PCC 589
Paleoclimatology

More on Isotopes in Ocean Sediments

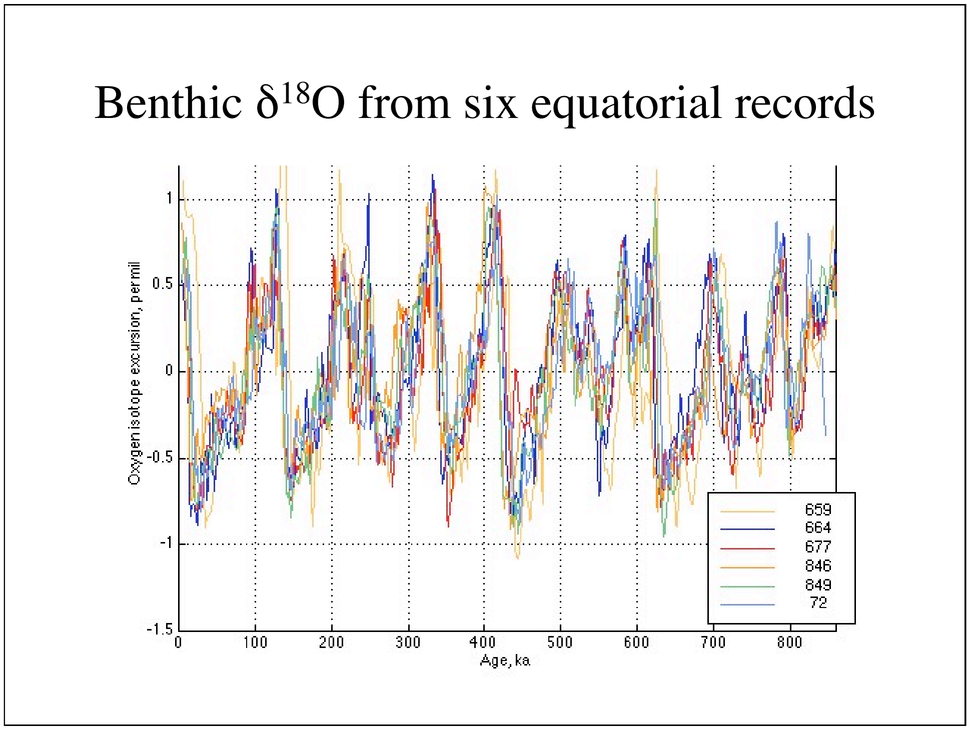
Isotopes in Ice Cores

Oxygen isotopes in ice cores

H_2O is composed of both $H_2{}^{16}O$ and $H_2{}^{18}O$

$$\delta^{18}O_{ice} = \frac{\left(\frac{H_2{}^{18}O}{H_2{}^{16}O}\right)_{ice} - \left(\frac{H_2{}^{18}O}{H_2{}^{16}O}\right)_{SMOW}}{\left(\frac{H_2{}^{18}O}{H_2{}^{16}O}\right)_{SMOW}} * 1000\ ‰$$

Review.



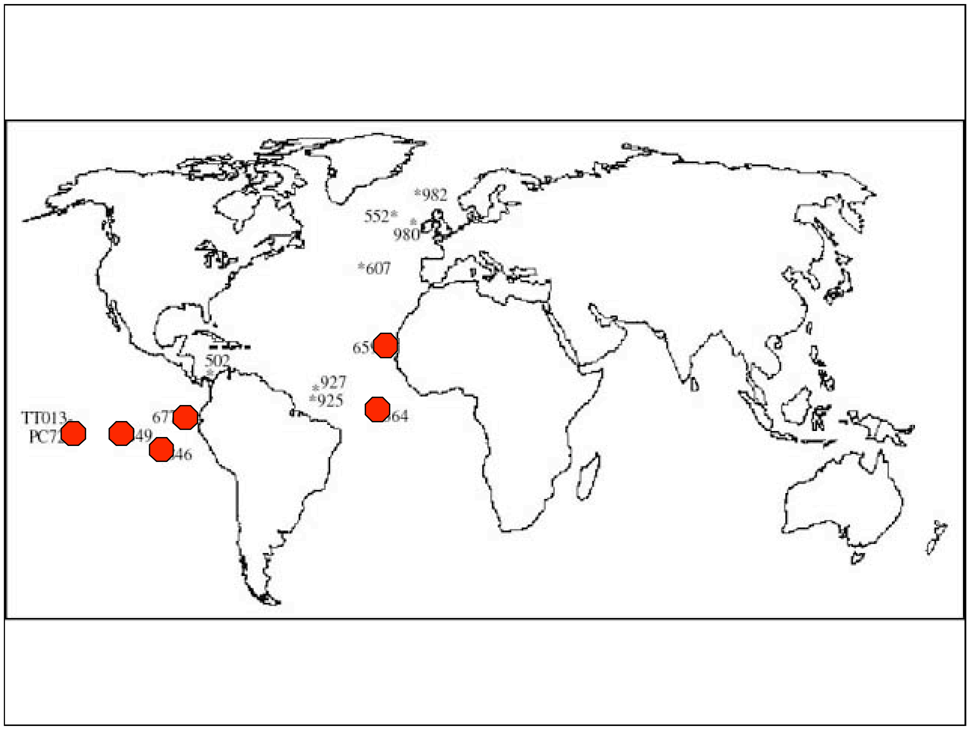
Last class we talked about the use of d18O in foraminifera as measures of the combination of temperature and ice volume.

