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Author(s)	TAKENO, Setuo
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A Note on Mackinawite (so-called Valleriite) from the Kawayama Mine, Japan

By

Setuo TAKENO

with 6 Text-figures and 1 Plate

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ABSTRACT : Mackinawite, a new species of copper-free iron sulfide mineral given by EVANS *et al.* (1964), has been described in connection with its paragenesis with some others. On the basis of its microtextures it is deducible that from the original ore solution four types of solid solutions A (rich in FeS), B (rich in ZnS), C (rich in CuFeS_2) and D (including all other sulfide minerals such as FeS_2 , PbS, etc.) might have been fractionated, and mackinawite is related only to the second type. The thermal effects on the specimens have been scrutinized and the results obtained evidently suggest that the mineral in question is reasonably contained in the system of Cu-Fe-S and gets to be immiscible at certain temperatures ($130^\circ\text{C}\sim 200^\circ\text{C}$) far lower than those shown in the preceding literatures.

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I. INTRODUCTION

Very recently, EVANS *et al.* (1964) described mackinawite, a new copper-free iron sulfide, from the Mackinaw mine, Washington. This seems to have vari-ously affected on the previous opinions of the ore microscopists studying especially on the sulfide minerals involved in Cu-Fe-S or Cu-Fe-Ni-S systems.

BLOMSTRAND (1870) was the first who discovered valleriite at Nya Kopparberg, Sweden almost a century ago. RAMDOHR and ÖDMAN (1932) identified the "unbekanntes Nickelerz" or "frägliches pleochroitisches Mineral" (SCHNEIDER-HÖHN, 1929) with valleriite obtained from Kaveltorp (ÖDMAN, 1933) because of its chemical composition of $\text{Cu}_2\text{Fe}_4\text{S}_7$ and of its crystal habit belonging to the hexagonal system.

Since that time, numerous ore microscopists have shown through examination of the polished sections that this strongly pleochroic and anisotropic mineral commonly occurs as a constituent of several types of the ore deposits at various

localities in the world. After RAMDOHR (1960), valleriite bears a chemical composition of $\text{Cu}_3\text{Fe}_4\text{S}_7$ (probably ranging to $\text{Cu}_2\text{Fe}_4\text{S}_7$ with variation in Cu content).

Concerning the chemical composition proposed by RAMDOHR and ÖDMAN, some opinions have been exhibited in the literatures. For instance, MERWIN and LOMBARD (1937) recognized a phase of $\text{Cu}_3\text{Fe}_4\text{S}_6$ and not that of $\text{Cu}_3\text{Fe}_4\text{S}_7$ in their experimental study of Cu-Fe-S system, whereas BARTHOLOMÉ (1958) concluded that valleriite does not belong to the Cu-Fe-S system at all.

On the other hand, the existence of another distinct sulfide phase having the optical properties similar to those of valleriite has just recently become to be suspected. MILTON and MILTON (1958, p. 432, footnote) alluded to a sort of iron sulfide mistaken as valleriite in their excellent study of Mackinaw ores. Subsequently, BIRKS *et al.* (1959) re-examined the Mackinaw mineral by means of recently developed "electron probe (x-ray) microanalyzer" (E.P.M.A.) making it possible to analyse the constituents contained in the specific areas of the specimen surface within an order of microns in diameter. They obtained the mineral, with contents of about 55 per cent iron and less than 5 per cent copper, pointing to an approximate formula of FeS , and suggested that the mineral previously termed valleriite in high temperature copper ores might be different from that of Kaveltorp and taken as an undescribed sulfide. Kouvo *et al.* (1963) described an optical alliance of valleriite with the beautiful tetragonal crystals of iron sulfide from the Outokumpu mine, Finland. Their analyses for this mineral revealed the contents of Fe: 64~54%, S: 35%, Ni: 0.2~8.3% and Co: 0.2~10%, and the characteristic absence of Cu, while their x-ray powder patterns were not congruent with those given for valleriite in the literatures but quite near to those for kansite (Fe_9S_8 ; ASTM, 7-26).

The most recent paper written by EVANS *et al.* (1964) gave a solution for the confusion between valleriite and the new mineral. According to them, the new copper-free iron sulfide designated as mackinawite is tetragonal in habit and characterized by space group P_4/nmm , and a unit cell with $a=3.679$, $c=5.047\text{Å}$ and with 2 molecules of FeS , while valleriite of the rhombohedral habit with space group $R3m$ or $R\bar{3}m$, and a unit cell with $a=3.792$, $c=34.10\text{Å}$, and with 6 molecules of CuFeS_2 was proposed. They emphasized the common and widespread occurrence of mackinawite compared with scarcity of valleriite as well as the misunderstanding for the latter because of the similarity in physical properties and of its extremely minute size. X-ray diffraction patterns obtained by them show a good identity with those of the Outokumpu mineral, kansite (Fe_9S_8) and BERNER's (1962) synthetical tetragonal iron sulfide. Thus, they concluded only the Outokumpu mineral to be same as the Mackinaw mackinawite.

In Japan, valleriite was reported first by TATSUMI (1953) from the Makimine mine, Kyûshû, and subsequently by TAKEUCHI *et al.* (1953, 1954) from the Ohmine and Akagane mines, Iwate Prefecture, by MATSUKUMA *et al.* (1957) from

the Obira mine, Ôita Prefecture, by MIYAHISA (1958) from the Besshi and Takara mines, Ehime Prefecture, by TAKEDA *et al.* (1960) from Sekizen mine, Ehime Prefecture, by SOEDA (1960) from several pyrometasomatic deposits locating in Chûgoku District and by the present writer (1963) from the Kawayama mine.

In all of these literatures, identification of the minerals with valleriite has been based ordinarily on the physical properties under microscope though there be room for further scrutiny because of obscurity resulted from their extremely minute size of some to hundreds microns.

IMAI and FUJIKI (1963), however, published a description on a valleriite-like mineral from the Kômori mine, Kyôto Prefecture and pointed out that on the basis of the chemical composition determined by means of E.P.M.A. might be identified with the nickel-bearing mackinawite (Cu: 4.0%, Fe: 52.1%, Ni: 5.6%, Co: 1.02~2.0%).

