

PREDICTING EQUILIBRIUM IRON ISOTOPE FRACTIONATIONS. E. A. Schauble, G. R. Rossman, and H. P. Taylor, Jr., Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125. *edwin@gps.caltech.edu*

Introduction: We report the results of a theoretical study of the equilibrium partitioning of iron isotopes among simple complexes and metallic iron. Theoretical calculations are based on a combination of force-field molecular modeling and existing vibrational spectroscopy data. This study is motivated by the discovery of transition-element (Fe, Cu, Zn, etc.) isotope abundance variations in natural terrestrial samples [1,2,3]. In the case of iron, isotope fractionations have also been observed in biological and inorganic laboratory experiments [4,5]. However, no one knows what ultimately controls the observed fractionations, so it is difficult to gauge their significance as biogeochemical and environmental probes. A basic theoretical understanding of the factors controlling equilibrium iron-isotope fractionations can help to bridge this knowledge gap.

Theoretical calculations based on ^{57}Fe -Mössbauer spectroscopy predict substantial inorganic fractionations [6]. We set out to confirm these predictions, and to develop a theoretical method that can be applied to elements lacking Mössbauer isotopes, like Cu and Zn.

Theory: Equilibrium stable-isotope fractionation is mainly caused by small differences in the vibrational energies of isotopically substituted substances. Substituting a heavy isotope for a lighter one reduces a substance's vibrational frequencies, leading to a small decrease in vibrational energy that varies from one substance to another. When two or more substances are at equilibrium, a heavy isotope will tend to be concentrated in the substance in which the vibrational energy is most sensitive to isotope substitution. Energy changes caused by isotope substitution can be determined if the vibrational spectra of isotopically heavy and light forms of a substance are known. Typically, however, only the spectra of substances containing the natural mixture of isotopes (dominated by ^{56}Fe) is known. So we developed a scheme for predicting the vibrational frequencies of ^{54}Fe -bearing analogues.

Method: Published vibrational spectra of metallic iron and simple complexes of iron with various ligands closely approximate the spectra of pure ^{56}Fe -bearing end members. The spectra of ^{54}Fe -bearing complexes are calculated using intra-molecular force-fields fitted to observed vibrational frequencies. Typically the Modified Urey-Bradley Force Field (MUBFF) is used. For tetrahedral and octahedral complexes, a MUBFF has three parameters that are adjusted to fit four or five measured frequencies. The accuracy of the theoretical calculation depends on the accuracy of the force-field applied to predict the vibrational frequencies of the

^{54}Fe -bearing complexes. Force-field predictions are tested by looking at complexes and molecules where the isotope effect has been measured or modeled in detail.

Results: Fractionations of up to several per mil are predicted between complexes in which iron is bonded to different ligands (i.e. 4‰ for $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ vs. $[\text{Fe}^{\text{III}}\text{Cl}_4]^-$). Similar fractionations are predicted between complexes with Fe(II) and Fe(III) (i.e. 5‰ between $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$). Our results (Fig. 1) suggest that heavy iron isotopes will be concentrated in complexes with high-frequency metal-ligand stretching vibrations. Thus, complexes with strongly bonding ligands like CN^- and H_2O will tend to concentrate the heavy iron isotopes when in equilibrium with complexes with weakly bonding ligands like Cl^- and Br^- . Fe(III)-bearing complexes will tend to concentrate the heavy iron isotopes relative to coexisting Fe(II)-bearing complexes. Iron in four-fold coordination will tend to concentrate the heavy isotopes relative to iron in six-fold coordination. Results for $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and metallic iron agree quantitatively with Mössbauer-based predictions [6]. Simple MUBFF force-field models accurately predict the effect of isotope substitution on vibrational frequencies.

References: [1] Beard B. L. and Johnson C. M. (1999) *GCA*, 63, 1653-1660. [2] Zhu X.-K. et al. (2000) *Science*, 287, 2000-2002. [3] Maréchal C. N. et al. (1999) *Chem. Geol.*, 156, 251-273. [4] Beard B. L. et al. (1999) *Science*, 285, 1889-1892. [5] Anbar A. D. et al. (2000) *Science*, 288, 126-128. [6] Polyakov V. B. (1997) *GCA*, 61, 4213-4217.

Fig. 1:

