite, pyrite, stability, kuroko deposits.

Introduction

ALTHOUGH great efforts have been made to elucidate the Cu–Fe–S system, many problems on phase equilibrium and mineral stability in this system remain unsolved. The phase relationship in the Cu-rich field is important in elucidating relatively oxidizing mineralization as observed in the kuroko-type deposits. Comprehensive phase relations in the ternary system have been reported by many workers including Merwin and Lombard (1937), Roseboom and Kullerud (1958), Yund and Kullerud (1966), Mukaiyama and Izawa (1970) and Sugaki *et al.* (1975, 1982). From systematic experiments under dry conditions, Yund and Kullerud (1966) and Mukaiyama and Izawa (1970) have confirmed a stable tie-line of

bornite–pyrite which is often observed in natural ores. However, Sugaki *et al.* (1975, 1982) have proposed, based on hydrothermal experiments in the temperature range 300–500°C, that the nukundamite + chalcopyrite assemblage is stable rather than that of bornite + pyrite. Czamanske (1974), Shima *et al.* (1982) and Kojima and Sugaki (1985) have shown that in the quaternary Cu–Fe–Zn–S system the bornite + pyrite assemblage is stable under hydrothermal conditions. This discrepancy was first assumed to be caused by an additional component such as zinc. However, in another quaternary system Cu–Fe–Bi–S, the nukundamite + chalcopyrite assemblage was obtained under hydrothermal conditions (Sugaki *et al.*, 1981, 1984). Thus, it is still uncertain which

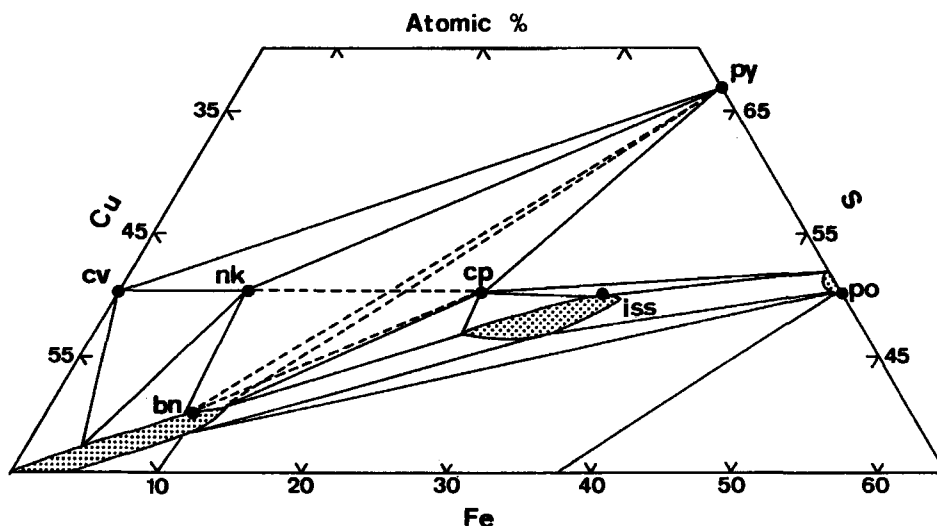


FIG. 1. Phase relations in the central portion of the Cu-Fe-S system at 300°C (modified from Sugaki *et al.*, 1975). Abbreviations: cv, covellite; nk, nukundamite; bn, bornite; cp, chalcopyrite; iss, intermediate solid solution; py, pyrite; po, pyrrhotite.

TABLE 1. Reported chemical compositions for natural and synthetic nukundamite.

	Cu	Fe	Zn	Ag	As	S	Total	Formula
Frenzel and Ottemann (1967)	56.3	9.8	-	-	-	33.7	99.8	
(Nukundamu)	41.9	8.3	-	-	-	49.7		$\text{Cu}_{5.05}\text{FeS}_{5.99}$
Colley and Rice (1975)	56.9	9.6	-	0.1	0.04	33.5	99.8	
(Nukundamu)	42.2	8.2	-	0.04	0.03	49.6		$\text{Cu}_{5.15}\text{FeS}_{6.05}$
Clark (1970)	56.7	9.5	-	-	-	33.9	100.1	
(Aucanquilcha)	42.1	8.0	-	-	-	49.9		$\text{Cu}_{5.26}\text{FeS}_{6.24}$
Sugaki <i>et al.</i> (1975)	56.9	9.0	-	-	-	33.8	99.7	
(synthetic)	42.4	7.6	-	-	-	49.9		$\text{Cu}_{5.58}\text{FeS}_{6.57}$
Sugaki <i>et al.</i> (1981)	55.9	10.0	-	-	-	33.8	99.8	
(synthetic)	41.6	8.5	-	-	-	49.9		$\text{Cu}_{4.89}\text{FeS}_{5.87}$
Sugaki <i>et al.</i> (1982)	55.7	10.4	-	-	-	34.2	100.2	
(synthetic)	41.2	8.7	-	-	-	50.1		$\text{Cu}_{4.73}\text{FeS}_{5.76}$
	55.5	10.4	-	-	-	34.0	99.9	
	41.2	8.7	-	-	-	50.0		$\text{Cu}_{4.73}\text{FeS}_{5.75}$
Kojima and Sugaki (1985)	55.3	9.8	0.4	-	-	34.0	99.4	
(synthetic)	41.2	8.3	0.3	-	-	50.2		
	56.5	9.9	0.5	-	-	33.8	100.7	
	41.8	8.3	0.3	-	-	49.6		
	56.0	9.4	0.2	-	-	33.8	99.6	
	41.8	8.0	0.2	-	-	50.0		

Weight and atomic percents are in the upper and lower rows, respectively.

