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METASTABLE CUBIC IRON SULFIDE—WITH SPECIAL REFERENCE TO MACKINAWITE

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ABSTRACT

Several iron sulfides including mackinawite, troilite, hexagonal pyrrhotite, metastable iron sulfide and others have been synthesized through immersion of pure iron plates in solutions saturated with hydrogen sulfide at 50°C and atmospheric pressure; and have been identified by means of X-ray diffraction and/or electron microprobe analysis.

Mackinawite is commonly recognized as fine-grained crystallites several microns in diameter; it is somewhat anisotropic and distinct in reflection pleochroism. Metastable iron sulfide is röntgenographically similar to sphalerite and is microscopically hexagonal, cubic, or rectangular in shape, usually less than about 30 μm in size, and has an approximate composition of stoichiometric FeS. This phase characteristically transforms gradually to mackinawite at room temperature and completely converts to the latter in a month.

With heating, the metastable iron sulfide and mackinawite change to hexagonal pyrrhotite at about 200°C and 170°C, respectively and finally to troilite under iron-rich conditions.

INTRODUCTION

Syntheses of iron sulfides in aqueous solutions have been extremely productive. Berner (1962, 1964 and 1967) examined the equilibrium conditions of Fe-S minerals in aqueous solutions at low temperatures. He distinguished mackinawite, a phase of tetragonal iron sulfide, which had been previously identified as kansite, a cubic phase, by many investigators (*e.g.* Meyer *et al.*, 1958). He also calculated the standard free energies of formation of mackinawite, greigite and some other iron sulfides through measurements of their equilibrium constants in aqueous solutions.

The present writers have already examined the stability relations of natural mackinawite (Takeno, 1965 and 1967) and decided to synthesize the mineral hydrothermally (Niihara *et al.*, 1969). A new phase with a sphalerite structure, found in the process of the experiments, is very characteristic in that it gradually changes to mackinawite at room temperature. Other than pyrite and marcasite, the only known cubic iron sulfide is greigite, having the spinel structure and the formula Fe_3S_4 (Skinner *et al.*, 1964).

Several years ago, R. A. Berner, Yale University, synthesized two new

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forms of iron sulfide, both apparently having the composition FeS. He was unsuccessful in reproducing the synthesis in order to obtain pure material, but he and B. J. Skinner, of the same institution, were successful in establishing that one of the forms of FeS had a sphalerite-type structure, cell edge 5.426 Å, and that the other had a wurtzite-type structure (Skinner, 1970, private communication).

Our new phase, metastable cubic FeS, is reproducible, euhedral in habit and very minute in size. In this paper, we will report on some properties of this new phase together with those of mackinawite.

EXPERIMENTAL METHODS

Iron sulfides have been produced through reaction of pure iron plate (about 30×45×3 mm in size) with hydrogen sulfide at 50°±2°C in solutions of various pH's. Prior to the experiments, distilled water was prepared while bubbling with nitrogen in order to exclude carbon dioxide or oxygen in the water. The pH values in solution were regulated with sulfuric acid and sodium hydroxide and measured by means of an Hitachi-Horiba D-5 pH-meter before and after the experiments. In all experiments, four iron plates were held in solution for 6, 16, 24, 60, 96, 162, 240 and 384 hours and were taken out at the different time intervals in order to examine the effects of the reaction. Hydrogen sulfide gas was passed through the vessel at a pressure of about 770 Torr.

RESULTS

During the study, the following phases were synthesized: mackinawite, troilite, hexagonal pyrrhotite, greigite and metastable cubic iron sulfide with composition approximating FeS. Melanterite was also identified as a thin film formed on the surface of the solution.

Mackinawite. Mackinawite was formed over a wide range of pHs, especially in alkaline solutions, and can be considered an important phase resulting from reaction of iron with hydrogen sulfide at low temperatures. X-ray powder data for the synthesized mackinawite and the product obtained by Berner (1962) are listed in the Table 1; there are some differences in intensities but a good coincidence in values of the spacings. Microscopic observation shows that the synthesized mackinawite commonly occurs as fine-grained crystallites, several microns in diameter, which are somewhat anisotropic and distinct in their reflection pleochroism.

