The Use of Isotope Geochemistry in Forensic Geology

Stable Isotopes

Modified from a PowerPoint presentation prepared by J. Crelling, Southern Illinois University
Isotopes

Two Categories

- **Unstable** – isotopes that continuously and spontaneously break down/decay in other lower atomic weight isotopes
- **Stable** – isotopes that do not naturally decay but can exist in natural materials in differing proportions
Stable Isotopes

- The absolute values of isotope concentrations are usually too small to measure and compare accurately.

- So the convention is to compare isotope ratios of any given element to a standard value for that element.
Stable Isotopes

- Elements can exist in both stable and unstable (radioactive) forms. Most elements of biological interest (including C, H, O, N, and S) have two or more stable isotopes, with the lightest of these present in much greater abundance than the others.
Isotopes of Major Elements of Interest in Plant Physiology and Ecology

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1H</td>
<td>99.985</td>
</tr>
<tr>
<td></td>
<td>2H</td>
<td>0.015</td>
</tr>
<tr>
<td>Carbon</td>
<td>12C</td>
<td>98.89</td>
</tr>
<tr>
<td></td>
<td>13C</td>
<td>1.11</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14N</td>
<td>99.63</td>
</tr>
<tr>
<td></td>
<td>15N</td>
<td>0.37</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16O</td>
<td>99.759</td>
</tr>
<tr>
<td></td>
<td>18O</td>
<td>0.204</td>
</tr>
<tr>
<td>Sulfur</td>
<td>32S</td>
<td>95.00</td>
</tr>
<tr>
<td></td>
<td>33S</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>34S</td>
<td>4.22</td>
</tr>
<tr>
<td></td>
<td>36S</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Stable Isotopes

Notation

$R$: “ratio”

$R = \frac{\text{heavy Element}}{\text{light Element}}$ for carbon: $^{13}\text{C}/^{12}\text{C}$
Stable Isotopes

More Notation

$\delta$: “del”

$\delta_{\text{heavy element}} = [(R_{\text{sample}}/R_{\text{standard}})-1]1000$ (‰, per thousand, also called per mil)

For carbon this becomes $\delta^{13}\text{C}$ (termed “del 13 C”)

For carbon, $R_{\text{standard}}$ comes from “Pee Dee Belemnite”, or “PDB” a limestone rock from South Carolina.

Plant carbon always has less of the heavy isotope compared with this standard, so the $\delta^{13}\text{C}$ of plant material is always a negative number.
Stable Isotopes

As the value of $\delta$ for a sample increases, the relative abundance of the rare (heavy) also isotope increases.

For carbon isotopes:

As the value of $\delta^{13}\text{C}$ increases i.e., “becomes more positive”

There is enrichment in $^{13}\text{C}$

As the value of $\delta^{13}\text{C}$ decreases i.e., “becomes more negative”

There is depletion in $^{13}\text{C}$
Stable Isotopes (Oxygen as an Example)

Same element with two different atomic masses:

\[
\delta^{18}O = \left[ \frac{^{18}O/^{16}O_{(\text{sample})} - ^{18}O/^{16}O_{(\text{SMOW})}}{^{18}O/^{16}O_{(\text{SMOW})}} \right] \times 1000
\]

Changes in $^{18}O/^{16}O$ ratios are too small to directly measure.

Sample is compared to a standard; in the case of oxygen, the standard is seawater:

$\text{SMOW} = \text{Standard Mean Ocean Water}$

$\delta^{18}O$ in units of per thousand, called 'per mil' and denoted as $\%_{\text{o}}$.

$\delta^{18}O = 0$ Sample has same ratio as that in seawater.

$\delta^{18}O > 0$ Sample enriched in heavy isotope ($^{18}O$) relative to seawater.

$\delta^{18}O < 0$ Sample depleted in heavy isotope ($^{18}O$) relative to seawater.
Range of carbon isotopes

Carbonates

Seagrass

Fish Zoopl. Plankton

C₄ plants

C₃ plants

Natural gas

PDB std

₀%o

₁₀%o

₂₀%o

₃₀%o

₄₀%o

Atmos. CO₂

₁³C enriched

= HEAVY

₁³C depleted

= LIGHT
Delta D Values of Selected Materials

Delta D, SMOW (per mille)
Delta 13C Values of Selected Materials

Delta 13C, PDB (per mille)
What accounts for the range of stable isotope composition?

