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Compositional Variations in Natural Mackinawite and the Results of Heating Experiments

By

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with 3 Tables, 16 Text-figures and 2 Plates

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Abstract: The compositions of natural mackinawites, $(Fe,Ni,Co,Cu)_{1+x}S$, from 14 different localities are presented. Heating experiments were performed and the temperature of observed breakdown to pyrrhotite does not appear to be a function of cation proportions. Indeed, the "breakdown" is not isochemical and involves the addition of sulfur from the surrounding minerals and therefore, is not representative of the upper thermal stability of mackinawite. In most natural occurrences, mackinawite occurs with chalcopyrite. Based on phase chemistry, this would appear to be a metastable assemblage. However, recent developments, particularly in the Cu–Fe–S system, suggest that at low temperatures several reactions may occur which could thereby permit the stable existence of this assemblage.

Contents

I. Introduction

Minerals within the Fe–S system are among the most common ore minerals occurring in nature. Although this system has received considerable attention in recent years, there remain many unsolved problems. One of these concerns the chemical composition and thermal stability of mackinawite.

The mineral mackinawite was proposed by Evans *et al.* (1962, 1964) for natural occurrences of a tetragonal compound near FeS in composition. A phase possessing the properties of this mineral had previously been described by Milton and Milton (1958), Kouvo and Vuorelainen (1959) and Kouvo *et al.* (1963).

Most mackinawite specimens found in ore deposits contain some Ni and Co; however, Berner (1962) has synthesized this phase in aqueous Fe–S solutions, thus demonstrating that Ni and Co are not essential components of the structure. Mackinawite has not been synthesized in the pure Fe–S system — i.e. without water.

Since the original description of mackinawite by Evans *et al.* (1962, 1964), it has been found in a variety of geological environments. BERNER (1964) stated that "the substance described as hydrotroilite ... is believed to be, at least in part, poorly crystallized tetragonal FeS" (BERNER used the term tetragonal FeS and mackinawite as synonyms). Thus, mackinawite is probably a common constituent of the amorphous, fine-grained, black iron sulfide mud of many Tertiary and Recent sediments. Mackinawite also commonly occurs in nickel-rich environments (CLARK, 1967), in contact metasomatic, pneumatolytic and hydrothermal deposits, in bedded cupriferous iron sulfide deposits within metamorphic rocks and in certain ultrabasic rocks (CHAMBERLAIN and DELABIO, 1965; RAMDOHR, 1967). It has even been found in association with troilite in several lunar rocks (TAYLOR *et al.*, 1971).

The chemical composition of mackinawite was originally given as $(Fe_{0.96}Ni_{0.04})S$ (EVANS *et al.*, 1964). KOUVO and VUORELAINEN (1963) obtained $M_{1.046}S$ to $M_{1.056}S$ where M represents Fe, Ni, and Co. Chemical analyses of mackinawite usually shows a slight excess of metal over a 1: 1 metal/sulfur ratio, and CLARK (1966) and TAKENO and CLARK (1967) represented the composition of the mineral as $(Fe,Ni,Co)_{1+x}S$, where x is 0.04 to 0.07. Recently, TAYLOR and FINGER (1971) performed a structure refinement on mackinawite and concluded that there is *a slight deficiency of sulfur in the structure* and *not metal excess* so that the formula should be written MS_{1-x} to be both compositionally and structurally correct. However, because of the entrechment of $M_{1+x}S$ in the literature, we shall continue to use this chemical formula.

The thermal stability of mackinawite is not known. The optical properties change to those of pyrrhotite when heated in vacuo at temperatures from 130° to 250°C. The relationship between the composition of mackinawite and the temperature of this phase change was examined previously (TAKENO, 1965; CLARK, 1967). It was concluded that the upper stability temperature of mackinawite is broadly related to the nickel and cobalt contents and increases markedly with increasing substitution of nickel and cobalt for iron. TAKENO (1965) noted that this transformation occurred at considerably different temperatures even in samples from within a single hand specimen. Actually, because all mackinawites in the specimens examined were fine-grained (5–100 μm), the heating experiments were conducted on "mackinawite-bearing assemblages" in which mackinawite was not the dominant phase. It is reasonable to expect that such a "breakdown" temperature depends not only on the chemical composition of the mackinawite, but also, and perhaps to a more important degree, on the sulfur fugacity controlled by the dominant phases of the assemblage. This is particularly true if the association represents a disequilibrium assemblage (TAKENO and TAYLOR, 1971).

Mackinawite should breakdown to Fe, Ni, Co native metal+FeS (troilite); however, this reaction has never been observed. The intergrown phases controlling higher sulfur fugacities provide the necessary sulfur for the sulfidation of mackinawite. It is suspected that many of the "breakdown" experiments reported in the literature do not represent the true thermal breakdown of mackinawite. The temperatures reported are simply those temperatures at which the reaction kinetics are sufficient for observation of the sulfidation of mackinawite (TAKENO and TAYLOR, 1971).

The association of mackinawite and hexagonal pyrrhotite appears to represent an obvious disequilibrium assemblage. Even within the Fe–Co–Ni–S system, the presence of tie lines between troilite and pentlandite should prevent the stable occurrence of this assemblage. The same statement can be made for mackinawite+chalcopyrite, the most common assemblage in which mackinawite occurs. It would be extremely unlikely that this mineral always in disequilibrium assemblages; instead, it is suggested that our knowledge of the phase equilibria in the various systems involved is lacking, particularly at temperatures below 200°C, the temperature range of most geologic importance for this problem.

In this paper, the compositions of natural mackinawites from 14 different localities are presented as obtained through use of an electron microprobe. The paragenesis of the minerals in each association is discussed. Although some of the assemblages containing the mackinawite may represent disequilibrium, heating experiments were performed in an attempt to obtain some insight into the stability relations of mackinawite.

Acknowledgements: The authors wish to express their grateful appreciation to Professor Y. UMEGAKI, the Dean of the Faculty of Science, Hiroshima University, for his continuing guidance. The Toyo Industrial Company is also acknowledged for kindly permitting use of their electron microprobe. A portion of this study was supported by N.S.F. grant GA 31988 to Prof. L. A. TAYLOR.

II. EXPERIMENTAL METHODS

The mackinawite-bearing specimens used for the experiments were approximately 1.0×0.5×0.5 cm. These were finely polished and examined with a reflected-light petrographic microscope. The specimens then were subjected to electron microprobe analyses. The carbon coating, necessary for microprobe examination, was removed, and the sample was placed in a sealed, evacuated silica-glass tube. The sample was annealed for a given time, the tube quenched and opened, and the sample was then reexamined both microscopically and with the microprobe.

The detailed occurrences of the specimes used in the present experiments are given in Table 1.

Electron Microprobe Analyses: The apparatus used for the chemical analyses was an ARL–EMX I electron microprobe manufactured by Shimazu Manufacturing Company, Ltd.

