12.740 Paleoceanography
Spring 2008

Oxygen isotope paleothermometry: the early applications

- 1950's: Emiliani

- A. Using Urey's mass spectrometer, which required about 5 mg of calcium carbonate (about 100-200 individuals of foraminifera), Emiliani analyzed a variety of species of planktonic foraminifera from the Caribbean and found an apparent depth stratification, with some species (G. sacculifer, G. ruber) recording isotopic temperatures close to that of surface seawater; others recording colder temperatures.

- B. Emiliani analyzed downcore records of apparent surface dwellers throughout the Atlantic; making a correction for changes in the isotopic composition of seawater (more about this later), he calculated a 6-8° decrease in tropical ocean surface temperatures during glacial periods (i.e. about 1.5‰ $\delta^{18}O$ increase). He found evidence for many glacial/interglacial cycles over the last half million years; he coined the isotope stage stratigraphy system (now commonly referred to as "MIS" (Marine Isotope Stage); and he argued that the data supported the Milankovitch mechanism of climate change.

Emiliani (1954, Am. J. Sci. 252☐:149) temperature calibration from Gulf of Mexico core tops

[AMERICAN JOURNAL OF SCIENCE, VOL. 252, MARCH, 1954, PP. 149-158]

DEPTH HABITATS OF SOME SPECIES OF PELAGIC FORAMINIFERA AS INDICATED BY OXYGEN ISOTOPE RATIOS
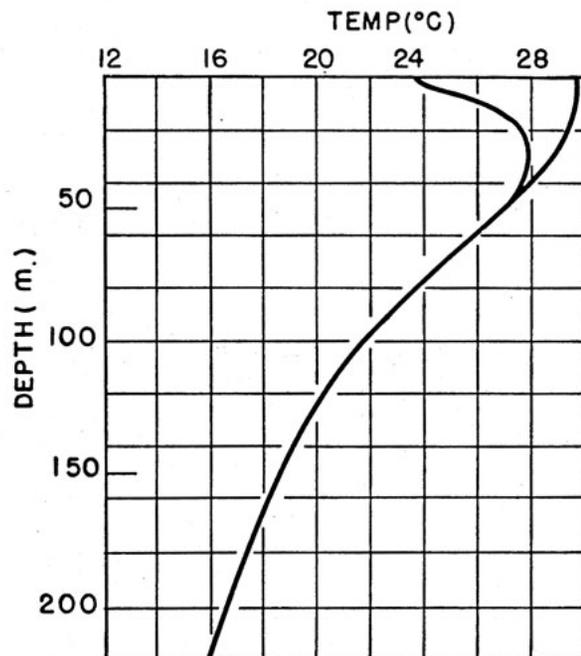
CESARE EMILIANI

Fig. 2. Variation of temperature with depth in the eastern Gulf of Mexico

Species	_Isotopic T_
G. rubra	27.2
G. sacculifera	25.1
G. conglobata	23.2
P. obliquiloculata	21.6
G. menardii	19.8
O. universa	19.8
G truncatulinoides	16.1

• Emiliani (1955 and other papers) then analyzed foraminifera from piston cores from the deep sea, and made temperature estimates:

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FIG.--Core A179-4: percentages of the fraction larger than 74 μ and isotopic temperatures obtained from Globigerinoides rubra (a) Globigerinoides sacculifera (b), Glabigerina dubia (c), and Gluborolalia menardii (d).

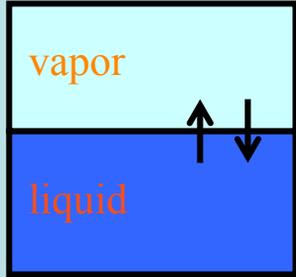• He found multiple cycles of cold and warm periods during the past ~500,000 years.

2. This work created quite a stir, and quickly was criticized on several grounds:

    a. It violated the prevailing 4-ice-age theory from continental geology.

    b. Meteorologists though that the tropical temperature change seemed excessive.

    c. Micropaleotologists thought that their micropaleontological work (G. menardii stratigraphy) contradicted with O-18 record.

    d. Biologists (e.g. Bé) argued that foraminiferal ecological shifts may have altered the depth habitat of organisms

    (and hence temperatures).

    e. The time scale (based on $^{230}Th/^{231}Pa$) was criticized.

    f. Various statistical errors were pointed out.

Oxygen isotope paleothermometry: the early applications

- Despite all of this criticism, with 1996 hindsight we can say that Emiliani was right about most of these points, with the major exception being the time scale and the amplitude of tropical cooling.

- The problem of the time scale: Emiliani derived his time scale from a core which had been dated by the "^{231}Pa/^{230}Th" method. This method assumes that the initial value of the ratio at zero age is the production rate from the ^{235}U and ^{234}U in seawater. We now know that this assumption is incorrect: Th and Pa are fractionated by their differential particle reactivity in the ocean.

