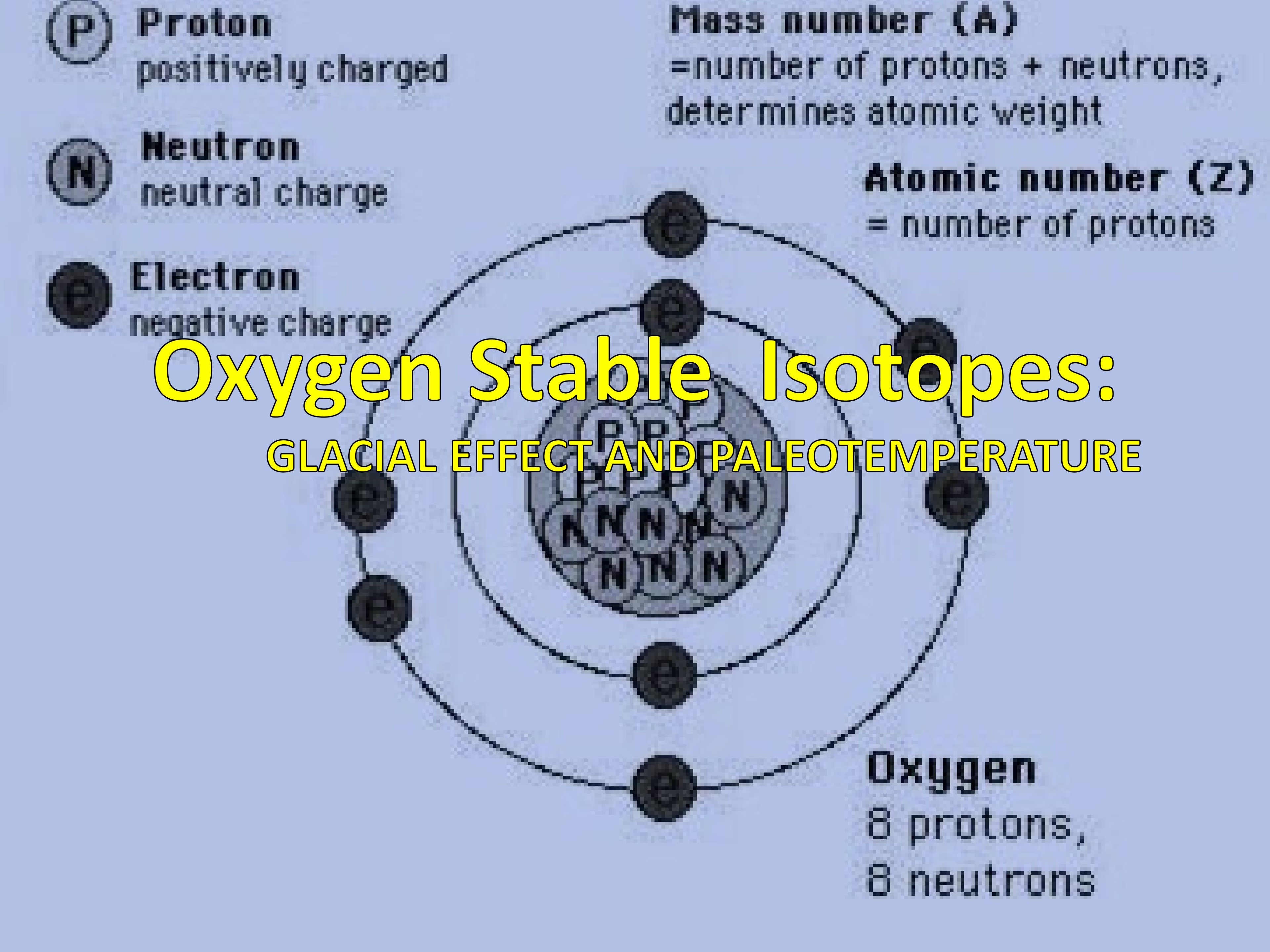
Oxygen Stable Isotopes:

GLACIAL EFFECT AND PALEOTEMPERATURE



SUMMARY

- PALEOTEMPERATURE EQUATION
- $\delta^{18}O$: PALEOTEMPERATURE
- $\delta^{18}O$: GLACIAL EFFECT

PREMISE

The analysis of stable oxygen and carbon isotopes in carbonate shells of planktonic and benthic foraminifera is a key component of research in stratigraphy, paleontology, paleoceanography, paleoclimatology, and paleoecology.

HAROLD UREY'S INTUITION - 1

***Harold Urey* (1893-1981)**. American chemist-physicist. He studied thermodynamics and molecular structures. This led him in 1931 to develop isotope separation techniques that allow him to discover deuterium and obtain **heavy water**. In 1934, he won the Nobel Prize in Chemistry. These discoveries were fundamental for the development of atomic energy. He was interested in geophysics and physics-chemistry of celestial bodies. With Stanley L. Miller he carried out an experiment on the origin of life on Earth in 1953, obtaining the synthesis of **amino acids** (the building blocks of living compounds) in a device that simulated the chemical and electrical conditions of the primordial earth's atmosphere.

PAST TEMPERATURE

Many principles of isotopic geochemistry trace back to Urey, who sought a method to determine past geological temperatures.

He deduced, through thermodynamic fractionation, that as temperature rises, more ^{16}O is incorporated into calcite shells of marine fossils, as ^{16}O has greater vibrational energy than ^{18}O and is more easily integrated into the crystalline structure.

HAROLD UREY'S INTUITION - 2

In 1948, Urey published a paper in Nature stating:

"The ratio of stable oxygen isotopes (^{18}O / ^{16}O) in $CaCO_3$ depends on the temperature of the water from which they precipitate."

In other words

Temperature (°T) controls the oxygen isotopic ratios between water (H_2O) and calcite ($CaCO_3$).

Urey believed that analyzing isotope ratios in fossil calcite could reveal the temperatures of the water where these organisms once lived. His vision was:

OXYGEN ISOTOPES IN CARBONATES COULD SERVE AS A PALEOTHERMOMETER

EPSTEIN ET AL.’ EQUATION (1951)...