The size of the included mackinawite in most specimens is small in width (i.e.<10 μm). It was considered of utmost importance to determine the best spot within each grain for the quantitative analyses. Therefore, each specimen was examined by linear scanning and a profile was thereby made in an attempt to ascertain the optimum site.

Microprobe Conditions : accelerating voltage 20KV; probe current 0.052 μA; spot diameter 2 μm; crystals used LiF and ADP; standards: synthetic FeS (36.47 wt%S) as S standard and pure metals of Fe, Ni, Co, Cu and Zn for cation contents.

The quantitative analyses were performed by repeated counting of the characteristic X-ray emission of a spot for 50 second intervals. In this manner, the average counts per second due to each element were determined. These raw data were reduced for standard corrections using the programs of PHILBERT (1962) and POOLE and THOMAS (1961).

TABLE 1. LIST OF THE SPECIMENS USED IN THE EXPERIMENTS

No.	Locality of Sample	Type of ore deposit	References
1	−240 meter level of the lower ore deposit of the Kawayama mine, Yamaguchi Pref., Japan	Hydrothermal fissure-filling and partly contact metasomatic ore deposit	TAKENO, 1965 a and b
2	70 meter level of the Mozumi ore deposit of the Kamioka mine, Gifu Pref., Japan	Pyrometasomatic and hydrothermal ore deposit	OKUNO, 1964
3	The Mackinaw mine, Snohomish County, Wash., U. S. A.	Fissure-filling in ultra basic rocks	MILTON and MILTON, 1958
4	N33058 from the drilling cores, Muskox, Canada	Layered ultramafic pluton in the Precambrian	CHAMBERLAIN and DELABIO, 1965
5	−25 meter level of the Tsumo mine, Shimane Pref., Japan	Contact metasomatic ore deposit	SHIMAZAKI, 1968 a and b
6	−350 meter level of Raiko No. 1 adit of the Komori mine,Kyoto, Pref., Japan	Fissure-filling in gabbroic rocks	FUJIKI, 1963
7	The Saezaki mine, Hiroshima Pref., Japan	Pyrometasomatic ore deposit	SOEDA, 1960
8	No. 2 adit of the Ohmine mine, Iwate Pref., Japan	Contact metasomatic ore deposit	TAKEUCHI *et al.*, 1953
9	The 1st sublevel of the Six ore deposit of the Akagane mine, Iwate Pref., Japan	ditto	TAKEUCHI and NAMBU, 1954
10	The Yaguki mine, Fukushima Pref., Japan	ditto	SHIMAZAKI, 1969
11	Senju adit of the Makimine mine, Miyazaki Pref., Japan	Bedded cupriferous iron sulfide ore deposit in the metamorphic rocks	TATSUMI, 1953
12	22 level of Honzan adit of the Besshi mine, Ehime Pref., Japan	ditto	MIYAHISA, 1958
13	The Shimokawa mine, Hokkaido, Japan	ditto	TAKENO, 1965 b
14	Stope U-27 of the Outokumpu mine, Finland	ditto	KOUVO *et al.*, 1963

III. RESULTS

The chemical compositions of mackinawites from 14 different localities were determined and are shown in Table 2. The results of the heating experiments are presented in Table 3. X-ray profiles for various elements were performed across the coexisting phases associated with the mackinawite. This gives a knowledge of the compositional variations between minerals but more importantly, it allows for the determination of a spot suitable for quantitative analyses. The linear profiles of the mineral assemblages from each locality are shown in figures 1–16. The elemental weight percentages are uncorrected values and are thus semiquantitative. The sulfur values shown have been multiplied by a factor of 2 in order to use the open portion of the graph.

TABLE 2. CHEMICAL ANALYSES OF MACKINAWITE (in wt.%)

No.	Specimen	Fe	Cu	Ni	Co	S	Total	$\frac{\text{Fe, Cu, Ni, Co}}{\text{S}}$	$\frac{\text{Fe, Ni, Co}}{\text{S}}$	$\frac{\text{Ni, Co}}{\text{Fe}}$
1	Kawayama	56.9	6.8	—	—	34.2	97.9	1.076	0.977	0.000
3	Mackinaw	59.1	1.9	2.8	0.1	36.1	100.0	1.011	0.984	0.047
4	Muskox I	60.8	—	2.0	4.9	34.5	102.2	1.119	1.119	0.103
4	〃 II	58.7	—	2.0	4.7	35.4	100.8	1.055	1.055	0.109
5	Tsumo I	57.0	0.1	6.9	0.2	35.0	99.2	1.060	1.046	0.119
5	〃 II	57.4	—	7.7	0.2	32.4	97.7	1.149	1.149	0.130
6	Kômori	55.9	3.2	4.2	1.9	35.7	100.9	1.039	0.994	0.104
7	Saezaki	55.4	6.2	3.6	2.6	36.4	104.2	1.053	0.967	0.106
8	Ohmine	53.1	5.1	3.9	4.7	37.2	104.0	1.014	0.936	0.155
9	Akagane	58.2	5.7	4.0	0.9	34.3	103.1	1.134	1.050	0.080
10	Yaguki	55.0	1.0	2.5	6.0	35.0	99.5	1.049	1.035	0.147
11	Makimine	53.5	2.2	—	12.7	36.0	104.4	1.076	1.045	0.224
12	Besshi	56.2	3.7	—	8.5	34.3	102.7	1.128	1.020	0.143
13	Shimokawa	53.2	8.8	0.3	8.6	33.2	104.1	1.200	1.066	0.159
14	Outokumpu	44.1	2.3	11.8	11.4	35.3	104.9	1.095	1.074	0.499

TABLE 3. "BREAKDOWN TEMPERATURE" OF MACKINAWITE

Specimen	Temp. (°C)	$\frac{\text{Ni, Co}}{\text{Fe}}$	Paragenesis
Tsumo I	120±5	0.119	in Cp with Pt, Py, Po
〃 II	〃	0.130	〃
Kawayama	125±5	0.000	in emulsoidal Cp dot in Sp with Po, Sp, Ga
Mackinaw	127±5	0.047	in Cp with Cb
Akagane	135±5	0.080	in Cp with skeletal Sp, Po
Muskox I	137±5	0.103	in Pt with Mt
〃 II	〃	0.109	〃
Ohmine	136±5	0.155	in Cp with skeletal Sp, Po
Saezaki	136±5	0.106	in Cp in Cb
Yaguki	140±5	0.147	in Cp with Po, Sp
Outokumpu	150±7	0.499	in Cp with Po, Sp, Pt
Besshi	153±6	0.143	in Cp with Py, Po
Kômori	140±10	0.104	in Cb and Cp with Po, Sp
Shimokawa	145±10	0.159	in Cp with Py, Sp, Po
Makimine	153±7	0.224	in Cp with Po, Py

Cp: chalcopyrite, Pt: pentlandite, Py: pyrite, Po: pyrrhotite Sp: sphalerite, Ga: galena, Cb: cubanite

In the next sections of this paper, the specimens from each locality are discussed as to assemblage, mackinawite composition, and results of heating experiments.

