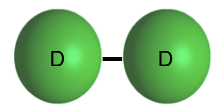
Clumped Isotope Geochemistry

Conventional Isotope Geochemistry

Clumped Isotope Geochemistry



A multiply-(rare)-substituted Isotopologue

Aka: 'clump'

The main reason this was not exploited in the past: clumped isotopologues are very rare and the minute differences ($1/10^6$) are difficult to measure.

From Weifu Guo

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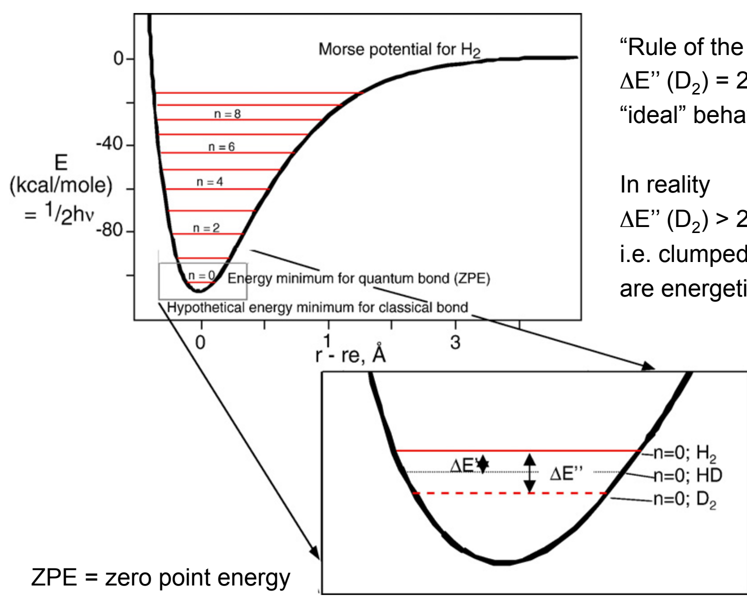
Energy Content of a Molecular Hydrogen Bond



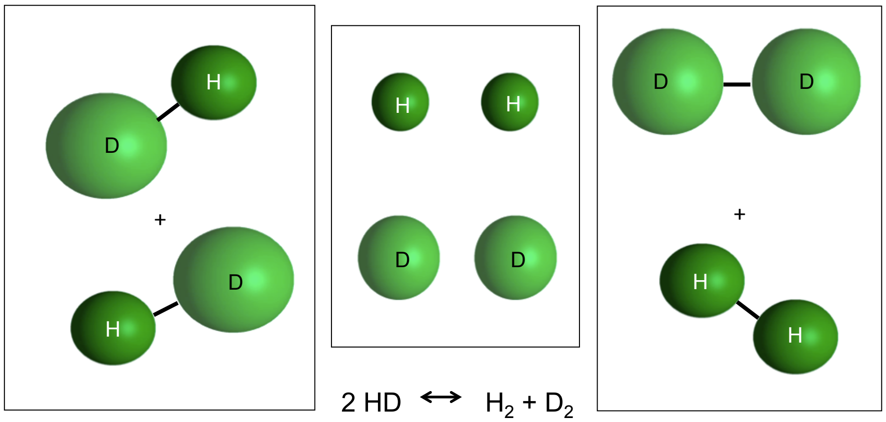
"Rule of the geometric mean":
$\Delta E''(D_2) = 2\,\Delta E'(HD)$
"ideal" behavior (>> T)

In reality
$\Delta E''(D_2) > 2\,\Delta E'(HD)$
i.e. clumped arrangements are energetically favored.