I noted that globally, the observation is that one benthic core is generally like another, but one planktonic record can be quite different than another.

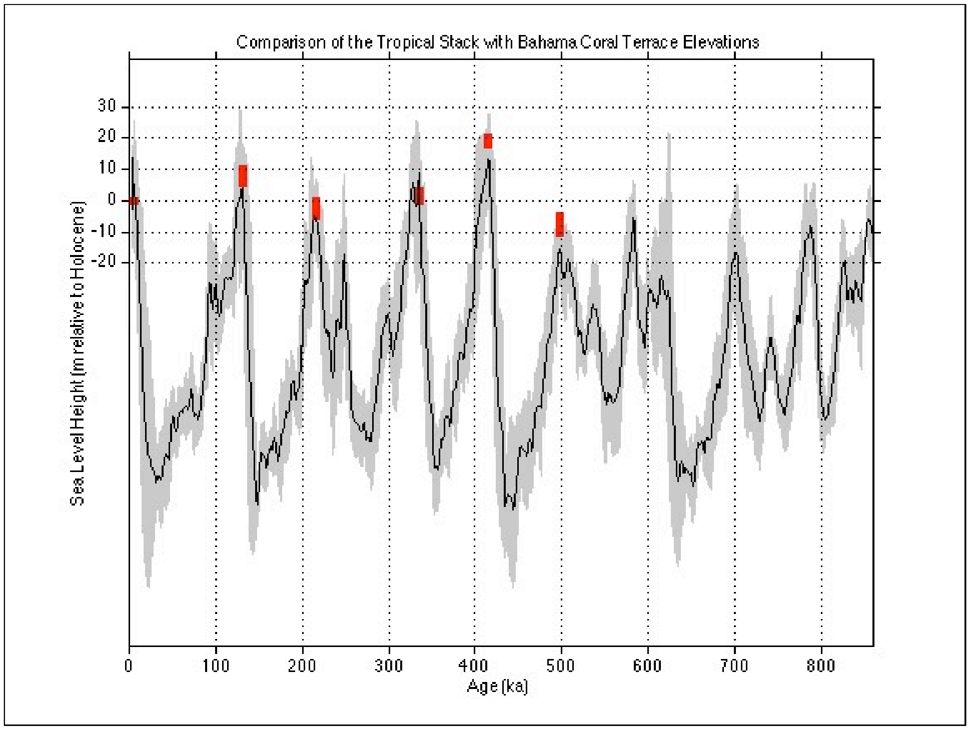
How similar are the benthic data? This graph shows a compilation of six equatorial records, locations shown on the next page.

This is from Karner at Berkeley.

http://jlevine.lbl.gov/BenStackCompare.html



This shows the locations used on the preceding slide. Note that cores shown but not marked with red were found to be "quite different" than the others. Nevertheless, that six cores from two different oceans give very similar results is strong support for the idea that the benthic records are "global" in what they represent.



How good is the assumption that the benthic data directly reflect ice volume (or sea level) rather than temperature change, as Shackleton suggestested?

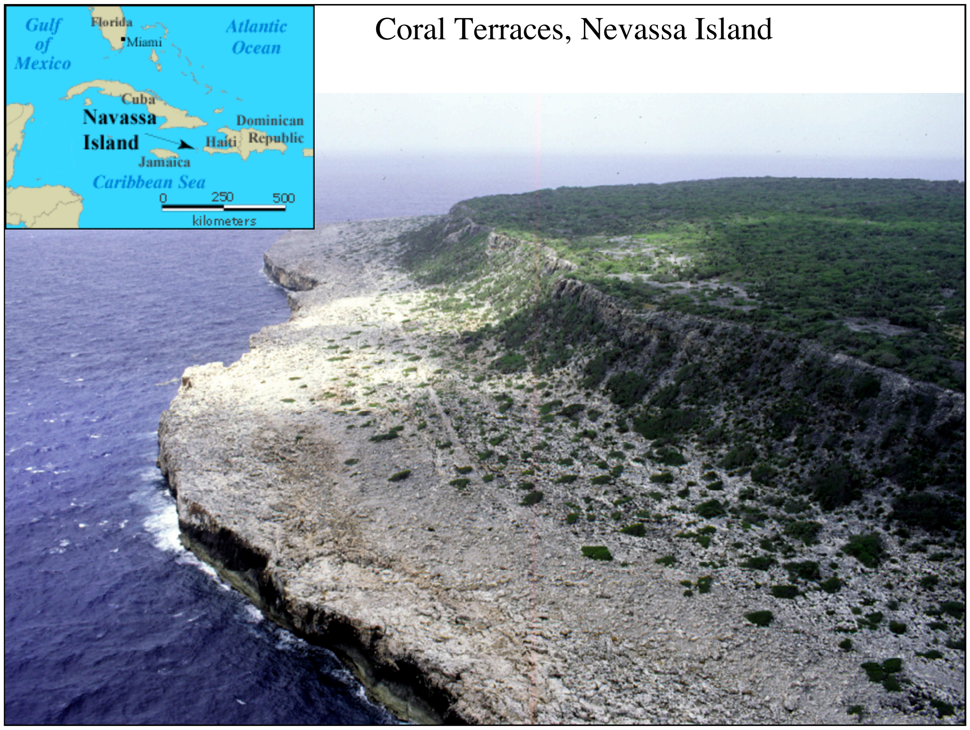
We'll make a calculation of this in our first problem set.

