Experimental determination of Fe isotope fractionation between aq. Fe(II), “green rust”, and siderite

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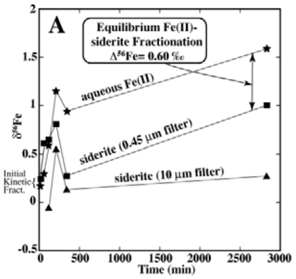
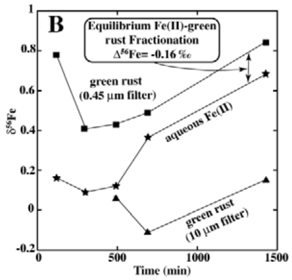
Interpretation of iron isotope variations in geologic materials is hampered by a lack of equilibrium fractionation factors among minerals and aqueuos fluids. Here we report on green rust ($Fe^{(II)}_4Fe^{(III)}_2(OH)_{12}CO_3$) and siderite ($FeCO_3$) synthesis experiments to constrain the equilibrium Fe isotope fractionation factor between aq. Fe(II), green rust, and siderite. Synthesis experiments were performed using oxygen-purged solutions of Fe(II) perchlorate and sodium bicarbonate (at ~20 ^{o}C). The identity of the precipitated phases were confirmed by XRD and SEM. Fe isotope analyses were performed using the Univ. of Wisconsin *IsoProbe.* Fe isotope compositions are reported as $\delta^{56}Fe = ([^{56}Fe/^{54}Fe]_{sample}/[^{56}Fe/^{54}Fe]_{TerrIgrocks}-1)10^3$. On this scale, the measured Fe isotope composition of the IRMM-014 Fe standard was $\delta^{56}Fe = -0.09 \pm 0.05$ ‰.

Preliminary results show a significant fractionation between the aq. Fe(II) and the precipitated green rust and siderite (Figs. A & B). The larger size siderite (>10 µm) has the lowest δ^{56}Fe values, whereas the smaller sized grains (<0.45 µm) appear to track the aq. Fe(II) Fe isotope composition, although at lower values. The larger mineral grains most likely record the evolving Fe isotope composition of the aq. Fe(II) and only the surface layer is probably in isotopic equilibrium with aq. Fe(II) at any given time. In contrast, we suspect that the smaller sized grains are more likely to maintain isotopic equilibrium with aq. Fe(II). We consider the isotopic difference between the 0.45 µm sized siderite and green rust and the aq. Fe(II) as one that closely approximates the equilibrium Fe isotope fractionation factor, where $\Delta^{56}Fe_{Fe(II)\text{-}siderite} = +0.6$‰ and $\Delta^{56}Fe_{Fe(II)\text{-}greenrust} = -0.16$‰ at room temperature. Comparison with fractionation factors obtained from spectroscopic data ($\Delta^{56}Fe_{Fe(II)\text{-}siderite} = +2.17$‰, 20^{o}C) , from natural samples in BIF’s ($\Delta^{56}Fe_{Fe(II)\text{-}siderite} = -1.7$ to 0.3‰) and from siderite produced by *Shewenella* suggests a distinct fractionation for biotic siderite production than for strictly abiotic siderite precipitation.





The effect of bacterial cell wall adsorption on mineral solubilities

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The transport of mass in geologic systems, such as liquid hydrocarbon migration in sedimentary basins or contaminant transport in groundwater systems, is strongly influenced by rock porosity and permeability. In turn, these rock properties are at least partially controlled by mineral solubilities and dissolution rates. Bacteria can affect the dissolution rates of rock-forming minerals. However, bacterial effects on mineral solubilities have not been studied. Here we demonstrate that the adsorption of mineral-forming cations onto a bacterial surface leads to enhanced mineral solubilities, and we present a thermodynamic approach for quantitatively modelling this bacterial effect. We determined the solubility of CuO in both abiotic and bacteria-bearing systems, measuring Cu concentrations, both in solution and adsorbed onto the bacteria. In the bacteria-bearing systems, we observed greatly elevated extents of mineral dissolution, caused by high concentrations of Cu adsorbed onto the cell walls. Our results are the first to indicate that bacterial cell wall adsorption can significantly lower mineral saturation states in geologic systems, causing both an increase in the extent of mineral dissolution as well as an inhibition of secondary mineral formation.