

## Formation of cubic FeS

JAMES B. MUROWCHICK,\* H. L. BARNES

Ore Deposits Research Section, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

### ABSTRACT

Metastable cubic FeS was synthesized by the sulfidation of powdered metallic Fe by aqueous H<sub>2</sub>S. Crystals of cubic FeS and troilite formed below 92°C between pH 2 and 6, with cubic FeS precipitating early in the 4–85-h-long experiments and then disappearing by conversion to mackinawite during aging. Above 92°C, troilite and/or mackinawite were the only products. Above pH 6, mackinawite was the only product.

Cubic FeS and troilite formed by reactions between aqueous H<sub>2</sub>S and Fe<sup>2+</sup>, but mackinawite formed by reactions involving solid phases such as Fe metal or previously formed cubic FeS. The short persistence of metastable cubic FeS makes it unlikely that this phase will be found in a natural occurrence.

### INTRODUCTION

Metastable cubic FeS occurs as a corrosion product in the Girdler-Sulfide process of heavy-water extraction (Shoesmith et al., 1980). Only superficial attention has been given to this phase (Table 1), so an investigation into the conditions of its formation was undertaken. The pH and temperature limits of formation were determined, and the likelihood of cubic FeS occurring as a mineral phase in nature was considered.

Cubic FeS was first identified by de Médicis (1970a, 1970b). In his study of the corrosion of iron by H<sub>2</sub>S, he placed blocks of pure iron in aqueous H<sub>2</sub>S solutions in closed containers at room temperature. The pH of the solutions ranged from 4.0 to 4.5 and the run duration from several hours to 4 d. A thin, adherent film of mackinawite, troilite, and cubic FeS formed on the metal blocks; identification of the phases was by X-ray diffraction methods. Formation of cubic FeS was inhibited by the presence of “foreign ions” such as Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> according to de Médicis. He characterized the cubic phase as having the sphalerite structure (F43m) with  $a = 5.423 \pm 0.001$  Å,  $D_{\text{calc}} = 3.661$  g/cm<sup>3</sup>, with bond lengths Fe–S = 2.348 Å, and Fe–Fe = S–S = 3.835 Å. The X-ray diffraction pattern for cubic FeS is indeed similar to that of sphalerite, both in peak positions and relative peak heights.

In the same year, Takeno et al. (1970) described their synthesis of a metastable cubic iron sulfide. They also used a pure iron plate in distilled water saturated with H<sub>2</sub>S at a pressure of 1 bar. Their experiments at 50°C covered a “wide range” of pH values, but only pH 5.7 was specified. The duration of their experiments ranged from 6 to 384 h. As in the work of de Médicis, the products were mackinawite, troilite, and cubic FeS. Takeno et al. found that mackinawite formed over a wide range of pH values, but especially in alkaline solutions. Troilite formation was

favored in acidic solutions, and cubic FeS seemed to form best in neutral solutions. Euhedral crystals of cubic FeS up to 30 μm across displaying the cube, positive tetrahedron, and negative tetrahedron were produced. These forms are consistent with the sphalerite structure proposed by de Médicis (1970a, 1970b). Electron-probe analyses (Takeno et al., 1970) of two samples of cubic FeS gave compositions of FeS<sub>0.973</sub> and FeS<sub>0.907</sub>. Takeno et al. also noted that cubic FeS inverted (in air) to mackinawite in 2 to 30 d.

A more recent study by Shoesmith et al. (1980) on the corrosion of unspecified stainless steels by aqueous sulfide solutions at 21°C produced similar results; i.e., mackinawite, troilite, and cubic FeS were the usual monosulfide products. Troilite and cubic FeS formed between pH 3 and 5. As in Takeno et al. (1970), troilite was favored at lower pH values, whereas mackinawite was more abundant at higher pH values (the pH ranged from 2 to 7). Shoesmith et al. examined the textures of their products and concluded that mackinawite formed by surface reaction of Fe metal with aqueous H<sub>2</sub>S, whereas the troilite and cubic FeS were formed by reaction of dissolved Fe<sup>2+</sup> and aqueous H<sub>2</sub>S. Cubic FeS was also observed to undergo solid-state reaction to mackinawite. Shoesmith et al. (1980)

Table 1. Syntheses of cubic FeS

Investigation*	pH	T (°C)	Products**
de Médicis (1970a, 1970b)	4.0–4.5	25	tr, cFeS, mk
Takeno et al. (1970)	5.7	50	tr, mk, cFeS
Shoesmith et al. (1980)	3, 4, 5	21	tr, cFeS
	6, 7	21	mk
	4	21–90	tr, cFeS
This work	2–6	55–85	tr, cFeS, mk
	6–7	55	mk, (tr)
	5	93	tr, mk

\* All four investigations used metallic iron and aqueous H<sub>2</sub>S.

\*\* Products are listed in order of decreasing abundance; tr = troilite, mk = mackinawite, and cFeS = metastable cubic FeS.

\* Present address: Department of Geology, University of Alberta, Edmonton, Alberta T6G 2E3, Canada.

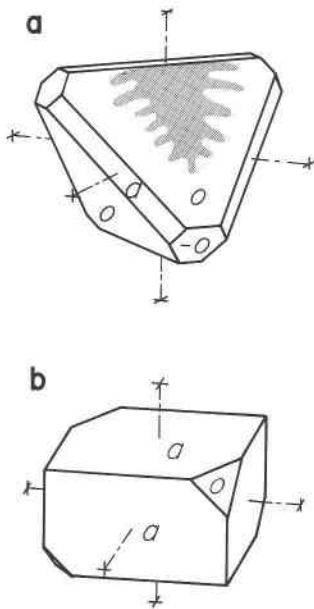


Fig. 1. Morphology of cubic FeS crystals. (a) Tetrahedron (*o*) modified by the cube (*a*) and negative tetrahedron (*-o*). The shaded area represents the replacement by mackinawite commonly observed in samples aged several hours to 2 d. (b) Cubic habit modified by the tetrahedron (*o*). This habit was rare and occurred with the tetrahedral crystals.

also investigated the effects of temperature on the products at pH 4 up to 90°C and found that cubic FeS was most abundant in the 35 to 50°C range, and a small amount formed at 90°C.

The purpose of the present study was to more fully determine the pH-*T* conditions of cubic FeS formation and to present proposed reaction mechanisms involved in its formation. Future studies should address the possibility of polymorphism between cubic FeS and mackinawite and the effects of other transition metals on the stability of cubic FeS.

Table 2. Experimental results

Run	<i>T</i> (°C)	<i>t</i> (h)	pH	<i>m</i> <sub>H<sub>2</sub>S</sub>	Products*		
					mk	tr	cFeS
7	55	48	4.24–4.54	0.05	4	2	3
8	93	70	4.50–4.97	0.05	3	2	0
9	65	39	4.60–4.20	0.05	3	2	1
10	60	30	4.34–4.23	0.05	3	4	2
11	60	30	4.54–4.13	0.05	3	4	2
12	60	30	4.24–4.40	0.05	3	4	2
13	56	85	4.87–4.30	0.05	3	4	2
14	55	27	5.95–5.60	0.1	3	4	2
15	55	67	6.97–6.64	0.1	3	2	0
16	55	6	2.99–3.92	0.1	2	3	3
17	55	4	2.6–3.5	0.1	2	2	3
18	65	5	2.6–3.5	0.1	2	3	2
19	75	15	2.3–3.5	0.1	3	4	2
20	83	22	2.1–3.5	0.1	2	4	3

\* Products are assigned relative abundances: 4 > 3 > 2, 1 = trace, 0 = absent. mk = mackinawite, tr = troilite, and cFeS = metastable cubic FeS.

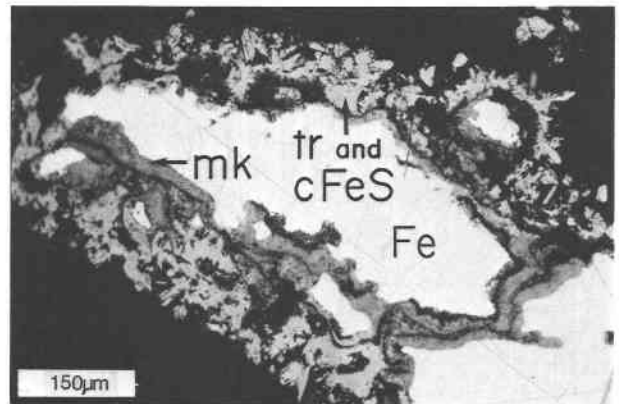


Fig. 2. Product textures. Mackinawite (mk) is shown replacing iron metal, with troilite (tr) and cubic FeS (cFeS, not visible) forming a corona of crystals around the Fe grain.