It is the first (polynomial) equation for reconstructing past paleotemperatures:

$$T = 16{,}5-4{,}3\ (\delta_{carb}-\delta_{seawater})+0{,}14\ (\delta_{carb}-\delta_{seawater})^2$$

δ_{carb} isotopic composition (measured) of the sample (carbonate)
$\delta_{seawater}$ sea water isotopic composition in which carbonate precipitates

This equation shows that by measuring the isotopic composition of carbonate, we can determine the temperature at which it formed.

Note: Both δ_{carb} and $\delta_{seawater}$ of modern oceans can be measured in labs. For fossil samples, $\delta_{seawater}$ was initially assumed to be constant.

OTHER PALEOTEMPERATURE EQUATIONS

Over time, Urey's original paleotemperature equation has been gradually refined based on experimental data. Below are some of the proposed equations:

PALEOTEMPERATURE EQUATIONS:

Epstein *et al.*, 1951

$T = 16.5 - 4.3\,(\delta_{sample} - \delta_{water}) + 0.14\,(\delta_{sample} - \delta_{water})^2$

Craig, 1965

$T = 16.9 - 4.2\,(\delta_{sample} - \delta_{water}) + 0.13\,(\delta_{sample} - \delta_{water})^2$

Shackleton, 1967

$T = 16.9 - 4.38\,(\delta_{sample} - \delta_{water}) + 0.1\,(\delta_{sample} - \delta_{water})^2$

O'Neil *et al.*, 1969

$T = 16.9 - 4.38\,(\delta_{sample} - \delta_{water}) + 0.10\,(\delta_{sample} - \delta_{water})^2$

Horibe & Oba, 1972

$T = 17.04 - 4.34\,(\delta_{sample} - \delta_{water}) + 0.16\,(\delta_{sample} - \delta_{water})^2$

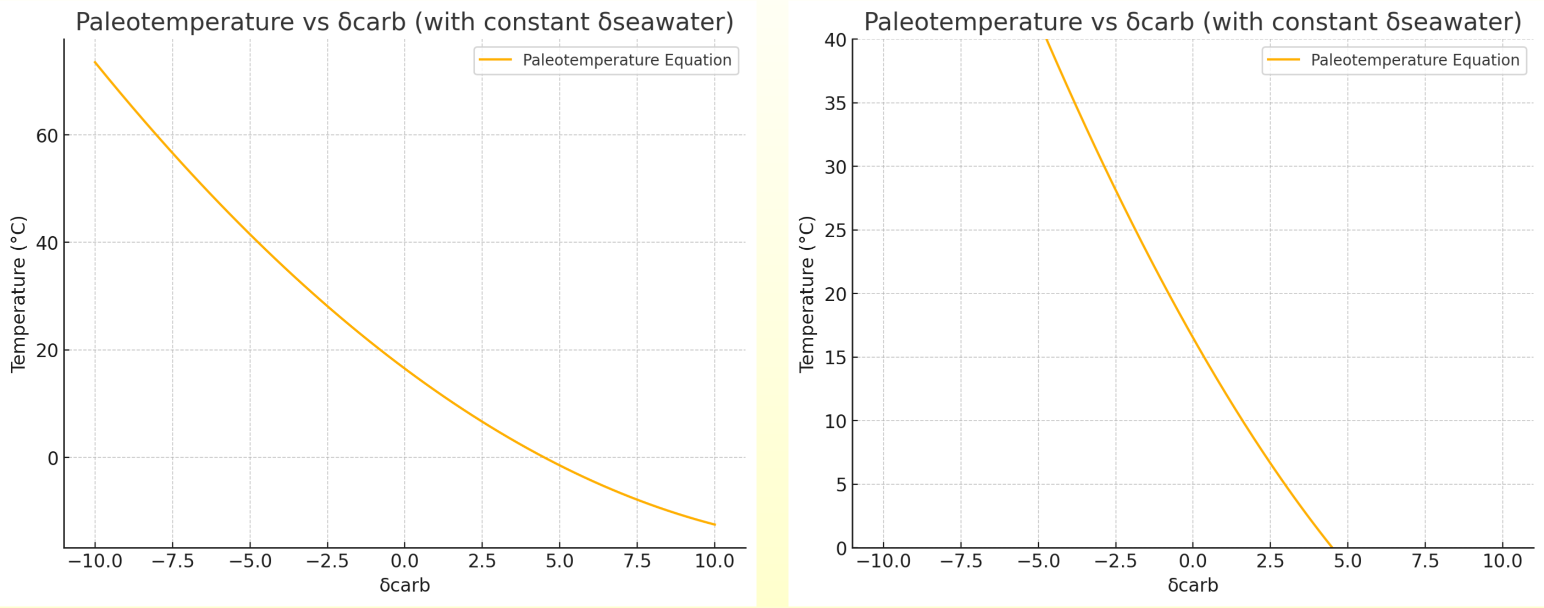
Erez & Luz, 1983

$T = 17 - 4.52\,(\delta_{sample} - \delta_{water}) + 0.03\,(\delta_{sample} - \delta_{water})^2$

$$\delta^{18}O = \frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{standard}}{{}^{18}O/{}^{16}O_{standard}} \times 1000$$

Relationship TEMPERATURE/δ_{carb}

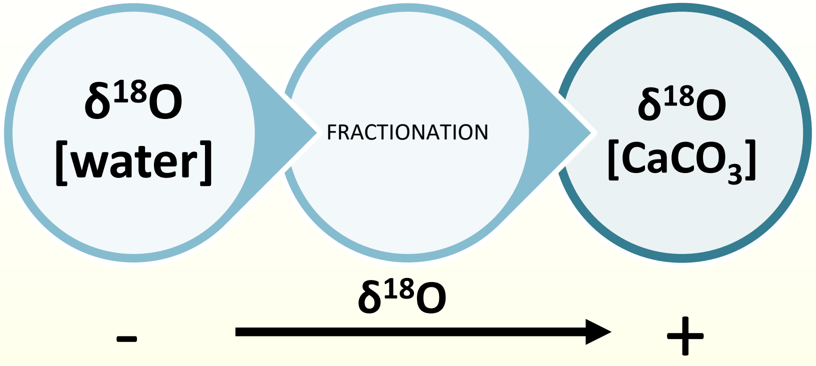
$$T = 16.5-4.3\ (\delta_{carb}-\delta_{seawater})+0.14\ (\delta_{carb}-\ \delta_{seawater})^2$$



$\delta_{seawater}$ = costant

The equation is a quadratic equation. Quadratic equations are second-degree polynomial equations. This results in a parabolic shape, typical of quadratic equations, where the curve first decreases and then increases.