TABLE 2. Free energy changes (ΔG_r°) for some univariant equilibria involving Cu-Fe-S minerals.

Reaction	ΔG_r° (kJ)				
	250°C	300°C	350°C	400°C	
1. $5\text{CuFeS}_2 + \text{S}_2 = \text{Cu}_5\text{FeS}_4 + 4\text{FeS}_2$	-86.1	-74.1	-62.1	-50.0	a
2. $2\text{Cu}_{5.5}\text{FeS}_{6.5} + \text{S}_2 = 2\text{FeS}_2 + 11\text{CuS}$	-65.7	-54.0	-42.3	-30.6	b
3. $\frac{22}{23}\text{Cu}_5\text{FeS}_4 + \text{S}_2 = \frac{20}{23}\text{Cu}_{5.5}\text{FeS}_{6.5} + \frac{2}{23}\text{FeS}_2$	-66.4	-56.0	-45.6	-35.2	b
4. $\text{Cu}_5\text{FeS}_4 + \frac{1}{2}\text{CuS} + \text{S}_2 = \text{Cu}_{5.5}\text{FeS}_{6.5}$	-66.3	-55.6	-45.0	-34.4	b

a, Schneeberg (1973); b, Barton and Skinner (1979).

of the two assemblages is indeed stable. In this study, thermodynamic calculations and hydrothermal experiments were performed in order to re-examine the stability of the two mineral assemblages observed in the kuroko-type deposits in Japan and Fiji.

Thermochemistry of the mineral assemblages

Calculation of free energy

In the temperature range below 500°C, the phase relations in the Cu-rich field of the Cu-Fe-S system are similar, so the phase diagram at 300°C is shown as an example in Fig. 1. Nukundamite, located on the Cu-rich side, is a hexagonal mineral which was recently reported in the Fijian kuroko deposit, and proved to be distinctly different from idaite with the ideal composition Cu_3FeS_4 (Rice *et al.*, 1979). Nukundamite corresponds to the synthetic phase referred to as Cu_5FeS_6 (Merwin and Lombard, 1937) or $\text{Cu}_{5.5}\text{FeS}_{6.5}$ (Yund and Kullerud, 1966). Chemical compositions reported for natural and synthetic nukundamite are listed in Table 1, indicating that nukundamite has a limited compositional range from $\text{Cu}_{4.7}\text{FeS}_{5.7}$ to $\text{Cu}_{5.6}\text{FeS}_{6.6}$. Sugaki *et al.* (1975) showed that

nukundamite has no solid solution field at 300°C and 350°C. In the present thermodynamic calculations, the formula given for the synthetic compound $\text{Cu}_{5.5}\text{FeS}_{6.5}$, was adopted as the ideal composition for nukundamite (Yund and Kullerud, 1966; Barton and Skinner, 1979). The maximum stability temperature of nukundamite has been found to be 501°C (Roseboom and Kullerud, 1958). Barton and Skinner (1979) have suggested from thermodynamic predictions that nukundamite becomes unstable below *c.* 227°C, decomposing to pyrite, covellite and bornite.

Although no thermodynamic data for nukundamite have been given, the free energy of formation for nukundamite can be indirectly determined by using free energy data of other associated Cu-Fe-sulphide phases and some univariant equilibria involving them. Table 2 summarizes the free energy changes (ΔG_r°) for selected univariant reactions in the temperature range 250–400°C, which equals the chemical potential of S_2 vapor (Barton and Skinner, 1979). The mineral phases in the reactions in Table 2, except low-temperature (<300°C) bornite phase in the reaction 1, are regarded as having nearly ideal compositions. The Gibbs free energies of formation (ΔG_f°) of the minerals in Table 3 have been determined by Toulmin and

TABLE 3. Free energies of formation (ΔG_f°) of some Cu-Fe-S minerals.