Rayleigh distillation of oxygen isotopes

vapor

liquid

Vapor pressure = f(T)

(Clausius-Clapeyron equation, exponential with increasing T)

At 25°C, the vapor pressure of $H_2^{16}O$ is 0.9% higher than $H_2^{18}O$

Imagine a 50-50 mixture of liquid $H_2^{16}O$ and $H_2^{18}O$, equilibrated with the vapor phase at 25°C. Separate the vapor from the liquid:

Cool the vapor to 20°C; allow liquid to condense from vapor:

$\delta^{18}O$ = -9‰   T=25°C

1009 $H_2^{16}O$ 1000 $H_2^{18}O$

$\delta^{18}O$ = -11‰   T=20°C

745 $H_2^{16}O$ 737 $H_2^{16}O$

264 $H_2^{16}O$ 263 $H_2^{18}O$

Rayleigh equation: $\dfrac{R}{R_0} = f^{\alpha-1}$

R_0 = initial isotope ratio
R = isotope ratio after cooling
f = fraction of water condensed
α = isotope fractionation factor

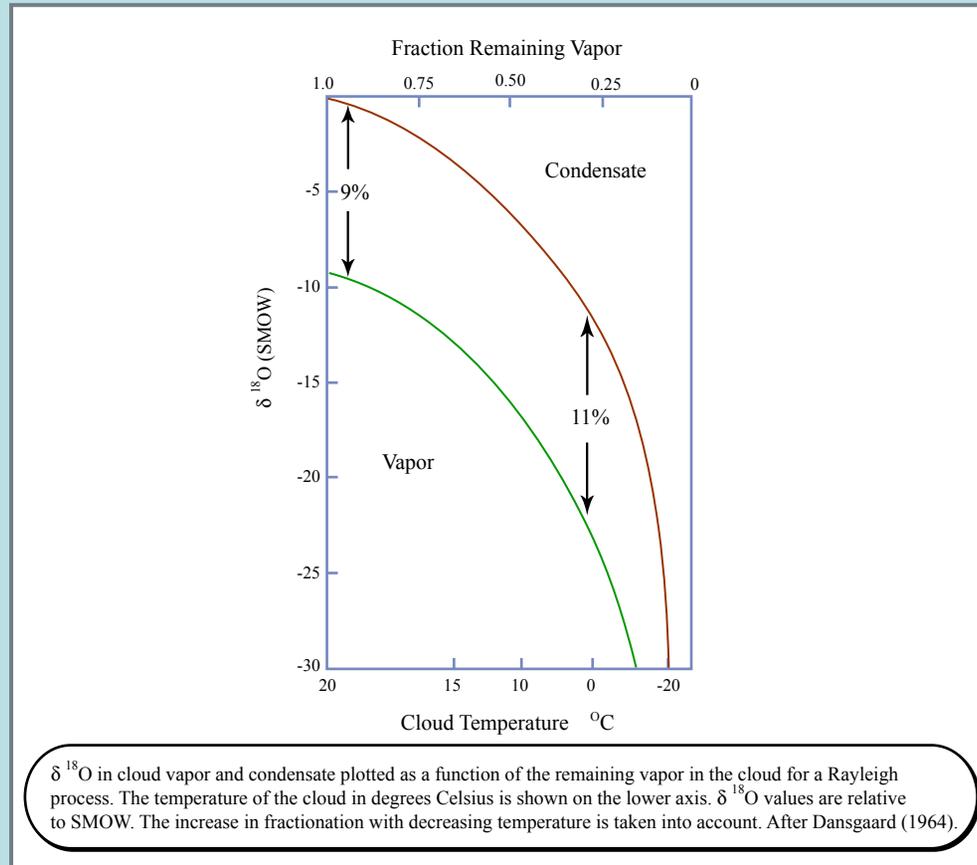# Cumulative Rayleigh Isotope Distillation as a function of temperature

$\delta\,^{18}O$ in cloud vapor and condensate plotted as a function of the remaining vapor in the cloud for a Rayleigh process. The temperature of the cloud in degrees Celsius is shown on the lower axis. $\delta\,^{18}O$ values are relative to SMOW. The increase in fractionation with decreasing temperature is taken into account. After Dansgaard (1964).

Observed $\delta^{18}O$ - surface temperature relationship

Mean annual $\delta^{18}O$ of precipitation as a function of the mean annual air temperature at the earth's surface. Note that $\delta^{18}O$ values are progressively lighter as the mean annual temperature becomes lower. After Dansgaard (1964).
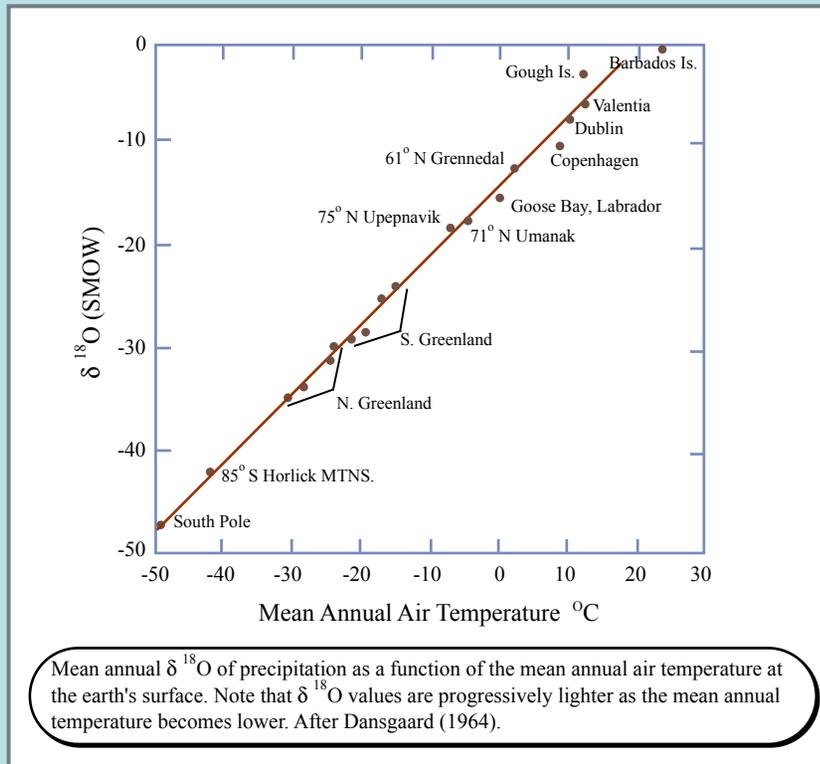
Figure by MIT OpenCourseWare.
Adapted from source: Broecker (1974)
Chemical Oceanography.