ZPE = zero point energy

Eiler, 2007

Isotopic Disproportionation Reaction



$$2\ HD \leftrightarrow H_2 + D_2$$

Random distribution: $K_{eq} = [D_2]\,[H_2]\,/\,[HD]^2$

$= [D]^2\,[H]^2\,/\,(2\,[H]\,[D])^2$

$= 0.25$

Eiler, 2007 *from W. Guo*

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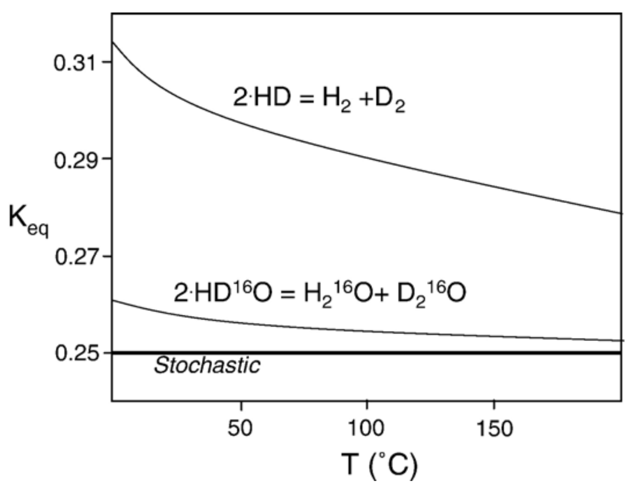
Temperature-dependence of Equilibrium Constant



D_2 more stable than predicted based on "rule of the geometric mean" – K_{eq} ↗

Entropy drives distribution towards randomness (increasingly so at >T) – K_{eq} ↘

Enthalpy of isotope exchange reactions are f(T), generally 1/T – K_{eq} ↘

Δ_i - Notation

Clumped isotope anomalies are not expressed as deviations from a known standard (as in conventional isotope geochemistry) or as deviation from mass-dependent behavior (as in mass-independent isotope geochemistry), but rather as deviation from a stochastic distribution (R^{x*}). For CO_2 ($R = x/^{12}C$, or $x/^{16}O$)

$$\Delta 47 = [\ (R47 / R47^* - 1) - (R46 / R46^* - 1) - (R45 / R45^* - 1)]\ \ 1000$$

with $R45^* = R^{13} + 2\ R^{17}$

$R46^* = 2\ R^{18} + 2\ R^{13}\ R^{17} + (R^{17})^2$

$R47^* = 2\ R^{13}\ R^{18} + 2\ R^{17}\ R^{18} + R^{13}\ (R^{17})^2$

Derived from calculations of isotope ratios based on stochastic distribution (see next table for corresponding isotopologues).

From Weifu Guo

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Calculating Stochastic Abundances

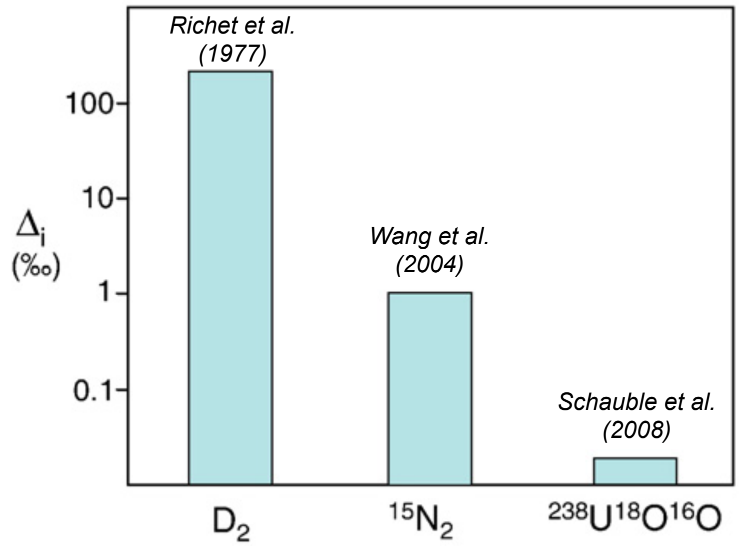
O_2	Isotopologue	Abundance	Calculation (from natural abundances)
32	$^{16}O_2$	99.50%	Ab (^{16}O) x Ab (^{16}O) = 0.9950…
33	$^{17}O^{16}O$	756 ppm	
34	$^{18}O^{16}O$	0.40%	
	$^{17}O_2$	0.144 ppm	
35	$^{18}O^{17}O$	1.52 ppm	Ab (^{18}O) x Ab (^{17}O) = 0.00000152
36	$^{18}O_2$	4.00 ppm	
CO_2			
44	$^{12}C^{16}O_2$	98.40%	
45	$^{13}C^{16}O_2$	1.11%	
	$^{12}C^{17}O^{16}O$	748 ppm	
46	$^{12}C^{18}O^{16}O$	0.40%	
	$^{13}C^{17}O^{16}O$	8.4 ppm	
	$^{12}C^{17}O_2$	0.142 ppm	
47	$^{13}C^{18}O^{16}O$	44.4 ppm	
	$^{12}C^{17}O^{18}O$	1.50 ppm	
	$^{13}C^{17}O_2$	1.60 ppb	
48	$^{12}C^{18}O_2$	3.96 ppm	
	$^{13}C^{17}O^{18}O$	16.8 ppb	
49	$^{13}C^{18}O_2$	44.5 ppb	