For now, note that independent measurements of sea level give a pretty consistent relationship with the benthic data.

This doesn't tell us what fraction of the d18O change is due to ice volume, but it suggests that they scale linearly with each other (when it gets cold in the deep ocean by some amount, there is a corresponding amount of ice on land).

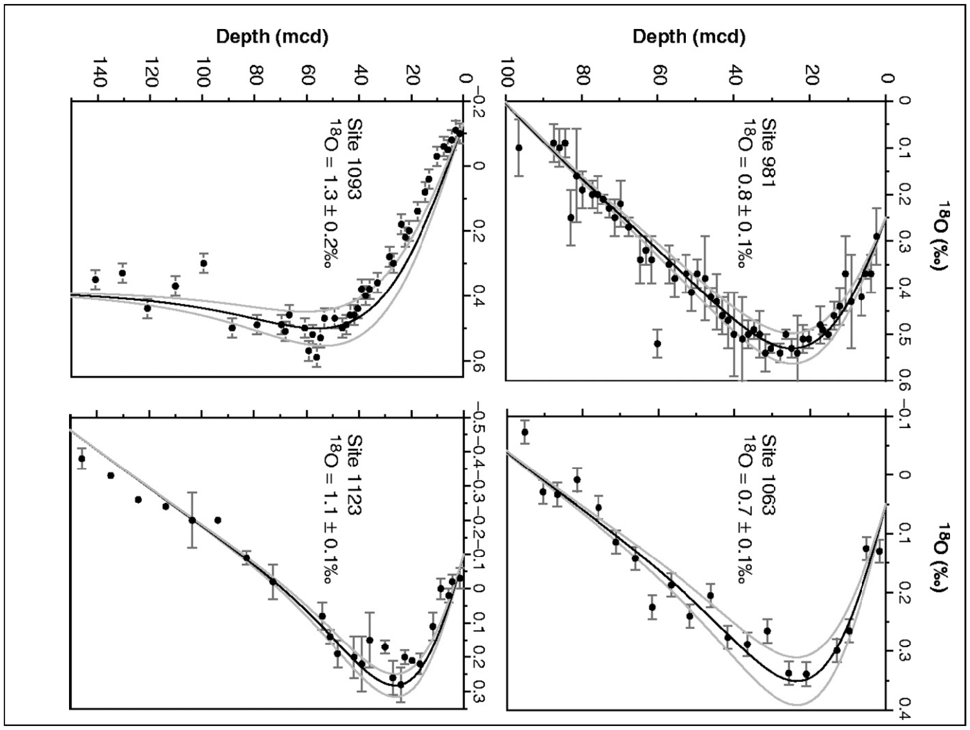
The sea level estimates are from Hearty and Kaufman (QSR, 2000), who have measured the elevations of coral terraces from the Bahamas, each the remnant of a different sea level highstand. The terrace elevation data cover the last six interglacial periods, and are plotted in red. The benthic stack is plotted behind them. The largest disagreement between the two data sets is about 8 m.

Note that the ages of the sea level high stands are NOT weel known except for the most recent on (~127,000 years ago). However, the assumpion that high sea level = either warm temperatures or little ice (or more likely both) is quite reasonably.



This is a photo of a coral terrace as an example -- note this one is quite a bit older (>3 Ma) than any we are discussing, but it shows the older sea level high stands (at least two of them) quite nicely.

Note that another way to form these terraces is to lift up the land, rather than lower sea level, so knowledge (e.g. from geodesy) of the tectonic uplift rate is important in estimates of sea level rise.

