

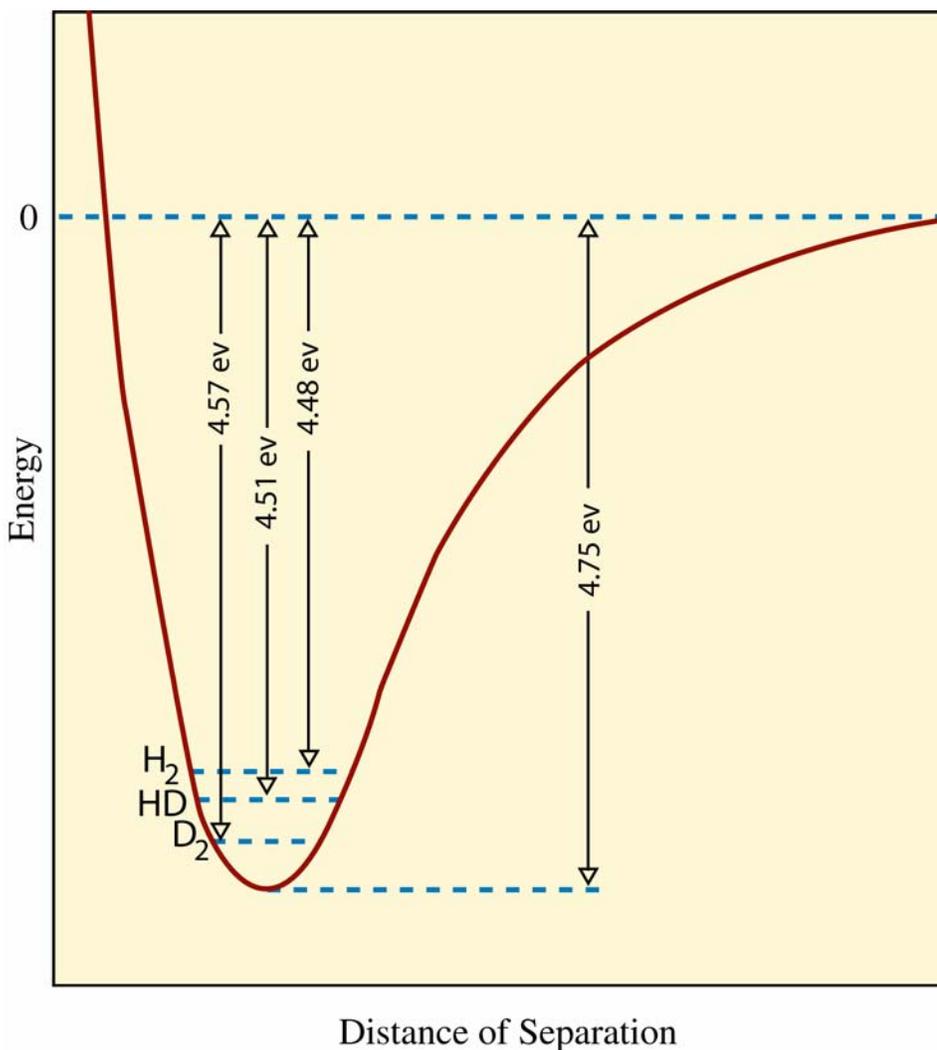
OXYGEN ISOTOPE PALEOCLIMATOLOGY

- I. Urey (1947) Thermodynamic properties of isotopes; statistical dynamical equations and infrared 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:



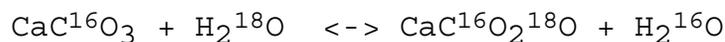
Schematic diagram showing the relationship between the zero-point energy and molecular mass for hydrogen (H_2), deuterium (D_2), and HD. The fundamental vibration frequencies are H_2 : 4405 cm^{-1} , HD: 3817 cm^{-1} , D_2 : 3119 cm^{-1} . The zero-point energy of H_2 is greater than that for HD which is greater than that for D_2 .

Adapted from source: Broecker and Oversby, Chemical Equilibria in the Earth, p. 151

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:



$$(1) \quad K(T) = \frac{[\text{CaC}^{16}\text{O}_2^{18}\text{O}] [\text{H}_2^{16}\text{O}]}{[\text{CaC}^{16}\text{O}_3] [\text{H}_2^{18}\text{O}]} = \exp[-\Delta G^\circ/RT]$$

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

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 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.						