OXYGEN ISOTOPE FRACTIONATION (CARBONATE) - 1



$\delta^{18}O$ [water]

FRACTIONATION

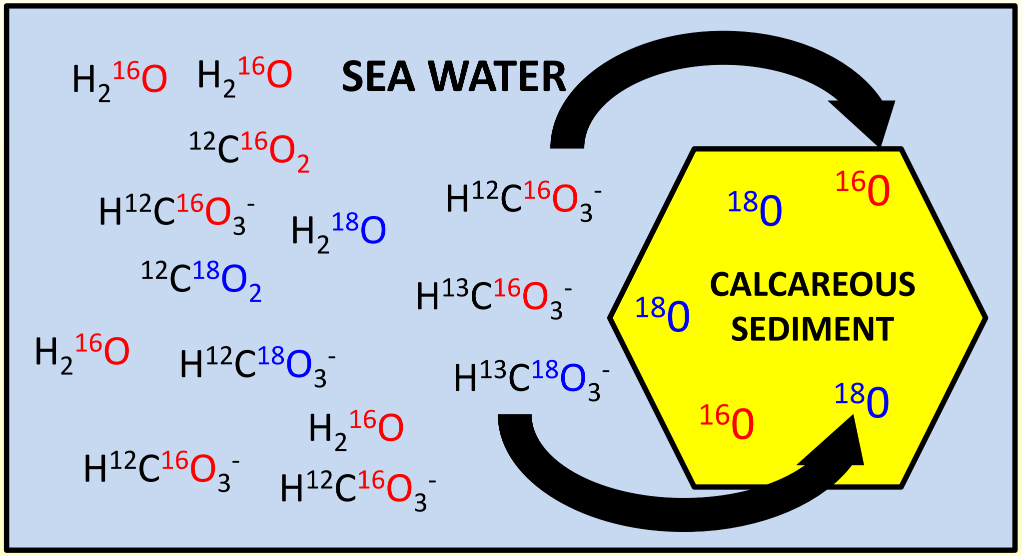
$\delta^{18}O$ [$CaCO_3$]

$\delta^{18}O$

\- → +

COSTANT TEMPERATURE

other fractionation processes, control the isotopic composition at the equilibrium between reactants ($\delta^{18}O_{SW}$) and products ($\delta^{18}O_{carb}$). Organisms secrete $CaCO_3$ "almost" in equilibrium with sea water, their shells are enriched (albeit slightly) in ^{18}O relative to the isotopic composition of water.



$H_2{}^{16}O$ $H_2{}^{16}O$ **SEA WATER**

$^{12}C^{16}O_2$

$H^{12}C^{16}O_3^-$ $H_2{}^{18}O$ $H^{12}C^{16}O_3^-$

$^{12}C^{18}O_2$ $H^{13}C^{16}O_3^-$

$H_2{}^{16}O$ $H^{12}C^{18}O_3^-$ $H^{13}C^{18}O_3^-$

$H_2{}^{16}O$

$H^{12}C^{16}O_3^-$ $H^{12}C^{16}O_3^-$

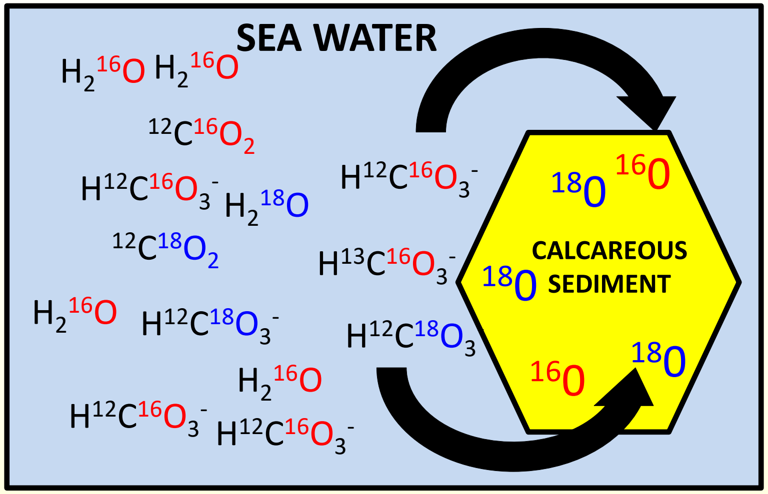
^{18}O ^{16}O

^{18}O **CALCAREOUS SEDIMENT**

^{16}O ^{18}O

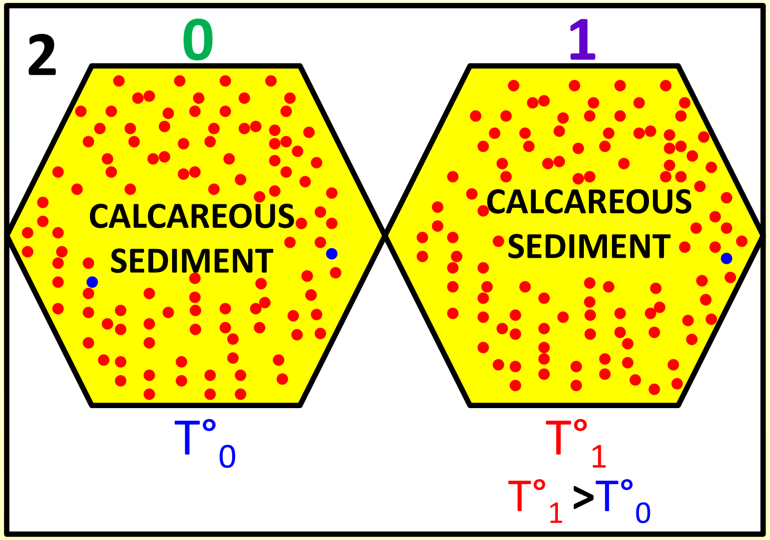
$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+}(Mg^{2+}) + 2HCO^{3-}$$

