

# Pyrite formation linked with hydrogen evolution under anaerobic conditions

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THE formation of pyrite ( $\text{FeS}_2$ ), an important factor in determining the global redox balance<sup>1</sup>, has recently attracted biological interest as a possible direct source of energy for early life<sup>2-5</sup>. The theory implies that carbon dioxide fixation, in competition with hydrogen formation, can serve as the electron sink for pyrite formation and it seems to be supported by the detection of minute grains of pyrite and iron sulphides inside bacteria<sup>5-8</sup>. Yet it clashes with the conventional assumption that elemental sulphur or a sulphur equivalent (polysulphide or thiosulphate) is the mandatory oxidant for pyrite formation<sup>9,10</sup>. It has been stressed that the reaction  $\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$  (with  $\text{H}^+$  as the oxidant) has "never been observed . . . during several years of experimentation"<sup>10</sup>. Here we report the formation of both pyrite and molecular hydrogen under fastidiously anaerobic conditions in the aqueous system of FeS and  $\text{H}_2\text{S}$ .

Of the geochemical environments in which pyrite can form, two are of particular biological significance: sedimentary systems, in which pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) is extremely rare<sup>11</sup> and in which pyrite seems to be formed from amorphous FeS<sup>10,12</sup>, and hydrothermal systems in which pyrite may be formed not only from amorphous FeS but also from pyrrhotite<sup>11</sup>. We have modelled these by reacting aqueous  $\text{H}_2\text{S}$  at 100 °C for 14 days, under strictly anaerobic and nearly neutral conditions, either with amorphous FeS, precipitated from aqueous  $\text{FeSO}_4$ , or with synthetic (metal basis) pyrrhotite. Our experiments show a linkage between pyrite formation (ascertained by X-ray diffraction) and hydrogen evolution (determined by gas chromatography). Typical results are shown in Table 1 and in Figs 1-3. The pyrrhotite crystals (runs 1, 2) seem to acquire a surface coating of pyrite as indicated by the hollow shells that remain if the

TABLE 1 Products of anaerobic FeS- $\text{H}_2\text{S}$  systems

No.	Starting materials		Products after 14 days	
	FeS	$\text{H}_2\text{S}$ (mmol)	$\text{H}_2$ ( $\mu\text{mol}$ )	Mineral products
1a	pyrrhotite 99%*	2	23 ± 3.5	pyrite
1b	(200 mg)	—	0.25	—
2a	pyrrhotite 99.99%*	2	18	pyrite
2b	(200 mg)	—	0.2	—
3a	FeS amorphous, wet†	2	15 ± 4	pyrite + mackinawite
3b	(precipitated with $\text{H}_2\text{S}$ ) (2 mmol)	—	0	—
4a	FeS amorphous, dried‡	2	40 ± 2.5	pyrite + mackinawite
4b	$\text{Na}_2\text{S}$ (200 mg)	—	0.2	—
5	—	2	0.2	—
6	—	—	0	—

All procedures were carried out under  $\text{CO}_2$ . The solutions were prepared from doubly distilled water, through which  $\text{N}_2\text{-CO}_2$  had been bubbled for 2 h. Serum bottles (120 ml) were charged with the suspension of FeS, stoppered and supplied with a  $\text{N}_2\text{-CO}_2$  atmosphere (80:20, 100 kPa) and then charged with an injection of 2 mmol  $\text{H}_2\text{S}$  gas and adjusted to pH 6.5 with NaOH. The  $\text{H}_2\text{S}$  gas was prepared by adding 50%  $\text{H}_2\text{SO}_4$  to  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  in an evacuated serum bottle. During incubation for 14 d at 100 °C in a rotary shaker (100 r.p.m.), the serum bottles were kept in anaerobic cylinders with an  $\text{N}_2\text{-CO}_2$  atmosphere (80:20, 180 kPa).  $\text{H}_2$  was determined by gas chromatography (Hewlett Packard 5890). A packed column filled with Molecular Sieve 5A (Supelco) was used (injection temperature, 190 °C; oven temperature, 140 °C; detection temperature, 220 °C; carrier gas,  $\text{N}_2$ ). For runs 1, 3 and 4, the averages and the standard deviations of the  $\text{H}_2$  measurements of three repeats of the reaction are given. Run 2 was not repeated. The traces of  $\text{H}_2$  in control runs 1b, 2b and 4b are barely above the background (detection limit 0.1  $\mu\text{mol}$ ) and may be due to the reaction  $2\text{FeS} + 2\text{H}^+ \rightarrow \text{FeS}_2 + \text{Fe}^{2+} + \text{H}_2$ . In control run 5, the trace of  $\text{H}_2$  may be due to thermal decomposition ( $\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + \text{S}$ ). The solid phase was dried in an anaerobic chamber ( $\text{N}_2:\text{H}_2 = 95:5$ ) and the mineral composition was analysed by X-ray diffraction.