Mineral	ΔG_f° (kJ)				Source
	250°C	300°C	350°C	400°C	
$\text{FeS}_2(\text{py})$	-195.2	-185.3	-175.5	-165.6	Toulmin and Barton (1964)
Cu_5FeS_4	-487.4	-477.2	-467.0	-456.9	Barton and Skinner (1979)
CuFeS_2	-236.7	-229.1	-221.5	-213.9	Robie <i>et al.</i> (1985)
CuS	-76.9	-73.3	-69.7	-66.0	Barton and Skinner (1979)
$\text{Cu}_{5.5}\text{FeS}_{6.5}$	-590.1	-567.2	-544.3	-521.4	calculated

Barton (1964), Barton and Skinner (1979) and Robie *et al.* (1985). By combining the free energy data in Table 3 with those for the reactions 2 to 4 in Table 2, ΔG_f° of nukundamite can be calculated. Due to appreciable uncertainties included in the thermodynamic data (Barton and Skinner, 1979) the three ΔG_f° values of nukundamite calculated using the reactions in Table 2 are slightly different, so the ΔG_f° of nukundamite at each temperature is presented as an average value in Table 3. Also, the calculated uncertainties in Tables 2 and 3 are not negligible. They are listed as follows: those for ΔG_f° of chalcopyrite and bornite and the related reaction (reaction 1 in Table 2) are $c. \pm 1.7$ kJ, and those for the others are $c. \pm 6.4$ kJ. Which of the nukundamite + chalcopyrite assemblage or the bornite + pyrite assemblage is thermodynamically stable, can be judged from ΔG_f° values for the following isochemical reaction:



The ΔG_f° values of the reaction computed by using the data in Table 3, are $94.5 (\pm 11.1)$ kJ at 250°C , $92.5 (\pm 14.0)$ kJ at 300°C , $90.9 (\pm 17.3)$ kJ at 350°C and $89.4 (\pm 20.7)$ kJ at 400°C . While the calculated uncertainties increase slightly with increasing temperature and thus their significant ranges cannot be disregarded, the ΔG_f° values are appreciably larger than the calculated uncertainties as shown in Fig. 2. Thus, the total free energy of formation of the nukundamite + chalcopyrite assemblage is higher than that of the bornite + pyrite assemblage in the temperature range below 400°C . Although Sugaki *et al.* (1975) have suggested that the bornite + pyrite assemblage does not become stable until the temperature decreases below 300°C , the stability of this assemblage is predicted above 300°C . Therefore, the assemblage of nukundamite + chalcopyrite in the Cu-Fe-S system is a metastable assemblage in this geologically important temperature range.

The effect of impurity elements on the stability

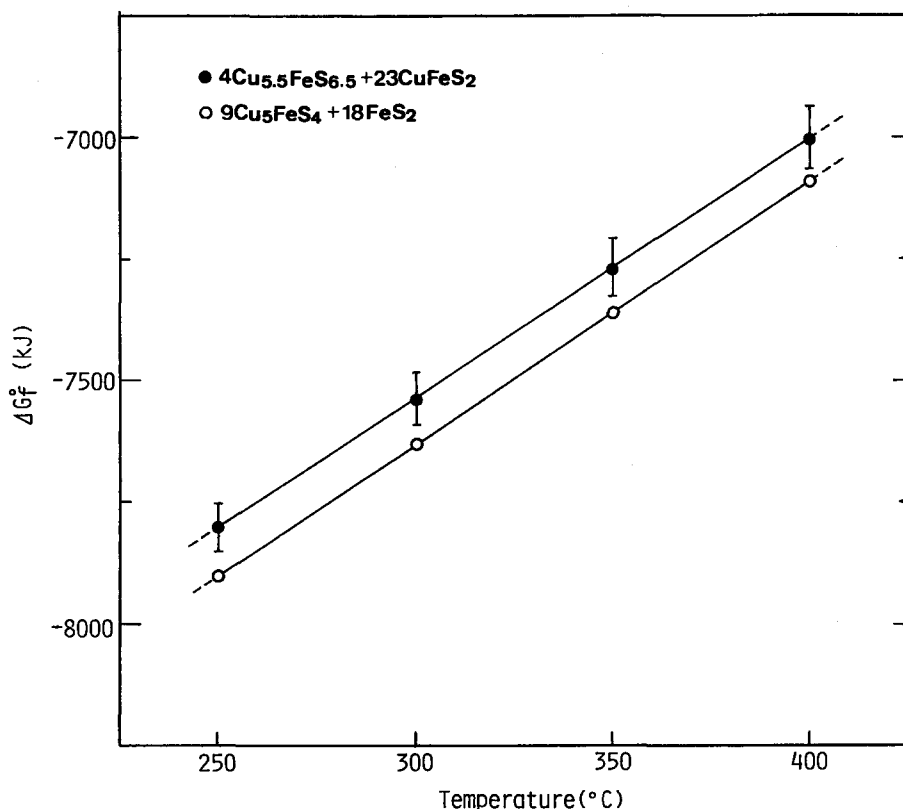


Fig. 2. Calculated free energies of formation (ΔG_f°) for the assemblages of $4\text{Cu}_{5.5}\text{FeS}_{6.5} + 23\text{CuFeS}_2$ and $9\text{Cu}_5\text{FeS}_4 + 18\text{FeS}_2$ in the temperature range $250 - 400^\circ\text{C}$. Vertical bars represent calculated uncertainties.