Recently, the present writer has re-examined the valleriite from the Kawayama mine by the electron microprobe analyses. The results deciphered from the diffraction images of the specimen are as follows:

- 1) Iron and sulphur are the principal constituents and the contents are nearly as high as those of the pyrrhotite associated.
- 2) Copper content is very low or null (cf. Plate 4, Fig. 1).
- 3) Nickel, cobalt, arsenic, lead and selenium were looked for, but not detected.

From these results and the description of EVANS *et al.* (1964), the mineral is naturally considered as mackinawite and not valleriite. According to FUJIKI (1963) and KATO (private communications) so-called valleriite from various kinds of Japanese ore deposits are actually mackinawite including nickelian (Kômori, Kyoto Pref.) and cobaltian (Shimokawa, Hokkaido) varieties.

In the light of the preceding circumstances, the paragenetic relations and genetical problems of mackinawite will be dealt with hereunder.

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assistance in carrying out his field work.

II. PARAGENESIS OF MACKINAWITE

A. MINERALOGY OF THE ORES FROM THE KAWAYAMA MINE

The Kawayama mine, situated about 40km north of Iwakuni City, Yamaguchi Prefecture, Southwest Japan, is one of the most important ones in Japan for production of the iron sulfide ores amounting to about 30,000 tons monthly. The main ore body of this mine consists of sulfides so far developed with a scale of more than 1,200m along the strike-side and 600m along dip-side. The ores of this deposit are, in general, bedded in form and nearly parallel to the plane of bedding schistosity (S_1) of the country rocks consisting of the semi-schist. The writer (1963) has already reported the outline of the mineralogy concerning the ores from this mine. The ores are composed of pyrrhotite with a little amount of sphalerite and chalcopyrite, while pyrite, marcasite, arsenopyrite, galena and cubanite are also observed in small quantity.

Pyrrhotite ($Fe_{1-x}S$) is observed mainly as massive ores and generally elongated along the S_1 direction of the country rock in the banded ores.

The paragenetic relations demonstrate that pyrrhotite might be deposited at least in four stages as follows: the first stage related to deposition of the massive ores from the original ore solution associating massive sphalerite, chalcopyrite, pyrite and galena and predominating in FeS , the second connected with formation of their lenses or blebs without chalcopyrite or cubanite in massive sphalerite, the third regarded to their genesis associated with chalcopyrite in a single grain and without mackinawite, and the fourth concerned with their production in each grain of chalcopyrite accompanying mackinawite. Such intergrowth as have been referred to in the latter three cases may be interpreted respectively as the unmixing products in different stages.

The other sulfide minerals associated intimately with mackinawite are examined in the following chapter.

B. GENERAL REMARKS OF MACKINAWITE

Almost all of the mackinawite, ranging from a few microns to about 40 microns in size, are enclosed within chalcopyrite blebs or blades in massive sphalerite. Its extraordinarily strong anisotropy and pleochroism and characteristic form in chalcopyrite blebs make it possible to be easily recognized.

Its microscopic characters are as follow:

Color under reflection microscope: pale yellowish pink (very little more pinkish than in case of chalcopyrite) to creamy gray (more brownish than in case of sphalerite) (in oil).

Anisotropism under crossed nicols: very strong and characteristic; brilliant yellow through bluish gray to dark gray (in oil).

Hardness: distinctly higher than that of chalcopyrite and cubanite, and slightly lower than that of pyrrhotite.

Etching reaction: (partly) darkend with saturated KOH and slightly darkend with conc. H_2SO_4 ; almost negative with 1:1 HNO_3 , 20% $FeCl_3$, and saturated $HgCl_2$, and negative with 1:1 HCl and 20% KCN.

EVANS *et al.* (1964) showed that both valleriite and mackinawite are extremely anisotropic and strongly pleochroic, though a slight difference of pleochroism is appeared in each case: that is, the former is pale yellow to deep creamy brown and the latter a pale pink to pinkish gray in color. Previous descriptions concerning so-called valleriite in Japan indicate its resemblance to mackinawite in color, as to which, for example, "light creamy yellow to purplish gray" (TAKEUCHI and NAMBU, 1954) and "pinkish cream to purplish gray" (SOEDA, 1960) were given. The specimen obtained from the Kawayama mine also has a similar resemblance. Nevertheless, it is regretful that there are no ways of justifying or rejecting the subjectivity exhibited by each investigator concerning this kind of tests.

The etching reactions reveal several discrepancies between the results obtained as to the mineral from the Kawayama mine by the present writer and those mentioned in some literatures. As has been referred to already, TAKEUCHI and NAMBU (1954) and SOEDA (1960) reported the so-called valleriite darkened slightly with 20% $FeCl_3$ and saturated $HgCl_2$, while the mackinawite from the Kawayama mine reacts almost negative by these chemicals. So-called valleriite from the Akagane mine is, after the private communications from A. KATO, considered as mackinawite through E.P.M.A. analyses and that from Saezaki is also so (IMAI and FUJIKI, 1963), and mackinawite in Japan is used to indicating variation in minor elements such as nickel or cobalt. The disagreement of the results obtained by the present writer with those in the literatures may be ascribed to the differences in the minor elements as well as in the chemical reactions for the mineral in question, extremely minute in size, and for its host mineral.

C. PARAGENESIS OF MACKINAWITE

Mackinawite is apt to show an intimate association with emulsoidal chalcopyrite blebs or blades in massive sphalerite. The latter is associated commonly with massive pyrrhotite and chalcopyrite and less commonly with pyrite but in parts included alone in such gangues as quartz, calcite and hisingerite. Sphalerite involving minute blebs or blades of chalcopyrite accompanied with mackinawite reveals more abundance on the lower levels especially on -240m

level where calcaceous rock is predominant, and a similar tendency in such parts as is situated on -110m and -140m levels at the upper deposit excepting that mackinawite appearing at the upper ore deposit is smaller in grain-size than that occurring at the lower one.

The paragenetic relations of mackinawite with some minerals are classifiable into the following four types:

1. *Sphalerite-chalcopyrite-mackinawite*

A paragenesis of mackinawite with chalcopyrite is most common, though in more or less amount.