OXYGEN ISOTOPE FRACTIONATION (CARBONATE) - 2



NON COSTANT TEMPERATURE

Urey et al. experimentally established the relationship between Temp (°C) and the isotopic composition of $CaCO_3$ in marine shells. **They found that as temperature increases, the $\delta^{18}O$ value becomes more negative (enrichment in ^{16}O).**



Initial State (Figure 2.0):

At time t_0 and temperature $T°C_0$:

$^{18}O/^{16}O\_sample = 2/100 = 0.02$

Final State (Figure 2.1):

At time t_1, with $T°C_1 > T°C_0$, organisms continue to fix ^{18}O, but to a lesser extent:

$^{18}O/^{16}O\_sample = 1/101 = 0.01$

NUMERICAL EXAMPLES

You are given the following isotope ratios for two samples:

- **SAMPLE A**:
  - R_sample = $^{18}O/^{16}O$ = 101/1000 = 0.101
  - R_standard = $^{18}O/^{16}O$ = 100/1000 = 0.100
- **SAMPLE B**:
  - R_sample = $^{18}O/^{16}O$ = 99/1000 = 0.099
  - R_standard = $^{18}O/^{16}O$ = 100/1000 = 0.100

Calculate the δ^{18}O for both samples using the formula:

$$\delta^{18}O = \left(\frac{R_{\ sample}}{R_{\ standard}} - 1\right) x\ 1000$$

After calculating the δ^{18}O values, which of the following statements is correct?

A) SAMPLE A is enriched in ^{16}O compared to SAMPLE B, indicating a higher temperature for SAMPLE A.

B) SAMPLE B is enriched in ^{16}O compared to SAMPLE A, indicating a higher temperature for SAMPLE B.

C) Both samples have the same temperature as their R_standard values are the same.

D) SAMPLE A has a higher temperature than SAMPLE B because it has a higher R_sample value.

After calculating the $\delta^{18}O$ values, which of the following statements is correct??

u are given the following isotope ratios for two samples:
AMPLE A:
- R_sample = $^{18}O/^{16}O$ = 101/1000 = 0.101
- R_standard = $^{18}O/^{16}O$ = 100/1000 = 0.100

AMPLE B:
- R_sample = $^{18}O/^{16}O$ = 99/1000 = 0.099
- R_standard = $^{18}O/^{16}O$ = 100/1000 = 0.100

lculate the **$\delta^{18}O$** for both samples using the formula:

$$\delta^{18}O = \left(\frac{R_{sample}}{R_{standard}} - 1\right) x\,1000$$

After calculating the $\delta^{18}O$ values, which of the following statements is correct?

1. SAMPLE A is enriched in ^{16}O compared to SAMPLE B, indicating a higher temperature for SAMPLE A — 0% — 0
2. SAMPLE B is enriched in ^{16}O compared to S — 0% — 0
3. Both samples have the same temperature a — 0% — 0
4. SAMPLE A has a higher temperature than S — 0% — 0

https://app.wooclap.com/events/PCCM24/0

NUMERICAL EXAMPLES

$$\delta^{18}0\ (‰)= [(R_{sample}/R_{\ stand})\ -1)x\ 1000$$

SAMPLE A

$R_{\ sample} = {}^{18}0\ /{}^{16}0 = 101/1000 = 0.101$

By convention we assume that

$R_{\ standard} = {}^{18}0/{}^{16}0 = 100/1000 = 0.100$

$\delta^{18}0\ (‰)= (R_{sample}/R_{\ stand})-1)\ x\ 1000$

$\delta^{18}0\ (‰)= (0.101/0.100\ -1)\ x\ 1000$

$\delta^{18}0\ (‰)= 0.01x\ 1000 = 10‰$

SAMPLE A is enriched in $^{18}0$ with respect to the standard

SAMPLE B

$R_{\ sample} = {}^{18}0\ /{}^{16}0 = 99/1000 = 0.099$

By convention we assume that

$R_{\ standard} = {}^{18}0/{}^{16}0 = 100/1000 = 0.100$

$\delta^{18}0\ (‰)= (R_{sample}/R_{\ stand})-1)\ x\ 1000$

$\delta^{18}0\ (‰)= (0.099/0.100\ -1)\ x\ 1000$

$\delta^{18}0\ (‰)= -0.01x\ 1000 = -10‰$

SAMPLE B is enriched in $^{16}0$ with respect to the standard

The $\delta^{18}O$ of **SAMPLE B** (-10‰) is relatively enriched in ^{16}O compared to **SAMPLE A** (+10‰) The $\delta^{18}O$ of **SAMPLE B** reflects a higher temperature than **SAMPLE A**

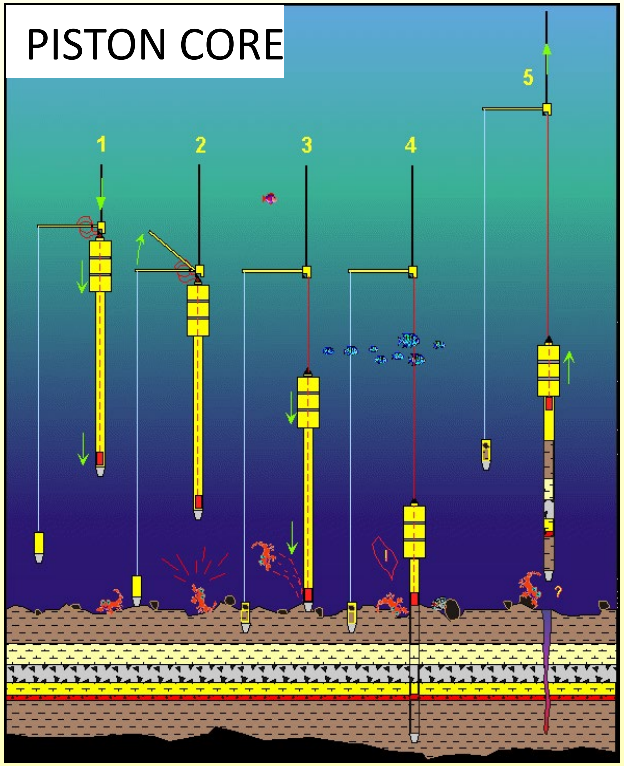
WHAT TO MEASURE?

