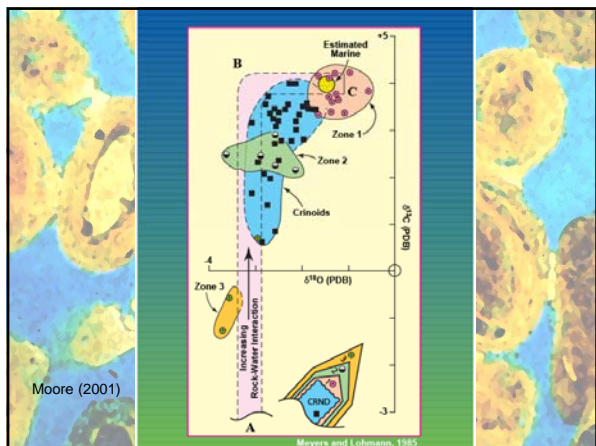
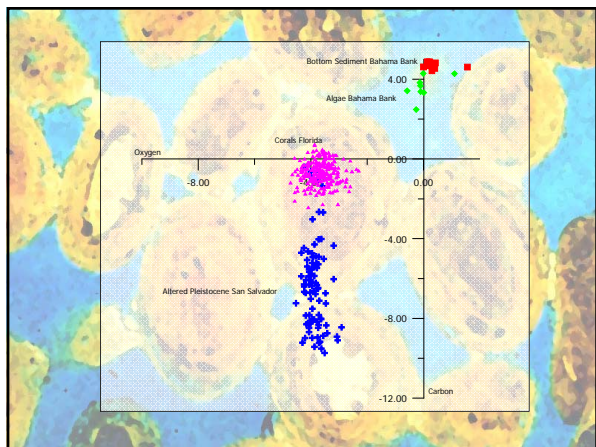


Moore 2001





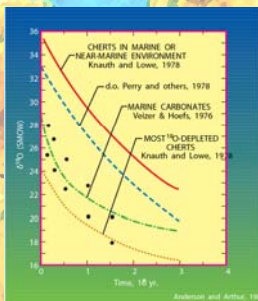
Oxygen Isotopes through time

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

Moore (2001)

Oxygen Isotopes through time

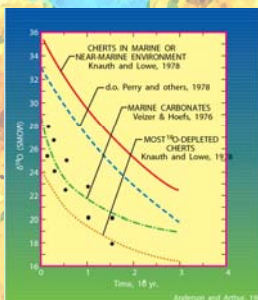
- Temperature
- In order to explain isotopic data temperatures would have had to have been about 15°C warmer than today. Organisms which are similar to those found today were apparently alive during the early Phanerozoic.



Moore (2001)

Oxygen Isotopes through time

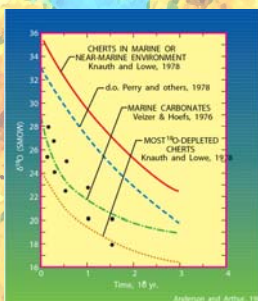
- Changing isotopic composition of oceans through time. The proposed mechanism is the cycling of ocean water through the crust. Most experts believe that this is impossible certainly on the time scale of millions of years. Other 'experts' disagree.



Moore (2001)

Oxygen Isotopes through time

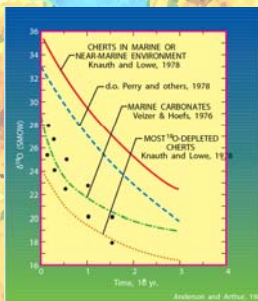
- Diagenesis tends to produce lighter carbonates both by involving meteoric fluids and through recrystallization at higher temperatures.
- Fossils exist which show very good preservation and are therefore argued to have preserved their isotopic integrity.
- Phosphates and carbonates can co-exist and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



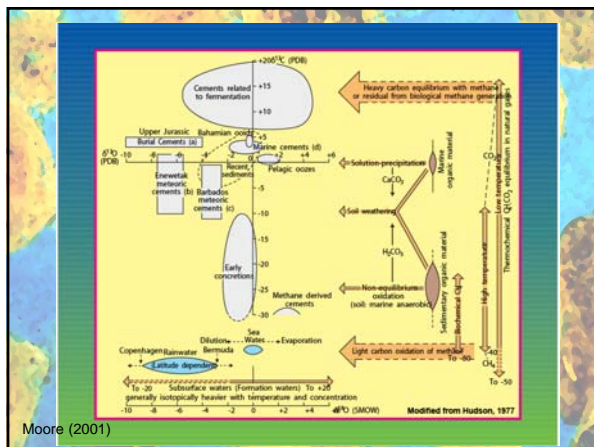
Moore (2001)

