Oxygen Isotopes: measuring temperature and ice volume

We've talked about major ice ages in the past.
How do we monitor the extent of glaciation in the past?
How do we take the planet's temperature?

Oxygen Isotopes are the major tool for paleoclimate reconstruction

Three stable isotopes

\[ ^{16}\text{O}: 99.76\% \]
\[ ^{17}\text{O}: 0.04\% \]
\[ ^{18}\text{O}: 0.20\% \]

Measured as \( \delta^{18}\text{O} \) values, where standards are either Standard Mean Ocean Water (SMOW) or a marine carbonate (PDB).

We'll take advantage of a few simple properties of the isotopes of oxygen to measure \( T \).

When a mineral forms from a solution, isotopes are differentially partitioned between liquid and solid due to differences in the stability of bonds they form.

For example: \( ^{18}\text{O} \) forms relatively stronger bonds in calcite than it does in water, so \( ^{18}\text{O} \) becomes enriched in calcite relative to the water from which it forms.

\[
\text{At } 25^\circ\text{C, } \alpha_{\text{calcite/water}} = 1.0288
\]

So if the water had a \( \delta^{18}\text{O} \) value of 0‰ (SMOW) then the calcite would be

\[
1.0288 = \frac{1000 + \delta^{18}\text{O}_{\text{calcite}}}{1000 + 0}
\]

\[
\delta^{18}\text{O}_{\text{calcite}} = (1000 \times 1.0288) - 1000 = 28.8 \text{‰ (SMOW)}
\]

To standardize relative to marine carbonate, use the following equation:

\[
\delta^{18}\text{O}_{\text{calcite}} \text{ (relative to SMOW)} = 1.03091 \times (\delta^{18}\text{O}_{\text{calcite}} \text{ relative to PDB}) + 30.91
\]

So: \( \delta^{18}\text{O}_{\text{calcite}} \text{ (PDB)} = -2.05\%\)

The fractionation of oxygen isotopes between calcite and water is not constant.

It varies with temperature

Greater fractionation at low temperatures.
Smaller fractionation at high temperatures.

Described by the following equation (note behavior as \( T \) changes)

\[
\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}} \approx 1000\ln \alpha_{\text{calcite/water}} = (2.78 \times 10^6/T^2) - 2.89, \text{ where } T \text{ is in K}
\]

Remember: \( K = {^\circ}\text{C} + 273.15 \)

DO IT YOURSELF!!!

At \( 25^\circ\text{C} \), \( \delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}} \approx 28.38\%\), solve the approximation for \( \alpha_{\text{calcite/water}} \) and show it is 1.0288. Next, plug in the correct temperature on the right-hand side of the equation, and again solve for \( \alpha_{\text{calcite/water}} \) and show it is 1.0288.

So, if we know \( \delta^{18}\text{O}_{\text{water}} \), we can solve for \( T \).

This relationship, and ones like it for other minerals, are the basis for marine paleothermometry

There is a well-developed marine temperature curve for last 100 Ma

We can even separate surface water temperature from deep-water temperature using "bugs" that live at different depths.
There is one major complication with this method
  Must assume $\delta^{18}O_{\text{water}}$ hasn't changed.
  This turns out to be a bad assumption.

$H_2^{16}O$ evaporates faster than $H_2^{18}O$, $H_2^{18}O$ condenses faster than $H_2^{16}O$

$^{18}O/^{16}O_{\text{vapor remaining}}/^{18}O/^{16}O_{\text{vapor initial (or Vo)}} = f \ (\text{or fraction of vapor remaining})^{(\alpha-1)}$
where $\alpha_{\text{water/vapor}}$ is the isotopic fractionation associated with the condensation of water from vapor
(1.0092 at 25°C)

When using $\delta^{18}O$ values, rather than $^{18}O/^{16}O$ ratios, the appropriate equations to calculate the oxygen isotope value of the remaining vapor or the rain that would condense from it are:

For vapor: $\delta^{18}O_{\text{vapor remaining}} = (\delta^{18}O_{\text{Vo}} + 1000)f^{(\alpha-1)} - 1000$
For rain: $\delta^{18}O_{\text{rain}} = \alpha(\delta^{18}O_{\text{vapor remaining}} + 1000) - 1000$

**DO IT YOURSELF!!!**
Below, assume that $\delta^{18}O_{\text{Vo}} = -9.1\%$ SMOW.
Convince yourself that before the rain begins to fall (i.e., when $f = 1$), the first equation yields $\delta^{18}O_{\text{vapor remaining}} = \delta^{18}O_{\text{Vo}}$. Convince yourself that when half the vapor has rained away (i.e., when $f = 0.5$), $\delta^{18}O_{\text{vapor remaining}} \approx -15.4\%$ SMOW and $\delta^{18}O_{\text{rain}} \approx -6.3\%$ SMOW.

This distillation process has three consequences that are important for paleoclimatology
1. Creates a regular relationship between MAT at a site and $\delta^{18}O_{\text{rain}}$
   $\delta^{18}O_{\text{rain}}$ is higher in warm areas and lower in cold areas
2. Creates a regular relationship between MAT and $\delta^{18}O_{\text{rain \& snow}}$ through time.
   $\delta^{18}O_{\text{rain \& snow}}$ is higher in warm times and lower in cold times
3. Causes glacial ice formed at high latitudes to be extremely enriched in $^{16}O$
   Formation of ice on land sucks $^{16}O$ out of the ocean and shifts raises its $\delta^{18}O$ value
   When there are big ice sheets on land, the $\delta^{18}O$ value of ocean water is higher