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# Thermal Studies on Mackinawite

By

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*with 1 Table, 8 Text-figures and 4 Plates*

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ABSTRACT: On mackinawite mistaken for valleriite, the specimens obtained from eleven localities have been investigated especially concerning its thermal behaviors. Those discriminated under the reflection microscope on the basis of their optical characters revealing abrupt change at 130°C~250°C are classifiable into A) Kawayama type (including the specimen from Mackinaw) losing its extraordinary pleochroism and anisotropism at 130°C~160°C, B) Kômori type (including those from Muskox, Tsumo, Akagane and Ohmine) showing the similar variation at intermediate temperature and C) Outokumpu type (including those from Makimine, Besshi and Shimokawa doing so above 200°C, among which the third type only discloses transformation from mackinawite to pyrrhotite. A considerable difference in transformation temperature is commonly observable even in the specimens collected from the same locality.

True valleriite, on the other hand, is stable at the temperature lower than about 500°C.

CONTENTS

## I. INTRODUCTION

Mackinawite which has hitherto been mistaken for valleriite in many localities is a new mineral reported first by EVANS *et al.* (1964), although details of its genesis or thermal behavior still remain to be scrutinized.

Since the first work given by BLOMSTRAND (1870) concerning valleriite from Nya Kopparberg, many ore-microscopists have described the mineral from various kinds of the ore deposits in the world.

The existence of a mineral different from valleriite was first being suspected when isolated successfully from the matrices of chalcopyrite associated most frequently in order to obtain a characteristic x-ray diffraction pattern.

MILTON and MILTON (1958) described an occurrence of a sulfide mineral identified with valleriite from the Mackinaw mine in Snohomish County, Washington mainly based on its physical properties under microscope. Their identification was tentative and a doubt arisen later in the related study was already pointed out. Examination for each grain of the mineral on a polished section with an electron-microprobe apparatus by Birks *et al.* (1959) showed copper to be very low in content and its composition to be approximately FeS.

Meanwhile, Kouvo *et al.* (1963) published a paper concerning a new iron-sulfide mineral resembling to, but differing from, valleriite from the Outokumpu mine, Finland. Their analyses for this mineral pointed to the characteristic absence of copper and led to such a formulation as $(Fe_{0.91}\ Ni_{0.13}\ Co_{0.007})\ S$, while the x-ray powder patterns were not congruent with those given for valleriite in the preceding literatures but quite close to those for kansite ($Fe_9\ S_8$). Inspection of its single crystals, up to 1mm in size, through Weissenberg method allowed these authors to reach such a conclusion that the crystals be composed of a tetragonal unit cell of probable space group *P4/mmm* with $a=3.676\pm0.002$Å and $c=5.032$Å.

This new phase designated by Evans *et al.* (1964) as mackinawite is very much similar in physical property to valleriite, causing a great deal of confusion. According to Evans *et al.* this new copper-free iron sulfide is of tetragonal space group, *P4/nmm* with $a=3.679$Å, $c=5.047$Å, and bears a unit-cell containing 2FeS, while valleriite is of rhombohedral space group, *R3m* or $R\bar{3}m$ with $a=3.792$Å, $c=34.10$Å, and its probable unit-cell contains $6CuFeS_2$. They emphasized common and widespread occurrence of mackinawite compared with scarcity of valleriite. Occurrences of authentic valleriite have been reported from only three localities such as Loolekop in South Africa, Kaveltorp in Southern Sweden and Muskox intrusion in Canada (Chamberlain and Delabio, 1965). X-ray diffraction patterns obtained by them show a good identity with those of the Outokumpu mineral described by Kouvo *et al.*

Occurrences of valleriite in Japan have been described from many ore deposits since its discovery by Tatsumi (1953) from the Makimine mine, Kyûshû. The present writer (1965), however, has already suggested that so-called valleriite from various kinds of the ore deposits in Japan should be taken as mackinawite.

On the other hand, because of no decisive data given so far for mackinawite, plenty of the ore-microscopists have dealt with the problem on the basis of the phase relations including valleriite and chalcopyrite as have been reported by some authors such as Borchert (1934) and Merwin and Lombard (1937).

However it may be, the present writer has reached a conclusion with respect to the mineral in question contained in the system Cu-Fe-S and its immiscibility at a certain temperature (130°C∼200°C) far lower than those shown in the previous literatures. On the other hand, Chamberlain and Delabio (1965) suggested in their discussion on the origin of mackinawite from the Muskox intrusion, Canada that the very mineral might have been formed at moderate or low temperatures during early stage of serpentinization of olivine.

The present experiment has been made with aim of proposing some clue to solution for the genetical condition and to discrimination of the mineral under consideration from valleriite.

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## II. SPECIMENS PROVIDED FOR EXPERIMENTS

### *1. Specimen from the Kawayama mine.*

The Kawayama mine is being worked for the large lenticular ore bodies developed so far with a scale of more than 1,200m along the strike-side and 600m along the dip-side. The ores consist of pyrrhotite associating a little amount of shalerite, chalcopyrite, marcasite, pyrite, galena and cubanite.

Under the microscope, mackinawite, a few to about 50 microns in size, is enclosed within the blebs or blades of chalcopyrite in massive sphalerite. The latter is associated commonly with massive pyrrhotite and chalcopyrite and less commonly with pyrite but in part included alone in such gangues as quartz, calcite and hisingerite (TAKENO, 1963).

Recently, the writer (1965) has described the paragenesis of mackinawite with some others in details and classified its paragenetic assemblages into four types: 1) sphalerite-chalcopyrite-mackinawite, 2) sphalerite-chalcopyrite-cubanite-mackinawite, 3) sphalerite-chalcopyrite-pyrrhotite-mackinawite and 4) sphalerite-chalcopyrite-cubanite-pyrrhotite-mackinawite. Its optical characters under the reflection microscope are as follows:

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

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

### 2. *Specimen from the Mackinaw mine.*

The Mackinaw mine, Snohomish County, Washington, is considered unique in occurrence of the ores consisting chiefly of niccolite, maucherite, pentlandite, chalcopyrite, cubanite and magnetite in an altered peridotite. Chalcocite and violarite or braboite are also present as the supergene minerals. Pyrrhotite and pyrite are absent. Mackinawite always occurs in chalcopyrite rather than in cubanite, as if it were considered either exsolved from, or replacing, chalcopyrite (MILTON and MILTON, 1958), but is found exceptionally within a single grain of pentlandite as small ragged bodies. The specimens used for the present experiment include the well-developed mackinawite, a few to hundreds microns in size, embraced in chalcopyrite and cubanite.

### 3. *Specimen from the Outokumpu mine.*

The specimen is that from Stope U 27 of Outokumpu mine, Finland, occurring in the serpentine rock. At Outokumpu, mackinawite is associated mainly with nickel pentlandite, chalcopyrite, cubanite, sphalerite and rarely with magnetite, especially replacing the former three of all. Macroscopically, its crystals are bronze-tinged, but the surfaces of fractures are white-gray in color and their powders are black. The mineral is soft and readily able to be scratched by a needle. The crystals are usually of tetragonal basal plates or of simple pyramid combined with perfect basal cleavage. The optical properties are virtually identical with those given previously for valleriite and are shown as follows:

Color: reddish gray (in air).

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

Hardness: greater than that of pyrrhotite but lower than that of cobalt pentlandite rich in cobalt.

(KOUVO *et al.*, 1963)

### 4. *Specimen from the Muskox intrusion.*

The Muskox intrusion was discovered in the Coppermine River area of northern Canada in 1956 by the Canadian Nickel Company, mapped by C. H. SMITH in 1959, 1960, and 1963, and drilled by the Geological Survey of Canada as a part of studies related to International Upper Mantle Project. Three vertical holes were drilled down to a combined depth of 10,000 feet, and the results obtained in this project are described by FINDLY and SMITH (1964). The Muskox intrusion is a Precambrian layered pluton, 74 miles in length, which is horizontally dike-like and in cross section funnel-shaped. Sulfides are most abundant in the intrusion along its margin and roof, and mackinawite together with valleriite have been observed in dunite and pyroxenite situating in the central series. The former occurs as a replacement product in pentlandite while the latter occurring in serpentine might have replaced secondarily magnetite and is not usually associated with other sulfides (CHAMBERLAIN and DELABIO, 1965), differing from mackinawite. The specimens provided for the experiments are those of No. N 33058 and No. E 21808 from the drilling cores. The optical properties of Muskox mackinawite are as follows:

Color: pinkish gray; resembling to pyrrhotite.
Bireflectance: moderate to high; pink to gray.
Anisotropism under crossed nicols: high, but decreasing with time after polishing; grayish white to dark gray under completely crossed nicols.

(CHAMBERLAIN and DELABIO, 1965)

### 5. *Specimen from the Makimine mine.*

The specimen is that from the Senju adit in the Makimine mine, Miyazaki Prefecture. The ores developing almost concordantly with the wall rock consist chiefly of chalcopyrite, pyrite, sphalerite and pyrrhotite in the Shimanto-Complex (Mesozoic?) consisting of black phyllite (TATSUMI 1953). Mackinawite included mainly in chalcopyrite and pyrrhotite is very fine-grained and irregular or rounded in shape.

### 6. *Specimen from the Kômori mine.*

The ore deposit of the Kômori mine in Kyoto Prefecture, produced in the gabbroic rocks, is of the vein-type. The ores of this mine consist of chalcopyrite, pyrrhotite, cubanite, Ni-bearing mackinawite, Co-bearing pentlandite, sphalerite, galena and so on. Mackinawite, a few to hundreds microns in size, is contained in chalcopyrite and cubanite lamellae revealing crystallographic intergrowth with each other (FUJIKI, 1963). The specimens used in the experiment are those from −380mL. of Raikô No. 1 adit of the Kômori mine.

### 7. *Specimen from the Besshi mine.*

The Besshi mine in Ehime Prefecture is famous for production of the greatest bedded deposit consisting of cupriferous iron sulfide ores (Kieslager) developed in a part of crystalline schist belonging to the Sambagawa metamorphic zone. Mackinawite, tens to hundreds microns in diameter, is associated with pyrrhotite, chalcopyrite, sphalerite and pyrite, occurring in rather lower part of the ore deposit (MIYAHISA, 1958). The specimens are those from 22L. of Honzan adit in the Besshi mine.