Oxygen Isotopes through time

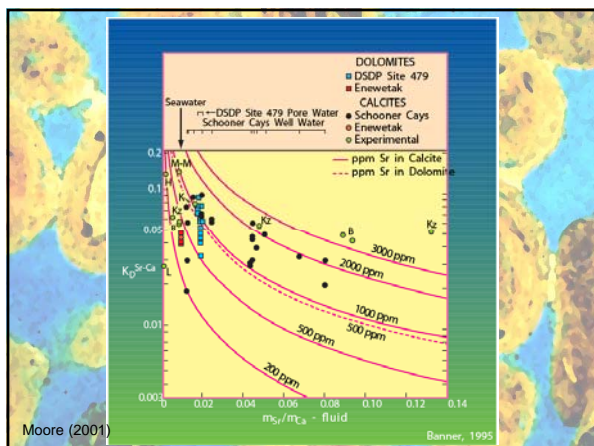
- Jury is still out on long term changes of the oxygen isotopic composition of the oceans with time and on secular variations which are argued by some to be even more difficult to explain.
- A Job for 'Clumped Isotopes'



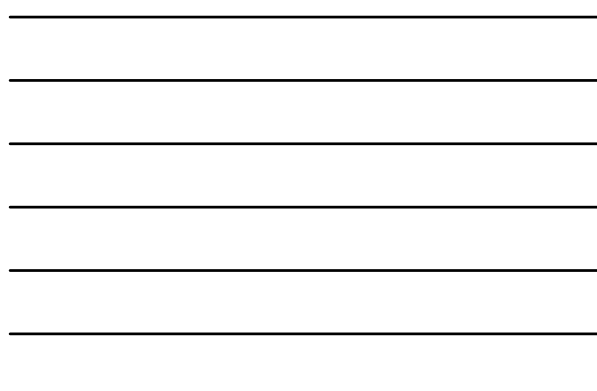
Moore (2001)

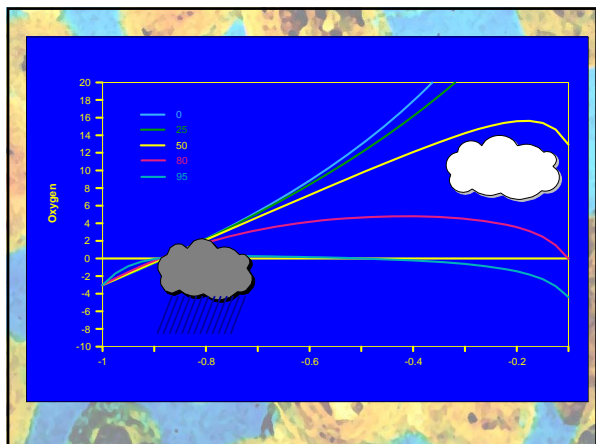


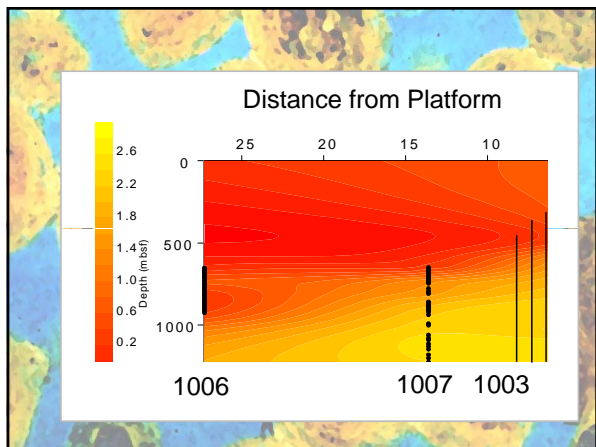
Moore (2001)