relationship between nukundamite + chalcopyrite and bornite + pyrite was not researched in this study. As stated earlier, the nukundamite + chalcopyrite assemblage appears in the Cu-Fe-Bi-S system, but not in the Cu-Fe-Zn-S system. According to the compositional data in Table 1, the nukundamite in the latter system contains trace amounts of Zn (<0.3 at.% Zn), and Bi is undetectable in the nukundamite of the former system. The bornite solid solution of the former system contains considerable amounts of Bi (<3.9 at.% Bi at 420°C; Sugaki *et al.*, 1984), whereas the dissolved Zn contents of the bornite in the latter system is very low (<0.4 at.% Zn below 400°C; Kojima and Sugaki, 1985). Assuming that such impurity contents increase ΔG_f° of bornite, the total free energy of the bornite + pyrite assemblage in the Cu-Fe-Bi-S system may be considered to be higher than that in the Cu-Fe-S system. In such a condition, it is likely that the nukundamite + chalcopyrite assemblage becomes thermodynamically stable. More detailed investi-

gations are required, so as to elucidate the stability relationship between the two assemblages in the multicomponent systems.

Conditions for formation of nukundamite-bearing assemblages

The aim of this section is to estimate the depositing environments for some assemblages including nukundamite. As described earlier, nukundamite was found as a primary mineral in a Fijian kuroko deposit, the Undu mine (Colley and Rice, 1975; Rice *et al.*, 1979). Also in the black-ore horizon of some Japanese kuroko deposits, hypogene nukundamite has been noted occasionally as follows: Kamikita mine (Takeuchi *et al.*, 1956), Hanawa mine (Kajiwara, 1970), Hanaoka mine (Takahashi and Suga, 1974) and the Nishi-Aizu mining district (Yamaoka and Asakura, 1974). In these deposits, the corresponding mineral was described as idaite or orange bornite. From the viewpoint of the

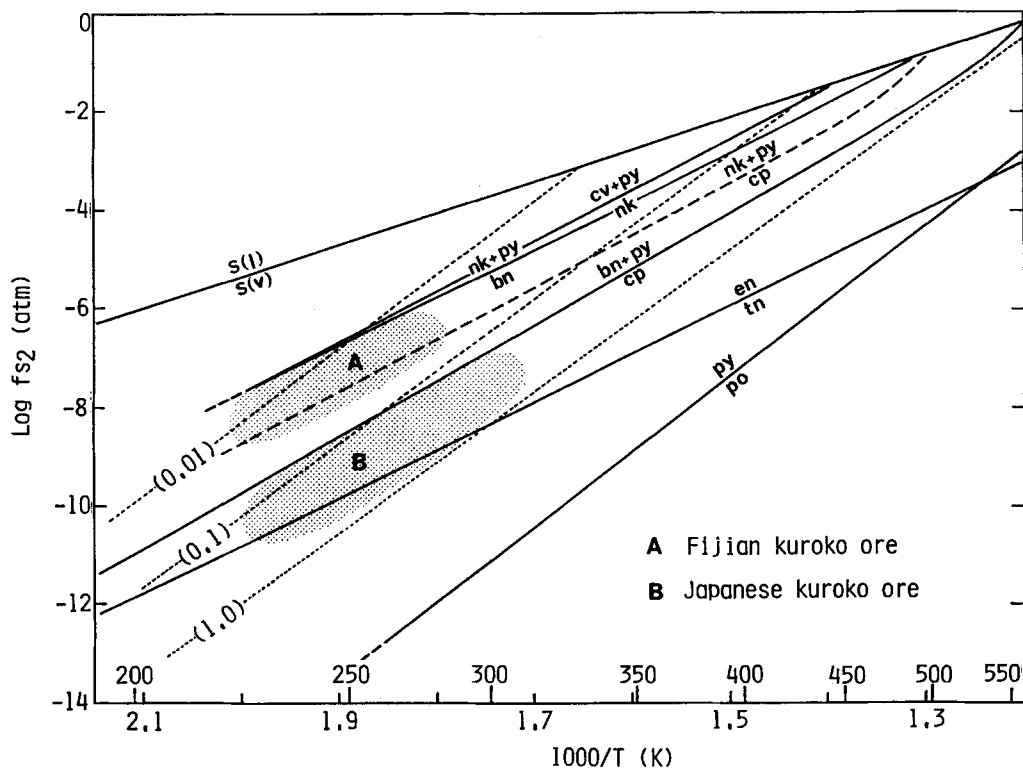


Fig. 3. $\log f_{S_2}$ -temperature diagram for various sulphidation reactions involving some Cu-Fe-S minerals and ranges inferred for the kuroko mineralizations in Japan and Fiji. Values in parentheses stand for mol.% FeS of sphalerite. Abbreviations: cv, covellite; nk, nukundamite; bn, bornite; cp, chalcopyrite; py, pyrite; po, pyrrhotite; en, enargite; tn, tennantite. See text for detailed explanations.

