Geophysical Research Abstracts
Vol. 21, EGU2019-14050, 2019
EGU General Assembly 2019

Mackinawite oxidation: Reaction pathways and kinetics

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There are many unknowns in prebiotic chemistry. Some of these involve sulphur, an essential component of all life on Earth that may have played a role in the earliest life. One of the oldest sulphur minerals, mackinawite (FeS), occurs in many anoxic environments and probably has existed since the Hadean eon. Mackinawite oxidises rapidly in air to produce pyrite, but can be preserved over extended periods in reduced aqueous solutions. It plays a pivotal role in the cycling of iron and sulphur in aqueous systems through its reactivity and the numerous pathways to stable phases. Many of these pathways are poorly understood, however, and are challenging to study due to the occurrence of multiple metastable intermediate species. Mössbauer spectroscopy offers a unique possibility to monitor these metastable phases. We undertook a study to address the following questions: Which reaction pathways are involved in the slow oxidation of mackinawite? What are the kinetics of these reactions?

We performed four types of experiments in a glove box under anoxic conditions. A solution containing freshly precipitated mackinawite was prepared and exposed to different oxidants. Four series were investigated: (1) addition of oxygen as air; (2) addition of synthetic lepidocrocite, gamma-FeOOH; (3) addition of polysulphide solution; and (4) no exposure to oxidants (reference run). The entire experiment ran over slightly more than five months. Samples were extracted at regular intervals and transferred anoxically to a continuous flow cryostat where Mössbauer spectra were collected at 5 K. Wet chemistry was performed at the same intervals as the Mössbauer measurements.

Mössbauer spectra analysis reveals that the single line of mackinawite evolves to a well defined magnetic sextet (16 T) that dominates in three of the experiments, accompanied by weaker sextets with 27 T and 45 T. All three sextets are attributed to non-stoichiometric FeS with excess sulphur. Correlation of wet chemistry results with Mössbauer spectral evolution is in progress and should yield a more complete picture of reaction pathways and kinetics.