### *8. Specimen from the Tsumo mine.*

The Tsumo mine in Shimane Prefecture is geologically found situating in the Palaeozoic formation. The ores replacing the calcareous shale consist of pyrrhotite, chalcopyrite and galena with some skarn minerals such as grossularite, diopside and wollastonite. Mackinawite is associated with chalcopyrite, pyrrhotite, cubanite and arsenopyrite. The specimens are those from −25mL. of the Tsumo mine.

### *9. Specimen from the Akagane mine.*

The ore deposit of the Akagane mine in Iwate Prefecture, developed in the Palaeozoic formation intruded by granitic rocks, is of a type of the contact metasomatic origin. Mackinawite is intimately associated with chalcopyrite, pyrrhotite, cubanite and, in part, with sphalerite and pentlandite. Based on the paragenetic relations of minerals TAKEUCHI and NAMBU (1954) classified valleriite (mackinawite) of this mine into three types: 1) irregular inclusions of mackinawite crystallized primarily from the ore-forming fluid in chalcopyrite and pyrrhotite, 2) small blade- or rod-like mackinawite derived from unmixing of solid solution along certain orientation in chalcopyrite, and 3) thin films of mackinawite occurring in the boundaries between chalcopyrite and pyrrhotite as the reaction products of the latters. The specimens are those sampled from the first sublevel of the second adit in the Sixth Ore Body of the mine concerned.

### *10. Specimen from the Ohmine mine.*

The Ohmine mine in Iwate Prefecture comprises a sort of contact metasomatic copper deposit developed in the Palaeozoic formation composed of slate, schalstein, hornfels and sandstone and intruded by granodiorite and quartz-diorite (TAKEUCHI *et al.*, 1953). The ores of this mine consist of pyrrhotite, chalcopyrite, pyrite, cubanite, violarite, pentlandite, sphalerite, tetrahedrite, magnetite and mackinawite. Mackinawite is intimately associated with chalcopyrite, cubanite, pyrrhotite and sphalerite. The specimens are those taken out from the No. 2 adit in the mine.

### *11. Specimen from the Shimokawa mine.*

The Shimokawa mine in Hokkaido is known for the bedded ore deposit of cupriferous iron sulfide developed along some fractured zone in Hidaka formation (Pre-Gretaceous) consisting of slate intruded by schalestein. The ores chiefly consist of pyrite, pyrrhotite, sphalerite, cubanite and so on. Mackinawite is in a close association with chalcopyrite and sphalerite ranging from a few microns to tens microns.

## III. EXPERIMENTS

### A. METHOD

The specimens, about $5 \times 5 \times 4$ mm$^3$ in size, were polished prior to the experiments.

After examined under reflection microscope, each of them was sealed in the hard-glass tube, 8~11mm in diameter and 20~30mm in length, evacuated to about $10^{-3}$ mm Hg, and then put in an electric furnace kept at a known temperature. After held for certain hours (usually, 1, 2, 3, 5, 10, 15, 20 and 24 hours) and quenched in water, the specimens were taken out and, after polishing of their surfaces, examined again under microscope.

Temperature was measured with almel-chromel thermocouple and mercurial thermometer. An automatic voltage-stabilizer was employed to keep constant at a known temperature.

### B. Experimental Results.

All the specimens of mackinawite are of size ranging from a few to hundreds microns and hence its structural variations with increasing temperature are hardly pursuable by means other than optical examination under microscope.

The mackinawite specimens revealing abrupt change of optical charaters at 130°C ~250°C are roughly classifiable into A) Kawayama type losing its extraordinary pleochroism and anisotropism at 130°C~160°C, B) Kômori type showing variation at the temperature ranging rather widely between A and B, and C) Outokumpu type doing so at the temperature higher than 200°C. In the following, the details will be described.

### 1. *Kawayama Type*

1) Kawayama mackinawite.

The lowest temperature revealing disappearance of the optical characteristic of mackinawite is rather variable. The maximum temperature for transformation with heating for an hour is observed at 147°C and the minimum at 130°C (1h), and with increase of heating time the temperature is lowered slightly but for more than 10 hours the change with temperature is generally small and in the range of 128°C~140°C.

At 130°C~150°C mackinawite alters to isotropic or very weakly anisotropic mineral ($M_1$ in Figs. 1 and 2) showing the following characters:

Color: pale pinkish cream to gray pinkish cream (in oil).
Reflection pleochroism: almost negative.
Anisotropism under the crossed nicols: very weakly recognizable.

In many cases, at the tip, or along the peripheries, of altered mackinawite original characters still remain at the temperature lower than 180°C (1h) as are shown in Fig. 1-b. In appearance, the altered mackinawite ($M_1$) is somewhat in resemblance to pyrrhotite in color but, owing to its extremely minute size, impossible to identify with each other only by means of the reflection microscope. $M_1$ is almost same as the original mackinawite in chemical composition through x-ray microprobe. Judging from its weak or almost negative anisotropism and reflection pleochroism it seems to be identified with undescribed iron sulfide, showing optical alliance (chiefly in its color) to chalcopyrrhotite reported by RAMDOHR (1960).

With increasing temperature, altered mackinawite gets to show rather strong reflection pleochroism and anisotropism at 200°C～350°C ($M_2$ in Figs. 2 and 3) and its optical characters are as follows:

Color: pinkish pale brown.
Reflection pleochroism: weak but distinct.
Anisotropism under the crossed nicols: strong; yellowish pale brown to pinkish dark brown (in oil).

$M_2$ is more brownish in color than $M_1$. With heating at about 170°C for an hour a linear mineral (LM in Figs. 1 and 2) begins to appear in the altered mackinawite. This is black to dark grayish brown in color, characterized with pleochroism ranging from yellowish brown to dark pinkish brown and strong anisotropism, and is generally arranged along certain orientation as are shown in Fig. 1. This characteristic mineral (probably graphite?) is stable at the temperature lower than about 380°C.

As for color and anisotropism in transformation of mackinawite, $M_2$ is more close to pyrrhotite than $M_1$; but growth of the linear mineral mentioned above causes an obscurity in determining the optical character of altered mackinawite with content of iron and sulfur nearly as high as those of pyrrhotite at the temperature between 200°C and 350°C.

With heating at about 350°C for an hour, the altered mackinawite almost loses its original form while chalcopyrite, the host mineral, remains just as it was. In this temperature range the former shows pyrite-like color (yellowish white～yellowish brown) with weak reflection pleochroism ($M_3$ in Figs. 1 and 2) and begins to form homogeneous solid solution with the latter from its peripheries or tips, culminating in its completion at the temperature higher than about 400°C (Figs. 1-j and 2-j). Figs. 1 and 2 illustrate the examples of the processes from original mackinawite to the end product of homogeneous solid solution with chalcopyrite.

In the course of these experiments, the variation of cubanite in natural state ($Cub_1$ in Figs. 1 and 2) to optically isotropic cubanite ($Cub_2$) at 230°C～240°C and furthermore its coincidence with the preceding works (BORCHERT, 1934 and SUGAKI, 1953) have been confirmed.

The pyrrhotite-like mineral reported by the present writer (1965, p. 67) also shows rather variable transformation temperature and in general form a homogeneous solid solution with altered mackinawite in the temperature range between 130°C and 150°C (Pol in Fig. 2), though occasionally preserved even at higher temperature (170°C～200°C), as is shown in Fig. 2. In a few cases, it is found preserving a strong anisotropism with increasing temperature and changing to normal pyrrhotite at the temperature up to 200°C.

It seems significant that the transformation temperature of mackinawite is variable even in the case of the same specimen although the deviation is usually smaller than 20°C and that difference of the transformation temperature caused by the paragenetic relation with some others is not recognized as a whole.

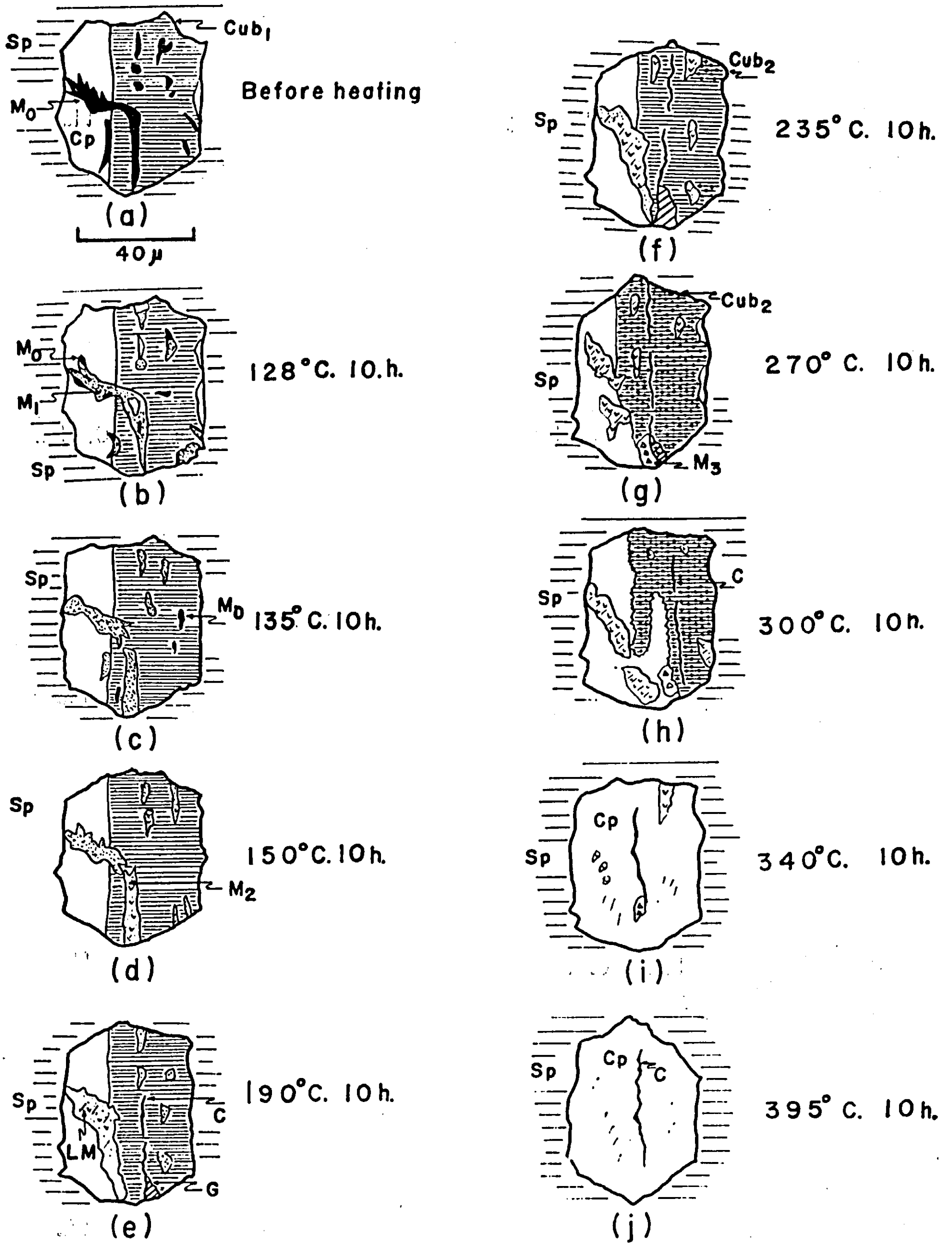

Fig. 1. Transformation of mackinawite from the Kawayama mine with increasing temperature (cf. Plate 54). Cp: chalcopyrite, Cub$_1$: ordinary cubanite, Cub$_2$: isotropic cubanite, Sp: sphalerite, C: cleavage yielded by heating, G: gangue mineral. These abbreviations will later be used in all figures.