compositions Cu_5FeS_6 or $\text{Cu}_{5.5}\text{FeS}_{6.5}$, however, they are regarded as nukundamite. Reported mineral parageneses in sulphide ores from the Fijian and Japanese kuroko deposits are usually similar (Table 4). Both types of kuroko deposits exhibit identical zoning of siliceous ore, yellow ore and black ore in ascending order, and typical black ores consist mainly of sphalerite, galena, pyrite, chalcopyrite and small amounts of covellite, marcasite, enargite and luzonite (e.g. Frenzel and Ottemann, 1967; Matsukuma and

Horikoshi, 1970; Shimazaki, 1974; Colley and Rice, 1975; Eldridge *et al.*, 1983). In addition to these minerals, black ores from the Japanese kuroko deposits frequently include tetrahedrite-tennantite and bornite in association with pyrite, and an appreciable amount of nukundamite is observed in the black ores from the Fijian deposit. As principal sulphide minerals in yellow and siliceous ores, chalcopyrite and pyrite with small amounts of sphalerite, galena and bornite occur commonly in both types of kuroko deposits. In the

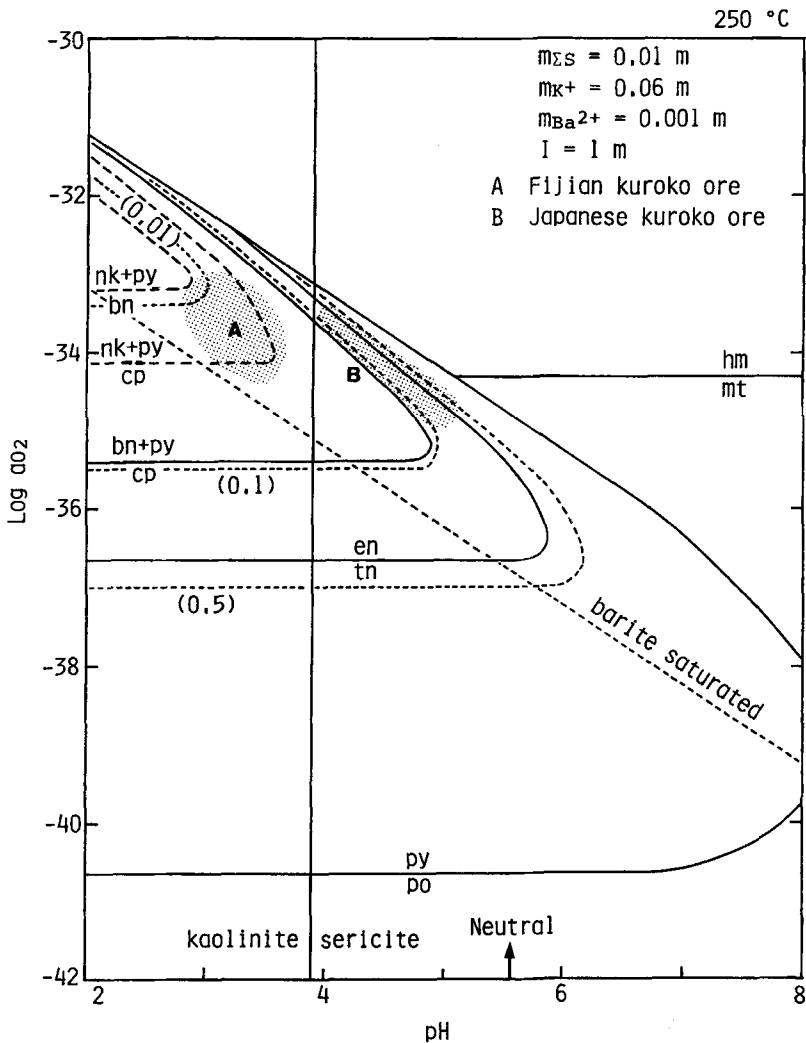


FIG. 4. Log a_{O_2} -pH diagram showing probable ranges for the kuroko mineralizations in Japan and Fiji. Values in parentheses represent mol.% FeS of sphalerite. Abbreviations: nk, nukundamite; bn, bornite; cp, chalcopyrite; py, pyrite; po, pyrrhotite; hm, hematite; mt, magnetite; en, enargite; tn, tennantite. See text for detailed explanations.

TABLE 4. Principal minerals occurring in the Fijian and Japanese kuroko deposits.

	Japanese kuroko	Fijian kuroko
Black ore	sphalerite, galena, pyrite, chalcopyrite, tetrahedrite-tennantite, bornite, covellite, enargite, electrum, luzonite, magnetite, marcasite, (nukundamite)	sphalerite, wurtzite, galena, pyrite, enargite, chalcopyrite, covellite, nukundamite, chalcocite, marcasite, luzonite
Yellow ore	chalcopyrite, pyrite, sphalerite, bornite, galena	chalcopyrite, pyrite, sphalerite, bornite, galena, tennantite, covellite
Siliceous ore	pyrite, chalcopyrite, sphalerite, galena, electrum	chalcopyrite, pyrite, sphalerite, covellite, nukundamite, enargite
Gangue minerals	gypsum, anhydrite, barite, calcite, silica minerals, sericite, smectite, kaolinite, sericite/smectite, fluorite, apatite	gypsum, anhydrite, barite, calcite, silica minerals, smectite, kaolinite

after Frenzel and Ottemann (1967), Matsukuma and Horikoshi (1970), Shimazaki (1974), Colley and Rice (1975), Eldridge *et al.* (1983).

case of the Fijian deposit, nukundamite also appears in the siliceous ore (Colley and Rice, 1975).