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

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

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

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

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

$$(6) \quad \Delta G^\circ = -RT \ln \frac{q_{\text{H}_2\text{O}(16)} q_{\text{CaCO}(16)} \text{O}_2(18)}{q_{\text{H}_2\text{O}(18)} q_{\text{CaCO}_3(16)}}$$

and

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

and

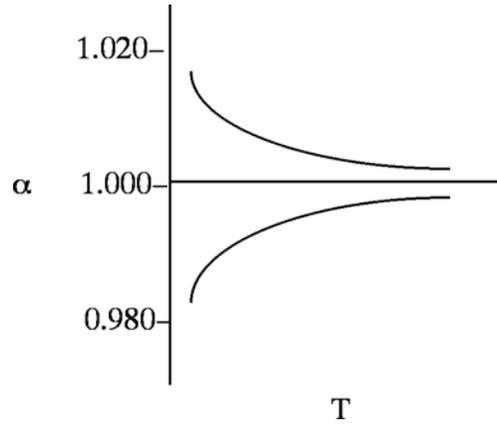
$$(8) \quad \frac{\partial \ln K(T)}{\partial T} = \frac{\Delta H_o}{RT^2}$$

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

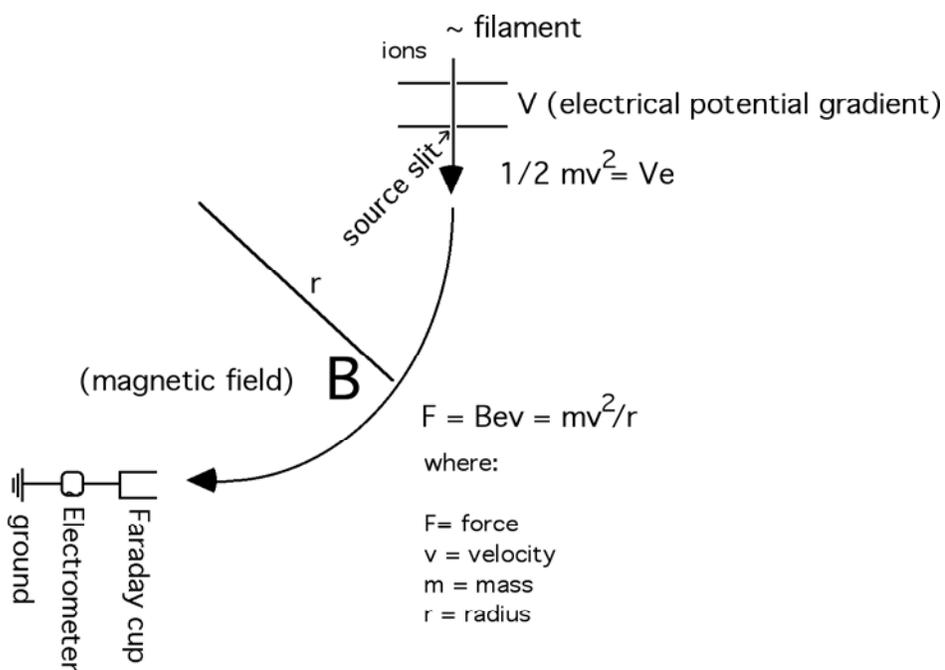
$$(9) \quad \alpha = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{calcite}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{water}}}$$

typically, fractionation factors are close to unity and approach closer as temperature increases:



II. Measurement

A. Mass spectrometer



Hence:

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

where

$M =$ atomic mass units

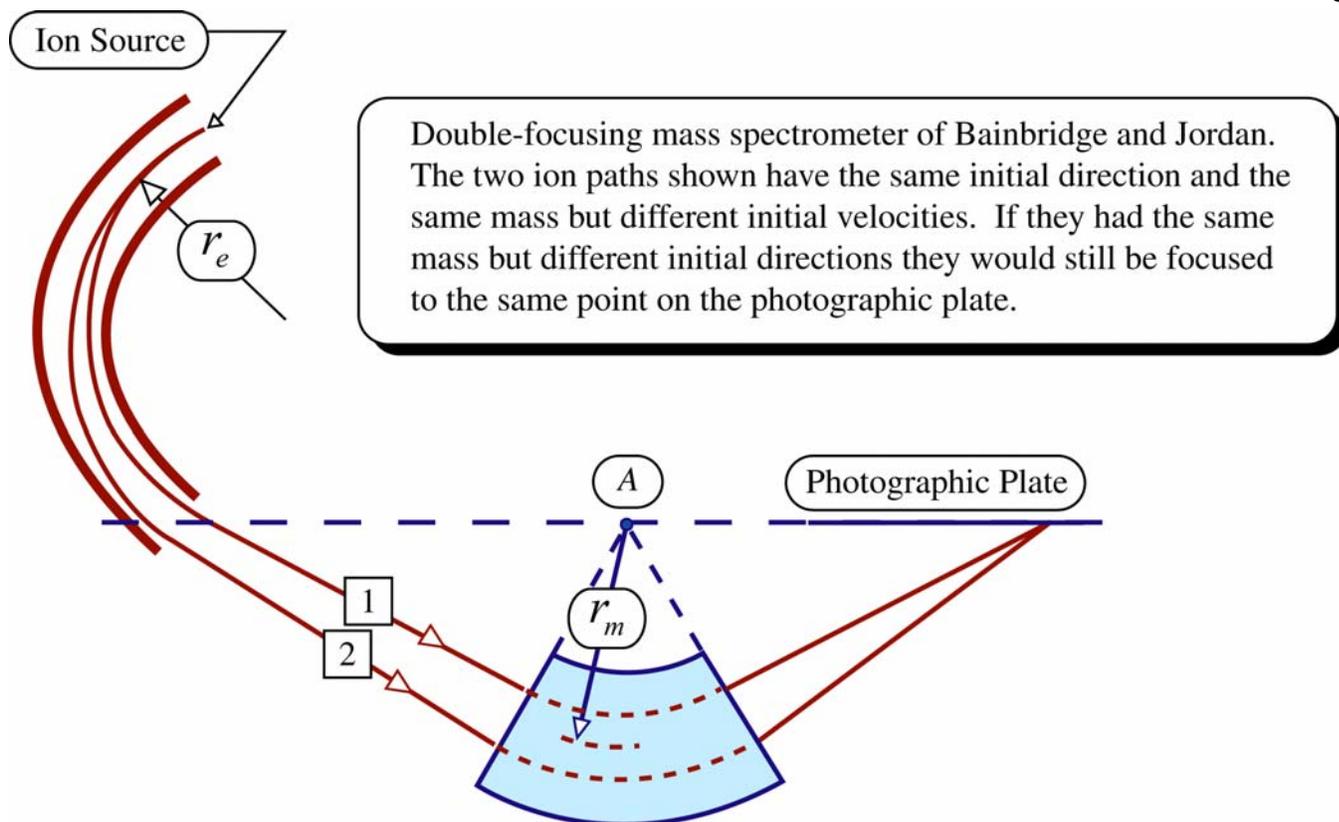
$e =$ electronic charge (1,2,3,...)

$r =$ radius (centimeters)

$V =$ acceleration potential (volts)

$B =$ magnetic field strength (gauss)

- B. 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.



Adapted from Source: Sproul (1963) *Modern Physics*

C. Practical measurement.

1. It is difficult to avoid some 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):

$$(10) \quad \delta^{18}\text{O} = 1000 \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right]$$

(units: ‰ (permil))

2. Measurements are made on CO_2 gas:

atomic mass unit (amu): 44: $^{12}\text{C}^{16}\text{O}_2$

45: $^{13}\text{C}^{16}\text{O}_2$, ($^{12}\text{C}^{16}\text{O}^{17}\text{O}$)

46: $^{12}\text{C}^{16}\text{O}^{18}\text{O}$

typical mass abundances:

$^{16}\text{O} = 99.759\%$ $^{12}\text{C} = 98.89\%$

$^{17}\text{O} = 0.037\%$ $^{13}\text{C} = 1.11\%$

$^{18}\text{O} = 0.204\%$

So for every measurement of $\delta^{13}\text{C}$, a small correction must be made for ^{17}O (estimated from $\delta^{18}\text{O}$). 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].

3. Other than for pure CO₂ gas, a procedure must be devised for conversion or isotopic equilibration with CO₂ gas. This requirement is at the root of many problems with the measurement - additional fractionations are introduced during the conversion process.
 - a. Calcium carbonate: Reaction with 100% phosphoric acid (because the oxygen atoms in phosphate exchange extremely slowly, and because H₃PO₄ has a low vapor pressure). Potential problems: CO₂ and H₂O 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 CO₂ 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).
 - b. Water: a known quantity of gaseous CO₂ 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 ‰.