Unheated mackinawite represented by $M_0$ is enclosed in emulsoidal chalcopyrite in sphalerite. At about 130°C (b) its characteristics disappear and a new phase (represented by $M_1$) is found preserving the original figure. This new phase shows a pale pinkish color with very weak anisotropism. From about 150°C $M_1$ changes to more anisotropic mineral ($M_2$) revealing some resemblances to ordinary pyrrhotite in its characteristics. LM in e, f, g and h is an undecided mineral (probably graphite) with characteristic optics. Above 235°C ordinary anisotropic cubanite (Cub$_1$) changes to isotropic one (Cub$_2$). At about 350°C $M_2$ together with Cub$_2$ yield a homogeneous solid solution with the host chalcopyrite.

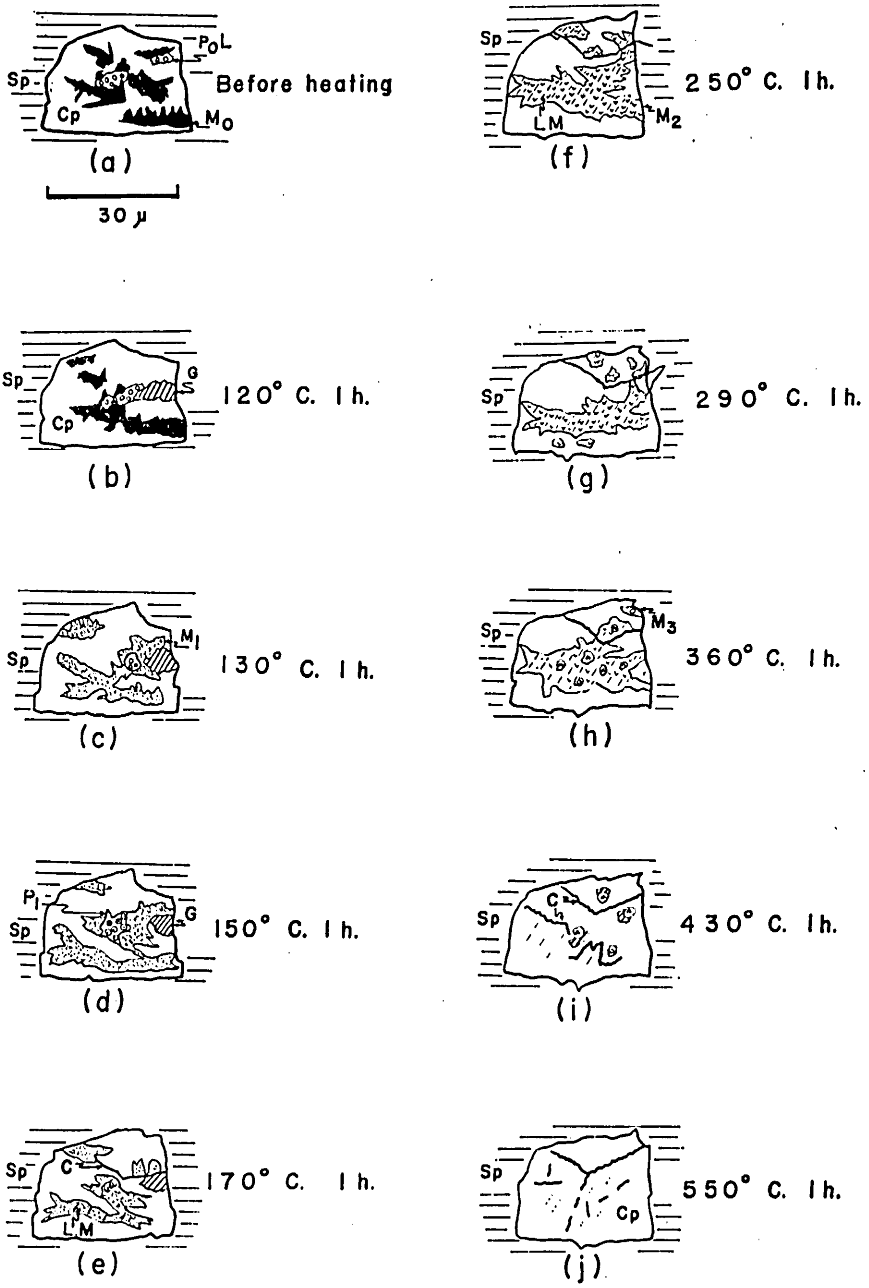

FIG. 2. Transformation of mackinawite from the Kawayama mine with increasing temperature. Unheated mackinawite represented by $M_0$ is included in the chalcopyrite grain in sphalerite. From 130°C its characteristics disappear almost completely and change to those of pinkish cream-colored one with rather strong reflection pleochroism and weak anisotropism ($M_2$). Above 340°C homogeneous solid solution is formed with the host chalcopyrite.

The optical characters of altered mackinawite are not identifiable with those of some known minerals especially at the temperature lower than about 200°C and their changes to those of normal pyrrhotite are rather certainly confirmed but not so much reliable as in the case of Outokumpu type.

2) Mackinaw mackinawite.

Mackinaw mackinawite holds its original optical characters at the temperature higher than in the case of Kawayama mackinawite, loses them at 145°C~165°C, and changes to the weakly anisotropic mineral ($Ma_1$ in Fig. 3), but the characteristics ($Ma_2$ in Fig. 3) resembling to those of the ordinary pyrrhotite are rather surely confirmable to appear at the temperature higher than 200°C.

At the first step, it loses its optical characteristics and alters to pale pinkish brown-colored mineral, more reddish than in the case of cubanite. In many cases, the original features are sustained sporadically in the central part of the grain ($Ma_0$ in Figs. 3-c and d) at the temperature lower than about 170°C, but in a few cases remain even at 180°C.

At the temperature lower than 200°C, the altered mackinawite is reddish brown (more reddish than in the case of cubanite) in color with distinct anisotropism. Above this temperature it shows pinkish brown color with reflectivity and anisotropism similar to those of the ordinary pyrrhotite ($Ma_2$ in Figs. 3-f, g and h). In this temperature range a linear mineral with the characteristics same as those of Kawayama mackinawite appears (LM in Figs. 3-f, g and h). At the temperature above 200°C the altered mackinawite ($Ma_2$) (probably pyrrhotite) preserves its characters up to rather high temperature. At the temperature above about 400°C more than half of the Mackinaw mackinawite together with the isotropic cubanite derived from the ordinary anisotropic one at 230°C~245°C disappear in chalcopyrite.

### 2. *Kômori Type*

1) Kômori mackinawite.

The Kômori mackinawite exhibits the complicated behaviors. In general, its optical characteristics disappear at 180°C~200°C, and change to those of the ordinary pyrrhotite. In many cases, its transformation to pyrrhotite is ascertained by the fact that the former is combined homogeneously with the adjacent latter.

One of the specimens obtained from −380mL. of Raikô No. I adit indicates the special behaviors as are described in details in the following.

Fig. 4 shows one of its change with increasing temperature. At 130°C~140°C its characteristics are lost in most part of the grain but remain as lenses or laths sporadically. This altered mackinawite has a pinkish brown color (rather reddish than that of, but more close to, pyrrhotite than that of the Kawayama type) with very weak anisotropism ($K_1$ in Fig. 4). With increasing temperature its original characters are completely extinguished but at 155°C~180°C nearly recovered sporadically as lenses or laths in the peripheries or sometimes in the central part of

