12.740 Paleoceanography
Spring 2008

Oxygen Isotope Paleoclimatology

12.740 Lecture 2 Spring 2008

Part 1:

DISCUSSION READING:

These notes!

SUPPLEMENTARY REFERENCES

Bemis, B. E., H. J. Spero, et al. (1998). "Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations." Paleoceanogr. 13: 150-160.

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Grossman, E. L. and T.-L. Ku (1986). "Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects." Chem. Geol. (Isotope Geosci.) 59: 59-74.

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Kim, S.-T. a. J. R. O'Niel (1997) "Equilibrium and non-equilibrium oxygen isotope effects in synthetic carbonates." Geochim. Cosmochim. Acta 61: 3461-3475.

Lynch-Stieglitz, J., W. Curry, et al. (1999). "A geostrophic transport estimate for the Florida Current from the oxygen isotope composition of benthic foraminifera." Paleoceanogr. 14: 360-373.

Matsumoto, K. and J. Lynch-Stieglitz (1999). "Similar glacial and Holocene deep water circulation inferred from southeast Pacific benthic foraminiferal carbon isotope composition." Paleoceanogr. 14: 149-163.

Rye, D.M. and M. Sommer II (1980) Reconstructing Paleotemperature and Paleosalinity Regimes with Oxygen Isotopes, in Skeletal Growth of Aquatic Organisms, eds. D.C. Rhodes and R.A. Lutz, Plenum, New York, pp. 169-202.

Urey, H.C. (1947) The thermodynamic properties of isotopic substances, J. Chem. Soc. 1947: 562-581.

Urey (1947) Thermodynamic properties of isotopes; statistical dynamical equations and infra-red spectroscopy

Because of the differences in the energy levels of the isotopes, isotope fractionation between equilibrium species is a function of temperature.

The vibration frequency of two objects connected by a spring depends on their masses (and the "spring constant"). Similarly, the rotation characteristics and translational movements depend on mass. These factors are the fundamental causes of isotopic fraction.

Ground-state energies:

Schematic diagram showing the relationship between the zero-point energy and molecular mass for hydrogen (H_2), deuterium (D_2), and HD. The fundamental vibration frequencies are H_2: 4405 cm^{-1}, HD: 3817 cm^{-1}, D_2: 3119 cm^{-1}. The zero-point energy of H_2 is greater than that for HD which is greater than that for D_2.
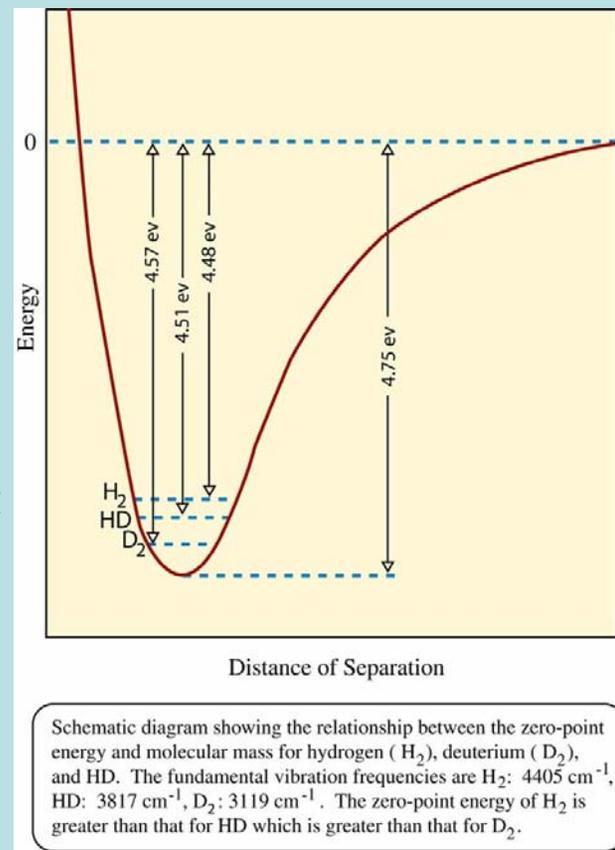
Figure by MIT OpenCourseWare.
Adapted from source: Broecker and Overs by
Chemical Equilibria in the Earth, p. 151.

