A quick primer on the use of d18O from deep sea sediments to get at global ice volue.

Introduction

Milankovich made a *prediction* that ice ages ought to follow the timing of orbital variations. This idea was very far ahead of its time, because we did not have the information we needed to test it for more than 50 years.

The important proof depended on

1) the discovery and measurement of stable oxygen isotope fractionation by Cohn and Urey
2) its application to marine sediment cores, most notably by Emiliani (temperature) and later by Shackleton and Opdyke (ice volume)
3) and finally analysis of the records (Hayes)

To understand how this works, we need a brief review of oxygen isotope exchange between water, water vapor, and carbonate.

Oxygen isotopes in water, water vapor, and calcium carbonate

Oxygen is composed of three stable isotopes:
^{18}O, ^{17}O, ^{16}O (99.76%, 0.04%, 0.2%)

Composition is written as

$$\delta^{18}O = \frac{\left(^{18}O/^{16}O\right)_{sample} - \left(^{18}O/^{16}O\right)_{\text{standard}}}{\left(^{18}O/^{16}O\right)_{\text{standard}}} * 1000‰$$

$$= \left(\frac{\left(^{18}O/^{16}O\right)_{sample}}{\left(^{18}O/^{16}O\right)_{\text{standard}}} - 1 \right) * 1000‰$$

Note that the “times 1000 per mil” is simply for convenience of units.

There are two important isotope exchange reactions we need to worry about:

1) Water-water vapor.
$$H_2{}^{16}O_{liquid} + H_2{}^{18}O_{vapor} \Leftrightarrow H_2{}^{18}O_{liquid} + H_2{}^{16}O_{vapor}$$

2) Water-calcium carbonate
$$H_2{}^{18}O_{liquid} + CaC^{16}O_3 \Leftrightarrow H_2{}^{16}O_{liquid} + Ca^{18}O^{16}O_2$$

For both of these exchanges, we can write a conventional equilibrium chemical reaction constant as follows:

$$K_{EQ} = \frac{[H_2{}^{18}O_{liquid}][H_2{}^{16}O_{vapor}]}{[H_2{}^{16}O_{liquid}][H_2{}^{18}O_{vapor}]}$$

$$= \frac{\left.\dfrac{[H_2{}^{18}O_{liquid}]}{[H_2{}^{16}O_{liquid}]}\right.}{\left.\dfrac{[H_2{}^{18}O_{vapor}]}{[H_2{}^{16}O_{vapor}]}\right.}$$

$$= \frac{\left(\dfrac{{}^{18}O}{{}^{16}O}\right)_{liquid}}{\left(\dfrac{{}^{18}O}{{}^{16}O}\right)_{vapor}} = \alpha_{liquid-vapor}$$

In this first example, the algebra happens to work such that we can cancel out the hydrogen atoms, and simply write the equilibrium constant in terms of the ratio of the abundance of the oxygen atoms. Written in this way, it is conventional to refer to this ratio as "alpha", <u>the equilibrium fractionation factor.</u>

For calcium-carbonate/water, the algebra doesn't work out quite so simply. But we can still define, and measure the value of, an equilibrium fractionation factor:

$$\alpha_{calcium\_carbonate-water} = \frac{\left(\dfrac{{}^{18}O}{{}^{16}O}\right)_{calcium\_carbonate}}{\left(\dfrac{{}^{18}O}{{}^{16}O}\right)_{water}}$$

The value of alpha in each case is temperature dependent, and the values at 25° C are:

$\alpha_{\text{calcium carbonate-water}} = 1.028$
$\alpha_{\text{liquid-vapor}} = 1.009$

From direct measurements in the lab, with inorganic calcium carbonate in equilibrium with water, we can write the following

$1000 \cdot \ln(\alpha_{\text{cc-water}}) = 2.78 \cdot 10^6/T^2 - 2.89$ (T in K; valid between 0 and 500 °C)

Laboratory experiments have also been done with living organisms that produce calcium carbonate from their shells, and the results are nearly indistinguishable from the inorganic experiments. Small differences between expected and observed values are generally attributed to "vital effects" reflecting different biology. In practice, we use measurements from organic carbonate in the lab. Given the way measurements are actually done, a typical calibration equation would look like this;

$T(°C) = 15.73 - 4.20\{\delta^{18}O_c(\text{PDB}) - \delta^{18}O_w(\text{SMOW})\}$

where δ^{18}Oc(PDB) refers to the oxygen 18 value of the carbonate, measured relative to a laboratory standard called PDB, and δ^{18}Ow(SMOW) refers to the oxygen 18 value of the water in which the carbonate formed

SMOW = “Standard mean ocean water”, which has a value close to the real ocean.