Isotopologues of the same nominal mass cannot be distinguished with current technology. Their contributions have to be modeled. Excellent chemical separation is required to minimize isobars of other elements.

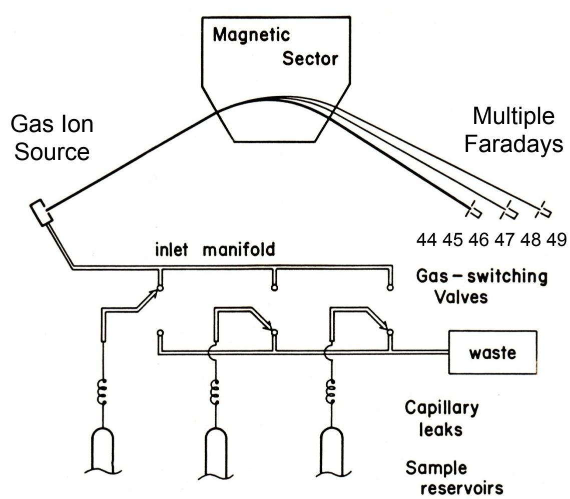
References: VSMOW and VPDB

Eiler, 2007, from Tab 1

(Reduced) Mass-dependency of Clumped Isotope Effects



Technological Advances



Larger detector blocks that can house up to nine ion collectors to simultaneously analyze multiple ion beams. Beams of abundant isotopologues are analyzed with Faraday cups equipped with $\Omega = 10^{11}$ or even $\Omega = 10^{10}$ resistors, while several weak ion beams (representing clumped isotopologues) require resistors with $\Omega = 10^{12}$.

Note: ensure that there is no "scrambling" of signals during preparation

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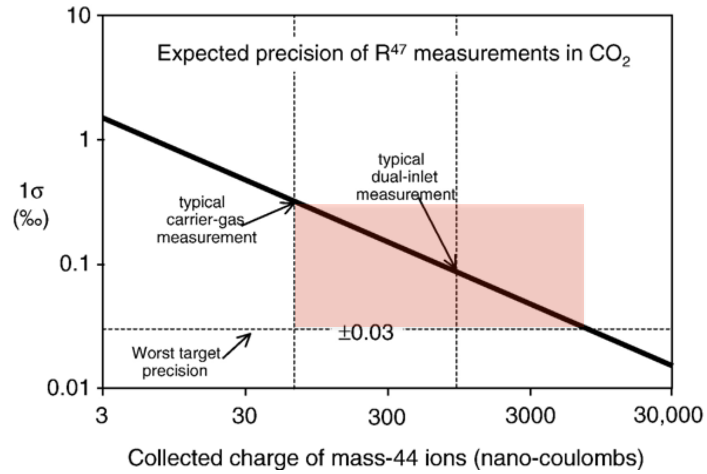
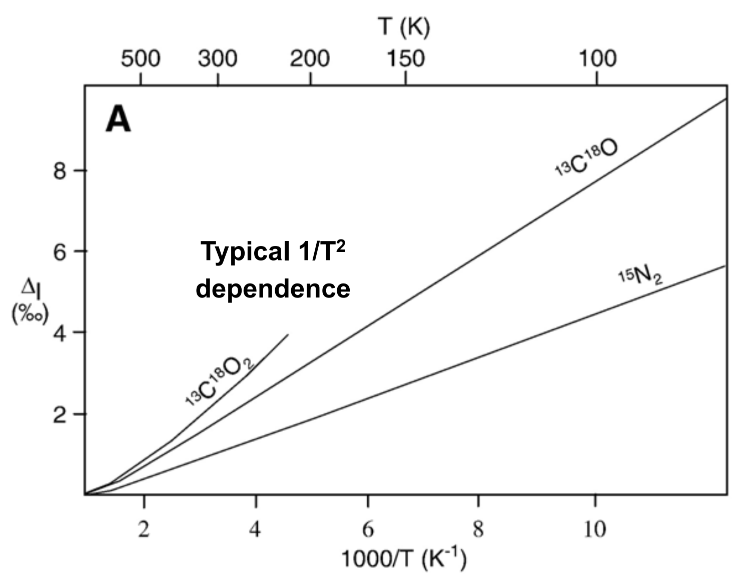
Statistical Limitations



