Stable Isotope Tracers

OCN 623 – Chemical Oceanography

5 March 2015

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

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Outline

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

- Determine sources/sinks and pathways of nutrients and chemicals in the ocean
- Tracers of biological, physical, geological ocean processes
- Record past changes in physical, chemical, and biological processes in the ocean
Uses of Stable Isotopes in Oceanography

- Most commonly studied:
  \[ ^2\text{H} \quad ^3\text{He} \quad ^{13}\text{C} \quad ^{15}\text{N} \quad ^{18}\text{O} \quad ^{34}\text{S} \]
- Food chain studies
- Horizontal mixing (water mass tracers)
- Paleoceanography
- 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 \(\text{C-12, C-13, C-14}\)
The chart of the nuclides (protons versus neutrons) for elements 1 (Hydrogen) through 12 (Magnesium) shows that most elements have more than one stable isotope (shaded), with the Valley of Stability highlighting regions of stability.
## Examples: H, He, C, N and O

<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></td>
<td>D (²H)</td>
<td>1</td>
<td>1</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T (³H)</td>
<td>1</td>
<td>2</td>
<td>10⁻¹⁴ to 10⁻¹⁶</td>
<td>T₁/₂ = 12.33 y</td>
</tr>
<tr>
<td>Helium</td>
<td>³He</td>
<td>2</td>
<td>1</td>
<td>0.000137</td>
<td></td>
</tr>
<tr>
<td></td>
<td>⁴He</td>
<td>2</td>
<td>2</td>
<td>99.999863</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>¹²C</td>
<td>6</td>
<td>6</td>
<td>98.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹³C</td>
<td>6</td>
<td>7</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁴C</td>
<td>6</td>
<td>8</td>
<td>10⁻¹⁰</td>
<td>T₁/₂ = 5730 y</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>¹⁴N</td>
<td>7</td>
<td>7</td>
<td>99.634</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁵N</td>
<td>7</td>
<td>8</td>
<td>0.366</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>¹⁶O</td>
<td>8</td>
<td>8</td>
<td>99.757</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁷O</td>
<td>8</td>
<td>9</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td></td>
<td>¹⁸O</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

All isotopes of a given element have the same chemical properties, yet there are small differences due to the fact that heavier isotopes typically form stronger bonds and diffuse slightly slower.
The “Delta” Notation

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

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{Sample} - (^{13}C/^{12}C)_{Standard}}{(^{13}C/^{12}C)_{Standard}} \cdot 1000 \text{‰}$$

‰ = per mil = 10⁻³

Negative delta values are depleted in $^{13}C$ ("light")
Positive delta values are enriched in $^{13}C$ ("heavy")

Example: $\delta^{13}C = -0.005 = -5\text{‰}$
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>²H/¹H</td>
<td>Standard Mean Ocean Water (SMOW)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP)</td>
</tr>
<tr>
<td>Helium</td>
<td>δ³He</td>
<td>³He/⁴He</td>
<td>Atmospheric He</td>
</tr>
<tr>
<td>Boron</td>
<td>δ¹¹B</td>
<td>¹¹B/¹⁰B</td>
<td>NIST SRM 951</td>
</tr>
<tr>
<td>Carbon</td>
<td>δ¹³C</td>
<td>¹³C/¹²C</td>
<td>Pee Dee Belemnite (PDB)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>δ¹⁵N</td>
<td>¹⁵N/¹⁴N</td>
<td>Atmospheric N₂</td>
</tr>
<tr>
<td>Oxygen</td>
<td>δ¹⁸O</td>
<td>¹⁸O/¹⁶O</td>
<td>Standard Mean Ocean Water (SMOW)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP)</td>
</tr>
<tr>
<td></td>
<td>δ¹⁷O</td>
<td>¹⁷O/¹⁶O</td>
<td>Pee Dee Belemnite (PDB)</td>
</tr>
<tr>
<td>Sulfur</td>
<td>δ³⁴S</td>
<td>³⁴S/³²S</td>
<td>Canyon Diablo Troilite (CDT)</td>
</tr>
</tbody>
</table>
SLAP2, Water

$^2$H and $^{18}$O in water samples, Water

- **Unit Size:** 20 ml
- **Price per Unit:** 180 EUR
- **Date of Release:** 2009-05-05
- **Reference Sheet:** SLAP2
- **Producing Laboratory:** email

SLAP2 (Standard Light Antarctic Precipitation 2) is an international measurement standard for stable isotope analysis. This water material was prepared at the IAEA Isotope Hydrology Laboratory in 2006 to replace the exhausting SLAP material. SLAP2 was mixed from several carefully calibrated natural water samples from the Antarctic in order to obtain a stable isotope composition as similar as possible to the original SLAP. Three selected laboratories provided calibration measurements in direct comparison to SLAP. All $\delta$-values will continue to be reported in the VSMOW/SLAP scale, using VSMOW2 and SLAP2 as calibration materials with their assigned stable isotope reference values.

### Analyte and Value

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2$H</td>
<td>-55.50</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>-427.5</td>
</tr>
</tbody>
</table>

- **Unit:** %
- **SD:** 0.02
- **R/C:** R

(Standard deviation calculated from results of calibrations performed at three laboratories.