- Molecules react at different rates depending on their isotopic composition

- All biological and chemical reaction could fractionate isotopes

- Electron structure determines chemical properties
- Nucleus determines physical properties
Stable Isotopes

Stable isotopes are useful as:

1. Tracers (for example, identifying food sources)

2. Indicators of physical or biological processes. (This is because fractionation can occur during many physical and biological processes).
Stable Isotopes

Because $^{12}\text{C}$ bonds are weaker than $^{13}\text{C}$ bonds all natural processes will tend to fractionate one or the other resulting in enrichment or depletion
Stable Isotopes

More Notation

\[ \alpha = \text{Isotope fractionation} = \frac{R_{\text{source}}}{R_{\text{product}}} \]

Fractionation is change in R that occurs during a physical or biological transformation
photosynthesis fixes preferentially more $^{12}\text{C}O_2$

leaving an increased abundance of $^{13}\text{C}O_2$ to form calcareous skeletal materials
$^{13}$C depends on enzyme pathway

![Graph showing the distribution of $\delta^{13}$C values for C$_3$ and C$_4$ plants with respect to atmospheric CO$_2$.](image)
In 1980 there was a large (80,000gal) gasoline spill from a service station.

Unusual large amounts of methane off gasses were found.

Borings showed the area was underlain by lake sediments and sawdust.

$\delta D$ (methane) plotted against $\delta^{13}C$ showed that the methane was coming from the sawdust and not the methane.
Figure 3. Service station site map showing original liquid gasoline plume and CH₄ concentrations measured in monitoring wells sample...
Areas showing $\delta^{13}C$ and $\delta D$ for methane generated by biological CO$_2$ reduction, biological fermentation and thermogenic processes.
<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C</th>
<th>$\delta^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biogenic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2$ reduction</td>
<td>-100 to -60</td>
<td>-150 to -250</td>
</tr>
<tr>
<td>Organic acid decomposition</td>
<td>-60 to -50</td>
<td>-250 to -350</td>
</tr>
<tr>
<td><strong>Thermogenic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early maturity</td>
<td>-50 to -40</td>
<td>-300 to -220</td>
</tr>
<tr>
<td>Optimum maturity</td>
<td>-40 to -30</td>
<td>-220 to -160</td>
</tr>
<tr>
<td>Late maturity</td>
<td>-30 to -15</td>
<td>-160 to -90</td>
</tr>
</tbody>
</table>
A chemical isotope field for CH₄ of different origins, yields after Coleman et al. (1995). Solid circles represent microbial fermentation, while dashed circles represent microbial CO₂ reduction.
Forensic Stable Isotope Cases

- Oil spills were found at an industrial facility where crude oil was stored
- Natural seeps of oil and gas were also present as well as numerous pipelines
- Large amounts of hydrocarbons, CO$_2$, CH$_4$, H$_2$ were present in the soil
- $\delta^D$ (methane) plotted against $\delta^{13}C$ (methane) showed that the methane was coming from microbial fermentation
The diagram depicts isotopic fields for CH₄ of different origins, yields after Coleman et al. (1995). Solid circles represent microbial fermentation.
When plants convert CO$_2$ into sugars by photosynthesis, they use two different processes yielding sugars with 3 carbon atoms (C3 plants) and 4 carbon atoms (C4) plants.

- **C3 plants** are barley, rice, etc.
- **C4 plants** are corn, cane sugar, etc.
- Each plant leaves its isotopic signatures in the resulting beer.
Figure 1. (A) Absolute frequencies of carbon isotope ratios ($\delta^{13}C$) of C$_3$ and C$_4$ plants. (B) Frequency of barley and corn in the USA and Canada. (C) Frequency of beans in Pacific Rim, Brazil, Mexico, and Europe.
The diagram shows the distribution of $C_4$ carbon in beers from around the world. Different symbols are used to represent the different regions and types of beer, such as Europe, Pacific Rim, Mexico, Canada, USA, Brazil, US Style, High ALC, and others. The amounts of $C_4$ carbon vary significantly across the regions and types, with some showing higher concentrations than others.
Gasoline Isotopes

- Gasoline from leaky service station tanks is a frequent ground water contaminant.
- I had a professor at Penn State who woke up one night to a popping sound in his basement.
- It turned out to be gasoline leaking into his sump pump from a leaky gas station up the hill from his house.
- The gasoline was exploding every time the pump came on.
Correlation of isotope ratios in groundwater extracts and two gasoline brands
Where Did the Oil Come From

Figure 9.9: BP “American Trader” accident in Huntington Beach, California, February 7, 1990. Correlation among Alaska and California crude oils and beach tar balls on Southern California beaches, based on their carbon isotope ratios.
You Are What You Eat & Drink

- The isotopic content of both food and water vary from place to place.

- People and animals eating and drinking in different places take on the isotopic signatures of their environment.

- Your travel history is in your hair, teeth, bones, etc.
Isotopic Composition of Water in the USA

source: Kendall and Coplen (2001)
You are what you eat!

Diet of C3-C4 mix

Diet of C3 only

Drank micro-brew beer
Isotopic values from the hair of an Inca mummy. The sinusoidal variations are thought to be related to seasonal variations (more corn in summer, etc.).
Forensic Stable Isotope Cases

From where did the Ice Man Commeth?

Research reported in Science (31 Oct 2003) compared Sr, Pb, O, and Ar isotopes from the iceman to the local geology and concluded that he originated within ~60 miles of where he was found and that he migrated through a number of local valleys.