Stable Isotopes

Principles of stable isotope fractionation

Annual layers in a tropical ice cap
Stable isotopes

• Many elements of low atomic weight have two or more stable isotopes, e.g.:
  Hydrogen - H, D, T
  Carbon - $^{12}$C, $^{13}$C
  Nitrogen - $^{14}$N, $^{15}$N
  Oxygen - $^{16}$O, $^{17}$O, $^{18}$O
  Sulfur - $^{32}$S, $^{33}$S, $^{34}$S, $^{35}$S

• The different masses cause isotopes to behave differently in physical and chemical processes. For example, $^2$H$_2$$^{18}$O is much heavier than $^1$H$_2$$^{16}$O and will be left behind during evaporation.
Stable isotopes

Stable Isotope geochemistry is concerned with variations of the isotopic compositions of elements arising from physicochemical processes (vs. nuclear processes).

Fractionation refers to the change in an isotope ratio that arises as a result of a chemical or physical process.

Occurs during:
- isotopic exchange reactions in which the isotopes are redistributed among different molecules containing that element
- unidirectional or incomplete reactions
- physical processes like evaporation/condensation, melting/crystallization, adsorption/desorption, diffusion

Characteristics of a useful stable isotope system:
1. large relative mass difference between stable isotopes ($\Delta m/m$)
2. abundance of “rare” isotope is high (0.1-1%)
3. element forms variety of compounds in natural system

Examples: $^2$H/$^1$H, $^7$Li/$^6$Li, $^{11}$B/$^{10}$B, $^{13}$C/$^{12}$C, $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, $^{26}$Mg/$^{24}$Mg, $^{30}$Si/$^{28}$Si, $^{34}$S/$^{32}$S, $^{37}$Cl/$^{36}$Cl, $^{40}$Ar/$^{36}$Ar, $^{44}$Ca/$^{40}$Ca, $^{56}$Fe/$^{54}$Fe
- note convention of putting the heavy isotope above the light isotope
Isotope fractionation

• The degree of fractionation depends on the relative weights of the isotopes.
  – Commonly fractionated: H, C, N, O, S
  – Somewhat fractionated: Si, Fe, Cl
  – Fractionation impossible (monoisotopic): Be, F, Na, Al, P

• Isotope fractionation during chemical processes is caused by exchange reactions of the type:

\[
\frac{1}{2}C^{16}O_2 + H_2^{18}O \leftrightarrow \frac{1}{2}C^{18}O_2 + H_2^{16}O
\]
At equilibrium, we have for the preceding reaction:

\[ K = \frac{\left[ \text{CO}_2^{18} \right]^2 \left[ \text{H}_2\text{O}^{16} \right]}{\left[ \text{CO}_2^{16} \right]^2 \left[ \text{H}_2\text{O}^{18} \right]} \]

We use molar concentrations and not activities because the activity coefficients cancel out.

If CO₂ and H₂O did not discriminate between ¹⁶O and ¹⁸O, then K would be equal to unity (K = 1.00).

However, at 25°C, K = 1.0412, which implies that CO₂ slightly prefers ¹⁸O and H₂O prefers ¹⁶O. This preference is small, but is large enough to cause isotopic fractionation.
Why is $K \neq 1.0$?

Because $^{18}$O forms a stronger covalent bond with C than does $^{16}$O. The vibrational energy of a molecule is given by the equations:

$E_{\text{vibrational}} = \frac{1}{2} h \nu$

$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$

Thus, the frequency of vibration depends on the mass of the atoms, so the energy of a molecule depends on its mass.

$h$ (Plank’s constant) = $6.63 \times 10^{-34}$ Js

$k$ (Boltzmann’s constant) = $1.38 \times 10^{-23}$ J/K

$m = \text{mass}$
• The heavy isotope forms a lower energy bond; it does not vibrate as violently. Therefore, it forms a stronger bond in the compound.