Troilite. This phase is common, especially in acidic conditions where needles several tens of microns in size are formed. Its composition was determined through measurement of the spacing of the main X-ray reflection, the result yielding 2.092±0.001Å for $d(102)$. In addition, microprobe analyses were carried out with ARL-EMXI manufactured by Shimazu Manufacturing Co., Ltd. Iron and sulfur in troilite and the

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC MACKINAWITE

hkl	Synthetic mackinawite: this paper				Synthetic mackinawite: Berner (1962), at 25°C (CuK radiation)	
	CuK radiation (Ni-filter)		CoK radiation (Fe-filter)			
	d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
001	5.05	100	5.04	100	5.03	10
101	2.97	40	2.97	58	2.97	8
110	2.60	10	2.60	3	2.60	2
111	2.31	45	2.31	46	2.305	8
200	1.840	25	1.837	28	1.835	6
112	1.808	35	1.806	40	1.805	8
201	1.726	15	1.724	16	1.723	6
003			1.676	3	1.677	2
211	1.563	10	1.562	8	1.564	4
103					1.527	2
202						
113	1.404	5			1.410	3
220	1.299	10	1.298	6	1.298	5
311			1.132	5		
312			1.055	6		

metastable iron sulfide were quantitatively determined by measurement of the intensities of the Fe-Kα and S-Kα reflections. A crystal of synthetic stoichiometric FeS(36.47 wt. percent of sulfur) was used as the

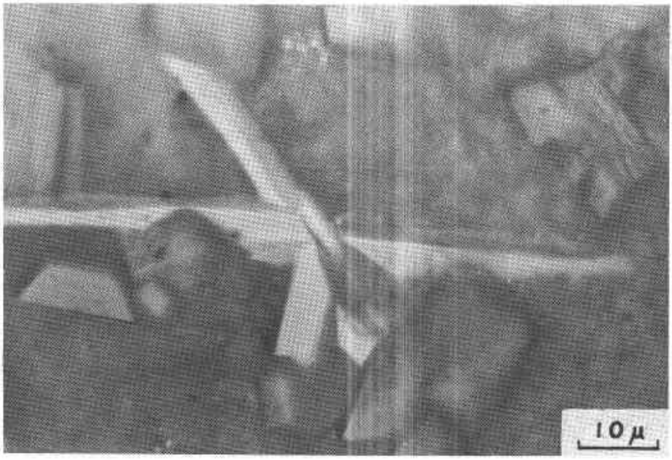

FIG. 1. Euhedral grain of synthetic troilite.

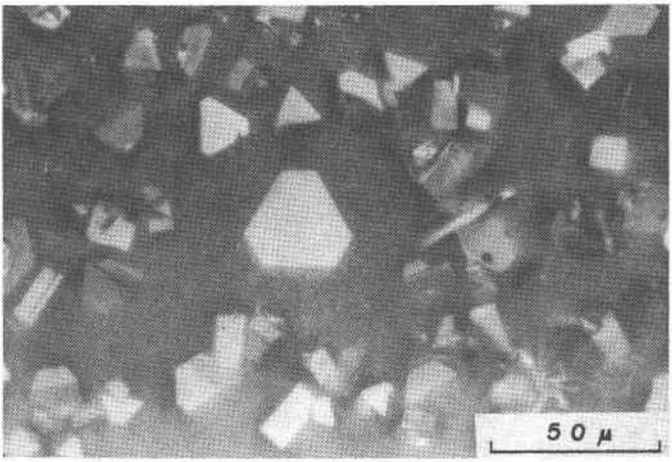

FIG. 2. Metastable cubic iron sulfide embraced in the ground-mass of the fine-grained mackinawite.

standard specimen for determination of iron and sulfur content. The chemical compositions of these phases, corrected for matrix absorption (*cf.* Philbert, 1962) and atomic number (*cf.* Poole and Thomas, 1961) are listed in Table 3.