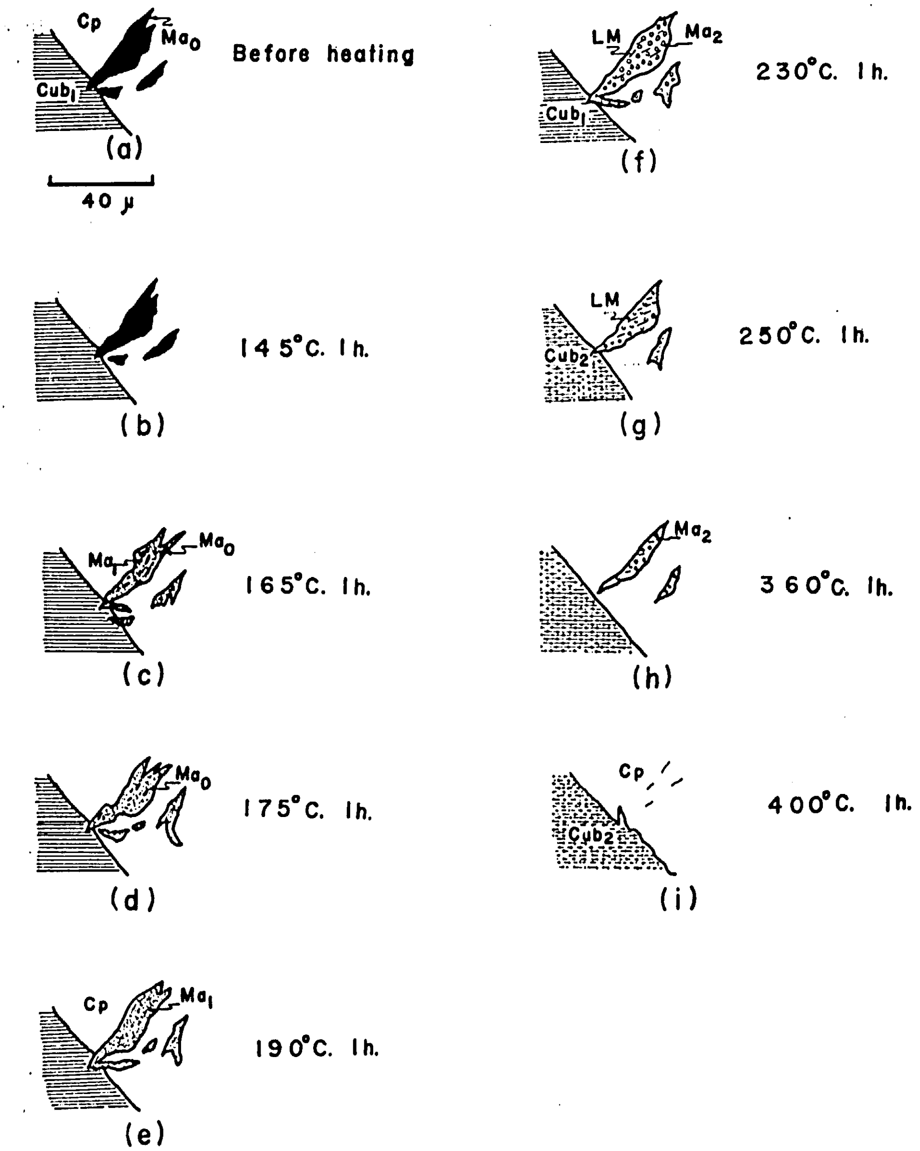

FIG. 3. Transformation of Mackinaw mackinawite with increasing temperature (cf. Plate 58, Fig. 3).

Unheated mackinawite (Ma$_0$) is comprised both in chalcopyrite and in cubanite with a pale pink to pinkish gray color. At 145°C (1h.) it shows no change. From 165°C its characteristics begin to disappear, change to those of reddish brown mineral (Ma$_1$) (more reddish one than Cub$_1$) preserving the original characters sporadically and above 190°C disappear completely, when it bears very similar color to that of the adjacent cubanite (but more reddish). Above about 230°C Ma$_1$ changes to pinkish brown-colored mineral with distinct reflection pleochroism and strong anisotropism similar to those of pyrrhotite (Ma$_2$). The adjacent cubanite become more pale in its color. Above 250°C Ma$_2$ becomes more similar to pyrrhotite in its characteristics, when the adjacent cubanite already extinguishes its anisotropism, and at about 360°C begins to disappear with Cub$_2$ in the host chalcopyrite.

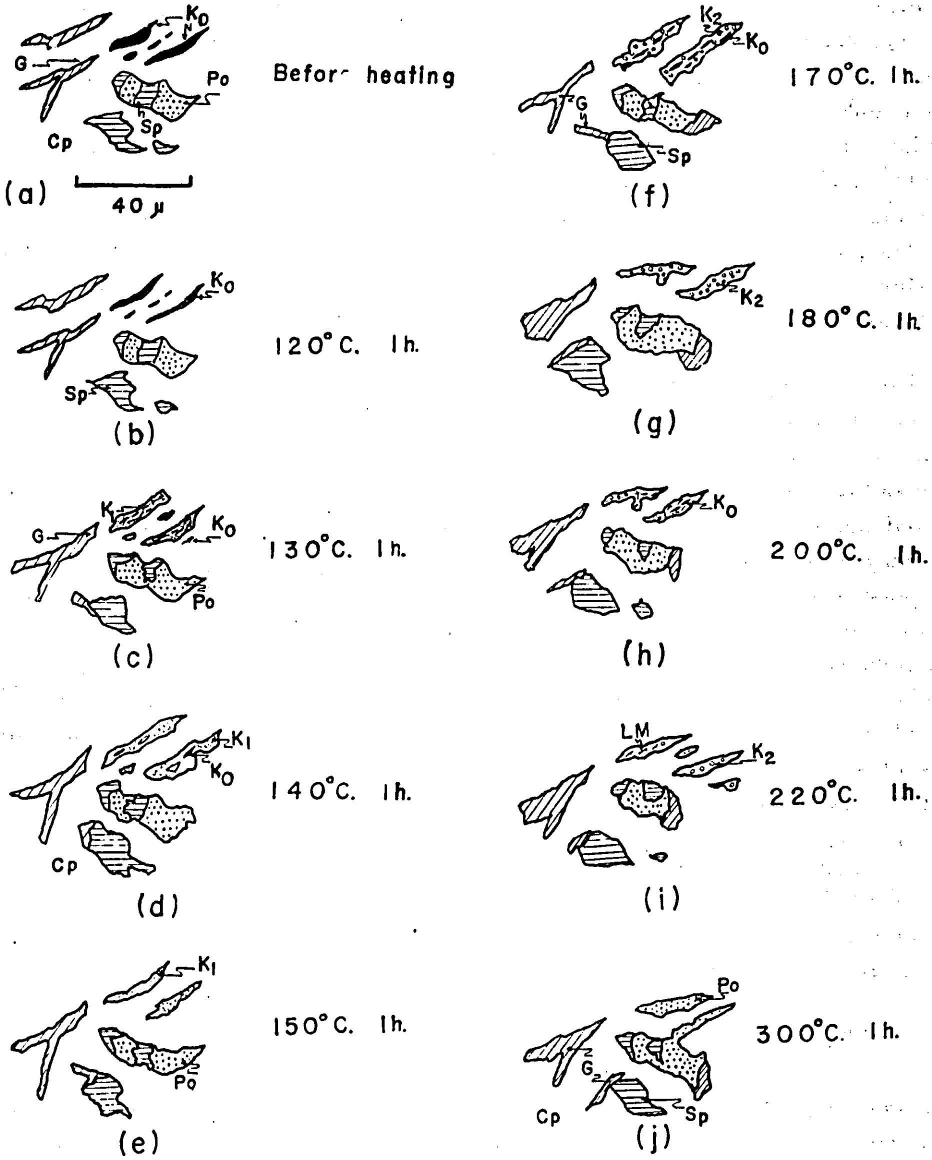

Fig. 4. Transformation of Kômori mackinawite with increasing temperature (cf. Plate 55).

Unheated mackinawite ($K_0$) is associased with chalcopyrite, pyrrhotite, sphalerite and cubanite. From 130°C its characteristics begin to disappear and change to those of pyrrhotite-like colored mineral ($K_1$), preserving the original charactres spordically. $K_1$ is similar to pyrrhotite in its color, but the anisotropism is rather weak. Above 145°C the original characteristics completely disappear and from 170°C reappear sporadically. The remaining part of the grain show the characteristics almost same as those of the ordinary pyrrhotite ($K_2$) in characteristics. Above about 180°C the reappeared phase with the characteristics similar to the original one disappears completely and at 200°C appears again. Above 200°C $K_2$ may safely be identified with pyrrhotite.

the grain. The reflection pleochroism and anisotropism of the remaining part ($K_2$ in Fig. 4) is, in details, very hardly discriminated because of emergence of such a new phase as disappears with increasing temperature completely and appears again at above 200°C.

The original characters disappear completely at the temperature higher than 200°C~230°C. To be noted is that the temperature range of these transformation is variable in each specimen and due to duration of heating.

Subsequent to these processes the alteration product becomes to be identified with pyrrhotite or in some cases combined homogeneously with the adjacent pyrrhotite, as is shown in Fig. 4-j. A linear mineral also appears at above 200°C (LM in Fig. 4).

### 2) Muskox mackinawite.

The Muskox mackinawite is very characteristic as for its paragenesis with true valleriite though in rare cases.

Its optical characters disappear at the temperature higher than 195°C. At first the altered mackinawite has a pale pinkish brown color (rather pale than that of the ordinary pyrrhotite). In general the original characters are kept remained along the peripheries or sometimes in the central part of the grain. The anisotropism, greenish yellow gray to pale greenish yellow, revealed by the new phase indicates some resemblance to that shown by pyrrhotite.

The original characters disappear completely at the temperature higher than 210°C and change to those of pyrrhotite-like mineral with hardness almost same as that of adjacent pentlandite. The optical characters of the altered mackinawite (210°C~240°C) are as follows:

Color under the reflection microscope: pinkish white (more pale pinkish than in the case of pentlandite).
Anisotropism under the crossed nicols: strong; grayish brown to greenish brown.

Above about 250°C the altered mackinawite begins to show almost same properties as that of the ordinary pyrrhotite.

### 3) Tsumo mackinawite.

The specimen begins to lose its original optical characters at rather low temperature between 135°C and 150°C but in part bears them at the temperature lower than 210°C. Through these processes some regularities are recognized: i.e. at 160°C ~180°C the part revealing the original characters is widely spread but at lower and higher temperature becomes to be restricted to the boundaries of the mineral in question or remains as narrow laths or lenses even if in the central part.

The altered mackinawite has a pale pinkish white color very similar to that of the adjacent pyrrhotite with weak anisotropism resembling to that of pyrrhotite.

At the temperature higher than 210°C complete alteration of the specimen to pyrrhotite is discernible in its formation of a homogeneous solid solution with the associated pyrrhotite.

4) Akagane and Ohmine mackinawite.

The specimens from these two localities show some alliance to each other in the transformation behaviors. The specimen from Akagane begins to diminish its original characters at 155°C and that from Ohmine does so at 180°C. Their original characters are in part still preserved to more or less extent up to 210°C or at a little higher temperature and then gradually disappear. As be nearly the case with the Tsumo specimen mentioned above, the altered product bears a pale reddish pink color with weak anisotropism showing some similarity to that of pyrrhotite. At the temperature higher than 200°C, the optical characters of the mineral become to be almost same as those of the ordinary pyrrhotite.

### 3. *Outokumpu Type*

1) Outokumpu mackinawite.

The thermal behaviors of the Outokumpu mackinawite have been preliminarily reported by Kouvo *et al.* (1963). The results obtained through heating of the mineral held in an opened crucible in a muffle furnace were as follows:

1. 40 min. at 200°C., no changes in the iron sulfide (mackinawite).
2. 40 min. at 210°C., the new phase bearing an x-ray pattern of hexagonal pyrrhotite with traces of strongest lines of the iron sulfide.
3. 40 min. at 230°C., no lines of the iron sulfide and only those of pyrrhotite.
4. 40 min. at 250°C., the homogeneous pyrrhotite.
5. 40 min. at 300°C., ditto.
6. 40 min. at 350°C., the product with a faint line at 2.50Å (probably due to some presence of magnetite included).

