A new sedimentary pyrite formation model

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Introduction

Conventional theories of sedimentary pyrite formation invoke the oxidation of precursor iron sulphides by elemental sulphur (Berner, 1970) or polysulphides (Rickard, 1975). The problems with these processes are that (a) the precursor iron suiphides are often hard to detect in sediments (viz. Morse and Cornwell, 1987) (b) the sedimentary process sometimes appears to involve rapid direct precipitation (e.g. Howarth, 1979) and (c) experimentally the process does not appear to result in framboids, one of the commoner sedimentary pyrite textures (e.g. Rickard, 1969). At the same time, some experimental data (e.g. Schoonen and Barnes, 1991) suggests that direct precipitation by this process does not occur: in the laboratory precursor phases always appear as intermediaries.

Methods

I examined the kinetics and mechanism of the rapid solution reaction between aqueous hexaquo-iron and sulphide at 25°C and showed that this process involved the formation of iron bisulphide complexes (Rickard, 1989a). Recently the original T-tube configuration (Rickard, 1989b) has been redesigncd to involve simultaneous measurements of pH and aS_{2-} and a stronger pump has permitted the reaction to be accessed down to <4ms. Taylor *et al.* (1979) showed that $FeS + H_2S \rightarrow FeS_2$ (pyrite) $+ H_2$ was rapid at hydrothermal temperatures. I am studying the kinetics and mechanism of this reaction at 60–80°C using mM H_2S concentrations in aqueous solutions of amorphous iron (II) sulphide. Product H_2 is measured by GC and pyrite formation is tracked by XRD and analysis of total product Fe and acid volatile sulphide.

Results

The results confirm that the mechanism of the fast reaction between aqueous iron (11) and dissolved sulphide involves the formation of a long-lived (<400ms) $Fe(SH)_x$ component that condenses to amorphous iron(II) monosulphide:

$$Fe^{2+} + HS^- \rightarrow Fe(SH)_x (fast)$$
$$Fe(SH)_x \rightarrow FeS(amorph) + SH^-(slow)$$
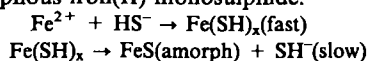
In a continuing programme on metal bisulphide complexing, using square wave voltammetry, we have shown (Luther *et al.*, 1994) that the iron (11) bisulphide complexes demonstrate a significant stability. The experimentally determined β_1 value for the formation of FeSHt is 5.5. The complex attains concentrations in the mM range in equilibrium with amorphous iron (II) monosulphide as the pH decreases. In the continued reaction between iron(II) monosulphide and hydrogen sulphide the preliminary results show that the reaction is rapid in the experimental temperature range with no remnant iron (11) monosulphide being detected after as little as 0.5 days at 80°C and with 4mM H_2S. The reaction is apparently first order with respect to H_2S and the Arrhenius activation energy is of the order that at 25°C and in mM H_2S concentrations the reaction will go to completion within weeks rather than months. Interestingly, the pyrite product is framboidal.

Discussion and conclusions

The sum of the reactions between hexaquoiron and bisulphide to form iron(II) monosulphide and between iron(II) monosulphide and hydrogen sulphide to form pyrite provides an alternative route for sedimentary pyrite formation. In its most literal form it would suggest that, in reactive iron-limited sedimentary systems the process would involve the continued reaction of iron salts with sulphide:

$$Fe^{2+} + HS^- \rightarrow FeS + H_2S \rightarrow FeS_2 + H_2$$
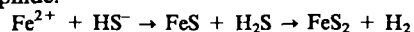
However, it is possible that a second and more rapid route may not involve iron (II) mono-sulphides as intermediaries:

$$Fe^{2+} + HS^- \rightarrow Fe(SH)_x + H_2S \rightarrow FeS_2 + H_2$$
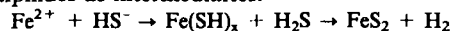
This second route is interesting because (a) it is likely to be more rapid since it does not require a solid phase intermediary (b) it is consistent with textural evidence regarding framboids that suggests direct precipitation and (c) it produces H_2 gas, a possibly important substrate for sulphate-reducing bacteria in sediments. Because (i) the rate dependence on HS^- of the initial reaction (ii) the increased stability of $FeSH_x$ at neutral to acid pH values and (iii) the rate dependence on H_2S of the pyrite-forming reaction

the process would appear to be favoured around pH = 7 where $H_2S \approx HS^-$. The requirement for excess H_2S indicates that the process might be enhanced in sedimentary systems where reactive iron is a limiting factor in pyrite formation. It is further possible that the same reaction process could be significant in higher temperature, hydrothermal enviroriments such as deep ocean hydrothermal vents.

Acknowledgements

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