Phase relation of some sulfide systems-(4)

Especially Cu-Fe-S system

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Abstract:

Phase relation studies for ternary Cu-Fe-S system have been performed by author and some students. Their results are described as mainly phase diagrams. Some diagrams are already reported, but adds additional new data and new knowledge.

Phase relations from 900 to 500°C were performed by evacuated silica glass tube method, and from 500 to 300°C were studied by thermal gradient transformation method under hydrothermal condition.

Phase relations at 900, 800, 700, 600 and 500 by dry method were obtained and their phase diagrams are given in the Figs. 5, 6, 7, 8 and 9 and at 500, 400, 300°C determined by hydrothermal synthesis under 29 MPa (300 kg/cm^2), 98 MPa (1,000 kg/cm^2) and 196 Mpa (2,000 kg/cm^2) are also given in Figs. 10, 11, 12, 13, 14, 15 and 16.

Introduction

Minerals which belong in the Cu-Fe-S system are the most important among ore minerals because they are persistent minerals occurring in many kinds of ore deposits. Accordingly, the phase relations in the Cu-Fe-S system are of great geological interest, and more time than 80 years since the first study was made by Merwin & Lombard [1] and effort have been expended in the determination of the phase relations in the Cu-Fe-S system by many authors than any other ternary sulfide system such as Schleger & Schuller [2] , Roseboom & Kullerud [3], Brett [4], Yund & Kullerud [5], Kullerud *et al*.[6], Mukaiyama & Izawa [7], Cabri [8], Barton [9] , Tsujimura & Kitakze [10], Kosyakov [11] and Kosyakov & Sinyakova [12]. They carried out a large number of systematic experiments on this system and determined the phase relations to be between 1200°C and 200°C.

The studies on the phase equilibrium in the Cu-Fe-S system below subsolidus are very important to know the formation conditions of mineral assemblages in the ores and the mechanism formed ore textures. The subsolidus phase relations in the phase diagram of the system we r e investigated by many authors such as Roseboom & Kullerud [3], Brett [4], Yund & Kullerud [5], Mukaiyama & Izawa [6], Barton [7] and Cabri [8]. All the experiments done by these authors were performed by the dry method using the evacuated silica glass-tube. However, the reaction rates below 400°C are sluggish. Therefore, it is

necessary very long time experiments to obtain the equilibrium state at such low temperature; especially in the experiments under dry condition below 300°C it is difficult to get the phase assemblages in equilibrium. Thus Sugaki *et al.* [13), 14), 15), 16)] tried hydrothermal synthesis of copper and iron sulfides using the thermal gradient method, which is apt to form relatively the equilibrium state at low temperature and obtained the isothermal phase diagrams of the system Cu-Fe-S at 500°C, 400°C, 350°C and 300°C.

The minerals found in the Cu-Fe-S system appeared in this paper are listed in Table 1 together with its compositions, abbreviations and their thermal stability.

Table 1. Minerals appeared in this study belonging within the Cu-Fe-S system

Minerals and phases	Abbreviations	Chemical formula	Stability limit	Remarks	References
Pyrite	py	FeS_2	<742	Decomposition	Yund & Kullerud[5)]
pyrrhotite	po	$Fe_{1-x}S$	<1190	Congruent melt	Yund & Kullerud[5)]
Fukuchilite	fk	Cu_3FeS_4	<200	Decomposition	Kajiwara[17)]
Isocubanite	icb	$CuFe_2S_3$	<930	Incongruent melt	Kosyakoc & Sinyakova[18)]
Chalcopyrite	cp	$CuFeS_2$	<547	Decomposition	Yund & Kullerud[5)]
Intermediate solid-solution	iss	$Cu_{1-x}Fe_{2+y}S_{2-z}$	<1012	Incongruent melt	Kosyakoc & Sinyakova[19)]
Talnakhite	tl	$Cu_9(Fe,Ni)_8S_{16}$	<186	Transform to intermediate phase	Cabri[8)]
Mooihoekite	mh	$Cu_9Fe_9S_{16}$	<167	Transform to intermediate phase	Cabri[8)]
Haycockite	hey	$Cu_4Fe_5S_8$	?		
Nukunadamite	nk	$Cu_{3.4}Fe_{0.6}S_4$	<501	Decomposition	Yund & Kullerud[5)]
Bornite	bn	Cu_5FeS_4	<1050	Congruent melt	This study
Covellite	cv	CuS	<507	Decomposition	Yund & Kullerud[5)]
Digenite	dg	Cu_2S	<1130	Congruent melt	Sharma & Chang[20)]

In this paper phase relations from 900 to 500°C determined using evacuated silica glass tube method and from 500 to 300°C determined by hydrothermal synthesis under high pressure condition of 29 ($300kg/cm^2$) or 98 ($1,000kg/cm^2$) and 196 MPa (2,000 kg/cm^2) are mainly described.

Experimental Procedure

Evacuated silica glass tube method

Synthetic experiments were mainly carried out by the evacuated silica-glass tube method which is about same described by Kitakaze *et. al.*[21), 22)] using pure copper and iron (over 99.99% in purity) and sulfur (99.99%).

Hydrothermal synthesis

Phase equilibrium from 500°C to 300°C in the central part of the system Cu-Fe-S has been studied by thermal gradient transporting method with 5 m NH_4Cl aqueous solution in gold tube at 500, 400 and 300°C under pressure of 29 or 98 and 196 MPa as same method described by Sugaki *et al.* [13),14),15),16)]. As nutrient materials, a mixture of powdered sulfides synthesized in advance by a reaction between metals and sulfur were used.

As a reaction vessel, a gold tube of 4 mm in inside diameter and about 50 mm in length was used. Nutrient materials of 10 to 50 mg and 0.1 to 0.3 ml of solution put into the gold tube sealed on one side, and then the another side of the tube was sealed by welding. The three or four sealed gold tubes were placed into a test-tube type pressure vessel and heated in a vertical electric furnace designed as to provide a linear thermal gradient by independently controlled separate upper and lower heating elements. The temperature during runs was measured by chromel-almel thermocouples (0.5 mm ϕ) inserted into the stainless steel pipe sealed on one side. Then, the pipe inserted into the inside of the vessel to get close to top of the gold tube. Pressure is measured by Bouedon's tube gauge as kg/cm^2 values, so recalculate to MPa values. At termination of the experiments, the furnace was pulled down and the pressure vessel around wet cloth wrapped was cooled rapidly to room temperature in an air blast.

