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Pyrite formation linked with hydrogen evolution under anaerobic conditions

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THE formation of pyrite (FeS_2), an important factor in determining the global redox balance[1], has recently attracted biological interest as a possible direct source of energy for early life[2–5]. 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[5–8]. Yet it clashes with the conventional assumption that elemental sulphur or a sulphur equivalent (polysulphide or thiosulphate) is the mandatory oxidant for pyrite formation[9,10]. It has been stressed that the reaction $FeS + H_2S \rightarrow FeS_2 + H_2$ (with H^+ as the oxidant) has "never been observed ... during several years of experimentation"[10]. Here we report the formation of both pyrite and molecular hydrogen under fastidiously anaerobic conditions in the aqueous system of FeS and H_2S.

Of the geochemical environments in which pyrite can form, two are of particular biological significance: sedimentary systems, in which pyrrhotite ($Fe_{1-x}S$) is extremely rare[11] and in which pyrite seems to be formed from amorphous FeS[10,12], and hydrothermal systems in which pyrite may be formed not only from amorphous FeS but also from pyrrhotite[11]. We have modelled these by reacting aqueous H_2S at 100 °C for 14 days, under strictly anaerobic and nearly neutral conditions, either with amorphous FeS, precipitated from aqueous $FeSO_4$, 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-H_2S systems

	Starting materials		Products after 14 days	
No.	FeS	H_2S (mmol)	H_2 (μmol)	Mineral products
1*a*	pyrrhotite 99%*	2	23 ± 3.5	pyrite
1*b*	(200 mg)	—	0.25	—
2*a*	pyrrhotite 99.99%*	2	18	pyrite
2*b*	(200 mg)	—	0.2	—
3*a*	FeS amorphous, wet†	2	15 ± 4	pyrite + mackinawite
3*b*	(precipitated with H_2S) (2 mmol)	—	0	—
4*a*	FeS amorphous, dried‡	2	40 ± 2.5	pyrite + mackinawite
4*b*	Na_2S (200 mg)	—	0.2	—
5	—	2	0.2	—
6	—	—	0	—

All procedures were carried out under CO_2. The solutions were prepared from doubly distilled water, through which N_2-CO_2 had been bubbled for 2 h. Serum bottles (120 ml) were charged with the suspension of FeS, stoppered and supplied with a N_2-CO_2 atmosphere (80:20, 100 kPa) and then charged with an injection of 2 mmol H_2S gas and adjusted to pH 6.5 with NaOH. The H_2S gas was prepared by adding 50% H_2SO_4 to $Na_2S \cdot 9H_2O$ 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 N_2-CO_2 atmosphere (80:20, 180 kPa). 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, N_2). For runs 1, 3 and 4, the averages and the standard deviations of the H_2 measurements of three repeats of the reaction are given. Run 2 was not repeated. The traces of H_2 in control runs 1*b*, 2*b* and 4*b* are barely above the background (detection limit 0.1 μmol) and may be due to the reaction $2FeS + 2H^+ \rightarrow FeS_2 + Fe^{2+} + H_2$. In control run 5, the trace of H_2 may be due to thermal decomposition ($H_2S \rightleftharpoons H_2 + S$). The solid phase was dried in an anaerobic chamber (N_2: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 H_2O. 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 H_2S gas to 10 ml 0.2 M $FeSO_4$ which had previously been freed of Fe^{3+} by treatment with elemental zinc at 60 °C for 2 h.

‡ Amorphous, dried FeS was prepared in an anaerobic chamber by adding $Na_2S \cdot 9H_2O$ (130 g) to 0.6 M $FeSO_4$ that had not been freed of Fe^{3+} filtering the precipitate, washing it with H_2O and drying it under CO_2. The dried precipitate was suspended in 10 ml H_2O.

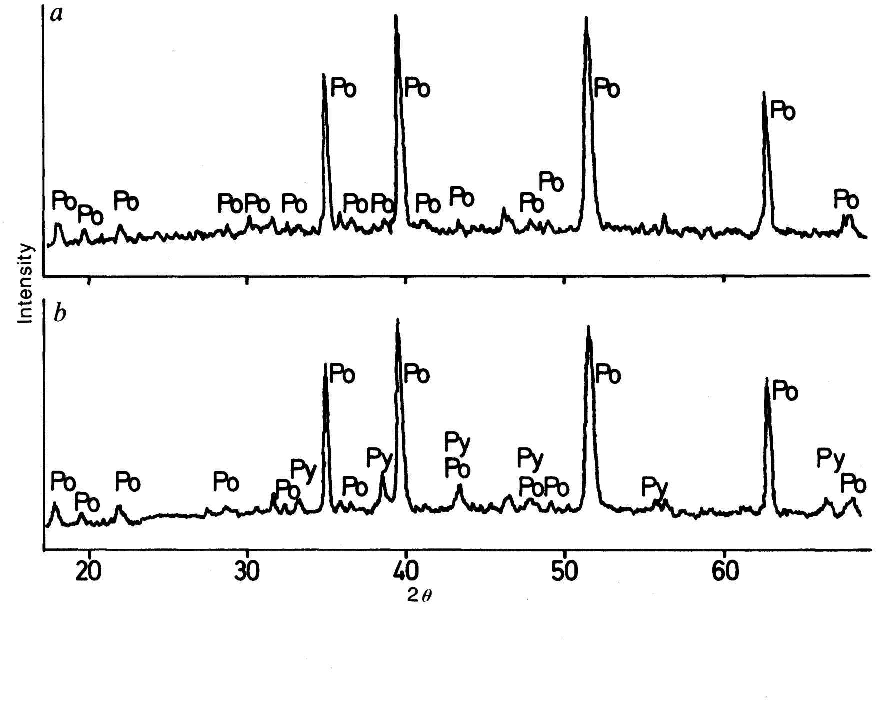

FIG. 1 X-ray diffraction pattern of pyrrhotite (99%; Johnson Matthey). *a*, Starting material. *b*, After incubation at 100 °C for 14 d in aqueous solution in the presence of H_2S. Po, pyrrhotite; Py, pyrite; 2*θ*, angle of reflection for Co K*α* radiation.

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