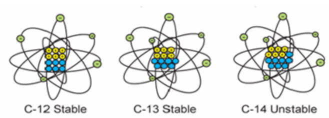
Isotopes as Climate Proxies

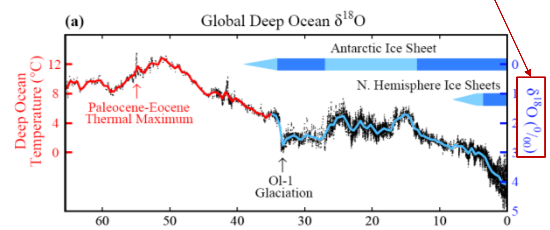
Richard McGehee



Seminar on the Mathematics of Climate Change
School of Mathematics
February 22, 2012

Isotopes as Proxies

What is this? δ18O (‰)



Isotopes as Proxies

What is this? $\delta^{18}O$ (‰)

‰ : "per mil," "per thousand"
1000‰ = 100% = 1
10‰ = 1% = 0.01
1‰ = 0.1% = 0.001

^{18}O: Oxygen 18: 8 protons 8 electrons 10 neutrons
^{17}O: Oxygen 17: 8 protons 8 electrons 9 neutrons
^{16}O: Oxygen 16: 8 protons 8 electrons 8 neutrons
Most of the oxygen atoms on Earth are ^{16}O.
About 1 in 500 atoms is ^{18}O. About 1 in 2500 is ^{17}O.
There are other oxygen isotopes, but they are unstable.

Isotopes as Proxies

What is this? $\delta^{18}O$ (‰)

Example

Given a sample of calcium carbonate ($CaCO_3$) from a foraminifera fossil, suppose that the ratio of ^{18}O atoms to ^{16}O is r = 0.002013 = 2.013‰. How would we report this finding?

How would we measure it in the first place?

The instruments measure the difference between two samples. Typically, one measures the difference between the sample of interest and a standard sample. A common standard is something called "Vienna Standard Mean Ocean Water" (VSMOW), for which the ratio of ^{18}O atoms to ^{16}O is s = 0.0020052. Then

$$\delta^{18}O = \frac{r-s}{s} = \frac{0.002013 - 0.0020052}{0.0020052} \approx 0.0039$$

So we would report

$\delta^{18}O$ = 3.9 ‰

Isotopes as Proxies

What is this? $\delta^{18}O$ (‰)

Going backwards, we have the formula

$$r = s(1+\delta)$$

For example, if the sample is reported as

$\delta^{18}O$ = 5‰

using the VSMOW standard, then we translate to the ratio of ^{18}O: ^{16}O

$$r = 0.0020052(1+0.005) = 0.002015$$

Isotopes as Proxies

Common Standards

Isotopes	Ratio	Standard	Source
D:H	0.0001558	VSMOW	Pierrehumbert[1]
^{13}C:^{12}C	0.0112372	PDB	Wikipedia[2]
^{18}O:^{16}O	0.0020052	VSMOW	Pierrehumbert[1]
^{18}O:^{16}O	0.0020672	VPDB	Pierrehumbert[1]

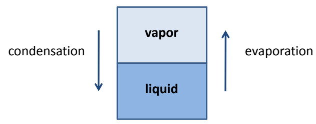
Standards:
VSMOW: Vienna Standard Mean Ocean Water
PDB: Pee Dee Belemnite
VPDB: Vienna Pee Dee Belemnite

[1]Raymond T. Pierrehumbert, Principles of Planetary Climate, Cambridge University Press, New York, 2010.
[2]http://en.wikipedia.org/wiki/%CE%9413C

Isotopes as Proxies

What does $\delta^{18}O$ (‰) tell us?

Fractionation
Example: Evaporation of Water



r_1 = ratio of ^{18}O:^{16}O in liquid
r_2 = ratio of ^{18}O:^{16}O in vapor
At equilibrium,

$$\boxed{r_2 = f r_1}$$

where f is the fractionation factor. (depends mostly on temperature)

Isotopes as Proxies

What does $\delta^{18}O$ (‰) tell us?

