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# CRYSTALLIZATION OF PYRITE FROM DEOXYGENATED AQUEOUS SULFIDE SOLUTIONS AT ELEVATED TEMPERATURE AND PRESSURE

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## ABSTRACT

Pyrite crystallized on the walls of a titanium autoclave containing a corroding carbon steel coupon and an aqueous solution of hydrogen sulfide at 160°C and 1.5 MPa initial pressure. External oxidants were excluded from the system. The pyrite formed well–developed cubes and octahedra indicating growth directly from solution. It appears that the disulfide ion ($S_2^{2-}$) required for pyrite crystallization was produced by an electro-oxidation reaction at the titanium surface, the reduction reaction involving the formation of hydrogen gas.

## SOMMAIRE

La pyrite a cristallisé sur les parois d'un autoclave en titane contenant un disque d'acier au carbone en voie de corrosion dans une solution aqueuse d'hydrogène sulfuré à 160°C et sous pression initiale de 1.5 MPa. Les oxydants externes étaient exclus du système. Cette pyrite se présente en cubes et en octaèdres bien développés ce qui indique une croissance au sein de la solution. L'ion bisulfure ($S_2^{2-}$) requis pour produire de la pyrite doit résulter d'une réaction électro-oxydante à la surface du titane, puisque toute réaction réductrice impliquerait la formation d'hydrogène gazeux.

(Traduit par la Rédaction)

## INTRODUCTION

Pyrite, cubic $FeS_2$, has a crystal structure closely related to the rocksalt-type (Wells 1962; Wyckoff 1965). Sulfur is bonded in pairs to form the disulfide ion ($S_2^{2-}$) such that each atom has a formal oxidation number of −1. During pyrite formation from sulfur species having an oxidation number of −2, e.g. $H_2S$, it is clear that an oxidation process must occur. There has been considerable geochemical interest in the formation of pyrite in natural aqueous environments where hydrogen sulfide is formed by the action of sulfate–reducing bacteria. Several investigators have concluded that an external oxidizing agent is required to produce $FeS_2$ in aqueous environments at low temperatures and pressures. The oxidant may be oxygen from the atmosphere, ferric iron in a reactant, or free sulfur produced by secondary reaction as shown by Berner (1964,1967), Rickard (1968,1969) and Roberts (1969).

In this note, we report preliminary observations of the crystallization of pyrite from aqueous solutions of hydrogen sulfide, but in the absence of external oxidants. These observations were made during on-going investigations into the mechanism of corrosion of carbon steel under the conditions of the Girdler-Sulfide process (Bebbington & Thayer 1959; Rae 1971) for producing heavy water. In this process, temperatures reach 160°C and $H_2S$ pressures are as high as 2 MPa. The main purpose of our corrosion studies is to examine the products formed at a carbon steel-aqueous hydrogen sulfide interface, but this aspect will be dealt with in a subsequent publication. We report here only our observation of pyrite crystal growth at a titanium*–aqueous hydrogen sulfide interface at 160°C and discuss the significance of this observation.

## EXPERIMENTS

The corrosion experiments were conducted in 1–liter titanium autoclaves containing a single carbon steel disc (51 mm in diameter by 1.6 mm thick) mounted on a stainless steel shaft. The disc was prepared by degreasing, buffing, and treating with 13% hydrochloric acid for 30 minutes. The autoclave was initially charged with 650 ml of triple–distilled water, purged with nitrogen (Linde, 30 ppm $O_2$), then purged with hydrogen sulfide (Matheson, CP grade), and finally pressurized to 1.5 MPa with the hydrogen sulfide gas. During each run, the disc was electrically insulated from the stainless steel shaft by Teflon spacers and rotated at a frequency of 1.7 Hz. Runs were conducted for periods ranging from one hour to one month with the temperature regulated at 160±5°C. These conditions result in an initial pH of ap-

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*Strictly speaking, the interface involves an oxide of titanium which may undergo sulfidation after prolonged exposure to aqueous $H_2S$.