Stable isotope ratios:
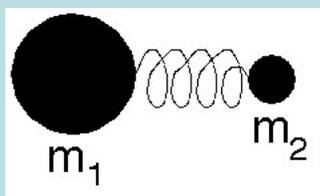
$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{standard}}} - 1 \right] \times 1000$$

Calcite geothermometer

- Ground-state differences lead to kinetic differences between isotopes (lower activation energies for lighter isotopes); differences in the energy-levels between the isotopes lead to changes in equilibrium distributions (rough rule of thumb: the heavier isotope "prefers" the more immobile state; i.e. at equilibrium water vapor is ~0.9% lighter than water).

- Rotation - Vibration - Translation

- Calcite geothermometer:

- $$CaC^{16}O_3 + H_2^{18}O \leftrightarrow CaC^{16}O_2^{18}O + H_2^{16}O$$

-
- (1) $K(T) = \dfrac{[CaC^{16}O_2^{18}O]\,[H_2^{16}O]}{[CaC^{16}O_3]\,[H_2^{18}O]} = \exp[-\Delta G_0/RT]$
-

- In theory, the equilibrium constant can be derived from the statistical mechanics of quantum energy states (in practice, not so easy; gases are not too bad, solids are possible, liquids are hard…):

Isotope Statistical Mechanics:

Assumes that all states which conserve total (quantized) energy are equally probable. For example, suppose there are 5 particles with a total energy of five units (with a range of zero to five quantized at 1). One possible state is for all five particles to have 1 unit of energy; another is for one particle (but which one?) to have all of the energy; these alternatives are considered equally probable.

```
Energy    5 _____    _a_____    __b_____    _____    _____
  Level   4 _____    _____     _____    _____    _____
          3 _____    _____     _____    ___c____    _____
          2 _____    _____     _____    __b_____    ___d___
          1 _abcde_     _____     _____    _____    _abc____
          0 _____     __bcde___    _a_cde_     _a__de_     _____e_
```

                                                                    etc.

$$(2) \qquad f_i \; = \; \frac{\exp \; [\; E_i / kT \;]}{\Sigma \; \exp \; [\; E_i / kT \;]}$$

Isotope Statistical Mechanics:

$$(2) \qquad f_i \quad = \quad \frac{\exp [E_i/kT]}{\Sigma \exp [E_i/kT]}$$

$$(3) \qquad q = \Sigma \exp [E_i/kt] \text{ for each mode (rot,vib,trans)}$$

$$(4) \qquad q_{tot} = [(q_{trans}q_{rot}q_{vib})^N /N!]^{1/N}$$

but for large N, $(N!)^{1/N} = e/N$, so

$$(5) \qquad q_{tot} = q_{trans}q_{rot}q_{vib} \ e \ / \ N$$

$$(6) \qquad \Delta G° = -RT \ \ln \frac{q_{H2O(16)} \ q_{CaCO(16)O2(18)}}{q_{H2O(18)} \ q_{CaCO3(16)}}$$

and

$$(7) \qquad S = E/T + R \ \ln q$$

Temperature dependence of equilibrium constant:

$$(8) \qquad \frac{\partial \ln K(T)}{\partial T} = -\frac{\Delta H_0}{RT^2}$$

As a generalization, we expect less isotopic fractionation at high temperatures, because differences between the occupancy of isotope energy levels becomes smaller (but note that this decrease depends on the specific molecules/phases involved; significant isotope fractionation exists for silicate phases at very high temperatures).

Fractionation factor:

$$(9) \qquad \alpha = \frac{\left(^{18}O/^{16}O\right)_{calcite}}{\left(^{18}O/^{16}O\right)_{water}}$$