4. Standards. An ideal standard is perfectly stable and available in perpetuity to anyone who wants it. Real standards:
 - a. PDB: a calcium carbonate powder prepared from the PeeDee Belemnite (a fossil from Georgia). This was the standard reference for carbonate analysis of δ¹⁸O and δ¹³C for many years. Practically, one measures samples against PDB by measuring CO₂ evolved under controlled conditions:



A problem: the water released in this reaction can react with the evolved CO₂ 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 δ¹⁸O than for δ¹³C, where differences of several tenths permil appear to occur at times. This is partly due to the greater scarcity of ¹⁸O compared to ¹³C, partly due to the "sticky" nature of H₂O (which can coat mass spectrometer surfaces), and partly due to small leaks in the vacuum system.

- b. 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 CO₂ 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!

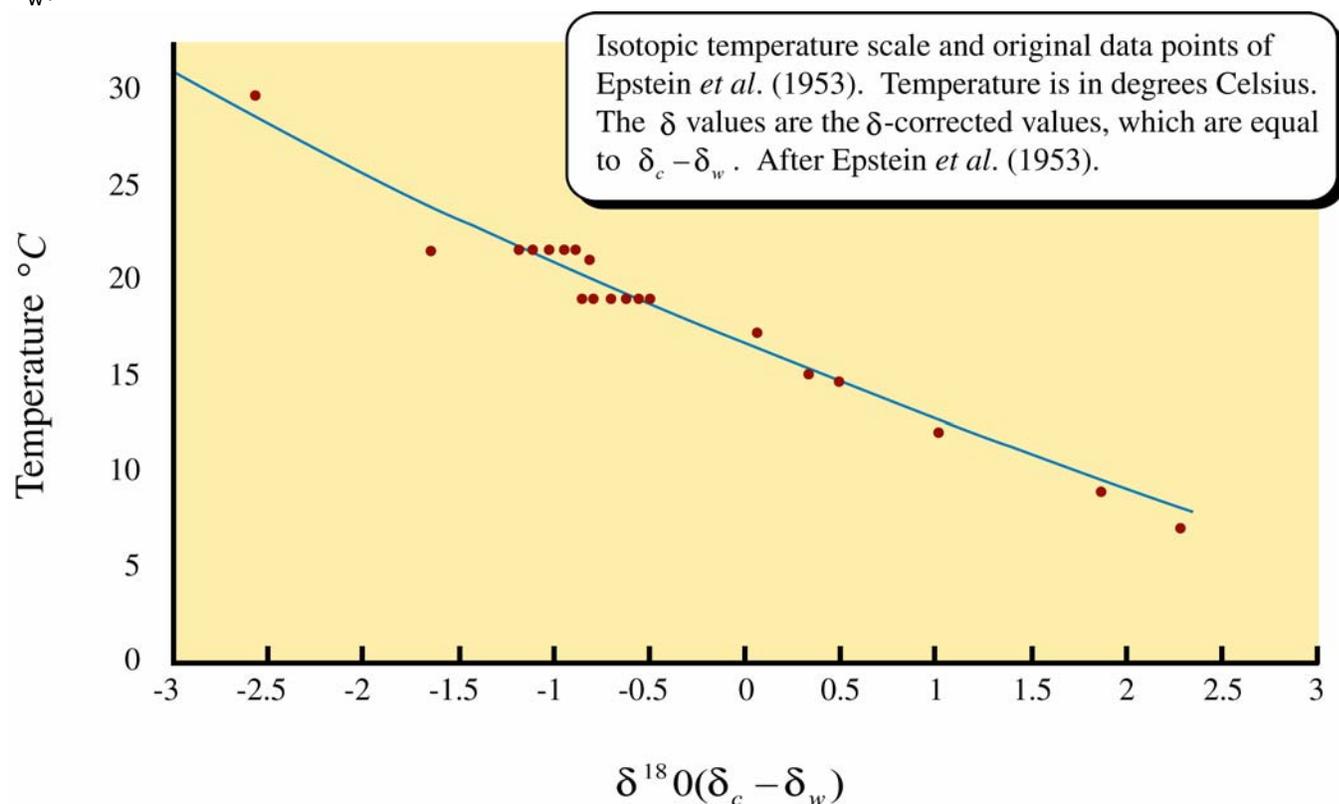
- c. VPDB, VSMOW: it has recently been declared that all $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements should be referenced to this standard, which in fact is not a standard but a definition based on actual standards (e.g., to convert to VPDB, convert the ratio measured on NBS19 to a certain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