Limitations from counting statistics (shot noise), √N / N, require long data acquisition and/or intense ion beams (good transmission)

Eiler, 2007

Temperature-dependence of Isotope Exchange Reactions



Eiler, 2007

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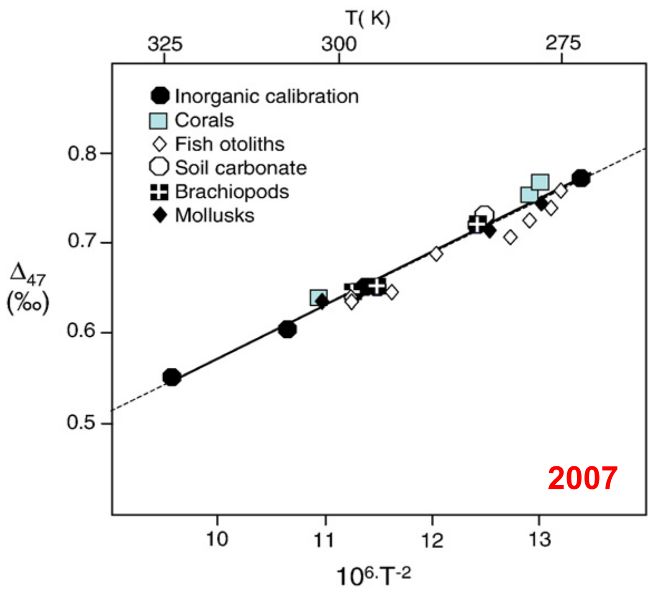
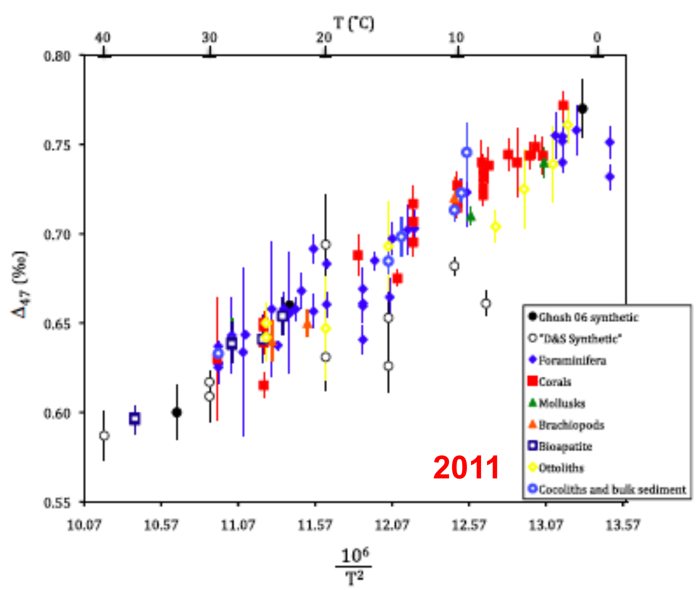