Identification of phases

All the run products obtained using the evacuated glass tube method were fine to coarse grained sulfide and their mixture, and examined by ore microscope and XRD by diffractometer for determination of phases and phase assemblages. Sometimes, XRD for some synthetic phases were performed using the Guinier method and cell parameters are refined by their data. Products obtained by the hydrothermally synthesis were found as aggregate of two or three sulfides grown near top of the gold tube.
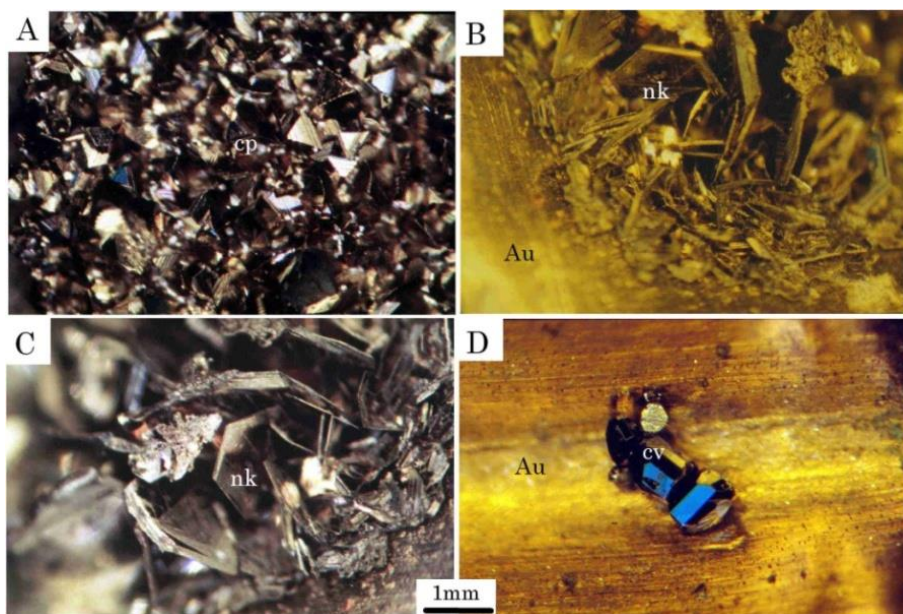
Fig. 1 Photographs under binocular microscope of sulfide crystals synthesized hydrothermally.
A: Chalcopyrite at 500°C,　　B, C: Nukundamite at 400°C,　　D: covellite at 400°C.
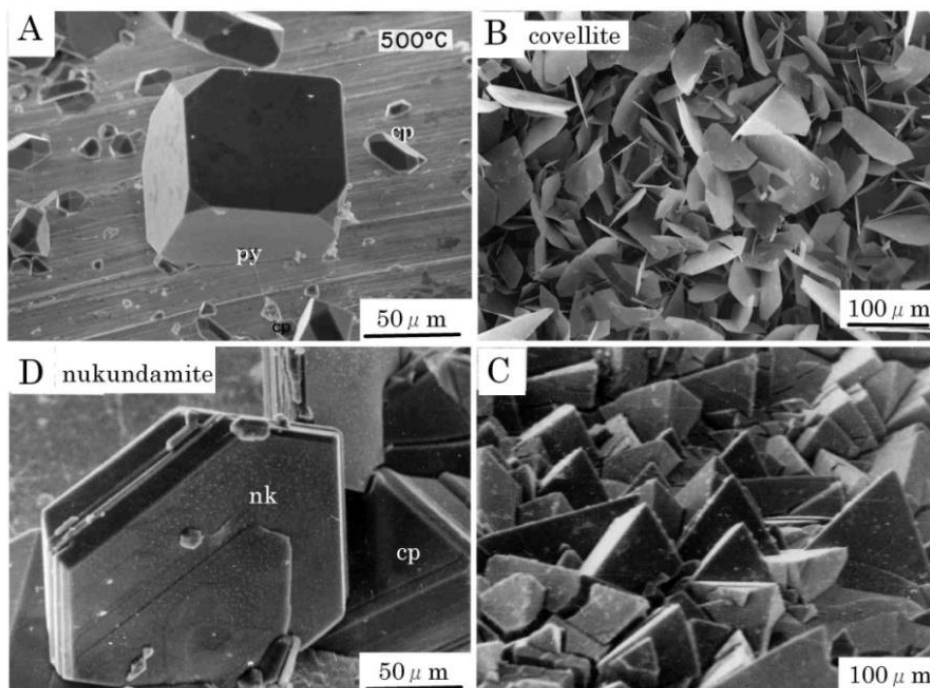

Fig. 2. Scanning electron micrographs (SEM) of sulfide crystals synthesized hydrothermally.

A: pyrite associating chalcopyrite at 500°C, B: covellite at 400°C,

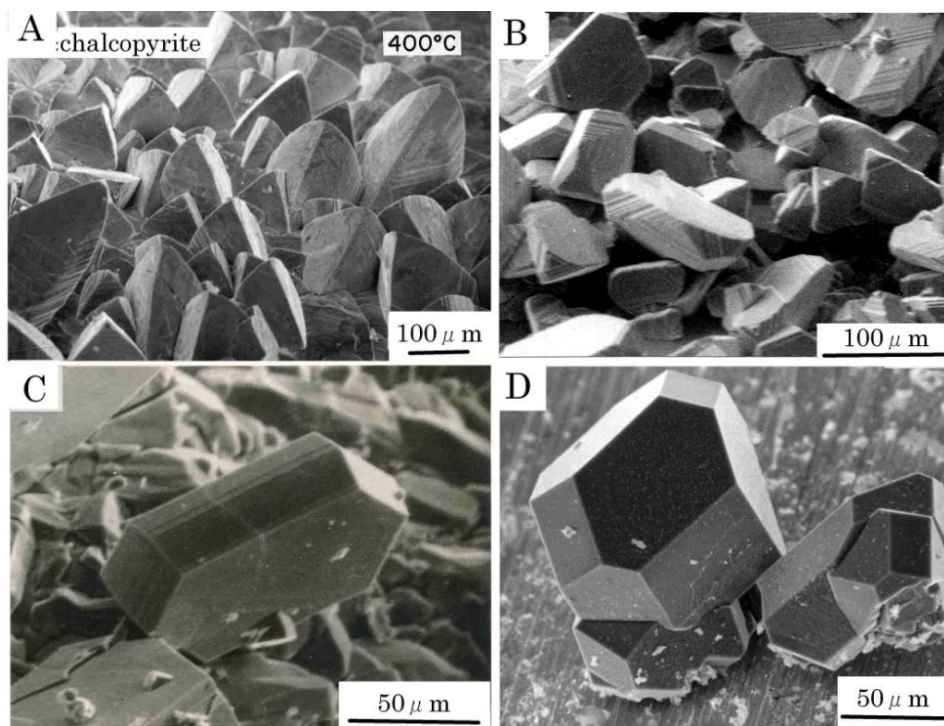D: nukundamite and chalcopyrite at 400°C, D: chalcopyrite at 300°C.

Fig. 3. SEM micrographs of euhedral sulfide crystals synthesized hydrothermally.
A: chalcopyrite at 500°C, B: iss at 500°C,
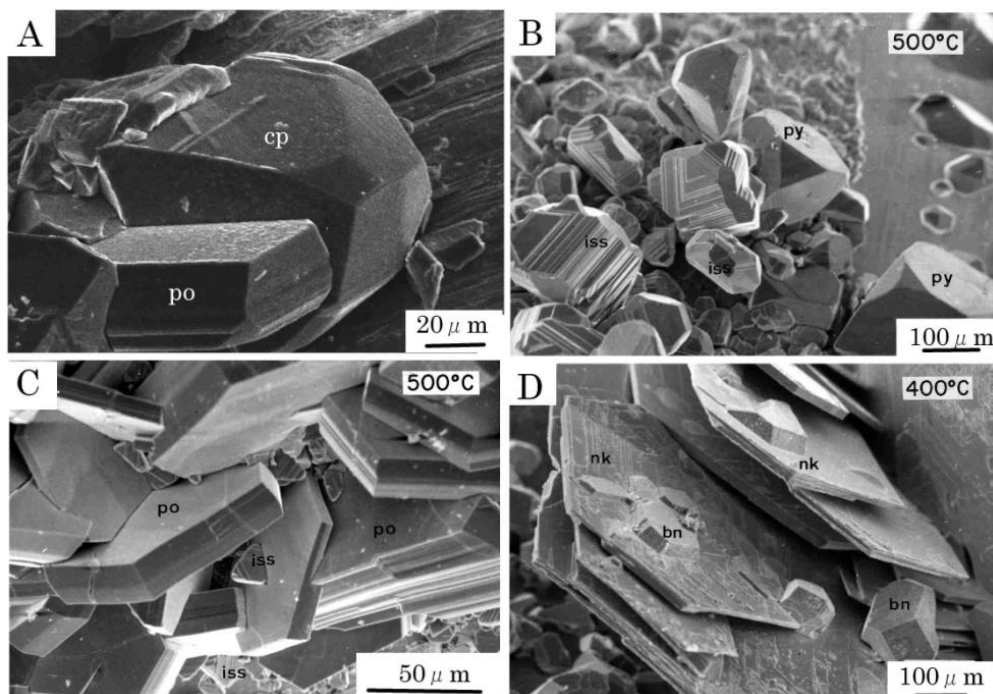C: pyrrhotite and iss at 500°C, D: bornite at 400°C.

Fig. 4. SEM images of euhedral sulfide crystals synthesized hydrothermally.
A: pyrrhotite and chalcopyrite at 300°C, B: pyrite and iss at 500°C,
C: pyrrhotite and iss at 500°C, D: nukundamite and bornite at 400°C.

They were identified by means of a binocular microscope, ore microscope, SEM, XRD by Gandolfi cameras and analyzed by EPMA. Because of the well-developed euhedral crystal forms, some phase can be identified by observation under a binocular microscope as seen as Fig. 1 and scanning electron microscope as Figs. 2, 3 and 4.