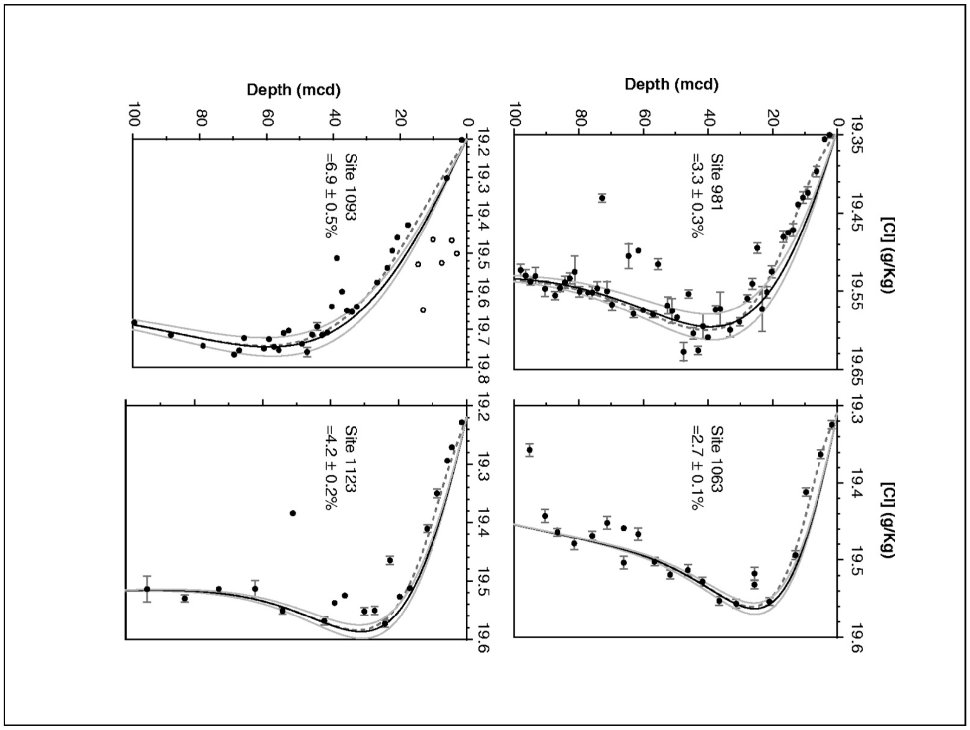


Another piece of evidence that supports the interpretation of benthic foram d18O in terms of ice volume is the del18O measurement of pore water, which is ancient sea water trapped in the sediment and cleverly retrieved without contamination. Because of diffusion the original d18O value of the sea water is not perfectly preserved, but there is memory of it, and if diffusion rates are known (or estimated), the original d18O of the ocean in the past can be deduced. The estimated last glacial maximum value is shown on each plot. It averages about 1 per mil.

Going back to figure (3), we can see that the total benthic d18O change from glacial to interglacial is about 1.5 per mil. Therefore, sea level change (or ice volume change) accounts for roughly 2/3 of the signal. The rest can be attributed to a cooling of about 2 degrees C, which is a satisfying number since deep ocean tempreatures are now about 2 degrees above the freezing point (and there is no evidence the deep ocean froze).

The four figures are from **The Salinity, Temperature, and 18O of the Glacial Deep Ocean Jess F. Adkins, Katherine McIntyre, Daniel P. Schrag** *Science*, Vol 298, Issue 5599, 1769-1773 , 29 November 2002.

The model fit to the data is a 1-D diffusion scheme that includes the effects of compaction advection but assumes there is no effect from externally forced advection through the sediment column. Effective diffusion coefficients were derived empirically from a best-fit to the data, in an iterative way assuming different possible sea level and ice volume histories.



The estimates from the del18 measurements can be validatd with salinity measurements, as shown here. The idea is simply that as sea level went down, salinity must have increased.

Also from Atkins et al., 2002.

Relationship between K and alpha for water evaporation

$$H_2O(g) + H_2{}^{18}O(l) \Leftrightarrow H_2{}^{18}O(g) + H_2O(l)$$

$$\Delta G = -RT\ln(K)$$

$$K \equiv {[H_2{}^{18}O(g)][H_2O(l)]} \Big/ {([H_2{}^{18}O(l)][H_2O(g)]}$$

$$1/K = \alpha = {\left(H_2{}^{18}O/H_2O\right)_{liquid}} \Big/ {\left(H_2{}^{18}O/H_2O\right)_{gas}}$$

Ice cores!

Recall that we can think of isotope exchange as chemical reactions.

For the simple evaporation of liquid water to water vapor, we can relate the fractionation factor alpha to the equilibrium constant K as shown.

(Note alpha does not always equal 1/K).

Note: l = liquid; g = gas (water vapor)

$$\Delta G_{rxn} = -RT\ln(K)$$
$$= 22 \text{ J at } 25 \text{ C}$$
$$\text{K} = 0.991$$
$$\alpha = 1/\text{K} = 1.009$$

In general, we can write deltaG = -RTln(K).

If the overall reaction has a positive deltaG, this means that free energy is gained by the reaction, so the lower energy side is the left side, and that is where the 18O will reside preferentially.

So our equations say that the water liquid slightly prefers the 18O.

$$\alpha = \left(H_2^{18}O / H_2O\right)_{gas} \Big/ \left(H_2^{18}O / H_2O\right)_{liquid}$$

$$= \left(H_2O_{gas} / H_2O_{liquid}\right) \Big/ \left(H_2^{18}O_{gas} / H_2^{18}O_{liquid}\right)$$

$$= p_{16} / p_{18}$$

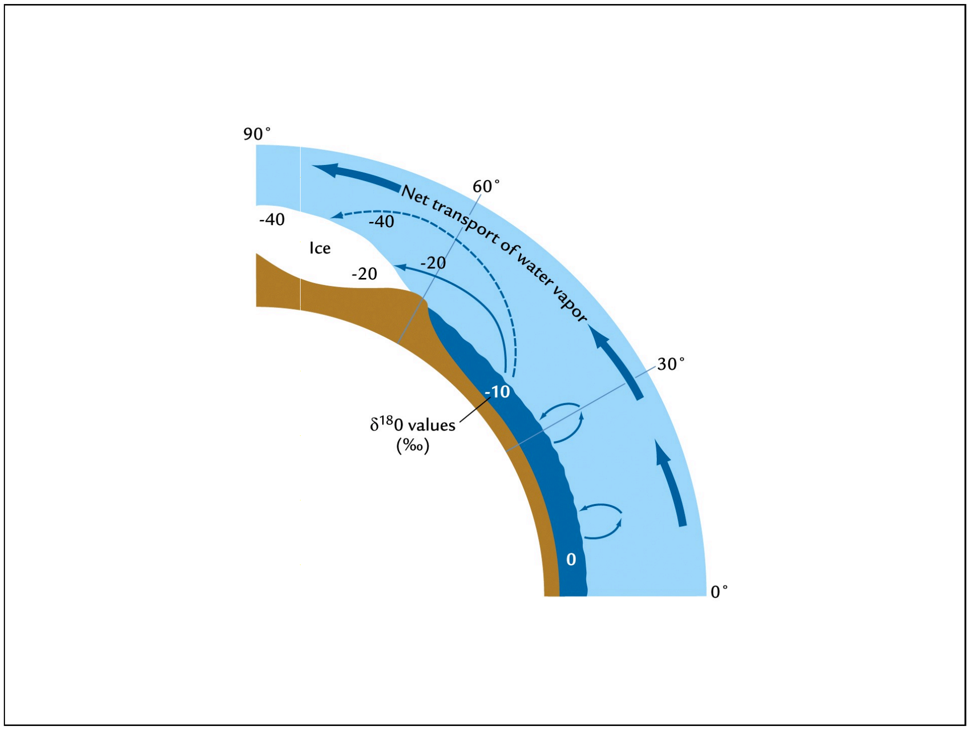
We can also express this as vapor pressure ratios.

