

# Theoretical Estimates of Equilibrium Fe-isotope Fractionations From Vibrational Spectroscopy

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## Abstract

As a step towards understanding the stable-isotope geochemistry of transition metals, the magnitude and direction of equilibrium iron-isotope  $^{54}\text{Fe}$  -  $^{56}\text{Fe}$  fractionations among simple iron-bearing complexes and  $\alpha$ -Fe metal are calculated. Calculations are based on a combination of force-field modeling and existing infrared, Raman, and inelastic neutron scattering measurements of vibrational frequencies. We use the theoretical model developed by Urey [1] and Bigeleisen and Mayer [2], which models equilibrium isotopic fractionations resulting from the effect of isotopic substitution on vibrational energies. Molecular force-field models are used to approximate unknown vibrational frequencies of isotopically substituted complexes. We predict that significant, measurable equilibrium fractionations will occur when iron is partitioned between two or more phases that are distinct with respect to a) the ability of bonding partners to form strong covalent bonds with iron, b) iron valency, and/or c) the coordination number of iron. Fractionations of up to several per mil are predicted between complexes in which iron is bonded to different ligands (i.e. 4 per mil for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  vs.  $[\text{FeCl}_4]^-$  at 25 °C). Similar fractionations are predicted between the different oxidation states of iron. The heavy iron isotopes will be concentrated in complexes with high-frequency metal-ligand stretching vibrations. That means  $^{56}\text{Fe}/^{54}\text{Fe}$  will be higher in complexes with strongly bonding ligands such as  $\text{CN}^-$  and  $\text{H}_2\text{O}$  relative to complexes with weakly bonding ligands like  $\text{Cl}^-$  and  $\text{Br}^-$ .  $^{56}\text{Fe}/^{54}\text{Fe}$  will also usually be higher in Fe(III) compounds than in Fe(II)-bearing species; the Fe(II) and Fe(III) hexacyano complexes are exceptions to this rule of thumb. Heavy iron isotopes will be concentrated in sites of 4-fold coordination relative to 6-fold coordination. Model results for a ferrous hexacyanide complex,  $[\text{Fe}(\text{CN})_6]^{4-}$ , are in agreement with analogous calculations based on Mössbauer spectra [3], suggesting that both approaches give reasonable estimates of iron-isotope partitioning behavior. References: [1] Urey (1947) J. Chem. Soc. (London), 562-581. [2] Bigeleisen and Mayer (1947) J. Chem. Phys. 15, 261-267. [3] Polyakov (1997) Geochim. Cosmochim. Acta 61, 4213-4217.

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