(R/C) Classification assigned to the property value for analyte (Recommended/Information/Conformed)

### References:


Isotopic Fractionation

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

- Lighter isotopes reacts faster, and to a greater extent
- Reaction products are enriched in the lighter isotopes
- Reservoir of reactants is depleted in the lighter isotopes

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

**Fractionation Factor** ($\alpha$):  
$$\alpha_{A-B} = \frac{R_A}{R_B}$$

where $R_A$ and $R_B$ are isotope ratios in materials A and B
Kinetic Fractionation

All isotope effects involving organic matter are kinetic. 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)

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

Terrestrial organic matter: ca. -19‰ (range -26 to -7‰)

Marine organic matter: ca. -14‰ (range -22 to -8‰)
Stable Isotope Applications 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 an indicator of the ice ages
Stable Isotope Applications in Oceanography

- $^3$He to study deep ocean circulation in the Pacific
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Figure 7-8. Section of excess $^3$He content (expressed as $\delta^3$He in percent) across the East Pacific Rise at 15° south (line A-B in figure 7-7). The westward extending plume of $^3$He originating at the crest of this spreading center is quite apparent. The measurements on which this diagram is based were made by John Lupton in the Laboratory of Harmon Craig at the Scripps Institution of Oceanography (280).
$^3\text{He}$ at 2500 m depth
$^3\text{He}$ Plume from Loihi Seamount (Hawaii)

Fig. 6. $\delta(^3\text{He})$% 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 $\delta(^3\text{He})$; 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, 23).
Stable Isotope Applications 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 an indicator of the ice ages
Balances of mass, salt, $\delta^{18}O$, and nutrients allow us to separate the contributions of the individual freshwater sources.

Schlosser et al., 1999

Freshwater balance in the Arctic Ocean

$S_i + S_r + S_p + S_d = 1$,

$f_a S_a + f_p S_p + f_r S_r + f_i S_i = S_m$,

$f_a \delta^{18}O_a + f_p \delta^{18}O_p + f_r \delta^{18}O_r + f_i \delta^{18}O_i = \delta^{18}O_m$,

$f_{aPO_4} + f_{pPO_4} + f_{rPO_4} + f_{iPO_4} = PO_4^*$,

Ekwurzel et al., 2001
Freshwater balance in the Arctic Ocean

from P. Schlosser
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Stable Isotope Applications 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 an indicator of the ice ages
Oceanic $\delta^{18}\text{O}-\text{H}_2\text{O}$ ($\delta^{18}\text{O}$)

$\delta^{18}\text{O}$ follows the water molecules (not $\text{O}_2$!)

Thus, excellent stable, conservative (SC) water mass tracer

In seawater:

$^{16}\text{O}$ (99.8%) $^{17}\text{O}$ (0.037%) $^{18}\text{O}$ (0.204%)

$\text{H}_2^{16}\text{O} / \text{H}_2^{18}\text{O} \approx 500 / 1$
Evaporation of $H_2^{16}O$ favored over heavier isotopes of water

During ice ages (net evaporation) O isotope balance in ocean changes

Can use $\delta^{18}O$ to get ice volume
Rayleigh Distillation

- Fractionation occurs when water molecules evaporate from sea surface.
- Equilibrium effect when water molecules condense from vapor to liquid form (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 masses transported to higher latitude/altitude where it is cooler.
- Water lost due to rain; raindrops are enriched in $^{18}O$ relative to cloud.
- Cloud gets lighter

\( \delta^{18}O \) in Average Rain vs. Temperature

This graph shows the relationship between mean annual air temperature (in °C) and the 
\( \delta^{18}O \) value of precipitation and snowfall. The data points represent various locations across different latitudes, indicating how temperature influences the isotopic composition of precipitation. The graph includes points from locations such as Barbados, Gough, Valentia, Dublin, Copenhagen, Grennedal, Scoresbysund, Angmagssalik, Goose Bay, Labrador, Upernavik, Umanak, South Greenland, Greenland, North Greenland, and Horlick Mtns., 85°S, South Pole.
Gridded Surface Seawater $\delta^{18}O$

Note the higher $\delta^{18}O_{sw}$ in the evaporation belts and the lower $\delta^{18}O_{sw}$ in the high latitudes, which are dominated by excess precipitation.

Any $\delta^{18}O$-temperature relationship depends primarily on the $\delta^{18}O$ of the water from which the carbonate is precipitated.

http://data.giss.nasa.gov/o18data/
\[ \delta^{18}O \] in Marine CaCO\(_3\)

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

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

2) \( \delta^{18}O \) of seawater that foraminifera are growing in:
   - Depends on latitude
   - Depends on global ice volume
Temperature dependence of equilibrium fractionation between $^{16}\text{O}$ and $^{18}\text{O}$ during precipitation of CaCO$_3$
Changes in ice volume also influence $\delta^{18}O$ of the ocean.
δ\textsuperscript{18}O in marine carbonates and paleotemperature records Vostok ice core

Figure 9.26. The lower curve shows smoothed δ\textsuperscript{18}O for marine carbonates (SPECMAP), the middle curve shows δD of ice in the Vostok ice core, and the upper curve the temperature calculated from δD at Vostok at the time of deposition of the ice relative to the present mean annual temperature. Vostok data is from Jouzel et al., (1987, 1993, 1996).
Stacked deep-sea benthic foraminiferal oxygen-isotope curve. The δ18O temperature scale, on the right axis, 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).

Zachos et al., 2008