Iron isotope fractionation at the hematite-water and goethite-water interface

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Density functional theory electronic structure calculations are used to compute equilibrium constants for iron isotope exchange among Fe^{2+}(aq), Fe^{3+}(aq), and hematite (a-Fe$_2$O$_3$). The hematite is represented in both bulk and surface environments. The iron-isotope fractionation between Fe^{2+}(aq) and Fe^{3+}(aq), determined using a range of exchange-correlation functionals and basis sets, is in good agreement with experimental measurements. The calculated reduced partition function ratio for bulk hematite is very close to previous estimates based on Moessbauer and inelastic nuclear resonance X-ray spectroscopy. However, the calculated fractionation between hematite bulk and the aqueous species Fe^{3+}(aq) and Fe^{2+}(aq) differs from experimental measurements carried out at the aqueous-hematite interface. We find a heavy iron enrichment trend in the order Fe^{2+}(aq) < hematite bulk $\approx$ hematite surface < Fe^{3+}(aq). It is surprising that the aqueous environment is predicted to be richer in heavy iron. The reason for this is that coupling of Fe-fractionating modes to wagging motions of water molecules near 1000 cm^{-1} give rise to a significant increase in the predicted reduced partition function ratio for the aqueous phase, while the highest-frequency motions in hematite are below than 700 cm^{-1}. In contrast to experimental studies, we find a significant positive fractionation (heavy enrichment) for Fe^{3+}(aq) relative to hematite, regardless of whether the hematite is represented by a bulk or a surface model. Our calculations indicate how isotope signatures might possibly be used constrain surface structures, and indicate that it is unlikely that the aqueous interfacial structure of hematite is a simple termination of the bulk structure. Calculated goethite-water interfacial fractionations are very close to those predicted for hematite-water.

Iron isotope fractionation in the lower mantle

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At the pressures of the Earth's lower mantle, crystalline and melt phases should preferentially take up heavy isotopes as bonds are compressed and vibrational frequencies increase. For the iron isotopes, the possibility of spin collapse may be expected to result in additional bond shortening which could further facilitate enrichment in heavy isotopes. A large fraction of the iron in the earth's lower mantle is dissolved in ferropericlase and ferroperovskite. The distinct coordination environments in these phases (6-fold versus 8-fold) and their influence on the spin state of iron would be expected to give rise to a fractionation of iron isotopes between these phases, most likely enriching heavy iron in the tighter six-fold coordination environment. In addition, during the crystallization of the mantle, these phases would have been in equilibrium with silicate melt exhibiting a variety of coordination environments for iron. Pressure effects on the fractionation will be counteracted to an unknown extent by increasing temperatures in the mantle.

Using density functional theory we have calculated isotope fractionation factors between these phases to pressures and pressures near the core-mantle boundary. We find that in ferropericlase, the predicted reduced partition function ratio (RFPR) is a strong function of the spin state. In contrast, the predicted RFPR of ferroperovskite is hardly affected by the spin transition. This appears to result from the asymmetric coordination environment of intermediate and low-spin Fe in perovskite, in which some bonds are lengthened and some are shortened relative to high-spin Fe. Surpisingly the RPFR values are very similar between ferropericlase and ferroperovskite. Although the immediate Fe-O bonds are indeed weaker in the eightfold coordination site, vibrational coupling of Fe-fractionating modes to Si-O stretching vibrations at high frequency raise the RPFR for Fe in ferroperovskite, compensating for the higher coordination environment. Ab initio molecular dynamics simulations of Fe in MgSiO$_3$ melt at lower mantle pressures give rise to a variety of coordination environments intermediate between ferropericlase and ferroperovskite. The presence of water in the melt seems to have little effect on the predicted isotopic signature.