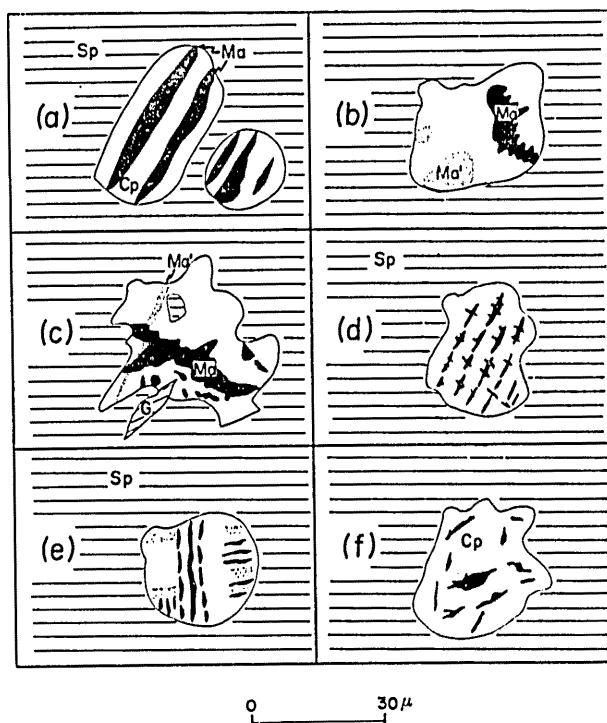


FIG. 1. Varieties of the shape of mackinawite in chalcopyrite grain.

Cp : chalcopyrite, Ma and Ma' : mackinawite, different in optical orientation from each other intersecting at 45 or 90 degrees, Sp : sphalerite, G : gangue.

In chalcopyrite blebs or blades microcrystals of mackinawite show variation in form, as are banded or lenticular along certain orientations of host individuals, comb-like, worm-like, lens- or lath-shaped, and irregular (Fig. 1). It seems common that a single grain of chalcopyrite, when larger than about 50 microns in diameter, bears no inclusion of mackinawite and is sometimes associated with pyrrhotite or cubanite. More larger grain of chalcopyrite in sphalerite is lack-

ing in inclusions though it be not the case with the skeletal crystals of sphalerite comprised in massive chalcopyrite (about up to 1mm in size) associating massive pyrrhotite, sphalerite, pyrite and galena.

In a bleb of chalcopyrite, mackinawite often shows two or three kinds of optical orientations and such reflection pleochroisms as are at the same time pale yellow and deep creamy brown in color. Moreover the apparent orientation of laths or lens of mackinawite is quite different from one another respectively in each grain of chalcopyrite.

2. Sphalerite-chalcopyrite-cubanite-mackinawite

Cubanite associated with mackinawite is easily distinguished by its characteristic bronzy tint and characteristic anisopism from chalcopyrite, appearing always in the grain of chalcopyrite enclosed in massive sphalerite. Its modes of occurrence are rich in variety, as were indicated by NAKAMURA (1949) and the writer (1963). Cubanite including mackinawite most often shows banded textures in a

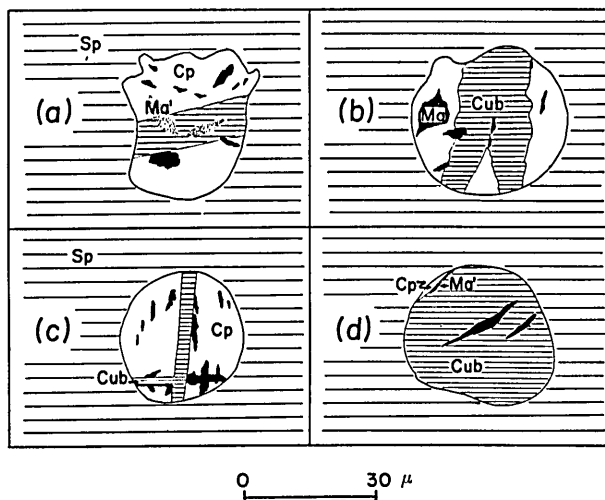


FIG. 2. Intergrowths of chalcopyrite-cubanite-mackinawite. The abbreviations are the same one as Fig. 1. Cub : cubanite.

grain of chalcopyrite (Fig. 2, a). In some cases cubanite grains accompanying chalcopyrite in more or less amount around their peripheries (from a few to 40 microns in size) include mackinawite of various forms (Fig. 2, b). In both cases, mackinawite occurs generally along the boundary between cubanite and chalcopyrite but less commonly in cubanite, most frequently cutting across the cubanite bands but being intersected rarely by the latter (Plate 4, Fig. 3). These associations seem to indicate the mackinawite to have been deposited later than the breakdown of chalcopyrite-cubanite intergrowth, since the mineral concerned is found traversing across cubanite as exsolution product.

3. *Sphalerite-chalcopyrite-pyrrhotite-mackinawite*

Pyrrhotite in emulsoidal grains of chalcopyrite associated with mackinawite seems somewhat harder than the adjacent minerals such as chalcopyrite and cubanite, in relation of its relief, commonly showing rather vague cleavages (Plate 4, Figs. 5 and 6).

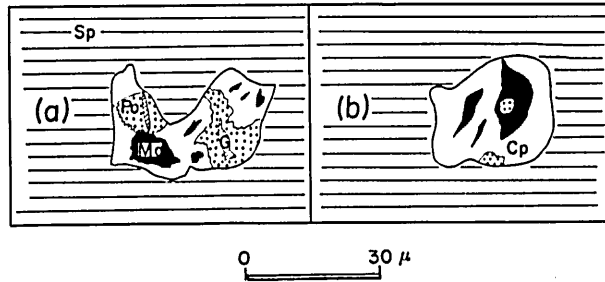


FIG. 3. Intergrowths of chalcopyrite-pyrrhotite-mackinawite. Po : pyrrhotite.

Pyrrhotite occurs as irregular inclusions in mackinawite within a single grain of chalcopyrite (Fig. 3, b) and those in chalcopyrite associated with mackinawite (Fig. 3, a), in general, includes no mackinawite, suggesting its own formation after the breakdown of chalcopyrite-mackinawite intergrowth along the cracks within the latter as later veinlets or by replacement.