The specimens used in the present experiments are from a few to some dozen microns in size and hence too minute to be subjected directly to an x-ray diffraction. Optical variation through thermal treatment of the mineral are as follows.

The original characters begin to disappear but still remain in most part ($O_0$ in Fig. 5) at 210°C, diminish gradually at higher temperature, change to those of pyrrhotite-like product ($O_1$ in Fig. 5) determined hardly because of coexistence with the still unaltered part, and then completely disappear at the temperature higher than 250°C as a result of formation of the ordinary pyrrhotite ($O_1$ in Figs. 5-f, g and h).

A mineral found partially at the temperature higher than 250°C along the boundaries between chalcopyrite and the altered mackinawite (pyrrhotite) (R in Fig. 5) has a yellowish brown color with very weak anisotropism changing from yellowish brown gray to grayish green. When etched with saturated KOH it changes its color to brown slowly and in many respects seems quite similar to such a reaction product between chalcopyrite and pyrrhotite as was reported by Sugaki (1955), according to whose suggestion cubanite or chalcopyrrhotite was possibly formed. Considering the present experimental results, its color differs from those of ordinary cubanite and isotropic cubanite. With increasing temperature its reflection color becomes

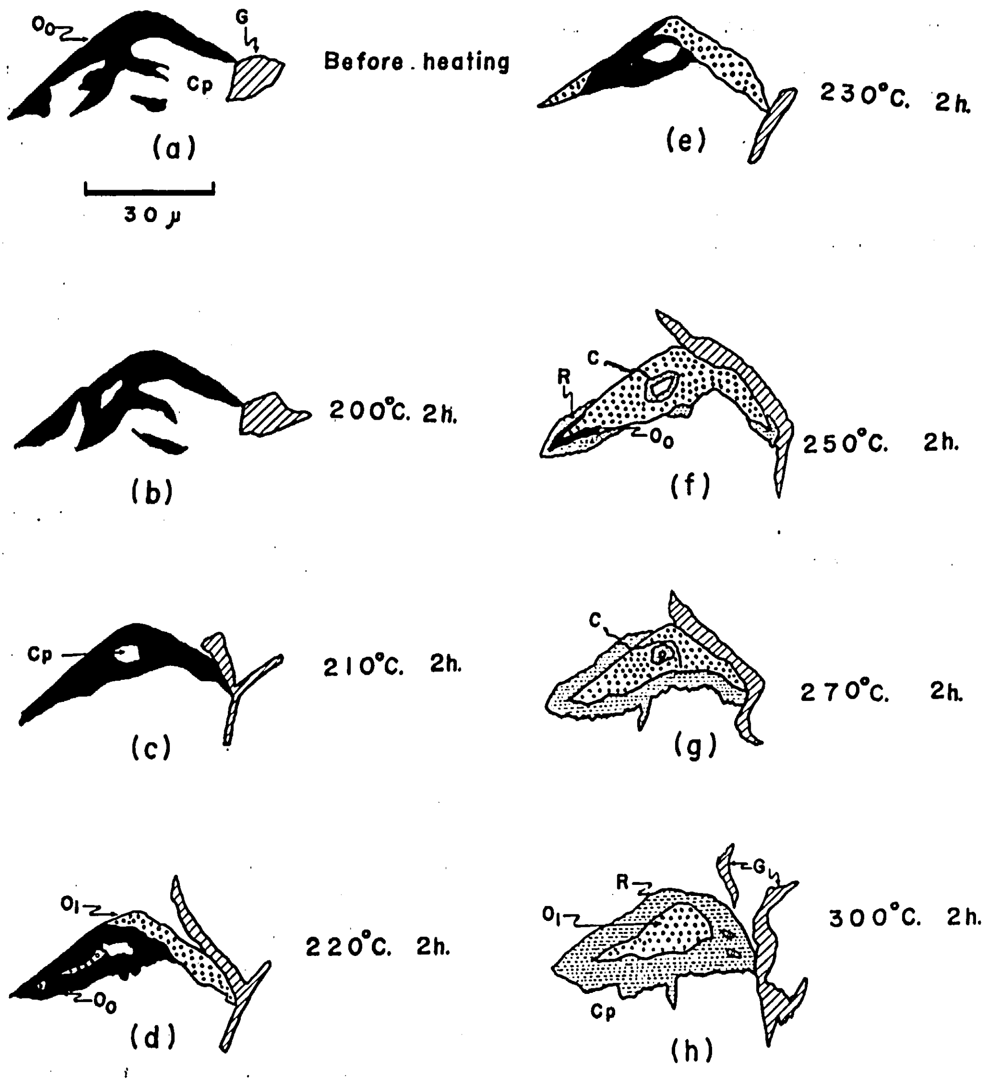

FIG. 5. Transformation of Outokumpu mackinawite with increasing temperature (cf. Plate 56). Unheated mackinawite is embraced in chalcopyrite ($O_0$). At the temperature higher than 210°C its characteristics begin to disappear and change to those of pyrrhntite-like colored mineral with weak anisotropism ($O_1$). Above about 230°C $O_1$ shows the characters almost same as those of the ordinary pyrrhotite, but there still remains the original one. $O_0$ completely disappears above about 255°C, and a yellowish brown-colored mineral (R) is found along the boundaries between $O_1$ (pyrrhotite) and the host chalcopyryte. This reaction product together with $O_1$ are preseved up to about 400°C.

more pale.

After all, transformation of mackinawite to pyrrhotite is performed rather gradually in the wide range of temperature (210°C~250°C).

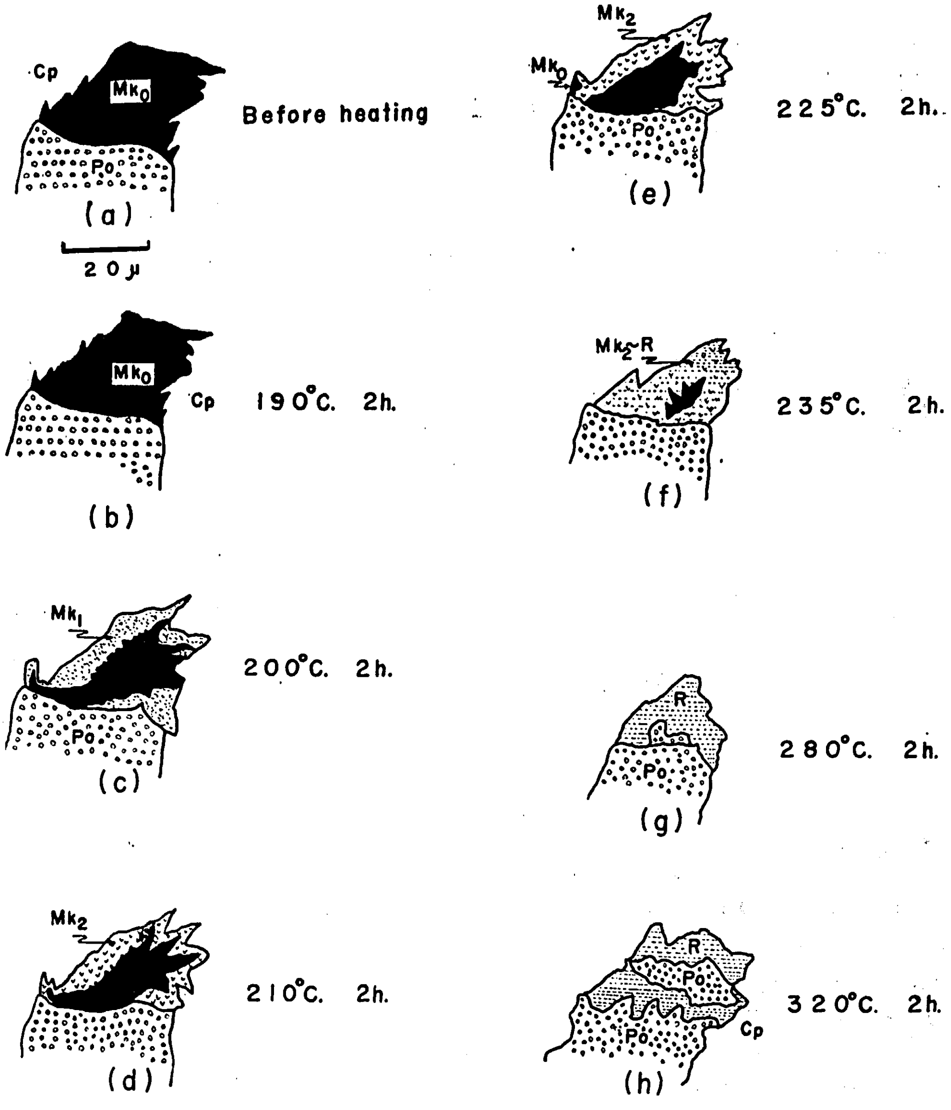

FIG. 6. Transformation of Makimine mackinawite with increasing temperature.

Unheated mackinawite is contained in chalcopyrite (Mk$_0$). At the temperature lower than 190°C there is no essential change in optics. Above 200°C its characteristics begin to disappear from its peripheries and change to those of the new phase with distinct reflection pleochroism and weak anisotropism (Mk$_1$). Above 210°C it is rather satisfactorily confirmed that Mk$_1$ shows the characteristics almost same as those of the ordinary pyrrhotite (Mk$_2$) but there still remain Mk$_0$ in some parts. Above about 240°C yellowish brown-colored mineral (R) appears along the boundaries of Mk$_2$ and its characteristics become rather complicated becuse of presence of Mk$_2$ occurring along the former. The original characteristics still remain at about 250°C. Above about 280°C Mk$_2$ is found combined with the adjacent pyrrhotite showing a homogeneous optical character.

2) Makimine mackinawite.

The optical characters of the specimen begin to disappear from its peripheries at the temperature higher than 200°C, as is shown in Fig. 6-c.

At first, the altered mackinawite ($Mk_1$ in Fig. 6) has a pale pinkish color differing from, and immediately changing to, that of pyrrhotite ($Mk_2$ in Figs. 6-d and e) but preserves the original state in more or less amount up to about 255°C.

The reaction product, yellowish brown in color, found above about 230°C (R in Fig. 6) as well as the altered mackinawite show the complicated characters and coexist with each other in the temperature range between 230°C and 250°C.