alpha can be viewed as the ratio of vapor pressures.

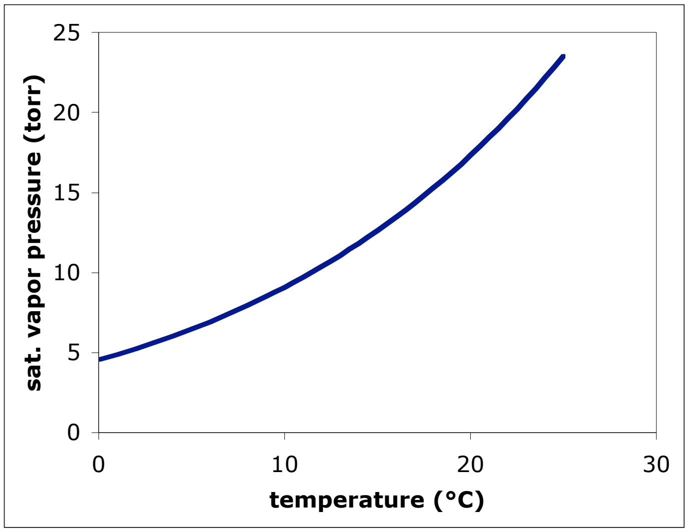
p is the partial pressure of vapor phase of the the pure substance (e.g. pure $H_2^{18}O$).

The “partial pressure” of the liquid phases of both are (at 1 atm) = 1 by definition, so these cancel.

$H_2^{16}O$ has a slightly higher vapor pressure than $H_2^{18}O$, so alpha > 1.



Dansgaard's (1973) pioneering work imagined a global "Rayleigh distillation" system, in which water evaporated from the ocean at low latitudes and moved towards the poles at high latitudes, with preferential loss of the heavier isotope as air masses cooled to the dew point and lost water vapor to condensation (I.e. cloud formation) and precipitation.



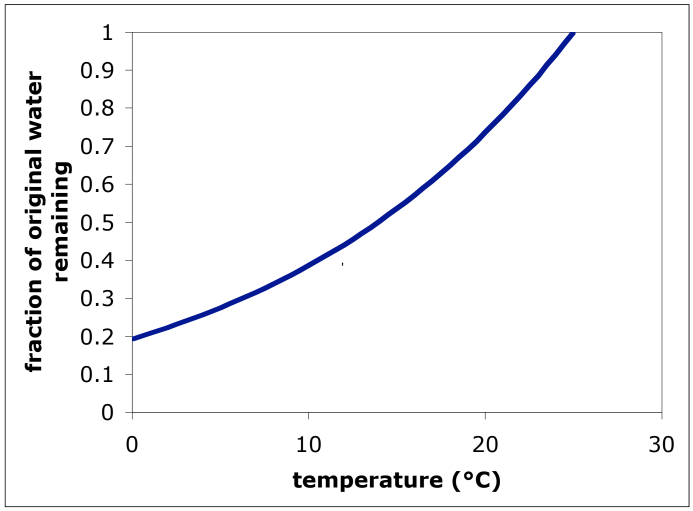
The conceptual model is as follows.

Start with a saturated air mass above the ocean surface at 25°C, and imagine that that the air travels poleward and that precipitation occurs as it cools.

Assume that

1) All cooling is by adiabatic processes.

2) The amount of water vapor remaining in the air at any point is determined by the satuation vapor pressure of water (see the figure).

