Geochemical Interlude:
Composition of the Earth and Isotope Geochemistry

Estimating the composition of the Earth

- Assuming chondritic relative abundances of refractory lithophiles, concentrations of other elements in the Earth can be estimated by observing their relationship to refractory lithophiles.
  - e.g., the K/U ratio of both the crust and the mantle are about 12,000. Since the U is a refractory lithophile element, and its abundance can be estimated from chondrites, we can then estimate the K concentration.
### Composition of the Silicate Earth

<table>
<thead>
<tr>
<th>Element</th>
<th>CI Chondrites</th>
<th>CI Chondritic Mantle</th>
<th>LOSIMAG (Hart and Zindler)</th>
<th>Pyrolite (Ringwood)</th>
<th>Pyrolite (Sun and McDonough)</th>
<th>PRIMA (Allegre et al.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>22.77</td>
<td>49.52</td>
<td>45.96</td>
<td>44.76</td>
<td>45.0</td>
<td>46.12</td>
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<tr>
<td>Al₂O₃</td>
<td>1.64</td>
<td>3.56</td>
<td>4.06</td>
<td>4.46</td>
<td>4.45</td>
<td>4.09</td>
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<tr>
<td>FeO</td>
<td>24.49</td>
<td>7.14</td>
<td>7.54</td>
<td>8.43</td>
<td>8.05</td>
<td>7.49</td>
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<tr>
<td>MgO</td>
<td>16.41</td>
<td>35.68</td>
<td>37.78</td>
<td>37.23</td>
<td>37.8</td>
<td>37.77</td>
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<tr>
<td>CaO</td>
<td>1.30</td>
<td>2.82</td>
<td>3.21</td>
<td>3.60</td>
<td>3.55</td>
<td>3.23</td>
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<tr>
<td>Na₂O</td>
<td>0.67</td>
<td>1.457</td>
<td>0.332</td>
<td>0.61</td>
<td>0.36</td>
<td>0.36</td>
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<tr>
<td>K₂O</td>
<td>0.067</td>
<td>0.146</td>
<td>0.032</td>
<td>0.029</td>
<td>0.029</td>
<td>0.034</td>
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<td>Cr₂O₃</td>
<td>0.39</td>
<td>0.412</td>
<td>0.468</td>
<td>0.43</td>
<td>0.384</td>
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<td>MnO</td>
<td>0.256</td>
<td>0.557</td>
<td>0.130</td>
<td>0.14</td>
<td>0.135</td>
<td>0.149</td>
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<td>TiO₂</td>
<td>0.073</td>
<td>0.159</td>
<td>0.181</td>
<td>0.21</td>
<td>0.20</td>
<td>0.18</td>
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<tr>
<td>NiO</td>
<td>1.39</td>
<td>0.244</td>
<td>0.277</td>
<td>0.241</td>
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<tr>
<td>CoO</td>
<td>0.064</td>
<td>0.012</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.07</td>
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<td>P₂O₅</td>
<td>0.274</td>
<td>0.018</td>
<td>0.019</td>
<td>0.015</td>
<td>0.021</td>
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<tr>
<td>Sum</td>
<td>69.79</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
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</tbody>
</table>

### Composition of the Earth: Bottom Line

- Relative to the Sun and chondrites, the Earth is depleted not only in the highly volatile elements (e.g., H, He, N), but in moderately volatile elements (e.g., Na, K, Pb) and even in slightly volatile elements (e.g., Si).
  - Extent of depletion highly volatile>moderately volatile>slightly volatile
- This depletion suggests that the Earth, or the material that it formed from, experienced high temperatures during the early solar system.
Geochemical Interlude: Some Background

- We want to understand not only current ideas about how the Earth has evolved, but *how* scientists have reached these conclusions.
- To do so, we need to understand some geochemical fundamentals.
  - Isotope geochemistry
    - Radiogenic isotopes
      - Important for understanding evolution of the Earth
    - Stable isotopes
      - Important for understanding atmosphere, hydrosphere, biosphere
  - Trace element geochemistry
    - Rare earth elements in particular

Stable Isotope Geochemistry

- Small differences in mass between isotopes of an element lead to small differences in chemical behavior. These in turn lead to small variations in isotopic abundance.
- Though the nucleus is not involved in chemical process, the mass of the nucleus influences bond strength and motion of atom, which in turn influences chemical behavior.
- Elements of interest are mainly light
  - This is because relative mass difference between isotopes must be large for mass to have significant effect
  - Principal elements of interest are: H, C, N, O, S
  - Also of interest: Li, B, Si, Cl, Fe, Cu, Zn, Mo, etc.
**Definitions:**

- **Fractionation.**
  - *Fractionation* is any process that affects the isotopes of an element differently and therefore changes the ratio of those isotopes.