Metastable cubic phase. Although there is room for further study, a neutral solution seems best suited for production of this phase with a well-developed crystal habit and sharp X-ray diffraction patterns. Standard X-ray powder diffraction techniques were employed and many specimens were examined with copper, iron, and cobalt radiation. X-ray powder data for the sample with the highest peak at 3.13Å are aligned in the Table 2. As is clear from inspection of the table, this phase reveals an identity with sphalerite in *d*-spacings and intensities; while the fact that specimens are microscopically hexagonal, cubic, and rectangular in shape (Fig. 2) makes it possible to analogize the sphalerite structure.

In Table 3, quantitative analytical data for two samples of the metastable cubic phase are shown as $Fe_{1.028}S$ and $Fe_{1.102}S$. The phase apparently has a composition slightly richer in metal than troilite.

The characteristic conversion of the phase to mackinawite at room temperature is illustrated in Figure 4. The most intense peak for mackinawite, (001), begins to emerge after two days and all of its peaks seem to be completed after about one month. It is to be noted that with decrease in intensity of the peaks representing the metastable cubic phase, the peaks for mackinawite become more and more conspicuous.

Table 2. X-Ray Powder Diffraction Data for Metastable Cubic FeS (CuK radiation, Ni-filter)

hkl	Synthesized at 50°C (pH=5.7)		β-ZnS (sphalerite) (XRDF: 5-0566)	
	d (Å)	*I*	*d* (Å)	*I*
111	3.130	100	3.123	100
200	2.709	6	2.705	10
220	1.914	43	1.912	51
311	1.633	20	1.633	30
222			1.561	2
400	1.354	5	1.351	6
331	1.242	6	1.240	9
440			1.209	2
422	1.1051	6	1.1034	9
	$a=5.417\pm0.004$ Å		$a=5.406$ Å	

Under the reflection microscope, grains of the metastable phase are often seen embraced in a groundmass of very fine-grained mackinawite (Fig. 2), are typically to 30 μm in diameter, and are optically isotropic and brownish grey in color somewhat resembling pyrrhotite. Conversion of the metastable cubic phase to mackinawite can be detected optically after several days and more than one half of each grain converts on the surface during a month. Figure 3 shows a completely converted grain with the characteristic anisotropism. Under the phase-contrast microscope, minute-scaled hollows representing the decrease of volume in the converted parts are clearly discernible.

Table 3. Quantitative Electron Microprobe Analyses of Iron Sulfides (Weight Percent)

	M-62-3 Ms	M-62-4 Ms	M-51-1 Ma	M-62-3 Tr	M-62-3 Tr
Fe	64.63	65.41	64.06	63.47	63.60
S	36.09	34.07	35.33	36.32	35.98
Total	100.72	99.48	99.39	99.79	99.58
Fe/S	1.028	1.102	1.042	1.003	1.015

Ms = metastable cubic iron sulfide, Ma = mackinawite.
Tr = troilite.

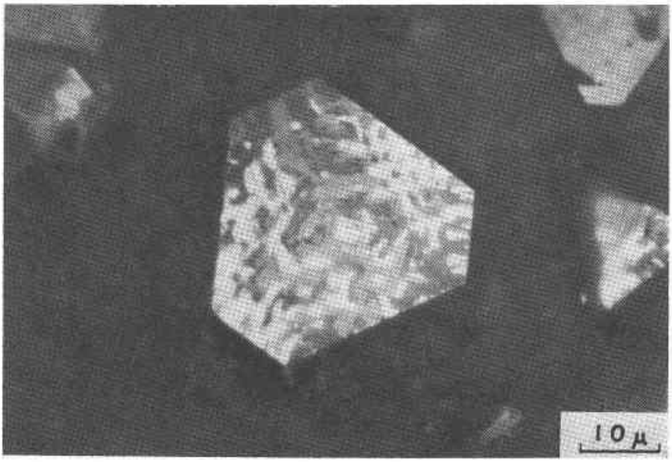

FIG. 3. Mackinawite grain derived from metastable cubic iron sulfide showing the characteristic optical properties.