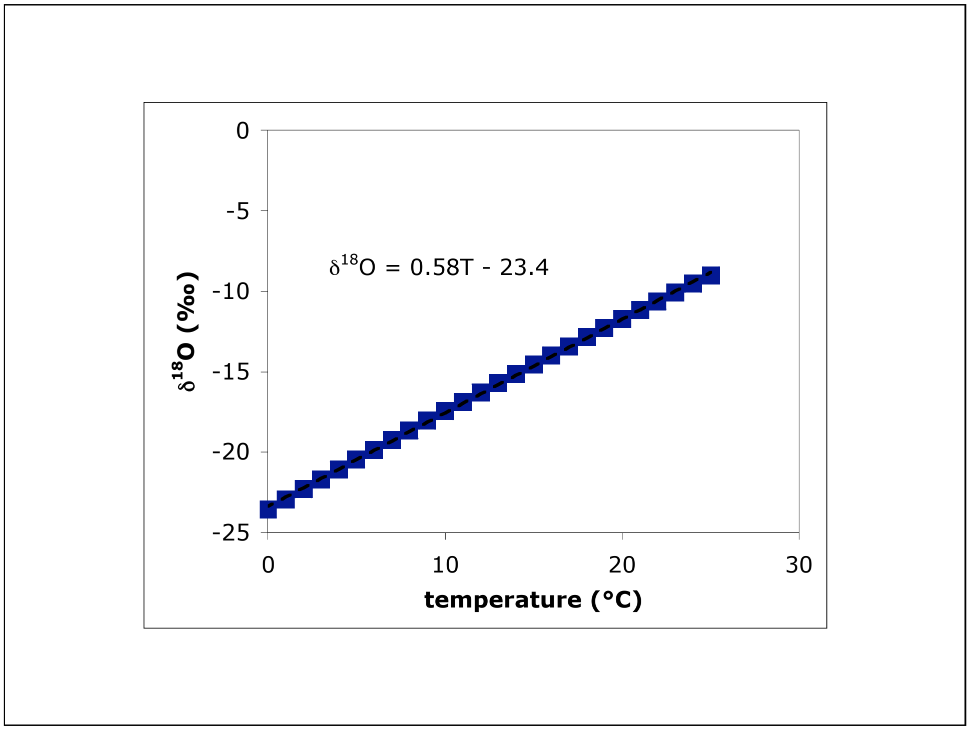


If there all isotopic exchange occurs in equilibrium, and if we approximate alpha as being independent of temperature, and we further assume that once water condenses it does not revaporate, and that the air mass obtains no "new" water vapor as it moves poleward, then the simple Rayleigh distillation equation applies:

Rayliegh distillation R/Ri = f(alpha-1)

where f is the "fraction of water remaining in the air mass", R is the 18O/16O ratio of the water vapor at any time, and R_i is the initial ratio.

Note that R/R_i = (del18O+1000)/(del18O(initial)+1000)



If we then plot T of the air mass vs. the del18O of the air mass, we obtain a slope of about 0.58, and a very nearly straight line.

Note that what is actually plotted is

(del18O(initial)+1000)*f^(alpha-1)-1000

Versus

T

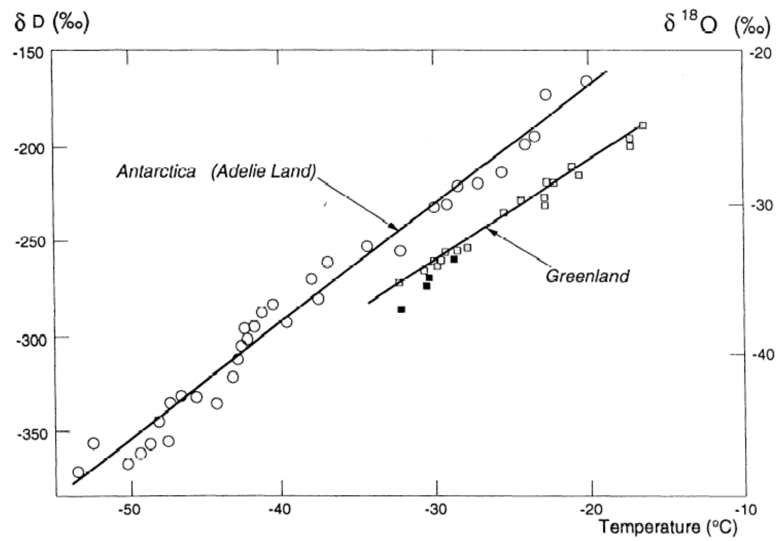


Figure 1. Isotope content of snow versus local surface temperature (annual average). Antarctic data (δD, left scale) are from *Lorius and Merlivat* [1977], and Greenland data ($\delta^{18}O$, right scale) are from *Johnsen et al.* [1989].

Dansgaard (and other since) have found that the spatial relationship between T and d18O in precipitation is very close to the value (about 0.6 per mil per degrees C) predicted by Dansgaard's Rayleigh model. That is, snow or rain from locations on the ice sheets that are colder (mean annual temperature) by some amount (x) also have mean annual del18O values that are lower by an amount ~x/0.6.

The assumption commonly made is that the SPATIAL relationship also ought to apply TEMPORALLY. That is, the idea is that going to a colder place is similar to staying in one place and getting colder.

If this is valid, then the del18O of snow (or ice) from an ice core ought to be a measure of temeprature over time.

Note two important additional assumptions for this to work: 1) the del18O of the source water must not change and 2) the T at the source area must not change.

Both of these assumptions are reasonable because we expect that variations in the ocean are only +/-1 per mil, but we find variations in the ice sheets >> 8 per mil from glacial to interglacial; we expect high latitude temperature changes to be much larger than low latitude changes. Also, the impact of Rayleigh distillation on del18O ought to be greatest towards the end -- so this ought to work better at high latitudes than at low latitudes.