Phase relation of Cu-Fe-S system

Phase relation at 900°C

The phase relations at 900°C obtained using the evacuated silica-glass tube method are shown in Fig. 5. There are two liquid phases of sulfur and the central sulfide liquids, three sulfide phases of bornite-digenite solid solution (below described as bnss), intermediate solid solution (below described iss) and pyrrhotite solid solution (below described poss) presented as blue area, and copper and iron in the isothermal diagram. As seen in the figure, the six univariant assemblages are shown as yellow area. Chalcopyrite with stoichiometric composition $CuFeS_2$ at 900°C still lies within the central sulfide liquid field. With further decrease in temperature, the central sulfide liquid field decreases in size, changing its composition to copper-rich and/or sulfur poor sides. It finally disappears on the Cu-S join at 813°C in a binary monotectic reaction, but it remain at 800°C in central portions as sulfide liquid as seen in Fig. 5.
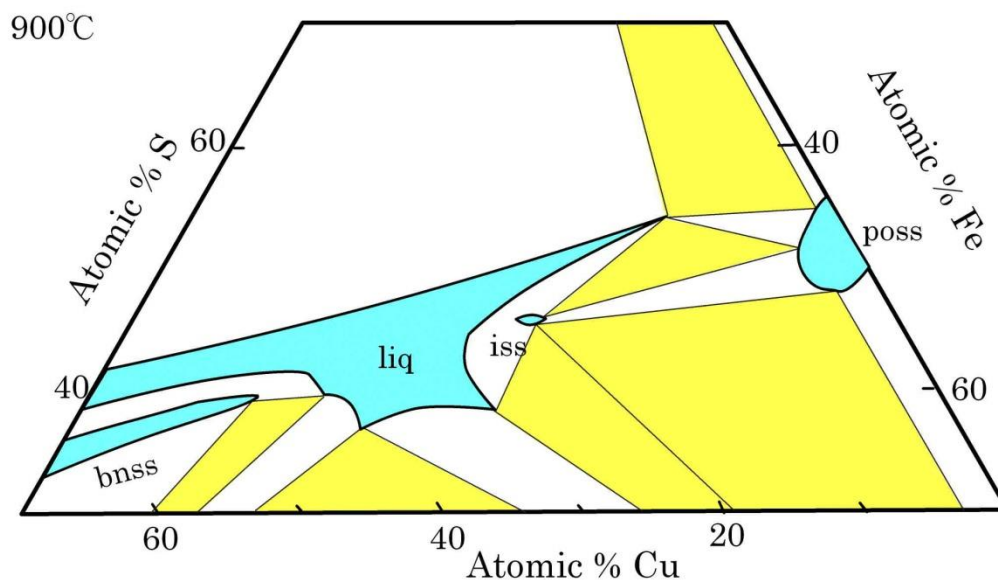

Fig. 5 Isothermal section in central portion of Cu-Fe-S system at 900°C

Phase relation at 800°C

The phase relations at 800°C obtained using the evacuated silica-glass tube method by

Taujimura and Kitakaze[10] and our data are shown in Fig. 6. There are the central sulfide liquids, three sulfide phases of bnss, iss and poss, and copper and iron in the isothermal diagram in central portion of Cu-Fe-S system. A sulfide liquid field becomes narrower than that of 800°C. The sulfide phase of iss filed was suddenly wider than that at 900°C. At 743°C pyrite produces by reaction between pyrrhotite and sulfur liquid, and the tie line between pyrite and iss is established at 739°C (Kullerud *et al*., [6]).
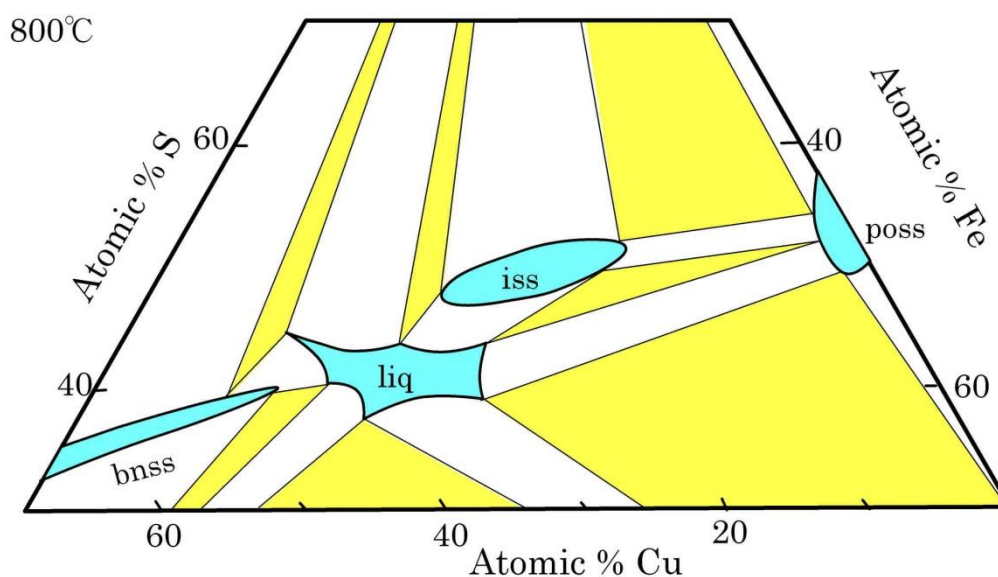

Fig. 6 Isothermal section in central portion of Cu-Fe-S system at 800°C.
after Tsujimura and Kitakaze[10] modified by author.

Phase relation at 700 ℃

The phase relations in the ternary system at 700°C are shown Fig. 7. There are four sulfides such as py, poss, iss and bnss, and no sulfide liquid because ternary sulfide liquid disappears at about 750°C. Tie lines between bnss and sulfur liquid, iss, poss, copper or iron, between iss and sulfur liquid, pyrite or poss, and between poss and pyrite or iron are established a this temperature. As the result, six univariant assemblages are formed. The iss assembled with pyrite and poss at 700°C has most iron-rich composition but at 600°C the iss composition with pyrite and poss varies remarkably in relatively wide range from iron-rich to copper-rich.
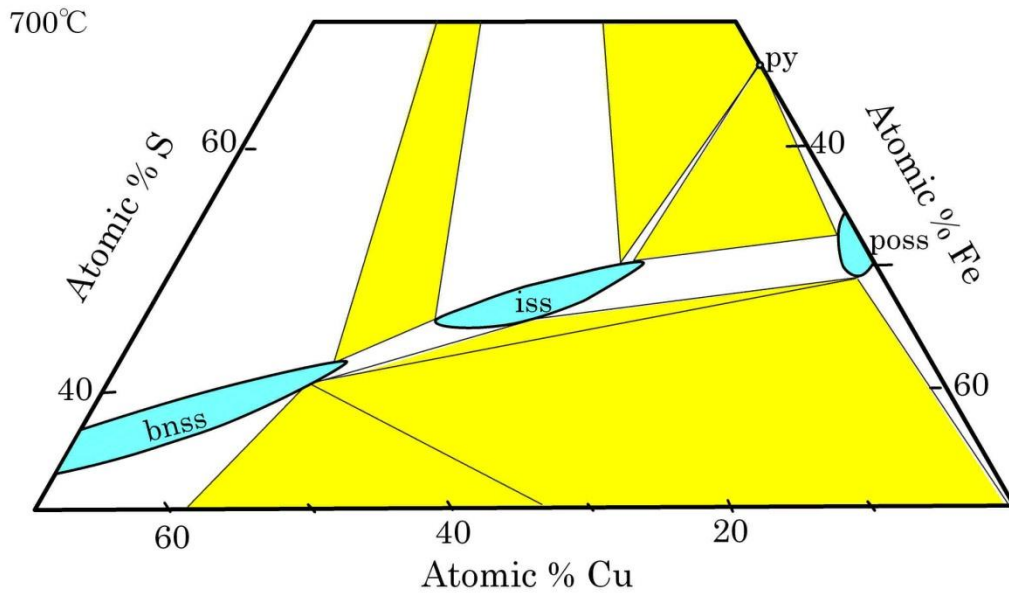
Fig. 7 Isothermal section in central portion of Cu-Fe-S system at 700°C.