typically, fractionation factors are close to unity and become closer as temperature increases:
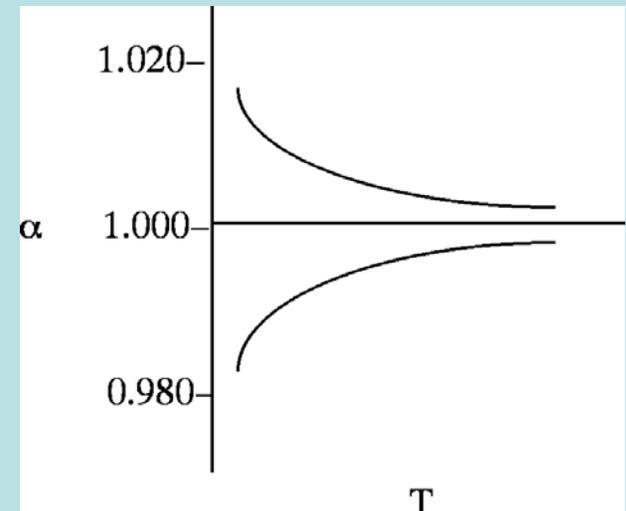
Isotope Measurement: the mass spectrometer
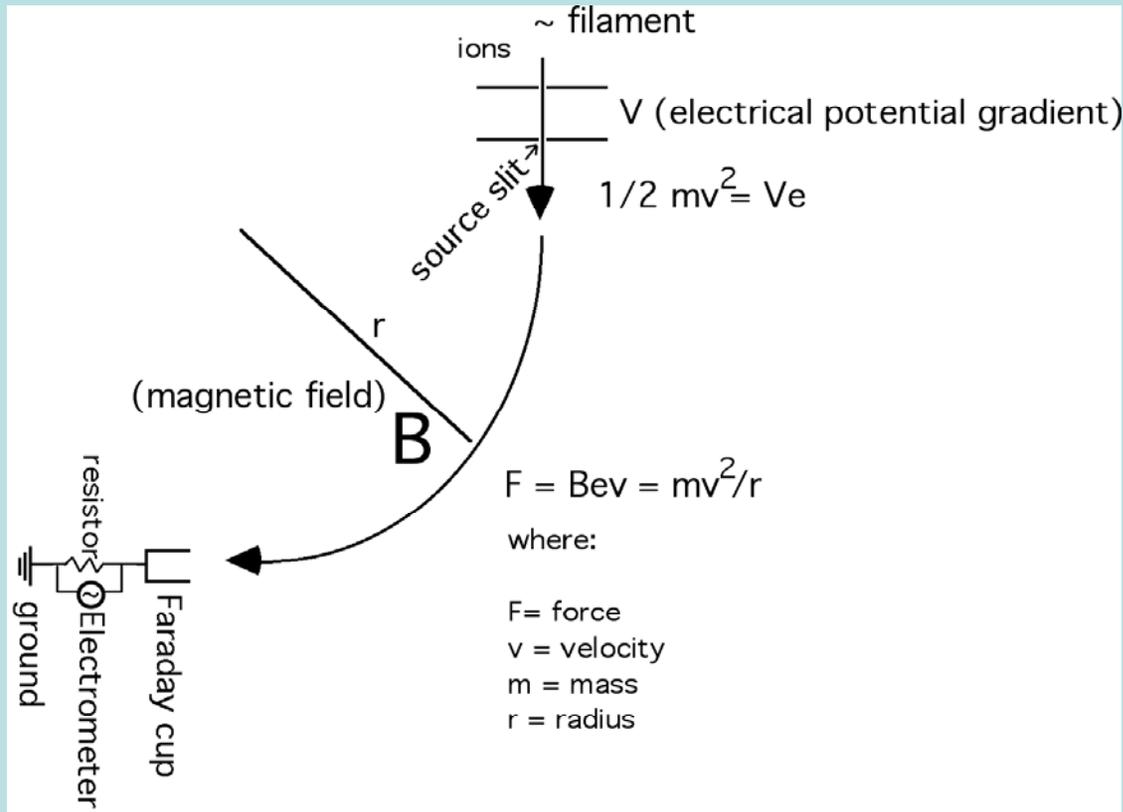
Hence:

$$M/e = 4.824 \times 10^{-5} \; r^2 B^2 / V$$

where

M = atomic mass units

e = electronic charge (1,2,3,...)

r = radius (centimeters)

V = acceleration potential (volts)

B = magnetic field strength (gauss)

1950: Nier double focussing mass spectrometer

Nier (1950): designed the modern double-focusing mass spectrometer, to compensate for differences in initial ion velocities Although the electrostatic acceleration by V is the same for all ions coming off of the filament, they start with slightly different velocities and directions. Bending the ion beam by an electrostatic field filters by energy rather than by mass, so combining an electrostatic filter with a magnetic filter produces better mass discrimination. Mass spectrometer in effect is an optical system producing an image of the source slit.