4. *Sphalerite-chalcopyrite-cubanite-pyrrhotite-mackinawite*

These assemblages are, in parts, recognized, as are shown in Fig. 4. In this case, pyrrhotite often has cracks similar to in the case of chalcopyrite-pyrrhotite-mackinawite intergrowth and is considered as the last product of all. Namely, it may be summarized that chalcopyrite blebs exsolve out from massive sphalerite at the first step, cubanite appears slightly later or, in some cases, simultaneously as exsolution product in chalcopyrite blebs, and mackinawite is produced at the last step concerning the chalcopyrite-cubanite-mackinawite intergrowth. In the case of chalcopyrite-cubanite-mackinawite intergrowth, as has already been stated, pyrrhotite is considered to have been formed subsequent

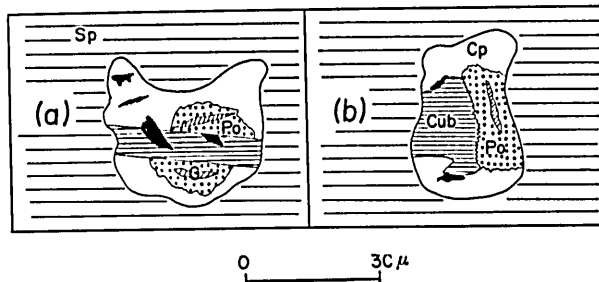


FIG. 4. Intergrowths of chalcopyrite-cubanite-pyrrhotite-mackinawite.

to the deposition of the former three in the latter. In this case, pyrrhotite appearing on unmixing of chalcopyrite-cubanite-mackinawite may have a crystal structure different from that produced ordinarily, and this kind of pyrrhotite-like mineral exhibiting weak anisotropism is surely recognized as will later be described.

5. *Pyrrhotite-like mineral associated with mackinawite*

A mineral, a few to 40 microns in size nearly similar to mackinawite, found out in the course of study on polished sections of the Kawayama mine is characterized by pyrrhotite-like anisotropism and colored pale pinkish brown or more pinkish to yellowish than in the case of ordinary pyrrhotite (in oil). Pleochroism is rather distinct but anisotropism is considerably weaker than that shown by ordinary pyrrhotite. Hardness is almost equal to the surrounding chalcopyrite and cubanite. The mineral concerned is comprised only in emulsoidal chalcopyrite blebs and frequently associated with cubanite or mackinawite.

Preliminary heat treatments for this mineral were carried out in a vacume of about 10^{-3} mm Hg in an electric furnace. It has been confirmed from the experiments that the specimen loses its pinkish color and produces a homogeneous solid solution with altered mackinawite* at the temperature range of $130^{\circ}\text{C}\sim 200^{\circ}\text{C}$.

The thermal studies of mackinawite as well as of the pyrrhotite-like mineral are here roughly outlined.

Both unmixing-textures and the results of heat treatment make it clear that the mineral is stable even at very low temperature lower than 200°C , revealing a structure of, so to speak, "low pyrrhotite". Furthermore details are however still now pending to be solved.

III. COMPARATIVE STUDIES OF PARAGENESIS

Mackinawite is surely a new mineral, so that there still remain confusion with valleriite from many localities. In spite of its common and widespread occurrence (EVANS *et al.*, 1964) description on mackinawite has been only a few in the literatures.

MILTON and MILTON (1958) described valleriite (identified later with mackinawite by EVANS *et al.*) from the Mackinaw mine, Snohomish County, Washington. At Mackinaw, it is considered unique that the ore consisting chiefly of niccolite, maucherite, pentlandite, chalcopyrite, cubanite and magnetite occurs in an altered peridotite, and mackinawite always occurs in chalcopyrite rather

* TAKENO and SOEDA (1964) reported a preliminary experimental results of thermal studies of "so-called" valleriite, suggesting that the mineral loses its characteristic pleochroism and anisotropism at $130^{\circ}\text{C}\sim 140^{\circ}\text{C}$, and alters optically to isotropic or weakly anisotropic mineral.

than in cubanite, but is found exceptionally within a single grain of pentlandite as small ragged bodies. The Mackinaw ore differs markedly from the Kawayama ore in the absence of pyrrhotite as well as in the existence of nickeliferous arsenides (niccolite and maucherite) and nickeliferous iron sulfide (pentlandite) and furthermore in its paragenesis with not emulsoidal chalcopyrite in sphalerite.

The Outokumpu ores described from a serpentine rock by Kouvo *et al.* (1963) also have some features in common with the Mackinaw ores but not with the Kawayama ores. At Outokumpu, mackinawite (described first as 'a tetragonal iron sulfide' and identified later with mackinawite) is associated mainly with nickel pentlandite, chalcopyrite, cubanite, sphalerite and pyrrhotite and rarely with magnetite, especially replacing the former three of all. At the Kawayama mine, nickeliferous sulfides are not found and mackinawite is always enclosed in chalcopyrite blebs in sphalerite accompanying hisingerite. In relation to this, the independent grains of mackinawite are included in the latter at Outokumpu.

Optical characters of the Outokumpu mackinawite were described by Kouvo *et al.* as follows:

Color: reddish gray (in air); internal reflections are not observed.

Pleochroism and anisotropy: very strong, gray to reddish (in air); undulatory extinction common.

Hardness: greater than that of pyrrhotite but lower than that of pentlandite rich in cobalt; Normarski equipment or simply diagonal illumination was used for observation.

The present writer also has got a chance to examine the same specimen given by Professor T. TATSUMI. Comparison of the color under reflection microscope and hardness show that mackinawite from Outokumpu is a little more reddish in color than that from Kawayama, while in talmage hardness the former is higher, and the latter is slightly lower, than pyrrhotite.

Moreover, thermal behaviors are quite different from each other: i. e. the former is altered to hexagonal pyrrhotite at up to 210°C (Kouvo *et al.*, 1963, p. 519) while the latter becomes isotropic or very weakly anisotropic at 130°C~140°C.

Valleriite described by SOEDA (1960) (later identified with mackinawite by IMAI and FUJIKI, 1963) from a deposit at Saezaki, Hiroshima Prefecture (considered by SOEDA to have been pyrometasomatically produced) discloses certain similarity to the Kawayama mackinawite in relation to its paragenesis with others. At Saezaki, the ore occurs in Paleozoic formation (alternation of slate and schalestein) intruded by granite, consisting chiefly of chalcopyrite, pyrrhotite, sphalerite, cubanite and arsenopyrite, and mackinawite is associated with chalcopyrite and cubanite. One of the SOEDA's figures (SOEDA, 1960, Fig. 12) illustrates the association of mackinawite with skeletal crystals of sphalerite in chalcopyrite whereas the Kawayama mackinawite is limited within the blebs of emulsoidal chalcopyrite and free from skeletal sphalerite. This may suggest a considerable difference of the thermal condition in each process of formation.

