

The stereochemistry of iron sulfides—a structural rationale for the crystallization of some metastable phases from aqueous solution¹

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Abstract

Stereochemical and topological arguments are used to rationalize the metastable occurrence of mackinawite and marcasite in laboratory experiments. The dimeric species, $(\text{FeS})_2$ and $(\text{FeS}_2)_2$, are postulated as intermediates in the crystallization of mackinawite and marcasite, respectively.

Introduction

The only stable binary solids in the Fe-S system above 200°C and near ambient pressure are the pyrrhotites, Fe_{1-x}S (including troilite, FeS) and pyrite, FeS_2 . Several other phases, at least some of which are metastable, occur widely at lower temperatures in both natural and artificial environments (Ward, 1970; Power and Fine, 1976). Many workers have studied the synthesis and interconversion of these phases (e.g. Berner, 1962, 1964, 1967; Rickard, 1969; Takeno *et al.*, 1970; Rising, 1973; Taylor *et al.*, 1979a,b; Shoesmith *et al.*, 1980; Wikjord *et al.*, 1980). In this paper, stereochemical arguments are used to postulate crystallization mechanisms for some iron sulfides. Intermediates proposed in these mechanisms may exist in solution, or they may occur only at surfaces. Similar concepts were first proposed by Bloom (1939). This work was part of an investigation of corrosion and deposition phenomena in Canadian Girdler-Sulfide heavy-water production plants.

Discussion

Iron monosulfides—mackinawite, troilite, and cubic FeS

A striking feature of the low-temperature formation of iron sulfides from aqueous solution is the frequent occurrence of mackinawite. It is typically the sole crystalline product of precipitation of ferrous ions by H_2S or its salts below 100°C, in the absence

of oxidants (Berner, 1964, 1967; Rickard, 1969). It also occurs widely in nature (e.g. Evans *et al.*, 1964; Schot *et al.*, 1972) and as a corrosion product on iron or carbon steel exposed to aqueous H_2S (Berner, 1962, 1964; Takeno *et al.*, 1970; Wikjord *et al.*, 1980; Shoesmith *et al.*, 1980). Pyrrhotites are not readily prepared from aqueous solution below 100°C, although troilite does occur as a low-temperature corrosion product (Takeno *et al.*, 1970; Wikjord *et al.*, 1980; Shoesmith *et al.*, 1980). Cubic FeS is known only as a corrosion product (Médicis, 1970a,b; Takeno *et al.*, 1970; Wikjord *et al.*, 1980; Shoesmith *et al.*, 1980).

The sluggish nature of most phase transformations in this system at low temperatures hinders the determination of equilibrium phase relations. One exception is the transformation of cubic FeS to mackinawite, which occurs spontaneously at room temperature, demonstrating that cubic FeS is not a stable phase (Médicis, 1970a,b; Takeno *et al.*, 1970; Shoesmith *et al.*, 1980).

The upper limit of thermal stability of mackinawite is about 130°C; small amounts of Ni and Co incorporated in the structure tend to enhance its stability (Takeno, 1965; Clark, 1966; Takeno and Clark, 1967). It is not known whether this limit reflects a true thermodynamic stability field, or kinetic limits on the transformation of a metastable phase.

Solubility studies (Berner, 1967; Tewari and Campbell, 1976; Tewari *et al.*, 1978) demonstrate that solutions which are saturated with respect to H_2S and synthetic mackinawite at ambient temperature and pressure are supersaturated with respect to troil-

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ite. However, since mackinawite usually has a metal:sulfur ratio greater than 1.00, the possible existence of a low-temperature stability field is not ruled out. Nonetheless, mackinawite is frequently formed under conditions where it is metastable with respect to troilite and/or more sulfur-rich sulfides.

Figure 1a shows the crystal structure of mackinawite (Berner, 1962; Taylor and Finger, 1971). Iron atoms occupy every site in alternate layers of tetrahedral interstices in a cubic close-packed (c.c.p.) sulfur sub-lattice. The Fe-S bonding network consists of interconnected Fe_2S_2 rings, and Fe-Fe bonding also occurs within the metal-atom layers. The Fe_2S_2 rings, and similar structural units discussed below, are not discrete moieties, but they are recognizable elements of the structural network.

Cubic FeS (Fig. 1b) is isostructural with sphalerite (Médicis, 1970; Takeno *et al.*, 1970), and differs from mackinawite in the distribution of iron atoms, which occupy one half of each layer of tetrahedral holes in the c.c.p. sulfur sub-lattice. The close structural relationship between these phases accounts for the ease of conversion of cubic FeS to mackinawite, cited above. Cubic FeS contains Fe_3S_3 , but not Fe_2S_2 rings, and there are no Fe-Fe bonds.

The structure of troilite is derived from the NiAs type. Both Fe and S are six-coordinate, and iron atoms are drawn together into triangular clusters. The topology of the structure is complex; both Fe_2S_2 and Fe_3S_3 rings can be discerned (Fig. 2) (Evans, 1970).

