Stable Isotope Tracers

OCN 623 – Chemical Oceanography

29 March 2016

Reading: Emerson and Hedges, Chapter 5, p.134-153

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Student Learning Outcomes

At the completion of this module, students should be able to:

1. Explain and use the “delta” notation commonly used with stable isotopes
2. Explain isotopic fractionation and how it can be used to elucidate oceanographic phenomena
3. Describe the common uses of stable isotopes as oceanic tracers
Outline

• Stable Isotopes - Introduction & Notation
• Isotope Fractionation
• Some Oceanographic Applications

Uses of Stable Isotopes in Oceanography

• Most commonly studied:
  • $^2$H  $^3$He  $^{13}$C  $^{15}$N  $^{18}$O  $^{34}$S
• Tracers of biological, physical, geological ocean processes
• Horizontal mixing (water mass tracers)
• Paleoceanography - Record past changes in physical, chemical, and biological processes in the ocean
• Pulse/chase experiments to determine metabolic rates and pathways (labeled tracers)
Isotopes of Elements

The chemical characteristic of an element is determined by the number of protons in its nucleus.

**Atomic Number** \( (Z) \) = number of protons = defines the chemistry

**Atomic Mass** \( (N) \) = protons + neutrons

**Isotopes** = atoms with same \( Z \) but different \( N \)

Abbreviated: \( ^{12}\text{C}, ^{13}\text{C}, ^{14}\text{C} \) or \( \text{C-12, C-13, C-14} \)

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**Nuclides of Elements 1 (Hydrogen) through 12 (Magnesium)**

Most elements have more than one stable isotope (shaded)
Most Commonly Used Isotopes

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Protons</th>
<th>Neutrons</th>
<th>% Abundance</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>0</td>
<td>99.985</td>
<td></td>
</tr>
<tr>
<td>Deuterium</td>
<td>D (H)</td>
<td>1</td>
<td>1</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Tritium</td>
<td>T (3H)</td>
<td>1</td>
<td>2</td>
<td>10^34 to 10^96</td>
<td>$\tau_{1/2} = 12.33 \text{ y}$</td>
</tr>
<tr>
<td>Helium</td>
<td>$^3\text{He}$</td>
<td>2</td>
<td>1</td>
<td>0.000137</td>
<td></td>
</tr>
<tr>
<td>$^4\text{He}$</td>
<td></td>
<td>2</td>
<td>2</td>
<td>99.998863</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>6</td>
<td>6</td>
<td>98.89</td>
<td></td>
</tr>
<tr>
<td>$^{12}\text{C}$</td>
<td></td>
<td>6</td>
<td>7</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td></td>
<td>6</td>
<td>8</td>
<td>10^-10</td>
<td>$\tau_{1/2} = 5730 \text{ y}$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N}$</td>
<td>7</td>
<td>7</td>
<td>99.634</td>
<td></td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td></td>
<td>7</td>
<td>8</td>
<td>0.386</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}\text{O}$</td>
<td>8</td>
<td>8</td>
<td>99.757</td>
<td></td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td></td>
<td>8</td>
<td>9</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td>$^{18}\text{O}$</td>
<td></td>
<td>8</td>
<td>10</td>
<td>0.205</td>
<td></td>
</tr>
</tbody>
</table>

% abundance is for the average Earth’s crust, ocean and atmosphere.

Red isotopes are radioactive.

All isotopes of a given element have the same basic chemical properties, yet heavier isotopes typically form stronger bonds and diffuse slightly slower.

The “Delta” Notation

- Absolute isotope ratios are measured for samples and a standard, and the relative measure “delta” is calculated:

$$
\delta^{13}\text{C} \equiv \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}} \cdot 1000_{\circ/\circ}
$$

- $\circ/\circ = \text{per mil} = 10^{-3}$
  - Example: 0.005 = 5$\circ/\circ$

- Samples with negative delta values are depleted in $^{13}\text{C}$ (they are “light”)
- Samples with positive delta values are enriched in $^{13}\text{C}$ (they are “heavy”)

- Red isotopes are radioactive.
Each isotopic measurement is reported relative to a standard:

<table>
<thead>
<tr>
<th>Element</th>
<th>δ value</th>
<th>Ratio</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>δD</td>
<td>$^2\text{H}/^1\text{H}$</td>
<td>Standard Mean Ocean Water (SMOW) ←</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP2)</td>
</tr>
<tr>
<td>Helium</td>
<td>δ$^3\text{He}$</td>
<td>$^3\text{He}/^4\text{He}$</td>
<td>Atmospheric He ←</td>
</tr>
<tr>
<td>Boron</td>
<td>δ$^{11}\text{B}$</td>
<td>$^{11}\text{B}/^{10}\text{B}$</td>
<td>NIST SRM 951 ←</td>
</tr>
<tr>
<td>Carbon</td>
<td>δ$^{13}\text{C}$</td>
<td>$^{13}\text{C}/^{12}\text{C}$</td>
<td>Pee Dee Belemnite (PDB) ←</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>δ$^{15}\text{N}$</td>
<td>$^{15}\text{N}/^{14}\text{N}$</td>
<td>Atmospheric $\text{N}_2$ ←</td>
</tr>
<tr>
<td>Oxygen</td>
<td>δ$^{18}\text{O}$</td>
<td>$^{18}\text{O}/^{16}\text{O}$</td>
<td>Standard Mean Ocean Water (SMOW) ←</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP2) ←</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pee Dee Belemnite (PDB) ←</td>
</tr>
<tr>
<td>Sulfur</td>
<td>δ$^{34}\text{S}$</td>
<td>$^{34}\text{S}/^{32}\text{S}$</td>
<td>Canyon Diablo Troilite (CDT) ←</td>
</tr>
</tbody>
</table>

Equilibrium Isotopic Fractionation

*Fractionation* occurs in reactions that do not go to completion:

- Lighter isotopes react faster, and to a greater extent
- Reactants are enriched in the heavier isotopes
- Reaction products are depleted in the heavier isotopes

Note: There is no equilibrium fractionation if a reaction goes to completion (*i.e.*, all of the reactants are consumed)

**Fractionation Factor ($\alpha$):** $\alpha_{A/B} = \frac{R_{\text{Prod}}}{R_{\text{React}}}$

where $R_{\text{Prod}}$ and $R_{\text{React}}$ are the isotope ratios of the Product and the Reactant after equilibrium is reached (*Reactant ↔ Product*)
**Kinetic Isotopic Fractionation**

Unidirectional reactions (e.g., those involving organic matter) show kinetic fractionation

Example:  
\[ {^{12}}\text{CO}_2 + \text{H}_2\text{O} \rightarrow {^{12}}\text{CH}_2\text{O} + \text{O}_2 \quad \text{faster} \]
\[ {^{13}}\text{CO}_2 + \text{H}_2\text{O} \rightarrow {^{13}}\text{CH}_2\text{O} + \text{O}_2 \quad \text{slower} \]

Thus, organic matter gets depleted in \(^{13}\text{C}\) during photosynthesis (i.e., \(\delta^{13}\text{C}\) becomes more negative)

Similarly, organic matter gets enriched in \(^{13}\text{C}\) during respiration (i.e., \(\delta^{13}\text{C}\) becomes more positive):  
\[ {^{12}}\text{CH}_2\text{O} + \text{O}_2 \rightarrow {^{12}}\text{CO}_2 + \text{H}_2\text{O} \quad \text{faster} \]
\[ {^{13}}\text{CH}_2\text{O} + \text{O}_2 \rightarrow {^{13}}\text{CO}_2 + \text{H}_2\text{O} \quad \text{slower} \]

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**Group Discussion**

![Graph showing the δ\(^{13}\text{C}\)DIC curve](image)

Why is the \(\delta^{13}\text{C}_{\text{DIC}}\) curve the shape it is? What processes are important? (Prepare an explanation of your interpretation)
Examples of Stable Isotopes in Oceanography

- $^3$He to study deep ocean circulation in the Pacific
- $^{18}$O to determine freshwater balance in the Arctic Ocean
- $^{18}$O as a recorder of the ice ages

$^3$He Plume from East Pacific Rise

Broecker and Peng, 1982
3He (%) at 2500 m depth

3He Plume from Loihi Seamount (Hawaii)