Note: this line is not the relationship predicted by the Rayleigh distillation curve. It includes many other effects: evaporation-precipitation cycles, cloud-T / surface-T relationships; multiple sources of water vapor at different temperatures, etc.

Oxygen isotopes of precipitation over North America

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Emiliani's ice volume correction

Although Emiliani knew that modern ice was relatively light and had an isotopic composition of about -25‰, he argued that the bulk of snowfall during the glacial maximum (where ice is accumulating at lower latitudes) must have an isotopic composition of about -15 ‰, because this is the composition of precipitation at ~-5 to 0°C (where the bulk of snowfall will occur because of the exponential dependence of vapor pressure on temperature). From then-current estimates of sea-level change (about 100m) and the assumption that ice sheets must have an isotopic composition of about -15‰, Emiliani calculated that the contribution of ice volume change to changes in the isotopic composition of the ocean corresponded to about $^1/_3$ of the total $\delta^{18}O$ change:

$$M_o\delta_o + M_i\delta_i = \text{constant}$$

$$M_o = 1.4 \text{ x } 10^{21} \text{ kg}$$

$$A_o = 361 \text{ x } 10^6 \text{km}^2$$

Because they flow, glaciers are filled from their summits:

Ice sheets don't represent average snowfall; wastage of the sheet is highest near the southern margin where snowfall is also the highest; glacial flow results in the bulk of the ice sheet representing the isotopic composition of the summits, with more negative $\delta^{18}O$ (-30 to -50 ‰).

Vertical cross section of an ice sheet resting on a horizontal subsurface. Ice particles deposited on the snow surface will follow lines that travel closer to the base the farther inland the site deposition. An ice mass formed around the divide (I-I) will be plastically deformed (thinned) with depth as suggested by the lined areas. The dashed curve along the vertical ice core (C-C) shows the calculated horizontal velocity profile V_x (Weertman 1968b). The horizontal arrows along C-C show the adopted approximation to V_x (Dansgaard et al. 1969).
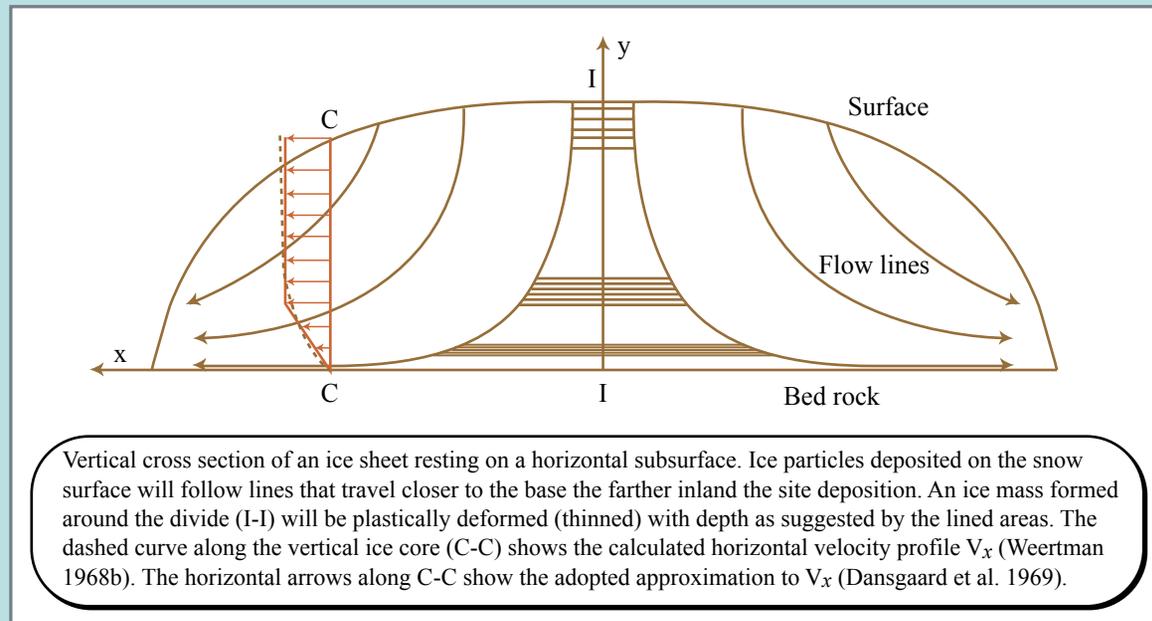
Figure by MIT OpenCourseWare.
Adapted from source: Dansgaard et al. (1971).

How can we know the isotopic composition of ice sheets from the last glacial maximum?

- It might seem that the isotopic composition of the Laurentide and Fennoscandian glacial ice is forever unknowable (because the ice is gone). Two ingenious ways of establishing isotopic composition of glacial ice have been suggested:

  - Hillaire-Marcel and Causse (1989) investigated the isotopic composition of carbonates precipitated from sub-glacial streams. The temperature is constrained to a narrow range (melting point as a function of pressure); modern analogues suggest that a range of -1.5 to 5 °C is reasonable. If the carbonates are at equilibrium, we can calculate the isotopic composition of the meltwater to better than 1‰. These results suggest that ice near the southern margins of ice Laurentide ice sheet was about -16 to -19‰, and that of the interior of the ice sheet about -30‰. In view of the likely flow lines, this result support the notion that the bulk of the ice sheet had an isotopic composition closer to -30‰ than to -15‰.