Fractionation
What about δ?

r_1 = ratio of ^{18}O:^{16}O in liquid
r_2 = ratio of ^{18}O:^{16}O in vapor

$$r_2 = f r_1$$

$$\delta_2 = \frac{r_2 - s}{s} = \frac{f r_1 - s}{s} = \frac{fs(1+\delta_1) - s}{s} = f(1+\delta_1) - 1$$

Note that the standard drops out.
f is usually close to 1, so let $f = 1+\varepsilon$

$$\delta_2 = (1+\varepsilon)(1+\delta_1) - 1 = \delta_1 + \varepsilon + \varepsilon\delta_1$$

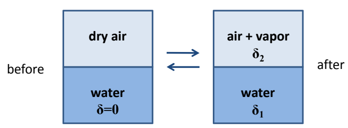
Since ε and δ are typically small, εδ is even smaller, so

$$\boxed{\delta_2 \approx \delta_1 + \varepsilon}$$

Isotopes as Proxies

What does $\delta^{18}O$ (‰) tell us?

Example: Evaporation of Water



$\delta^{18}O$(water) = 0 $\delta^{18}O$(water) = δ_1 f = 0.99 = 1+ε
$\delta^{18}O$(vapor) is undefined $\delta^{18}O$(vapor) = δ_2 ε = -0.01 = -10‰

$$\delta_2 \approx \delta_1 + \varepsilon$$

Suppose that 1% of the water becomes vapor.

$$\delta_1 \approx \delta = 0, \qquad \delta_2 \approx \delta_1 + \varepsilon = -0.01,$$

Is there a better approximation for δ_1 ?

Isotopes as Proxies

What does $\delta^{18}O$ (‰) tell us?

Example: Evaporation of Water

before
water
x_0 = moles of ^{16}O
y_0 = moles of ^{18}O

after
water
x_1 = moles of ^{16}O
y_1 = moles of ^{18}O

vapor
x_2 = moles of ^{16}O
y_2 = moles of ^{18}O

$$y_i = r_i x_i, \quad i = 0,1,2$$

$$r_1 = \frac{y_1}{x_1} = \frac{y_0 - y_2}{x_0 - x_2} = \frac{y_0 - r_2 x_2}{x_0 - x_2} = \left(\frac{y_0}{x_0}\right)\frac{1-(r_2/y_0)x_2}{1-(x_2/x_0)} = \left(\frac{y_0}{x_0}\right)\frac{1-r_2(x_0/y_0)(x_2/x_0)}{1-(x_2/x_0)}$$

Since x_2/x_0 is small,

$$r_1 \approx \left(\frac{y_0}{x_0}\right)\left(1+\left(1-r_2\frac{x_0}{y_0}\right)\frac{x_2}{x_0}\right) = r_0\left(1+\left(1-\frac{r_2}{r_0}\right)\frac{x_2}{x_0}\right)$$

In this case,

$$r_0 = s, \quad x_2/x_0 = h \approx 0.01, \quad r_2/r_0 = 1+\delta_2$$

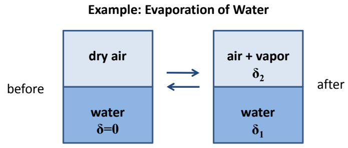
so

$$r_1 \approx s(1-\delta_2 h), \quad \boxed{\delta_1 \approx -\delta_2 h}$$

Isotopes as Proxies

What does $\delta^{18}O$ (‰) tell us?

Example: Evaporation of Water



$\delta^{18}O$(water) = 0 $\delta^{18}O$(water) = δ_1 f = 0.99 = 1+ε
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Suppose that 1% of the water becomes vapor.

Summary

$$\delta_1 \approx -\delta_2 h \approx +0.0001, \qquad \delta_2 \approx \varepsilon = -0.01,$$

Isotopes as Proxies

Deuterium Example

What if the all the glaciers melted?
How would the deuterium content of seawater change?

$$\delta_1 D \approx h\delta_2 D$$

sea water ↗ ↖ glaciers

About 2% of the Earth's water is in glaciers, vs. 98% in the oceans, so we take

$h \approx 0.02.$

According to Ray,

δ_2D ≈ -420‰,

so

δ_1D ≈ -8.4‰

Isotopes as Proxies

Everything Depends on Temperature

Water Evaporation Fractionation Factors for ^{18}O

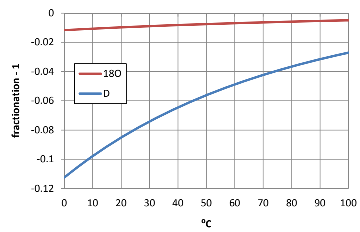
Temperature (°K)	Temperature (°C)	Temperature (°F)	$\delta^{18}O$
273	0	32	-11.7‰
290	17	62	-10.1‰
350	77	170	-6.0‰

Raymond T. Pierrehumbert, Principles of Planetary Climate, Cambridge University Press, New York, 2010.