Urey and his team initially used **bivalves** for their experiments but soon realized it was better to use more common fossils, found more consistently and across various environments.


BIVALVES

By the 1950s, rudimentary techniques had been developed to collect 10-20m long **ocean floor cores** ("piston cores").
These contained abundant and continuous **planktonic foraminifera**, while benthic foraminifera were present in much lower frequencies in pelagic deposits.

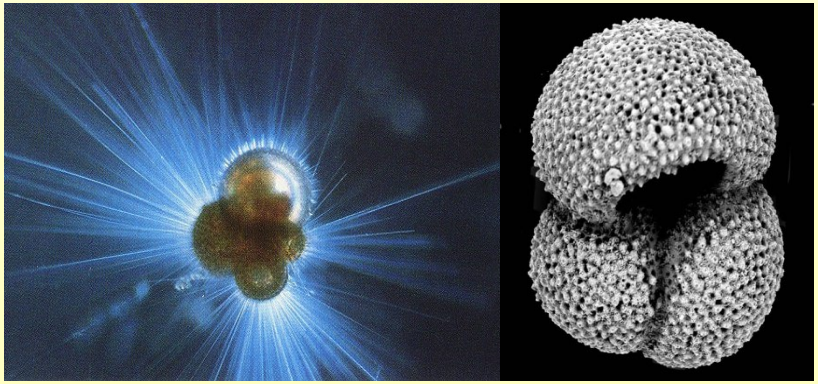
Urey established a position in his lab to study stable oxygen isotopes in planktonic foraminifera shells, which was filled by a young Italian micropaleontologist.


PISTON CORE

CESARE EMILIANI: ISOTOPES E FORAMS

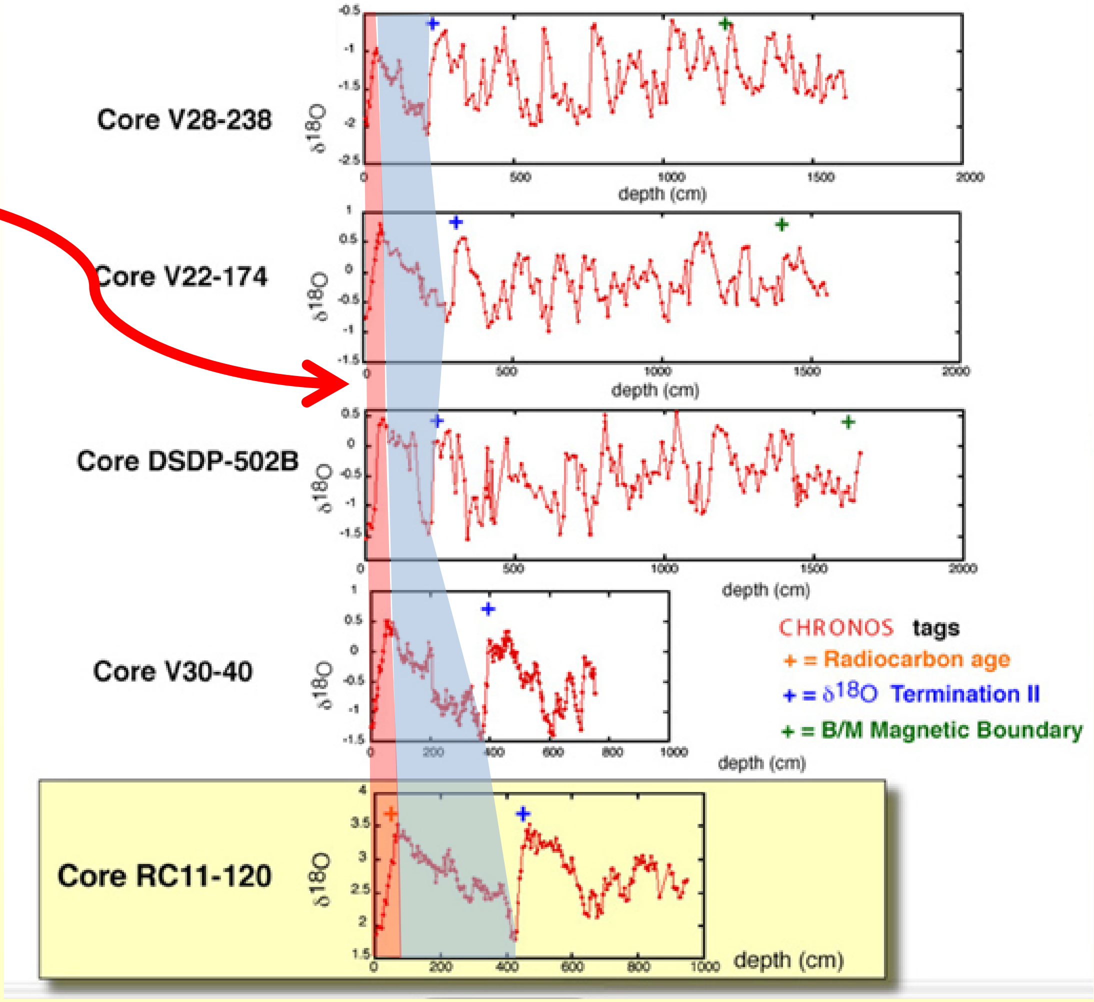
Born in Bologna in 1922, he graduated in Natural Sciences in 1945 with a thesis in Micropaleontology. After working for AGIP, he joined Urey's lab in 1950 to pursue a doctorate, focusing on stable oxygen isotopes in foraminifera, which he had studied in Italy. Later, he moved to the University of Miami and became a pioneer of modern Paleoceanography. He passed away in 1992.