Phase relation at 600℃

The isothermal phase relations in the central portion of the Cu-Fe-S system at 600°C obtained by Cabri[8] and Kitakaze et al. (un publish data) using the evacuated silica glass-tube method are shown in Fig. 8. The composition of bnss with poss and copper becomes to more copper-rich.
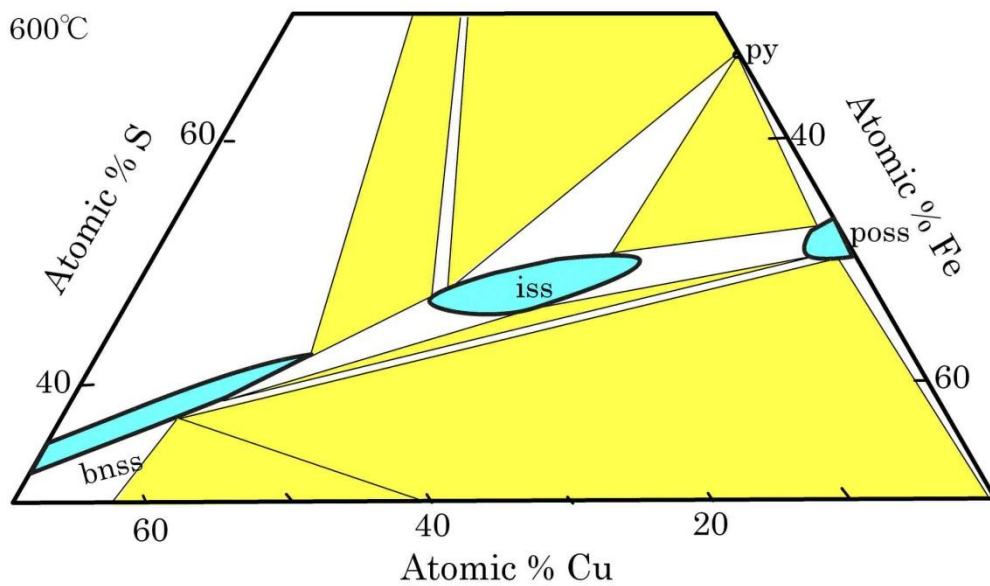

Fig. 8 Isothermal section in central portion of Cu-Fe-S system at 600°C
after Cabri[8] and Kitakaze (unpublished data) modified by author.

There is no chalcopyrite at 600°C because it breaks down to the iss and sulfur (l) above 550°C. However, on cooling chalcopyrite crystallizes at this temperature as a stable phase.

Covellite (CuS) and nukundamite appear at 507°C and 501°C (Yund & Kullerud[5]), respectively.

Phase relation at 500°C

Isothermal phase diagram at 500°C is shown in Fig. 9 obtained by Kitakaze (unpublished data) using evacuated glass-tube method. There are seven sulfides of pyrite, poss, chalcopyrite, iss, nukundamite, covellite and bnss, and ten three univariant assemblages. Chalcopyrite appears at 500°C associating with bnss, iss and pyrite, but no assembles with poss, but no assemble with sulfur liquid at this temperature. Covellite and nukundamite also appear at 500°C because they are stable below 501°C and 507°C, respectively, and assemble with pyrite. Tie line between nukundamite and chalcopyrite was not observed in dry synthetic method, but this tie line appears under hydrothermal synthesis.
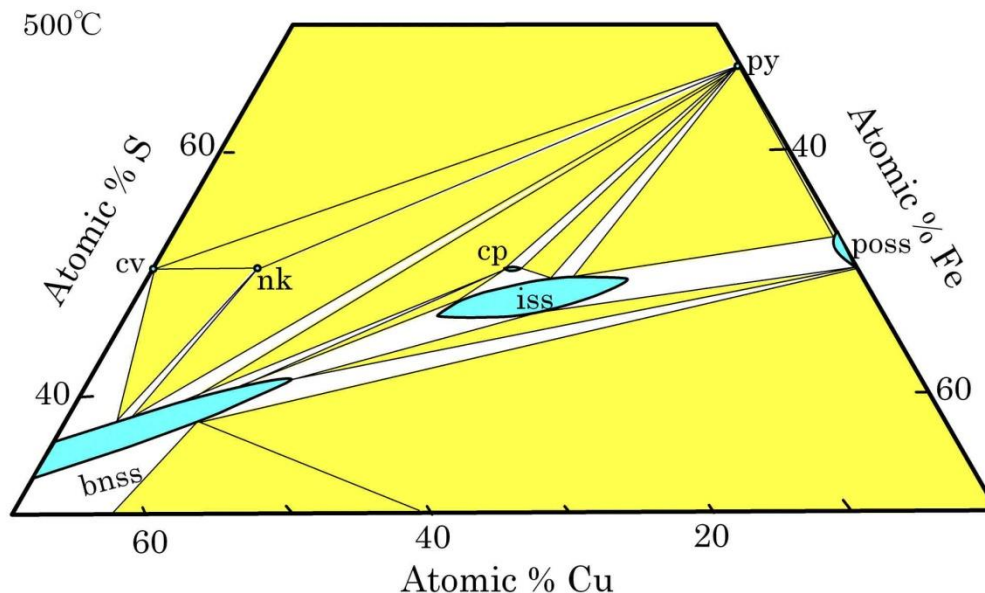

Fig. 9. Isothermal section in central portion of Cu-Fe-S system at 500°C by dry method.

The phase relations of the central portion in the Cu-Fe-S system at 500°C and 98 MPa and 196 MPa obtained by Sugaki *et al*. [16] and Kitakaze *et al*. (unpublished data) using hydrothermal recrystallization method are shown in Figs. 10 and 11. There are found

bnss, iss, chalcopyrite, nukundamite, pyrite and covellite as crystalline sulfide phases in the diagram. The tie lines between bnss and covellite, nukundamite, chalcopyrite, iss or poss, between iss and chalcopyrite, pyrite or poss, between covellite and nukundamite, between nukundamite and chalcopyrite, and between pyrite and poss also exist as stable at 500°C under hydrothermal condition.
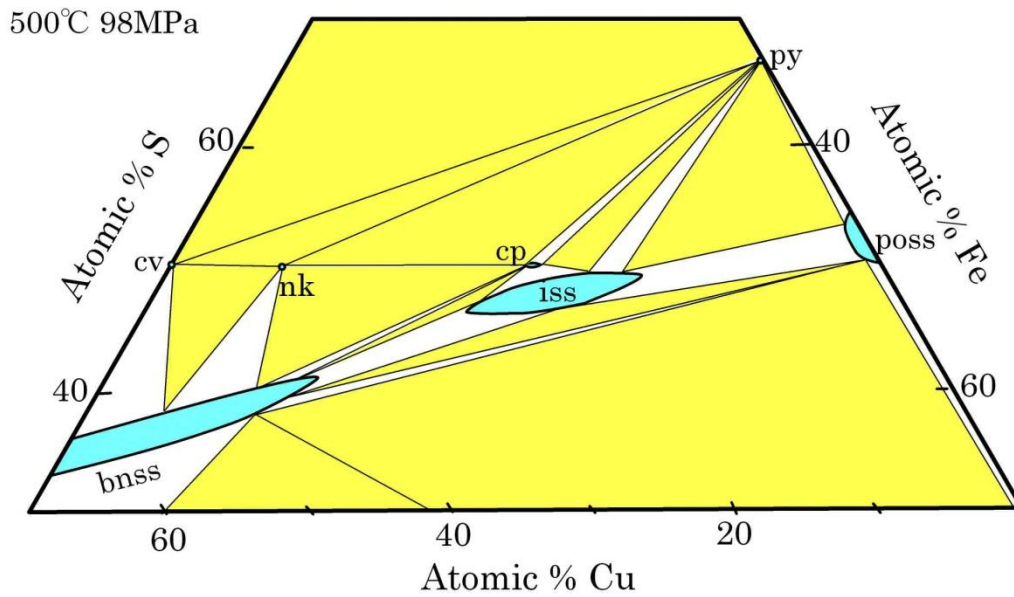

Fig. 10. Phase relations in the central portion of the Cu-Fe-S system at 500°C and 98 MPa under hydrothermal conditions after.
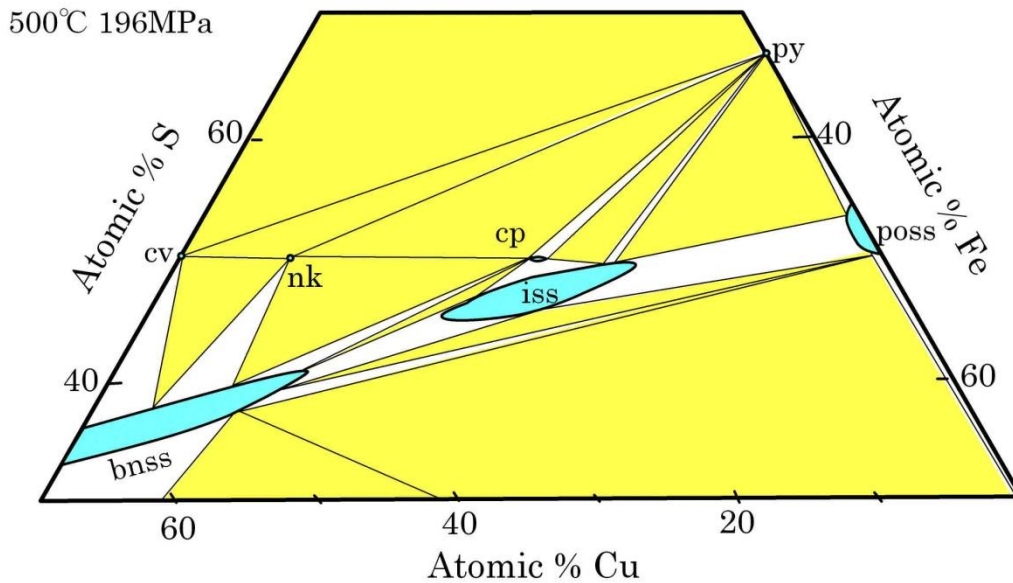

Fig. 11. Phase relations in the central portion of the Cu-Fe-S system at 500°C and 196 MPa under hydrothermal conditions after Sugaki *et al.* [16] modified by author.