The metastable cubic FeS changes to hexagonal pyrrhotite with heating above about 200°C. Owing to their unstable nature under atmospheric conditions, specimens were taken immediately after synthesis and sealed in hard glass tubes evacuated down to about 10^{-3} mm Hg, and then put in an electric furnace kept at known temperatures. Figure 5 shows the conversion of metastable FeS to hexagonal pyrrhotite with heating. Because of difficulty in manipulation of the minute materials obtained through synthesis, the heating experiments were carried out with the iron plate. Metastable cubic FeS changes to hexagonal pyrrhotite (48.10 to 48.40 atomic percent iron) at about 200°C after heating for one or two hours; however the pyrrhotite gradually becomes more iron-rich with increase of the heating time and temperature (300°C for 4 hr: 49.65; 400°C for 4 hr: 49.75; and 500°C for 4 hr: 49.90 atomic percent iron) and finally reaches the composition of troilite. This behavior is probably due to the presence of excess iron in the plate. In Figure 5, the (110) reflection of α-iron is represented by the highest peak at 2.0268 Å. It seems that the inversion temperature of the metastable phase to troilite is lowered with increase of heating time. Metastable FeS begins to change to troilite ($d_{102} = 2.091$ Å) with heating at 170°C for 30 days, but alters to mackinawite if heated at temperatures lower than 170°C.

Mackinawite converts to hexagonal pyrrhotite with heating (Fig. 7). The peaks of mackinawite gradually weaken on heating, and diminish at 140°∼150°C while those of the hexagonal pyrrhotite ($d_{102} = 2.0690$Å) begin to appear at about 170°C. It is worth mentioning that at the intermediate step of the heating process, the mackinawite reflections (101

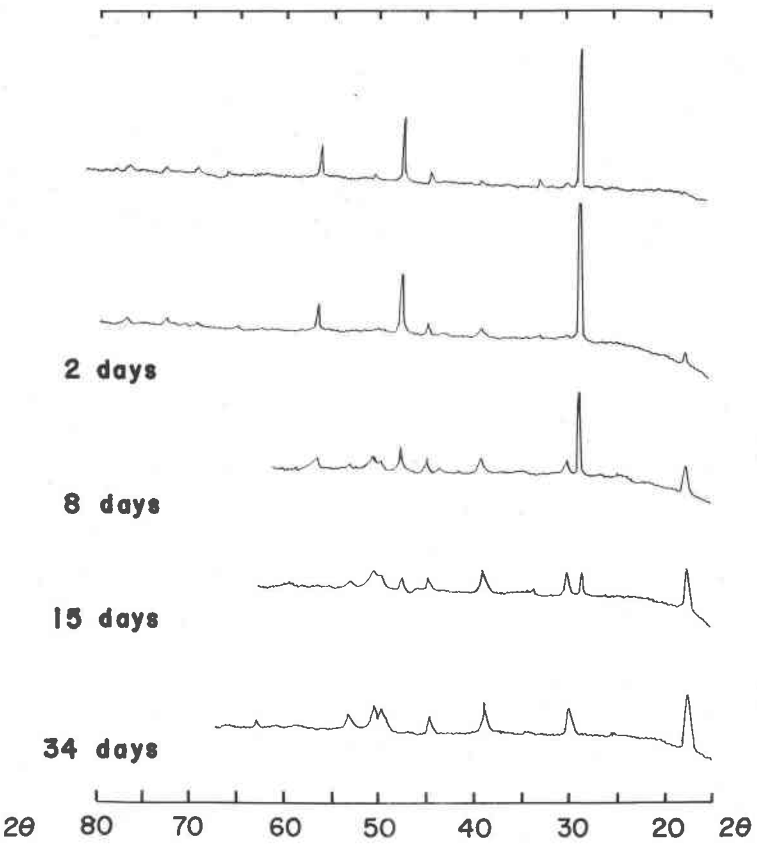

Fig. 4. X-ray diffraction patterns showing the phase change of the metastable cubic iron sulfide to mackinawite with duration of time. CuK radiation with Ni-filter.

at 2.97Å and (201) at 1.73Å still remain, but convert respectively to (100) and (110) for hexagonal pyrrhotite with further heating (see Fig. 7). It is also to be noticed that mackinawite accompanied by the metastable FeS is stable at about 200°C and that prior to disappearance of the (001) reflection of the former, the peaks of hexagonal pyrrhotite already emerge (Fig. 5).