Double-focusing mass spectrometer of Bainbridge and Jordan. The two ion paths shown have the same initial direction and the same mass but different initial velocities. If they had the same mass but different initial directions they would still be focused to the same point on the photographic plate.
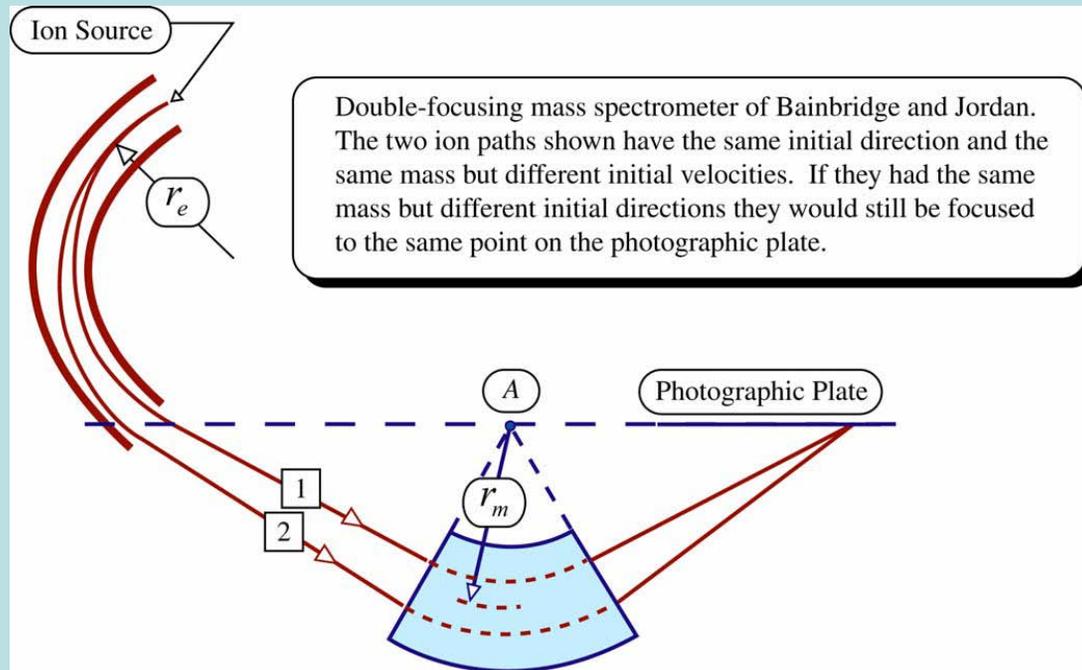
Figure by MIT OpenCourseWare.
Adapted from Source: Sproul (1963) Modern Physics.

Mass spectrometric isotope measurement of CO_2

- It's difficult to avoid mass fractionation within the instrument, so rather than attempt to measure absolute ratios, we measure isotope ratio differences between standards and samples (compared alternately in the instrument by switching a valve at the inlet):

- Measurements are made on CO2 gas:

atomic mass unit (amu): 44: $^{12}C^{16}O_2$
45: $^{13}C^{16}O^2$, ($^{12}C^{16}O^{17}O$)
46: $^{12}C^{16}O^{18}O$

- typical mass abundances:

- $^{16}O = 99.759\%$ $^{12}C = 98.89\%$
- $^{17}O = 0.037\%$ $^{13}C = 1.11\%$
- $^{18}O = 0.204\%$

- So for every measurement of $\delta^{13}C$, a small correction must be made for ^{17}O (estimated from $\delta^{18}O$). As a generality, isotope fractionation for 2-mass-unit difference is usually ~twice that for a 1-mass-unit difference. [Warning: some unusual processes violate this rule! For example, the process that produces ozone in the stratosphere has mass-independent fractionation- so the isotopic composition of ozone (and the residual oxygen in the atmosphere) is anomalous].