The tie line between bnss and pyrite is still stable at this temperature as seen Fig. 9 and Yund & Kullerud[5] also accepted the tie line between bnss and pyrite instead of the tie line between nukundamite and chalcopyrite as seen Fig. 12. Such disagreement on the stable tie line remains as unsolved problem. However, it may be due to difference of the experimental conditions in the equilibrium works, dry (solid state reaction) and wet (hydrothermal reaction) methods.
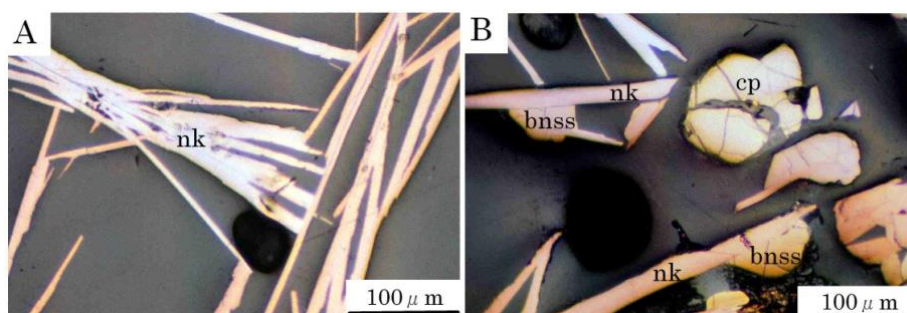

Fig. 12. Photomicrographs of nukundamite and associating minerals synthesized hydrothermally.
A: Platy crystal of nukundamite at 400°C, 98 MPa, B: association with nukundamite, chalcopyrite and bnss at 400°C, 98 MPa

Chalcopyrite has extremely limited solid solution. The chalcopyrite ss field at 500°C is not so wide as Yund & Kullerud[5] and Barton & Skinner[23] have suggested, and has a very narrow range from nearly stoichiometric $CuFeS_2$ to somewhat iron-rich composition: $Cu_{0.99}Fe_{1.01}S_{2.00}$ along a line of metal to sulfur ratio of approximately 1.0. However, Mukaiyama & Izawa[7] recognized no the solid solution field of chalcopyrite. The compositions of the chalcopyrite ss with bornite and/or nukundamite concentrate into stoichiometric $CuFeS_2$ and the chalcopyrite ss in the univariant assemblage with the iss and pyrite becomes most iron rich. The iss, as stated above, has a considerably wide field extending from near the stoichiometric isocubanite ($CuFe_2S_3$) composition toward the copper-rich and sulfur-deficient composition as is seen in Fig. 16.

The field includes isocubanite as well as the compositions of mooihoekite and haycockite described by Cabri & Hall[24]. Although the iron-rich and copper-rich ends of the iss field have not been determined precisely, the most copper-rich phase of the iss synthesized at 500°C and 98 MPa was the composition of $Cu_{1.88}Fe_{1.34}S_{2.81}$ with Cu/Fe atomic ratio of 1.38.

The iss coexists stably with Cu/Fe atomic ratio of 1.38. The iss coexists stably with pyrite, pyrrhotite, chalcopyrite, and bnss. The

composition of the iss in equilibrium with pyrite and pyrrhotite at 500°C and 96 MPa is Cu 18.2, Fe 32.1 and S 49.7 in atomic% corresponding to $Cu_{1.09}Fe_{1.92}S_{2.98}$ which is close to stoichiometric cubanite $CuFe_2S_3$. Also, the composition of the iss in the univariant assemblage with chalcopyrite and pyrite at 500°C and 98 MPa is Cu 18.2, Fe 32.1 and S 49.7 in atomic % corresponding to $Cu_{1.09}Fe_{1.93}S_{2.98}$.

The bnss field extends to beyond its stoichiometric composition toward a more iron-rich side. The most iron rich composition of the bnss at 500°C and 98 MPa gives the formula $Cu_{4.42}Fe_{1.43}S_{4.15}$ and 3.09 in Cu/Fe atomic ratio. The bnss assembled with only chalcopyrite has a composition range from 4.00 to 4.75 in Cu/Fe atomic ratio. The composition of the bnss in the univariant assemblages of bnss + chalcopyrite + iss is $Cu_{4.80}Fe_{1.20}S_{4.00}$. Also the bnss composition of the univariant assemblage bnss + nukundamite + chalcopyrite is $Cu_{4.99}Fe_{1.05}S_{4.97}$ which is very close to stoichiometric composition of bornite. On the other hand, the bornite composition in equilibrium with covellite and nukundamite is $Cu_{5.67}Fe_{0.51}S_{3.82}$.

Nukundamite always occurs in a crystal of thin hexagonal plates, as shown in Figs. 1, 2, 3 and 4. The chemical composition of nukundamite synthesized hydrothermally at 400°C is almost equivalent to $Cu_{3.36}Fe_{0.64}S_{4.00}$. These values are in good accordance with those of nukundamite synthesized by using the evacuated glass-tube (Yund[25]) and synthesized hydrothermally at 350° and 300°C by Sugaki *et al*.[13),16)]. It can coexist stably with pyrite, covellite, bnss and chalcopyrite below 500°C. Nukundamite is stable at below 501°C, but breaks down to bnss, covellite and pyrite above this temperature.

Phase relation at 400 ℃

The phase relations in the Cu-Fe-S system at 400°C, and 98 MPa and 196 MPa obtained by Sugaki *et al*.[16)] and Kitakaze et al. (unpublished data) using hydrothermal method are shown in Figs. 13 and 14.
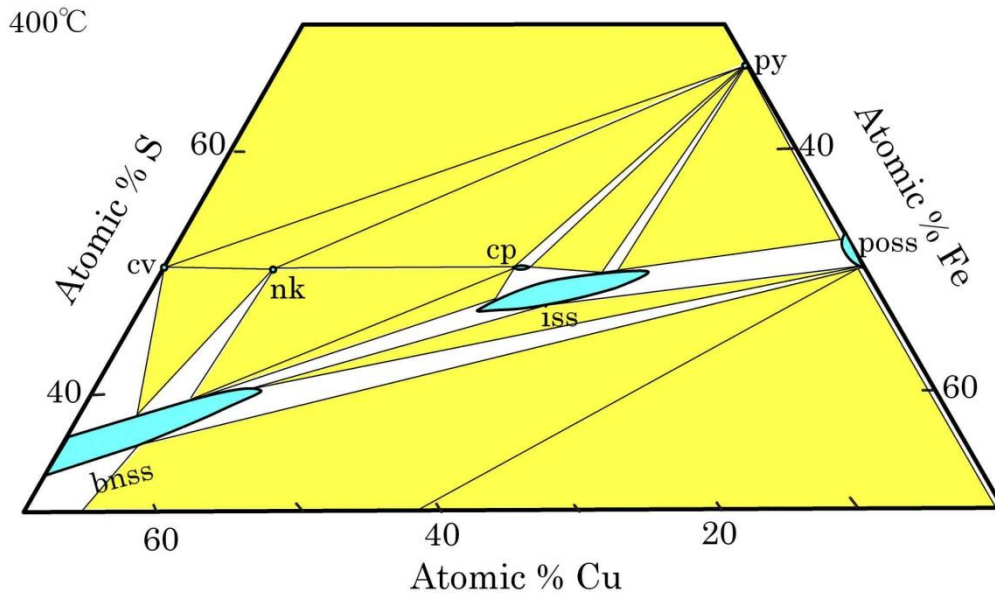
Fig. 13. Phase diagram of central portion in the Cu-Fe-S system at 400°C obtained by dry synthetic method.