- **Delta (δ) Notation:**
  - Isotopic compositions of stable isotopes are reported as *per mil variation from some standard.* This is denoted as δ. For example, the isotopic composition of oxygen would be calculated as:

  \[
  \delta^{18}\text{O} = \left( \frac{^{18}\text{O} / ^{16}\text{O}}{^{18}\text{O} / ^{16}\text{O}}_{\text{std}} \right) \times 1000
  \]

  - Standards:
    - For H(D) and O (except for carbonates): SMOW (standard mean ocean water)
    - For C and O (in carbonates): PDB (*Pee Dee Belemite*)
    - For N: ATM (atmospheric nitrogen)
    - For S: CDT (Canyon Diablo Troilite - a sulfide in an iron meteorite)

**Fractionation Factors**

- Expresses the relationship between isotope ratios of two phases (A and B) at equilibrium or as a consequence of a kinetic fractionation

  \[
  \alpha_{A-B} = \frac{R_A}{R_B}
  \]

- Also often written as

  \[
  \Delta_{A-B} = \delta_A - \delta_B
  \]

- The two are related by
  - \( \Delta \approx (\alpha - 1)10^3 \)
  - or \( \Delta \approx 10^3 \ln \alpha \)
A little bit of theory

- **Why do isotopes fractionate?**
  - Isotope fractionations can originate as a consequence of both equilibrium and kinetics
  - **Equilibrium**
    - Refers to most stable distribution of chemical components between phases
    - Components are distributed among phases so as to minimize the energy of a system (specifically, the Gibbs Free Energy)
    - Equilibrium fractionations arise because concentration of the heavy isotope of an element in phase with the strongest bond reduces the overall energy of the system
  - **Kinetics**
    - Kinetics refers to the reaction process
    - Kinetic fractionations arise because the light isotope of an element reacts more rapidly and diffuses faster than heavier isotopes

Atomic Vibrations

- Atoms in molecules or crystal lattices are constantly vibrating.
- The frequency of these vibrations depends on a number of things, including the bond strength, the mass of the atoms involved, and temperature.
- It is primarily the effect of mass on atomic vibrations that lead to isotopic fractionations.

*Two of the vibrational modes of the water molecule*
Equilibrium Fractionations

• Vibrations of atoms in molecules and crystals approximates harmonic oscillator:

• For a diatomic molecule, we can apply Hooke’s Law:

\[ \nu = \frac{1}{2} \sqrt{\frac{k}{\mu}} \]

- Where \( \mu \) is the “reduced mass”:
  \[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

- \( \nu \) is vibration frequency and \( k \) is a constant
- Energy is proportional to \( \nu \), so substituting heavy isotope for light one decreases \( \nu \), lowering energy of the system
- The stronger the bond, the greater this effect

Equilibrium Fractionations: Temperature Effect

• The theoretical expected dependence of the fractionation factor is:

  - At low temperature: \( \alpha \propto \frac{1}{T} \)
  - At high temperature: \( \alpha \propto \frac{1}{T^2} \)

• This means isotope ratios may be used as geothermometers
  - i.e., knowing the different of stable isotope ratios between two phases that formed at equilibrium, we can calculate the temperature at which they formed.
Temperature dependence of fractionation factor

- Comparison of the two approximations for the fractionation of oxygen isotopes between CO$_2$ and water.

Example: determining ancient seawater temperature from fossil carbonate shells
**Kinetic fractionations**

- **Kinetic fractionations occur because:**
  - Light isotopes diffuse faster
    - Equipartition of energy: all kinds of molecules in a gas have same energy
    - Translational energy given by $E = \frac{1}{2}mv^2$
      - If $E$ is the same, the $v$ must be greater for isotope with lower $m$
  - Light isotopes react more rapidly
    - Light isotopes form weaker bonds
    - These bonds break more readily
    - Therefore, light isotopes available for reaction sooner