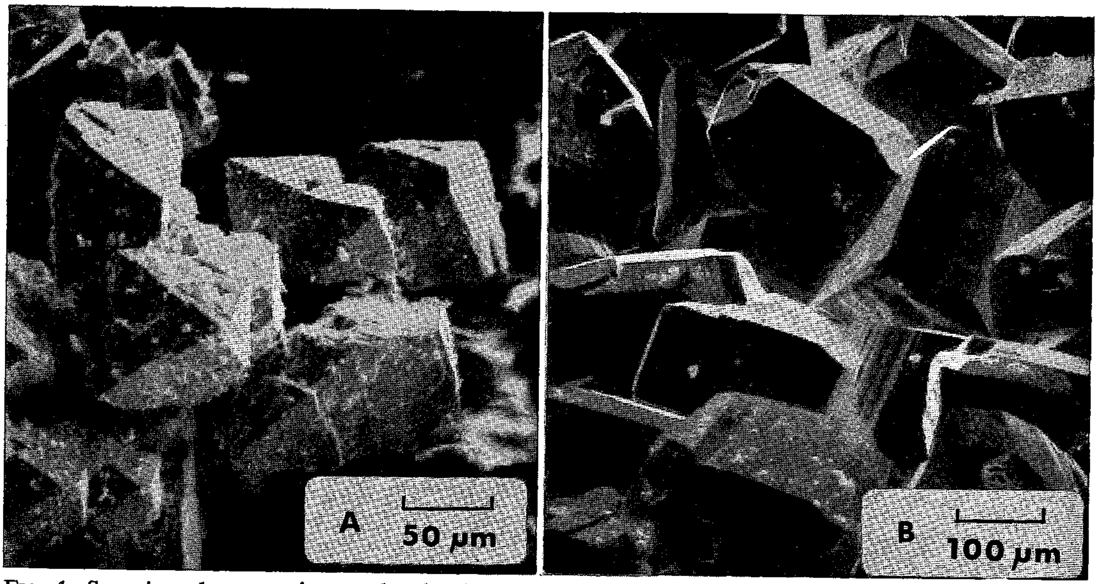

FIG. 1. Scanning electron micrographs showing crystals of pyrite, grown on the wall of a titanium autoclave from an aqueous solution of $H_2S$ (total initial pressure 1.5 PMa) during 1-month experiments at 160°C. The octahedrons shown in (a) formed when the autoclave was recharged several times with $H_2S$ (their yield was about 2 g); the intergrown truncated cubes shown in (b) formed when the $H_2S$ was not replenished (the yield in this case was about 10 g). These forms are well-established variants of the crystal habit of pyrite (Sunagawa 1975).

proximately 4.0 at 160°C and an estimated initial partial pressure of oxygen of 0.5 Pa. In most of the experiments, the initial charge of $H_2S$ was not replenished; however, in a few cases, it was recharged periodically by a bleed-and-feed procedure.

After each experiment, the autoclave was depressurized and drained and the identity and morphology of the crystals adhering to the titanium wall were established using standard X-ray diffraction and scanning electron microscopic techniques. In all cases, pyrite crystals had grown at the wall of the autoclave. Their habit varied from regular octahedra to truncated cubes as depicted in Figure 1.

The well-defined morphology of these crystals suggests that they formed directly from ionic species rather than by reaction of an intermediate lower sulfide, such as mackinawite (tetragonal $FeS_{1-x}$), with dissolved $H_2S$ or $HS^-$. Because the crystals adhered to the wall of the autoclave and neighboring crystals were often extensively intergrown as shown in Figure 1, we conclude that growth occurred directly on the titanium surface.

