# PCC 589 Paleoclimatology

1. Oxygen Isotopes, Temperature and Ice Volume

First of four lectures covering:

1) Oxygen isotope in carbonate shells, and how they reflect a combination of ice volume (or sea level) and temperature.

2) Oxygen isotopes in ice cores, and why they reflect temperature according to a simple Rayleigh distillation model.

3) Milankovich forcing ideas, and the link between ocean and ice cores via the d18O of atmospheric O2.

4) CLIMAP, the problem of low latitude SSTs, and the observation that glaciation is synchronous in both hemispheres.

The oxygen isotope paleothermometer

$$H_2{}^{18}O + CaC{}^{16}O_3 <--> H_2{}^{16}O + CaC{}^{18}OO_2$$
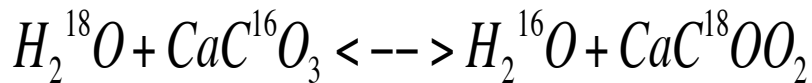
$$\Delta G_{rxn} = -RT\ln(K)$$

$$\alpha = \frac{\left({}^{18}O/{}^{16}O\right)_{CaCO_3}}{\left({}^{18}O/{}^{16}O\right)_{H_2O}}$$

Oxygen is composed of about 0.04% ${}^{17}O$, 0.2% ${}^{18}O$, and the balance (>99.7%) ${}^{16}O$. For most purposes we measure the ${}^{18}O/{}^{16}O$ ratio and ignore ${}^{17}O$.

The formation of calcium carbonate (CaCO3) via the net reaction $Ca^{2+} + 2HCO_3{}^- --> CaCO_3 + H_2O + CO_2$ results in a slight enrichment of ${}^{18}O$ in the $CaCO_3$ compared with the H_2O.

This can be expressed as an isotopic equilibrium reaction, where the equilibrium constant K is defined as in normal chemical equilibrium as the ratio of the activities (or, approximately, the concentrations) of the products and reactants $K = ([CaC^{18}OO_2][H_2O])/([H_2{}^{18}O][CaCO_3]$. If written in this way, then the free energy change (deltaG) of the reaction is a negative value; that is, the energy state is lowered by preferentially concentrating the more massive isotopes of oxygen in the $CaCO_3$ rather than the water. Note that deltaG is a SMALL negative number though. There is not a very strong preference, and so the ratio of 18O/16O in the water will be only slightly less than that same ratio in the calcium carbonate.

In general, we express this difference as an equilibrium fractionation factor, alpha, which is closely related to the K and, like K, is temperature dependent. At 25°C, alpha for this reaction is about 1.024. Alpha is smaller for warmer temperatures and approaches 1 at very high temperatures.

Note: R = universal gas constant, T = temperature, K = equlibrium constant.

The possibility of using the temperature dependence of the isotope equilibrium was first recognized by Urey, and first applied to paleoceanography by Emiliani.

Definition of "del18O"