Eiler, 2007

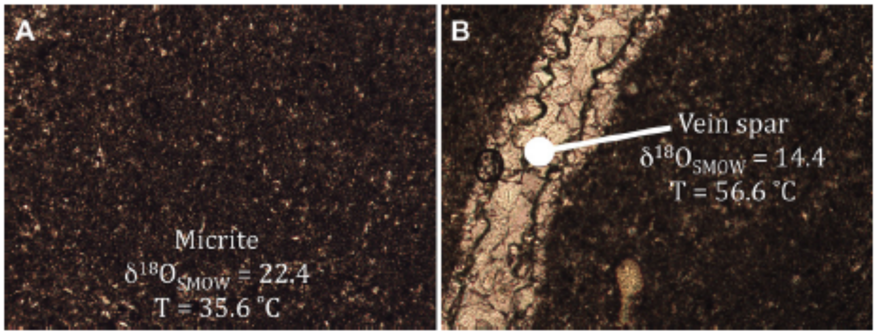
Temperature-dependence of Isotope Exchange Reactions



Eiler, 2011

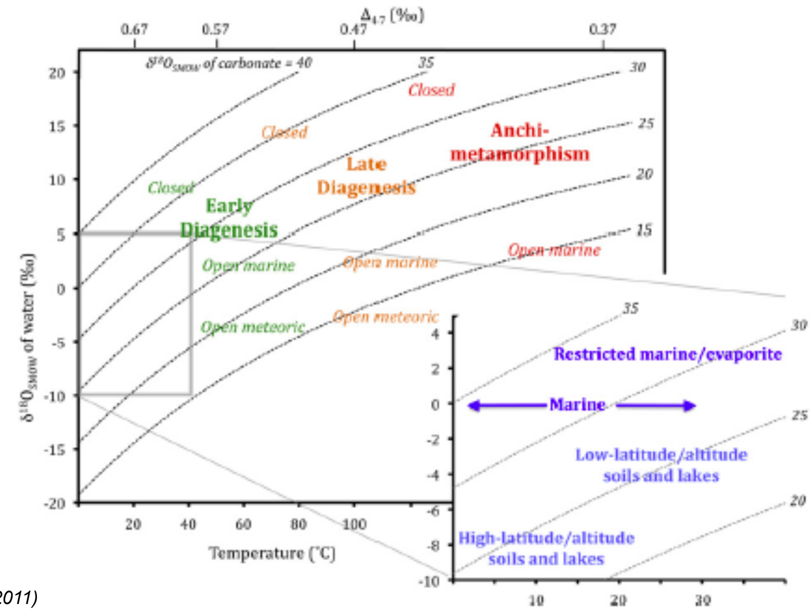
Problem of Secondary Alteration

54.1 Ma soil carbonate (Cc) nodule from the Bighorn Basin.
Field of view is 1.4 mm wide.
Temperatures are derived from "clumped" isotope ratios.



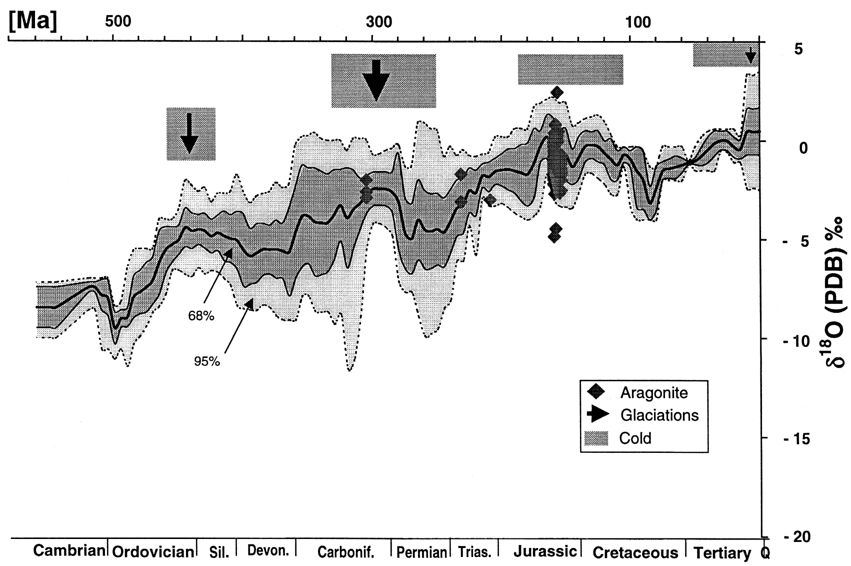
Photos from K. Snell, in Eiler (2011)