Mass spectrometric isotope measurement of CO_2

- Other than for pure CO_2 gas, a procedure must be devised for conversion or isotopic equilibration with CO_2 gas. This requirement is at the root of many problems with the measurement - additional fractionations are introduced during the conversion process.

- Calcium carbonate: Reaction with 100% phosphoric acid (because the oxygen atoms in phosphate exchange extremely slowly, and because H_3PO_4 has a low vapor pressure). Potential problems: CO_2 and H_2O left over from previous reactions can affect current reaction; problem may be minimized by using fresh aliquot of acid each time or by minimizing the volume of the reaction bath, and heating acid in vacuo to drive off water. The resulting CO_2 is then distilled by a freezing/warming cycle to free it of water and other volatiles. Many workers "roast" samples in vacuo or in helium to "drive off organics" that might interfere; documentation on this practice is sparse and it may lead to problems (e.g. phase changes).

- Water: a known quantity of gaseous CO_2 of known isotopic composition is equilibrated with a larger quantity of water.

- Procedural precision should be better than 0.1 ‰. Modern mass spectrometers can usually reproduce measurements on standards to better than 0.05 ‰ *in the short term*.

Mass spectrometric isotope measurement of CO_2

- Standards: An ideal standard is perfectly stable and available in perpetuity to anyone who wants it. Real standards:

- PDB: a calcium carbonate powder prepared from the PeeDee Belemnite (a fossil from Georgia). This was the standard reference for carbonate analysis of $\delta^{18}O$ and $\delta^{13}C$ for many years. Practically, one measures samples against PDB by measuring CO_2 evolved under controlled conditions:

- $$3CaCO_3 + 2H_3PO_4 \rightarrow 3CO_2 + 3H_2O + Ca_3(PO_4)_2$$

- A problem: the water released in this reaction can react with the evolved CO_2 to change its isotopic composition. The extent of this back reaction depends critically on experimental conditions (temperature, mixing rate, previous samples analyzed...). Two experimental conditions are common: "common acid bath" (samples dumped into large bath in sequence) and "single drop" (drop of phosphoric acid placed on each sample). In principle, the latter should avoid memory problems better; in practice, it seems that either method works reasonably well in the hands of a careful analyst.

- Another problem: PDB doesn't exist anymore!. As a result, people actually use other available standards which supposedly have been calibrated with respect to PDB (major ones: NBS-20, a 'dirty' limestone powder, and NBS-19, a coarse marble sand). Personal preferences, less than full competence, and personality differences between labs results in some confusion over interlaboratory comparisons. These problems seem to be worse for $\delta^{18}O$ than for $\delta^{13}C$, where differences of several tenths permil appear to occur at times. This is partly due to the greater scarcity of ^{18}O compared to ^{13}C, partly due to the "sticky" nature of H_2O (which can coat mass spectrometer surfaces), and partly due to small leaks in the vacuum system.

Mass spectrometric isotope measurement of CO_2

- SMOW: "Standard Mean Ocean Water", an artificial standard which approximates the oceanic mean, formerly maintained and recreated by Harmon Craig's laboratory, which refers to the isotopic composition of CO_2 equilibrated with SMOW, not to the actual isotopic composition of the water; this doesn't matter for measurements relative to SMOW but confuses many people when comparing absolute fractionations and converting to PDB. Problem: An infinite quantity of SMOW wasn't made; several batches of it have been used up. Supposedly these batches have been carefully intercalibrated over the last 20 years. Unfortunately, more recent measurements (GEOSECS) of deep ocean water appear to be 0.2 permil offset with respect to the classic "Craig and Gordon" reference, suggesting that the standard has drifted over time!

- VPDB, VSMOW: it has recently been declared that all $\delta^{18}O$ and $\delta^{13}C$ measurements should be referenced to this standard, which in fact is not a standard but a definition based on actual standards (e.g., to convert to VPDB, convert the ratio measured on NBS19 to a certain value). The wrath of the IUPAC gods to anyone who ignores this convention!

Oxygen isotope paleothermometry

Stable isotope ratios:
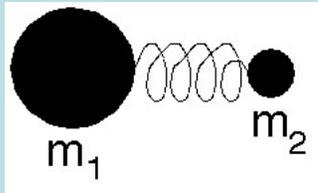
$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right] x \ 1000$$

- Urey (1947) calculated that the oxygen isotope fractionation between calcium carbonate and water should be temperature-dependent.