• The Rule of Bigeleisen (1965) - The heavy isotope goes preferentially into the compound with the strongest bonds.
Fractionation during physical processes

- Mass differences also give rise to fractionation during physical processes (diffusion, evaporation, freezing, etc.).

- Fractionation during physical process is a result of differences in the velocities of isotopic molecules of the same compound.

- Consider molecules in a gas. All molecules have the same average kinetic energy, which is a function of temperature.

\[ E_{\text{kinetic}} = \frac{1}{2} mv^2 \]
Because the kinetic energy for heavy and light isotopes is the same, we can write:

\[
\frac{v_L}{v_H} = \sqrt{\frac{m_H}{m_L}}
\]

In the case of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ we have:

\[
\frac{v_L}{v_H} = \sqrt{\frac{28.99827}{27.994915}} = 1.0177
\]

Regardless of the temperature, the velocity of $^{12}\text{C}^{16}\text{O}$ is 1.0177 times that of $^{13}\text{C}^{16}\text{O}$, so the lighter molecule will diffuse faster and evaporate faster.
• Regarding kinetics, lighter isotopes form weaker bonds in compounds, so they are more easily broken and hence react faster. Thus, in reactions governed by kinetics, the light isotopes are concentrated in the products.

• At high temperatures, the equilibrium constant for isotopic exchange tends towards unity, i.e., at $T \rightarrow \infty$, $K \rightarrow 1$, because small differences in mass are less important when all molecules have very high kinetic and vibrational energies.

So at colder temperatures, isotopes will be more heavily fractionated.
The isotope fractionation factor

The isotope fractionation factor is defined as: \( \alpha_b^a = \frac{R_a}{R_b} \)

where \( R_A \), \( R_B \) are the isotope ratios in two phases (e.g., carbonate and water, or water vapor and water)

For example, consider: \( H_2O(l) \leftrightarrow H_2O(v) \) at 25°C

\[ \alpha_v^l(O) = \frac{R_l}{R_v} = \left( \frac{^{18}O/^{16}O}{^{18}O/^{16}O} \right)_v = 1.0092 \]

The differences in isotope ratios are relatively small and are expressed as parts per thousand (per mil) deviations from a standard.
If $\delta > 0$, this means that the sample is enriched in the heavy isotope relative to a standard. If $\delta < 0$, this means that the sample is depleted in the heavy isotope relative to a standard.

The relationship between $\alpha$ and $\delta$ is:

$$\alpha_b^a = \frac{\delta_a + 10^3}{\delta_b + 10^3}$$

The fractionation factor is a function of temperature:

$$1000 \ln \alpha_b^a = \frac{A \times 10^6}{T^2} + B$$

where $A$ and $B$ are constants.
Experimentally determined equilibrium oxygen isotope fractionation factors as a function of temperature.

\( \alpha \) varies inversely with T
Experimentally determined equilibrium carbon isotope fractionation factors as a function of temperature.

\( \alpha \) varies inversely with \( T \).
A useful approximation

Natural logarithms of small numbers like 1.00X have the property that

$$1000 \ln 1.00X \approx X$$

as long as $X \leq 9$.

This approximation holds for $\alpha^a_b$ for C, N, O and S isotopes in many systems. This leads to the following:

$$10^3 (\alpha^a_b - 1) \approx 10^3 \ln \alpha^a_b \approx \delta_a - \delta_b = \Delta^a_b$$

so

$$10^3 \ln \alpha^a_b \approx \Delta^a_b \approx \frac{A \times 10^6}{T^2} + B$$
Each isotopic measurement is reported relative to a **standard**