Problem of Secondary Alteration



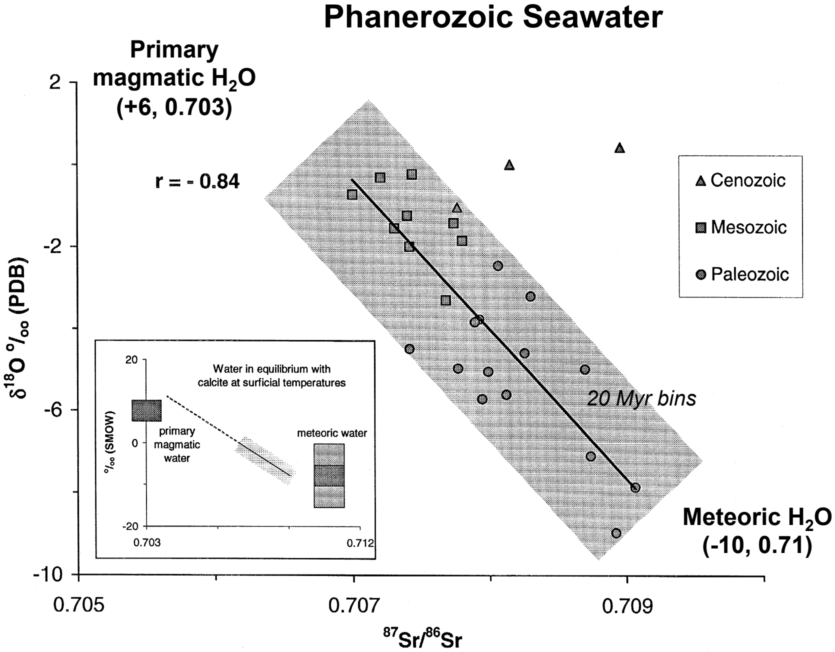
Eiler (2011)

Application: $\delta^{18}O$ of Phanerozoic seawater



Veizer et al. (1999)

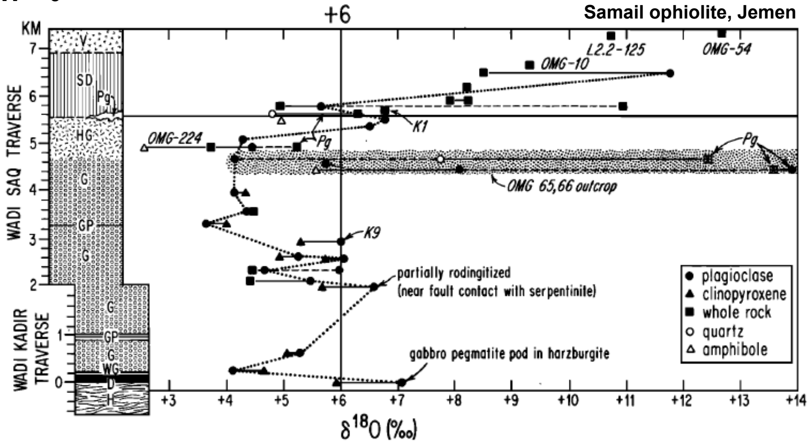
Phanerozoic Seawater



Veizer et al. (1999)