After a few years of work, Emiliani published his first isotopic curves based on planktonic foraminifera from cores collected in the Caribbean and Mediterranean.
These cores spanned from the Holocene to the late Pleistocene and revealed that...



EXAMPLES OF ISOTOPIC Δ18o CURVES

Holocene



1) The $\delta^{18}O$ varies cyclically
2) The Holocene values (hot-red) are "lighter"
3) The underlying Pleistocene values (glacial-blue) are "heavier" (Δ = ~ 1.5-2 ‰)
4) The curves are similar in various areas and perfectly correlated.

δ^{18}O CURVES AS A PROXY FOR PAST CLIMATE

The oxygen isotopes reflect the glacial-interglacial climatic cycles that geologists had been studying for over a century on the land, with enormous difficulties in establishing NUMBER and CHRONOLOGY (Alpine chronology).

The enthusiasm was enormous, but discussions began.

The first inconsistencies began to emerge.

Almost all the scientists believed that $\delta^{18}0$ was a "proxy" of the climate, but **many were skeptical about the value of the direct (and quantitative) correlation between oxygen isotopes and temperature**.

δ^{18}O: IS IT A PALEOTEMPERATURE PROXY?

Urey and Emiliani speculated that δ^{18}O was a paleotemperature proxy, but solving the paleotemperature equation requires knowing two variables: δ_{carb} and $\delta_{seawater}$.

$T = 17-4.52\ (\delta_{carb}-\delta_{seawater})+0.03\ (\delta_{carb}-\delta_{seawater})^2$ => Erex & Luz (1983)

δ_{carb} measurable in the rocks
$\delta_{seawater}$?

Initially, it was assumed $\delta_{seawater}$ **remained constant throughout geological time**, but this proved unrealistic.

Assuming constant $\delta_{seawater}$ led to inconsistent paleotemperature values, as δcarb variations couldn't be explained by temperature alone without suggesting implausible temperature changes (see next slide).

δ^{18}O: IS IT A PALEOTEMPERATURE PROXY?

Example:

$\delta_{seawater} = 0$ $\delta_{carb} = 5$

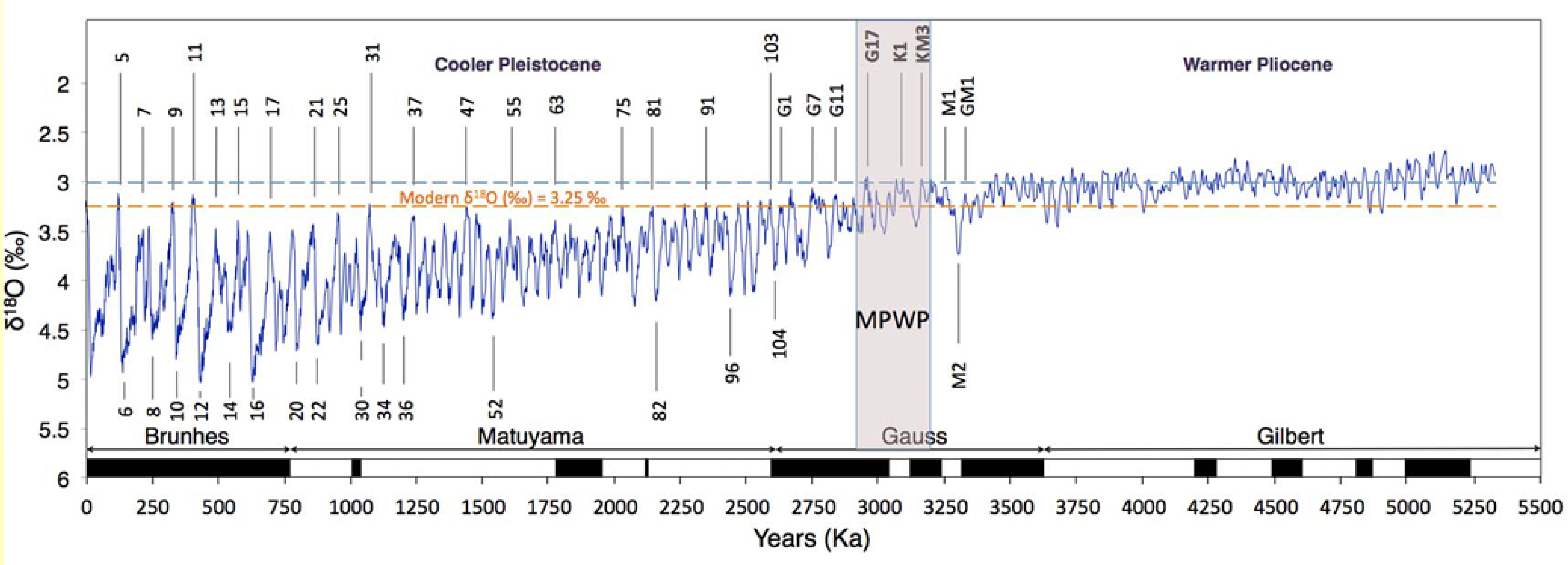
$T = 17-4.52(5-0)+0.03(5-0)^2=17-22.6+0.75= -4.85$