We define a measurement reporting convention (\(\delta\) or “delta” units):

\[
\delta^{18}O = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}\right) \times 10^3 = \frac{^{18}O/^{16}O_{\text{sample}} - ^{18}O/^{16}O_{\text{standard}}}{^{18}O/^{16}O_{\text{standard}}} \times 10^3
\]

\[
\delta^{13}C = \frac{\left(^{13}C/^{12}C\right)_{\text{sample}} - \left(^{13}C/^{12}C\right)_{\text{standard}}}{\left(^{13}C/^{12}C\right)_{\text{standard}}} \times 10^3
\]

\[
\delta D = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{standard}}}{(D/H)_{\text{standard}}} \times 10^3
\]

**Note that ‘deltas’ are named after the heavy isotope**

<table>
<thead>
<tr>
<th>Table 9.1. Isotope Ratios of Stable Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
<tr>
<td>Lithium</td>
</tr>
<tr>
<td>Boron</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
<tr>
<td>Sulfur</td>
</tr>
</tbody>
</table>

Canyon Diablo meteorite from Meteor Crater, Arizona (CDT).
Isotope fractionation in the hydrosphere

Evaporation of surface water in equatorial regions causes formation of air masses with H₂O vapor depleted in ¹⁸O and D compared to seawater. This moist air is forced into more northerly, cooler air in the northern hemisphere, where water condenses, and this condensate is enriched in ¹⁸O and D compared to the remaining vapor.

The relationship between the isotopic composition of liquid and vapor is:

\[ \delta^{18}O_l = \alpha^l \left( \delta^{18}O_v + 10^3 \right) - 10^3 \]
Assuming that $\delta^{18}O_v = -13.1\%$ and $\alpha^1_v(O) = 1.0092$ at 25°C, then

$$\delta^{18}O_l = 1.0092\left(-13.1 + 10^3\right) - 10^3 = -4.0\%$$

and assuming $\delta D_v = -94.8\%$ and $\alpha^1_v(H) = 1.074$ at 25°C, then

$$\delta D_l = 1.074\left(-94.8 + 10^3\right) - 10^3 = -27.8\%$$

These equations give the isotopic composition of the first bit of precipitation. As $^{18}O$ and D are removed from the vapor, the remaining vapor becomes more and more depleted. Thus, $\delta^{18}O$ and $\delta D$ values become increasingly negative with increasing geographic latitude (and altitude).

$\delta > 0$, sample *enriched* in the heavy isotope

$\delta < 0$, sample *depleted* in the heavy isotope
Map of North America showing contours of the approximate average $\delta D$ values of meteoric surface waters.
Seasonal variations in snow and firn at stake 25 of the South Pole accumulation network

Variation of $\delta^{18}O$ in ice cores from Byrd Station, Antarctica, and Camp Century, Greenland
(a) $\delta^{18}O$ values of foraminifera in Pacific and Caribbean Sea cores during the Brunhes epoch. The variations of $\delta^{18}O$ are attributable to temperature fluctuations of surface water in the oceans during the Pleistocene epoch. (b) Generalized paleotemperature curve and time scales (from Emiliani and Shackleton, 1974).
Increase of $\delta^{18}O$ in tests of a benthic foraminifer in a core collected in 2200 m of water in the equitorial Pacific. The increase in $\delta^{18}O$ of the carbonate indicates a decrease in the temperature of bottom water at this site 16 Ma and was associated with the growth of continental ice sheets in Antarctica.
Because both H and O occur together in water, $\delta^{18}O$ and $\delta D$ are highly correlated, yielding the meteoric water line:

$\delta D \approx 8\delta^{18}O + 10$
Rayleigh distillation

Isotopic fractionation that occurs during condensation in a moist air mass can be described by Rayleigh distillation. The equation governing this process is:

\[ R_v = R_v^o f^{\alpha-1} \]

where \( R_v \) = isotope ratio of remaining vapor, \( R_v^o \) = isotope ratio in initial vapor, \( f \) = the fraction of vapor remaining and

\[ \alpha = \frac{R_l}{R_v} \]
Effect of Rayleigh distillation on the $\delta^{18}$O value of water vapor remaining in the air mass and of meteoric precipitation falling from it at a constant temperature of 25°C.