  - McDuff (1984) pointed out that the delay in diffusion of salt and isotopes into the pore waters of oceanic sediments should lead to a maximum of salinity and a minimum in $\delta^{18}O$ near 40 m depth, because of the time scale of diffusion:

$$t \sim \overline{x^2} / D \approx (16 \times 10^6 \text{ cm}^2) / (2 \times 10^{-6} \text{ cm}^2/\text{sec}) \approx 250{,}000 \text{ years}$$

So pore waters at that depth are closer to the average salinity and $\delta^{18}O$ over the past several glacial cycles rather than to the current oceanic values which are less salty and isotopically lighter. Schrag and DePaolo (1993) applied this technique and estimated that seawater $\delta^{18}O$ shifted by -1.0±0.25‰ since the last glacial maximum. Assuming a sea-level change of ~120 m suggests that the isotopic composition of the latest Pleistocene ice sheet was about −32 ± 8‰. Later, Adkins et al. (2002) extended this approach to paleosalinity estimation, which allows for estimation of sea level change. Taken at face value, this data implies ~150 m fall in sea level at the Last Glacial Maximum (LGM), which is 20-30 m more than estimated from sea level observations.

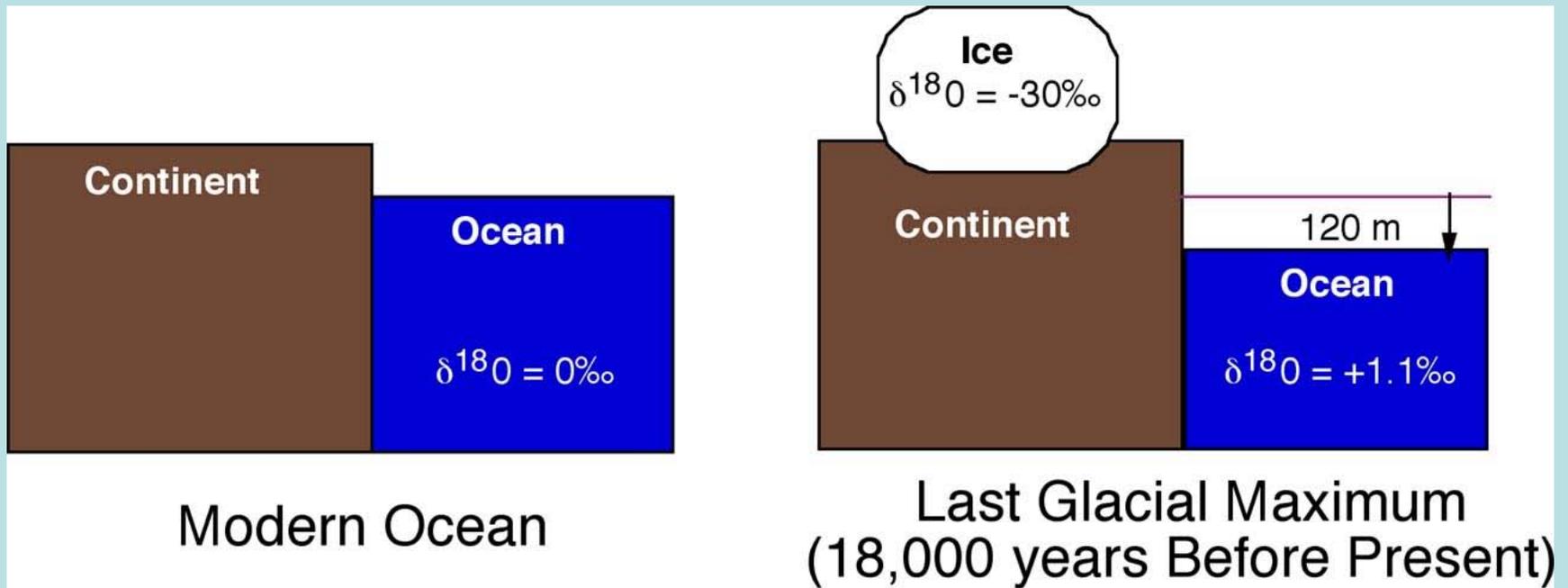# Pore water chlorinity and oxygen isotopes

Image removed due to copyright restrictions.

Adkins, Schrag, and McIntyre (2002)

Image removed due to copyright restrictions.

