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Pyrite Formation in an Anoxic Chemostatic Reaction System

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Introduction

Like many sparingly soluble salts, pyrite does not rapidly nucleate from supersaturated solutions, and the Fe-S system follows the Ostwald step-rule, whereby the first precipitated phase (FeS_{am}) is the most soluble and least thermodynamically stable. The mechanism by which iron (II) monosulphide transforms to pyrite is the subject of debate. Transformation to pyrite may proceed via oxidation:

$FeS_{(aq)} + H_2S_{(aq)} = FeS_{2(s)} + H_{2(occluded)}$ (1) Rickard (1997)

Reaction (1) is rapid, once initiated, involves a transport phase via an $FeS_{(aq)}$ cluster complex, and S(-II) is oxidised to S(-I) in pyrite while Fe(II) remains unoxidised. Alternatively, the transformation may proceed by addition of zero-valent sulphur:

$FeS_{(s)} + S_n{}^{2-}{}_{(aq)} = FeS_{2(s)} + S_{n-1}{}^{2-}{}_{(aq)}$ (2) Luther (1991)

Reaction (2) is considerably slower than (1) by several orders of magnitude, and low concentrations of polysulphide in natural systems may preclude it as a pathway for rapid pyrite formation. Finally, the transformation to pyrite may proceed by iron loss via a greigite intermediate:

$4FeS$(sub>(s) $+ 1/2O_{2(aq)} + 2H^+{}_{(aq)} = Fe_3S_{4(s)} + Fe^{2+}{}_{(aq)} + H_2O_{(l)}$ (3)
$Fe_3S_{4(s)} + 2H^+{}_{(aq)} = 2FeS_{2(aq)} + Fe^{2+}{}_{(aq)} + H_{2(occluded\ ?)}$ (4)
Wilkin and Barnes (1996)

This reaction scheme is a solid phase process, with step (3) involving oxidation of 2/3 of the Fe(II) to Fe(III) while S(-II) remains unoxidised, and step (4) requiring reduction of Fe(III) to Fe(II) while S(-II) is oxidised to S(-I).

Methods and Results

Ageing of precipitated FeS in the presence of aqueous hydrogen sulphide at pH 6-6.5, 40ºC, and in the absence of O_2 was investigated using an anoxic chemostatic reaction system (Butler *et al.*, 1999). Aqueous Fe^{2+} and H_2S are added by peristaltic pump to the reaction vessel. Environmental conditions such as pH, a_{HS^-}, temperature and reaction volume are controlled by electrode, thermocouple and transducer feedback to process controllers. Anoxia is maintained using N_2 gas scrubbed with a Zr-ZrO_2 buffer at 300ºC. The headspace of the reaction vessel is maintained at positive pressure, and all reservoir solutions are purged continuously with N_2. Experimental runs were performed over periods of 1 to 5 weeks.

Suspensions of FeS are stable in the presence of H_2S for extended periods (2-3 weeks), and no conversion of FeS to pyrite was observed. A second set of experiments were performed with polished pyrite blocks present in the reaction vessel. In these experiments, concentrations of dissolved sulphide were lower than in the first set, and in order to maintain a stable dissolved sulphide concentration, S and Fe were added continuously by pump from reservoirs, otherwise reaction conditions were identical to those experiments in which there was no pyrite formation. Where pyrite blocks were present in the reaction vessel, pyrite formation was rapid and extensive.

A range of pyrite textures was developed, including epitaxial overgrowth of the pyrite block (Figure 1a), clusters of euhedral pyrite, framboidal pyrite (Figure 1b), globular pyrite, and an unusual acicular pyrite texture, indicating enhanced growth rates at cube face centres or octahedral apices (Figure 1c).

Discussion

The observed stability of FeS in the presence of H_2S, but absence of O_2 or any oxidised S source, is consistent with the observations of Wilkin and Barnes (1996), Butler *et al.*, (1999), and others. This apparent contradiction with the results of Rickard (1997) is explained by partial oxidation of the FeS surface in the experiments of Rickard (1997). Rickard (1999) considered that limited oxidation of the FeS surface may initiate reaction (1) by enhancing pyrite nucleation kinetics.

Pyrite formation in the absence of O_2, but where a pyrite seed is provided, is consistent with the hypothesis proposed by Rickard (1999), and the framboid formation model of Butler and Rickard (in press). Pyrite provides a nucleation surface for further pyrite formation from solutions where unoxidised precipitated FeS and H_2S are the sole reactants. In natural ambient temperature anoxic environments, where H_2S is the dominant S form, low concentrations of O_2 or polysulphides close to the redoxcline may facilitate conversion of small amounts of FeS to FeS_2 via reactions 2,3 and 4. Subsequent rapid pyrite formation, and pyrite formation in strictly anoxic environments proceeds via the H_2S oxidation pathway, utilising oxidised FeS or FeS_2 as a nucleation/growth surface.

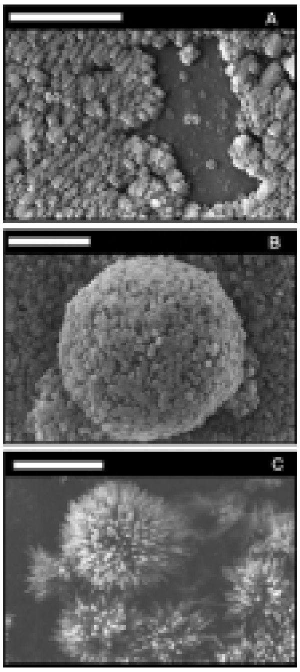

Figure 1: a) Epitaxial overgrowth (EO) of cubic pyrite crystals covering the original surface (OS) of the pyrite seed. Crystals nucleated on the surface of the seed share a common orientation. Scale bar = 4µm. b) Framboidal pyrite composed of numerous cubic microcrystals. Framboidal structures develop on the epitaxial overgrowth on the pyrite seed, and in places develop into polyframboidal structures by sequential nucleation and growth. Scale bar = 2µm c) Globular radiating acicular pyrite developed on the surface of the pyrite seed. The needle-like crystals are suggestive of extremely rapid crystal growth, and examples of this texture often display preferential growth towards octahedral apices. Scale bar = 2µm.

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