From the above information on mineral paragenesis, ore-forming conditions for the Fijian and Japanese kuroko deposits can be quantitatively illustrated on the diagrams in Figs. 3 and 4. The univariant reactions treated in the former section and some available equilibria are shown graphically in the fugacity of S_2 (f_{S_2})–temperature diagram (Fig. 3), where the ranges inferred for both the Fijian and Japanese kuroko deposits are indicated together. Thermochemical data used in constructing the diagram were from Craig and Barton (1973), Schneeberg (1973) and Barton and Skinner (1979). As suggested by many workers (e.g. Ohmoto *et al.*, 1983), f_{S_2} conditions for the Japanese kuroko deposits are regarded to be close to the bornite + pyrite/chalcopyrite line, ranging above the sphalerite isopleth of 1.0 mol. % FeS. Assuming that the temperatures of ore-forming fluid responsible for the Fijian and Japanese kuroko deposits are nearly equal, the region interposed between the nukundamite + pyrite/bornite and bornite + pyrite/chalcopyrite curves is inferred for the Fijian kuroko deposit. This condition is compatible with the f_{S_2} range estimated from the observed FeS content (~0.02 mol. %) of sphalerite (Colley and Rice, 1975), so it is suggested that the Fijian kuroko deposit was formed under relatively high- f_{S_2} conditions compared with the Japanese kuroko deposits.

The oxygen activity (a_{O_2}) and pH of the ore-forming environments can be specified on the log

a_{O_2} –pH diagram (Fig. 4), where the regions inferred for the Fijian and Japanese kuroko deposits at 250°C are illustrated together. The concentration levels of dissolved species (dissolved sulphur species, K^+ and Ba^{2+}) and ionic strength used in calculating the activity coefficients were from Ohmoto *et al.* (1983). The activity coefficients of the species were calculated using the extended Debye-Hückel equation (Helgeson *et al.*, 1981). Equilibrium constants used in constructing the diagram are given in Table 5.

Fig. 4 shows that the a_{O_2} level for the Fijian kuroko deposit is slightly higher than that for the Japanese kuroko deposits. As shown in Table 4, sericite is usually observed in the Japanese kuroko deposits. In the Fijian deposit, sericite is absent and kaolinite is the dominant gangue mineral (Colley and Rice, 1975). Therefore, an acidic solution is assumed to have been generated in the Fijian kuroko mineralizations. This feature is consistent with the result that the quench pH of the experimental solutions in coexistence with nukundamite + chalcopyrite is much lower than that of the solutions with bornite + pyrite in the Cu–Fe–Zn–S system (Kojima and Sugaki, 1985). Assuming that pertinent chloride complexes dominate as metal-carrying aqueous species, hydrothermal solutions responsible for the Fijian kuroko deposition should be capable of transporting higher contents of metallic species as compared with that for the Japanese kuroko deposition. In such conditions, it is likely that a situation leading to precipitation of the nukundamite + chalcopyrite assemblage was metastably

TABLE 5. Equilibrium constants used in constructing Figs. 3 and 4.

Reaction	log K(250°C)	Source
1. $S_2(v) = 2S(l)$	4.7	a
2. $H_2S(aq) + \frac{1}{2}O_2 = \frac{1}{2}S_2(v) + H_2O$	15.4	b
3. $H_2S(aq) = H^+ + HS^-$	7.6	c
4. $H_2S(aq) + 2O_2 = H^+ + HSO_4^{2-}$	61.4	b
5. $HSO_4^- = H^+ + SO_4^{2-}$	-5.1	b
6. $BaSO_4 = Ba^{2+} + SO_4^{2-}$	-11.0	b
7. $BaCl^+ = Ba^{2+} + Cl^-$	-2.0	b
8. $H_2O(l) = H^+ + OH^-$	-11.2	d
9. $4Fe_3O_4 + O_2 = 6Fe_2O_3$	-34.2	e
10. $2Fe_2O_3 + 4S_2 = 4FeS_2 + 3O_2$	-59.7	e
11. $Fe_3O_4 + 3S_2 = 3FeS_2 + 2O_2$	34.3	e
12. $FeS + \frac{1}{2}S_2 = FeS_2$	6.7	a
13. $2Fe_3O_4 + 3S_2 = 3FeS + 4O_2$	-70.9	a
14. $5CuFeS_2 + S_2 = Cu_5FeS_4 + 4FeS_2$	8.6	f
15. $\frac{22}{23}Cu_5FeS_4 + S_2 = \frac{20}{23}Cu_{5.5}FeS_{6.5} + \frac{2}{23}FeS_2$	6.6	a
16. $\frac{22}{9}CuFeS_2 + S_2 = \frac{4}{9}Cu_{5.5}FeS_{6.5} + 2FeS_2$	7.6	g
17. $2Cu_{12}As_4S_{13} + 3S_2 = 8Cu_3AsS_4$	29.2	h
18. $2KAl_3Si_3O_{10}(OH)_2 + 3H_2O + 2H^+ = 3Al_2Si_2O_5(OH)_4 + 2K^+$	5.4	i

a, Barton and Skinner (1979); b, Drummond (1981); c, Naumov *et al.* (1974); d, Busey and Mesmer (1978); e, Robie *et al.* (1978); f, Schneeberg (1973); g, Calculated from 14 and 15; h, Craig and Barton (1973); i, Montoya and Hemley (1975).

