Stable Isotopes: Natural variations in the ratios of isotopes can be used to trace the flow of mass or the extent to which a process has occurred.

Issues of Notation: Example is from C isotopes, but the same conventions apply to O.

Stable Carbon Isotopes: $^{12}\text{C}: 98.89\%$ $^{13}\text{C}: 1.11\%$

Isotopic fractionation: Sorting of isotopes between substances as a consequence of differences in molecular bond energies or rates of transport for different isotopes of an element.

Isotopic Notation: Because one isotope is common and the other is rare, and because isotope fractionations are often small, naturally-occurring isotopic differences between substances are often very small, in the range of parts per thousand. They are easier to remember if we report isotopic compositions of materials using: $\delta$ values

$$\delta^{13}\text{C} = \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}\right)_{\text{sample}} - \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}\right)_{\text{standard}} \times 1000 = \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}\right)_{\text{sample}} - 1 \times 1000$$

$\delta$ values indicate relative enrichment or depletion in $^{13}\text{C}$ to $^{12}\text{C}$.

Higher $\delta$ values, relatively more $^{13}\text{C}$, less $^{12}\text{C}$: Heavier

Lower $\delta$ values, relatively less $^{13}\text{C}$, more $^{12}\text{C}$: Lighter

The units are parts per thousand or per mil (‰)

Fractionations are measured using fractionation factors or isotopic offsets.

The Fractionation Factor ($\alpha$) between two substances, $a$ and $b$, is defined as:

$$\alpha_{a/b} = \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}\right)_a \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}\right)_b = \frac{1000 + \delta^{13}\text{C}_a}{1000 + \delta^{13}\text{C}_b}$$

The Isotopic Offset between $a$ and $b$, is defined as:

$$\Delta^{13}\text{C}_{a/b} = \delta^{13}\text{C}_a - \delta^{13}\text{C}_b \approx 1000 \ln \alpha_{a/b}$$

Why are C isotopes useful in constraining the burial history of carbon?

Photosynthesis strongly favors $^{12}\text{C}$ over $^{13}\text{C}$-bearing CO$_2$

During CaCO$_3$ precipitation, $^{13}\text{C}$-bearing HCO$_3^-$ forms stronger bonds than $^{12}\text{C}$-bearing HCO$_3^-$

Plants (C-H materials) are light. Calcite (C-O material) is heavy.

$$\Delta^{13}\text{C}_{\text{CO}_2/\text{plant}} = 16\%$$

$$\Delta^{13}\text{C}_{\text{CO}_2/\text{calcite}} = -9\%$$

| marine algae modern $\delta^{13}\text{C} = -23\%$ | dissolved CO$_2$ modern $\delta^{13}\text{C} = -7\%$ | protist calcite modern $\delta^{13}\text{C} = +2\%$ |

BIOLOGICAL CARBON PUMP

Bury greater amounts of C-H material, suck $^{12}\text{C}$ out of surface environment.

Bury greater amounts of C-O material, suck $^{13}\text{C}$ out of surface environment.

Volcanic outgassing pumps CO$_2$ into the system with a known, relatively constant value.

Changes in C isotope ratios of surface waters are recorded in rocks and fossils.

Isotopes monitor the balance between volcanic input, organic C burial, and carbonate C burial.
How can we calculate the rate of organic carbon burial?

1. At steady state, amount of carbon entering and exiting the ocean must be the same.

\[ \text{Flux}_{\text{in}} \ (\text{Gt/yr}) = \text{Flux}_{\text{out}} \ (\text{Gt/yr}) \]

Where \( \text{Flux}_{\text{out}} = \text{Flux}_{\text{organic}} + \text{Flux}_{\text{carbonate}} \). \( \text{Flux}_{\text{in}} \) comes from volcanoes and weathering.

Rather than deal with true fluxes, which may be hard to quantify, we’ll convert to proportional fluxes. Divide both sides of the flux equation above by \( \text{Flux}_{\text{in}} \).

\[ 1 = f_{\text{carb}} + f_{\text{org}} \]

Where \( f_{\text{carb}} \) and \( f_{\text{org}} \) are the proportions of C buried as organic matter and carbonate.