A. KAWAYAMA AND KAMIOKA MINES

The mackinawite present in samples from these mines occurs within chalcopyrite blebs contained in a sphalerite host. The Ni and Co contents are characteristically low and these mackinawites are similar in composition to those collected from other localities such as Tsumo and Nakase. It is believed that the 6.8 wt percent Cu found in this mackinawite is real; the metal/sulfur ratio is typical for a mackinawite formula, $M_{1.076}$ S. The traverse from right to left in figure 1 shows a gradual increase in sulfur and iron contents from sphalerite towards mackinawite; this may be due to the fact that the mackinawite here is not "infinitely thick" to the electron beam. That is, other mineral(s) occur just below the polished surface.

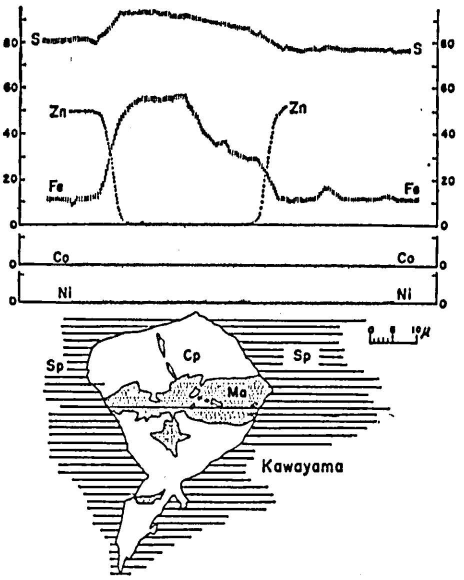


FIG. 1. Textural relationships of mackinawite from the Kawayama mine. The position of the microprobe traverse for the various elements is depicted across the specimen. The elemental weight percentages are uncorrected and the sulfur values shown have been multiplied by a factor of 2 in order to use the open portion of the figure.
Ma: mackinawite, Cp: chalcopyrite, Sp: sphalerite, These abbreviations are used in all figures.

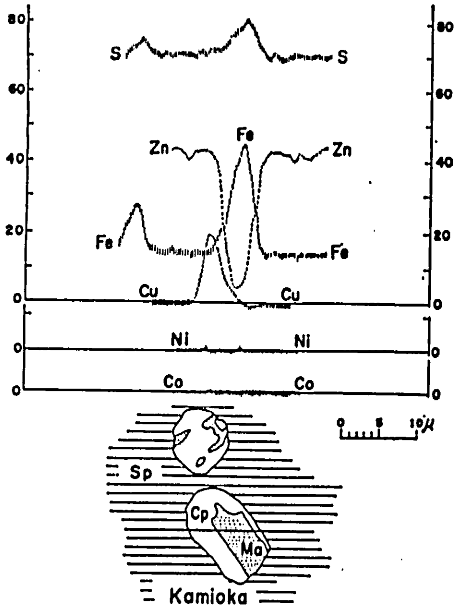


FIG. 2. Textural relationships of mackinawite from the Kamioka mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

The compositions of the associated pyrrhotite and sphalerite were determined and found to contain 46.63 wt percent Fe, 53.37 wt percent S and 89 mol percent ZnS, 11 mol percent FeS, respectively. The pyrrhotite is of the monoclinic variety.

B. Mackinaw mine

This region in the state of Washington is the type locality for mackinawite. The Ni content of the mineral examined is 2.8 wt percent and the grains are homogeneous (Figure 3). The apparent variation in Cu content of the mackinawite, as seen in figure 3, is probably due to chalcopyrite just below the polished surface.

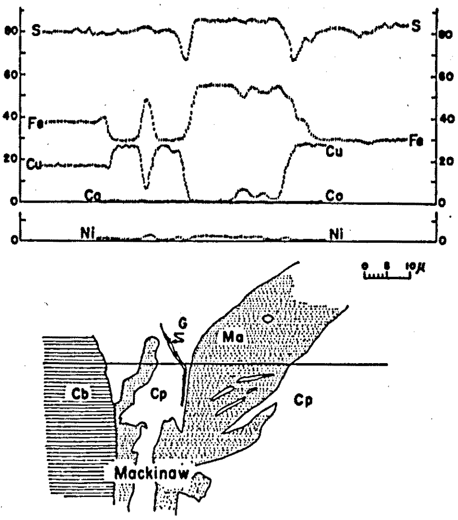


Fig. 3. Textural relationships of mackinawite from the Mackinaw mine. G: gangue minerals, Cb: cubanite.

The sulfur content appears to abruptly decrease at the boundaries between mackinawite and chalcopyrite. This may be an edge effect caused by the relief developed as a result of differences in polishing hardness; however, this behavior was not observed in other sections. The "upper stability" of mackinawite in this assemblage was determined to be 127° ± 5°C.

C. Muskox intrusion

The mackinawite occurrence from this locality has been described by Chamberlain and Delabio (1965). A portion of a drill core collected by Dr. J.A. Chamberlain of the Geological Survey of Canada was examined and mackinawite was found in association with magnetite and pentlandite (figure 5–a). The contents of Ni and Co in the associated pentlandite are 26.7 and 6.7 wt. percent, respectively. The breakdown temperature is higher than for the specimens previously discussed (confer table 2). This relation was considered by Takeno *et al.* (1970) as indicative of a hypothesis that in creased contents of Ni+Co stabilized mackinawite to higher temperatures.

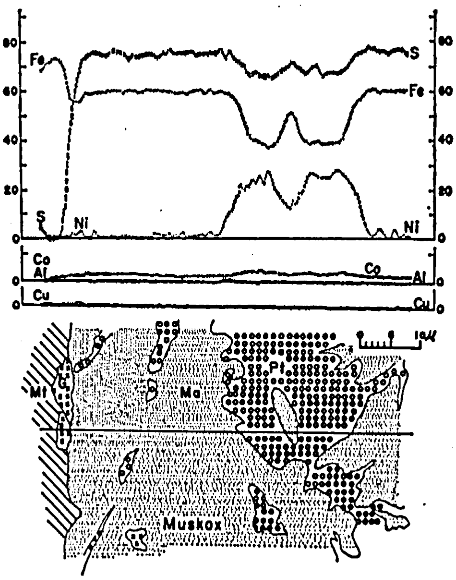


FIG. 4-a. Textural relationships of mackinawite from the Muskox intrusion. The position of the microprobe traverse is depicted across the specimen. Pt: pentlandite, Mt: magnetite.

