

In situ determination of the stability of iron monosulphides and kinetics of pyrite formation

L. G. Benning
H. L. Barnes

Pennsylvania State University, Department of Geosciences,
University Park, PA, 16802, USA

Pyrite (FeS_2), the most abundant sulphide in the Earth's crust plays a key role in the global iron and sulphur geochemical cycles. Until recently, it was accepted that in highly reducing, low temperature environments, pyrite formed via an iron monosulphide precursor, which served both as iron source and nucleation site. Either polysulphide or elemental sulphur were assumed to be the sulphur source (Berner, 1967; Rickard, 1975, Wilkin and Barnes, 1996 and references therein). However, recently Rickard (1997), following Drobner *et al.* (1990) postulated the 'H₂S pathway' ($\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$) as the fastest process for pyrite formation in reduced, low temperature environments. This suggestion has stirred controversy due to its implications for primordial metabolic cycles.

To test that hypothesis, new experimental data are presented here on *in situ* nucleation, growth, and stability of iron monosulphides below 100°C and their *in situ* replacement by pyrite. In addition, for the first time equilibrium constants for mackinawite up to 100°C have been calculated. Such data are vital for understanding the overall reaction rates for pyrite formation.

Methods

In situ precipitation, ageing and conversion experiments were conducted under highly reduced, variable pH conditions for up to 4 months. The instantaneous precipitation of iron monosulphides is induced by injecting a known amount of oxygen-free 1 N NaOH into an oxygen-free Fe(II) solution saturated with 100% H₂S_{gas}. The resulting suspension (except in specified 'intentional oxidation' runs) was kept under a constant, positive partial pressure of reduced gas (variable H₂S/H₂ mixtures) ensuring a constant $\Sigma\text{S}_{\text{red}}$ and a fixed oxidation potential. During each experiment the diffraction pattern, morphology, and magnetic character of the solids, and the pH, ΣFe , ΣNa , $\Sigma\text{S}_{\text{red}}$ of the solutions have been monitored.

In selected experiments, intentional oxidation was used to test for changes in reaction speed and mechanism for pyrite formation. In such experiments

the initially precipitated monosulphide (mackinawite) was aged for 4–15 days and subsequently oxygen or air was allowed to equilibrate with the suspensions for a known time interval. In these experiments, to measure the conversion rate of iron monosulphides to pyrite, the relative amounts of 'FeS' to FeS₂ were determined via a sequential extraction method using a sulphur coulometer.

Results and discussion

Various long-term experiments were conducted at T < 100°C, variable reduced sulphur concentrations and pH 3.5 to 12. In all cases, the only solid phase stable in equilibrium with the highly reduced H₂S solution was mackinawite (Fig. 1a). Only due to slow diffusion of oxygen into the reaction vessel was the formation of greigite and pyrite observed after extended time intervals (30 to 120 days). We conclude that under highly reduced conditions in a system where only mackinawite and H₂S are present, pyrite formation does not occur under low temperature acid to alkaline conditions. A stronger oxidant than H₂S is required to start these reactions.

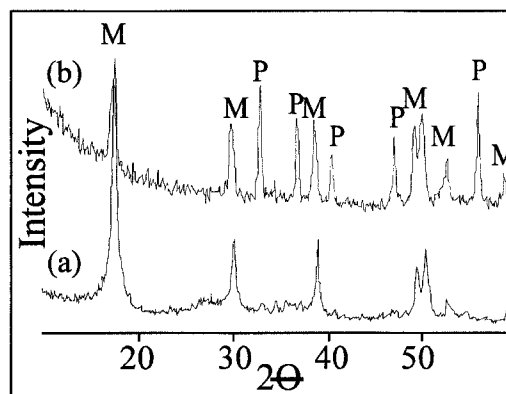


FIG. 1. X-Ray diffraction patterns for (a) a reduced and (b) an oxidised experiment. Conditions: (a) 80 days, pH = 4.32, T = 80°C; (b) 65 days, pH = 4.32, magnetic, T = 50°C.

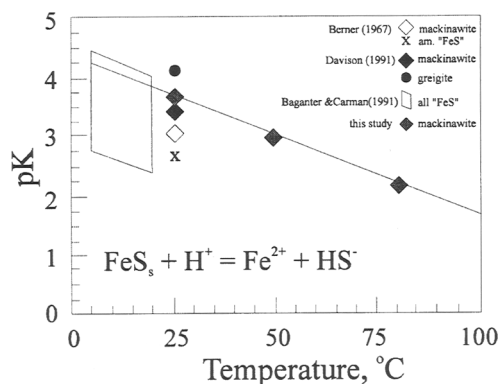


FIG. 2. Low temperature equilibrium constants for amorphous iron monosulphide, greigite and mackinawite from this study and from the literature.

From all experiments carried out under totally reduced conditions, the solubility constants for mackinawite to 80°C have been calculated from the concentrations of ΣS_{red} and ΣFe^{2+} in equilibrium with the solid. These constants were fitted to a temperature dependent equation and are plotted in Fig. 2 together with data from the literature.

Intentional oxidation, of either the precursor solid phase or the aqueous sulphur species, causes a dramatic increase in the reaction rate, thereby implying a reaction mechanism different from the 'H₂S pathway' suggested by Rickard (1997). In these experiments the formation of greigite, followed by pyrite, occurred within days. When the conversion rates of mackinawite to pyrite obtained from 'intentional oxidation' experiments (Fig. 1b) are calculated using the kinetic rate law suggested by

Rickard (1997), the comparison shows the rates measured in the current study to be, nevertheless, up to 100 times slower. The 'H₂S pathway' is in contradiction with the overall pyrite formation pathway which follows the reaction sequence mackinawite → greigite → pyrite.

Conclusions

(1) Mackinawite, not troilite or pyrrhotite, is apparently the stable iron monosulphide in low temperature reduced hydrosulphide solutions.

(2) For the first time *in situ* determined stability constants are presented for the dissolution of mackinawite up to 100°C.

(3) The conversion to the less reduced greigite and, finally, to pyrite or marcasite, occurs *only* when a more reactive oxidant promotes the formation of intermediate sulphur species is present.

Acknowledgements

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