$$\delta^{18}O_{sample} = \left(\frac{\left(^{18}O/^{16}O\right)_{sample}}{\left(^{18}O/^{16}O\right)_{standard}} - 1 \right) \times 1000\%o$$
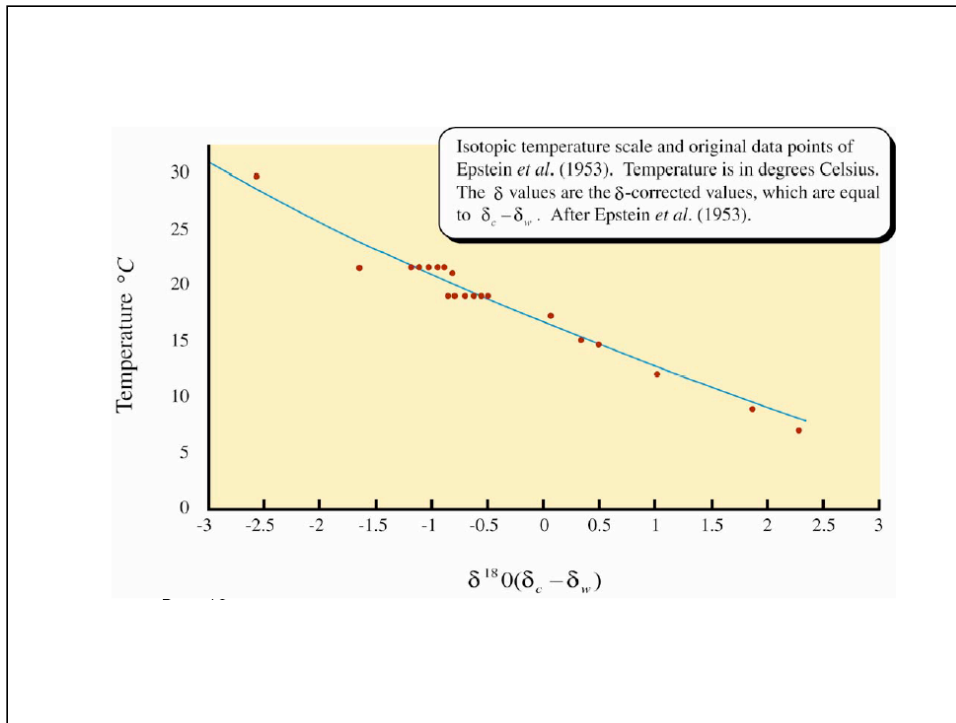
$$\delta^{18}O_{PDB} \equiv 0 \text{ on the PBD scale}$$

$$\delta^{18}O_{SMOW} \equiv 0 \text{ on the SMOW scale}$$

We generally express isotope ratios in terms of a deviation from a standard, rather than an absolute ratio, because absolute ratios are very very hard to measure.

For oxygen isotopes, we reference the "del18O" value either to PDB (which is a marine carbonate) or to "Standard Mean Ocean Water" (SMOW). Both are DEFINED to be zero *ON THEIR RESPECTIVE SCALES. A typical ocean water sample will have del18O close to zero on the SMOW scale, but about -24‰ (parts per thousand) on the PDB scale. A typical marine carbonate will have del18O of about 0 ‰ on the PDB scale, or about 24‰ on the SMOW scale.*

It sounds complicated, but this is a sensible way to do things because a carbonate sample in isotopic equilibrium with water will be about 24‰ apart. When we express the difference del18O (calcium carbonate) (PDB scale) - del18O (water) (SMOW scale) we will get ~zero if they are in equilibrium at 25°C. If the difference is greater than 0 (but equilibrium is stil valid) then the temperature must have been colder than 25°C. If the difference is less than zero, then the temperature must have been warmer.

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).

The relationship between alpha and temperature can in principle be determined from statistical mechanics if we know the vibrational characteristics of the molecular bonds, but in practice it is determined empirically. Most textbooks will cite the equation of Epstein, who found that the difference between the delta_18_O values of the calcite of mollusc and the delta_18_O of the water in which they grew fit a line that is sometimes expressed as a 2nd-order polynomial.

$T = 16.5 - 4.3(delC-delW)+0.14(delC-delW)^2$.