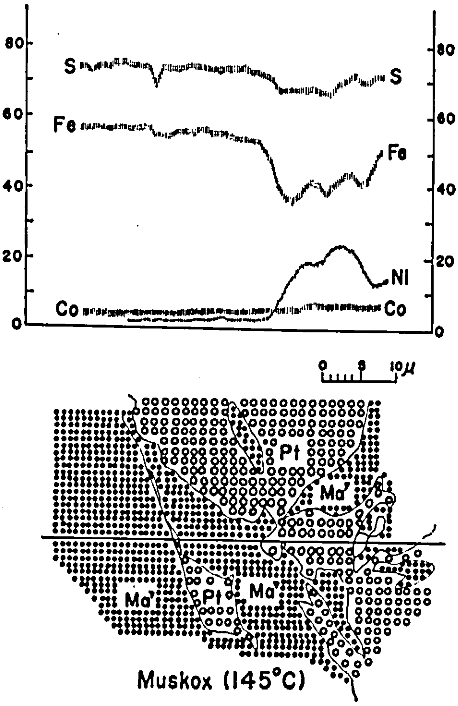


FIG. 4-b. Textural relationships of pyrrhotite (Ma′) derived from mackinawite as a result of annealing the specimen shown in FIG. 4-a at 145°C for 4 hours.

After annealing at 145°C for 4 hours, the mackinawite has been completely converted to pyrrhotite (see, figure 5-b). As seen by comparison afthe Fe tracings in figures 5-a and 5-b, there appears to be a decrease in the iron content after the annealing process. Therefore, the "transformation" does not appear to have been isochemical.

D. TSUMO MINE

The mackinawite from this locality occurs in an assemblage with chalcopyrite and pentlandite (29.0 wt percent Ni; 2.3 wt percent Co). Its chemical composition is unusual in that the Ni content is high (~7.3 wt percent) whereas the Co content is low (0.1 ~0.2 wt percent). The breakdown temperature is also very low at 120°C (Table 3). The altered mackinawite is optically similar to pyrrhotite, and with reference to figures 5-a and 5-b, it can be seen that there is an apparent slight decrease in iron content due to the annealing process.

E. KÔMORI MINE

The specimen obtained from this mine displays a complicated paragenesis which was previously reported by FUJIKI (1963). The mackinawite occurs as lamellae and blades within chalcopyrite in association with cubanite, sphalerite, pyrrhotite and

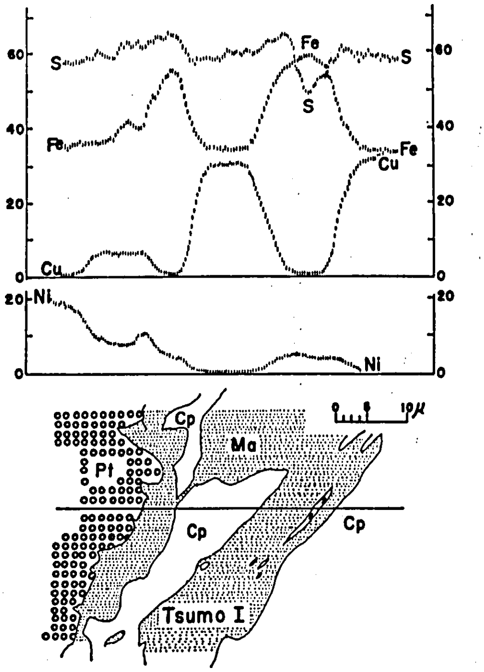


FIG. 5-a. Textural relationships of mackinawite from the Tsumo mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

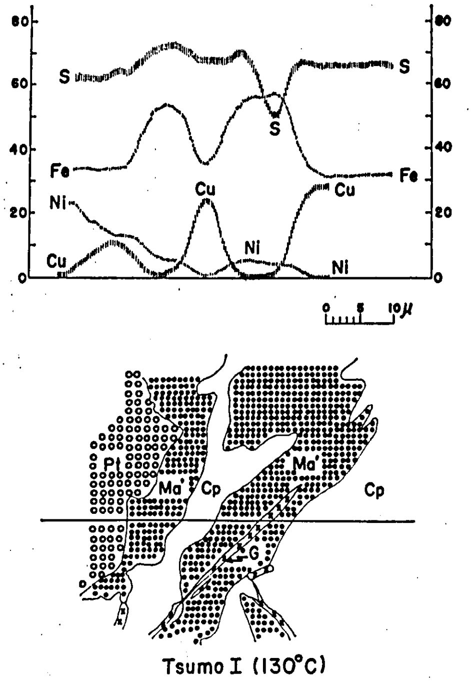


FIG. 5-b Textural relationships of mackinawite altered to pyrrhotite (Ma′) by annealing the specimen shown in Fig. 5-a at 130°C for 4 hours.

pentlandite. Although the ratios of metal/sulfur, Ni+Co/Fe and Ni+Co+Cu/Fe are relatively low (table 2), the breakdown temperature is not low (140°C, table 3). The pyrrhotite (Ma′ in figure 7–b) formed as a result of the annealing, has a lesser amount of iron compared to the original mackinawite. However, even at 240°C, there does not appear to be extensive diffusion of the various components.

F. SAEZAKI, OHMINE, AKAGANE AND YAGUKI MINES

The mackinawite from the first three mines occurs as laths and blades in chalcopyrite associated with cubanite and some pyrrhotite and pentlandite. The Yaguki mackinawite is present in an assemblage which consists of pyrrhotite with some chalcopyrite (figure 11). Because of the minute size of the mackinawite grains, it was difficult to perform accurate chemical analyses; therefore, some of the Cu reported is undoubtedly due to excitation of adjacent or underlying chalcopyrite.

G. MAKIMINE MINE

Mackinawite from this locality is characterized by a paucity of Ni and the highest Co contents (12.7 wt. percent) found during this study (table 2). This phase occurs in

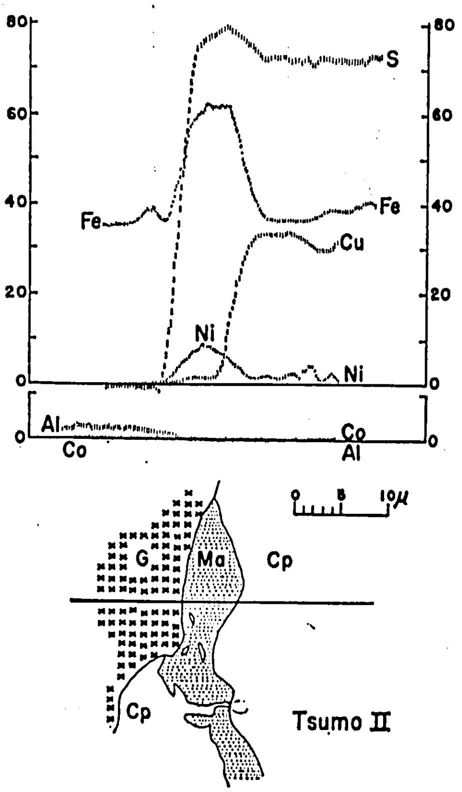


Fig. 6. Textural relationships of mackinawite from the Tsumo mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

association with pyrrhotite, sphalerite and pentlandite. The pyrrhotite at the contact with mackinawite is stoichiometric FeS whereas only 50 μm away, the pyrrhotite only contains 47.8 atomic percent metals.