Discussion

Paragenetic relationships of natural mackinawite are broadly indicative of relatively low temperature of formation. Differences in the temperature of conversion for synthesized mackinawite and for the natural phase (*cf*. Kouvo *et al.*, 1963, Takeno, 1965, Clark, 1966 and 1968) may most probably be ascribed to differences in the sulfur fugacities, but it

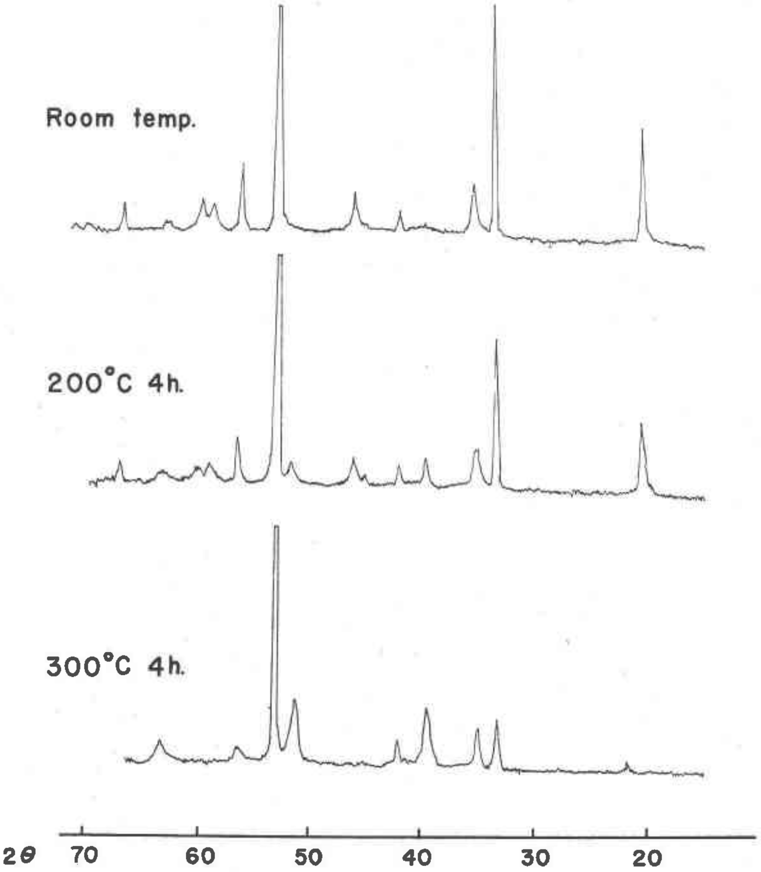

FIG. 5. X-ray diffraction patterns showing the phase change of the "metastable cubic iron sulfide-mackinawite-α-iron" assemblage with heating. CoK radiation with Fe-filter.

is an important problem to study the stability of the synthesized products in more detail. Naturally occurring mackinawite converts to hexagonal pyrrhotite (130°∼240°C) at the temperatures lower than those for conversion of the synthesized phase. Possibly this is caused by higher fugacities of sulfur associated with natural occurrences. In preliminary attempts to determine the influence of sulfur fugacity on the phase transformation temperature, experiments were carried out at various temperatures with saturated sulfur vapor. The experiments demonstrate a considerable lowering of the transformation temperature with increased sulfur fugacity. The temperature of the phase transformation determined