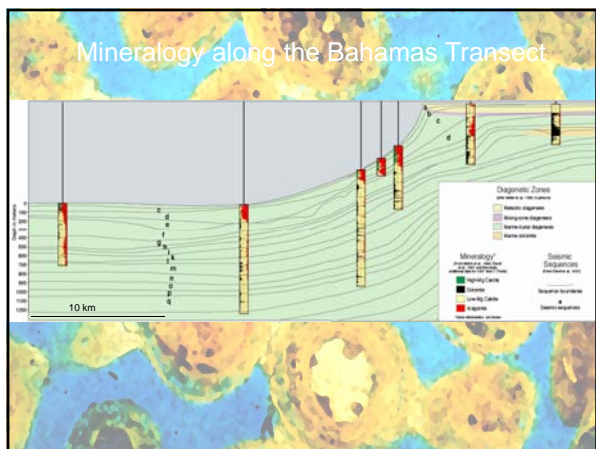


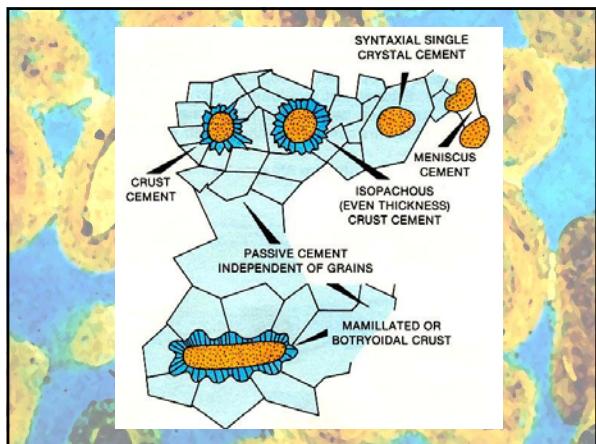
Moore (2001)