The 2nd order relationship is probably not warranted, and most people use a linear relationship. Remembe that in general, we are dealing with living organisms and precise equilibrium may not apply -- differences from the "expected" relationship are referred to as "vital effects" which vary from species to species.
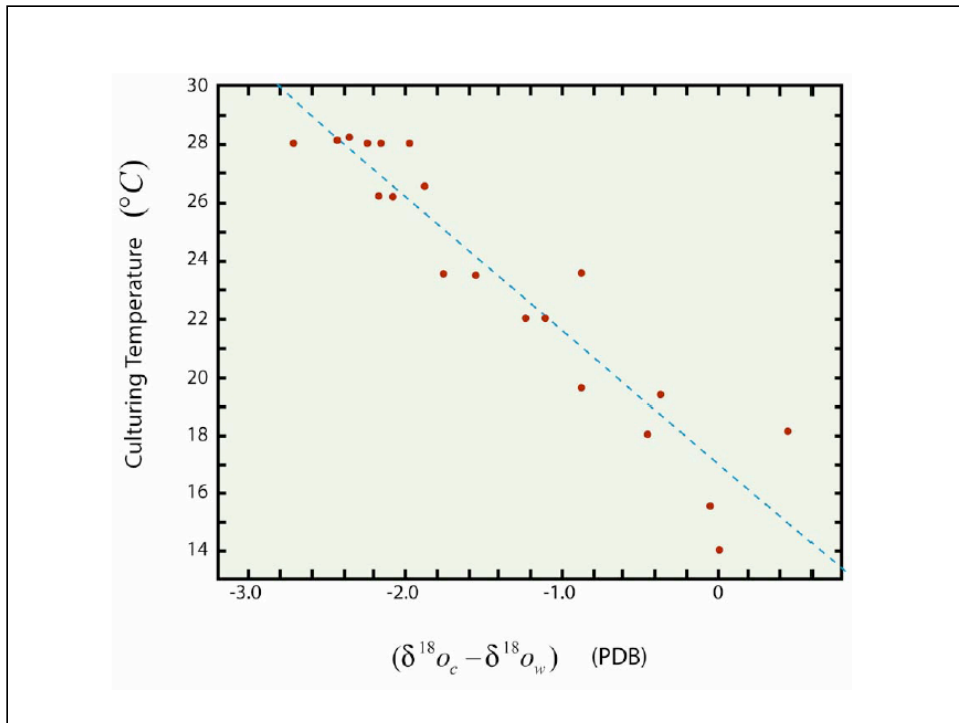
Shown here is a culturing experiment using a planktonic foraminifera grown in the lab, by Erez et al. (1983) (planktonic G. sacculifer). The relationship is similar to the mollusc culture, with T = 17-4.52(delC-delW)+0.03(delC-delW)^2. Inorganic precipitation of carbonate in the lab gives a similar relationship to the culturing work, showing that the vital effects are not large.
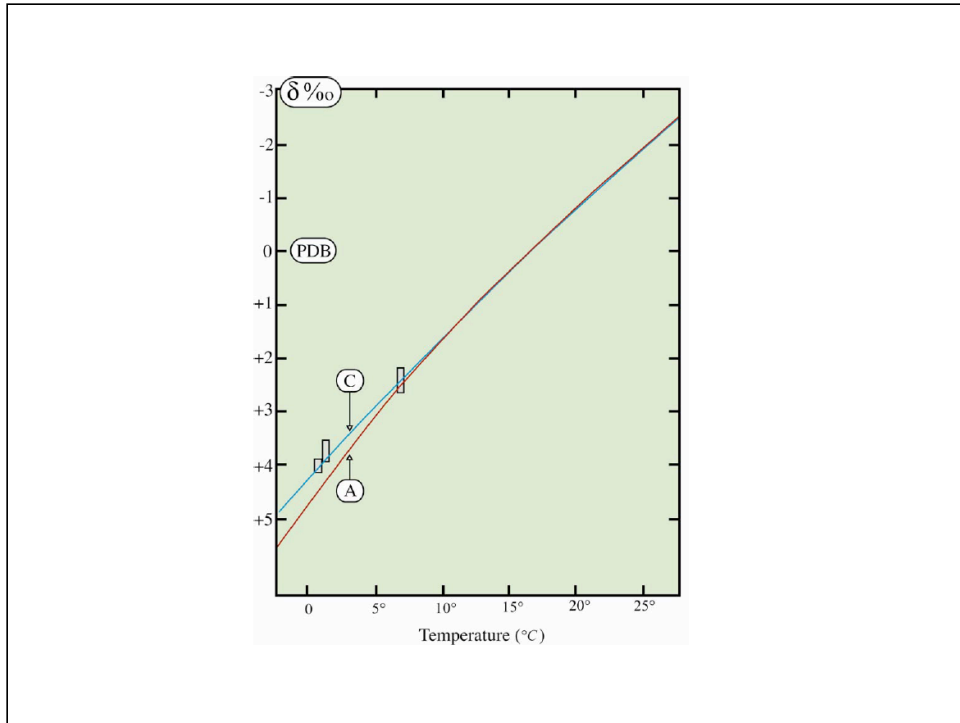
What we really want to know is: do these relationships work in the ocean. Shown here are data from core tops (surface sediment), with measurements done on the benthic foraminifera Uvigerina by Shackleton (1974). Equation A is Epstein's. Equation C is the best fit, which gives T = 16.9 - 4.2(delC-delW) + 0.13(delC-delW)^2.