- Epstein (1953) grew molluscs in the laboratory and empirically determined the ^{18}O-T relationship (arbitrary parabolic curve fit):

$$T = 16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2$$

Isotopic temperature scale and original data points of Epstein *et al.* (1953). Temperature is in degrees Celsius. The δ values are the δ-corrected values, which are equal to $\delta_c - \delta_w$. After Epstein *et al.* (1953).
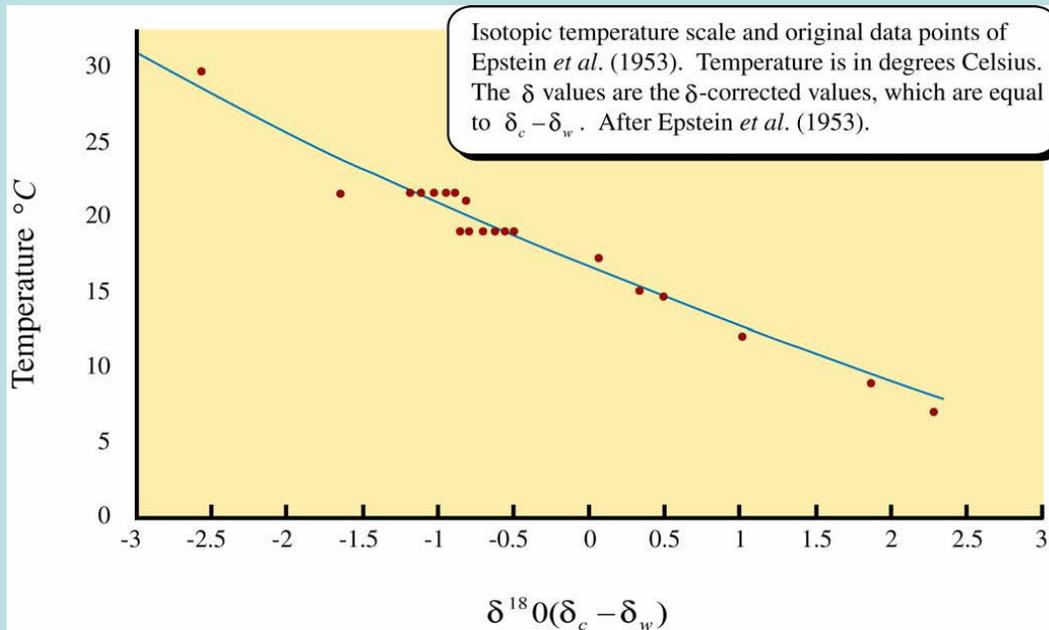
Figure by MIT OpenCourseWare.
Adapted from source: Rye and Sommer (1980).

Oxygen isotope paleothermometry equations
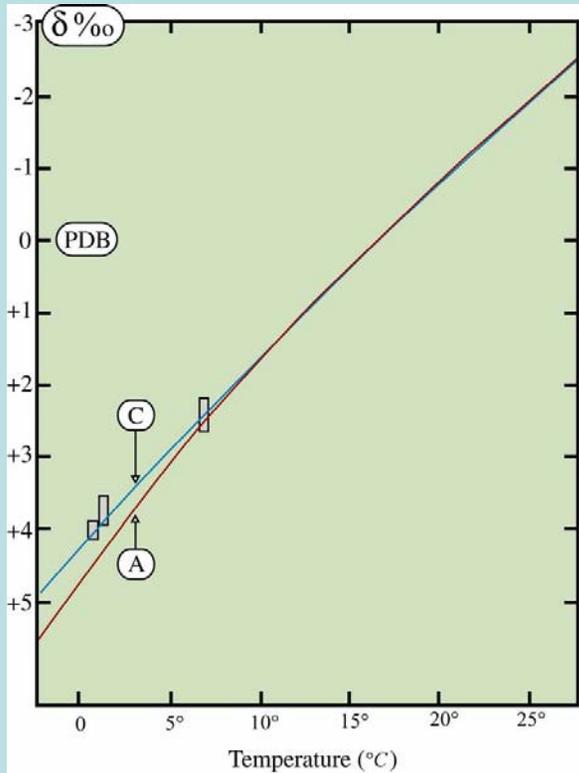
Analyses of *Uvigerina* sp from recent section of three cores (Tables 1 and 2) plotted against temperature, and compared with two alternative expressions of isotopic equilibrium.

$$AT = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$
$$CT = 16.9 - 4.38(\delta_c - \delta_w) + 0.10(\delta_c - \delta_w)^2$$

Figure by MIT OpenCourseWare.