CARBONATE PALEOTEMPERATURE EQUATIONS

- I. Epstein data (experimental growth of molluscs), fit to an (arbitrary) parabolic curve (because the relationship seemed slightly non-linear):

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

$\delta_w)^2$



Adapted from source: Rye and Sommer (1980)

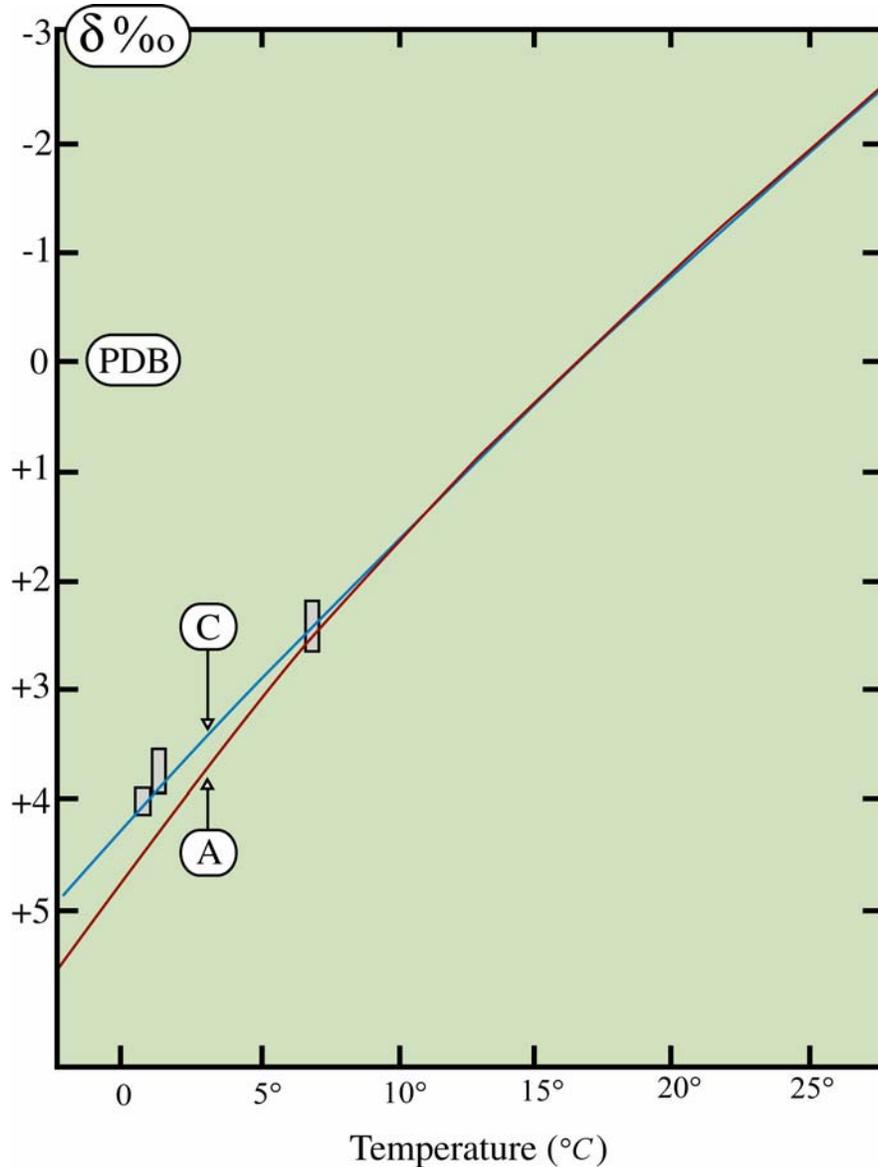
Craig reworked a curve fit to Epstein data:

$$T = 16.9 - 4.2 (\delta_c - \delta_w) + 0.13 (\delta_c - \delta_w)^2$$

O'Neil data (inorganic precipitation experiments, lower-temperature interval), Shackleton curve fit:

$$T = 16.9 - 4.38(\delta_c - \delta_w) + 0.10(\delta_c - \delta_w)^2$$

Shackleton (1974) *Uvigerina* data :



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.