The ease of precipitation of fine-grained ($<1 \mu\text{m}$) mackinawite demonstrates that homogeneous nucleation of this phase is facile. This nucleation presumably proceeds by complexation of Fe^{2+} and SH^- (1),

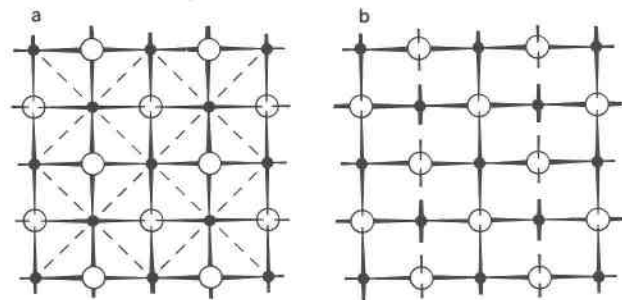


Fig. 1. (a) Projection of four unit cells of the crystal structure of mackinawite down the *c* axis. Large open and small closed circles represent S and Fe atoms, respectively; this convention is used in all figures. Dashed lines delineate Fe-Fe interactions. (b) Projection of the crystal structure of cubic FeS down the *a* axis. Broken bonds proceed to Fe atoms above and S atoms below those shown.

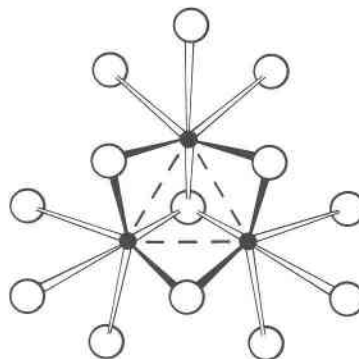
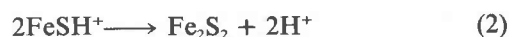


Fig. 2. Part of the crystal structure of troilite, showing the environment of one Fe_3 cluster. Interactions with neighboring Fe_3 clusters are omitted. The solid bonds delineate an Fe_3S_3 ring which may be a precursor to troilite crystallization. Dashed lines show Fe-Fe interactions.

and subsequent polymerization of FeSH^+ with elimination of protons and water of solvation. A similar mechanism has been proposed for the growth of thioferrite salts from aqueous solution (Taylor and Shoemsmith, 1978). Few SH^- complexes of transition metals are known, but CrSH^{2+} has been reported (Ramasami and Sykes, 1976). If the initial polymerization step is a dimerization (2), then further association of the dimer is readily envisaged to lead to the layer structure of mackinawite by a simple tessellation, with formation of additional bonds.



Although Fe_2S_2 rings are also present in the troilite structure, the greater complexity of their interconnection may account for the evident difficulty of troilite nucleation. Analogous situations, in which phases with high coordination numbers and complex structural networks are more difficult to crystallize than metastable polymorphs with simpler structural networks, are common, *e.g.*, GeO_2 (Rochow, 1973, p. 26), NaFeO_2 (Okamoto, 1968).

When troilite occurs as a corrosion product on iron or carbon steel in aqueous H_2S at low temperatures, it appears to arise from high local iron concentrations at the corroding surface (Shoemsmith *et al.*, 1980). A trimeric precursor, Fe_3S_3 , may be involved in its nucleation.

The absence of close Fe-Fe contacts in cubic FeS

probably results in a low activation energy for its nucleation, but its low stability confines its occurrence to conditions of high supersaturation and short reaction times. Like troilite, its formation as a corrosion product is associated with high local supersaturation. There is evidence for competition between these two phases as sinks for dissolved iron at corroding surfaces (Shoosmith *et al.*, 1980).

Iron disulfides—pyrite and marcasite

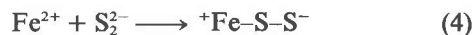
Both pyrite and marcasite have compositions very close to $\text{FeS}_{2.00}$. Buerger (1934) suggested that an apparent slight sulfur-deficiency of marcasite (*ca.* $\text{FeS}_{1.985}$) might be related to its mechanism of formation. However, Kullerud and Yoder (1959) concluded that the two phases are true dimorphs of $\text{FeS}_{2.00}$. Although the possible occurrence of a low-temperature stability field for marcasite cannot be completely ruled out, there is evidence that it is often formed under conditions where it is metastable with respect to pyrite. It may well be metastable under all conditions (Rising, 1973).

Recent work by Shoosmith *et al.* (1979), Taylor *et al.* (1979b), and Wikjord *et al.* (1980) showed that pyrite is the sole ultimate product of reaction of aqueous H_2S with iron, carbon steel, troilite, or mackinawite at 100–160°C, in the absence of oxidants other than H_2S . However, in the presence of oxygen or sulfur, or under the application of an anodic current at the crystallization site, marcasite is formed in addition to pyrite. Formation of a metastable phase under these enhanced oxidizing conditions is not unexpected. These observations are consistent with the literature, as reviewed by Rising (1973).