- **Consider two molecules of carbon dioxide, $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{18}\text{O}_2$, in a gas.**
  - If their energies are equal, the ratio of their velocities is $(45/44)^{1/2}$, or 1.011.
  - Thus $^{12}\text{C}^{18}\text{O}_2$ can diffuse 1.1% further in a given amount of time at a given temperature than $^{13}\text{C}^{16}\text{O}_2$. This result, however, is limited to ideal gases.
  - For the case where molecular collisions are important, the ratio of their diffusion coefficients is the ratio of the square roots of the reduced masses of CO$_2$ and air (mean molecular weight 28.8):
    $$\sqrt[2]{\frac{\mu_{^{12}\text{CO}_2}}{\mu_{^{13}\text{CO}_2}}} = \frac{17.561}{17.406} = 1.004$$
  - Bottom line: $^{12}\text{C}^{16}\text{O}_2$ will diffuse in air 4.4 per mil faster than $^{13}\text{C}^{16}\text{O}_2$
Kinetic fractionation: faster reaction

- The energy required to dissociate the D₂ molecule is 441.6 kJ/mole, whereas the dissociation energy for the H₂ molecule is 431.8 kJ/mole.
- Therefore it is easier to break H-H bonds than H-D bonds.
- Where equilibrium is attained, isotopic fractionations will be determined by equilibrium fractionation. When it is not, the lighter isotope will be concentrated in the reaction products.

Isotope fractionation in the hydrologic system

- “Light” water (water containing light isotopes of hydrogen and oxygen) evaporates more readily than “heavy water” (water containing either ²H or ¹⁸O)
  - Therefore, atmospheric water vapor has lower δ than it source (usually the ocean)
  - Upon condensation, this is reversed:
    - Rain has higher δ than the vapor it condenses from
    - But: all the vapor does not condense at once
    - Residual vapor becomes “lighter” as condensation proceeds
  - Fractionation factor increases with decreasing T
- **Bottom line:**
  - Rain becomes more negative inland and at colder temperatures
Isotope fractionation in rain

Biological fractionation of carbon isotopes

- Biological processes are principle source of fractionation of carbon isotopes
  - Mainly due to photosynthesis
- Fractionation during photosynthesis is primarily kinetic and has several causes
  - $^{12}\text{CO}_2$ diffuses into plants more quickly than $^{13}\text{CO}_2$: CO$_2$ in plant interior has $\delta^{13}\text{C}$ of -4.4‰.
  - Next step in photosynthesis involves breaking one of the C=O bonds to form phosphoglyceric acid (in C$_3$ plants).
    - Since $^{12}\text{C}=\text{O}$ bond is weaker than the $^{12}\text{C}=\text{O}$ bond, $^{12}\text{CO}_2$ participates in this reaction more readily than $^{13}\text{CO}_2$. 
Carbon isotope fractionation in photosynthesis

- C₃ plants (most terrestrial plants) have $\delta^{13}C$ of -20 to -30‰.
- C₄ plants (many grasses, including maize) have $\delta^{13}C \approx -13‰$.
- Photosynthetic bacteria have $\delta^{13}C \approx -13‰$.
- Marine algae have $\delta^{13}C$ of -5 to -30‰.
  - Difference is due to fractionation between CO₂ and HCO₃ and to greater variation in dissolved CO₂ availability in seawater
- Other metabolic processes produce only small carbon isotope fractionations.

Take-Home Message from Biological Isotope Fractionation

- Only biological processes are known to produce $\delta^{13}C$ values of -20‰ and lower in nature.
- Isotopic composition of animals closely matches their diet.
Oxygen Isotope Fractionation during water-rock interaction

- O is the most abundant element in the silicate part of the Earth.
  - $\delta^{18}O$ of the mantle (and therefore the Earth) is about +5.7 (relative to SMOW).
  - Only small (few per mil) fractionations occur as magmas crystallize
- $^{18}O$ partitions preferentially into rock (actually, minerals of the rock) when water and rock react
  - Effect decreases with decreasing T

Take-home message for water-rock interaction

- Rocks whose $\delta^{18}O$ deviates significantly (more than a couple per mil) from 5.7 must have either been affected by low-T reaction with water or contain a component that reacted with water at low-T.
If an element has 3 isotopes or more isotopes (e.g., $^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$), the fractionation between isotopes is generally proportional to the difference in mass:

- e.g., $\delta^{17}\text{O} \approx 0.52 \delta^{18}\text{O}$
- This is called mass-dependent fractionation

Chemical reactions involving photodissociation appear to violate this rule.

- This is known as mass-independent fractionation.
- Examples include O isotopes in meteorites, in stratospheric ozone, and sulfur in Archean sedimentary rocks.

O isotope ratios in meteorites & planetary bodies