$\delta_{seawater} = 0$ $\delta_{carb} = 3$

$T = 17-4.52(3-0)+0.03(3-0)^2=17-13.9+0.27=3.37$

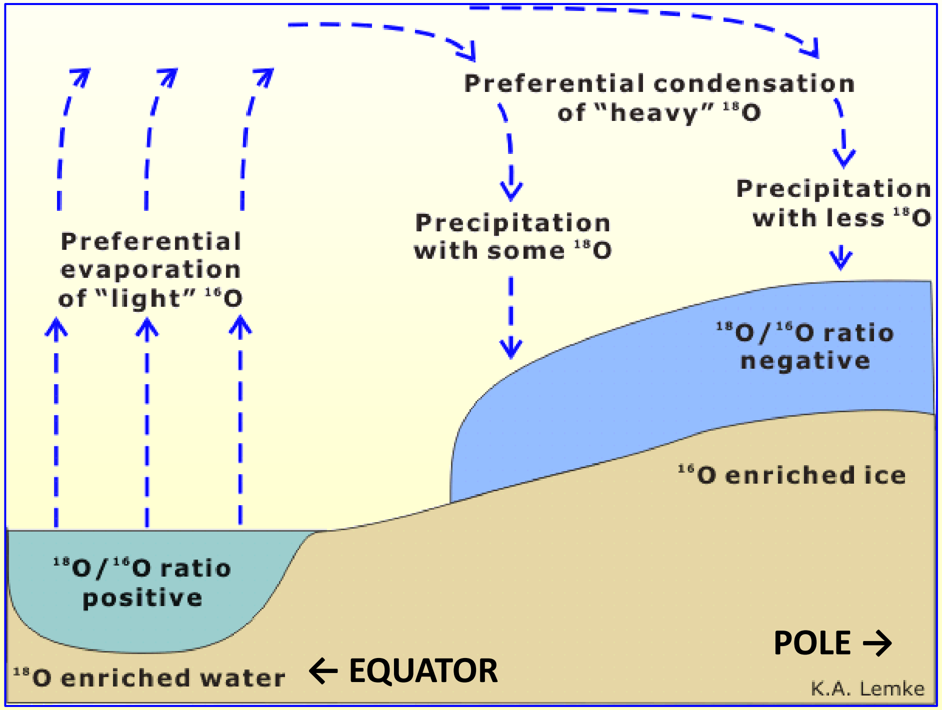
ΔT=4.7 – (-1.5)= 8.2 °C

Estimated by other proxies ca. 3°C



GLACIAL EFFECT

It was thought that the growth and melting of Pleistocene ice caps (waxing and waning) must have influenced the $\delta_{seawater.}$ and $\delta_{carb.}$



Isotopic Fractionation of Oxygen Between Equator and Poles during glacial periods

GLACIAL PERIODS

Ice Sheet Growth.

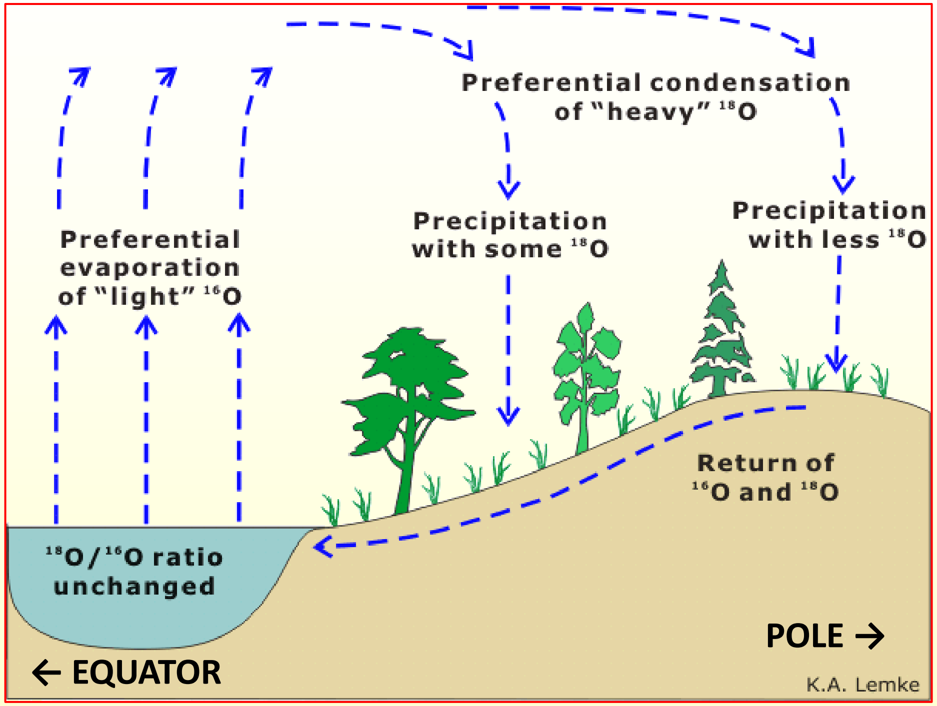
During glaciation, large amounts of water, enriched in the lighter isotope ^{16}O, are trapped in ice sheets. This leaves the ocean relatively enriched in the heavier isotope ^{18}O, increasing the $\delta^{18}O$ value in seawater ($\boldsymbol{\delta}_{seawater}$). As a result, the calcium carbonate ($CaCO_3$) formed by foraminifera reflects higher $\delta^{18}O$ values ($\boldsymbol{\delta}_{carb}$).

GLACIAL EFFECT

DEGLACIATION + INTERGLACIAL PERIODS

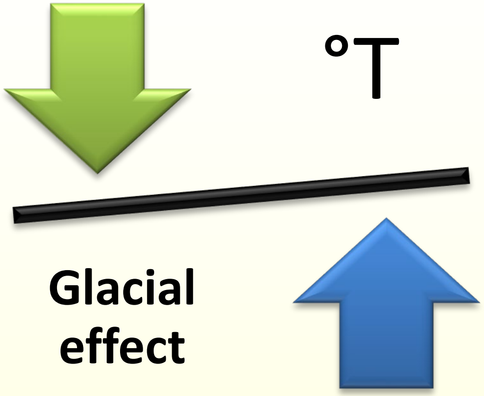
Ice Sheet Melting.

When ice sheets melt, ^{16}O-rich water is released back into the ocean, lowering the δ^{18}O value of seawater ($\delta_{seawater}$). Consequently, the δ^{18}O values recorded in foraminifera shells decrease, reflecting this change in seawater composition (δ_{carb}). The "light" H_2O, sequestered at the poles in the glacial, will return to the sea, the sea level will rise and the average composition of the $\delta_{seawater}$ will "lighten“.



Isotopic Fractionation of Oxygen Between Equator and Poles during interglacial periods

HOW TO QUANTIFY THE GLACIAL EFFECT



By the 1960s, the influence of glacial effects on $\delta^{18}O$ values was undeniable. The challenge was determining whether the glacial effect was more significant than temperature in shaping $\delta^{18}O$ values.