Hydrothermal Alteration of Oceanic Crust

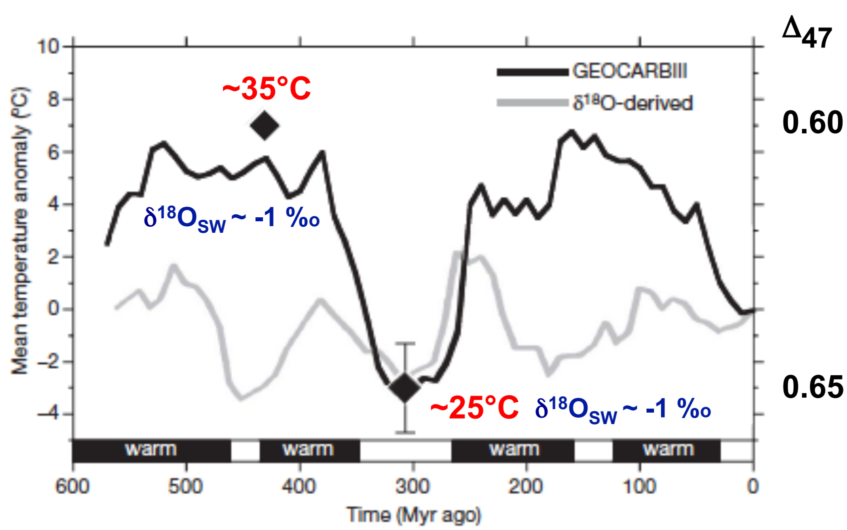
SMOW = 0



Seawater-plagioclase interactions at high temperature (500°C) result in $\delta^{18}O$ values of the fluid of +7.5. When this fluid reacts with plagioclase at low temperature (200°C), the plagioclase acquires $\delta^{18}O$ values of of +10 to +17, depending on...

Gregory & Taylor (1981), idea proposed by Muehlenbachs & Clayton (1976)

Tropical air temperature anomalies in the Phanerozoic



Came et al. (2007) Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic era. Nature 449, 198-201.

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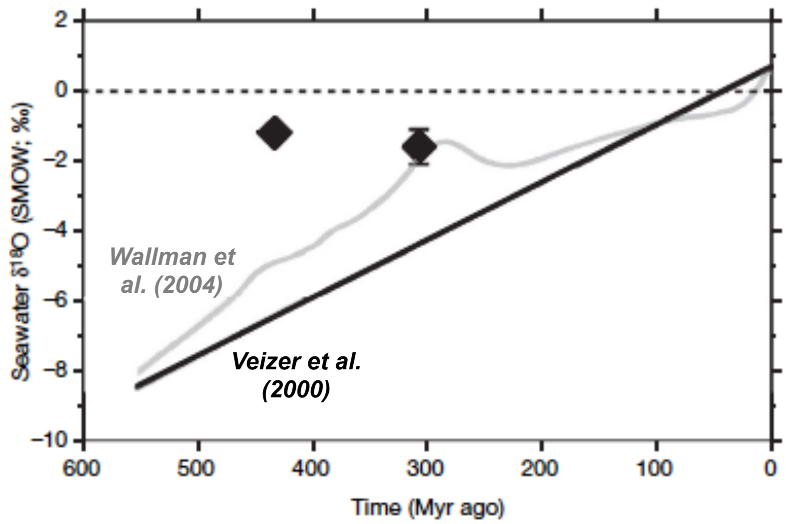
$\delta^{18}O$ of Phanerozoic seawater



Came et al. (2007) Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic era. Nature 449, 198-201.