Fig. 6. δ(3He)% contoured on a surface at a depth of 1100 m, showing the broad lateral extent of the Loihi plume. In some cases, bottle data were interpolated to 1100-m deep surface. The contour interval is 1% in δ(3He), the accuracy of the measurements is 0.25% (1σ). This figure includes data from eight different expeditions spanning the time interval from 1985 to 1994. Although these data are not synoptic, the sampling period is relatively short compared with the time scale for circulation at this depth. Helium data along WOCE lines P4 and P16 were provided by W. Jenkins (4, 29).
Examples of Stable Isotopes in Oceanography

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Freshwater Balance in the Arctic Ocean

We can use salt, $\delta^{18}$O, and nutrients to separate the contributions of the individual freshwater sources.

\[ f_s + f_r + f_w = 1. \]
\[ f_o S_o + f_r S_r + f_w S_w = S_w. \]
\[ f_o \delta^{18}O_o + f_r \delta^{18}O_r + f_w \delta^{18}O_w = \delta^{18}O_w. \]
\[ f_o PO_4^{3-} + f_r PO_4^{3-} + f_w PO_4^{3-} = PO_4^{3-}. \]

Schlosser et al., 1999 Ekwurzel et al., 2001
Examples of Stable Isotopes in Oceanography

- $^3$He to study deep ocean circulation in the Pacific
- $^{18}$O to determine freshwater balance in the Arctic Ocean
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Oceanic $\delta^{18}O$-$H_2O$ ($\delta^{18}O$)

- $\delta^{18}O$ follows the water molecules (not $O_2$!)
  - Thus, excellent stable, conservative (SC) water mass tracer

- In seawater:
  \[ H_2^{16}O / H_2^{18}O \approx 500 / 1 \]

- $H_2^{16}O$ evaporation favored over $H_2^{18}O$ evaporation

Rayleigh Distillation - Global Hydrological Cycle

- Equilibrium fractionation when water molecules evaporate from sea surface
- Equilibrium fractionation when water molecules condense from vapor to liquid (rain is heavier than vapor)
- Vapor becomes progressively lighter (i.e., $\delta D$ and $\delta^{18}O$ get lower) with distance from source

- Evaporation from ocean creates depleted clouds
- Air mass transported to higher latitude (cooler)
- Water lost due to rain; raindrops enriched in $^{18}O$ relative to cloud
- Cloud gets lighter as it moves poleward

**FIGURE 29.4. Schematic fractionation in the atmospheric water cycle. Source: Lectures in Isotope Geology, U. Siegenthaler (eds.: E. Jager and J. C. Hunziker), copyright © 1979 by Springer-Verlag, Heidelberg, Germany, p. 266.**
Group Discussion

Using this figure...what percent of the cloud vapor is lost in the first rainout episode below (when $\delta^{13}C_{\text{vapor}}$ changes from $-13\%$ to $-15\%$)?

How did you figure this out?

$\delta^{18}O$ in Average Rain vs. Temperature, Location
Surface Seawater $\delta^{18}O$  

Higher $\delta^{18}O_{sw}$ in the net evaporation belts  

Lower $\delta^{18}O_{sw}$ at high latitudes, which are dominated by net excess precipitation

The large mass of surface seawater keeps the range from being larger

Foraminiferal $\delta^{18}O$-CaCO$_3$  

A Paleotemperature Recorder

The $\delta^{18}O$ of the CaCO$_3$ is a function of:

1) **Temp of seawater** that forams are growing in:  
   Warmer water $\rightarrow$ lighter $\delta^{18}O$-CaCO$_3$

2) **$\delta^{18}O$ of seawater** that forams are growing in:
   - Depends on latitude
   - Depends on glacial/interglacial state:
     - Freshwater is light compared to seawater
     - **Glacial** – heavier sw; **Interglacial** – lighter sw
Deep-sea benthic foraminiferal $\delta^{18}O$ curve. The $\delta^{18}O$ temperature scale was computed on the assumption of an ice-free ocean; it therefore applies only to the time preceding the onset of large-scale glaciation on Antarctica (about 35 million years ago).