At 400°C the isothermal phase relations, especially appeared phases and their assemblages, of the Cu-Fe-S system are entirely the same as those at 500°C mentioned above, but the solid solution fields of the bnss, iss and poss become more or less small or narrow in comparison with those at 500°C.
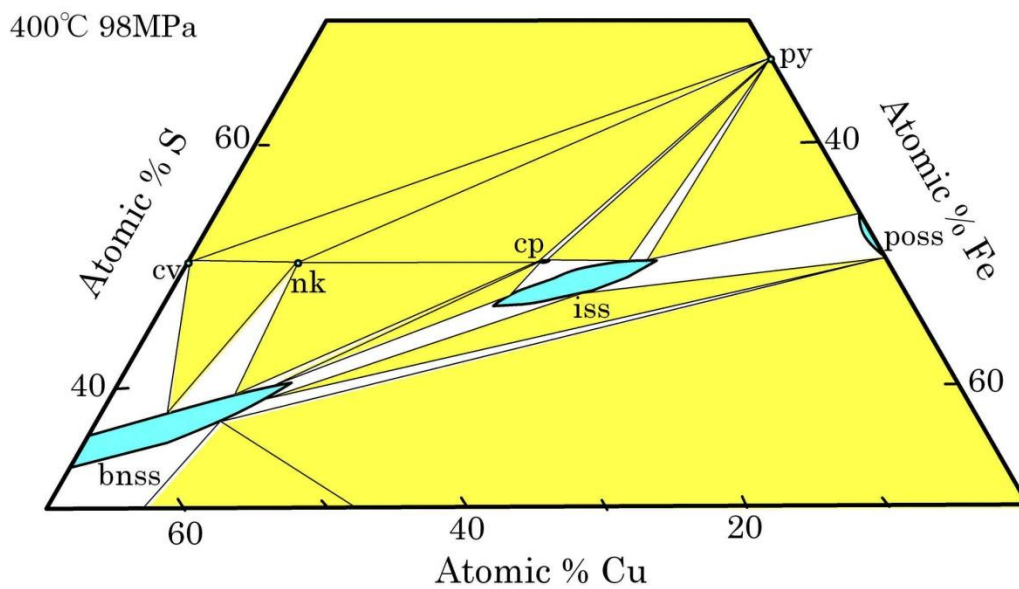

Fig. 14. Phase relations of central portion in Cu-Fe-S system at 400°C, 98 MPa under hydrothermal condition.

Although the iron-rich or/and copper-rich ends of the solid solution fields have not determined precisely, the most copper-rich phase of the iss synthesized at 400°C and 196 MPa was the composition of $Cu_{1.80}Fe_{1.41}S_{2.79}$ with Cu/Fe atomic ratio of 1.29.

Also the compositions of the iss and bnss with the univariant assemblages described at 500°C slightly vary at 400°C.

That is, at 400°C and 196 MPa the composition of the iss in equilibrium with pyrite and pyrrhotite is $Cu_{1.04}Fe_{1.96}S_{3.00}$ which is very close to stoichiometric composition. The composition of the iss in the univariant assemblage with chalcopyrite and pyrite is $Cu_{1.11}Fe_{1.90}8_{3.00}$.

The maximum iron content of the bnss is $Cu_{4.76}Fe_{1.20}S_{4.04}$ of 3.97 in Cu/Fe atomic ratio. The bnss associated with chalcopyrite and nukundamite has a composition of Cu 68.5, Fe 7.1 and 8 24.0 in weight % (8.46 in Cu/Fe atomic ratio). The bnss composition in equilibrium with covellite and nukundamite is given as $Cu_{5.95}Fe_{0.32}S_{3.73}$ (18.6 in CufFe atomic ratio) nearly close to high-digenite composition. Chalcopyrite has a limited range solid solution from nearly stoichiometric to $Cu_{0.98}Fe_{1.02}S_{2.00}$. The range corresponds to 1.00 to 0.96 in the Cu/Fe atomic ratio along a line of the metal/sulfur ratio 1.0.

Nukundamite can coexist stably with pyrite, covellite, bnss, and chalcopyrite as the same as at 500°C. Because the tie line between nukundamite and chalcopyrite is still stable at 400°C, the assemblage of bnss and pyrite accepted by Yund & Kullerud (1966) is not found. Also, the tie line between the iss and pyrite still occurs in a stable assemblage at this temperature. So, the assemblage of chalcopyrite and pyrrhotite does not appear.
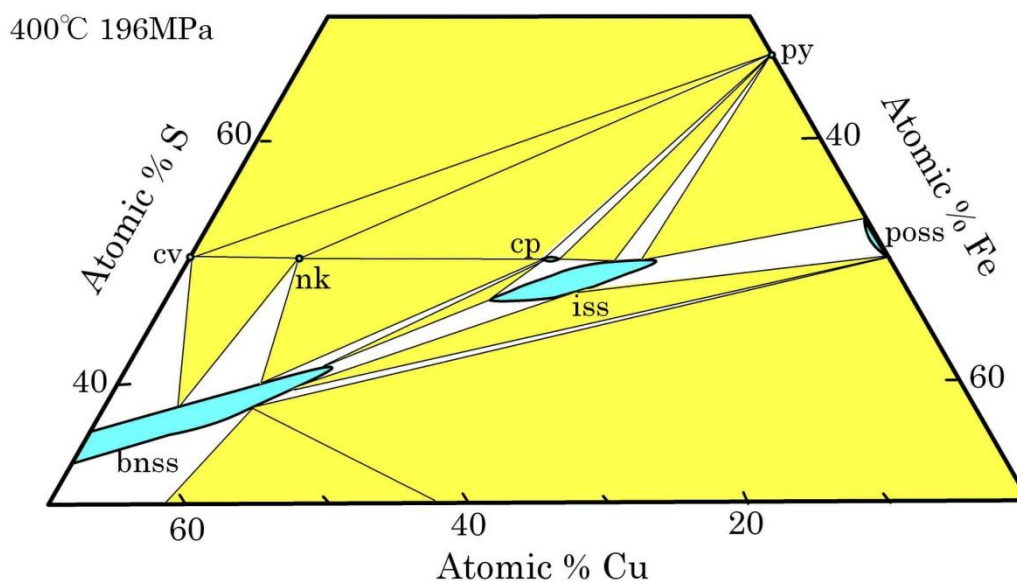

Fig. 15. Phase elations in the central portion of the Cu-Fe-S system at 400°C and 196 MPa Under hydrothermal conditions after Sugaki *et al.*[16] modified by author.

Phase relations at 300°C

According to them, at 350°C the stable phase assemblages and coexistence of the solid solution such as bnss, iss and poss are very similar to those of 400°C (and 500°C), except the fields of these solid solutions reduce their area to somewhat small. They confirmed that chalcopyrite synthesized has a limited composition range as the solid solution from nearly stoichiometric $CuFeS_2$ to approximate $Cu_{0.9}Fe_{1.1}S_{2.0}$ corresponding to 1.00 to 0.87 in Cu/Fe atomic ratio along metal to sulfur ratio of approximate 1.0.

The equilibrium works of the Cu-Fe-S system at low o temperatures at 350° and 300°C were done by Sugaki *et al*. (1975) using hydrothermal recrystallization technique.

The phase diagram in the central portion of the system Cu-Fe-S at 300°C is shown in Fig. 16 (Sugaki *et al*.[13]). Except for a small reduction of the solid solution fields and tie line change from the iss-pyrite join to the chalcopyrite-pyrrhotite join, the phase relations of the system are essentially the same as those at 400°C.
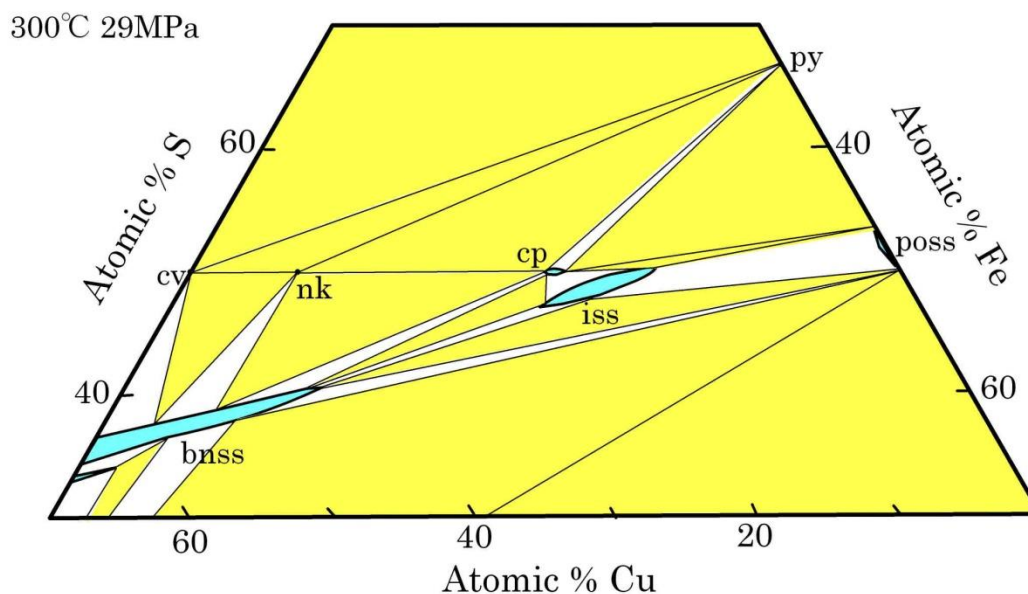

Fig. 16. Phase relations in the central portion of the Cu-Fe-S system at 300°C and 29 Mpa under hydrothermal conditions after Sugaki *et al*. [14] modified by author.

