

Iron in Sulfate brines and minerals: Roles in amino acid preservation

A. JOHNSON* AND L. PRATT

1001 E. 10th Street, Bloomington, IN 47405,
(*correspondence: adjohns@indiana.edu)

Data returned from the MER rovers indicate that systems of acidic, oxidizing water once existed on or near the surface of Mars [1]. As the planet cooled, these would have been intermittently frozen and evaporated away, precipitating a variety of mineral assemblages along with potential biological molecules. It is imperative we identify those particular mineral environments that maximize detection of a biologically relevant signal. Experiments were carried out to mimic the present Martian diurnal cycling of a Mg-Fe-Ca-Na-SO₄ brine derived from acidic weathering of olivine-laden basalt [2] and laced with an enantiomeric excess of amino acids. Experimental conditions and end member products are analogues for evaporation and sublimation processes in a Martian paleolake and subsurface groundwater or permafrost system, i.e. systems with and without exposure to the photolytic effects of UV radiation.

Results indicate that iron containing brines in the presence of UV are prone to increased levels of amino acid degradation due to photo-Fenton oxidation reactions. In the absence of UV, iron-rich brines provide enhanced preservation, with half lives 200-300% longer than systems lacking iron. Racemization half lives are 30 and 50 times greater than corresponding degradation half lives in iron and non-iron samples, respectively. These initial results provide interesting scenarios in the preservation of organic matter on Mars; an iron-rich subsurface groundwater system, such as those attributed to hematite concretion formation [3], may provide increased organic matter preservation. Additionally, a limiting factor in life detection may not be the detection of an enantiomeric excess of amino acids but detecting a pool of amino acids at all.

- [1] Squyres, S.W & Knoll, A.H. (2005) *EPSL* **240**, 1-10.
[2] Tosca, N.J. & McLennan, S.M. *et al.* (2004) *J. Geophys. Res-Planets* **109**, E05003. [3] Squyres, S.W. *et al.* (2004) *Science* **306**, 1709-1714.

Temporal variations in Fe isotope compositions of banded iron formations record changes in the nature of redox cycling

C. JOHNSON, B. BEARD AND E. RODEN

Univ. Wisconsin - Madison (clarkj@geology.wisc.edu,
beardb@geology.wisc.edu, eroden@geology.wisc.edu)

The largest range in Fe isotope compositions of sedimentary rocks is defined by Archean and Proterozoic banded iron formations (BIFs), where $\delta^{56}\text{Fe}$ values range from -2 to +2 ‰. Fine-scale isotopic variations in magnetite in BIFs on the mm- and cm-scale indicate that their $\delta^{56}\text{Fe}$ values do not generally record the Fe isotope compositions of ancient seawater, but instead record the isotopic compositions of precursor Fe(III) oxides, as well as early diagenesis prior to lithification. The oldest BIFs, ~3.7-3.8 Ga in age, have exclusively positive $\delta^{56}\text{Fe}$ values for magnetite, reflecting incomplete oxidation of hydrothermal Fe(II), most likely by anaerobic photosynthetic Fe(II) oxidation. The largest BIF inventories are found in 2.5 Ga age sequences, and $\delta^{56}\text{Fe}$ values for magnetite extend from slightly positive values to significantly negative values; the negative $\delta^{56}\text{Fe}$ values probably record Fe(II)_{aq} produced by Fe(III)-reducing bacteria and not abiologic Fe(II)-oxide interaction because such interaction should have occurred in BIFs of all ages, but negative $\delta^{56}\text{Fe}$ values are apparently restricted to ~2.5 Ga sequences. The extensive 2.5 Ga BIFs may record a period of maximum expansion of bacterial Fe(III) reduction, prior to establishment of widespread bacterial sulfate reduction. Magnetite from BIFs of ~1.8 Ga age have near-zero to slightly positive- $\delta^{56}\text{Fe}$ values. Although Fe(III)-reducing bacteria existed at this time, mobilization of significant quantities of low- $\delta^{56}\text{Fe}$ Fe(II)_{aq} may have been inhibited by high levels of sulfide produced by bacterial sulfate reduction.

In contrast to magnetite, a large portion of the inventory of siderite and Fe(II) silicates in BIFs appear to have formed in Fe isotope equilibrium with seawater. Exceptions include high- $\delta^{56}\text{Fe}$ carbonates, which cannot be explained using known Fe(II)_{aq}-siderite fractionation factors, and these most likely reflect reduction of high- $\delta^{56}\text{Fe}$ precursor oxides by Fe(III)-reducing bacteria. Additional evidence for a role by Fe(III)-reducing bacteria in siderite formation comes from C isotope compositions, where $\delta^{13}\text{C}$ values are as low as -16 ‰ in BIF carbonates. We conclude that temporal variations in Fe isotope compositions of BIFs record global changes in Fe(II) oxidation rates, but also changes in microbial metabolisms that are involved in C-S-Fe cycling.