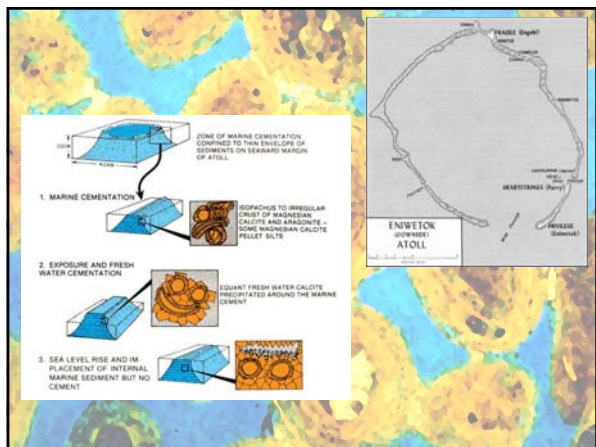


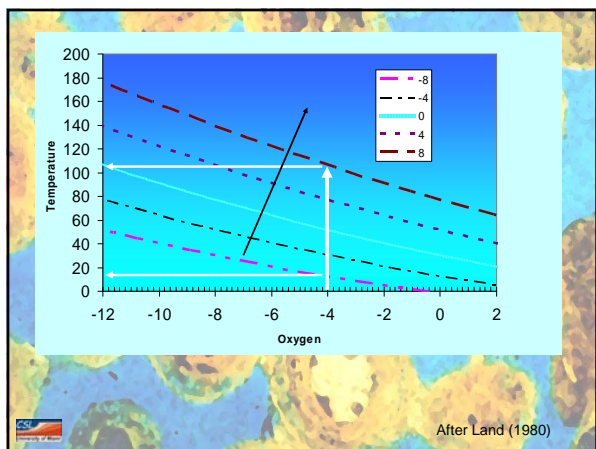


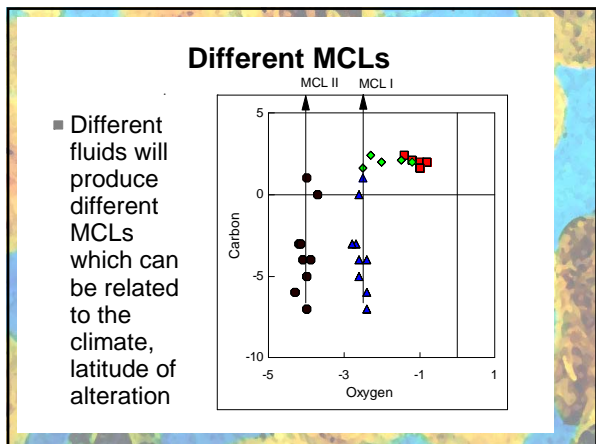


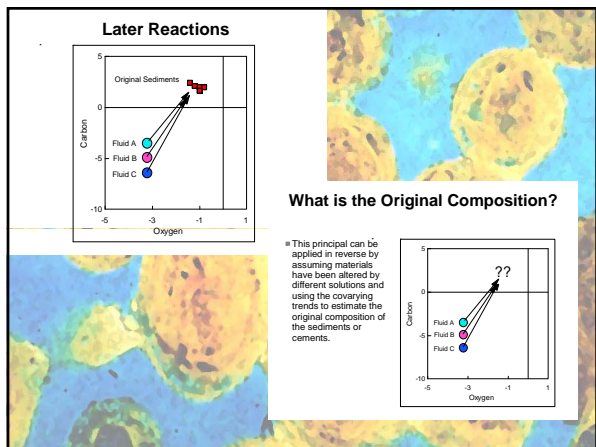


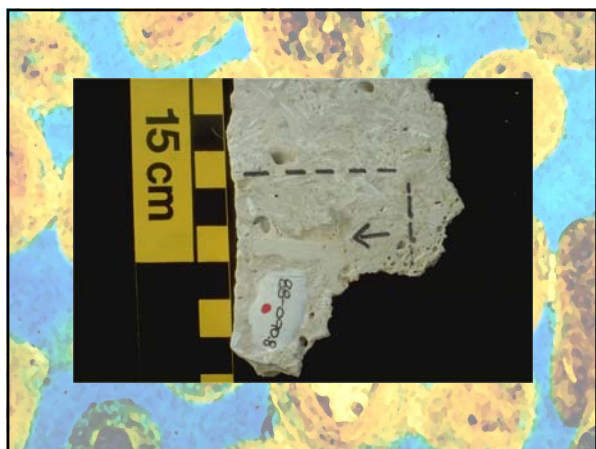


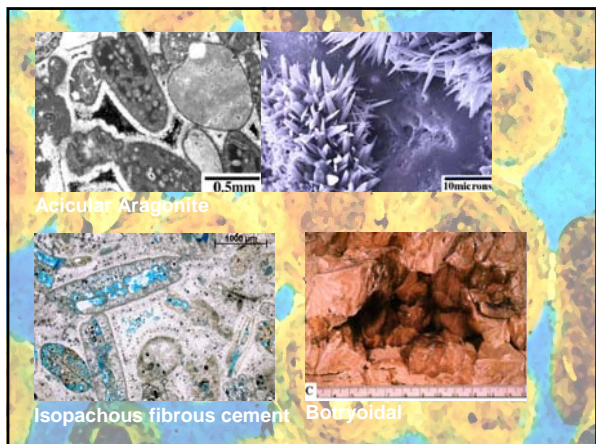


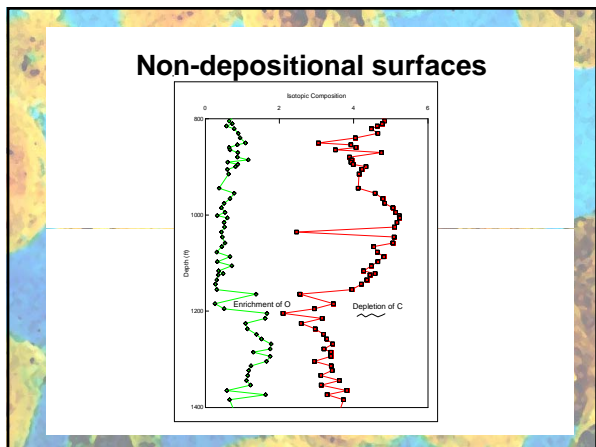


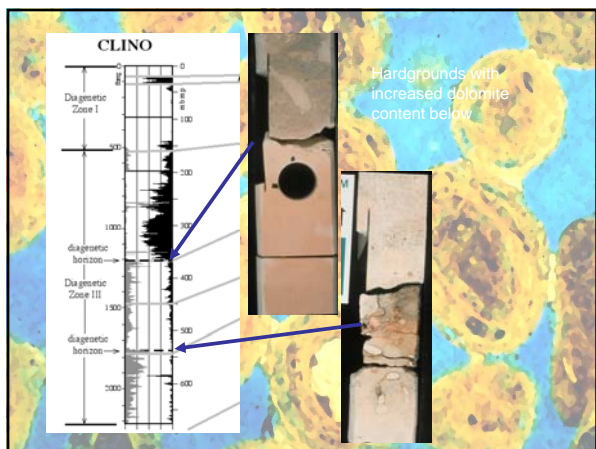


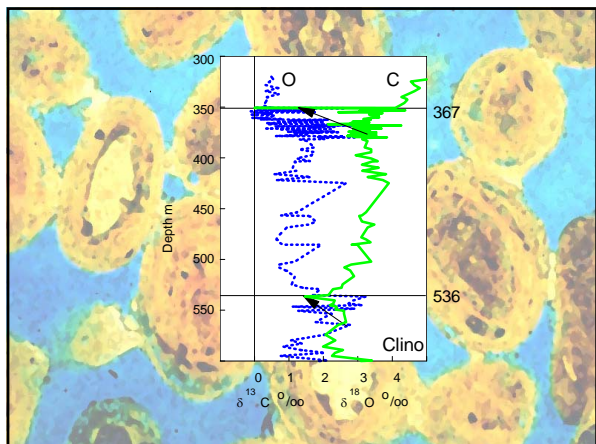










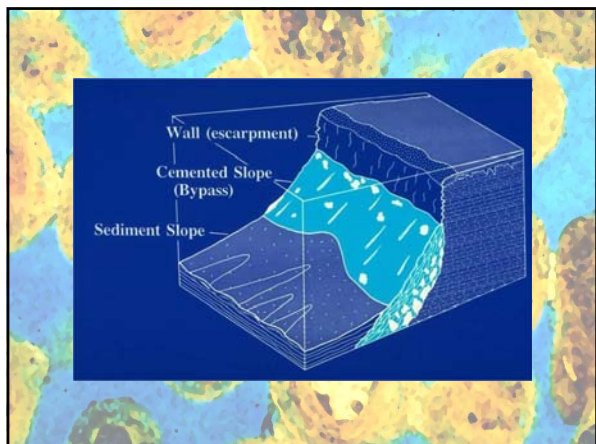


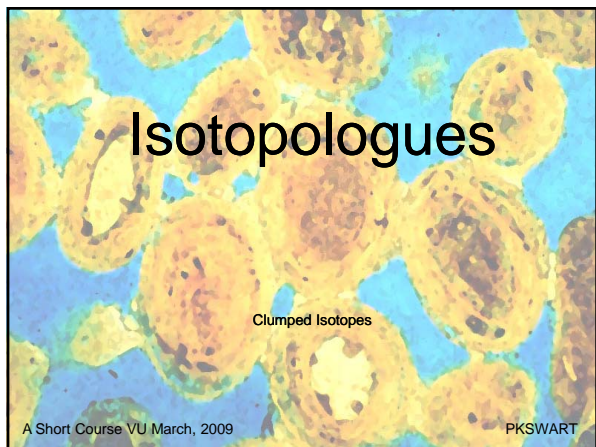