At the temperature higher than 250°C the altered mackinawite clearly changes to the normal pyrrhotite, and the reaction product between chalcopyrite and pyrrhotite grows in more amount with increasing temperature (see Fig. 6-g and h). The latter is found in the most part of boundaries between chalcopyrite and pyrrhotite and bears such distinct reflection pleochroism and weak anisotropism as are almost same as in the case of Outokumpu specimens.

It thus follows that the Makimine mackinawite begins to lose its original characters from 200°C and alters completely at a certain temperature lower than 255°C, forming a sort of reaction product with chalcopyrite.

3) Besshi mackinawite.

The original characters begin to disappear at 200°C, but in the adjoining part between the specimen and pyrrhotite the former reveals no change in its optical characters and is traversed by the latter showing the comb-shaped boundaries in the temperature range from 190°C (see Fig. 7-d).

At first, the altered mackinawite ($B_1$ in Fig. 7) is tinted with a pinkish white color with weak anisotropism but immediately changes clearly its color similar to that of the ordinary pyrrhotite. Original characteristics are held invariable at the temperature lower than 250°C. In some cases, an undulatory extinction is observable both in reflection pleochroism and in anisotropism even at the original state at the temperature between 220°C and 235°C.

In some specimens, the reaction product between chalcopyrite and the altered mackinawite or pyrrhotite are recognized when heated at the temperature higher than about 250°C and its characteristics seem under the reflection microscope almost same as those of the preceding specimens.

4) Shimokawa mackinawite.

The original characters begin to disappear at 210°C, but invariably remain in more or less amount up to 250°C, as are almost in the case of Outokumpu mackinawite. The reaction product between the altered mackinawite or ordinary pyrrhotite and chalcopyrite is also found above 250°C.

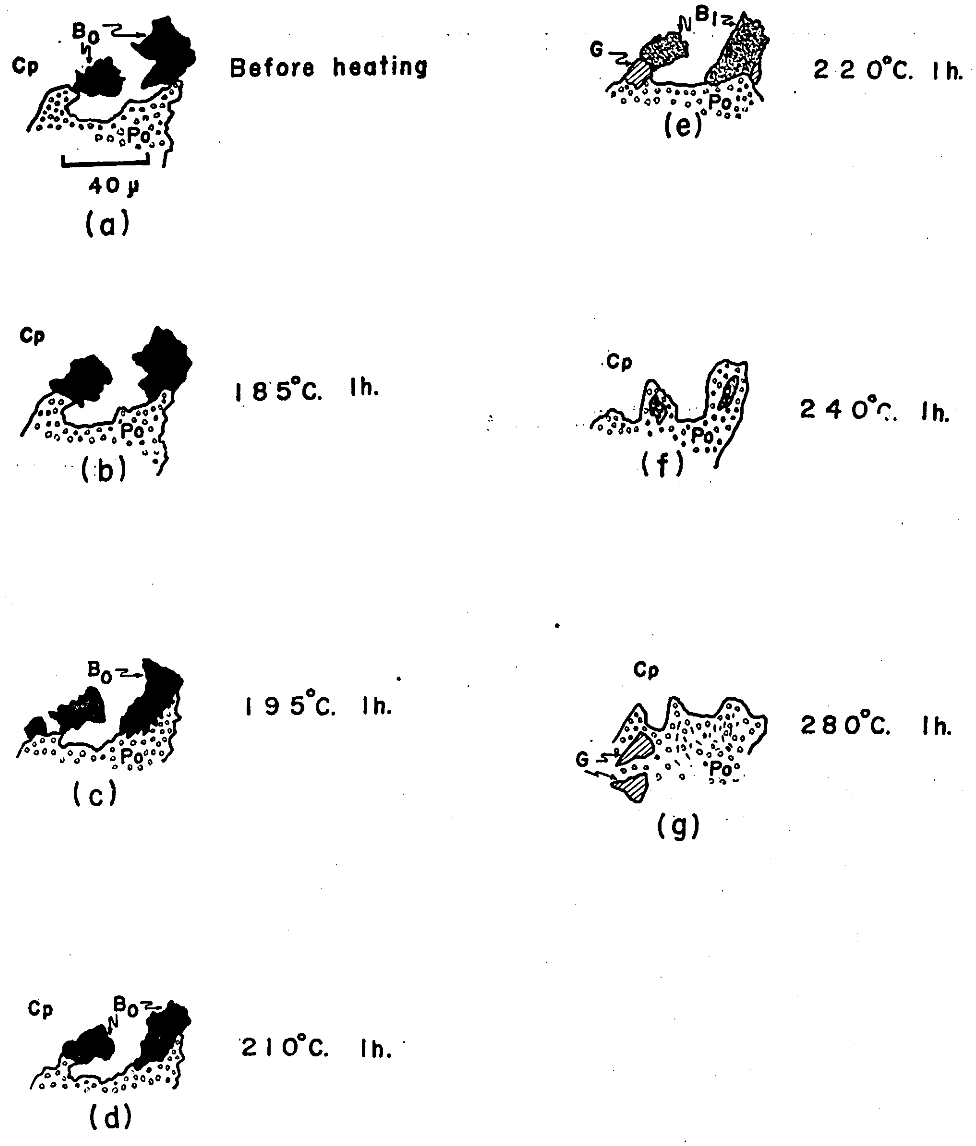

FIG. 7. Transformation of Besshi mackinawite with increasing temperature.

Unheated mackinawite is involved in chalcopyrite associated with pyrrhotite ($B_0$). From about 190°C $B_0$ and pyrrhotite show a comb-shaped boundary. The original characteristics begin to disappear above about 210°C and change to those of pinkish white-colored mineral (more white than that of Cp) ($B_1$). This new phase shows undulatory extinction both in reflection pleochroism and in anisotropism. Above 250°C the altered mackinawite is combined with the adjacent pyrrhotite showing homogeneous characteristics.

## 4. *True Valleriite*

True valleriites from two localities, of which one is from Kaveltorp in Southern Sweden and the other is from Parabra in South Africa, have been preliminarily investigated as are described in the following.

Characteristic differences in physical and optical properties of valleriite from mackinawite in natural state are recognized in two respects: i. e. one is appeared in polishing condition and the other in its color under reflection microscope. It is impossible to polish valleriite to such an extent as shows a semi-matt surface even in small grains, as has already been pointed out by CHAMBERLAIN and DELABIO (1965) in the case of Muskox valleriite. In spite of difficulty in polishing, a distinct difference between valleriite and mackinawite in reflection color is recognizable: that is, the former is clearly reddish or brownish in color compared with the latter revealing yellowish color.

Moreover, thermal behaviors are quite different from each other. The optical characteristics of valleriite in natural state are invariable at the temperature lower than, at least, 500°C far higher than in the case of mackinawite. At the temperature higher than 500°C the original characters begin to vanish and change to those of pale orange yellow colored mineral with distinct anisotropism. This new phase is very close to chalcopyrite in its optical characters and the x-ray powder-diffraction patterns show some identity with those of $\beta$-chalcopyrite (ASTM, 11-515).

## 5. *Summary of the Experimental Results*

(a) Mackinawite and valleriite are quite different from each other in thermal behaviors: that is, the former has a distinct modification at the temperature surely lower than about 250°C and commonly changes to pyrrhotite while the latter yields a chalcopyrite-like phase at the temperature higher than 500°C. Thus the mineral "valleriite" identified earlierly in the literatures in Japan is assuredly mackinawite.

(b) Kawayama mackinawite is used to losing its optical characters at 130°C~150°C though there be remarkable differences even in a single specimen. Identification of the altered mackinawite with some known mineral is rather difficult especially at the temperature lower than 200°C and its resemblance to chalcopyrrhotite in color is however recognizable.

(c) Mackinawite specimens obtained from various types of ore deposits are on the basis of its transformation temperature to be classified into three types: the first is transformable at the lowest temperature (130°C~160°C), the second at the intermediate temperature, and the third at the highest temperature. Of three, transformation of mackinawite to pyrrhotite is clearly discernible only in the third type and slightly in the second type. Nevertheless, there may be some transitional phases among them.

(d) Prior to complete loss of the original characters, mackinawite shows a delicate change especially in reflection pleochroism: with heating the original pleochroism displaying change of pale pinkish gray to pale yellowish pink inclines to the final one revealing variation of pinkish white (similar to in case of arsenopyrite) to pinkish gray.

(e) Reaction products between chalcopyrite and the altered mackinawite or pyrrhotite are recognized at the temperature higher than 250°C in many specimens but restricted to in the case of the third type.

## IV. DISCUSSION

The present writer has already suggested in the previous work (TAKENO, 1965) that difference in transformation temperature of mackinawite obtained from various types of the ore doposits may be attributed mainly to the iron-sulfur ratio held in the respective inner structures. While Dr. G. KULLERUD of Carnegie Institute of Washington and Dr. C. MILTON, one of the discoverer of mackinawite, of U. S. Geological Survey of Washington are of opinion (1964, private communication) that it may be related to the chemical compositions, i. e. the proportion of Ni, Co, and the like, and this view is supported by Dr. A. KATŌ of the National Science Museum, Tokyo (1965, private communication) based on the stability range of a certain solid solution concerning mackinawite. In either cases, the compositional variation is believed to relate intimately to transformation temperature. In the present experiments, however, variation expected in the inner structures has not decisively been determined owing to difficulty in sampling of extremely minute crystals, and the chemical analyses of the mineral concerned by means of electron microprobe analyser remain to have not yet been carried out. A few data given by this means in the previous literatures are shown in Table 1.

TABLE 1. CHEMICAL ANALYSES OF MACKINAWITE (in wt. %)

| | Fe | S | Ni | Co | Formula (4) |
|---|---|---|---|---|---|
| Mckinaw (1) | 63.0 | 34.0 | 1.0~2.0 | — | $(Fe_{0.96}Ni_{0.04})S$ |
| Muskox (2-a) | 55±5 | — | 2.3±1 | 1.5±1 | |
| Kômori (2-b) | 52.1 | — | 5.6 | 1.0~2.0 | (Fe, Ni) S (5) |
| Outokumpu (3) | 50.4<br>52.4 | 31.8<br>32.6 | 7.4<br>7.6 | 0.38<br>0.34 | $(Fe_{0.91}Ni_{0.13}Co_{0.007})S$ |

(1) EVANS *et al.* (1964)
(2-a) CHAMBERLAIN and DELABIO (1965)
(2-b) IMAI and FUJIKI (1963)
(3) KOUVO *et al.* (1963)
(4) Taking S as 1.00
(5) Proposed as a general formula by IMAI and FUJIKI.