The most important lesson here is that while we get slighly different answers in varying environments (we are dealing with living organisms after all) the relationship is APPROXIMATELY 4°C change for each per mil change in the difference between the water and the calcium carbonate d18O values, with larger differences corresponding to colder temperatueres.

Globigerina bulloides
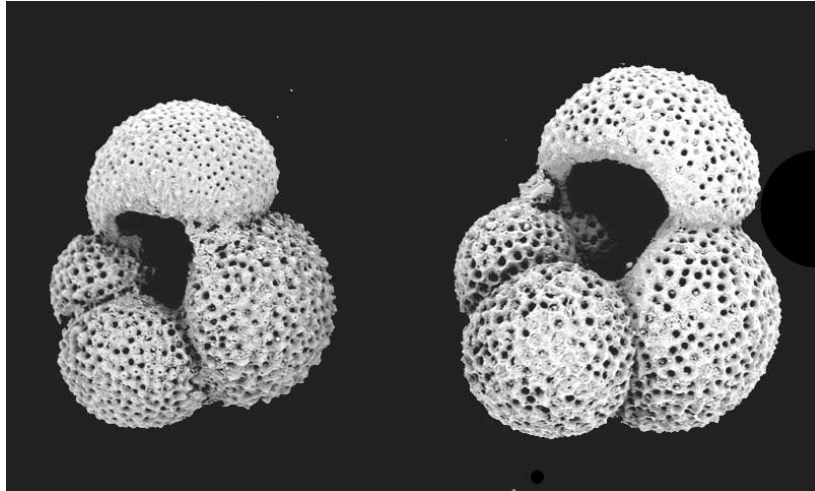
As Emiliani discovered, different foraminfera -- small microscopic animals that live in all the worlds oceans at virtually all depths -- from the same sediment cores give different del18O histories when plotted vs. depth in the core. This is because different forams live at different ocean depths. Globigerina species are easily identified by their round shapes, and these all live in the near surface ocean, generally within or just below the mixed layer. Such planktonic foraminifera therefore record ocean temperatures at the surface. When they die, their shells sink to the bottom but retain the d18O value they had when the organism was alive.

Uvigerina cushmani
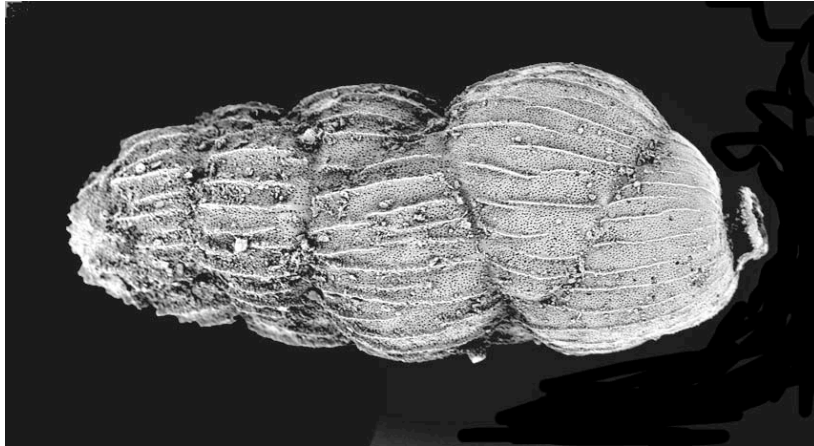
Benthic foraminfera live much deeper, in some cases quite close to or at the bottom. The most commonly used are various species of the genus Uvigerina. Because they live in the deep ocean, their del18O values reflect deep ocean temperatures.