Mechanism for Change at Non-Depositional Surface

- 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.

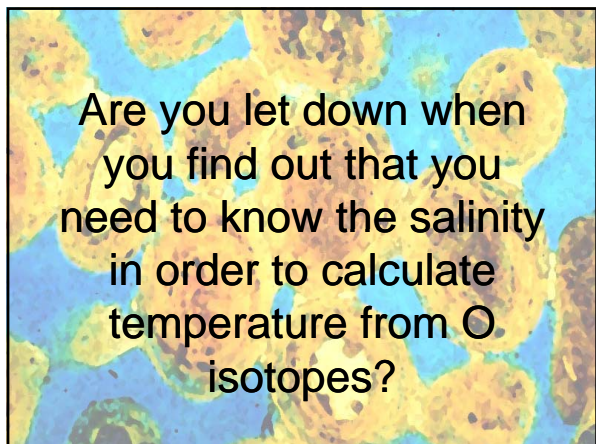
Differences between sub-aerial and non-depositional surfaces

- 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)

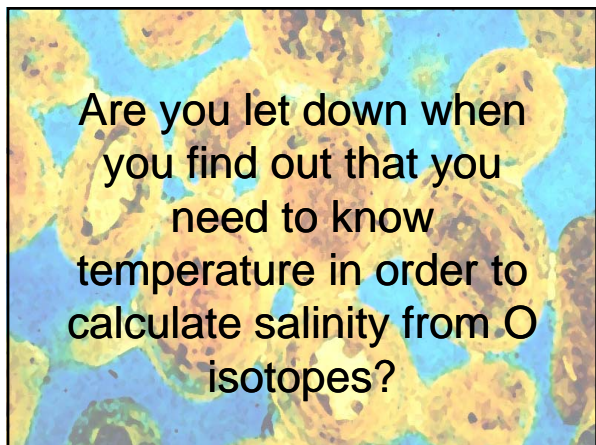








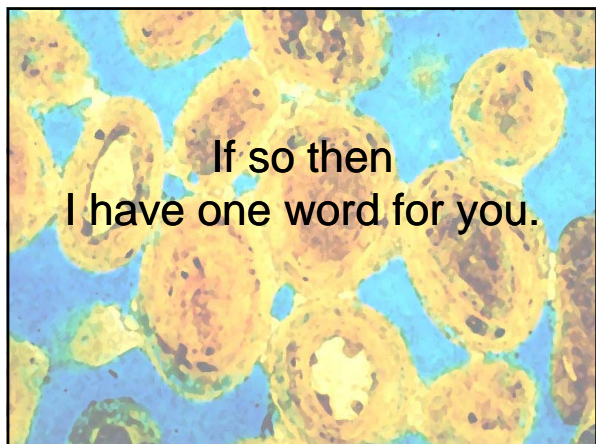
Are you let down when you find out that you need to know the salinity in order to calculate temperature from O isotopes?