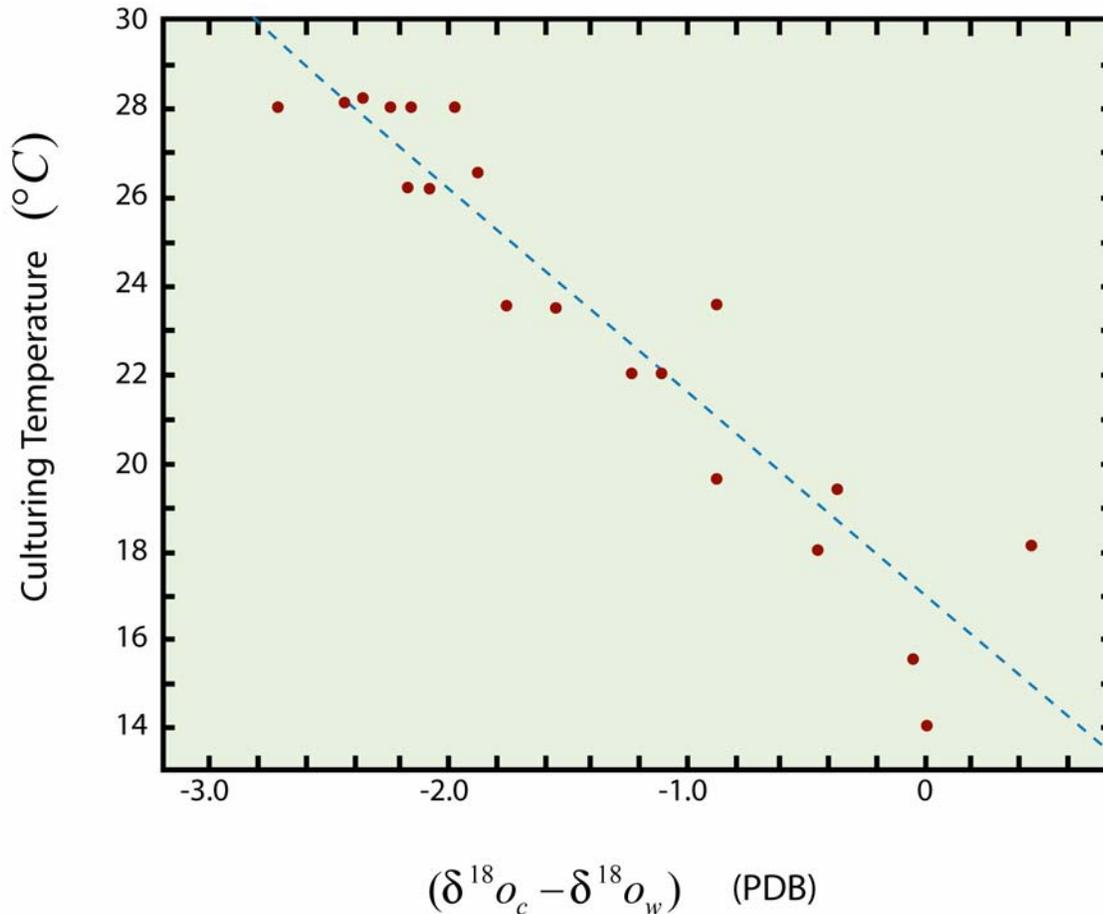
$$AT = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

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

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)



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

Note: To use these all of these paleotemperature equations, the isotopic composition of the water must be known! δ_w must be referenced to the PDB scale if δ_c is! Note that if "the CO₂ equilibrated with SMOW" has a δ_w which is 0.2 ‰ heavier than δ_w referred to PDB; i.e.:

$$\delta_w (\text{PDB}) = \delta_w (\text{SMOW}) - 0.2$$

Also note that the actual absolute isotopic composition of water is 30‰ depleted compared to the absolute isotopic composition of the CO₂ it is equilibrated with!

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 devise 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 $\delta^{18}\text{O}$ 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 equilibrium when we have shown that the same value is obtained when approaching equilibrium from above and below.* If carbonates take millions or more 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.

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) 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.

DISCUSSION READING:

These notes!

SUPPLEMENTARY REFERENCES

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