Uvigerina (benthic), core V1930
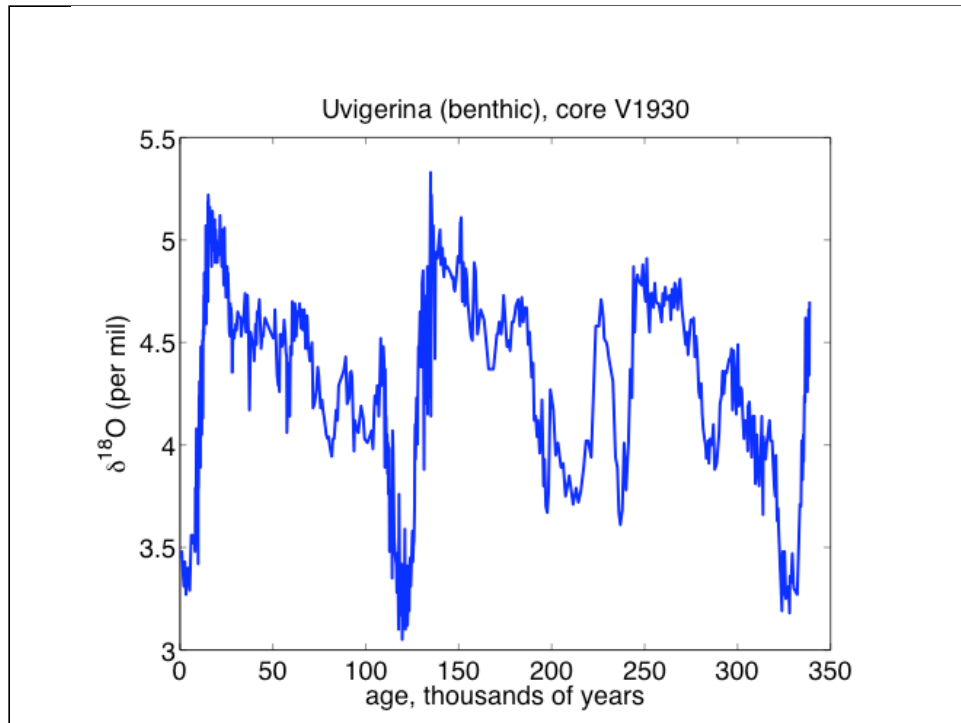
Shackelton's data from benthic forams on the core V1930 off the coast of Peru shows large variations in del18O. Emiliani originally interpreted such variations as due to temperature change associated with the waxing and waning of ice ages. Taken at face value, the observed changes would imply variations in deep ocean temperature of about 6 °C. Shackelton, however, noted that it deep ocean temperatures probably don't change much, and interpreted the benthic data in terms of changes in delW rather than delC -- 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. His explanation was that the lighter isotopes were preferentially evaporated and deposited as ice in the great ice sheets that grew on the northern hemisphere continents.

Following Shackelton's work, it became commonplace to think of d18O curves from benthic forams as "ice volume" records.