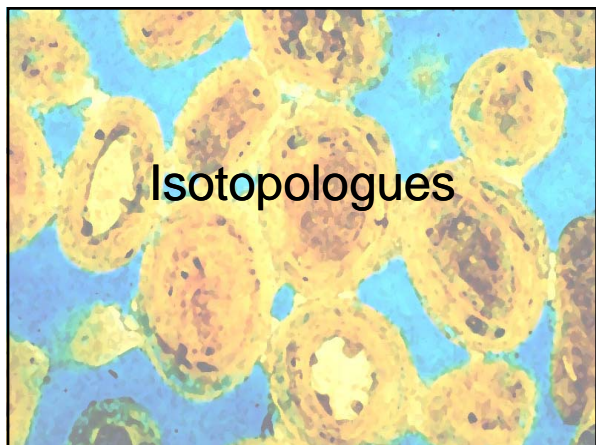
Are you let down when you find out that you need to know temperature in order to calculate salinity from O isotopes?



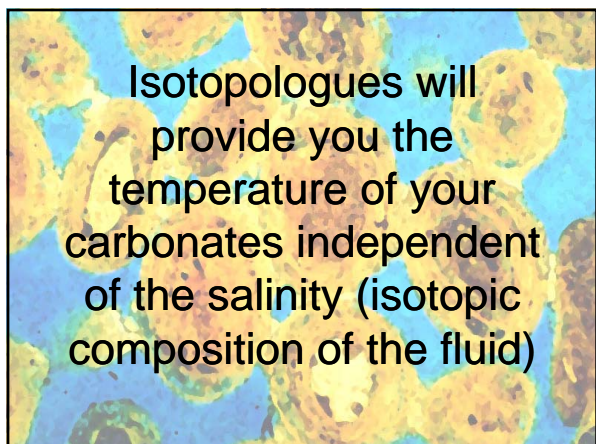
Do fluid inclusions leave you confused and feeling inadequate?



If so then
I have one word for you.

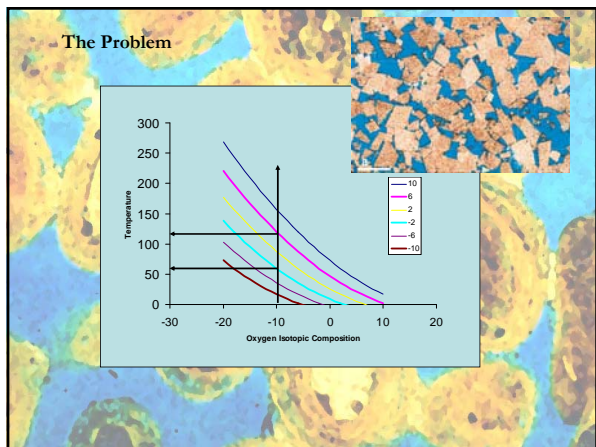


Isotopologues



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





- 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?

$^{13}\text{C}, ^{18}\text{O}$

Carbonate plus phosphoric acid = $\text{CO}_2 + \text{H}_2\text{O}$
 (Dolomite, Calcite, Siderite)

WHAT


44 $\text{C}^{12}\text{O}^{16}\text{O}^{16}$
 45 $\text{C}^{13}\text{O}^{16}\text{O}^{16}, \text{C}^{12}\text{O}^{16}\text{O}^{17}$
 46 $\text{C}^{12}\text{O}^{16}\text{O}^{18}, \text{C}^{12}\text{O}^{17}\text{O}^{17}, \text{C}^{13}\text{O}^{16}\text{O}^{17}$

$R_{45} = 45/44 = R_{13} + R_{17}$ $\delta^{18}\text{O} = (R_{18}/R_{18_{\text{std}}}-1)*1000$
 $R_{46} = 46/44 = R_{18} + R_{17}R_{17} + R_{13}R_{17}$ $\delta^{13}\text{C} = (R_{13}/R_{13_{\text{std}}}-1)*1000$

$R_{13} = ^{13}\text{C}/^{12}\text{C}$ $\delta^{17}\text{O} = (R_{17}/R_{17_{\text{std}}}-1)*1000$
 $R_{17} = ^{17}\text{O}/^{16}\text{O}$ $\delta^{17}\text{O} = 1/2 \delta^{18}\text{O}$
 $R_{18} = ^{18}\text{O}/^{16}\text{O}$