After annealing the specimen at 320°C, a new phase X (figure 12–b) was observed in the mackinawite which has been altered to pyrrhotite. It is pinkish white in color and is nearly as anisotropic as the enclosing pyrrhotite. Diffusion of certain elements has occurred. The different degrees of diffusion probably reflect the kinetics for the elements within each phase.

H. Besshi and Shimokawa mines

The specimens collected from these mines are similar to the other samples described above in that chalcopyrite is the dominant phase. The pyrrhotite immediately adjacent to the mackinawite contains approximately 49.7 atomic percent metals. The sphalerites from the Shimokawa mine contains 11 to 19 mol percent FeS. The mackinawite

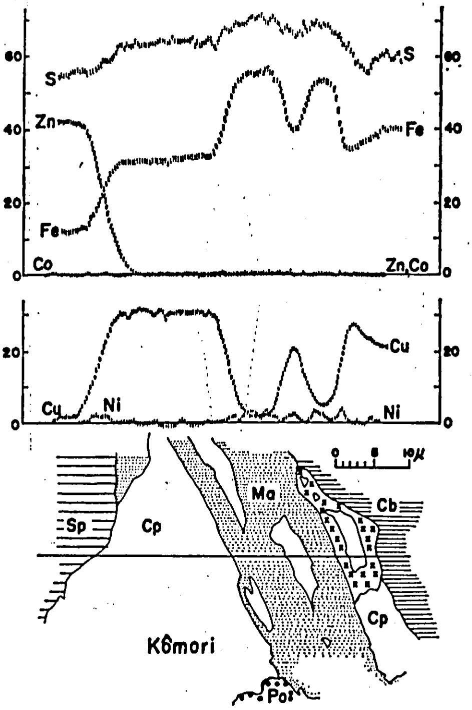


Fig. 7-a. Textural relationships of mackinawite from the Kômori mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

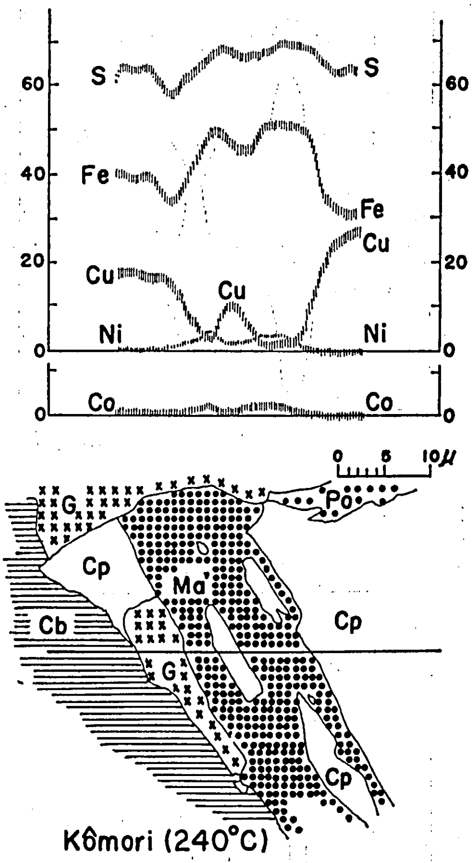


Fig. 7-b. Textural relationships of pyrrhotite (Ma′) derived from mackinawite by annealing the specimen shown in Fig. 7-a at 240°C for 4 hours.

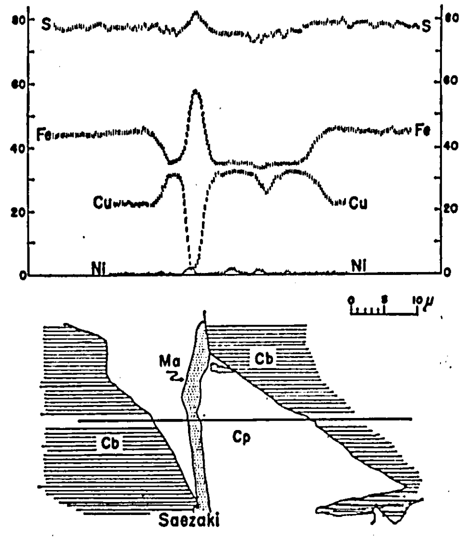


Fig. 8. Textural relationships of mackinawite from the Saezaki mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

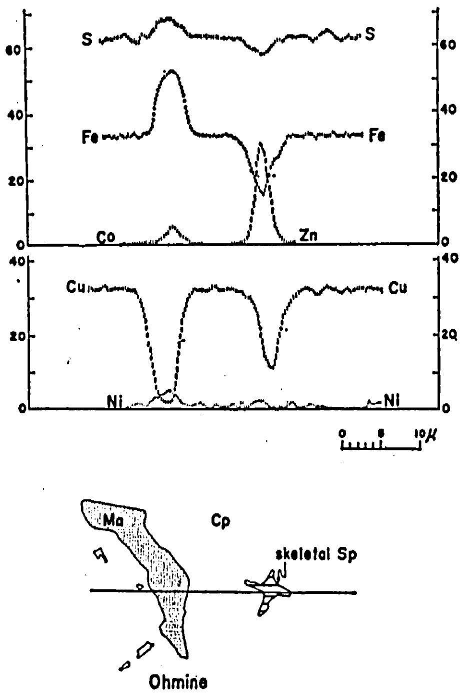


FIG. 9.

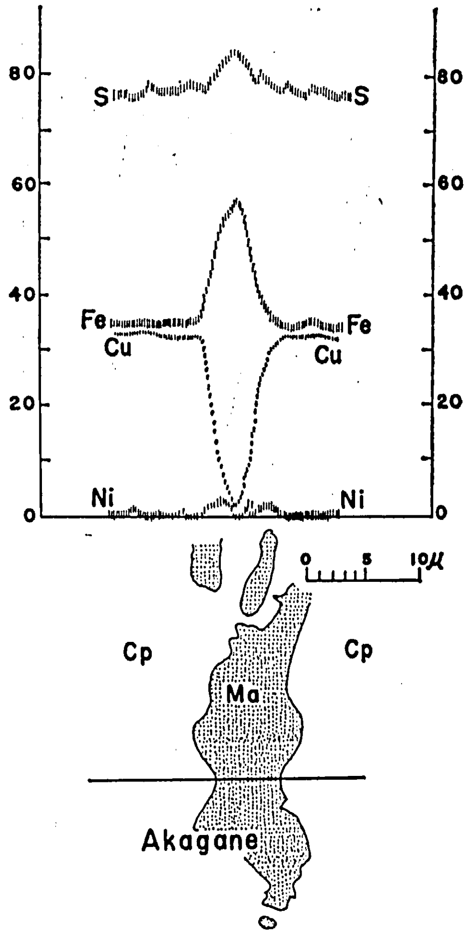


FIG. 10.