Ni-bearing mackinawite described by FUJIKI (1963) from the Kômorî mine, Kyôto Prefecture is associated with chalcopyrite, cubanite, pyrrhotite and Cobearing pentlandite in the vein-type deposit produced in gabbroic rocks. After FUJIKI, the ores showing exsolution textures are divided into two types: one (including five subtypes) is characterized with lamellar texture and the other with non-lamellar texture. Mackinawite is found comprized in subtypes 3 and 5. Subtype 3 indicates the lamellar texture of chalcopyrite-cubanite, wherein cubanite involves the regular intergrowth of the exsolved lamellar texture of pyrrhotite bearing the unmixed cobalt-bearing pentlandite accompanied furthermore with the unmixed nickel-bearing mackinawite along its crystallographic orientation. Subtype 5 shows an assemblage of the major minerals quite similar to in the former case, though the unmixed nickel-bearing mackinawite is contained in the chalcopyrite lamellae in crystallographic intergrowth. Mackinawite from the Kawayama mine is sometimes arranged beautifully along certain crystallographic orientation in chalcopyrite (Fig. 1, a), but not in cubanite. Lamellar textures of chalcopyrite-cubanite observed in the Kawayama ores are not so much well-developed as in the case of Kômorî ores.

These studies concerning the paragenesis of mackinawite seem to offer a conclusion that its association with chalcopyrite is most common and that with cubanite is subordinate but its occurrence in emulsoidal chalcopyrite is rare, while its association with nickeliferous sulfides is also common. It may be unique that the Kawayama mackinawite is contained in the host free from nickeliferous minerals. At any rate, an intimate co-existence of mackinawite with chalcopyrite and cubanite may give an important clue to serutiny for the origin of mackinawite.

IV. DISCUSSION

I. As for the ore minerals produced in the Kawayama mine, pyrrhotite, chalcopyrite, sphalerite (including marmatite), pyrite, and a few amount of cubanite, mackinawite, native-bismuth, Cu-Bi-S minerals, marcasite, galena and so on were already mentioned in the previous work (TAKENO, 1963). The mutual relationships among some pairs of such minerals as pyrrhotite, sphalerite, chalcopyrite and cubanite with mackinawite will hereunder be discussed.

In this case, most of the sulfide minerals are interpreted as might have been exsolved from a certain phase of homogeneous ore solution with complex compositions rich in FeS.

On cooling, this phase is considered to exsolve four fractionated phases, such as, 1) solid solution A (predominant in FeS), 2) solid solution B (rich in ZnS), 3) solid solution C (rich in CuFeS₂) and solid solution D (including FeS₂ and PbS etc. in no direct relations to mackinawite). Various deductions may be led

through inspection of the unmixed products. The relative abundances of A, B, C and D are thereby estimated 5:2:1:1.

Solid solution A is inferred to have contained iron, copper and zinc sulfides approximately as FeS together with only few per cent of ZnS and CuFeS₂.

Solid solution C might have contained copper, iron and zinc sulfides approximately as CuFeS₂ accompanying a few per cent of FeS and ZnS.

Solid solution D is to have included all other sulfide minerals such as FeS₂, PbS, FeAsS and so on. This may be furthermore divided into several phases in no relation to mackinawite.

Mackinawite is in connection only with solid solution B containing zinc, iron and copper sulfides in an approximate proportion of 3:1:1.

First, most proportion of pyrrhotite (Fe_{1-x}S) are exsolved from solid solution A, coming into contact with massive sphalerite, chalcopyrite, pyrite, and so on. Contemporaneously or a little later, most of sphalerite and chalcopyrite are derived from B and C through unmixing with descending temperatures, and sphalerite from B becomes to split into the blebs of pyrrhotite, chalcopyrite and cubanite in order through exsolution. Far later, so-called emulsoidal chalcopyrite (rich in FeS) blebs are brought forth from the residual solution of B through double unmixing, and at last cubanite, pyrrhotite and mackinawite are settled up in the emulsoidal chalcopyrite blebs through triple unmixing.

The relations among the solid solution A, B, C and D together with paragenesis of the ore minerals from the Kawayama mine are schematically illustrated in Fig. 5.

Sphalerite indicates at least three stages of deposition: 1) massive sphalerite (represented by Sp₁ and Sp₃ in Fig. 5) associated with massive pyrrhotite, chalcopyrite and other sulfide minerals such as pyrite and galena, 2) massive sphalerite (Sp₂) derived from S. S. B. a little later than from S. S. A and S. S. C and 3) skeletal sphalerite (Sp₄, Sp₅ and Sp₆) in chalcopyrite. All of these might have become immiscible at the same stage at the temperature range of 450°C~550°C, as were discussed in many literatures.

Chalcopyrite, though more complicated, reveals at least three stages of deposition: 1) massive chalcopyrite (Cp₁ and Cp₂ in Fig. 5) associated with massive pyrrhotite, sphalerite and other sulfide minerals, 2) chalcopyrite in pyrrhotite (Cp₃ and Cp₅), sometimes associated with cubanite and skeletal sphalerite and 3) chalcopyrite of so-called "emulsion" or "mottled" texture frequently shows a wide range in size and an unequal distribution throughout a single sphalerite crystal.

