

Arsenic Incorporation into Pyrite at low Temperature, Experimental Results

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Pyrite is one of the major authigenic minerals in sediments, and an important sink for arsenic in the anoxic environment (Huerta-Diaz and Morse, 1992). Prior investigations of the geochemistry of arsenic focused mainly on the oxic part of its geochemical cycle. Studying the process of incorporation of arsenic into sedimentary pyrite encompasses unravelling probably the most important step in the anoxic part of its geochemical cycle. The purpose of our study is to determine the mechanism of arsenic incorporation into pyrite at low temperature, and to determine the reaction conditions under which incorporation takes place. We focused on the H₂S oxidation pathway of pyrite formation as described by Rickard and Luther (1997), in which amorphous FeS is oxidised by H₂S to form pyrite (FeS₂).

Incorporation of arsenic into pyrite was examined using the experimental methods of Rickard (1997). The reaction of disordered mackinawite with H₂S and arsenic solutions was investigated in the absence of O₂ at pH 6 and 25 °C, with a reaction time of 4 weeks. The arsenic was added as arsenate (As(V)) or arsenite (As(III)); the dominant arsenic species in natural anoxic environments is arsenite, but the more oxidised species, arsenate, can still be present (Edenborn et al., 1986). Furthermore continuous experiments were performed in the chemostated system described by Butler et al. in this volume, with the exception of doping the 0.6 mM iron reservoir solution with 0.6 µM arsenite. Experimental runs with and without polished pyrite blocks in the main reaction vessel were performed for 1 to 2 weeks at 40 °C, pH 6 and a total sulphide concentration of 2 mM.

Results from the batch experiments show that arsenite present in concentrations higher than 0.5 µM inhibits pyritisation of FeS. In 0.5 µM arsenite experiments a small amount of FeS was converted to pyrite. Preliminary data indicate that arsenate has the same effect as arsenite at concentrations of 0.5 M. No pyrite was formed in these experiments; arsenate oxidised ferrous iron to green rust and sulphide to sulphur. Preliminary results from the continuous flow experiments confirm the batch experiments, and show that arsenic either co-precipitated with or adsorbed onto FeS in the end product.

The results indicate that arsenic can inhibit pyrite formation following the H₂S oxidation pathway. While arsenate completely oxidises the FeS precursor, arsenite adsorbs onto the FeS surface and prevents the conversion to pyrite. This implies that, in natural ambient temperature anoxic environments, arsenic may be incorporated into pyrite via adsorption onto an existing pyrite surface. That is, in solutions with high arsenic concentrations (circa 1 ppm and higher) arsenic content is a secondary feature of pyrite (related to a later event) and not inherited from precursor FeS.

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