Cements are indicative of diageneric environments.
Oxygen Isotopes through time

- Increasing temperature
- Changing water composition in the oceans
- Diagenesis
- Over past 600 myrs there is about a 4 per mil decrease

Moore (2001)
Oxygen Isotopes through time

- Temperature
- In order to explain isotopic data, temperatures would have had to have been about 15°C warmer than today. Organisms which are similar to those found today were apparently alive during the early Phanerozoic.

Moore (2001)

Oxygen Isotopes through time

- Changing isotopic composition of oceans through time. The proposed mechanism is the cycling of ocean water through the crust. Most experts believe that this is impossible on the time scale of millions of years. Other experts disagree.

Moore (2001)

Oxygen Isotopes through time

- Diagenesis tends to produce lighter carbonates, both by involving meteoric fluids and through recrystallization at higher temperatures.
- Fossils that show very good preservation and are therefore argued to have preserved their isotopic integrity.
- Phosphates and carbonates can co-exist and therefore provide independent evidence of temperature by eliminating the water variable.

Moore (2001)
Oxygen Isotopes through time

- Jury is still out on long term changes of the oxygen isotopic composition of the oceans with time and on secular variations which are argued by some to be even more difficult to explain.
- A Job for ‘Clumped Isotopes’

Moore (2001)
Different MCLs

- Different fluids will produce different MCLs which can be related to the climate, latitude of alteration.

![Different MCLs Graph](image)

Later Reactions

- What is the Original Composition?

![Later Reactions Graph](image)
Acicular Aragonite
Botryoidal
Isopachous fibrous cement
Botryoidal

Non-depositional surfaces

Increasing depletion of C during increased dolomite content below.
**Mechanism for Change at Non-Depositional Surface**

- Organic carbon is concentrated in burrows and degrades imparting an isotopically negative carbon isotopic signature.
- Cementation at the sea-floor could produce dolomite (isotopically heavy), and calcite (+ve if formed at low temperatures).
- BUT Marshall and Ashton claimed non-depositional surfaces are heavy as a result of the precipitation of heavy inorganic cements.

**Differences between sub-aerial and non-depositional surfaces**

- Both surfaces can have isotopic depletions in carbon and enrichments in oxygen.
- However, subaerial surfaces tend to be much more extreme (4 to 6 per mille).
- In contrast hardground show only small deviations in carbon (1 per mille).
- Also subaerial surfaces should be surrounded by other evidences of exposure (petrographic and geochemical).
Isotopologues

Are you tired of the promise of Stable Oxygen Isotopes?
Are you let down when you find out that you need to know the salinity in order to calculate temperature from O isotopes?

Are you let down when you find out that you need to know temperature in order to calculate salinity from O isotopes?

Do fluid inclusions leave you confused and feeling inadequate?
If so then I have one word for you.

Isotopologues

Isotopologues will provide you the temperature of your carbonates independent of the salinity (isotopic composition of the fluid)
The Problem

Outline

- What exactly are Isotopologues?
- How do they work?
  - What do they reflect
    - Temperature
    - Salinity
- How are Isotopologues measured?
- What are the applications and the challenges?
Carbonate plus phosphoric acid = CO₂ + H₂O
(Dolomite, Calcite, Siderite)

<table>
<thead>
<tr>
<th>WHAT</th>
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</thead>
<tbody>
<tr>
<td>44</td>
<td>C₁²O₁⁶O₁⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>C₁³O₁⁶O₁⁶, C₁²O₁⁶O₁⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>C₁²O₁⁶O₁⁸, C₁²O₁⁷O₁⁷, C₁³O₁⁶O₁⁷</td>
<td></td>
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</tbody>
</table>

\[ R_{45} = \frac{45}{44} = R_{13} + R_{17} \]
\[ R_{46} = \frac{46}{44} = R_{18} + R_{17} \]
\[ R_{13} = \frac{13}{12} \]
\[ R_{17} = \frac{17}{16} \]
\[ R_{18} = \frac{18}{16} \]

\[ \delta^{18}O = \frac{R_{18}}{R_{18}(st)} - 1 \times 1000 \]
\[ \delta^{13}C = \frac{R_{13}}{R_{13}(st)} - 1 \times 1000 \]
\[ \delta^{17}O = \frac{R_{17}}{R_{17}(st)} - 1 \times 1000 \]
\[ \delta^{17}O = \frac{1}{2} \delta^{18}O \]
Isotopologues