II. As has already been stated, mackinawite from the Kawayama mine is associated with chalcopyrite, cubanite and pyrrhotite in massive sphalerite of solid solution B, and exsolved from emulsoidal chalcopyrite blebs. Mackinawite (approximately FeS), chalcopyrite (CuFeS₂), cubanite (CuFe₂S₃) and pyrrhotite (Fe_{1-x}S) are all included in the system Cu-Fe-S, as to which there have so far

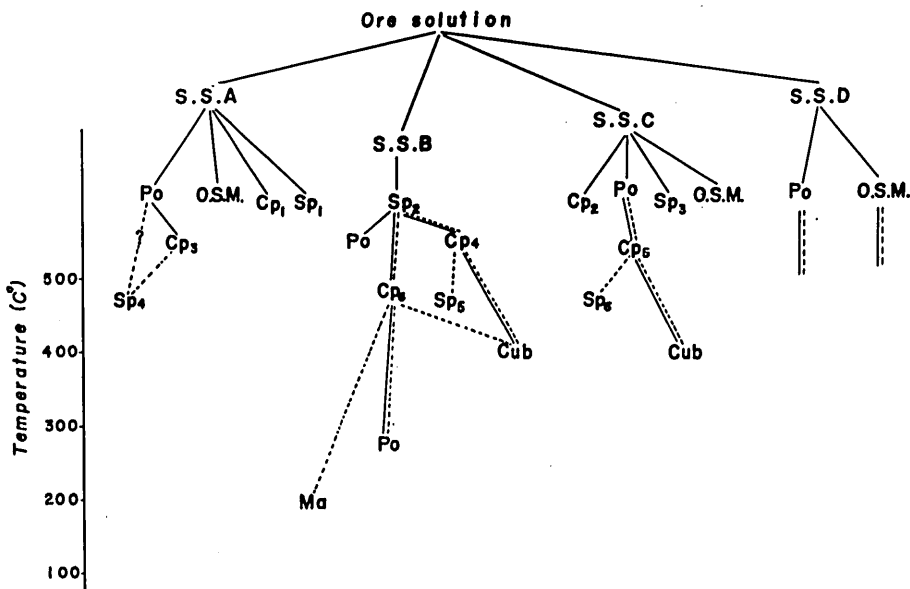


FIG. 5. Paragenetic relation of the ore minerals from the Kawayama mine.

The dotted lines represent the immiscibility and the solid lines indicate the mutual contact or replacement relation. S.S. A, S.S. B, S.S. C and S.S. D : solid solution A, B, C and D. Po : Pyrrhotite, Cp : chalcopyrite, Sp : sphalerite, Cub : cubanite, Ma : mackinawite, O.S.M. : other sulfide minerals such as pyrite, galena, arsenopyrite, and so on.

been some experimental works. In particular, the nature and history of our solid solution B as well as the paragenesis of the related minerals are here dealt with in details.

After HEWITT (1938), pyrrhotite and chalcopyrite form two kinds of solid solution and pyrrhotite can be dissolved in chalcopyrite above 300°C. These two minerals then react with each other, resulting in formation of chalcopyrrhotite displaying a very fine intergrowth with the latter around the former as an aureole. At ca. 600°C, the latter is dissolved in the former and, upon unmixing, forms oriented laths in the former. The textures produced by pyrrhotite and chalcopyrite was described by SCHWARTZ (1937), who stated that the latter occurs as veinlets or as replacement products in the former and as alternating bands with the former. The solid solution A seems to correspond to such a product as was described by HEWITT.

The solid solution B is more difficult to be solved. In relation to this, solubility of FeS in ZnS in appreciable amounts has long been known. In nature, colorless ZnS in pure state is extremely rare. In numerous ore deposits, pyrrhotite is found intimately connected with sphalerite (marmatite). Owing to an abundance of iron during the process of ore formation, it is safely assumed that a sort of equilibrium might have existed between free pyrrhotite and FeS con-

tained in the sphalerite lattice at the stage of sphalerite formation. KULLERUD (1953) obtained an equilibrium diagram of FeS-ZnS system as a result of more than 250 runs of experiments concerning the mixtures of FeS and ZnS in various proportions. These data are unreasonable to be applied to the solid solution B on account of contamination with a considerable amount of CuFeS_2 and CuFe_2S_3 . On the other hand, BEURGER (1934) reported that sphalerite and chalcopyrite are capable of forming solid solution to certain extent at the temperature above 350°C to 400°C and chalcopyrite dissolved in sphalerite becomes immiscible nearly at these temperatures.

Cubanite (CuFe_2S_3) commonly occurs as parallel laths or bands along the [111] direction of chalcopyrite. After SCHWARTZ (1927), these textures of cubanite are found only in the high-temperature deposits, and cubanite is possible to enter into solid solution in chalcopyrite when heated above 450°C . Chalcopyrite and cubanite from the Kawayama ores show no parallel intergrowth in typical form.

SCHWARTZ (1931) was of opinion that cubanite occurs only in a close association with pyrrhotite and chalcopyrite, and EDWARDS (1954) pointed out the composition in paragenetic relations among pyrrhotite, chalcopyrite and sphalerite. MERWIN and LOMBARD (1937), in their investigations on the system Cu-Fe-S, show that under suitable conditions pyrrhotite and chalcopyrite may react with each other to form cubanite. This relation was also illustrated in a series of experiments carried out by BORCHERT (1934/35), according to whom the solid solution that is stable only at temperatures above 255°C but seems preservable through quenching to room temperature is called chalcopyrrhotite while cubanite and vallerite become stable on further cooling. To be noted is that he also found a naturally occurring mineral identified by himself as chalcopyrrhotite. After RAMDOHR (1960), chalcopyrrhotite is isotropic or very weakly anisotropic, brownish but a little more yellowish than pyrrhotite in color and reveals a similar reflectivity, occurring alone or as intergrowth with chalcopyrite or cubanite.

Concerning the pyrrhotite-like mineral, two species such as the ordinarily anisotropic cubanite I and the isotropic cubanite II were discerned from each other by RAMDOHR (1960). The latter was regarded as an intimate intergrowth of chalcopyrite and chalcopyrrhotite by BORCHERT (1934/35) who suggested the transformability of cubanite I to cubanite II at the temperature higher than 235°C . Nevertheless, trimorphism of cubanite represented by the orthorhombic one at the natural state, the tetragonal one derived by heating of the former at $200^\circ\text{C}\sim 260^\circ\text{C}$, and the cubic one stable at the temperature higher than 270°C was reported by YOUND and KULLERUD (1961). The interrelation of the latter two modifications to cubanite II still remains to be solved. The relation of the solid solution B to three modifications mentioned above is also of obscurity. On the other hand, the writer and SOEDA (1964) carried out the thermal studies

of so-called valleriite (mackinawite) from the Kawayama mine and found out that its characteristic pleochroism and anisotropism disappear, when heated at $130^{\circ}\text{C}\sim 140^{\circ}\text{C}$. This implies the complicated problems existing in the Cu-Fe-S system at lower temperature below 200°C .