\* Pyrrhotite (99% or 99.99%) (Johnson Matthey) was suspended in 10 ml  $\text{H}_2\text{O}$ . Both pyrrhotites were free of elemental iron as indicated by the lack of hydrogen evolution upon dissolution in concentrated HCl.

† Amorphous wet FeS was precipitated directly in the serum bottles used in the experiment by adding 2 mmol  $\text{H}_2\text{S}$  gas to 10 ml 0.2 M  $\text{FeSO}_4$  which had previously been freed of  $\text{Fe}^{3+}$  by treatment with elemental zinc at 60 °C for 2 h.

‡ Amorphous, dried FeS was prepared in an anaerobic chamber by adding  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (130 g) to 0.6 M  $\text{FeSO}_4$  that had not been freed of  $\text{Fe}^{3+}$  filtering the precipitate, washing it with  $\text{H}_2\text{O}$  and drying it under  $\text{CO}_2$ . The dried precipitate was suspended in 10 ml  $\text{H}_2\text{O}$ .

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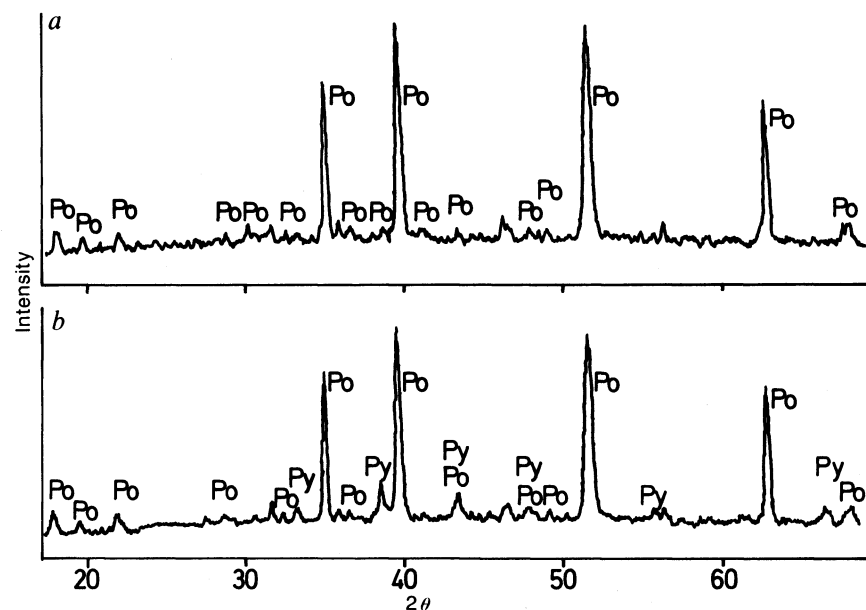


FIG. 1 X-ray diffraction pattern of pyrrhotite (99%; Johnson Matthey). a, Starting material. b, After incubation at 100 °C for 14 d in aqueous solution in the presence of  $\text{H}_2\text{S}$ . Po, pyrrhotite; Py, pyrite;  $2\theta$ , angle of reflection for  $\text{Co K}\alpha$  radiation.

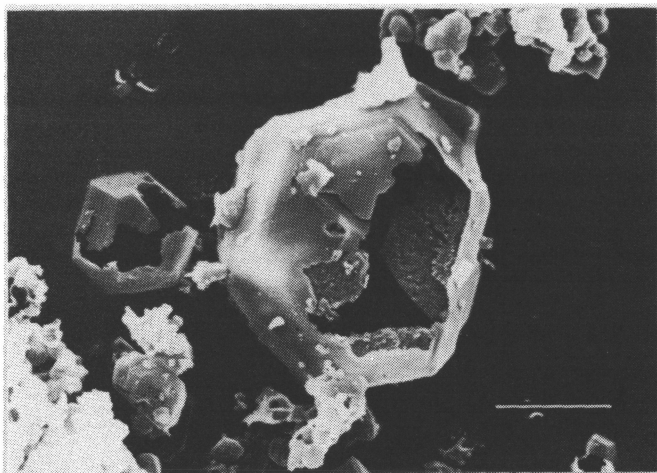


FIG. 2 Scanning electron micrograph of pyrite shells with pyrrhotite pseudomorphs (run 1a) after dissolution of pyrrhotite by treatment with 6N HCl. Scale bar, 0.5  $\mu\text{m}$ .