induced. It is likely that nukundamite would be considerably more soluble in comparison with the other Cu-Fe-S minerals, although any experimental data on the solubility of nukundamite have not yet been obtained. Furthermore, it is noteworthy that wurtzite frequently occurs in the black ore from the Fijian kuroko deposit (see Table 4). According to Kojima and Ohmoto (1991), wurtzite is regarded as a metastable mineral formed under a high degree of supersaturation in contrast to sphalerite. This suggestion may give indirect support for the metastability of the nukundamite + chalcopyrite assemblage. Considering all these estimates, it is concluded that the Fijian kuroko deposit was formed under fairly high-sulphidation and low-pH conditions from highly supersaturated solutions.

Experimental

An attempt was made to produce experimentally the stable assemblage of bornite + pyrite in the Cu-Fe-S system. All experiments were carried out at 350°, 300° and 250°C by a conventional method using transport driven by a temperature-gradient under hydrothermal conditions. This

method is based on dissolution of nutrient materials, transportation by convection along a thermal gradient, and precipitation of the stable mineral assemblage (e.g. Sugaki *et al.* 1975, 1982; Kojima and Sugaki, 1985). Nutrient materials and an appropriate solvent were sealed in the reaction capsule, a silica glass tube of about 3.5 mm inside diameter, and enclosed in the autoclave together with distilled water. The autoclave was heated in a vertical electric furnace, whose temperature was directly controlled by the upper and lower heaters. A small temperature-gradient of approximately 2°C/cm was imposed outside the vessel to avoid metastabilities induced by supersaturation. The temperatures of mineral precipitation were controlled within $\pm 3^\circ\text{C}$ during the run, and directly measured near the top of the reaction capsule by using a chromel-alumel thermocouple inserted into the inner vessel. The pressure in the autoclave, which is balanced with that of the inner capsule, was maintained at 200 to 250 kgf/cm² in all runs, and monitored via a Bourdon-type pressure gauge.

The nutrient materials used were mixed powders of the Cu-Fe-sulphide minerals synthesized previously by a conventional evacuated

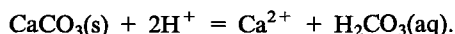
TABLE 6. Results of hydrothermal recrystallization experiments between 350°C and 250°C.

Run No.	T(°C)	Starting materials			Solvent	Run period (days)	pH ¹	Product	
		Assemblage	Bulk composition						
			Cu	Fe	S				
HS01	350	cv+nk+py	23.9	21.7	54.3	2 m NH ₄ Cl	10	2.4	bn+nk
HS02*	350	cv+nk+py	23.9	21.7	54.3	2 m NH ₄ Cl	10	6.4	bn+cp
HS03	350	nk+bn+py	36.2	13.8	50.0	5 m NH ₄ Cl	9	4.8	nk+bn+py
HS04*	350	nk+bn+py	36.2	13.8	50.0	5 m NH ₄ Cl	9	6.8	nk+bn+py
HS05	350	nk	42.3	7.7	50.0	2 m NH ₄ Cl	9	2.0	cv+nk+bn
HS06*	350	cv+tr	30.0	20.0	50.0	5 m NH ₄ Cl	9	6.8	bn+cp
HS07	350	bn+cp+py	29.2	20.8	50.0	5 m NH ₄ Cl	10	6.8	bn+cp
HS08	350	nk+py	12.8	25.6	61.6	5 m NH ₄ Cl	10	4.2	nk+cp
HS09*	350	nk+py	12.8	25.6	61.6	5 m NH ₄ Cl	10	7.2	nk+py
HS10	350	bn+py	22.7	22.7	54.5	2 m NH ₄ Cl	11	3.8	nk+bn
HS11	350	bn+py	22.7	22.7	54.5	5 m NH ₄ Cl	10	5.8	bn+py
HS12	350	nk+cp+py	8.3	29.3	62.4	5 m NH ₄ Cl	11	4.2	nk+bn
HS13*	350	nk+cp+py	8.3	29.3	62.4	5 m NH ₄ Cl	11	7.4	bn+py
HS14	300	nk+cp+py	8.3	29.3	62.4	5 m NH ₄ Cl	11	4.8	cv+nk+py
HS15*	300	cv+tr	30.0	20.0	50.0	5 m NH ₄ Cl	11	6.6	bn+cp+py
HS16*	300	nk+py	12.8	25.6	61.6	2 m NH ₄ Cl	11	6.4	bn+cp+py
HS17*	300	nk+py	12.8	25.6	61.6	5 m NH ₄ Cl	9	6.4	bn+py
HS18*	300	nk+bn+py	36.2	13.8	50.0	5 m NH ₄ Cl	11	6.6	nk+bn
HS19	300	nk	42.3	7.7	50.0	5 m NH ₄ Cl	13	4.8	cv+nk+bn
HS20	300	nk	42.3	7.7	50.0	2 m NH ₄ Cl	11	4.6	nk+bn
HS21	250	cv+nk+py	23.9	21.7	54.3	2 m NH ₄ Cl	16	1.6	cv+nk+bn
HS22*	250	cv+nk+py	23.9	21.7	54.3	2 m NH ₄ Cl	16	6.2	bn+cp
HS23	250	nk+bn+py	36.2	13.8	50.0	2 m NH ₄ Cl	11	2.4	bn+cp
HS24*	250	nk+bn+py	36.2	13.8	50.0	5 m NH ₄ Cl	13	6.4	bn+cp+py
HS25	250	nk+py	12.8	25.6	61.6	5 m NH ₄ Cl	12	1.4	cv+py
HS26	250	nk	42.3	7.7	50.0	5 m NH ₄ Cl	23	4.8	nk+bn+cp
HS27*	250	nk+py	12.8	25.6	61.6	5 m NH ₄ Cl	23	6.6	nk+bn+py
HS28	250	nk+cp+py	8.3	29.3	62.4	5 m NH ₄ Cl	14	3.6	cv+nk+bn