Caution: this method requires some knowledge of past water mass distributions in the ocean
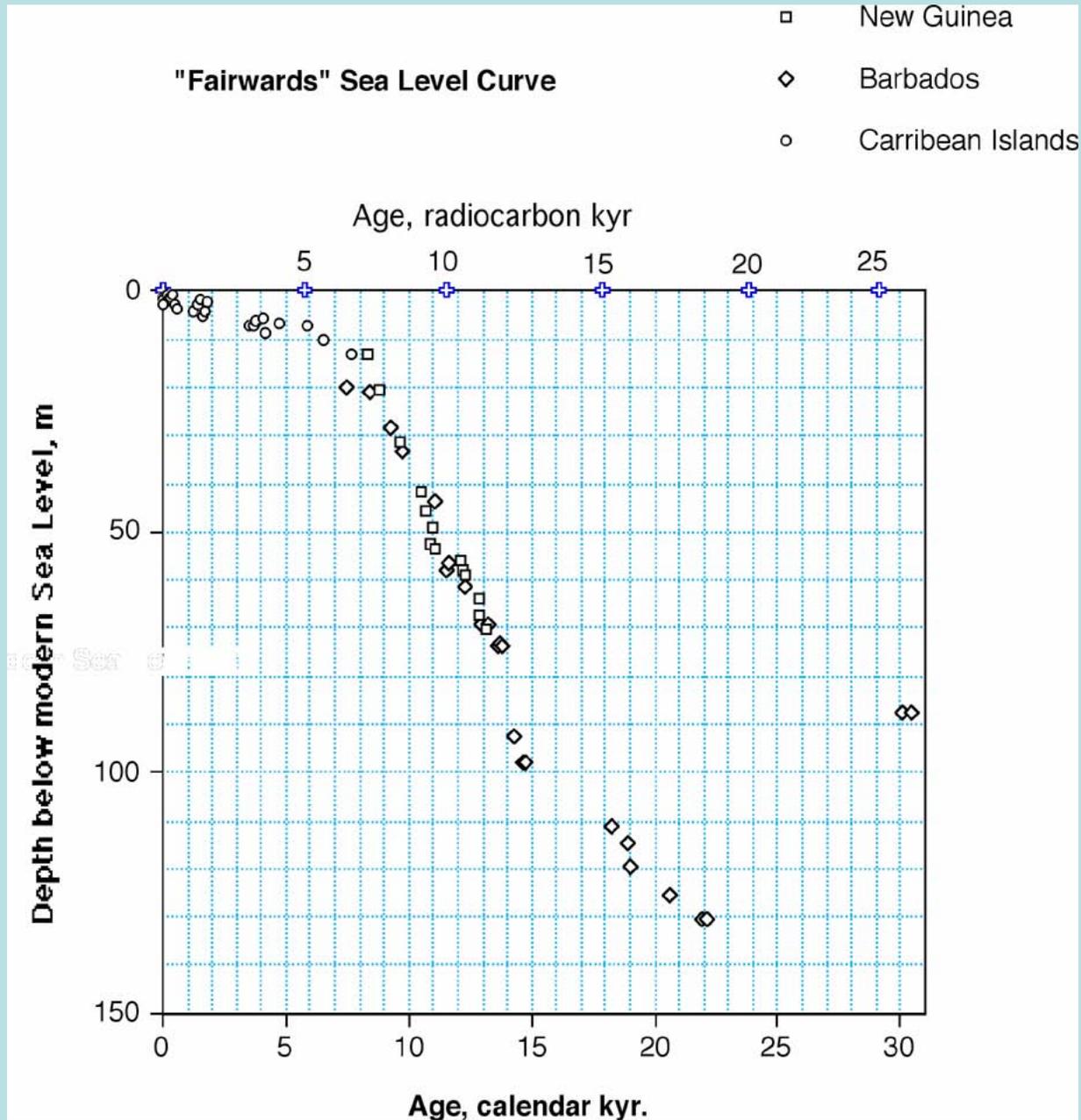(salinity and $\delta^{18}O$ variations)

Effect of glaciation on the oxygen isotope composition of the ocean

Ice
$\delta^{18}O = -30‰$

Continent

Ocean

$\delta^{18}O = 0‰$

Modern Ocean

Continent

120 m

Ocean

$\delta^{18}O = +1.1‰$

Last Glacial Maximum
(18,000 years Before Present)

Isotope Mass Balance Equation:

$$M_o\delta_o + M_i\delta_i = M_t\delta_t$$

Sea-level estimates from drilling submerged coral terraces

Shackleton benthic foram $\delta^{18}O$

At about the same time as Dansgaard's ice core work, N.J. Shackleton came to the same conclusion based on the similarity between planktonic and benthic foraminiferal $\delta^{18}O$. He argued that temperature change in the cold deep ocean must have been small (at least some waters certainly could not have been colder than the freezing point), so that $\delta^{18}O$ in benthic foraminifera would represent mainly ice-volume changes. Problem: benthic foraminifera are scarce (only a few percent of total foraminifera), so in general one requires ~100x the raw sample size to find enough benthic foraminifera. Shackleton collaborated with workers who developed an improved mass spectrometer that required 10x less sample, which made benthic foram analysis possible.

Image removed due to copyright restrictions.

Shackleton

Shackleton benthic foram $\delta^{18}O$

Shackleton's first paper compared <u>mixed</u> benthic species with surface planktonic species and found a 1:1 correlation. So Shackleton argued that most ("at least $^2/_3$") of the planktonic and benthic $\delta^{18}O$ change was due to ice volume. This would imply that tropical surface temperatures did not change very much, contrary to Emiliani's conclusion of 8-10°C cooling. As this idea came to be accepted, it was common to find "at least $^2/_3$" drift to "more than $^2/_3$" or even "most of the benthic isotopic change is due to ice volume changes".

Work over subsequent years indicates that the $^2/_3$ number was probably just about on the mark. The arguments require that you know more about the physical evidence for paleo sea level [to be covered later].

Image removed due to copyright restrictions.

Shackleton

Oxygen isotope stratigraphy

- Shackleton pointed out that if most of the oxygen isotope signal is due to ice volume, $\delta^{18}O$ records from throughout the ocean are "globally synchronous" (within the ~1000 year mixing time of the ocean) and can serve to establish a globally synchronous relative chronology. He also established several "sub-stages" to Emiliani's stratigraphy that enhanced the corrrelation precision of this stratigraphy.