44 $^{12}C^{16}O^{16}O^{16}$
45 $^{13}C^{16}O^{16}O^{16}$, $^{12}C^{16}O^{16}O^{17}$
46 $^{12}C^{16}O^{16}O^{18}$, $^{12}C^{17}O^{17}O^{17}$, $^{13}C^{16}O^{17}O^{17}$
47 $^{13}C^{16}O^{16}O^{18}$, $^{13}C^{12}O^{12}O^{17}$, $^{12}C^{12}O^{17}O^{18}$
48 $^{13}C^{18}O^{17}O^{17}$, $^{12}C^{18}O^{18}O^{18}$
49 $^{13}C^{18}O^{18}O^{18}$

Isotopologues

44 $^{12}C^{16}O^{16}O^{16}$
45 $^{13}C^{16}O^{16}O^{16}$, $^{12}C^{16}O^{16}O^{17}$
46 $^{12}C^{16}O^{16}O^{18}$, $^{12}C^{17}O^{17}O^{17}$, $^{13}C^{16}O^{17}O^{17}$
47 $^{13}C^{16}O^{16}O^{18}$, $^{13}C^{13}O^{17}O^{17}$, $^{12}C^{12}O^{17}O^{18}$
48 $^{13}C^{18}O^{17}O^{17}$, $^{12}C^{18}O^{18}O^{18}$
49 $^{13}C^{18}O^{18}O^{18}$

Isotopologues 'Clumped' Isotopes

45/44 = $\delta^{45}$
46/44 = $\delta^{46}$
47/44 = $\delta^{47}$

<table>
<thead>
<tr>
<th>R47</th>
<th>44 ppm</th>
<th>1.5 ppm</th>
<th>1.6 ppm</th>
</tr>
</thead>
</table>

1. Theoretical $R47 = 47/44 = R_{18}R_{13} + R_{13}R_{17}R_{17} + R_{17}R_{18}$
2. Measured $R47 = 47/44$
3. $\Delta 47 = (\text{Measured } R47 - \text{Theoretical } R47) \times 1000$
How and Why?

- The theoretical distribution of the isotopologues of CO₂ is governed by the 'Rule of Means'.
- The 'Rule of the Means' predicts that the abundance of ¹³C¹⁸O is the product of the abundance of ¹³C times ¹⁸O.
- Departure from the rule of the means occurs because decreases in the vibrational energy of the atoms occurs which slightly exceeds that predicted.

How and Why?

- Vibration energies of the C-O bonds differ slightly between the ¹⁸O-C-¹⁶O and ¹⁶O-C-¹⁶O and this gives rise to a preferential partitioning of ¹³C into ¹⁸O-C-¹⁶O which decreases with increasing temperature.
- Differences in the actual concentrations of ¹³C and ¹⁸O are taken into consideration by subtracting the theoretical distribution from the actual measured value.

How and Why?

- Δ⁴⁷ is rigorously independent of both the δ¹⁸O and δ¹³C of the water because variations in these are taken care of by the theoretical 47/44 which is calculated from the actual δ¹⁸O and δ¹³C.
- Δ⁴⁷ is therefore ONLY dependent upon the temperature of formation which causes preferential partitioning of ¹³C into ¹⁸O-C-¹⁶O which decreases with increasing temperature.
And the Result is

\[ y = 0.0599x - 0.0252 \]

\[ R^2 = 0.9228 \]

Ghosh et al., 2006

HOW CAN WE MEASURE THEM?

- Multi-collector

How are they measured?

Triple Collector (251 Type)
What do you Need to get into the Clumped Isotope Game?

- Multiple collector MS
- Software which can collect data increased dynamic range of the amplifiers
- More sensitive amplifiers for masses 47-49
- Basically we need new instrumentation
Applications

• Paleoceanography

• Long term changes
  – Temperature
  – Changes in Ocean δ¹⁸O
  – Diagenesis

• Diagenesis
Some References