Geochemistry 5 (Mineral Physics 4.5): Experimental and Stable Isotope Perspectives on Planetary Cores

Credit: Kevin Righter (and LPI's Leanne Woolley)

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These effects decrease with the inverse square of temperature and usually are negligible at mantle temperatures. Thus stable isotopes fractionate only at the surface of the Earth.
Look for elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass (enough to measure)
Stable Isotopes

Look for elements that have more than one non-radiogenic isotope, for which the mass difference between isotopes is a significant fraction of the atomic mass (enough to measure).
Fractionation refers to the partial separation of two isotopes of the same element, producing reservoirs with different ratios of the isotopes.

Isotopic fractionations occur due to:

- Differences in bond energies (equilibrium)
- Reaction rates (kinetics)

\[
\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}
\]
$E_n = h\nu(n + \frac{1}{2})$
\[ E_n = \hbar \nu (n + \frac{1}{2}) \]

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]
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Zero-point energy differences drive typical equilibrium stable isotope fractionations.
Heavy isotopes have lower vibrational frequencies.
Stiffer bonds concentrate the heavy isotopes
- shorter bonds
- higher oxidation state
- low coordination number

\[ v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]
O’Neil 1986 tabulated five common characteristics that are shared by elements that show large variations in isotopic compositions in nature:

- low atomic mass
- relative mass difference between isotopes is large
- tendency to form covalent bonds
- elements exist in more than one oxidation state
- abundances are high enough that we can measure them
AX' + BX = AX + BX'

\[ K_{eq} = \frac{Q(AX)Q(BX')}{Q(AX')Q(BX)} \]

\[ Q_{total} = Q_{translation}Q_{rotation}Q_{vibration} \]
\[ Q_{\text{vib}} = \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}} \]

\[ u_i = \frac{h\nu_i}{k_B T} \]

\[ Q_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} \ V \]

\[ Q_{\text{rot}} = \frac{8\pi^2 l kT}{h^2} \]

\[ Q_{\text{total}} = Q_{\text{vib}} Q_{\text{rot}} Q_{\text{trans}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \frac{8\pi^2 l kT}{\sigma h^2} \frac{(2\pi mkT)^{3/2}}{h^3} \ V \]
\[ \alpha_{XR-X} = \left[ \prod_i \frac{v_{heavy \ XR}}{v_{light \ XR}} \times \left( \exp\left[ -\frac{\hbar v_{heavy \ XR}}{2kT} \right] \right) \times \left( \frac{1 - \exp\left[ -\frac{\hbar v_{heavy \ XR}}{kT} \right]}{\exp\left[ -\frac{\hbar v_{light \ XR}}{2kT} \right]} \right) \right]^{1/n} \]
The extent of isotope separation in a particular reaction is the $\alpha$

$$\alpha_{A-B} = \frac{R^{i/j}_A}{R^{i/j}_B}$$

where $R^{i/j}_A$ is the ratio of isotopes $i$ and $j$ in material $A$. 
The extent of isotope separation in a particular reaction is the α

\[ \alpha_{A-B} = \frac{R_{i/j}^A}{R_{i/j}^B} \]

where \( R_{i/j}^A \) is the ratio of isotopes i and j in material A and

\[ \delta^i = \left[ \frac{R_{i/j}^{\text{sample}}}{R_{i/j}^{\text{standard}}} - 1 \right] \times 1000 \]

\[ \delta_A - \delta_B = \Delta_{A-B} \approx 10^3 \ln \alpha_{A-B} \]

\[ 10^3 \ln \alpha_{a-b}^{i/j} = \frac{10^3}{24} \left( \frac{h}{k_BT} \right)^2 \left( \frac{1}{m_j} - \frac{1}{m_i} \right) \left[ \sum_{x=1} K_{f,x,a} \frac{1}{4\pi^2} - \sum_{x=1} K_{f,x,b} \frac{1}{4\pi^2} \right] \]
Schauble (2004) suggested the following rules governing equilibrium stable isotope fractionations:

- decrease as temperature increases
- fractionation scales with mass
- heavy isotopes of an element will tend to be concentrated in substances with stiffest bonds (high spring constants)
  - high oxidation state; highly covalent bonds; low coordination number; for anions high oxidation state to which the element of interest is bonded; bonds involving elements near the top of the periodic table; low-spin electronic configurations
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It is important to point out that these rules (particularly 3 and 4) are largely untested with respect to fractionations in the less-well studied elements (those other than H, C, N, O, and S) at the present time. Furthermore, within rule (3), it is not known which chemical properties

\[
10^3 \ln \alpha_{a-b}^{i/j} = \frac{10^3}{24} \left( \frac{h}{k_b T} \right)^2 \left( \frac{1}{m_j} - \frac{1}{m_i} \right) \left[ \sum_{x=1}^{4} \frac{K_{f,x,a}}{4\pi^2} - \sum_{x=1}^{4} \frac{K_{f,x,b}}{4\pi^2} \right]
\]
O’Neil 1986 tabulated five common characteristics that are shared by elements that show large variations in isotopic compositions in nature:

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Fayalite

Fe\(^{2+}\) in octahedral coordination

Magnetite

Fe\(^{3+}\) in tetrahedral coordination

Fe\(^{2+}\) and Fe\(^{3+}\) in octahedral coordination
The heavier isotope will be concentrated in stiffer bonds, which are associated with (among others):
- higher oxidation state
- low coordination number

Therefore, magnetite should be more enriched in $^{57}$Fe than fayalite.
Reaction Sequence -

\[ \text{Fa} + \text{Hem} + \text{Qtz} \]

\[ \rightarrow \]

\[ \text{Fa} + \text{Hem} \rightarrow \text{Mgt} + \text{Qtz} \]

\[ \rightarrow \]

\[ \text{Fa} + \text{H}_2\text{O} \leftrightarrow \text{Mgt} + \text{Qtz} + \text{H}_2 \]

OR

\[ \text{Fa} + \text{O}_2 \leftrightarrow \text{Mgt} + \text{Qtz} \]
Shahar, Young, and Manning (2008)

Fractionation $\Delta_{\text{mgf-fay}}^{57}$ versus $10^6/T^2$.
Fractionation $\Delta_{\text{mgt-fay}}^{57}$ as a function of $10^6/T^2$ for different temperatures, as reported by Shahar, Young, and Manning (2008).
Density and Composition of Mantle and Core

Francis Birch

Harvard University, Cambridge, Massachusetts

Abstract. Two new density distributions are obtained, closely related to the seismic velocities. In the upper mantle and transition layer, density is assumed to be proportional to the velocity of compressional waves, with ratios consistent with experimental studies of rocks. In the lower mantle and core, the density variation is found by the Adams-Williamson method. The resulting densities in the lower mantle are found to be in good agreement with shock-wave measurements on rocks having FeO contents in the range 10 ± 2% by weight, and may be accounted for in terms of mixtures of close-packed oxides, silica transforming to stishovite in the transition layer. Except for iron oxide, the chemical composition of the mantle is indeterminate. The density of the outer core is lower than that of iron by about 10%. The estimated density of the inner core, based on shock-wave measurements of metals and considerations of abundance, is no higher than 13.5 g/cm³.
Something Lighter

Depth

Density

Pure Iron
Core
Georg et al., 2007

- 

Earth's mantle

Sun

10% Si in core

5% Si in core

Mg/Si

Al/Si

Mass-dependant fractionation line: x0.5178

- Mean terrestrial mantle
- Mean lunar basalts
- Mean achondrites (martian, eucrites and aubrites)
- Mean chondrites

Georg et al., 2007
Georg et al., 2007

By comparing,

We can learn about
Fitoussi and Bourdon, 2012
Pringle et al., 2013

(a) Bulk 4-Vesta with 10% Si

(b) Bulk 4-Vesta with 18% Si

Si in 4-Vesta's core (wt%)

log fO₂ (ΔIW)
Since the core is not pure iron, is there a compositional effect on the iron isotopes?
The interior of Mars

- **CRUST**: 10-50 km thick
- **MANTLE**
  - Olivine-pyroxene-garnet
  - Spinel-majorite
  - Magnesiowustite-perovskite
- **CORE**
  - Metallic iron (w/nickel and sulfur)

(Illustration by Brooks Bays, PSRD graphics artist.)
\[ \alpha_{XR-X} \approx 1 + \frac{\hbar^2 \sum_i v_{\text{light}}_{XR}^2 - v_{\text{heavy}}_{XR}^2}{24nk^2T^2} \]

\[ \left( \frac{\partial \ln \beta}{\partial P} \right)_T = -\frac{\Delta V}{nRT} \]
Fig. 2. Isotopic fractionation between CaCO₃ and water at 500°C as a function of pressure. Below 12 kbar, calcite is stable; above 12 kbar, aragonite is stable. Error bars show mean deviations from mean at each pressure.

Clayton et al., 1975
$10^3 \ln \beta$ (1 GPa - 1 atm) vs. $10^6 / T^2$ (K)

Graphite, Quartz, Albite, Calcite (18O), Calcite (13C), Rutile, Diamond

Polyakov and Kharlashina, 1994; Horita, 2005
• FeO - 5, 20, 25, 40 GPa
• Fe3C - 2, 5 GPa
• -120 meV to +150 meV
• Energy resolution of 2 meV
• 6-7 seconds counting time,
• 19-50 scans per pressure point
• Panoramic diamond anvil cells
• Be gasket
• $^{57}$FeO powder
Jacobsen et al. 2005 noted that the rhombohedral phase was more compressible.
The diagram shows the relationship between $1000 \times \ln \beta$ and $10^6 / T^2$ for different temperatures: 3000°C and 800°C. The phases Fe, Fe$_3$C, and FeO are indicated on the graph.