- Epstein curve: $T = 16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2$

- Craig reworked a curve fit to Epstein data:
$$T = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

- O'Neil performed inorganic precipitation experiments, Shackleton fit lower-temperature interval to this equation:'
$$T = 16.9 - 4.38(\delta_c - \delta_w) + 0.10(\delta_c - \delta_w)^2$$

<-- Shackleton (1974) *Uvigerina* core top data :

- Shackleton (1974) linear fit to *Uvigerina* data:
$$T = 16.9 - 4.0(\delta_c - \delta_w)$$

- Erez et al. (1983) (planktonic *G. sacculifer* laboratory experiment)
$$T = 17.0 - 4.52(\delta_c - \delta_w) + 0.03(\delta_c - \delta_w)^2$$

Oxygen isotope paleothermometry equations
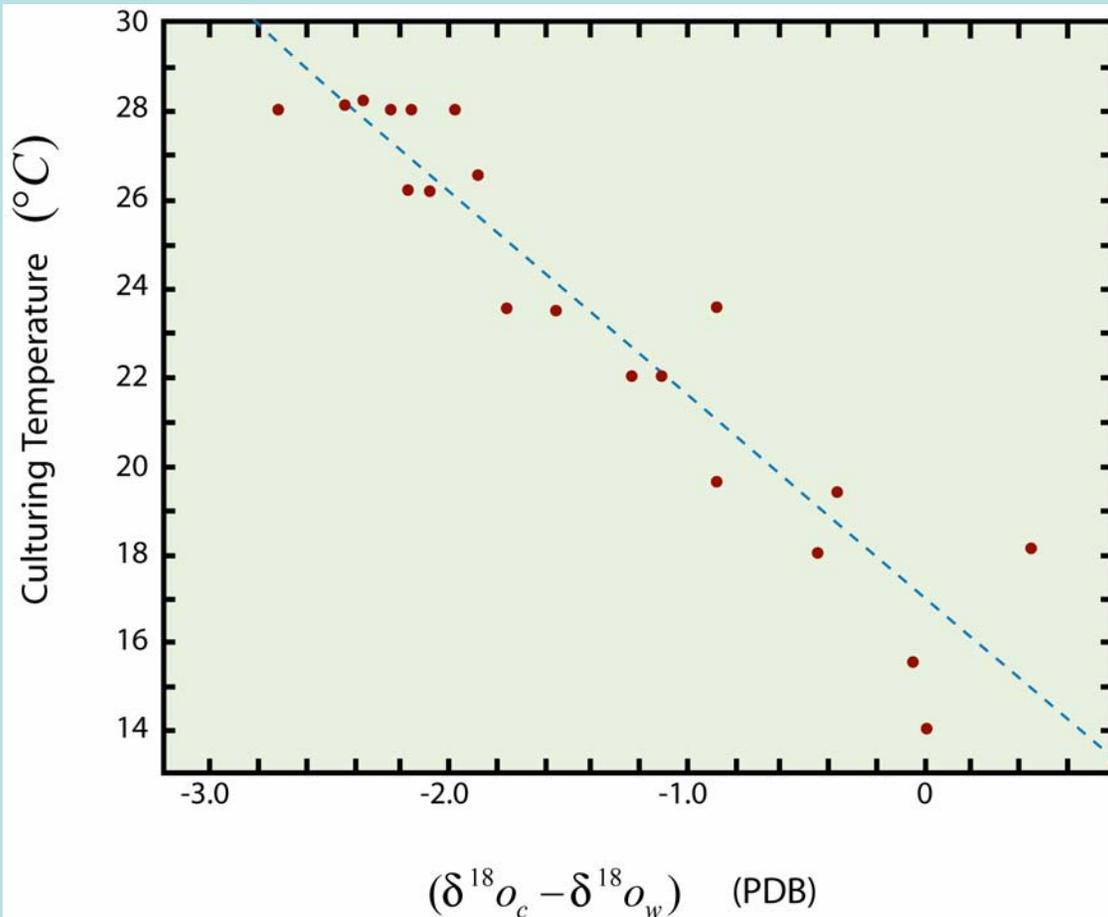
Erez et al. (1983)
(planktonic *G. sacculifer*
laboratory experiment)