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

Isotopologues



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


Isotopologues



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

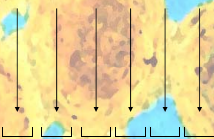
$R_{47} = 47/44 = R_{18}R_{13} + R_{13}R_{17}R_{17} + R_{17}R_{18}$
44 ppm 1.6 ppm 1.5 ppm

Isotopologues 'Clumped' Isotopes




45/44 = δ45
 46/44 = δ46
 47/44 = δ47

44 45 46 47 48 49




1- Theoretical $R_{47} = 47/44 = R_{18}R_{13} + R_{13}R_{17}R_{17} + R_{17}R_{18}$
 2- Measured $R_{47} = 47/44$
 3- $\Delta 47 = (\text{Measured } R_{47} - \text{Theoretical } R_{47}) * 1000$

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.

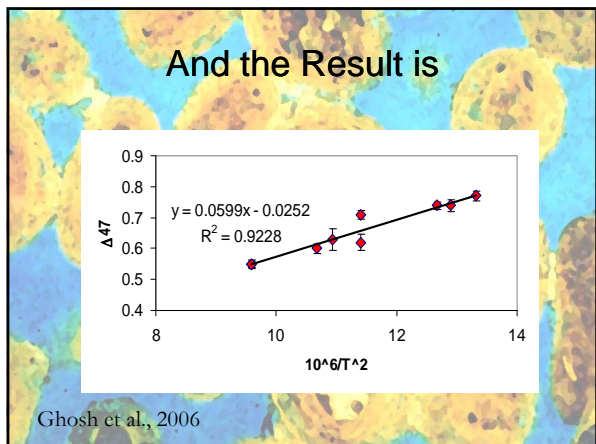
How and Why?



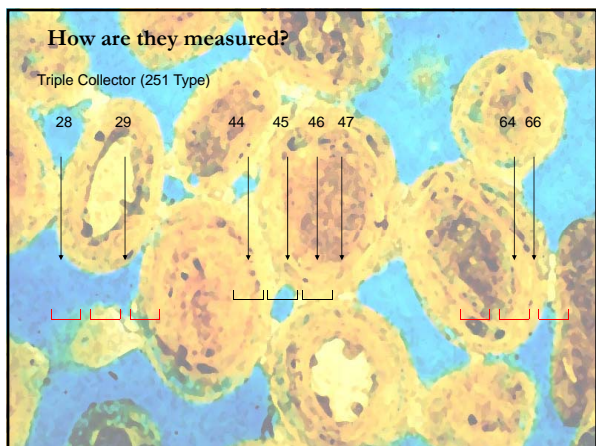
- Vibration energies of the C-O bonds differ slightly between the ¹⁸O-C-¹⁶O and ¹⁶O-C-¹⁶O and this gives rise to a preferential partitioning of ¹³C into ¹⁸O-C-¹⁶O which decreases with increasing temperature
- Differences in the actual concentrations of ¹³C and ¹⁸O are taken into consideration by subtracting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

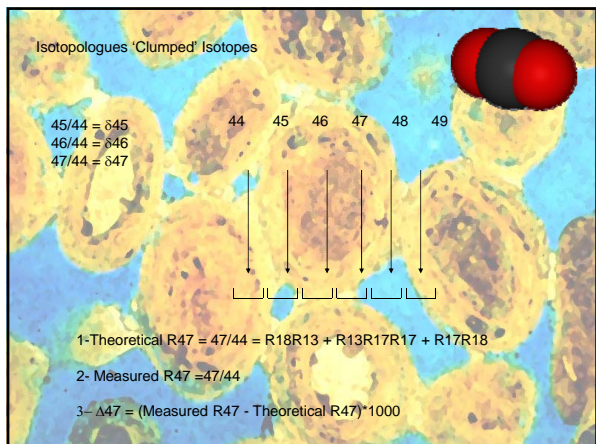
How and Why?

