Fractionation of Fe isotopes during biogenic mineral formation by dissimilatory Fe(III) reduction (DIR)

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

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

Iron isotope fractionation between aqueous Fe(II) and biogenic magnetite and Fe carbonates produced during reduction of hydrous ferric oxide (HFO) by *Shewanella putrefaciens, Shewanella algae,* and *Geobacter sulfurreducens* in laboratory experiments is a function of Fe(III) reduction rates and pathways by which biogenic minerals are formed. High Fe(III) reduction rates produced ^{56}Fe/^{54}Fe ratios for Fe(II)$_{aq}$ that are 2-3 per mil lower than the HFO substrate, reflecting a kinetic isotope fractionation that was associated with rapid sorption of Fe(II) to HFO. In long-term experiments at low Fe(III) reduction rates, the Fe(II)$_{aq}$ - magnetite fractionation is -1.3 per mil, and this is interpreted to be the equilibrium fractionation factor at 22 ^{o}C in the biological reduction systems studied here. In experiments where Fe carbonate was the major ferrous product of HFO reduction, the estimated equilibrium Fe(II)$_{aq}$ - Fe carbonate fractionations were ca. 0.0 per mil for siderite ($FeCO_3$) and ca. +0.9 per mil for Ca-substituted siderite. Formation of precursor phases such as amorphous non-magnetic, non-carbonate Fe(II) solids are important in the pathways to formation of biogenic magnetite or siderite, particularly at high Fe(III) reduction rates, and these solids may have ^{56}Fe/^{54}Fe ratios that are up to 1 per mil lower than Fe(II)$_{aq}$. Under low Fe(III) reduction rates, where equilibrium is likely to be attained, it appears that both sorbed Fe(II) and amorphous Fe(II)(s) components have isotopic compositions that are similar to those of Fe(II)$_{aq}$.

The relative order of δ^{56}Fe values for these biogenic minerals and aqueous Fe(II) is: magnetite > siderite ≈ Fe(II)$_{aq}$ > Ca-bearing Fe carbonate, and this is similar to that observed for minerals from natural samples such as Banded Iron Formations (BIFs). Where magnetite from BIFs has δ^{56}Fe>0 ‰, the calculated δ^{56}Fe value for aqueous Fe(II) suggests a source from mid-ocean ridge (MOR) hydrothermal fluids. In contrast, magnetite from BIFs that has δ^{56}Fe ≤0 ‰ apparently requires formation from aqueous Fe(II) that had very low δ^{56}Fe values. Based on this experimental study, formation of low-δ^{56}Fe Fe(II)$_{aq}$ in non-sulfidic systems seems most likely to have been produced by dissimilatory reduction of ferric oxides by Fe(III)-reducing bacteria.

Modeling stable isotope fractionation in crystals

EDWIN A. SCHAUBLE

Dept. of Earth and Space Sciences, UCLA, Los Angeles, CA 90095-1567 USA (schauble@ess.ucla.edu)

New techniques and instrumentation have made it possible to analyze the isotopic compositions of many elements to such high precision that we can now detect natural variations of ~0.1‰ or less. In order to use these new measurements most effectively, it is crucial to work towards a quantitative understanding of the geochemical mechanisms that cause isotope fractionation. Theoretical models, based on the calculation of thermodynamic partition function ratios, are helping to establish a framework for predicting the chemical systematics of natural fractionations. Models can also help verify experimental results, and allow extrapolation to temperatures where isotopic exchange is too slow to achieve equilibrium on laboratory time scales. These models require detailed knowledge of the vibrational frequencies of both common and rare isotopic forms of the substances being modeled. The complexity and long-range order of crystals make it difficult to obtain these frequencies using conventional spectroscopy, presenting a hurdle to accurate modeling. However, minerals are the most durable repository of ancient geochemical signatures, and are a natural focus for modeling efforts despite their complexity.

One promising approach is to combine first-principles lattice dynamics with careful sampling of the vibrational density of states of each crystal to obtain an accurate representation the complete vibrational spectrum. Early results show that accurate vibrational frequency estimates can be achieved using free open-source software like ABINIT (*www.abinit.org*), and that the method can be applied to many geochemically relevant materials. Case studies of zinc and calcium isotopic fractionation in oxides, sulfides and carbonates illustrate the potential of these *ab initio* techniques. Calculated Zn-isotope fractionations between ZnS and ZnO minerals suggest that ^{68}Zn/^{66}Zn will be ~1‰ higher in oxides in equilibrium with sulfides at 25ºC. The results also suggest that oxides and dilute aqueous solutions with 6-coordinate Zn will have ~0.5‰ lower ^{68}Zn/^{66}Zn than coexisting phases where Zn is in 4-fold coordination with oxygen. Initial Ca-isotope modeling also shows a coordination number effect, with ^{44}Ca/^{40}Ca in calcite (6-coordinate) predicted to be ~4‰ higher than in aragonite (9-coordinate). This effect is in the same direction, but larger than experiments indicate.