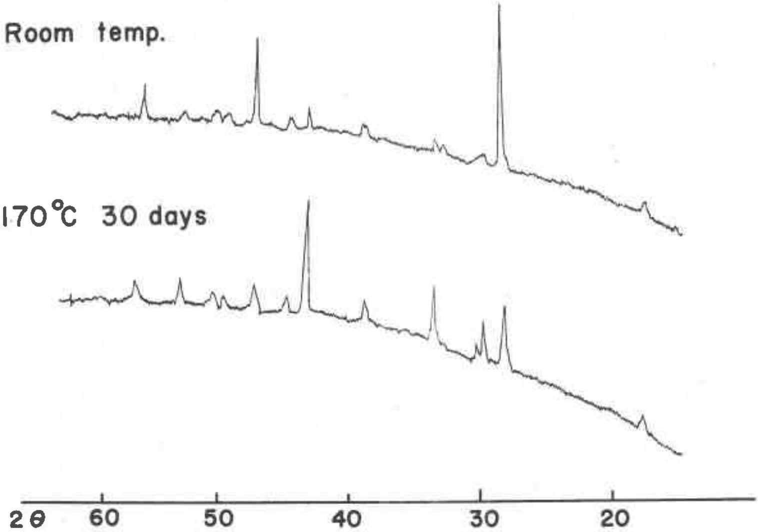

FIG. 6. Phase change of the metastable cubic iron sulfide to troilite with long time heating. CuK radiation with Ni-filter.

optically (210°C) corresponds to that at the intermediate step of the process pursued röntgenographically.

The stability field of nickel- and cobalt-free mackinawite is tentatively shown by Clark (1968). According to his $T-X$ diagram, mackinawite is flanked by the two-phase fields, mackinawite+α-iron and mackinawite+troilite, at temperatures lower than about 140°C. The experimental results show that mackinawite converts to hexagonal pyrrhotite (47.40~47.50 atomic percent iron) at the first step of the heating process even in iron-rich circumstance (Fig. 7). But with heating for sufficient time (or at higher temperature), mackinawite converts to troilite, as is indicated in Clark's diagram. It is to be noted that the composition of the hexagonal pyrrhotite derived from mackinawite exactly corresponds to that of the sulfur-rich limit (47.45 atomic percent iron) for the temperature range below 325°C, as studied by Yund and Hall (1969). However, it still remains to be more accurately confirmed whether or not mackinawite, troilite and α-iron may stably coexist with one another at about 170°C.

On the other hand, with heating at about 200°C, the metastable phase of cubic FeS changes to more iron-rich hexagonal pyrrhotite (48.10~48.40 atomic percent iron) than does mackinawite. In connection with this, Arnold (1967) examined the composition and structure of the phases in

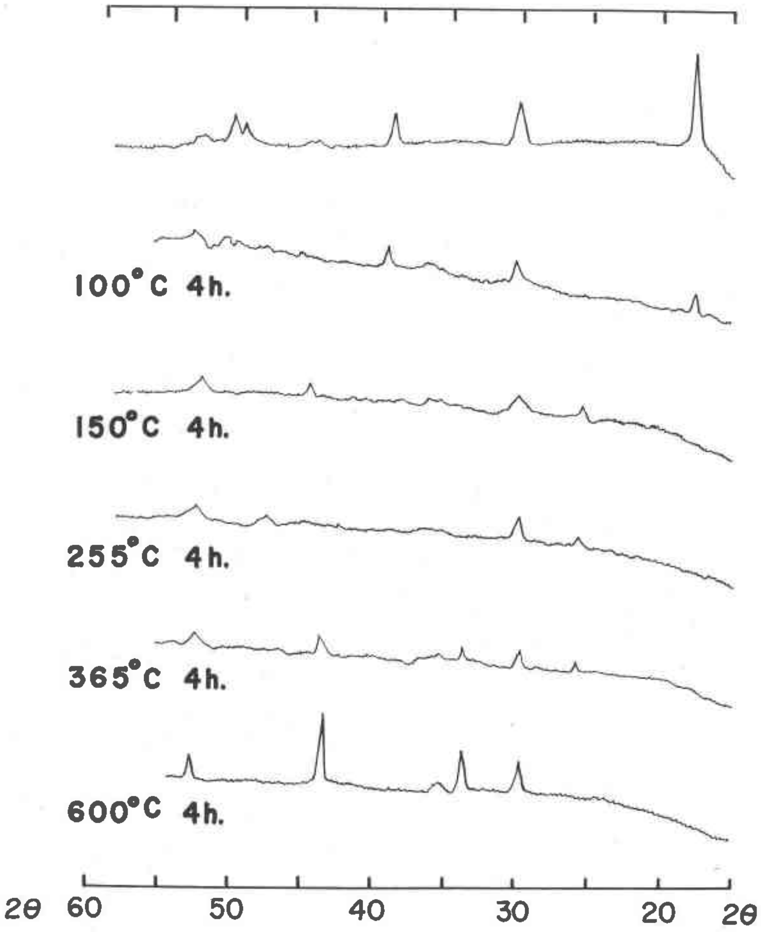

FIG. 7. X-ray diffraction patterns showing the phase change of mackinawite to hexagonal pyrrhotite with heating. CuK radiation with Ni-filter.