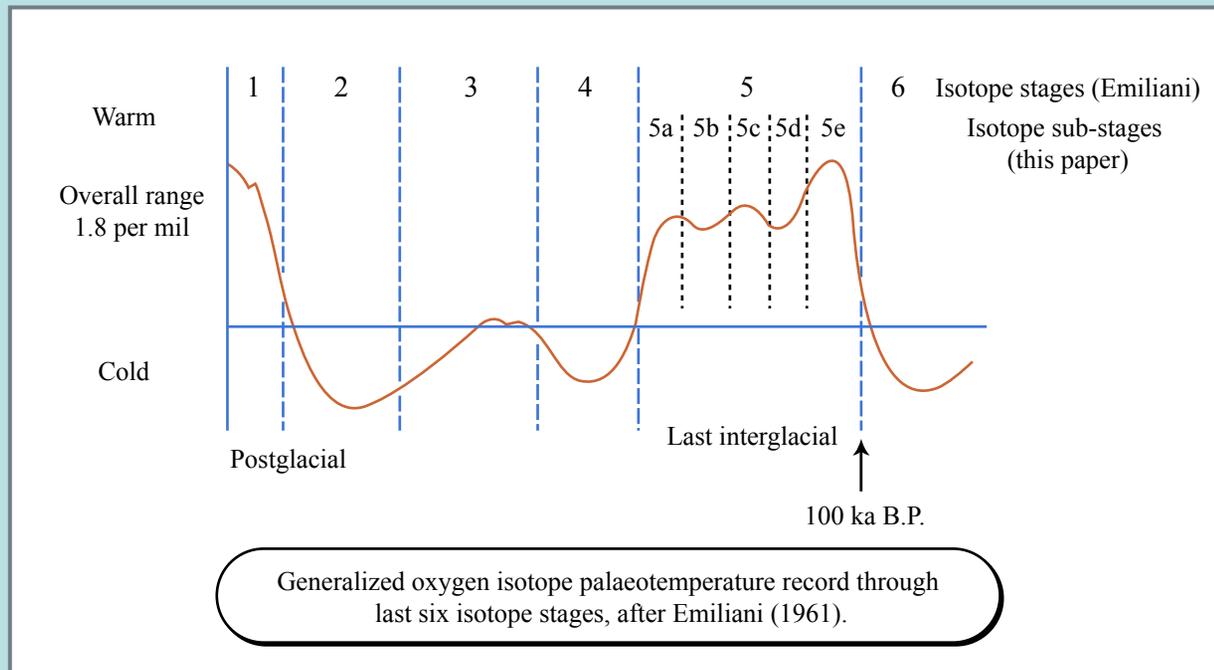Generalized oxygen isotope palaeotemperature record through last six isotope stages, after Emiliani (1961).

Figure by MIT OpenCourseWare.

- Broecker and van Donk (1970) noted that in many data sets, deglaciations were often much more extreme than glacial inceptions ("sawtooth" records) and introduced the concept of "Terminations" which are the large abrupt deglaciations such as the transition out of the last glacial maximum, which was dubbed "Termination I".

V19-29 (Eastern Tropical Pacific)
Shackleton's first high resolution $\delta^{18}O$ record

Image removed due to copyright restrictions.

V28-238 (Western Pacific) paleomagnetic stratigraphy: the (more) correct $\delta^{18}O$ chronology
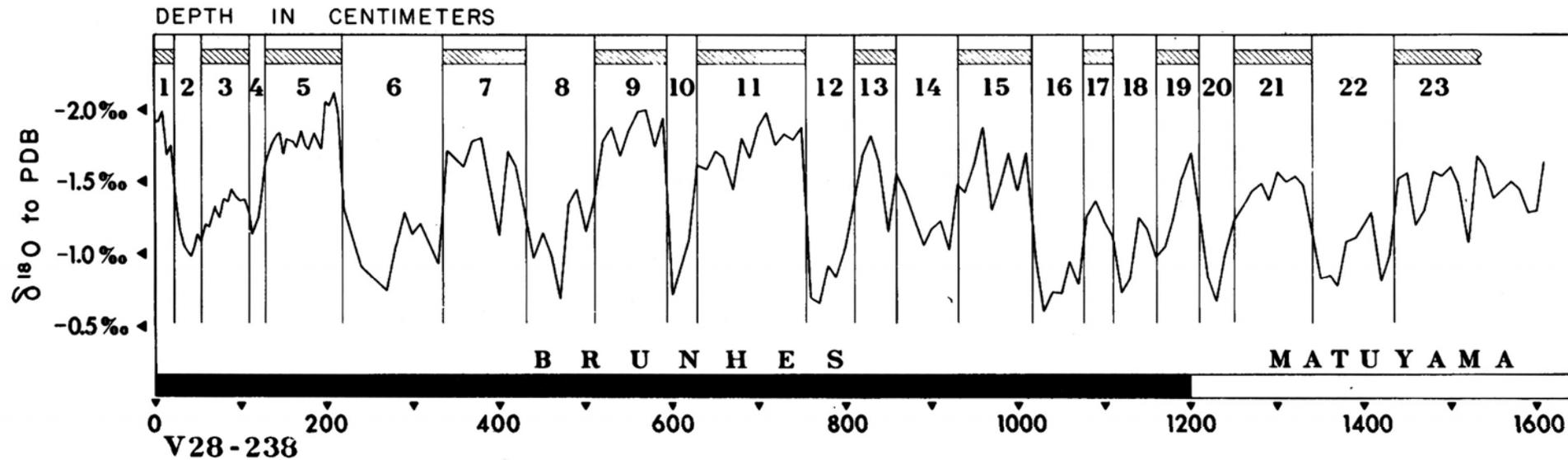

Figure 2. Oxygen-isotope and paleomagnetic record in upper 880 cm of cores V28-238

Life gets complicated:
Duplessy et al. (1970) find species-dependent $\delta^{18}O$

Pyrgo sp.