## METHODS AND MATERIALS

Experiments were performed in this study using an airtight, 1460-mL capacity, glass reaction kettle (Murowchick, 1984) containing a pH electrode, gas bubbler, stirrer assembly, and a thermometer, which together occupied the four ports in the lid. The kettle was completely filled with deoxygenated, deionized water and then purged with methane (Matheson, high purity, >99.99% CH<sub>4</sub>). The excess water was displaced by the supernatant CH<sub>4</sub> until 500 mL of solution remained. This procedure minimized O<sub>2</sub> contamination. During the methane purge, the kettle was heated in a constant-temperature bath. After purging, the gas was switched to pure H<sub>2</sub>S or 50/50 H<sub>2</sub>S/CH<sub>4</sub> (Matheson, CP grade, 99.5% H<sub>2</sub>S) and the solution saturated at about 1-bar total pressure. A slight positive gas pressure was maintained to minimize the amount of oxygen entering the kettle. After saturation with H<sub>2</sub>S, approximately 5 to 10 g of powdered iron (Fisher, electrolytic, 100 mesh) was quickly poured into the kettle by slightly opening one port. By displacing the air in the kettle with CH<sub>4</sub>, O<sub>2</sub> was effectively eliminated as an oxidizing agent. The metallic Fe was then oxidized by H<sup>+</sup> instead. By bubbling H<sub>2</sub>S through the solution, subsequent O<sub>2</sub> contamination was minimized and a low *f*<sub>O<sub>2</sub></sub> maintained.

The pH was adjusted by injecting small amounts of HCl, H<sub>2</sub>SO<sub>4</sub>, or NaOH through one of the rubber stoppers with a hypodermic syringe. The runs covered the pH range from 2 to 7 and temperatures from 55 to 93°C. Samples were taken at intervals during each experiment by inserting a pipette into the port normally containing the pH electrode. (This port was sealed with a 20-cm length of 2.5-cm diameter, thin-walled rubber tubing (Gooch tubing), which acted as an airlock and permitted sampling to be conducted without appreciable air contamination.) The precipitates, containing cubic FeS, mackinawite, and/or troilite, were filtered, rinsed with acetone, dried, and examined using reflected-light microscopy and X-ray diffraction.

The reflectance of cubic FeS was measured on well-formed crystal faces using a Vickers Visual Microphotometer with a 580 nm (green) filter. Because of the reactivity of cubic FeS, polished sections were not used for the reflectance measurements. The bulk sample was sprinkled on a glass slide. Ten cubic FeS crystals, each with a well-formed, horizontally oriented {111} face (Fig. 1) exhibiting maximum reflectance, were selected for measurement. Ten replicate measurements were made on each of the ten

crystals, yielding an average reflectance of  $28 \pm 1\%$ . Cubic FeS is isotropic, and is neutral gray against the pinkish tan of troilite and the beige to medium gray of mackinawite.

For the X-ray examination,  $\text{CuK}\alpha$  radiation was used with a monochromator, a scan speed of  $2^\circ/\text{min}$ , and a 2-s time constant, on a Rigaku Geigerflex automated diffractometer operated at 40 kV and 20 mA. The minimum detectable amounts of each phase were not determined but are conservatively estimated at 5 wt%. Confirmation of the presence of particular phases, or the identification of phases present in abundances not detectable by X-ray diffraction, was accomplished using incident-light microscopy. Examination had to be completed within several hours because of the moderately rapid oxidation in air of the cubic FeS and mackinawite. The samples were stored in glass vials that were subsequently evacuated or filled with  $\text{CH}_4$  or  $\text{H}_2\text{S}$ .

### EXPERIMENTAL RESULTS

The reaction of powdered metallic iron with aqueous  $\text{H}_2\text{S}$  produced three iron monosulfide phases: mackinawite, troilite, and metastable cubic FeS (Fig. 2). The relative amounts of each phase depended on pH, temperature, and time (Table 2). The variation in the proportion of the run products as a function of pH indicated that, as in previous studies, troilite precipitation was favored at low pH values, cubic FeS at intermediate pH values (3 to 5), and mackinawite at even less acidic pH values in the range of the experiments (pH 2 to 7).