Fortunately, the data of (1), (2) and (3) correspond to those of the present specimens respectively. Mackinaw mackinawite (the Kawayama type) showing a low transformation temperature contains iron in maximum and nickel in minimum, Outokumpu mackinawite yields the relation reverse to the former in their contents, and Muskox and Kômori mackinawites are of the intermediate. In addition, this order just corresponds to transformation temperature determined in the present experiments: i. e. that of the Kawayama type is 130°C~160°C, that of the Kômori type is intermediate and that of the Outokumpu type is higher than 200°C. Nevertheless, it still remains to be solved whether these temperatures may be ascribed to the contents of iron (iron-sulfur ratio) and/or nickel (and cobalt) or not. The ratio of iron to sulfur or iron deficiency in the inner structure of iron sulfide with the stoichiometric composition is preferably considered to play an important rôle compared with the contents of minor elements such as nickel and cobalt, as was already suggested in the preceding work (1965).

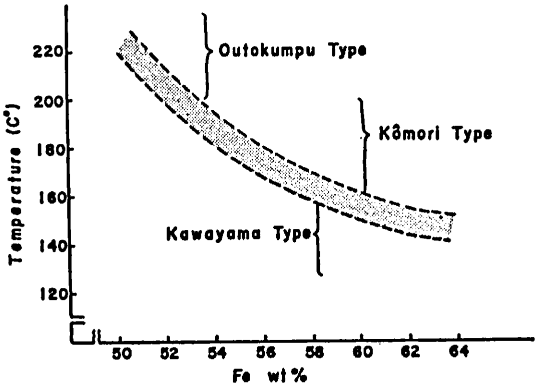

FIG. 8. A tentative curve showing the relation between transformation temperatures and Fe content of mackinawite.

On the other hand, BORCHERT (1934) gave the phase diagram between chalcopyrite and pyrrhotite, and reported that unmixing of pyrrhotite and chalcopyrrhotite from solid solution begins at 550°C and reaches the end at 255°C. Chalcopyrrhotite is unstable at the temperature lower than 255°C while cubanite and valleriite become stable on further cooling. In these processes, pyrrhotite may be exsolved from chalcopyrrhotite with excess of iron at the temperature lower than 250°C. This was proved in the assemblage of pyrrhotite with mackinawite in a crystal of chalcopyrite (TAKENO, 1965, Fig. 5).

Recently, YUND and KULLERUD (1960) reported the equilibrium relation in the system Cu-Fe-S at 700°C. Their data roughly coincide with the results obtained by MERWIN and LOMBARD (1937). To be solved is a detailed phase diagram for the combination of pyrrhotite (approximately FeS), cubanite ($CuFe_2S_3$) and chalcopyrite ($CuFeS_2$) together with mackinawite. In both studies mentioned above, chalcopyrrhotite proposed by BORCHERT was not ascertained at all, but the altered mackinawite, especially in the case of the Kawayama mackinawite, shows a good identity with chalcopyrrhotite in its optical characters. In the system of Cu-Fe-S, mackinawite may probably be formed in an intimate relation to chalcopyrrhotite associated with free ZnS and $CuFeS_2$.

Instead of the reaction product formed seemingly by solid diffusion between chalcopyrite and pyrrhotite (or altered mackinawite) as rim-shaped bodies when heated at about 250°C for 2 hours in the present experiment, Sugaki (1955) obtained the similar mineral with yellowish brown color when heated at above 330°C for 5 hours and furthermore considered possibility of solid reaction between chalcopyrite and pyrrhotite on the basis of the assumed formulae:

$$\begin{array}{llll} & \mathrm{CuFeS_2} & +\ \mathrm{FeS} & = \mathrm{CuFe_2S_3} \\ & \text{chalcopyrite} & \quad \text{pyrrhotite} & \quad \text{cubanite} \\ \text{or} & \mathrm{CuFeS_2} & +\ 3\mathrm{FeS} & = \mathrm{CuFe_4S_5} \\ & \text{chalcopyrite} & \quad \text{pyrrhotite} & \quad \text{chalcopyrrhotite} \end{array}$$

In relation to this, cubanite of natural state may become unstable at high temperature. The yellowish brown mineral obtained in the present experiment indicates some differences from ordinary cubanite and isotropic cubanite (above 235°C) in its optical properties. On the other hand, it seems more problematical whether chalcopyrrhotite may exist or not, as was suggested by Merwin and Lombard (1937) and Yund and Kullerud (1960).

It is reasonably concluded that in the system Cu-Fe-S and especially in the relation between $\mathrm{CuFeS_2}$-$\mathrm{CuFe_2S_3}$-FeS together with chalcopyrrhotite, a mysterious mineral, there still remain many problems to be inspected and in addition the true valleriite may be excluded from the system. Moreover, the accurate determination of the chemical composition of mackinawite from various localities will give a significant clue to solving the problems concerning its own genesis.

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# EXPLANATION OF PLATE LIV

Transformation of Kawayama mackinawite with increasing temperature.
All figures are taken under oil immersion lens (×2500).

FIG. 1. Before heating.
FIG. 2. 128°C 10h.
FIG. 3. 190°C 10h.
FIG. 4. 235°C 10h.
FIG. 5. 270°C 10h.
FIG. 6. 300°C 10h.
FIG. 7. 395°C 10h.

Each figure corresponds respectively to FIG. 1, a, b, e, f, g, h and j described already in the main report.

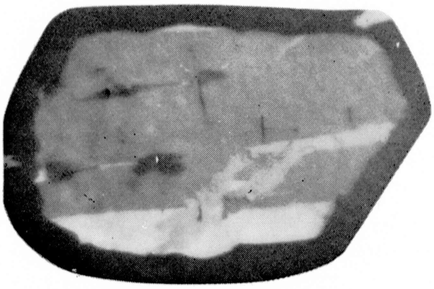


FIG. 1.

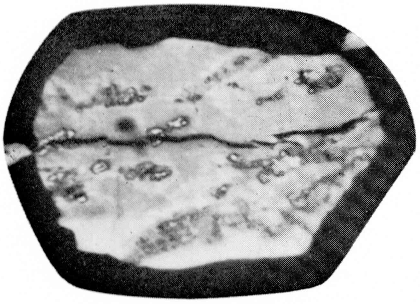
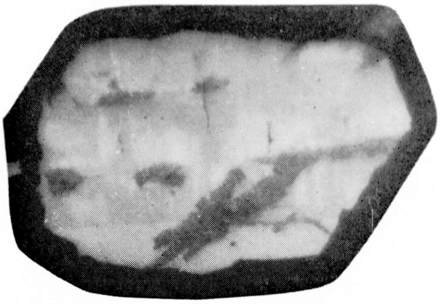


FIG. 5.



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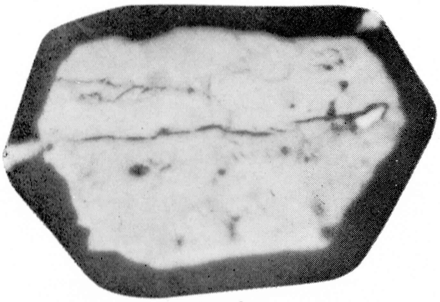

FIG. 2.

FIG. 3.

FIG. 7.

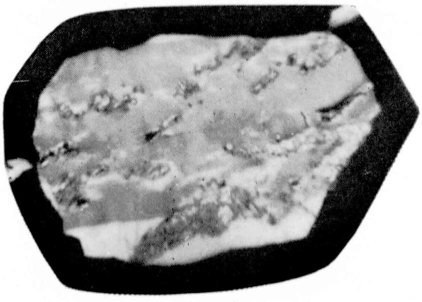

FIG. 4.

## EXPLANATION OF PLATE LV

Transformation of Kômori mackinawite with increasing temperature. All figures are taken under oil immersion lens (×2000).

FIG. 1. Before heating.
FIG. 2. 130°C 1h.
FIG. 3. 170°C 1h.
FIG. 4. 180°C 1h.
FIG. 5. 200°C 1h.
Fig. 6. 220°C 1h.

Each figure corresponds respectively to FIG. 4, a, c, f, g, h and i described already in the main report.

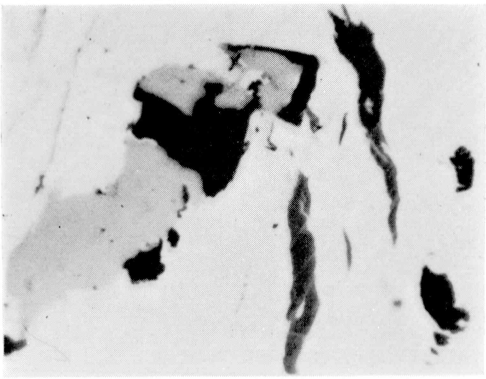

FIG. 1.

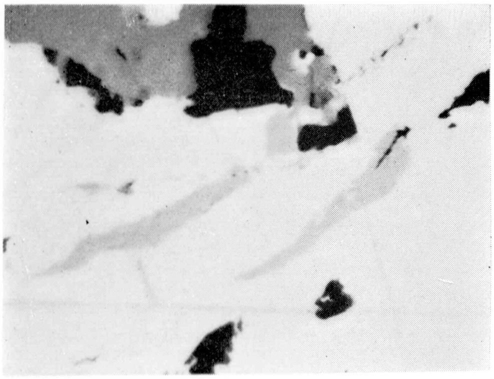

FIG. 4.

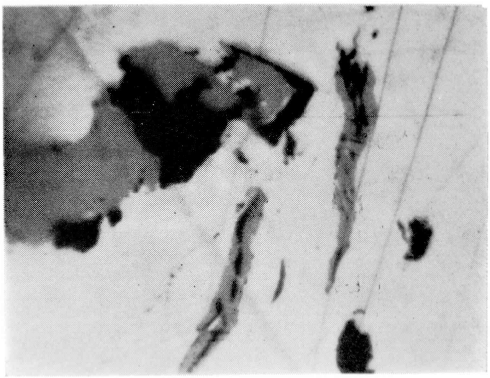

FIG. 2.

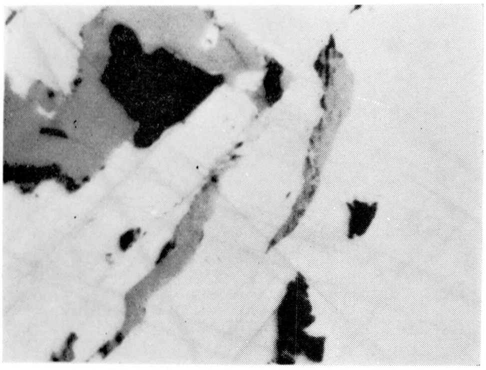

FIG. 5.