So far as the chemical composition given in the BORCHERT's diagram is concerned, valleriite is to be combined with mackinawite, but the temperature considered suitable for this mineral is really lower than that proposed by him, as was already suggested by Kouvo *et al.* (1963) as well as the present writer (1964) and it is also problematical to include valleriite simply in the Cu-Fe-S system, inasmuch as the considerable amounts of Al_2O_3 and MgO were verified in the analyses of the related minerals from Nya Kappenberg by BLOMSTRAND (1870) and in the one from Kaveltorp by EVANS *et al.* (1964).

As for optical property, altered mackinawite shows some resemblances to chalcopyrrhotite or cubanite II, but details of the system at the lower temperature range remain yet to be pursued.

As a result, an interpretation may be that the solid solution B exsolves in sphalerite from the original ore solution at an early stage at a considerably high temperature (up to 600°C), chalcopyrite is then produced as a myriad of minute blebs at the temperature range of $350^{\circ}\text{C}\sim 400^{\circ}\text{C}$, and mackinawite is finally formed in chalcopyrite blebs as triple unmixing probably at the temperature range lower than 200°C .

III. Any considerations on the occurrence of extremely minute mackinawite have not been dealt with. Naturally occurring minerals belonging to the Fe-S system are represented ordinarily by the hexagonal pyrrhotite (Fe_{1-x}S or FeS_{1+x}) and pyrite ($\text{Fe}_{1+x}\text{S}_2$). Kouvo *et al.* described the tetragonal FeS changing to normal hexagonal Fe_{1-x}S through heating and examined the cell dimension of FeS and Fe_{1-x}S with various quantity of x .

The physical properties of iron sulfides Fe_{1-x}S have, almost simply from the standpoint of solid physics, been studied by many investigators but no experimental works of Fe_{1-x}S have ever been given from the geological point of view. For instance, the iron sulfides revealing very complicated magnetic behaviors have been investigated similarly from crystallographical and electrical fields. UEDA *et al.* (1950) show in their study of synthetical pyrrhotite that the lattice constant c of $\text{FeS}_{1.01}$ contracts abruptly at 120°C . HARALDSEN (1937, 1941) and HIHARA (1960) have investigated the magnetic properties of synthetic iron sulfides and presented the magnetic susceptibility versus temperature curve with some knicks of transformation, for instance, T_{α} pointing to that at $90^{\circ}\sim 140^{\circ}\text{C}$.

After HARALDSEN (1937, 1941), UEDA *et al.* (1950), BERTAUT (1953) and HIHARA (1960), T_{α} shifts to the lower temperatures side with increasing x , T_{α} for stoichiometric FeS ($x=1.00$) is 140°C , and the crystal structure of FeS_x ($1.00 \leq x \leq 1.44$) is of hexagonal NiAs-type with no essential change at T_{α} , but at the temperature below T_{α} a superlattice structure is present.

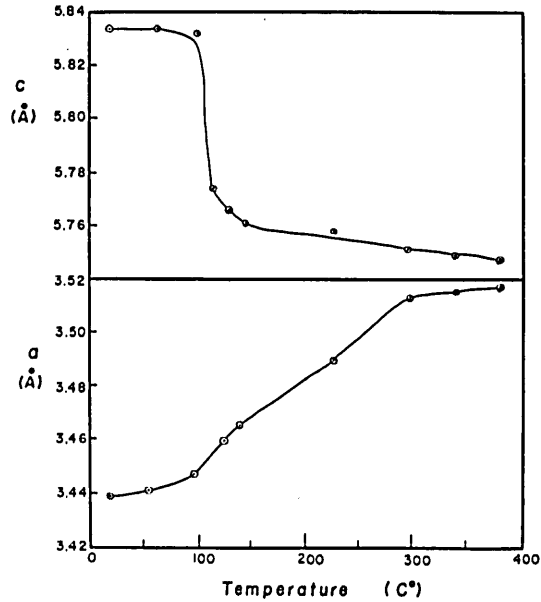


FIG. 6. Lattice constant a and c of $\text{FeS}_{1.01}$ (50.2% S mol.) versus temperature curve. (After UEDA *et al.*, 1950).

Stoichiometrically, mackinawite may have a composition of FeS , and the Kawayama mackinawite changes to a new phase at $130^{\circ}\text{C}\sim 140^{\circ}\text{C}$ just corresponding to T_{α} (at 140°C for $\text{FeS}_{1.00}$). This fact may justify the transformation of mackinawite at $130^{\circ}\text{C}\sim 140^{\circ}\text{C}$.

Difference in transformation temperature of the Outokumpu specimens from that of the Kawayama ones and even in that of each one from the same locality may be mainly owing to the Fe deficiency in the respective inner structure rather than to contents of the minor elements. Moreover, immiscibility appearing in the intimate association of chalcopyrite with mackinawite suggests that the latter might have been derived from the solid solutions of the definite composition of CuFeS_2 with a very little amount of FeS at a certain stage and at extremely low temperature far lower than those shown in the geological literatures.

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INSTITUTE OF GEOLOGY AND MINERALOGY,
FACULTY OF SCIENCE,
HIROSHIMA UNIVERSITY.

EXPLANATION OF PLATE IV

- FIG. 1. Photograph of X. M. A. (Cu $K\alpha$), showing FeS (Ma) in CuFeS_2 (Cp) grain in ZnS (Sp). (25kV, 25mA. Analyser : LiF, System : air)
- FIG. 2. Intergrowth of chalcopyrite-mackinawite in sphalerite. Under oil immersion lens.
- FIG. 3. Intergrowth of chalcopyrite-cubanite-mackinawite. Under oil immersion lens.
- FIG. 4. Intergrowth of chalcopyrite-cubanite-mackinawite. Crossed nicols. Under oil immersion lens.
- FIG. 5. Intergrowth of chalcopyrite-pyrrhotite-mackinawite. Under oil immersion lens.
- FIG. 6. Intergrowth of chalcopyrite-cubanite-pyrrhotite-mackinawite. Under oil immersion lens.

Ma and Ma' : mackinawite revealing different orientation intersecting with each other at about 90 degrees. Cp : chalcopyrite, Cub : cubanite, Sp : sphalerite, Po : pyrrhotite, G : gangue.