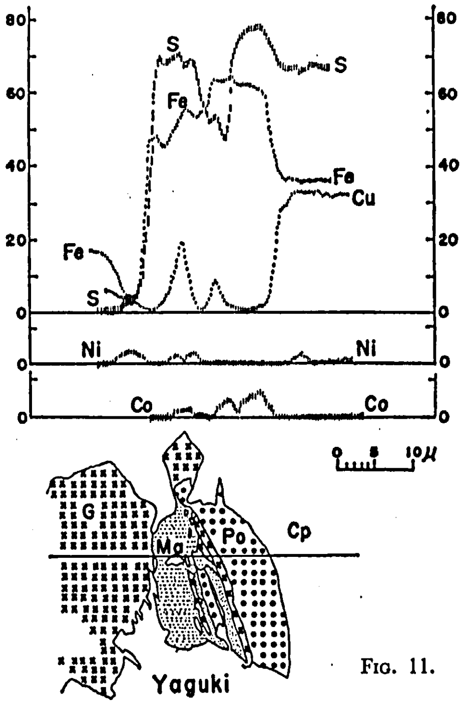


FIG. 11.

FIG. 9. Textural relationships of mackinawite from the Ohmine mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

FIG. 10. Textural relationships of mackinawite from the Akagane mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

FIG. 11. Textural relationships of mackinawite from the Yaguki mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

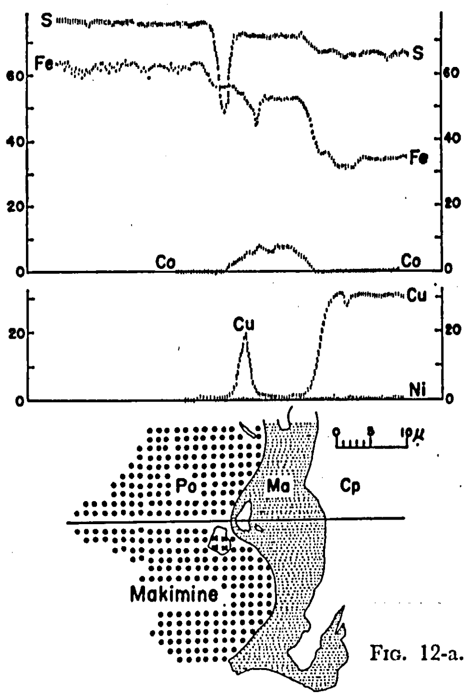


FIG. 12-a.

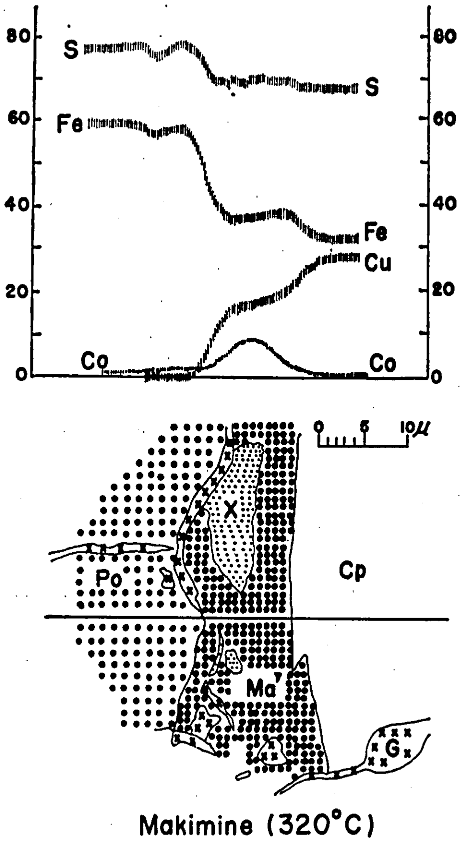


FIG. 12-b.

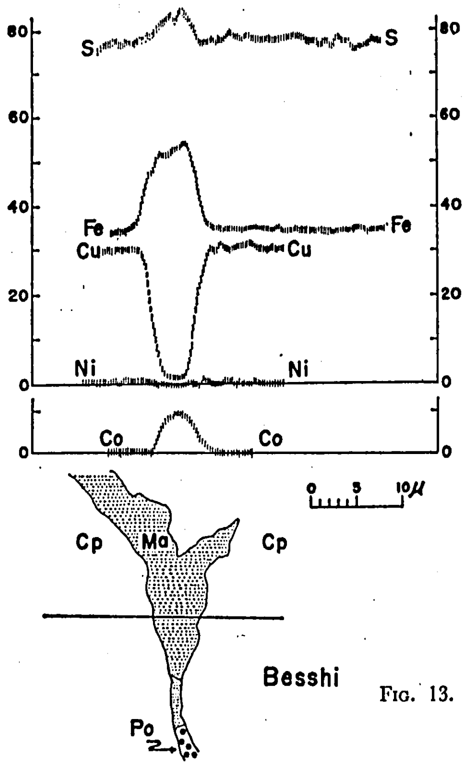


FIG. 13.

FIG. 12-a. Textural relationships of mackinawite from the Makimine mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

FIG. 12-b. Textural relationships of pyrrhotite (Ma′) derived from mackinawite as a result of annealing the specimen shown in FIG. 12-a at 320°C for 4 hours. The phase X is pinkish white in color and distinctly anisotropic, this latter property similar to that of pyrrhotite.

FIG. 13. Textural relationships of mackinawite from the Besshi mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

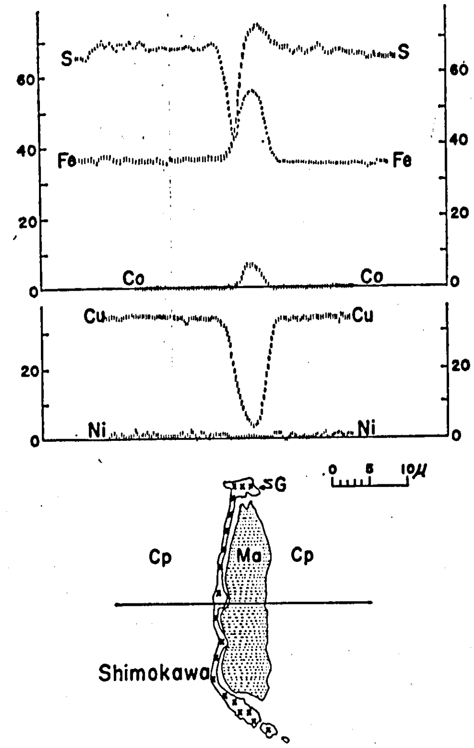


FIG. 14. Textural relationships of mackinawite from the Shimokawa mine. The position of the microprobe traverse for the various elements is depicted across the specimen.

from Besshi is similar to that from Makimine in that it contains high Co (8.5 wt percent) and undetectable Ni (0.02 wt percent).

I. OUTOKUMPU MINE

This occurrence of mackinawite has been discussed in detail by KOUVO *et al.* (1963). The assemblage here includes major chalcopyrite with pyrrhotite, sphalerite and pentlandite. These mackinawite grains contain the lowest amount of Fe (44 wt percent) and the highest amounts of Ni and Co (11.8 and 11.4 wt percent, respectively) of the mackinawites examined during this study.