Temperature also influenced the product composition. Mackinawite and troilite maintained their relative abundances from 55 to  $93^\circ\text{C}$ , but the rates of formation increased with temperature. From the shape of X-ray diffractogram peaks, the crystallinity of the mackinawite product appeared to increase with temperature. The best-formed crystals of cubic FeS were produced at  $55^\circ\text{C}$  (pH 4 to 5), mimicking the results of Shoesmith et al. (1980). The proportion of cubic FeS in the products decreased above  $55^\circ\text{C}$  to about  $93^\circ\text{C}$  where no cubic FeS was detected. Above and below  $55^\circ\text{C}$  at pH 3 to 5, the size of the cubic FeS crystals decreased from that of the  $55^\circ\text{C}$  crystals, but the number of crystals increased below  $55^\circ\text{C}$ .

The composition of the products also changed as a function of time. In general, mackinawite and cubic FeS formed early in a given experiment, followed by a decrease in the abundance of cubic FeS and Fe metal with a concurrent increase in the abundance of troilite. In addition, the cubic FeS content of the product decreased with age as the cubic FeS converted to mackinawite over the course of several hours to 2 d.

### DISCUSSION

Cubic FeS has been found to form in acidic,  $\text{H}_2\text{S}$ -rich environments below  $92^\circ\text{C}$  where the corrosion of ferrous metals is occurring. Associated phases include mackinawite and troilite, the relative amounts being a function of pH, temperature, and time.

Two reactions are proposed to explain the observed products. The first is a surface reaction to form mackinawite:

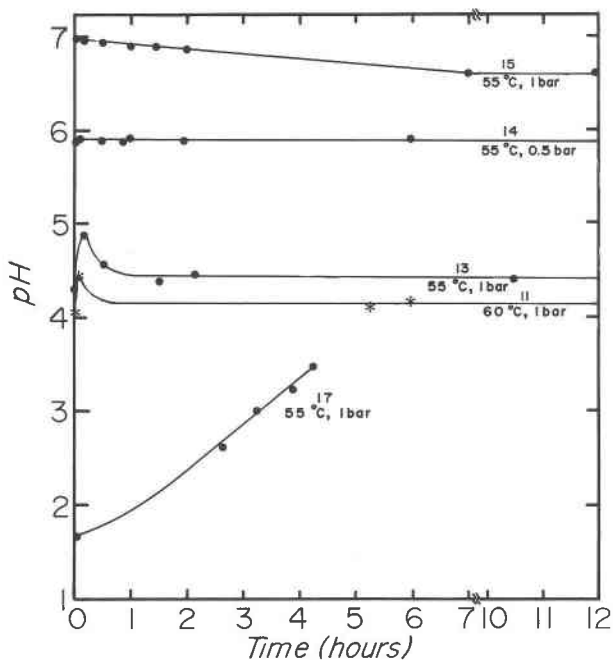
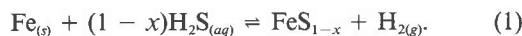
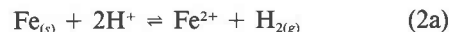


Fig. 3. Variation of pH with time for selected experiments. Run numbers are given above the curves, and temperature and  $P_{\text{H}_2\text{S}}$  are given below the curves.  $\text{H}_2\text{S}$  was in great excess for both  $P_{\text{H}_2\text{S}} = 1$  bar and 0.5 bar, and the curves are not appreciably altered by changing from 1 bar to 0.5 bar  $P_{\text{H}_2\text{S}}$ . The dots are for  $55^\circ\text{C}$  and the stars for  $60^\circ\text{C}$  runs. See the text for a full explanation.



This reaction is pH independent, so there is little pH drift during experiments in which Reaction 1 is dominant. The second reaction involves aqueous  $\text{Fe}^{2+}$  and takes two steps:



The pH-time relationships for several experiments are shown in Figure 3. At pH 6 and 7, Reaction 1 dominates, as indicated by the constancy of pH with time. The cause of the gradual pH drop in Run 15 is not clear, but might have been due to air contamination (causing oxidation of the  $\text{H}_2\text{S}$ ) or pH electrode drift, although electrode instability was not a common problem. Run 14, which used  $P_{\text{H}_2\text{S}} = 0.5$  bar showed no detectable variation of pH with time.