Neogloboquadrina dutertrei (planktonic)
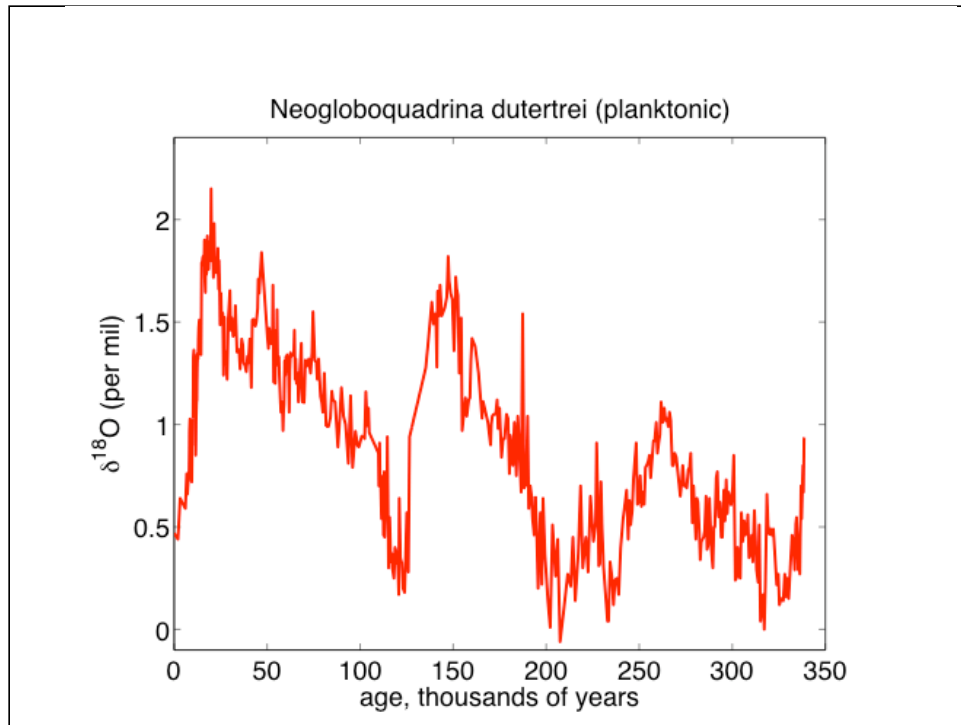
Planktonic forminifera from the same core showed similar variations to the benthic data, but larger in magnitude, supported Shackleton's idea. The suggestion is that the surface ocean del18O value changed, just as the deep ocean del18O did, as ice sheets built up, but that temperature changes were also important.

V1930 Planktonic – Benthic
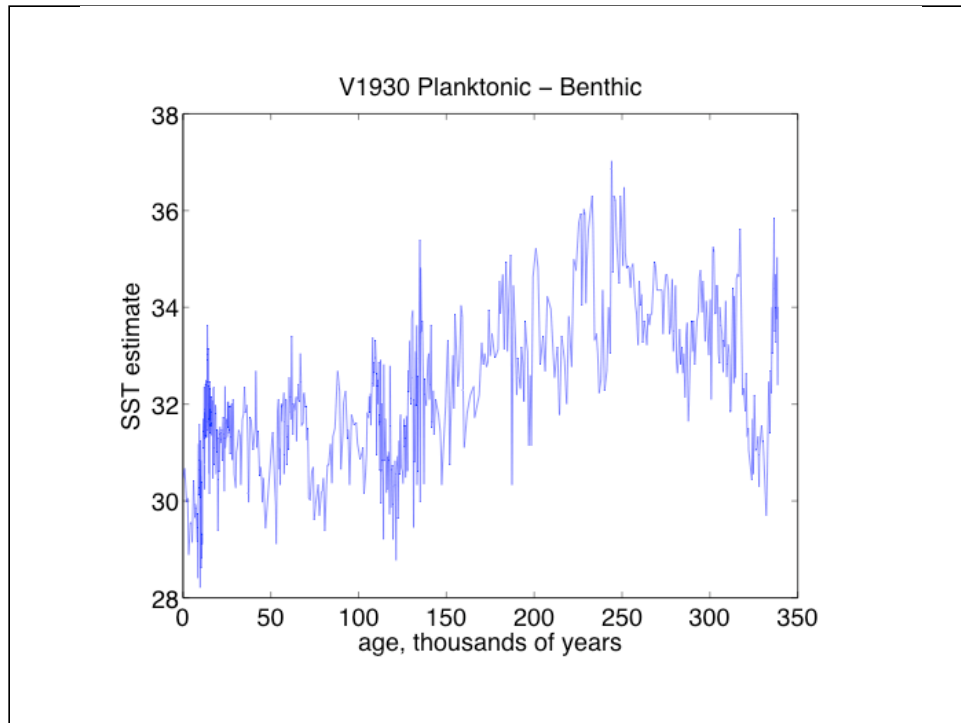
Assuming that the benthic foram d18O changes are due only to ice volume changes, then we can estimate the temperature change over time at the V1930 site by subtracting the two preceding curves and multiplying by -4. We obtain a temperature history that suggests ever-cooler temperatures throughout the 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 waterr 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.