Complications:
1) Re-evaporation
2) Temperature dependency of $\alpha$

$\delta^{18}$O increasingly negative with continued precipitation
Oxygen isotope fractionation in clays

• Oxygen in igneous and metamorphic rocks is enriched in $^{18}$O relative to SMOW.

• When these minerals react with acidic meteoric waters during weathering to form clays, the amount of isotopic fractionation depends on:
  – The isotope composition of the meteoric water.
  – The isotope composition of the original minerals.
  – The water/rock ratio.
  – Temperature.
  – The fractionation factors.
• To form clays, high water/rock ratios are required, so the O-isotope composition will be dictated by that of meteoric water; the composition of the rock will have little influence.

• Similar remarks apply for H-isotopes, except that igneous and metamorphic rocks are depleted in D relative to SMOW.

• We find that the following equations relate $\delta^D$ and $\delta^{18}O$:

  $$\delta^D = 7.3 \ \delta^{18}O - 260 \text{ (montmorillonite)}$$

  $$\delta^D = 7.5 \ \delta^{18}O - 220 \text{ (kaolinite)}$$

• Once clays are formed, they do not re-equilibrate unless heated to $T > 100^\circ C \ (H)$ or $T > 300^\circ C \ (O)$. 
Schematic representation of the isotope composition of H and O in clay minerals formed from meteoric water.
Oxygen isotope geothermometry

• The fractionation of oxygen isotopes among coexisting minerals can be used as a geothermometer.

• It must be assumed that the minerals crystallized at the same time at equilibrium, and were not subsequently altered afterwards.

• If the fractionation of oxygen isotopes between several mineral pairs yield the same temperatures, then we have more confidence in the temperature estimate.
An example

Consider a hydrothermal vein in which quartz, calcite and chlorite were deposited together. The minerals were analyzed for their O-isotopes which resulted in:

\[ \delta^{18}O_{\text{quartz}} = 5.1 \, \text{‰}; \quad \delta^{18}O_{\text{calcite}} = 3.8 \, \text{‰}; \quad \delta^{18}O_{\text{chlorite}} = -1.5 \, \text{‰}. \]

Assuming these three minerals were all in equilibrium with one another, calculate the temperature of formation. First, we need the fractionation factors for these minerals:

\[
10^3 \ln \alpha_{w}^{qtz} = \frac{3.38 \times 10^6}{T^2} - 3.40 \approx \Delta_{w}^{qtz} = \delta^{18}O_{qtz} - \delta^{18}O_{w}
\]

\[
10^3 \ln \alpha_{w}^{cc} = \frac{2.78 \times 10^6}{T^2} - 2.89 \approx \Delta_{w}^{cc} = \delta^{18}O_{cc} - \delta^{18}O_{w}
\]

\[
10^3 \ln \alpha_{w}^{chl} = \frac{1.56 \times 10^6}{T^2} - 4.70 \approx \Delta_{w}^{chl} = \delta^{18}O_{chl} - \delta^{18}O_{w}
\]
\[
\Delta_{cc}^{qtz} = \Delta_{w}^{qtz} - \Delta_{w}^{cc} = \frac{3.38 \times 10^6}{T^2} - 3.40 - \frac{2.78 \times 10^6}{T^2} + 2.89
\]

\[
= \frac{0.6 \times 10^6}{T^2} - 0.51 = 5.1 - 3.8 = 1.3 \%_00 = \delta^{18}O_{qtz} - \delta^{18}O_{cc}
\]

\[
T = 575.75 \text{ K} = 302.6^\circ \text{C}
\]

\[
\Delta_{chl}^{qtz} = \Delta_{w}^{qtz} - \Delta_{w}^{chl} = \frac{3.38 \times 10^6}{T^2} - 3.40 - \frac{1.56 \times 10^6}{T^2} + 4.7
\]