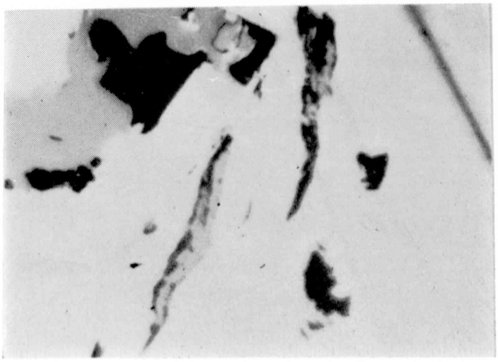

FIG. 3.

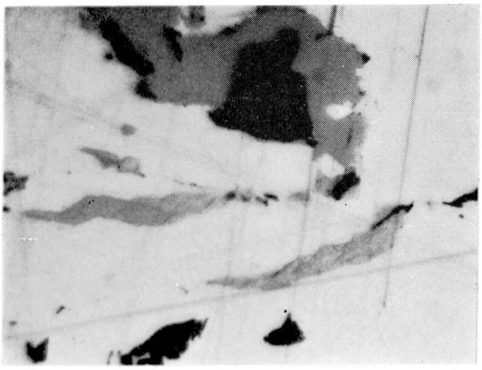

FIG. 6.

## EXPLANATION OF PLATE LVI

Transformation of Outokumpu mackinawite with increasing temperature.
All figures are taken under oil immersion lens (×2000).

FIG. 1. Before heating.
FIG. 2. 200°C 2h.
FIG. 3. 230°C 2h.
FIG. 4. 250°C 2h.
FIG. 5. 270°C 2h.
FIG. 6. 300°C 2h.

Each figure corresponds respectively to FIG. 5, a, b, e, f, g and h described already in the main report.

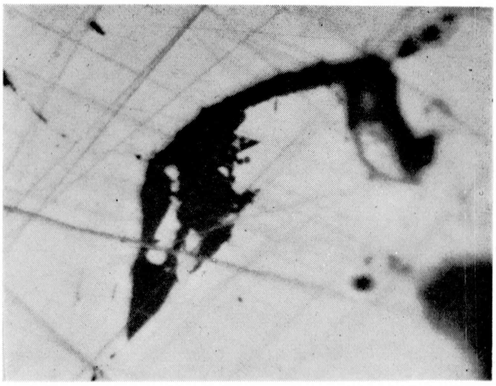

FIG. 1.

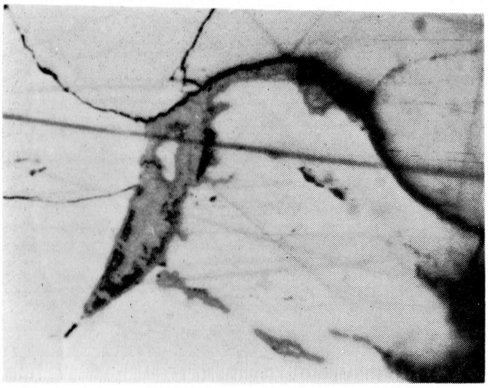

Fig. 4.

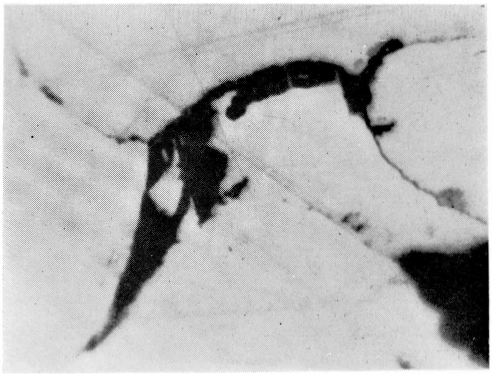

FIG. 2.

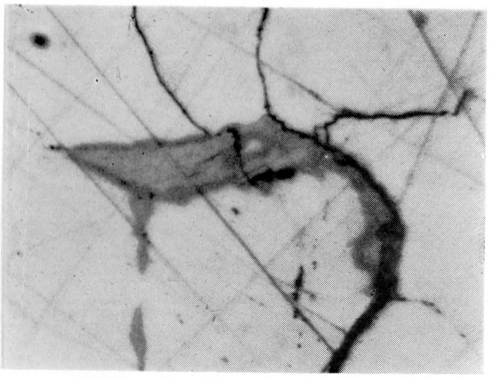

FIG. 5.

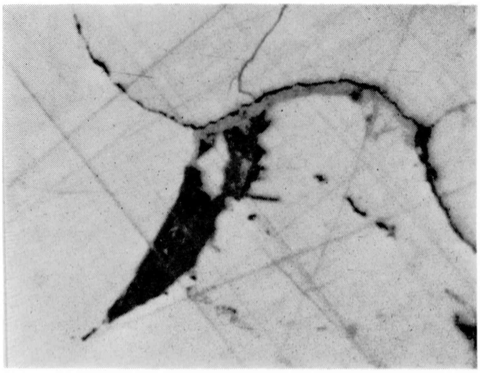

Fig. 3.

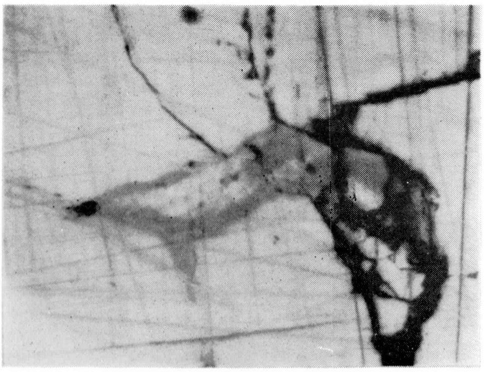

FIG. 6.

## Explanation of Plate LVII

Fig. 1-a. Muskox mackinawite (Before heating).
Fig. 1-b. 〃 (230°C 2h.)
(×250)
Fig. 2-a. Shimokawa mackinawite (Before heating).
Fig. 2-b. 〃 (225°C 2h.).
(under oil immersion lens. ×2500)
Fig. 3-a. Mackinaw mackinawite (Before heating).
Fig. 3-b. 〃 (360°C 1h.) (×1500).
Cp: chalcopyrite, $\mathrm{Cub}_1$: ordinary cubanite, $\mathrm{Cub}_2$: isotropic cubanite, M: mackinawite, M′: altered mackinawite, Mg: magnetite, Po: pyrrhotite, Pt: pentlandite, G: grangue.

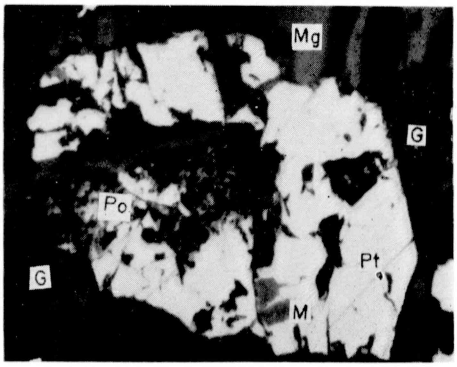

FIG. 1-a.

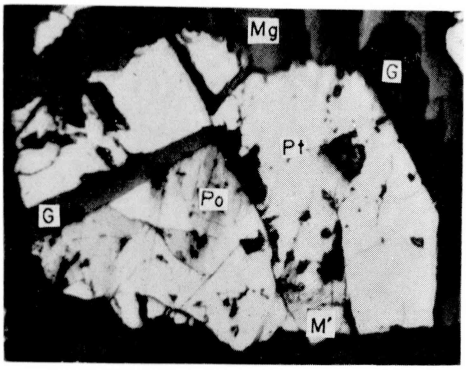

FIG. 1-b.

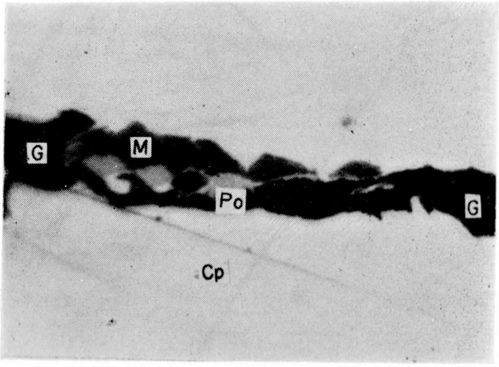

FIG. 2-a.

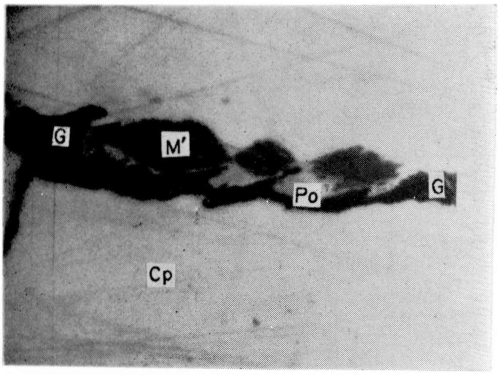

FIG. 2-b.

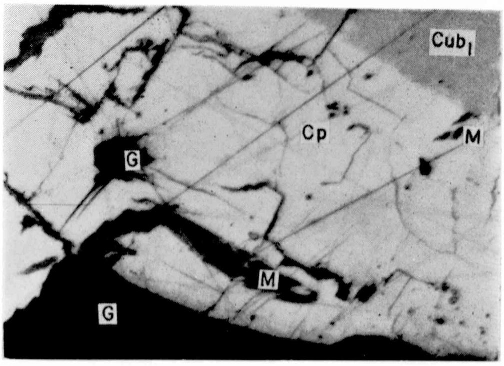

FIG. 3-a.

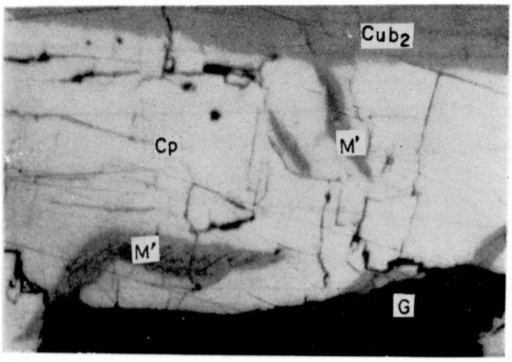

FIG. 3-b.