The pH in Runs 11 and 13 rose rapidly, then dropped back to a steady level for the remainder of the experiment. This type of behavior may be explained by the initial, temporary dominance of Reaction 2a. As Reaction 1 slowly coated the iron with mackinawite, Reaction 2a became inhibited. Furthermore, once FeS nucleation occurred, Reaction 2b became dominant and the pH began to drop. The pH then leveled off to a constant value controlled by Reactions 2a and 2b and FeS saturation. At the pH reversal in some of the runs, a darkening of the solution occurred, caused by the nucleation and growth of FeS.

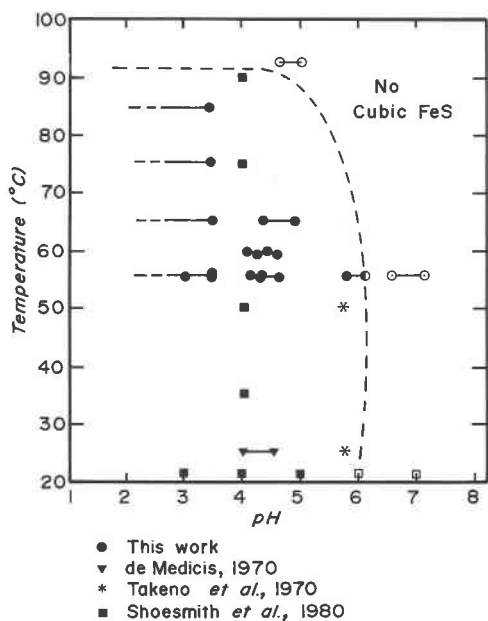


Fig. 4. The conditions of formation of cubic FeS. Filled symbols = cubic FeS present, half-filled symbols = possible cubic FeS, open symbols = cubic FeS absent.

A very low starting pH resulted in a lively effervescence of  $H_2$  and a steady rise in pH throughout the duration of the experiment. This behavior reflects the dominance of Reaction 2a to the degree that, even after FeS saturation was reached, the rate of FeS precipitation (Reaction 2b) was slower than the rate of  $Fe^{2+}$  production (Reaction 2a) for the duration of the experiment. Reaction 2a was not hindered because the high solubility of mackinawite at those low pH values prevented passivation of the metal surface by a mackinawite coating.

The textures of the products also reflect the proposed mechanisms. The tendency of a growing crystal to produce well-developed crystal faces increases as the difference between the surface tensions of the crystal and the host phase increase (Spry, 1969, p. 145). Therefore, a crystal growing from an aqueous solution will often have well-developed faces, whereas a crystal growing by replacement of another solid phase will usually be anhedral. Troilite and cubic FeS produced in our experiments were euhedral crystals, substantiating their proposed precipitation from aqueous phases via Reaction 2b. Cubic FeS formed modified tetrahedra (occasionally twinned on  $\{111\}$ ) and cubes (Fig. 1). Troilite formed hexagonal plates, prisms, and blades, and twins were common (cf. Takeno et al., 1970, Figs. 1 and 2). Mackinawite formed by Reaction 1 and solid-state conversion of aged cubic FeS as indicated by the rims of anhedral mackinawite replacing the iron grains

(Fig. 2) and as oriented intergrowths in aged cubic FeS (Fig. 1).

### SUMMARY AND CONCLUSIONS

Metastable cubic FeS forms as a product of the corrosion of iron metal in  $H_2S$ -rich aqueous solutions below pH 6 and at temperatures below  $92^\circ C$  at 1 bar total pressure (Fig. 4). It is associated with mackinawite ( $FeS_{1-x}$ ) and troilite (hexagonal FeS) with the ratio of mackinawite to troilite increasing with pH. The rate of formation of cubic FeS increases with decreasing pH and increasing temperature, but the best-formed crystals grow between pH 4 and 5 at temperatures between 35 and  $60^\circ C$ . The phase is metastable with respect to mackinawite and troilite and converts to mackinawite within hours to several days after formation. The spontaneous conversion of cubic FeS to mackinawite, and their similar compositions, suggest that they might be polymorphs. Investigations of the relationship between cubic FeS and mackinawite, and the effects of other transition metals on the stability of cubic FeS, remain to be done.

Cubic FeS has not yet been found in nature. The metastable nature of the phase and its short persistence even at ambient temperature make it unlikely that cubic FeS will be found in a natural occurrence. However, it may occur as a corrosion product or byproduct in low-temperature experimental studies in which metallic iron and aqueous  $H_2S$  are present. Even if the cubic FeS crystals have not been preserved, mackinawite pseudomorphs after cubic FeS may provide evidence of their former existence.

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