The solid solution area of chalcopyrite at 300°C is slightly decreased in comparison with that at 350°C. The most iron-rich chalcopyrite, which coexists with iss and pyrrhotite, has a composition of $Cu_{0.97}Fe_{1.04}S_{1.99}$.

The chalcopyrite ss extends form 1.0 to

approximate 0.93 in the Cu/Fe atomic ratio along a line of the metal/ sulfur ratio 1.0. The tie line between iss and pyrite, existing stably at 350° and 400°C, is replaced by the tie line between chalcopyrite and pyrrhotite at 300°C (Fig. 16).

The iss still having a remarkable area in the system at 300°C extends to the range between 0.51 and 1.04 in the Cu/Fe atomic ratio. It assembled with chalcopyrite and pyrrhotite has a composition of $Cu_{1.10}Fe_{1.97}S_{3.02}$ which is very close to stoichiometric cubanite $CuFe_2S_3$. While the iss coexisting with bnss and chalcopyrite has a composition of $Cu_{1.63}Fe_{1.57}S_{2.81}$. The solid solution field of iss includes the compositions of mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$.

The bnss field extends still far beyond the stoichiometric composition. The maximum iron content of the bnss is approximated by the composition of bnss coexisting with iss, that is Cu 57.2, Fe 15.7 and S 26.2 in weight % (Cu/Fe atomic ratio of 3.19). Meanwhile, bnss in equilibrium with chalcopyrite has a relatively wide composition range from about 3.5 to 7.2 in Cu/Fe atomic ratio at 300°C. The composition of bnss coexisting with chalcopyrite and nukundamite is Cu 57.1, Fe 9.0 and S 33.9 in weight % (5.5 in the Cu/Fe atomic ratio, a metal and sulfur ratio of approximately 1.0).

Nukundamite has no field of solid solution at 300°C, and its composition is very close to $Cu_{3.38}Fe_{0.62}S_{4.00}$ as proposed by Sugaki et al. [13].

All pyrrhotite synthesized at 300°C were found to be of a hexagonal type as a result of reexamination by Sugaki et al.[16], although Sugaki et al.[13] reported that pyrrhotite has two structure types, hexagonal and monoclinic.

Temperature and pressure dependence of the iss

The experimental results are given that the solid solution field of the iss moves by temperature and pressure. Fig. 17 shows the change of iss field by temperature of 400 and 500°C under constant pressure of 98 MPa (Sugaki et al.[16]). Also in this figure, the range of iss field at 300°C (29 MPa) by Sugaki et al.[13] is indicated. According to this figure, the field of the iss moves to the more iron-rich side reducing that as the temperature decreases. In this case, the movement of the most copper-rich end to the copper side is noticeable, and the iron-rich end does not move to the iron side. As shown in Fig. 18, exsolution texture of bornite or chalcopyrite from the iss are considered due to the movement and shrinkage of the solid solution field due to temperature decrease and these exsolution were often observed during cooling after completion of the synthesis experiments.

The stoichiometric compositions of mooihoekite and haycockite are included in the iss field at 500°C, but isocubanite composition is at outside of the iss field. At 400°C the iss field encloses the mooihoekite composition, but not haycockite and isocubanite compositions.

Although the iss field at 300°C reduces its area, it still includes the composition of mooihoekite. Because moving the iss field toward the more iron-rich side in the diagram, the stoichiometric isocubanite composition is included in the iss field. Accordingly, with decreasing temperature the exsolution of bnss and/or chalcopyrite from iss is expected. The iss is unquenchable, and it is very difficult to keep its high-temperature form and composition at room conditions. Indeed exsolution texture as lamellar form of bornite and chalcopyrite in iss occurred on cooling was often observed during experiments (Fig. 18).
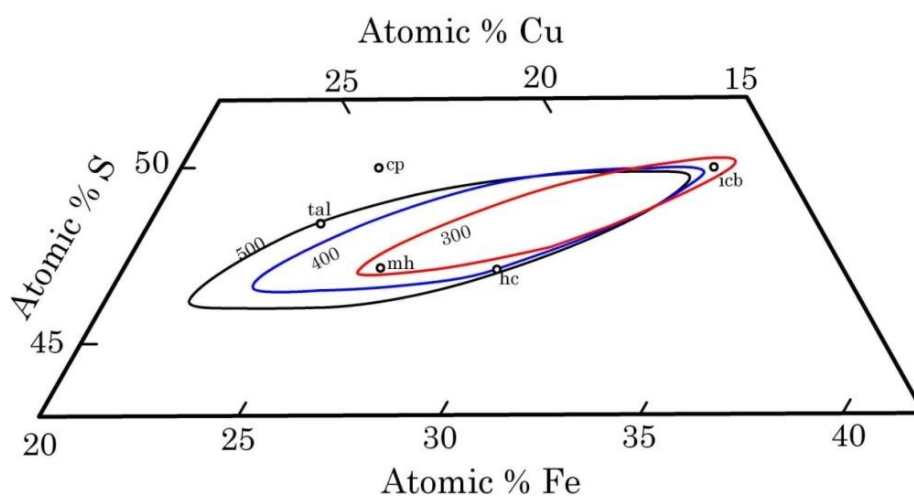

Fig. 17. Solid solution area of iss under hydrothermal conditions at 500 (black line) and 400°C (blue line) under 98 MPa and 300°C (red line) under 29 MPa after Sugaki et al.[16] modified by author. Open circles show stoichiometric compositions.
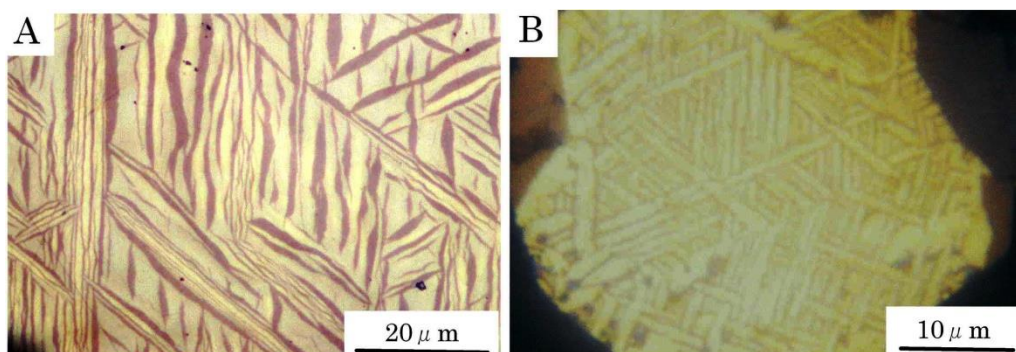

Fig. 18. Photomicrographs of exsolution lamellae appeared by cooling after runs.
A: Exsolution lamellae of bornite (brown) in iss (yellow).
B: Exsolution lamellae of chalcopyrite (light yellow) in iss (brownish yellow)

The experimental results revealed that the field of iss moves not only by temperature but also by pressure. The shift of the iss field is not only due to temperature, but with pressure.