Isotopes as Proxies

Everything Depends on Temperature

Water Evaporation Fractionation Factors

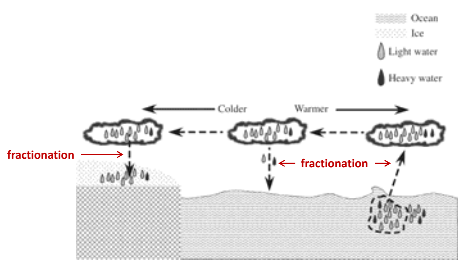


Formulae from Gerrit Lohmann, 2007

Isotopes as Proxies

Everything Depends on Temperature

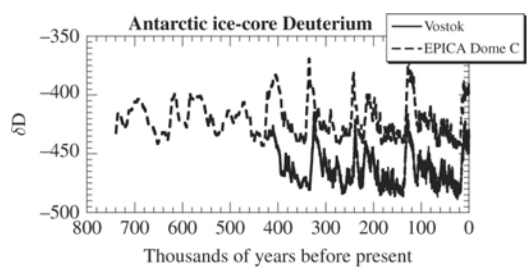
And it's even more complicated.



Raymond T. Pierrehumbert, Principles of Planetary Climate, Cambridge University Press, New York, 2010.

Isotopes as Proxies

Vostok and Dome C are Different



Raymond T. Pierrehumbert, Principles of Planetary Climate, Cambridge University Press, New York, 2010.

Isotopes as Proxies

Biology Matters

and is yet still more complicated.

atmosphere ↘ ocean ↙

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$
$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3$$

↖ foraminifera

Temperature dependent fractionation occurs at every step.

The result: the $\delta^{18}O$ in foram shells is about +30‰ compared with the surrounding water (depending on temperature).

$(\delta^{18}O)/dT \approx -0.25$ ‰/ °C

(Reference: Ray's book)

And then there's carbon.

Isotopes as Proxies

Biology Matters

And then there's carbon.

photosynthesis ↓

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

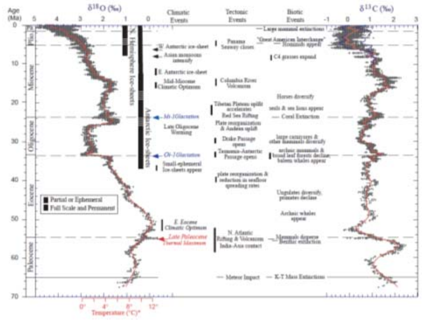
$\delta_1 = \delta^{13}C$ ↗ ↖ $\delta_2 = \delta^{13}C$

Fractionation is about -25‰.

$$\delta_2 \approx \delta_1 - 0.025$$

Result: Plants, animals, coal, and oil are all lighter in ^{13}C than inorganic carbon.

Isotopes as Proxies



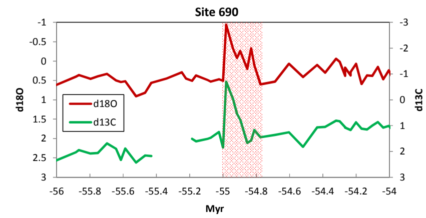
Zachos, *et al*, *Science* **292** (2001), p. 689

Isotopes as Proxies

Paleocene-Eocene Thermal Maximum (PETM)

Sharp decrease in $\delta^{18}O$, interpreted as a rapid increase in temperature.

Sharp decrease in $\delta^{13}C$, interpreted as massive oxidation of sequestered organic carbon.

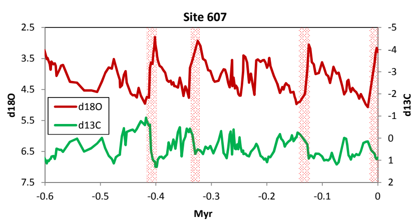


Isotopes as Proxies

Late Pleistocene Glacial Cycles

Sharp decreases in $\delta^{18}O$, interpreted as a rapid deglaciations.

Sharp **increase** in $\delta^{13}C$, interpreted as increase in biological activity. Since the atmospheric CO2 increased during these periods, there must have been a large release of inorganic carbon, presumably from the oceans.



Isotopes as Proxies

What is this?