Both the pyrite and marcasite crystal structures are

three-dimensional networks of inter-linked Fe and S_2 moieties (Brostigen and Kjekshus, 1969; Brostigen *et al.*, 1973 and references therein). In each structure, iron has approximate octahedral coordination by sulfur, and sulfur has a distorted tetrahedral coordination by three iron atoms and the second sulfur atom of the S_2 unit. The two structures differ in their network geometries, and can be described in terms of fused Fe–S ring systems (Rising, 1973).

The pyrite structure consists entirely of Fe_2S_3 rings, I (Figs. 3a and 4), whereas marcasite contains Fe_2S_2 and Fe_2S_4 rings, II and III (Figs. 3b and 4) as well. There is no significant Fe–Fe bonding in either structure. Clearly, a crystallization mechanism which favors the formation of rings II or III will favor formation of marcasite rather than pyrite, as outlined by equations (4) to (6).



Although $(\text{FeS}_2)_2$ could have any of the structures I to III, III is most likely on the basis of the structural chemistry of related species. Six-membered polysulfide rings are known in $(\text{NH}_4)_2\text{Pt}(\text{S}_3)_3 \cdot 2\text{H}_2\text{O}$ (Jones and Katz, 1967) and $(\pi\text{-C}_5\text{H}_5)_2\text{TiS}_5$ (Koeppel *et al.*, 1968). Units of the type R–S–S–R are generally more stable than $\text{R}_2\text{S}=\text{S}$, with the exception of S_2F_2 (Schmidt and Siebert, 1973, p. 843–844). An example of a solution species containing an M–S–S–M linkage, $[\text{Cr-S-S-Cr}]^{4+}$, has recently been reported (Ramasami *et al.*, 1976). If III has a chair configuration, as do the rings in the compounds mentioned above and in S_6 (Donohue *et al.*, 1961), then a simple

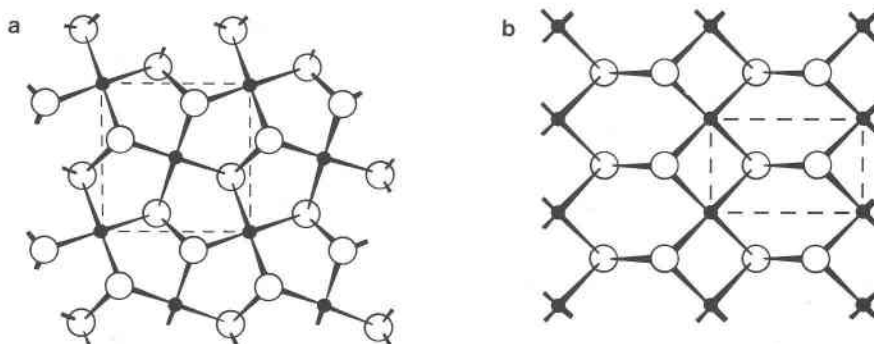


Fig. 3. (a) Part of the crystal structure of pyrite, viewed in projection down the a axis, showing the system of fused Fe_2S_3 rings. Bonds nearly vertical to the projection are omitted for clarity. The dashed lines delineate the unit cell. (b) Part of the crystal structure of marcasite, viewed in projection down the a axis, showing the system of fused Fe_2S_2 and Fe_2S_4 rings. Some bonds are omitted for clarity, as in Fig. 3a. The dashed lines delineate the unit cell; b - and c -axis projections closely resemble Fig. 3a.

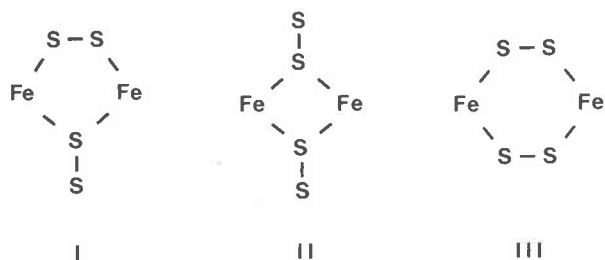


Fig. 4. Possible structures for an $(\text{FeS}_2)_2$ dimer.

three-dimensional tessellation of such units leads directly to the marcasite structure (Fig. 3b). This involves the formation of additional Fe-S bonds, but no further rearrangement of the structural net.

High concentrations of S_2^{2-} would favor the reaction sequence (4) to (6), although not necessarily to the exclusion of pyrite precipitation. This is consistent with the observations that oxidizing conditions, which favor polysulfide generation, also favor marcasite formation. It is noted that the equilibrium concentration of S_2^{2-} in the system $\text{H}_2\text{S}-\text{S}-\text{H}_2\text{O}$ is extremely low at $\text{pH} = 4$ (Giggenbach, 1972; Teder, 1971). However, the same structural arguments apply if the S_2 moiety is generated only as a surface species at the crystallization site, or if FeS_2 monomer is produced by an alternative route.

Unfortunately, iron sulfide formation is not amenable to most probes which might test the hypotheses put forward here. Some relevant information might be obtained from a matrix isolation spectroscopic study of the reactions of Fe atoms with S atoms and S_2 molecules, or from the chemistry of other systems in which similar polymorphism occurs.

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