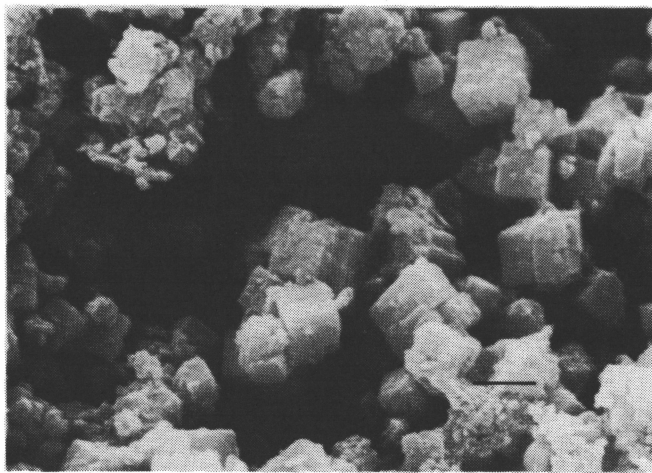
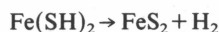
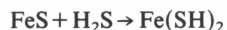


FIG. 3 Scanning electron micrograph of cubic pyrite crystals formed from amorphous FeS (run 4a). Scale bar, 1  $\mu\text{m}$ .

pyrrhotite is leached out with HCl (Fig. 2). Amorphous FeS, precipitated in the absence of  $\text{Fe}^{3+}$  and of sulphur or sulphur equivalents (run 3), seems to produce pyrite in the form of discrete crystals (Fig. 3) as well as some mackinawite ( $\text{FeS}_{1-x}$ ). Hydrogen evolution is also observed with an amorphous FeS precipitated with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (containing polysulphide) without removing  $\text{Fe}^{3+}$  (run 4).

The results may best be represented by the following overall reactions



The reaction mechanism may be a concerted four-centre reaction with a simultaneous formation of the covalent bonds of  $\text{H}_2$  and  $\text{S}_2^{2-}$ , but radical or hydride involvement cannot be excluded. The reaction of pyrrhotite seems to be a surface redox reaction with a concomitant rearrangement of the  $\text{S}^{2-}/\text{S}_2^{2-}$  lattice and a diffusion of ferrous ions. The electron transfer may well be promoted by the semiconductor properties of pyrite.

The considerable variety of geochemical environments that give rise to pyrite may indicate a variety of pyrite-forming pathways using different oxidants. By contrast, the conventional assumption that pyrite formation requires not only  $\text{H}_2\text{S}$  (for FeS formation) but also elemental sulphur or polysulphide as the oxidant placed severe restrictions on the possible geochemical explanations of pyrite formation. In particular, it was difficult to explain sedimentary pyrite formation under anaerobic conditions. For example, Boesen and Postma<sup>12</sup> demonstrated that the freshwater *Ancylus* clay in the Gotland deep of the Baltic Sea (deposited 9,200–7,700 years ago) is presently being sulphidized by the downward diffusion of  $\text{H}_2\text{S}$  from the overlying marine muds. In this process the ferrous ions in the clay are first converted into FeS and subsequently into  $\text{FeS}_2$ . On this conversion they comment "... unless a hitherto unknown oxidant exists the only explanation seems to be either downward diffusion of polysulfides or that the FeS/FeS<sub>2</sub> distribution reflects a historical change [of the redox conditions]. The latter possibility seems, however, unlikely ...." Our results show that the system FeS– $\text{H}_2\text{S}$  is a powerful reducing agent and that  $\text{H}^+$  can indeed serve as oxidant for pyrite formation. Thus, the somewhat implausible assumption of a slow diffusion of metastable polysulphides in, for example, the sediments of the Gotland deep is no longer required.

The pyritization of fossils is also a highly variable and complex process. For some of these pyritization processes, our results seem to offer straightforward explanations if we assume: (1) diffusion of dissolved ferrous ions and  $\text{H}_2\text{S}$ , at concentrations too small for FeS precipitation (at lower pH, for example) into the site of fossilization; (2) the formation of  $\text{FeS}_2$  and  $\text{H}_2$  under the pH conditions of the site of fossilization; (3) the diffusion of  $\text{H}_2$  out of the site of fossilization. As a variation of this scheme, we may assume diffusion of sulphate ions into the site of fossilization and the formation of hydrogen sulphide by organotrophic sulphate-reducing bacteria at the site of fossilization. In any case, the implausible assumption of a conversion of hydrogen sulphide into elemental sulphur<sup>13</sup> under the reducing conditions at the site of fossilization is no longer necessary.

The production of  $\text{H}_2$  in nature has previously been attributed to biogenic origins, geothermal exhalations and tropospheric decompositions<sup>14</sup>. Our results establish the system FeS– $\text{H}_2\text{S}$  as an alternative source of hydrogen. This source is ubiquitous, which correlates well with the ubiquitous occurrence of hydrogen-consuming bacteria, such as methanogens, sulphur and sulphate reducers and hydrogen-oxidizing bacteria. Finally, our findings suggest that a functional evolutionary connection might exist between the hydrogen-producing system FeS– $\text{H}_2\text{S}$  and the hydrogen-producing iron-sulphur centres of hydrogenases and nitrogenases. □

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