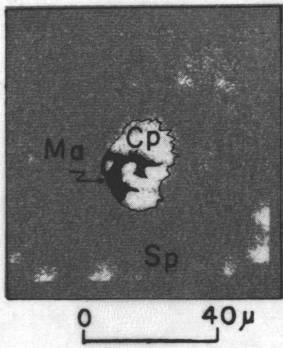


FIG. 1.

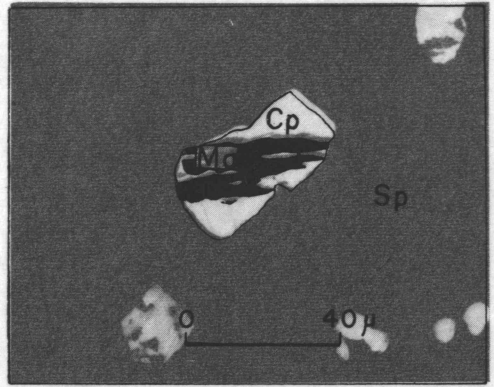


FIG. 2.

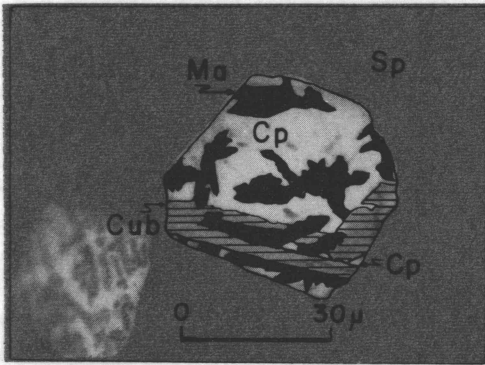


FIG. 3.

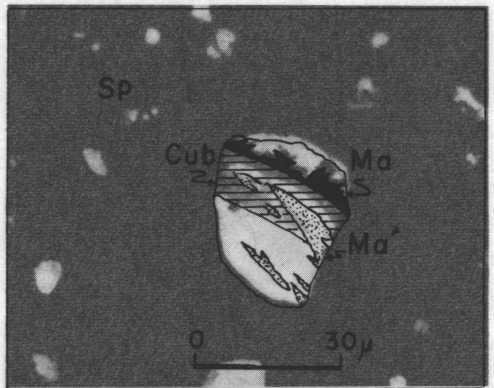


FIG. 4.

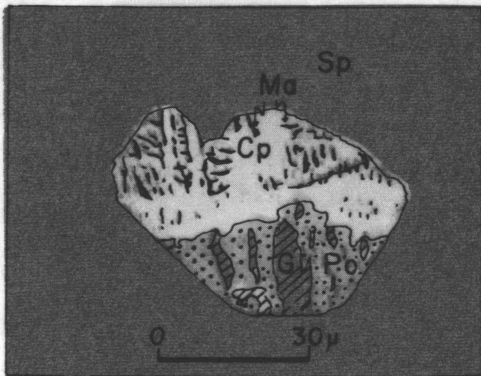


FIG. 5.

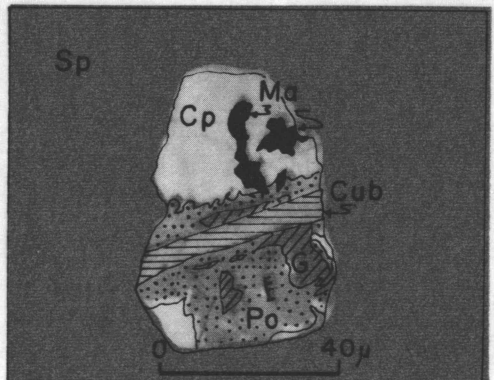


FIG. 6.



FIG. 1.

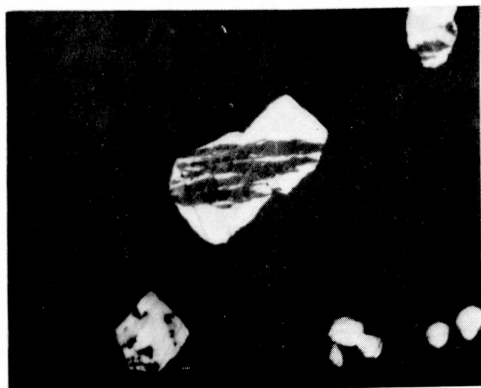


FIG. 2.

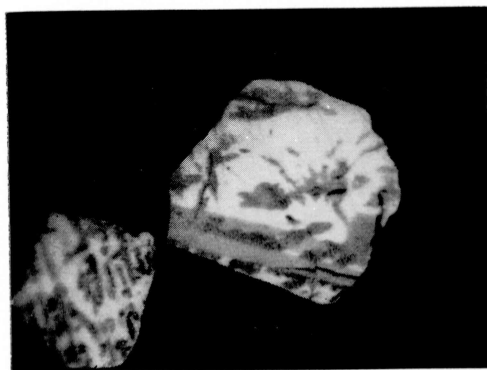


FIG. 3.

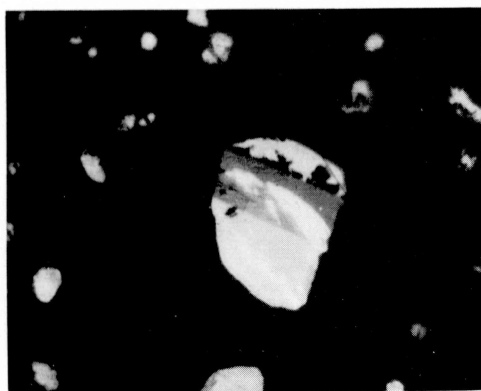


FIG. 4.

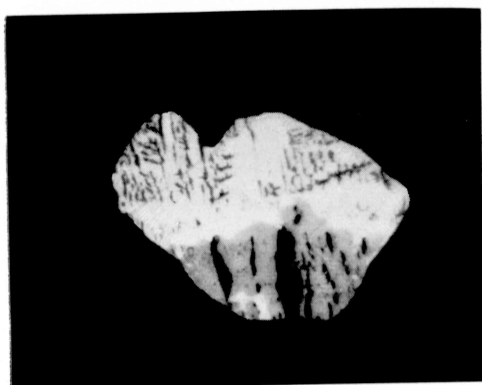


FIG. 5.



FIG. 6.