

Mechanisms of Fe isotope fractionation during dissimilatory Fe(III) reduction (DIR)

HEIDI A. CROSBY, CLARK M. JOHNSON,
BRIAN L. BEARD AND ERIC E. RODEN

Department of Geology and Geophysics, University of
Wisconsin, 1215 W. Dayton St., Madison, WI 53706

Iron isotopes provide a powerful means for constraining the Fe pathways involved during DIR. Previous work has measured low $\delta^{56}\text{Fe}$ values for $\text{Fe(II)}_{\text{aq}}$ during DIR, but it has also been suggested that sorption of Fe(II) to ferric hydroxides may produce low- $\delta^{56}\text{Fe}$ $\text{Fe(II)}_{\text{aq}}$; in neither case, however, has the high- $\delta^{56}\text{Fe}$ component been analyzed directly. In the present study the mechanisms of Fe isotope fractionation during DIR were investigated through direct measurement of the isotopic composition of aqueous Fe(II), adsorbed Fe(II), and the outermost layer of Fe(III) and tightly bound Fe(II) on the oxide surface. The obligate anaerobe *Geobacter sulfurreducens* was grown with hematite and goethite as its terminal electron acceptor for 280 days, over which time less than 4% of the available ferric iron was reduced; this slow rate of growth best simulates natural conditions and minimizes kinetic isotope effects. The aqueous Fe(II) was isotopically light, in agreement with previous studies, and direct measurement of the adsorbed Fe(II) shows that its isotopic composition is similar to that of aqueous Fe(II). The outermost layer of Fe(III), as determined by step-wise leaching/partial dissolution, has high $\delta^{56}\text{Fe}$, and this represents the first time that an isotopically heavy component (required by mass balance) has been identified in DIR experiments.

Beard et al. (2003 Chem. Geol.) proposed a ligand exchange model to explain Fe isotope fractionation during DIR, in which the major fractionation step is between ligand-bound pools of Fe(III) and Fe(II). Our results instead suggest that the major fractionation step may occur during electron transfer from sorbed or aqueous Fe(II) to Fe(III) at the ferric oxide/hydroxide surface, following the bacterial reduction step. We find no evidence that sorption produces the large Fe isotope fractionations reported by Icopini et al. (2004 Geology). Instead, the measured $\delta^{56}\text{Fe}$ values for $\text{Fe(II)}_{\text{aq}}$ are produced by creation of a high- $\delta^{56}\text{Fe}$ ferric oxide/hydroxide layer, where $\text{Fe(II)}_{\text{aq}}$ is ~ 3 per mil lower in $^{56}\text{Fe}/^{54}\text{Fe}$. At the extent of reduction in these experiments, this is equivalent to about one Fe atom thickness; it is not yet clear if this mechanism occurs at larger extents of reduction. These results provide the first evidence that redox cycling of Fe atoms occurs at the ferric oxide/hydroxide surface during DIR.

Isotope fractionation of Cadmium on the Moon

J. R. DE LAETER, K. J. R. ROSMAN AND S. SCHEDIWIY

Department of Applied Physics, Curtin University of
Technology, Perth, Western Australia

The absence of a lunar atmosphere enables bombardment of the lunar surface by high energy particles and micro-meteorites to occur. Some of the sputtered material escapes from the small gravity field of the Moon, and may leave the residue preferentially enhanced in "heavy" isotopes of certain elements with respect to a terrestrial standard. A mass spectrometric study of the volatile element cadmium revealed evidence of isotope fractionation (Sands et al., 2001).

To accurately ascertain the magnitude of this fractionation and the elemental abundance of cadmium, a number of lunar samples were analysed by Thermal Ionization Mass Spectrometry, using the double spike technique. Five lunar soils gave a positive isotope fractionation ranging from + 3.1 to + 5.2 ‰ per mass unit, in which the "heavy" isotopes of cadmium are enhanced relative to the "light" isotopes. A mare basalt from the lunar surface gave zero fractionation, which is identical to BCR-1, indicating that the isotope fractionation of the Moon and Earth are identical. An orange glass from Shorty Crater in the Taurus-Littrow region, however, gave a negative fractionation of -2.6 ± 0.8 ‰ per mass unit, as a result of re-deposition of cadmium from the volatile-rich cloud associated with lunar volcanism.

Reference

Sands D., Rosman K.J.R. and De Laeter J.R. (2001) *Earth Planet. Sci. Lett.* 186, 103-111.