Stacked Records
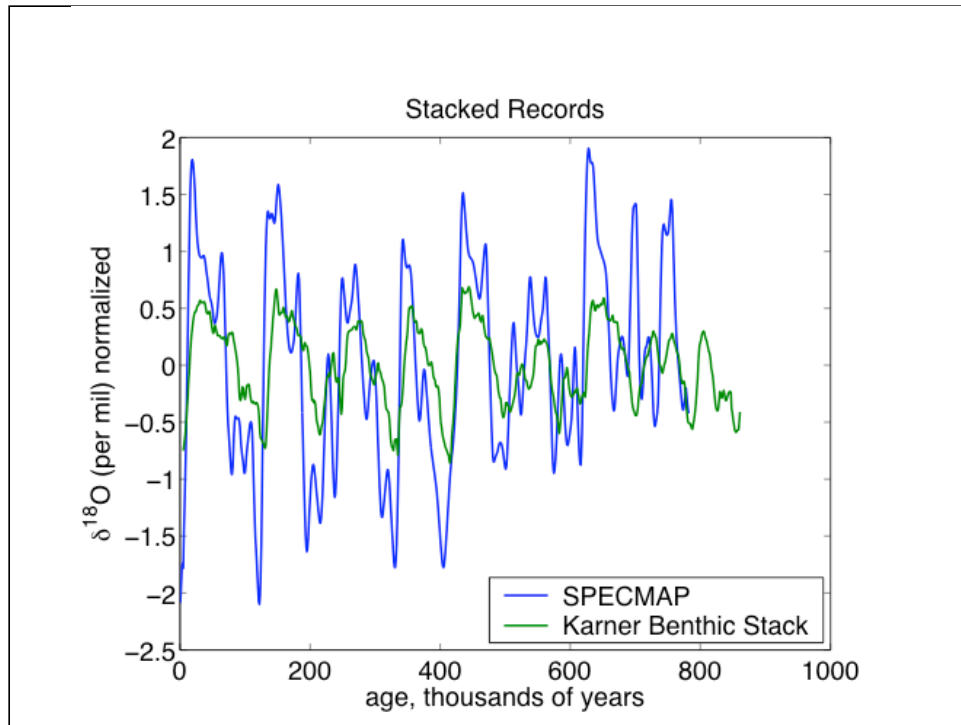
A major project in the 1970s resulted in the "SPECMAP" stack of planktonic foraminifera. More recently, Karner and others have produced a "benthic stack". In general, benthic d18O variations from core to core are not as large as planktonic d18O variations, so there has not been a lot of use of the Karner or other averaged benthic records (as the next slide shows, V1930 alone is very similar).

