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Sulphur Isotope Discrimination During Experimental Formation of Pyrite

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Introduction

A means of elucidating pyrite forming processes is to use reactants of known stable sulphur isotopic composition as tracers for reaction pathways, and indicators of S sources in experimental systems. Experiments on the fast precipitation of FeS gave only small isotope fractionation compared to $H_2S_{(aq)}$ and $HS^-_{(aq)}$ (Böttcher *et al.*, 1998). Wilkin and Barnes (1996) examined pyrite formation by ageing FeS in the presence of H_2S, polysulphide and S with low concentrations of O_2 in aqueous solution (70 C; pH 6-8), using isotopically characterised reactants. The product pyrite inherited the isotopic composition of the precursor FeS, indicating that pyrite formation proceeds via Fe loss rather than addition of S. On the other hand, Sweeney & Kaplan (1973) observed an intermediate isotope signature for pyrite after synthesis from S and FeS end-members between 60 and 85 C. A resolution of these different experimental results has implications for the interpretation of pyrite formation in nature.

Methods

The reaction of precipitated, freeze dried FeS with excess H_2S and Na_2S_4 was investigated in anoxic aqueous solution at pH 6 (H_2S) and pH 8 (S_4^{2-}) and 25 to 100 ºC using the methods of Rickard (1997). FeS was prepared from $Na_2S.9H_2O$ with a $\delta^{34}S$ of +6.0 ±0.2 (1σ). Reactant sulphide was produced by acid decomposition of ZnS with a known $\delta^{34}S$ composition. Sodium tetrasulphide was produced by fusing elemental S with anhydrous Na_2S. Reaction products were characterised using XRD to confirm Fe-S mineralogy. Excess S in products from tetrasulphide reactions was removed by Soxhlet extraction. Sulphur for isotopic analysis was extracted from the products using acid $Cr(II)Cl_2$ distillation, precipitated as ZnS, transformed to Ag_2S and analysed by means of C-irmMS using Finnigan MAT 252 or Delta+ mass spectrometers.

Results and Disscussion

Ageing of FeS (+5.94) in the presence of tetrasulphide (+12.1) at 25 without conversion to FeS_2 resulted in the formation of disordered mackinawite with isotopic compositions (+8.9 to +9.9 ‰) intermediate between those of the initial reactants (see figure 1b). For experiments using FeS (+5.94) and H_2S (+17.5 and +15.5) or tetrasulphide (+12.1 and +13.0) which proceeded to complete FeS_2 conversion (figure 1 a & b), the isotopic composition of FeS_2 products (+8.8 to +11.6) was also found to be intermediate between that of the initial compositions of the reactants, but strongly dominated by that of the S source. For reactions with $S_4^{2-}{}_{(aq)}$, product FeS_2 (+11.2‰ to +13.3) is close or identical in isotopic composition to the reactant polysulphide (+12.1 and +13.0).

For an aqueous suspension of precipitated FeS in the presence of H_2S, where $\delta^{34}S_{FeS}$ $\pm\delta^{34}SH_2S$, isotope exchange between dissolved and precipitated sulphur species will be controlled by the equilibria:

$Fe^{2+}{}_{(aq)} + H_2S_{(aq)} = FeS_{(s)} + 2H^+{}_{(aq)}$ (1)
$Fe^{2+}{}_{(aq)} + HS^-{}_{(aq)} = FeS_{(s)} + H^+{}_{(aq)}$ (2)
$H_2S_{(aq)} = HS^-{}_{(aq)} + H^+{}_{(aq)}$ (3)

Rickard (1995) demonstrated that equilibria 1 and 2 are rapidly established, so isotope exchange equilibrium between aqueous and precipitated FeS should be rapidly achieved. This has been demonstrated with radiotracers by Fossing & Jørgensen (1990). Similar arguments apply to systems containing FeS and polysulphide.