PBD = PeeDee Belemnite (Belemnites are ancient relatives of the modern cuttlefish; the PeeDee formation is in North Carolina and is of late Cretaceous age). The use of this standard is arbitrary, but it was living in the ocean, and was presumably in equilibrium with the ocean, so it a reasonable representation of “average” marine carbonate.

On an absolute scale SMOW is about 30 ‰ lower than PDB. (That is, it contains 3 per cent fewer ^{18}O atoms).

<u>The important point</u> – from a paleoclimatologists viewpoint – is that the empirical equation for temperature has two isotopic terms:

1) δ^{18}O of the water
2) δ^{18}O of the carbonate.

The *difference* between them is dependent on temperature, with a sensitivity of about 4.2°C per ‰ change in the oxygen isotope ratio.

If we measure the δ^{18}O of the shells of carbonate organisms that lived in the past ocean, and they are abundant enough that we can measure a lot of them, we can get an estimate of temperature (if we assume $\delta^{18}O_w$ is constant). Importantly, if we have an independent estimate of temperature, then we can determine $\delta^{18}O_w$. Making these measurements on microscopic animals with carbonate shells (e.g. *foraminfera*) – allows us to do this.

One of the most famous and important records is Nick Shackleton’s data from benthic (deep water) forams on the sediment core V1930 off the coast of Peru. Emiliani originally interpreted all such variations as due to temperature change associated with the waxing and waning of ice ages. Taken at face value, the observed changes would imply variations in deep ocean temperature of about 6 °C.

Shackleton, however, noted that deep ocean temperatures probably don’t change much, and interpreted the benthic data in terms of changes in $\delta^{18}O_W$ rather than δ^{18}O -- that is, he interpreted the data as showing that the ocean (which is very well mixed on a timescale of about 2000 years) had gotten isotopically heavier during the cold phase of ice ages and isotopically lighter during interglacial periods. <u>$\delta^{18}O_w$ represents ice volume, because the ocean is enriched in ^{18}O as the ice sheets build up. Put another way, the ocean tends to lose ^{16}O preferentially, so as ice volume goes up (and sea level goes down), the ocean ^{18}O/^{16}O ratio will increase.</u>

Following Shackelton’s work, it became commonplace to think of δ^{18}O curves from benthic forams as “ice volume” records.

Planktonic forminifera from the same core showed similar variations to the benthic data, but larger in magnitude, supported Shackleton’s idea. The suggestion is that the surface ocean δ^{18}O value changed, just as the deep ocean δ^{18}O did, as ice sheets built up, but that temperature changes were also important.

Assuming that the benthic foram δ^{18}O changes are due only to ice volume changes, then we can estimate the temperature change over time at the V1930 site by subtracting the two preceding curves and multiplying by -4. We obtain a temperature history that suggests ever-cooler temperatures throughout the last 250,000 years. Is this correct?

It might be, but if so it is probably only of local significance, since there is no reason to assume that SSTs changed uniformly throughout the globe. Furthermore, local variations in surface water d18O unrelated either to temperature or ice volume can result from e.g. river runoff (meteoric water generally has much lower d18O than ocean water).

If we are interested in the global story, then it makes sense to combine or “stack” a large number of sediment cores to get a sense of the average temperature and ice volume change over time.

A major project in the 1970s resulted in the “SPECMAP” stacks of planktonic foraminifera. This was tuned to the Milankovich curves, so is a weak test of Milankovich theory. More recently, Huybers produced a new set of stacked records, with the dating independent of any Milankovich assumptions.

When we combine many sediment cores together, and subtract their average benthic d18O variations from their average planktonic d18O variations, we obtain a representative sea surface temperature estimate that will look familiar to most paleoclimatologists. It implies about a 10 degree change in temperature between interglacials (such as today) and the maximum cooling of ice ages, such as ~20,000 years ago.

Validation: at least two pieces of evidence validate the use of benthic d18O as a measure of ice volume

1) independent estimates of sea level from coral reefs dated by U-Th isotopes
2) independent direct measurements of the water remaining from the last glacial period, preserved interstices in marine sediment – the water is both saltier and d18O enriched