The culturing temperature *vs.* the difference $(\delta^{18}Oc - \delta^{18}Ow)$ (*i.e.*, the carbonate minus the water oxygen isotopic composition). The line is the best fit for the date and yields the following paleotemperature equation: $\hat{t} = 17.00 - 4.52(\delta^{18}Oc - \delta^{18}Ow) + 0.03(\delta^{18}Oc - \delta^{18}Ow)^2$ with $r = 0.95$.

Oxygen isotope paleothermometry equations

- These equations are empirical curve fits to data, and their functionality is not specified by theory. Ultimately, we can't prove that any of these relationships describe isotope equilibrium, because the carbonate is precipitated rapidly and does not re-equilibrate with the surrounding water after precipitation.

- In recent years, several groups have tried to devised new "equilibrium" paleotemperature equations based on inorganic precipitation in the laboratory (e.g. Kim and O'Neil (1997), core top calibrations (e.g. Lynch-Stieglitz et al., 1999, Matsumoto and Lynch-Stieglitz, 1999; and Grossman and Ku, 1986 for aragonite) or experimental manipulations of foraminifera (e.g. Bemis et al., 1998). Often, these studies suggest that their new equation is the "true equilibrium paleotemperature equation" or that some species are closer to equilibrium than others. Despite acknowledging the value of the experiments (see below), I believe that claims concerning the "true" equilibrium relationship are unsupportable. Consider the following truisms:

  * Different species of foraminifera living in the same environment have different $\delta^{18}O$ values.

  * At least some of them are NOT in equilibrium.

  * We expect foraminifera to retain their oxygen isotope composition for (millions-tens of millions-100's of millions?) of years. If they manage to do this, then the rate of re-equilibration with their environments must be vanishingly small on the time scale of human laboratory experiments.

- Inorganic precipitates may form out of equilibrium under certain conditions – but how can we know which conditions are "equilibrium"? It is a tenet of physical chemistry that we can only prove equilibrum exists when we have shown that the same value is obtained when approaching equilibrium from above and below. If carbonates take millions (or tens of millions) of years to re-equilibrate with solutions, no laboratory experiment can approach equilibrium from both directions. Hence we cannot know the true equilibrium value for carbonate isotopic composition.

Oxygen isotope paleothermometry equations

In my estimation, the search for the "true paleotemperature equation" is akin to the search for the Holy Grail. It is better suited for Monty Python than for paleoceanographers.

In the absence of knowing true equilibrium, the best approach is a "modified empirical approach":

(1) Use calibrations appropriate for the species in question (because we know that biological fractionations are possible.

(2) (2) Use calibrations that most closely approximate natural conditions (because the biological fractionations may depend on environmental conditions).

(3) This situation may be seen as a curse upon proving equilibration, but it is necessary if environmental carbonates are to be used as paleotemperature recorders over tens of millions of years.

Oxygen isotope paleothermometry: the early applications

- 1940's: Kullenberg's invention of the piston core. Previously, deep-sea coring was done by gravity coring, where a pipe with an in-line stopper at the top and "core catcher" at the bottom (interleaved flexible metal fingers) was dropped into the seafloor. Friction against the walls of the pipe limited the length of core that could be obtained. Modern gravity cores can get cores ~ 5 m in length; older ones obtained only a meter or two. Kullenberg introduced a piston into the pipe; the piston was rigged with a cable that prevented it from moving down with the pipe, creating "suction" which helped force the sediment into the pipe as it moved down into the sediment. Modern piston cores can obtain as much as ~50 m of sediment (although more typically, ~20 m).

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