2. \( \delta \) values can serve as labels of mass flow of different types of carbon.

\( \delta \) values can be manipulated algebraically. For example, if you want to balance isotope as well as the mass fluxes, all you need to do is multiply the fluxes above by their isotope values.

\[
(1) \quad \delta^{13}\text{C}_\text{input} = (f_{\text{carb}})\delta^{13}\text{C}_\text{carb} + (f_{\text{org}})\delta^{13}\text{C}_\text{org}
\]

We can make two useful equations relating \( f_{\text{org}} \) (which is related to \( \text{O}_2 \) input to the atmosphere) \( \delta^{13}\text{C}_\text{carb} \) to out of this relationship if we rearrange and substitute.

Remember/define:
\( \delta^{13}\text{C}_\text{input} = -5\% \) (volcanism, weathering)
\( \Delta^{13}\text{C}_{\text{carb-org}} = \delta^{13}\text{C}_\text{carb} - \delta^{13}\text{C}_\text{org} = +25\% \) (fractionation of C b/w inorganic and organic pools)
\( f_{\text{org}} = 1 - f_{\text{carb}} \)

Time for some algebra
\[
\delta^{13}\text{C}_\text{input} = (1 - f_{\text{org}})\delta^{13}\text{C}_\text{carb} + (f_{\text{org}})(\delta^{13}\text{C}_\text{carb} - \Delta^{13}\text{C}_{\text{carb-org}})
\]
\[
\delta^{13}\text{C}_\text{input} = \delta^{13}\text{C}_\text{carb} - f_{\text{org}}\delta^{13}\text{C}_\text{carb} + f_{\text{org}}\delta^{13}\text{C}_\text{carb} - f_{\text{org}}\Delta^{13}\text{C}_{\text{carb-org}}
\]
\[
\delta^{13}\text{C}_\text{input} = \delta^{13}\text{C}_\text{carb} - f_{\text{org}}\delta^{13}\text{C}_\text{carb} + f_{\text{org}}\delta^{13}\text{C}_\text{carb} - f_{\text{org}}\Delta^{13}\text{C}_{\text{carb-org}}
\]
\[
\delta^{13}\text{C}_\text{input} = \delta^{13}\text{C}_\text{carb} - f_{\text{org}}\Delta^{13}\text{C}_{\text{carb-org}}
\]

Equation 1: \( f_{\text{org}} = (\delta^{13}\text{C}_\text{carb} - \delta^{13}\text{C}_\text{input})/\Delta^{13}\text{C}_{\text{carb-org}} \)

Substitute using modern values: \( f_{\text{org}} = (\delta^{13}\text{C}_\text{carb} + 5)/25 \)

Equation 2: \( \delta^{13}\text{C}_\text{carb} = \delta^{13}\text{C}_\text{input} + f_{\text{org}}\Delta^{13}\text{C}_{\text{carb-org}} \)

Substitute using modern values: \( \delta^{13}\text{C}_\text{carb} = -5 + 25f_{\text{org}} \)

Higher \( \delta^{13}\text{C}_\text{carb} \) values indicate higher proportional burial of \( ^{12}\text{C} \)-enriched organic matter. Lower \( \delta^{13}\text{C}_\text{carb} \) values indicate proportionally greater burial of \( ^{13}\text{C} \)-enriched carbonate.

The second equation and the equation for \( \delta^{13}\text{C}_\text{org} \) are plotted on the next page. They illustrate, quantitatively, how \( \delta^{13}\text{C}_\text{carb} \) and \( \delta^{13}\text{C}_\text{org} \) change with changes in the burial flux of organic C.
\[ \delta^{13}C_{\text{carb}} = -5 + 25f_{\text{org}} \]

\[ \delta^{13}C_{\text{input}} = -5 \]

\[ \delta^{13}C_{\text{org}} = \delta^{13}C_{\text{carb}} - 25 \]