Various benthic species

Planulina wuellestorfi

Globorotalia hirsuta

Orbulina universa

Globorotalia truncatulinoides

δ^{18}

Depth in the core (mm)

Variation of $\delta^{18}O$ in three benthic and three pelagic species of Foraminifera in the core.
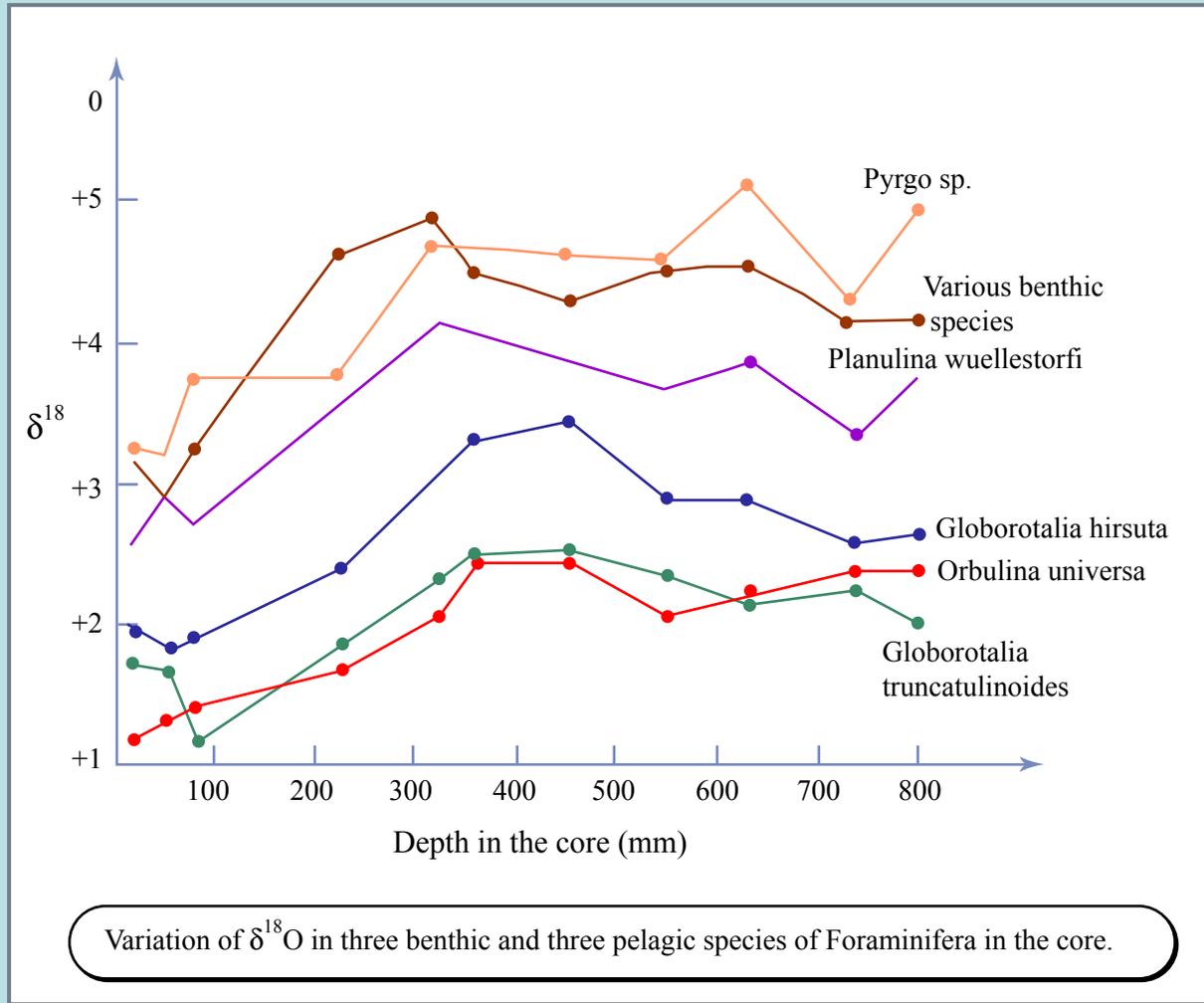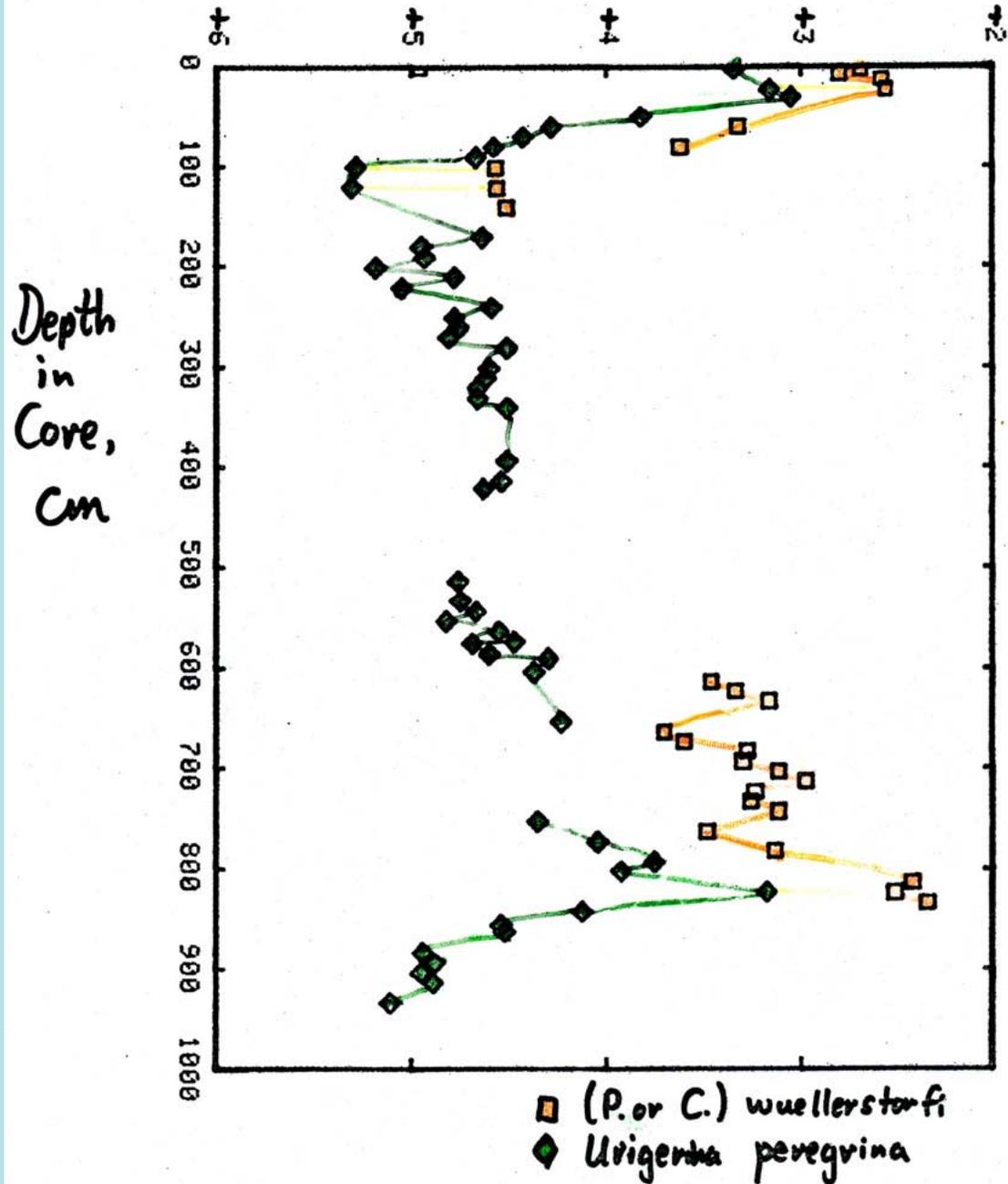
Figure by MIT OpenCourseWare. Source: Duplessy et al. (1970).