The amount of pyrite formed at the titanium surface increased with time. The quantity formed after one hour was negligible and only milligram amounts were present after one day. However, after one month, about 10 g of $FeS_2$ formed when the $H_2S$ was not replenished and about 90% of the initial charge of $H_2S$ was converted to $H_2$. When the $H_2S$ was replenished several times during the experiment, the yield of $FeS_2$ was reduced because of diminished iron release from the carbon steel surface. This implies that a more protective sulfide film was formed on the carbon steel disc when the $H_2S$ pressure was maintained near its initial value. Consequently, the rate of formation of ferrous ions at the iron disc became rate-determining in the sequence,

$$\begin{tikzcd}
\text{Fe (carbon steel)} \arrow[d, "\text{SULFIDATION}"] \arrow[dd, bend right] \\
\text{FeS}_x\text{ (surface)} \arrow[d, "\text{DISSOLUTION}"] \\
\text{Fe}^{2+}\text{ (solution)} \arrow[d, "\text{TRANSPORT}"] \\
\text{Fe}^{2+}\text{ (titanium wall)}
\end{tikzcd} \qquad (1)$$

Hydrogen was identified as a reaction product by mass spectrometric analysis of residual gases. Also, the pressure in the autoclave increased during the course of the experiment because $H_2$ is less soluble than $H_2S$ under these conditions. One source of hydrogen production is certainly the corrosion of the carbon steel coupon, but, as discussed later, hydrogen may also be formed during $FeS_2$ synthesis at the titanium wall.

Although the trace quantities of oxygen present in the reactants may not have been purged completely from the system, there is no doubt that the level of residual oxygen (estimated $\leq$1–2 μg) cannot account for the large quantities of pyrite formed in many of our experiments. Hence, we suggest that the mechanism of formation of $S_2^{2-}$ at 160°C in these experiments is different than that at lower temperatures, where external oxidants are apparently required for pyrite to form at measurable rates (Berner 1964,1965; Rickard 1968,1969; Roberts 1969).

## INTERPRETATION

The mechanism of pyrite formation at the titanium wall has not yet been established. We tentatively propose a mechanism involving the electro-oxidation of a sulfide species such as the hydrosulfide ion at the titanium surface, the counter reaction being the reduction of hydrogen ions to liberate $H_2$ gas

anodic reaction: $2HS^- \rightarrow S_2^{2-} + 2H^+ 2e$ (2)

cathodic reaction: $2H^+ + 2e \rightarrow H_2$ (3)

(Equation (2) may involve the electrochemical formation of free sulfur and the concomitant formation of higher polysulfides [$S_n^{2-}$, $n>2$]). The $S_2^{2-}$ ions produced in equation (2) react with $Fe^{2+}$ ions transported from the corroding carbon steel (equation (1)) according to the reaction $Fe^{2+} + S_2^{2-} \rightarrow FeS_2$. It is not known whether the $S_2^{2-}$ ions are incorporated directly into the $FeS_2$ lattice, or whether they go into solution prior to incorporation. Another possibility which has not been ruled out, however, involves the formation of free sulfur by the thermal dissociation of $H_2S$: $H_2S \rightleftarrows H_2 + S^0$. The free sulfur so produced could then facilitate the formation of pyrite by way of solution reactions involving polysulfides as proposed by Rickard (1975). $H_2S$ decomposition has been shown to occur at temperatures of 140–200°C if one or other of the decomposition products is removed (Holtslander 1975). In these experiments, pyrite formation could effectively remove the free sulfur.

It is also noteworthy that iron monsulfides can be converted to the disulfide by heating them in oxygen-free solutions of $H_2S$. Korolev & Kozerenko (1965) converted a freshly precipitated sulfide, presumably mackinawite, to both pyrite and marcasite (orthorhombic $FeS_2$) at temperatures between 90°C and 240°C. Similar experiments in this laboratory have transformed troilite (hexagonal FeS) to pyrite in oxygen-free solutions at temperatures greater than 130°C within 1-2 weeks. Although these transformation studies support the thesis that pyrite can form at higher temperatures without the action of external oxidants, it is not clear whether the transformations involve prior dissolution of the lower sulfides.

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