IV. CONCLUSIONS

The present study has provided much additional data with which to interpret the compositional and stability limits of mackinawite. It is obvious from the analytical data that mackinawite always contains metal in excess of sulfur — i.e. a $(Fe,Ni,Co,Cu)_{1+x}S$ chemical formula. The substitution of Ni,Co etc. for Fe can be appreciable such as in the Outokumpu specimens. However, even though mackinawite composition plots

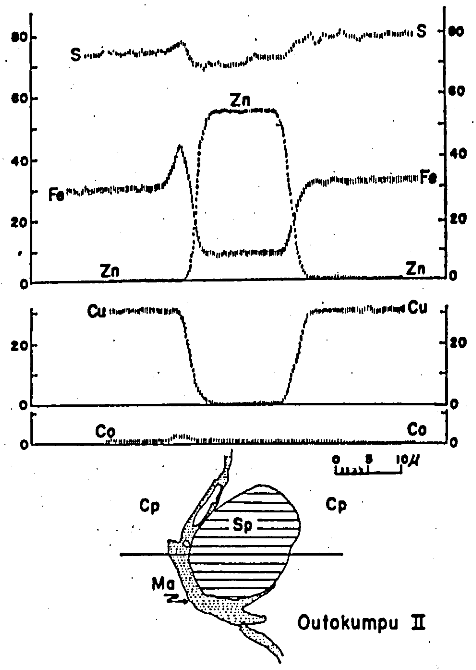
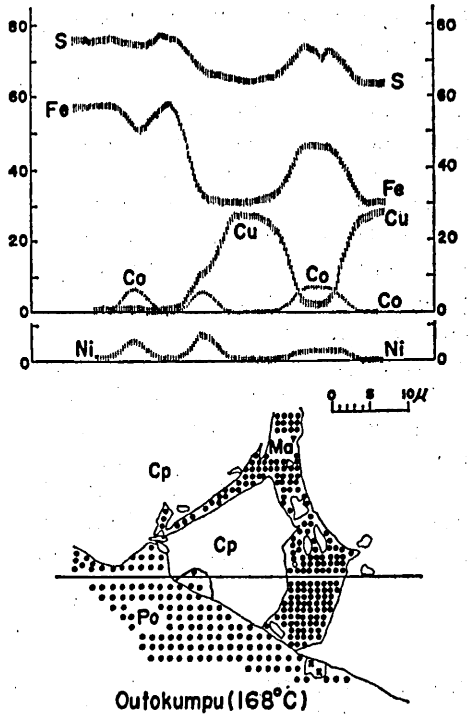


FIG. 15. Textural relationships of mackinawite from the Outokumpu mine. The position of the microprobe traverse for the various elements is depicted across the specimen.



F G. 16. Textural relationships of pyrrhotite (Ma') derived from mackinawite as a result of annealing at 168°C for 4 hours (confer Table II, FIG. 8-a and FIG. 8-b).

between FeS and native metal, it has never been observed to breakdown to this assemblage during heating experiments.

TAKENO *et al.* (1970) reported that mackinawite initially breaks down to pyrrhotite with ~47.4 atomic percent Fe and this pyrrhotite changes to troilite with longer annealing times or at higher temperatures under iron-rich conditions. This is highly unlikely since this would necessitate an initial gain of sulfur followed by a loss to become more metal rich. As observed during the present study, mackinawite does convert to pyrrhotite of a more sulfur-rich composition, and therefore, the breakdown is not isochemical. This also explains why the ideal reaction has never been reversed.

It would also appear that the idea that increased contents Ni+Co stabilized mackinawite to higher temperatures is not valid at least for the specimens examined by the heating experiments described. As discussed by TAKENO and TAYLOR (1971), the temperatures at which "breakdown" is observed may represent only the temperatures at which the kinetics of the "sulfidation" of mackinawite are rapid enough to occur in the annealing time (~4hours). In such cases, it is the availability of sulfur in the vapor, which is a function of the associated minerals, which is most important. It is reasonable to expect that the higher the sulfur fugacity, the lower the temperature will be at which the phase change is observable. There is a need for long-term experiments at lower temperatures with pure starting material. Such experiments are currently in progress in our laboratory.

In almost all natural occurrences, mackinawite is in an assemblage with chalcopyrite. Based on our present knowledge of the Cu–Fe–S or Cu–Fe–Ni–S systems, it would appear that these are not equilibrium assemblages. Tielines between Cu and FeS would necessitate this. However, how much do we really know about phase equilibria in these systems below 200°C. For example, until recently chalcopyrite and cubanite were the only yellow-colored phases in the central portion of the Cu–Fe–S system. Cabri and Hall (1972) have shown that there are at least 3 new minerals, all similar to chalcopyrite, within a few percent of $CuFeS_2$ composition. In fact, haycockite ($Cu_4Fe_5S_8$) is optically identical to chalcopyrite. It is highly probable that much of what has been called chalcopyrite, even during the present study, is indeed this new mineral.

The stable coexistence of chalcopyrite or haycockite and mackinawitew ould necessitate that several invariant reactions would have to occur between 200°C and room temperature. However, the assemblages are trying to tell us something about this. It will take considerable detailed microprobe work, supplemented by phase equilibria studies, before we understand fully the reactions of the mackinawite assemblages. This present study has moved us an additional step closer to much an understanding.

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Explanation of Plate VI

Fig. 1. Mackinawite from the Kawayama mine occurring within chalcopyrite bleb in a sphalerite.
Fig. 2. Mackinawite from the Mackinaw mine associated with chalcopyrite and cubanite.
Fig. 3. Mackinawite from the Muskox intrusion found in association with pentlandite and magnetite.
Fig. 4. Mackinawite from the Tsumo mine associated with chalcopyrite, pentlandite and pyrite.
Fig. 5-a. Mackinawite from the Komori mine occurring within chalcopyrite in association with cubanite and sphalerite.
Fig. 5-b. Pyrrhotite (Ma′) derived from mackinawite as a result of annealing at 150°C for 4 hours.

Explanation of Plate VII

Fig. 6-a. Mackinawite in chalcopyrite in association with skeletal sphalerite as found in the specimen from the Ohmine mine.
Fig. 6-b. Pyrrhotite (Ma′) derived from mackinawite as a result of annealing the specimen shown in Fig. 6-a at 144°C for 4 hours.
Fig. 7-a. Mackinawite from the Makimine mine associated with chalcopyrite and pyrrhotite.
Fig. 7-b. Pyrrhotite (Ma′) derived from mackinawite as a result of annealing the specimen shown in Fig. 7-a at 245°C for 4 hours.
Fig. 8-a. Mackinawite from the Outokumpu mine associated with chalcopyrite and pyrrhotite.
Fig. 8-b. Pyrrhotite (Ma′) derived from mackinawite as a result of annealing the specimen shown in Fig. 8-a at 158°C for 4 hours.