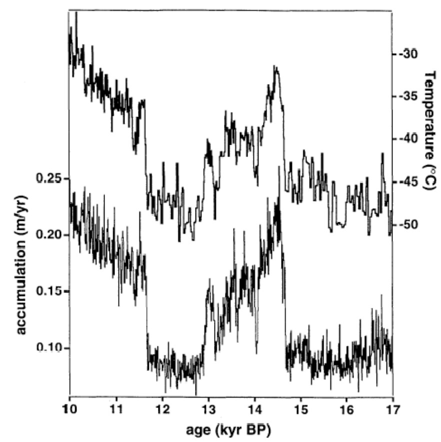
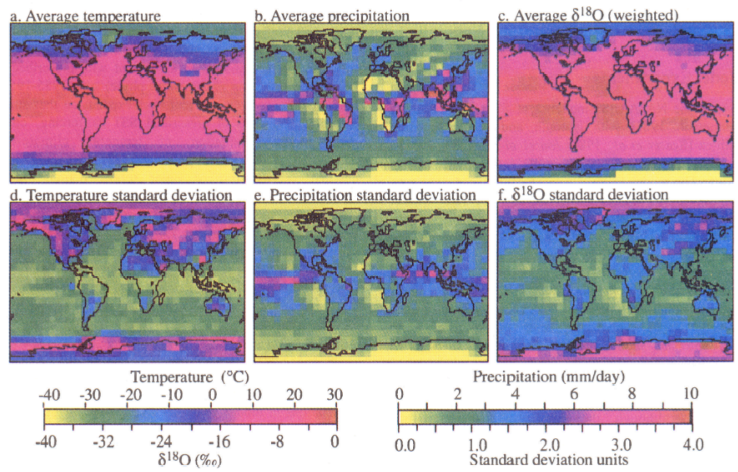


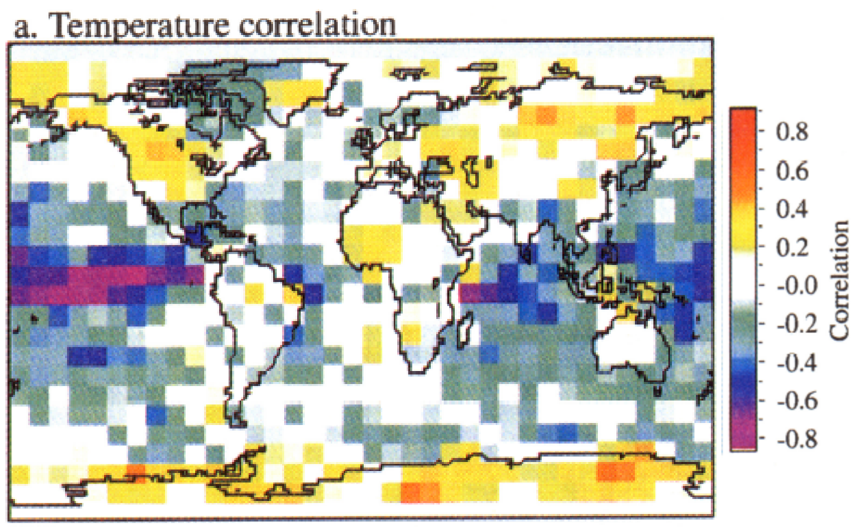
Figure 4. Comparison of the accumulation and δ records at the GISP2 site for the period between 18 and 10 kyr B. P. (adapted with permission from *Nature* [*Kapsner et al.*, 1995]; copyright Macmillan Magazines Limited), in using a calibration of 0.33‰/°C instead of 0.53‰/°C (see text).

Some evidence that the general idea that the d18O is controlled by temperature via the "fraction of water remaining" is supported by the observation that on timescales of thousands of years, there is a very strong correlation between del18O (shown here converted to temperature) and precipitation rate on the Greenland ice sheet (this also works pretty well for the Antarctic ice sheet).

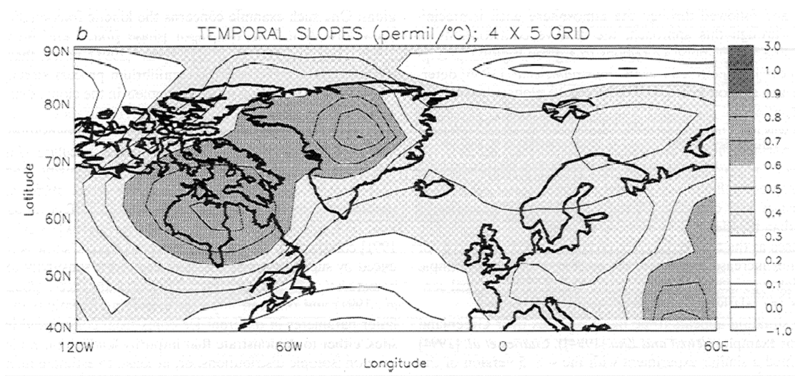
[Note though that the inferred slope of the T-del18O relationship is ~0.3 per mil per °C, rather than 0.6]).



General circulation model simulations confirm that the temperature/del18O relationship should be quite strong spatially, with lower del18O values at higher latitudes. This suggests that the real complexities of the climate system that are ignored in the simple Rayleigh model are roughly averaged out, at least when considering high latitudes and long timescales.