Eventually, Shackleton reports the same thing:
core M12392
(northeast tropical Atlantic)

Core Meteor 12392   Shackleton, 1977

□ (P. or C.) wuellerstorfi
◆ Uvigerina peregrina

Oxygen isotopes, phases 1 & 2, the plateau

• Shackleton showed that *Uvigerina* appears to be in equilibrium (compared to the 1970 O'Niel inorganic equation), and focused on developing benthic isotope stratigraphies based on this species. The conclusions remained much the same as his previous work, and people (other than an angry Emiliani) began to view benthic $\delta^{18}O$ records as proxy sea-level records. For a period in the 1970's (and unfortunately, even today…), it was common for people to label benthic $\delta^{18}O$ records as "ice volume", virtually neglecting any possible role for deep ocean temperature variations. We eventually learn otherwise…

• The argument against Emiliani's tropical paleotemperature interpretation was strengthened by John Imbrie's paleo-ecological temperature method, which also indicated that that tropical sea surface temperatures had not changed much. This method needs to be covered in some detail before we proceed.

Part 2: supplementary references

Classics: These are key papers in the development of our understanding of oxygen isotope paleoclimatology. Some of the arguments have not survived over the years, but the papers will help you understand how the current state of knowledge developed. (*) are worth more time than the others.

Emiliani, D. (1954) Depth habitats of some species of pelagic foraminifera as indicated by oxygen isotope ratios, Am. J. Sci. 252:149-158.

Emiliani, C. (1955) Pleistocene temperatures, J. Geol. 63: 538.

Dansgaard, W. (1964) Stable isotopes in precipitation, Tellus 16:436.

*Shackleton, N.J. (1967) Oxygen isotope analyses and Pleistocene temperatures re-assessed, Nature 215:15-17.\

Shackleton, N.J. (1969) The last interglacial in the marine and terrestrial records, Proc. Roy. Sco. Lond. B 174:135-154.

*Dansgaard, W. and H. Tauber (1969) Glacier oxygen-18 content and Pleistocene ocean temperatures, Science 166:499-502.

Duplessy, J.C., Lalou, C. and Vinot, A.C., 1970. Differential isotopic fractionation in benthic foraminifera and paleotemperatures re-assessed. Science, 168:250-251.

Shackleton, N.J. and N.D. Opdyke (1973) Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V28-238: oxygen isotope temperatures and ice volumes on a 105 to 106 year time scale, Quat. Res. 3:39-55.

Other Papers:

*Adkins, J. F. and D. P. Schrag (2003). "Reconstructing Last Glacial Maximum bottom water salinities from deep-sea sediment pore fluid profiles." Earth Planet. Sci. Lett. 216: 109-123.

Broecker, W.S. and J. van Donk (1970) Insolation changes, ice volumes, and the O18 record in deep sea cores, Rev. Geophys. Space Phys. 8:169.

Duplessy J. C., Lalou C. ,and Vinot A. C. (1970) Differential isotopic fractionation in benthic foraminifera and paleotemperatures re-assessed. Science. 168, 250-251.

Hillaire-Marcel C. ,and Causse C. (1989) The late Pleistocene Laurentide glacier: Th/U dating of its major fluctuations and d18O range of the ice. Quat. Res. 32, 132-138.

McDuff R. E. (1984) The chemistry of interstitial waters, Deep Sea Drilling Project Leg 86. In Init. Repts. Deep Sea Drilling Project (ed. G. R. Heath and e. al.), Vol. 86, pp. 675-687.

Schrag D. P. ,and DePaolo D. J. (1993) Determination of δ18O of seawater in the deep ocean during the last glacial maximum. Paleoceanogr. 8, 1-6.

Schrag D. P., Hampt G., and Murray D. W. (1996) Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean. Science 272, 1930-1932.