1, Quench pH; *, Runs using CaCO₃ powder as a pH buffer.

Abbreviations: cv, covellite; nk, nukundamite; bn, bornite; cp, chalcopyrite; py, pyrite; tr, troilite.

silica-tube method using pure metals and sulphur (>99.9% purity). As solvents, NH₄Cl aqueous solutions of 2*m* or 5*m* (pH = 4.8–4.6 at 25°C) were used. As shown in Fig. 4, solution pH is an important factor controlling stable assemblages in the Cu-Fe-sulphide minerals. Therefore, a small amount of fine-grained CaCO₃ reagent was added as a pH buffer to the starting materials in some experimental runs: primary pH of the experimental solutions is buffered near neutral through the following reaction (Bourcier and Barnes, 1987).



After 9–23 days at the experimental temperatures, the reaction vessel was quenched using an electric fan and the capsules were removed from the furnace. Precipitated products in the upper

(cooler) end of the capsule were mounted as polished sections, and identified using a reflected light microscope.

More than 70 runs were carried out, 28 of which were successful. The experimental results are summarized in Table 6, where the observed assemblages are shown. Generally, the amount of run products in the CaCO₃-free runs is abundant compared with the CaCO₃-bearing runs, and increases with increasing run temperature. The assemblages including nukundamite and chalcopyrite were produced only in the CaCO₃-free runs (run nos. HS08, HS26), and the quench pH values of the experimental solutions in coexistence with the above assemblage were less than 4.8. Frequently, a thin layer of chalcopyrite coated nukundamite and bornite crystals. Since such a chalcopyrite is regarded as a quench product, it was excluded from the equilibrium assemblages in

Table 6. Alternatively, in the experiments using CaCO_3 reagent, the quench pH values of the experimental solutions range from 6.2 (at 250°C) to 7.4 (at 350°C). Although pyrite is difficult to nucleate under low degrees of supersaturation (Murowchick and Barnes, 1987), it occurred in some of the runs as discrete grains and minute inclusions in bornite crystals. The assemblages including bornite and pyrite, which were obtained mostly in the CaCO_3 -bearing runs (run nos. HS03, HS04, HS11, HS13, HS15, HS16, HS17, HS24, HS27), occurred under nearly neutral pH conditions (quench pH ≥ 4.8). This feature agrees well with the thermochemical prediction made in the earlier section. In this manner, the present hydrothermal experiments have suggested that thermochemical predictions for primary assemblages including the Cu-Fe-S minerals can give significant information on the ore-forming environments.

Conclusions

In order to specify which of the two assemblages nukundamite + chalcopyrite or bornite + pyrite is stable in the Cu-Fe-S system, thermodynamic calculations were made by using the previously published data on ΔG_f° in the temperature range 250–400°C. The calculations indicate that the total free energy of the nukundamite + chalcopyrite assemblage is significantly higher than that of the bornite + pyrite assemblage. It is therefore suggested that the nukundamite + chalcopyrite assemblage is thermodynamically metastable in the probable temperature range for common hydrothermal deposits. A comparison of the ore-forming environment for the Fijian kuroko deposit with that for the Japanese kuroko deposits suggests that the nukundamite + chalcopyrite assemblage as included in the Fijian deposit is likely to occur under relatively high-sulphidation and low-pH conditions. This estimate is supported by the experimental results in this study, which indicate that the bornite + pyrite assemblage can be formed in the temperature range 350–250°C by using nearly neutral solutions.

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