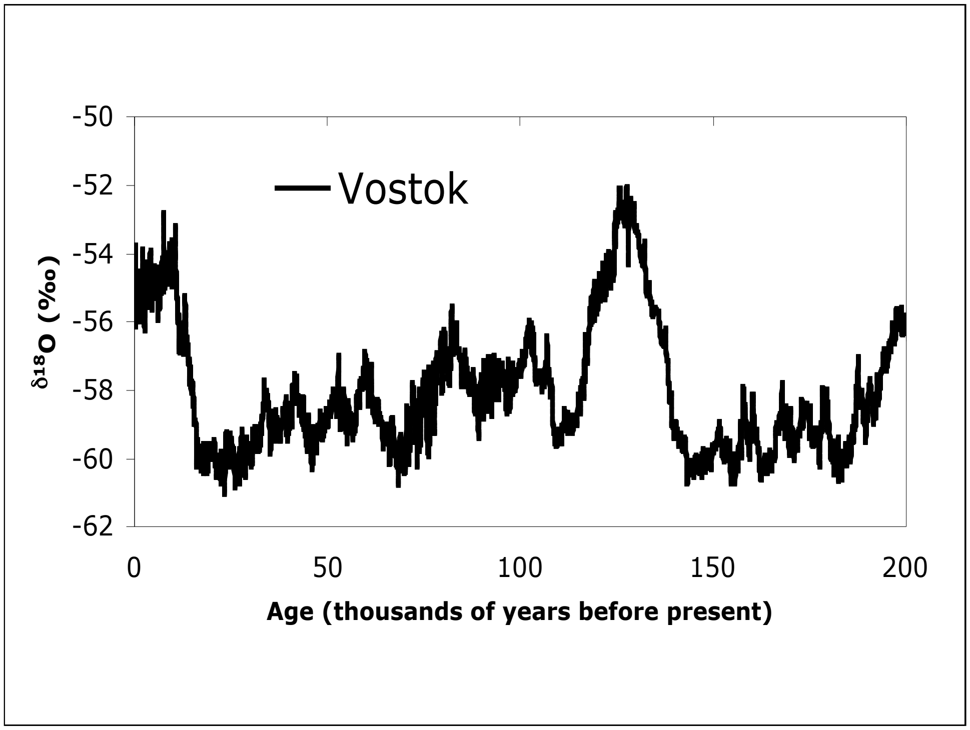
This shows the correlation, in a GCM simulation, between year-to-year variations in del18O and in temperature. Note that the idea that the simply Rayleigh model ought to work on such short timescales is asking a lot. Yet at high latitudes it isn't so bad -- roughly 50% of the variability in del18O can in fact be explained by temperature on these timescales. Note that the relationship falls apart completely, and actually comes negative, at low latidues. So caution is urged in trying to interpret del18O directly in terms of temperature.



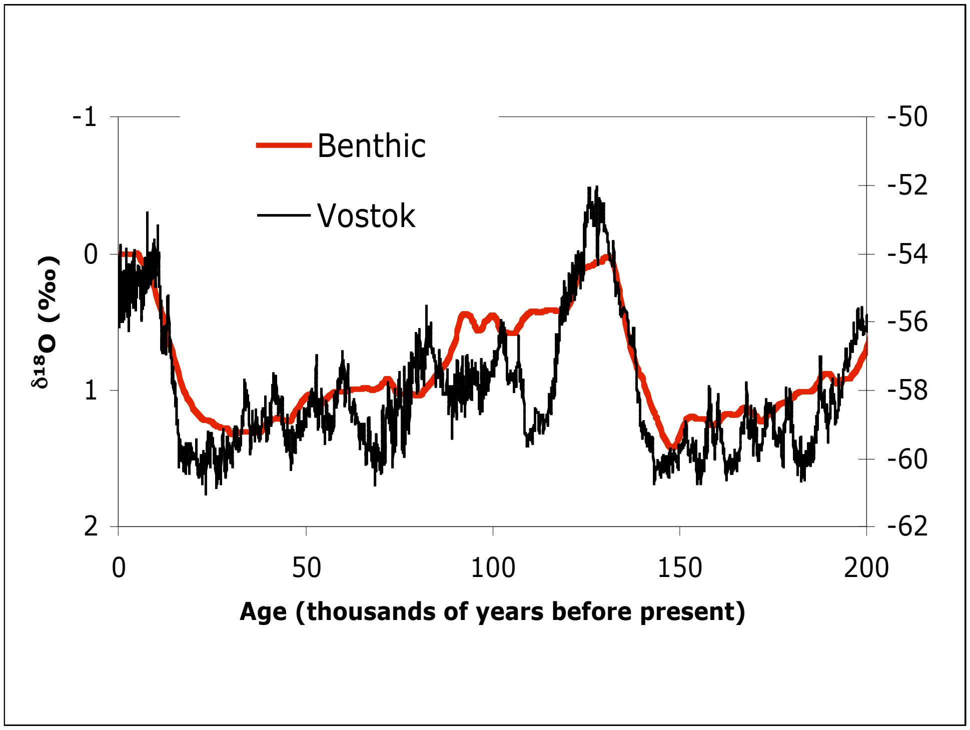
Nevertheless, it does seem to work pretty weell on long timescales, at high latitudes where the ice cores are from.

This is another GCM simulation, which shows an estimate of how sensitive del18O is to temperature change as we go from glacial to interglacial climate. The results suggest that for Greenland, a change of 0.33 per mil implies a 1°C change. (Note the figure title is wrong -- this should read °C/permil).

This is in agreement with the estimates from slide 17.



Is there therefore reasonable to interpret this figure -- from the very famous Vostok ice core from central East Antarctica -- as a temperature history..



The relationship between ice volume (from benthic del18O, left axis) and temperature (from Vostok ice core del18O) is remarkably good.