Results of our experimental study indicate that for FeS in the presence of aqueous H_2S or S_4^{2-}, isotopic exchange between aqueous and precipitated sulphur species results in the formation of FeS with $\delta^{34}S$ approaching 1:1 mixtures of the two S sources. Product pyrite shows $\delta^{34}S$ compositions characteristic of H_2S or S_4^{2-} dominated mixtures of the reactants, suggesting that the reactions:

$FeS_{(s)} + H_2S_{(aq)} = FeS_{2(s)} + H_{2(occluded)}$ (5)
$FeS_{(s)} + S_4^{2-}{}_{(aq)} = FeS_{2(s)} + S_3^{2-}{}_{(aq)}$ (6)

are associated with a distinct isotope fractionation which, in the case of (6), is significantly larger than experimental uncertainty. The data suggest that isotope exchange during pyrite formation takes place between $FeS_{(s)}$ and $H_2S_{(aq)}$ or $S_4^{2-}{}_{(aq)}$ and is an overall result of equilibria (1) to (3) (above), with an additional, distinct, isotope fractionation resulting from reactions (5) and (6). Thus, the sulphur isotopic signature of sedimentary pyrite will closely reflect the signature of the aqueous sulphur source.

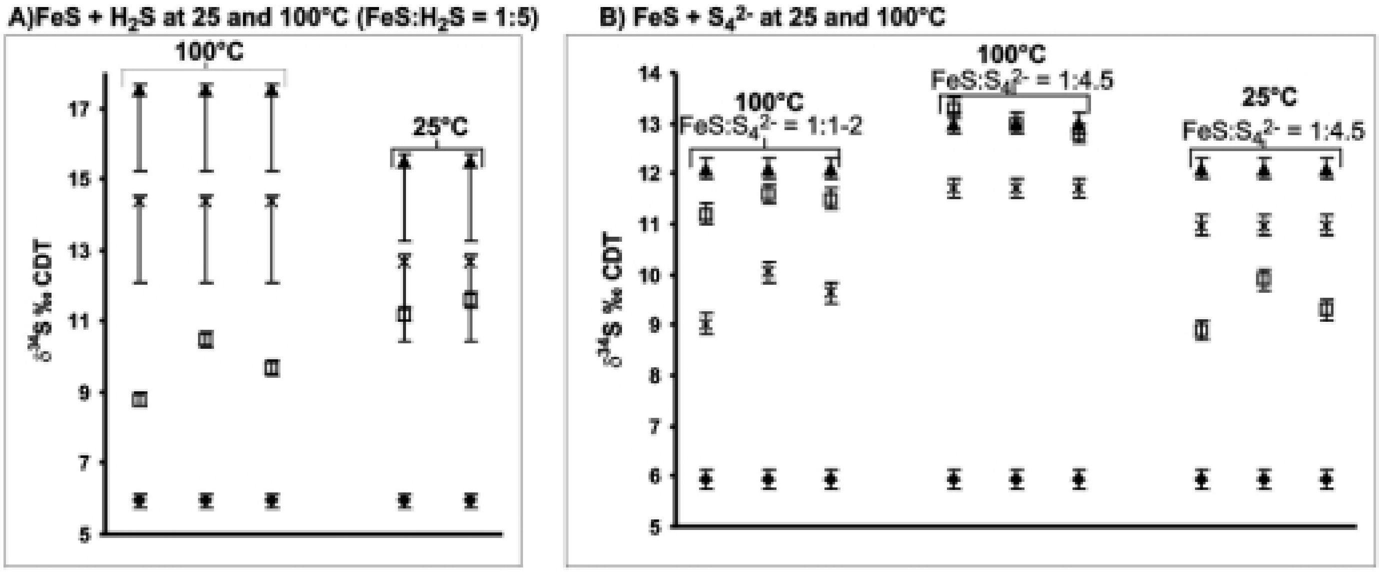

Figure 1: Experimental results for reactions of FeS with $H_2S_{(aq)}$ and $S_4^{2-}{}_{(aq)}$ at 25 and 100ºC. Filled diamonds = reactant FeS, filled triangles = reactant H_2S or $S_4^{2-}{}_{(aq)}$, open squares = product FeS_2 (with the exception of open squares for $S_4^{2-}{}_{(aq)}$ reactions at 25ºC, which is disordered mackinawite), crosses = calculated equilibrium isotopic mixture of reactants. Error bars = ±0.2 ‰ (1σ), except for H_2S experiments where $\delta^{34}SH_2S$ is subject to a repeatable fractionation of -2.3 ±0.3 ‰.

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