\[
= \frac{1.82 \times 10^6}{T^2} + 1.30 = 5.1 - (-1.5) = 6.6 \%_00 = \delta^{18}O_{qtz} - \delta^{18}O_{chl}
\]

\[
T = 586.0 \text{ K} = 312.9^\circ \text{C}
\]
\[ \Delta_{chl}^{cc} = \Delta_{w}^{cc} - \Delta_{w}^{chl} = \frac{2.78 \times 10^6}{T^2} - 2.89 - \frac{1.56 \times 10^6}{T^2} + 4.7 \]
\[ = \frac{1.22 \times 10^6}{T^2} + 1.81 = 3.8 - (-1.5) = 5.3 \%_00 = \delta^{18}O_{cc} - \delta^{18}O_{chl} \]

\[ T = 591.2 \text{ K} = 318.1^\circ\text{C} \]

The average of these three values is 311±8°C. Within experimental error, these values are identical, lending confidence that the minerals were deposited at the same time, in equilibrium, at the same temperature.
## Oxygen fractionation in rock-forming minerals

### Table 25.2 Geothermometry equations based on fractionation of oxygen isotopes between mineral pairs

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$A^a$</th>
<th>$B$</th>
<th>Temperature Range, °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz-albite</td>
<td>0.50</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-jadeite</td>
<td>1.09</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-anorthite</td>
<td>1.59</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-diopsite</td>
<td>2.08</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-wollastonite</td>
<td>2.20</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-magnetite</td>
<td>6.11</td>
<td>0</td>
<td>400 to 800</td>
<td>1</td>
</tr>
<tr>
<td>Quartz-magnetite</td>
<td>7.8 ± 0.4</td>
<td>0</td>
<td>600</td>
<td>2</td>
</tr>
<tr>
<td>Quartz-magnetite</td>
<td>6.1 ± 0.2</td>
<td>0</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>Quartz-calcite</td>
<td>0.50</td>
<td>0</td>
<td>500 to 700</td>
<td>3</td>
</tr>
<tr>
<td>Quartz-zoisite</td>
<td>1.56</td>
<td>0</td>
<td>500 to 700</td>
<td>5, 6</td>
</tr>
<tr>
<td>Quartz-muscovite</td>
<td>2.20</td>
<td>−0.60</td>
<td>&gt;500</td>
<td>5, 6</td>
</tr>
<tr>
<td>Quartz-plag.</td>
<td>(0.79 + 0.90β$^b$)</td>
<td>−(0.43−0.30β)</td>
<td>400–500</td>
<td>4</td>
</tr>
</tbody>
</table>

\[
10^3 \ln \alpha_b^a \approx \Delta_b^a \approx \frac{A \times 10^6}{T^2} + B
\]
Variation of $\Delta^{18}\text{O}$ with temperature, where $\Delta^{18}\text{O}$ is the difference between $\delta^{18}\text{O}$ values of two coexisting minerals that have equilibrated oxygen with the same isotope reservoir at the same temperature.
Range of $\delta^{18}O$ values of igneous rocks and stony meteorites
Sulfur isotopes

The stable sulfur isotopes are: $^{32}\text{S}$, $^{33}\text{S}$, $^{34}\text{S}$, $^{35}\text{S}$, but the fractionation between $^{32}\text{S}$ and $^{34}\text{S}$ is the most studied.

$$
\delta^{34}\text{S} = \frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{sample}} - \left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{standard}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_{\text{standard}}} \times 10^3
$$

The most important cause of S-isotope fractionation is the metabolism of the bacteria *Desulfovibrio* and *Desulfatomaculum*. These bacteria flourish in anoxic environments by oxidizing organic matter using oxygen from $\text{SO}_4^{2-}$. The $\text{SO}_4^{2-}$ is reduced to $\text{H}_2\text{S}$, which is enriched in $^{32}\text{S}$ relative to sulfate.
Sulfate reduction

• The reaction can be written:
  \[ \text{CH}_4 + \text{SO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{S}(g) + \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

• For this reaction at 25°C, \( \Delta G_r^\circ = -26.324 \) kcal mol\(^{-1} \) or log \( K = 19.3 \), so the reaction is highly favored thermodynamically, but is slow in the absence of bacteria.