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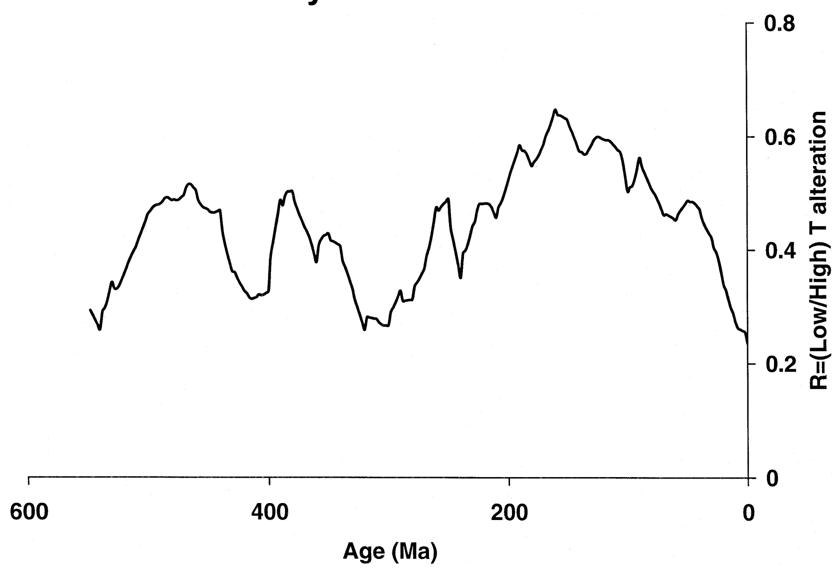
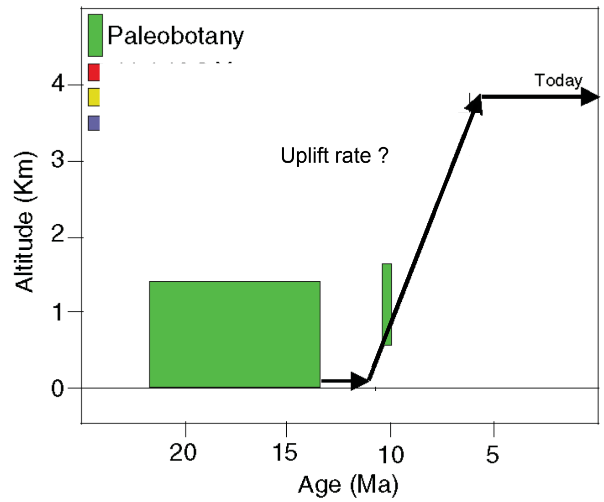
Stable $\delta^{18}O$ of Phanerozoic seawater with variable LT vs. HT hydrothermal alteration



Veizer et al. (1999)

Another Application: Paleoaltimetry



Ghosh et al. (2006) Rapid uplift of the Altiplano revealed through ^{13}C-^{18}O bonds in paleosol carbonates. Science 311, 511.

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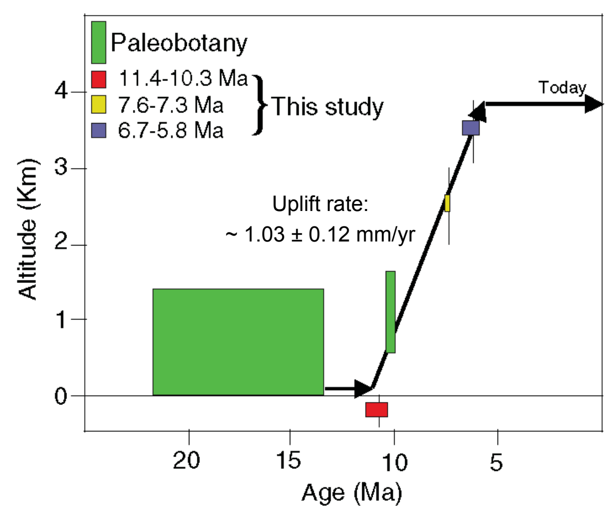
Paleoaltimetry



Ghosh et al. (2006) Rapid uplift of the Altiplano revealed through ^{13}C-^{18}O bonds in paleosols carbonates. Science 311, 511.

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"Clumped"

- Clumped isotopes provide another paleoclimate proxy, without assumptions about seawater $\delta^{18}O$, but also not without complications (alteration).
- John Eiler and co-workers at Caltech started this field, but many labs (>13, *including WHOI: Weifu Guo, in G&G*) are now set up to do these measurements.
- The clumped isotope community has established a wiki on the web, where published clumped isotope papers, recipes, data reduction calculations, etc. are complied:

http://daeron.fr/wiki/doku.php

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Stable Isotope Summary

- "Conventional" stable isotope geochemistry relies on mass-dependent fractionation ($\delta^{18}O \sim 2 \times \delta^{17}O$; $\delta^{33}S \sim 0.5 \times \delta^{34}S$; $\delta^{36} \sim 2 \times \delta^{34}S$).
- Mass-independent fractionation (MIF) refers to rare fractionations that do not follow mass-dependant laws. The (stratospheric) mechanisms are still not fully understood…(e.g. O_3 formation, S isotopes).
- Clumped isotope geochemistry deals with the special cases of (very) rare multiply-substituted isotopologues and their (slightly) different behaviors.

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