Ma: mackinawite, Cp: chalcopyrite, Cub: cubanite, Sp: sphalerite, Pt: pentlandite, Mt: magnetite, G: gangue minerals

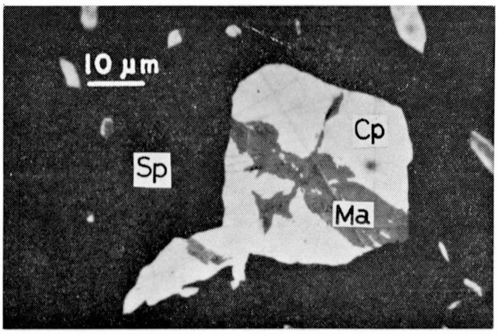


Fig. 1.

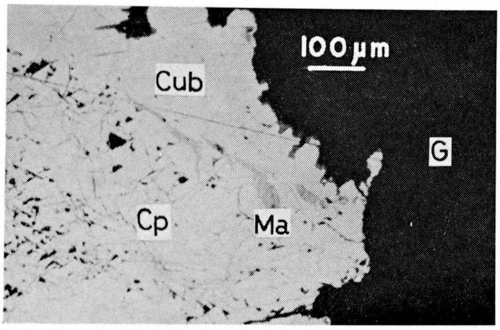
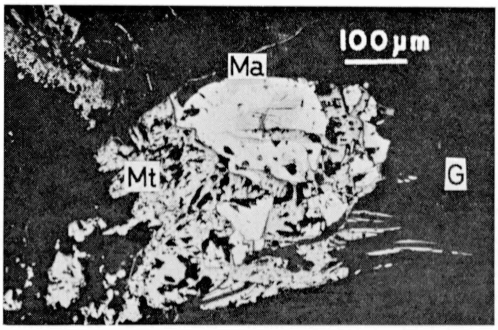


Fig. 2.



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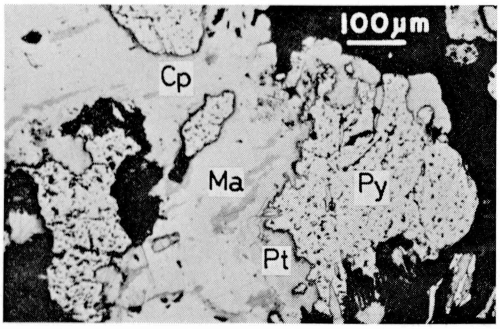

Fig. 4.

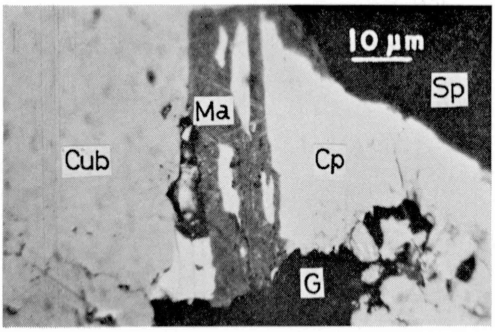

Fig. 5–a.

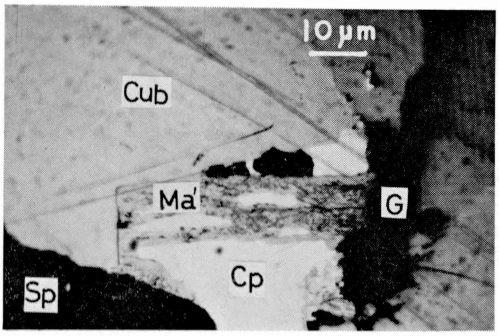

Fig. 5–b.

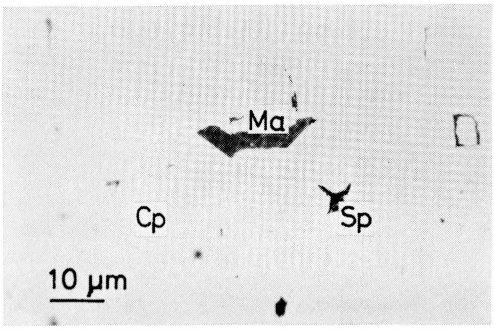

FIG. 6–a.

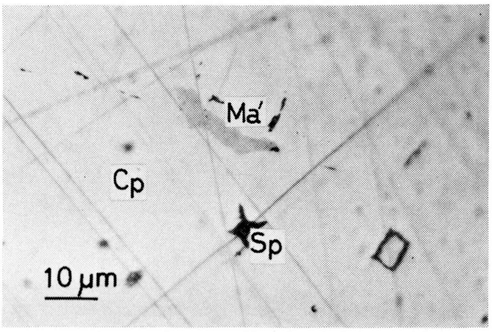

FIG. 6–b.

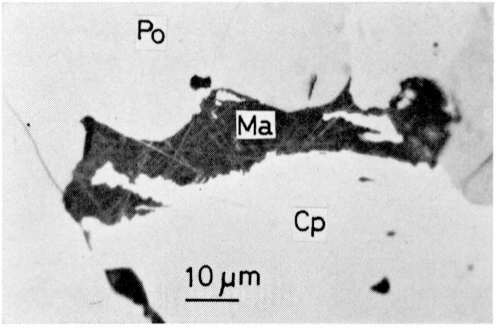

FIG. 7–a.

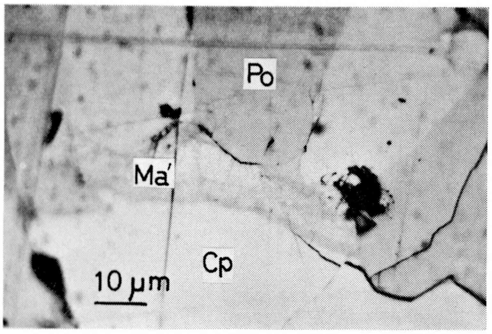

FIG. 7–b.

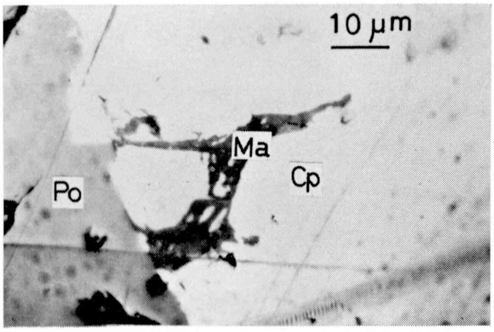

FIG. 8–a.

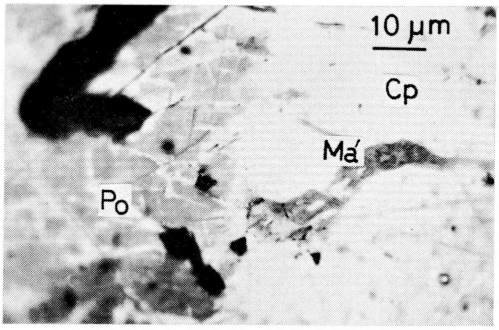

FIG. 8–b.