Stacked Planktonic – Benthic
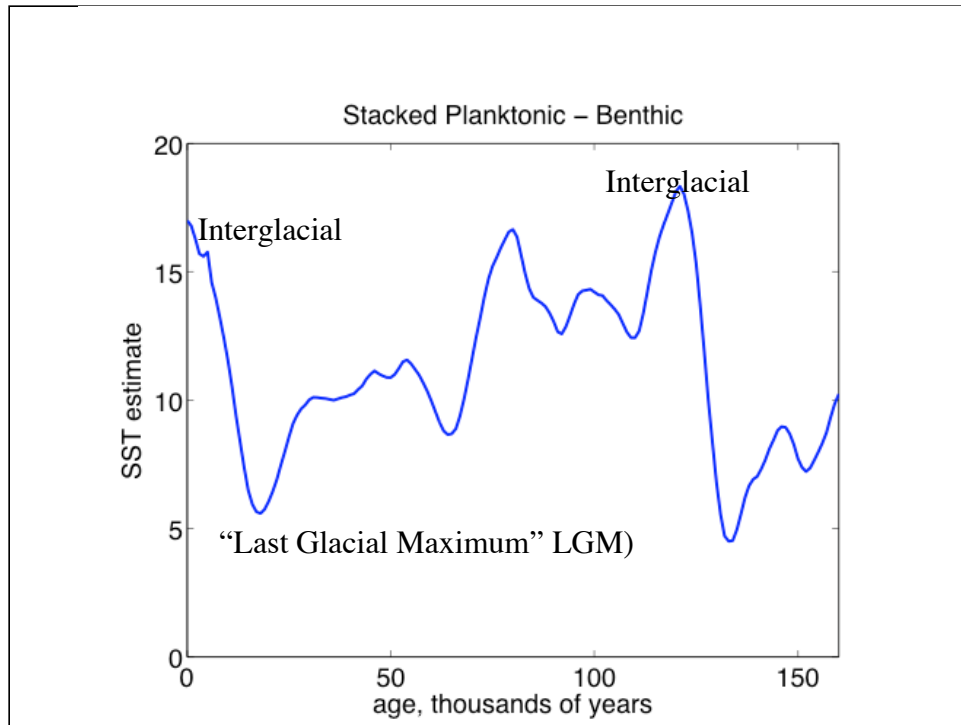
When we combine many sediment cores together, and subtract their average benthic d18O variations from their average planktonic d18O variations, we obtain a representative sea surface temperature estimate that will look familiar to most paleoclimatologists. It implies about a 10 degree change in temperature between interglacials (such as today) and the maximum cooling of ice ages, such as ~20,000 years ago.
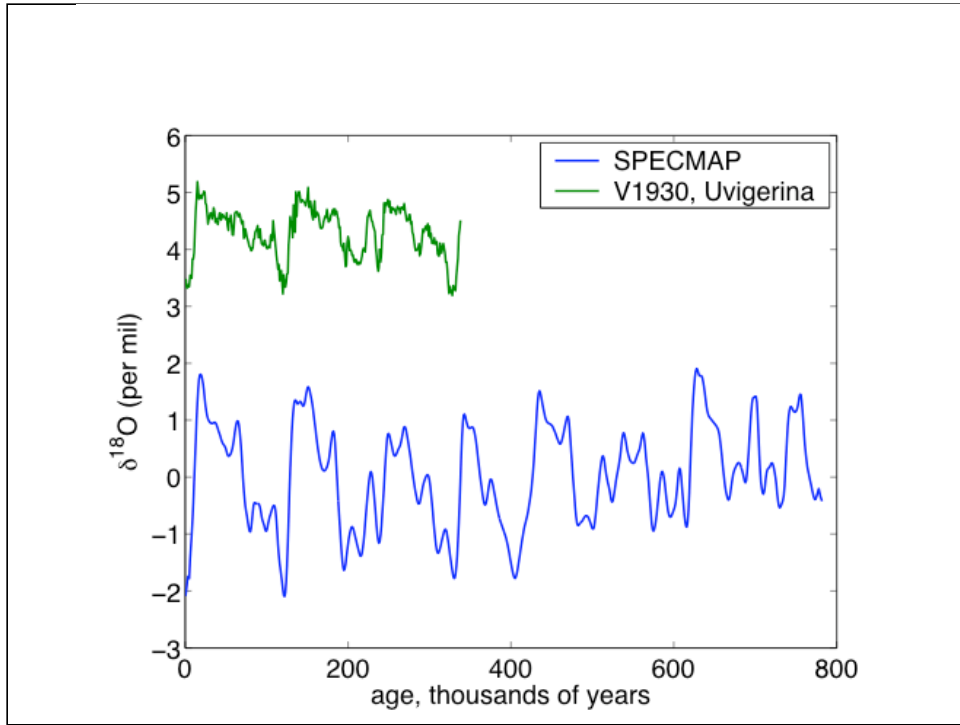
This shows SPECMAP and the V1930 benthics for comparison.