• The reaction is not at equilibrium and a large kinetic isotope fractionation factor between sulfate and sulfide occurs when bacteria are involved.
Sulfide/sulfate fractionation

The extent of fractionation of S-isotopes between sulfate and sulfide depends on:
1) The rate of metabolism by bacteria.
2) Composition and abundance of food supply.
3) Size of sulfate reservoir.
4) Temperature.
5) The rate of removal of H$_2$S.
Alternative scenarios

• Closed system - the concentration of H$_2$S may build up until it poisons the bacteria, e.g., in the Black Sea. The H$_2$S is then strongly depleted in $^{34}$S.

• Open system - the sulfate reservoir is virtually infinite, and H$_2$S is removed. Metabolized sulfide is depleted in $^{34}$S, but the isotope composition of sulfate remains constant.

• Open system, sulfate-limited - H$_2$S is free to escape. Rayleigh distillation occurs. The remaining sulfate and each new batch of H$_2$S become enriched in $^{34}$S.
Distribution patterns for $\delta^{34}\text{S}$ values of $\text{H}_2\text{S}$ and sulfide minerals when sulfate of $\delta^{34}\text{S} = 20\%$ is reduced by various mechanisms.
S isotopes as tracers

Metabolic H\textsubscript{2}S may react with metals and form sulfides. These generally have $\delta^{34}$S $< 0$, but this may vary stratigraphically (and may even be $> 0$) depending on the extent of Rayleigh distillation.

Thus, sedimentary and igneous sulfides tend to exhibit different trends in their $\delta^{34}$S values.

- Sedimentary sulfides - $\delta^{34}$S exhibits a wide range, generally towards negative values.
- Igneous sulfides - $\delta^{34}$S values close to 0 ‰.
Sulfur isotope variation in nature
Caveats!

We need to be careful in using S-isotopes as tracers because:

1) $\delta^{34}S$ of some sedimentary sulfides can be near zero or positive.

2) $\delta^{34}S$ of some magmatic sulfides could be negative if the S originally came from sedimentary rocks that were melted.

3) $\delta^{34}S$ values of igneous rocks can vary from zero depending on pH and partial pressure of oxygen.

4) $\delta^{34}S$ of sulfides in igneous and metamorphic rocks can be changed by isotope exchange during alteration.
Variation of isotope composition of S and Sr in Phanerozoic time. Note that both $\delta^{34}S$ and the $^{87}$Sr/$^{86}$Sr ratio declined irregularly during the Paleozoic Era from the Cambrian to the Permian periods. During the Mesozoic, both parameters had low values but began to rise during the Cretaceous and continued to rise in the Tertiary. The observed variations in isotopic compositions of S and Sr in the oceans were caused by global changes in the geochemical cycles of these elements.
S-isotope geothermometry

We can use sulfur isotopic fractionation in sulfide and sulfate minerals as a geothermometer if all minerals precipitated at the same time in equilibrium with one another.

For example, consider the fractionation between galena and sphalerite:

\[ \Delta_{sp}^{gn} = \delta^{34}S_{sp} - \delta^{34}S_{gn} \approx 1000 \ln \alpha_{gn}^{sp} = \frac{7.2 \times 10^5}{T^2} \]

Suppose we determine that:

\[ \Delta_{sp}^{gn} = 4.0^{\circ/oo} \]

Then we calculate:

\[ T = \left( \frac{7.2 \times 10^5}{4.0} \right)^2 = 424 \text{ K} = 151^{\circ} \text{C} \]
Experimentally determined equilibrium sulfur isotope fractionation factors as a function of temperature.
Carbon isotopes as tracers:
The carbon isotopic variation in nature.