Mechanisms of Fe isotope fractionation during dissimilatory Fe(III) reduction by *S. putrefaciens* and *G. sulfurreducens*

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Microbial dissimilatory iron reduction (DIR) is widespread in anaerobic sediments and is a key producer of aqueous Fe(II) in suboxic sediments that contain reactive ferric oxides. Here we compare Fe isotope fractionations produced by similar cultures of *G. sulfurreducens* and *S. putrefaciens* during reduction of hematite and goethite. Both species produce aqueous Fe(II) that is depleted in the heavy Fe isotopes, as expressed by a decrease in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios or $\delta^{56}\text{Fe}$ values. The low $\delta^{56}\text{Fe}$ values for aqueous Fe(II) produced by DIR reflect isotopic exchange among three Fe inventories: aqueous Fe(II) (Fe(II)$_{aq}$), sorbed Fe(II) (Fe(II)$_{sorb}$), and a reactive Fe(III) component on the ferric oxide surface (Fe(III)$_{rec}$). The fractionation in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios between Fe(II)$_{aq}$ and Fe(III)$_{rec}$ was 2.95‰, and this remained constant over the timescales of the experiments (280 d). The Fe(II)$_{aq}$-Fe(III)$_{rec}$ fractionation was independent of the ferric Fe substrate (hematite or goethite) and bacterial species, indicating a common mechanism for Fe isotope fractionation during DIR. Moreover, the Fe(II)$_{aq}$-Fe(III)$_{rec}$ fractionation in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios during DIR is identical within error of the equilibrium Fe(II)$_{aq}$-ferric oxide fractionation in abiologic systems at room temperatures. This suggests that the role of bacteria in producing Fe isotope fractionations during DIR lies in catalyzing coupled atom and electron exchange between Fe(II)$_{aq}$ and Fe(III)$_{rec}$ so that equilibrium Fe isotope partitioning occurs.

Although Fe isotope fractionation between Fe(II)$_{aq}$ and Fe(III)$_{rec}$ remained constant, the absolute $\delta^{56}\text{Fe}$ values for Fe(II)$_{aq}$ varied as a function of the relative proportions of Fe(II)$_{aq}$, Fe(II)$_{sorb}$, and Fe(III)$_{rec}$ during reduction. In the case of hematite reduction, the effect of Fe(II)$_{aq}$ on the $\delta^{56}\text{Fe}$ values of Fe(II)$_{aq}$ was insignificant, <0.05‰. Sorption of Fe(II) produced small, but significant effects during reduction of goethite, reflecting the higher proportion of Fe(II)$_{sorb}$ and larger measured Fe(II)$_{aq}$-Fe(II)$_{sorb}$ fractionation. The isotopic effects of sorption on the $\delta^{56}\text{Fe}$ values for Fe(II)$_{sorb}$ were largest during the initial stages of reduction when Fe(II)$_{sorb}$ was the major ferrous Fe species during goethite reduction, on the order of 0.3 to 0.4‰, but decreased to <0.2‰ with continued reduction; our results show that the effect of sorption is much less than has been proposed in other studies. These experiments provide a breakthrough in our understanding of the mechanisms that produce Fe isotope fractionation during DIR, and form the basis for interpretation of Fe isotope variations in modern and ancient natural systems where DIR may have driven Fe cycling.