The solid solution fields at 98 MPa and 196 MPa at the temperature of 500°C are shown in Fig. 19. In addition, the field of the iss determined by the dry method at 500°C is also shown in the figure. It is clearly recognized in the figure that the iss field shifts toward the more iron-rich side of the diagram with decreasing pressure as the same as the case of temperature. In this case, the moving of the most copper-rich end also is remarkable more than that of the iron-rich end of the field as

similar to the case of decreasing temperature. It is an interest and significant notice that the iss field is moved not only by temperature, but by pressure. So, it is expected an exsolution from the iss by its retreat toward the more iron-rich composition with decreasing pressure. In the case interpreting the mineral assemblages and their textures in the ores, the effect of pressure has to be considered not only the temperature.
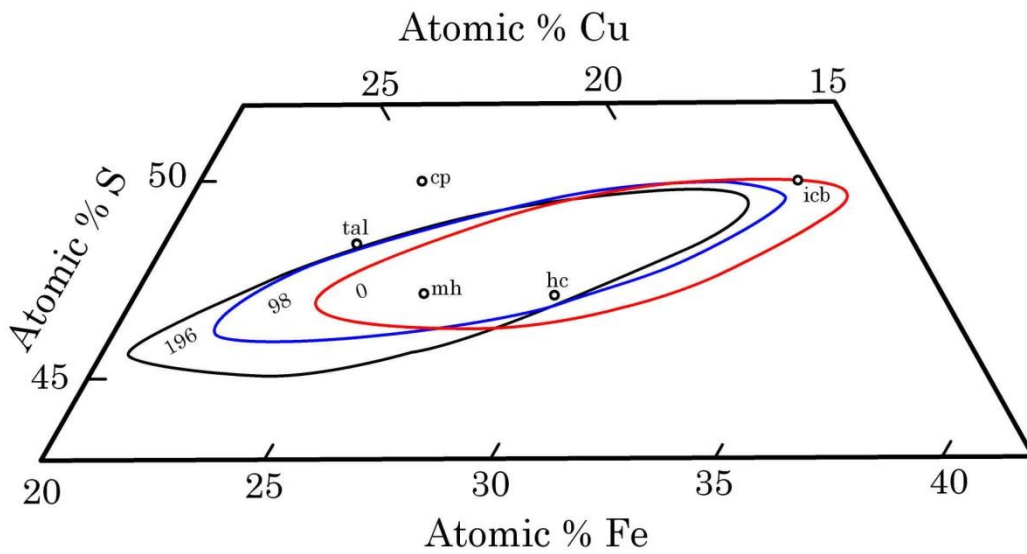

Fig. 19. Solid solution area of iss under hydrothermal conditions at 500°C under 196 (black line) and 98 MPa (blue line) and dry conditions (red line) after Sugaki et al.[16] modified by author.

In addition, as shown in Fig. 20, the relationship between the composition (iron content) of most copper- and iron-rich ends for iss, and the relationship between temperature and pressure is shown. The temperature-pressure dependence of the iss can be understood well. The figure also shows the

temperature-pressure change of the most iron-rich composition of the bornite solid solution.

The composition of the most iron-rich bnss is also affected by both the temperature and pressure, and retreats to the copper-rich side as

reducing its area with increasing pressure, although it becomes gradually more iron-rich composition with increasing temperature. The compositional change of the most iron-rich bnss and the copper-and iron-rich ends of the iss by temperature and pressure are shown in Fig. 20 (Sugaki *et al.*,[16]).

The field of the iss reduces its area with decreasing temperature and it suggests that the iss compositions have a tendency as converging into stoichiometric isocubanite composition, $CuFe_2S_3$ at room temperature and pressure, although a process of its change below 300°C is not yet made clear. Also the composition of the bnss may be astringed into its stoichiometric composition Cu_5FeS_4 at room conditions.
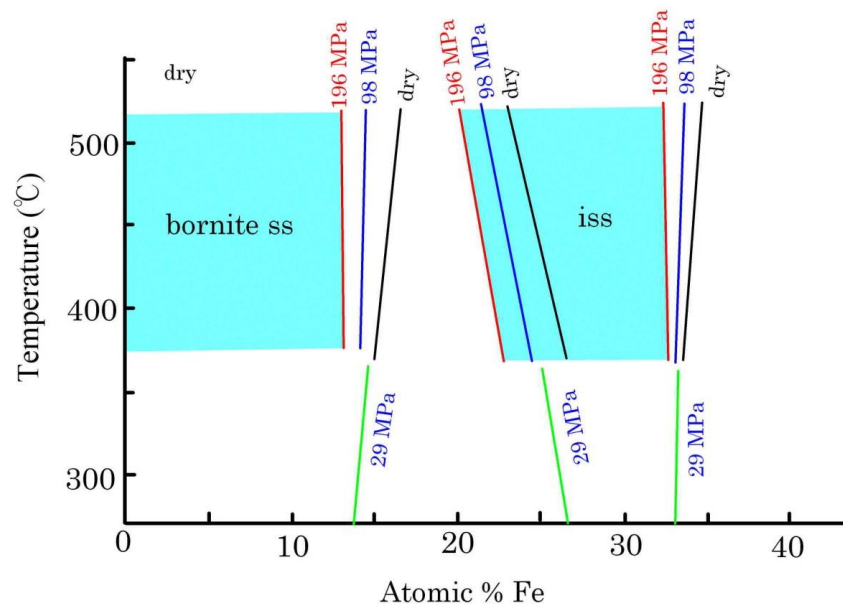
Fig. 20. Composition change of Cu-rich and Fe-rich ends of iss and Fe-rich end of bns by temperature and pressure of 196 MPa (red line), 98 Mpa (blue line), 29 MPa (green line) and dry condition after Sugaki *et al.*[16] modified by author. Light blue area show of solid solution ranges of bornite and intermediate solid solution.

Tie line change of pyrite-iss to chalcopyrite-pyrrhotite

In the temperature range of 500 and 400°C, the iss - pyrite tie line exists stably, so that chalcopyrite + pyrrhotite tie line in natural copper ore does not occur. On the other hand, according to the experiment of Sugaki *et al.* (1975), at 350°C, iss-pyrite tile line is stable, but in 300°C, chalcopyrite-pyrrhotite tie line occurs, replacing iss-pyrite tie line. Yund & Kullerud[5] determined the temperature of tie line change as 328°C. The latter experiment is a dry method and the influence by pressure is not examined.

Therefore, the Sugaki *et al.*[16] conducted experiments under the conditions of temperature 300, 320, 330, 350, 400 and 500°C, and pressure 29 to 196 MPa (300 to 2,000 kg/cm^2) in order to further examine the tile line change while considering the influence of pressure by the hydrothermal synthesis method . The results of these experiments are shown in Figure 10. In addition to the above experimental results, the figures also show the data obtained by the dry method by the author. From the experimental results, the tie line change from iss - pyrite to chalcopyrite - pyrrhotite is between 320 and 330°C, which is considered to be below 325°C. This temperature is hardly affected by the pressure of about 200 MPa. Therefore, natural chalcopyrite + pyrrhotite assemblage occurs at a temperature below 325°C.
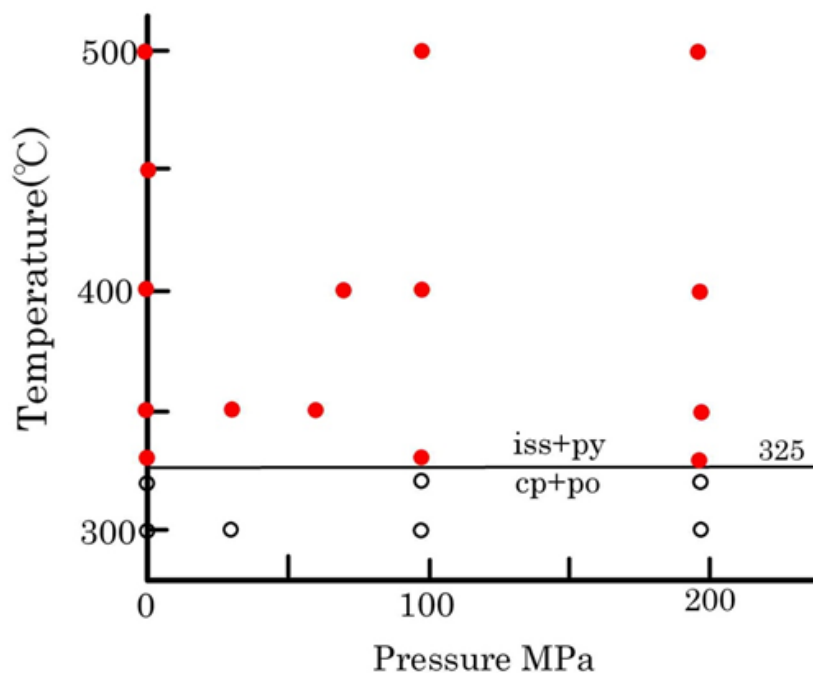
Fig. 21. Results of experiments on the tie line change from iss-pyrite to chalcopyrite-pyrrhotite under hydrothermal conditions.

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