natural pyrrhotite and classified them into three groups, hexagonal FeS (50.0 atomic percent metals), Hexagonal $Fe_{1-x}S$(48.1～47.5) and monoclinic $Fe_{1-x}S$(46.5). The composition of the hexagonal pyrrhotite derived from the metastable phase is situated in the two-phase field (troilite and hexagonal pyrrhotite). Coexistence of the metastable phase and mackinawite seems to stabilize the latter to higher temperatures (above 200°C) than can be attained by mackinawite (above 170°C).

Considering the X-ray powder data, the crystal habit, and the optical properties observed under the reflection microscope, it appears clear that the metastable iron sulfide has the sphalerite structure. The writers are now continuing the experimentation especially concerning: the synthesis of larger crystals more suitable for the single crystal analyses, and the synthesis of the stable phase under atmospheric conditions.

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REFERENCES

ARNOLD, R. G. (1967) Range in composition and structure of 82 natural terrestrial pyrrhotites. *Can. Mineral.* **9,** 31–50.

BERNER, R. A. (1962) Tetragonal iron sulfide. *Science,* **137,** 669.

——— (1964) Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure. *J. Geol.* **72,** 293–306.

——— (1967) Thermodynamic stability of sedimentary iron sulfides. *Amer. J. Sci.* **265,** 773–785.

CLARK, A. H. (1966) Some comments on the composition and stability relations of mackinawite. *Neues Jahrb. Mineral. Monatsh.* **10,** 300–304.

———, AND A. M. CLARK (1968) Electron microprobe analysis of mackinawite from the Ylöjärvi deposit, Finland. *Neues Jahrb. Mineral. Monatsh.* **6,** 259–268.

EVANS, H. T., C. MILTON, E. C. T. CHAO, I. ADLER, C. MEAD, B. INGRAM, AND R. A. BERNER (1964) Valeriite and the new iron sulfide, mackinawite. *U.S. Geol. Surv. Prof. Pap,* **475**-D, 6—69.

KOUVO, O., Y. VUORELAINEN, AND J. V. P. LONG (1963) A tetragonal iron sulfide. *Amer. Mineral,* **48,** 511–524.

MEYER, F. H., O. L. RIGGS, R. L. MCGLASSON, AND J. D. SUDBURY, (1958) Corrosion products of mild steel in hydrogen sulfide environments. *Corrosion,* **14,** 109t–115t.

NIIHARA, T., H. ZÔKA, S. TAKENO (1969) Studies of synthetic mackinawite (I) *Kobutsugaku Zasshi,* **9,** 311–323 [in Japanese].

PHILBERT, J. (1962) *Proc. 3rd. Int. Symp. on X-ray optics and X-ray microanalysis.* Stanford, New York, Academic Press.

POOLE, D. M., AND P. M. THOMAS, (1962) Quantitative electron-probe microanalysis. *J. Inst. Metals,* **90,** 228–232.

SKINNER, B. J., R. C. ERD, AND F. S. GRIMALD, (1964) Greigite, the thio-spinel of iron; a new mineral. *Amer. Mineral.,* **49,** 543–555.

TAKENO, S. (1965) A note on mackinawite (so-called valleriite) from the Kawayama mine, Japan. *Geol. Rep. Hiroshima Univ.,* **14,** 59–76.

——— (1965) Thermal studies on mackinawite. *J. Sci. Hiroshima Univ. Ser. C,* **4,** 455–478.

——— AND A. H. CLARK, (1967) Observations, on tetragonal (Fe, Ni, Co)$_{1+x}$S, mackinawite. *J. Sci. Hiroshima Univ. Ser. C,* **5,** 287–293.

YUND, R. A. AND H. T. HALL, (1969) Hexagonal and monoclinic pyrrhotites. *Econ. Geol.* **64,** 420–423.

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