- 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



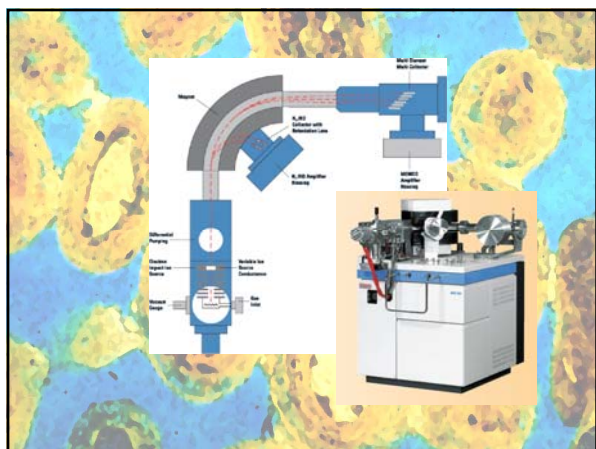


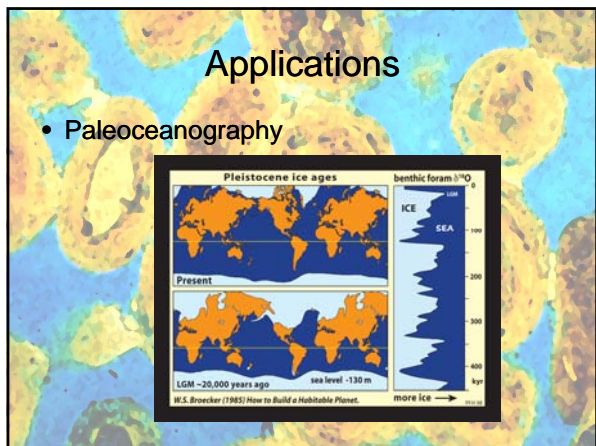


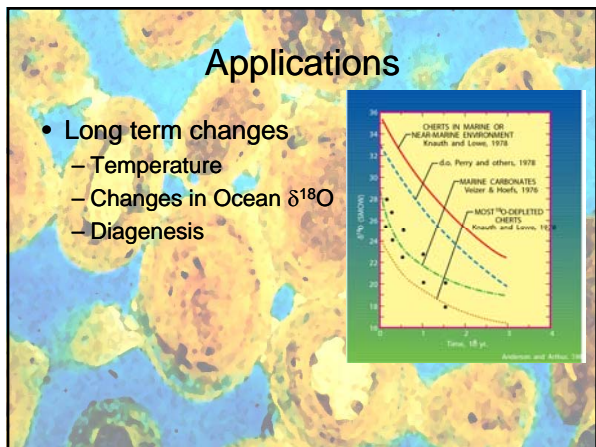


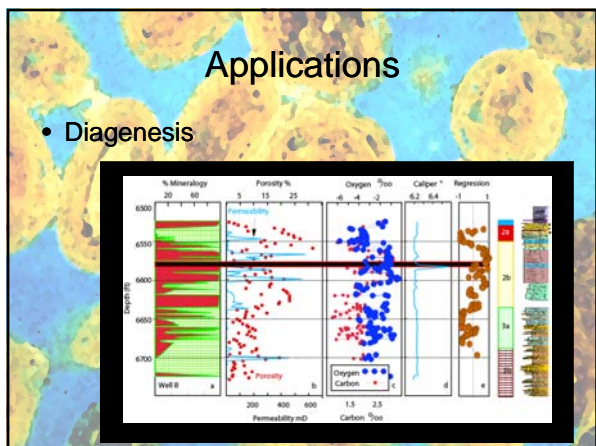
What do you Need to get into the Clumped Isotope Game?

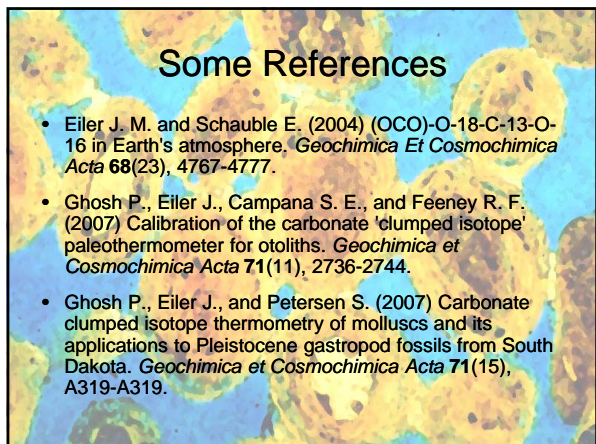
- Multiple collector MS
- Software which can collect data Increased dynamic range of the amplifiers
- More sensitive amplifiers for masses 47-49
- Basically we need new instrumentation











Some References

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- Ghosh P., Eiler J., Campana S. E., and Feeney R. F. (2007) Calibration of the carbonate 'clumped isotope' paleothermometer for otoliths. *Geochimica et Cosmochimica Acta* **71**(11), 2736-2744.
- Ghosh P., Eiler J., and Petersen S. (2007) Carbonate clumped isotope thermometry of molluscs and its applications to Pleistocene gastropod fossils from South Dakota. *Geochimica et Cosmochimica Acta* **71**(15), A319-A319.