The $\delta^{18}O$ of marine carbonates follows these rules:

$\delta^{18}O$ increases as temperature decreases and ice caps grow.

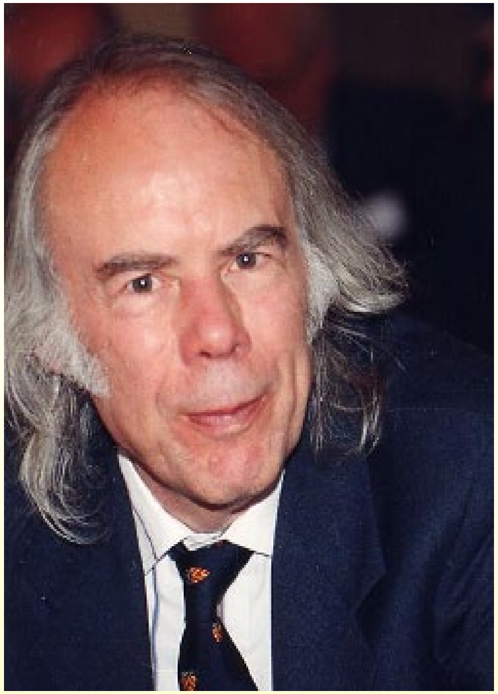
$\delta^{18}O_{carb}$ > ↓ **°T**
↑ **ICE CAP**

$\delta^{18}O$ decreases as temperature rises and ice caps shrink.

$\delta^{18}O_{carb}$ < ↑ **°T**
↓ **ICE CAP**

During this "impasse," another prominent figure in modern Earth Sciences emerged.

NICK SHACKLETON'S IDEA

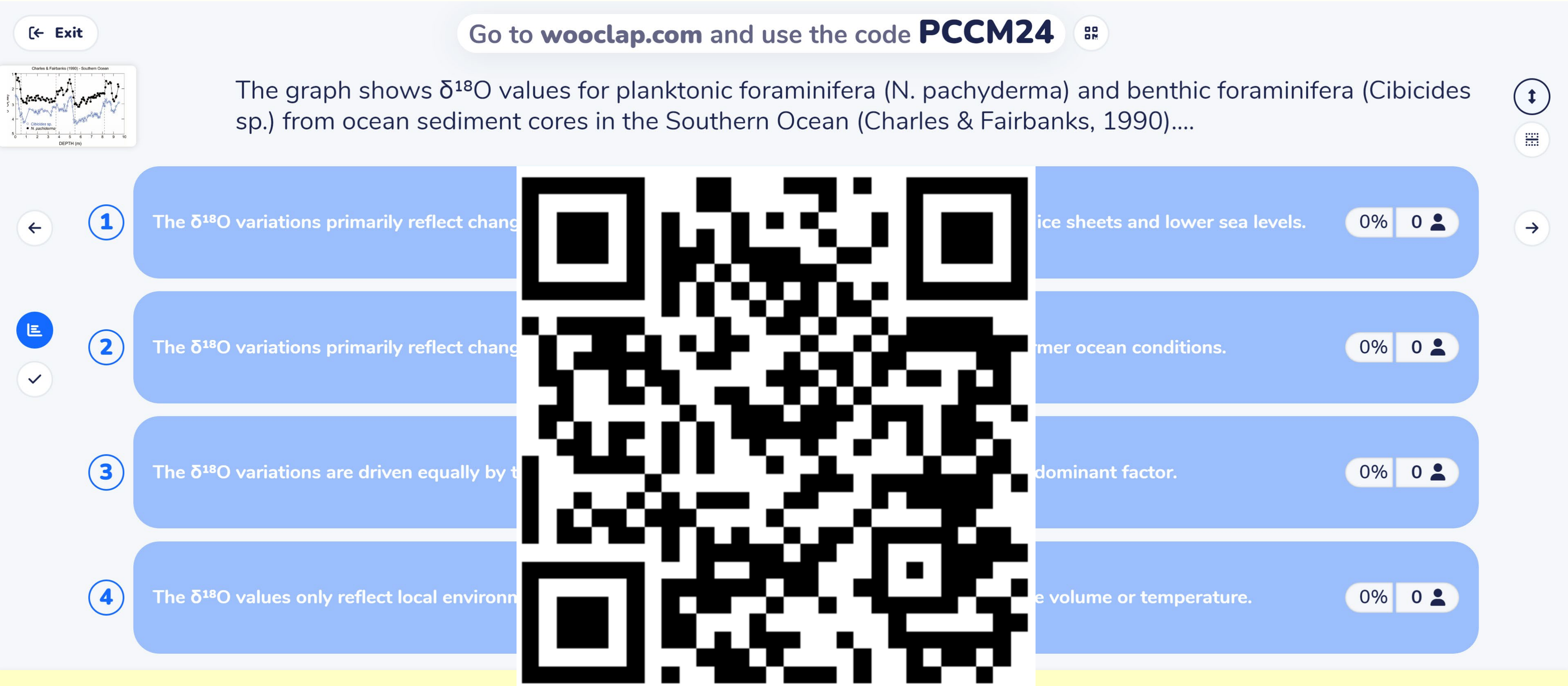


At Cambridge University, a young student named Nick Shackleton (1937-2006), with a background in Physics and a family legacy in geology and Antarctic exploration, was not convinced by Urey and Emiliani's interpretations. **He believed that the glacial effect was far more significant than temperature in shaping the $\delta^{18}O$ of planktonic foraminifera**. Shackleton made fundamental contributions to many topics in this field. He was knighted by the Queen of England, awarded the Crafoord Prize in 1995, and received an the PhD honorary degree in Geology from the University of Padua.

The simple and brilliant idea:
Study the isotopic composition of benthic foraminifera, which live on the ocean floor where temperatures remain nearly constant during glacial and interglacial periods.

Let's compare the results!

The graph shows δ¹⁸O values for planktonic foraminifera (*N. pachyderma*) and benthic foraminifera (*Cibicides* sp.) from ocean sediment cores in the Southern Ocean (Charles & Fairbanks, 1990). Which of the following statements best explains the primary driver of the observed δ¹⁸O variations in the graph?

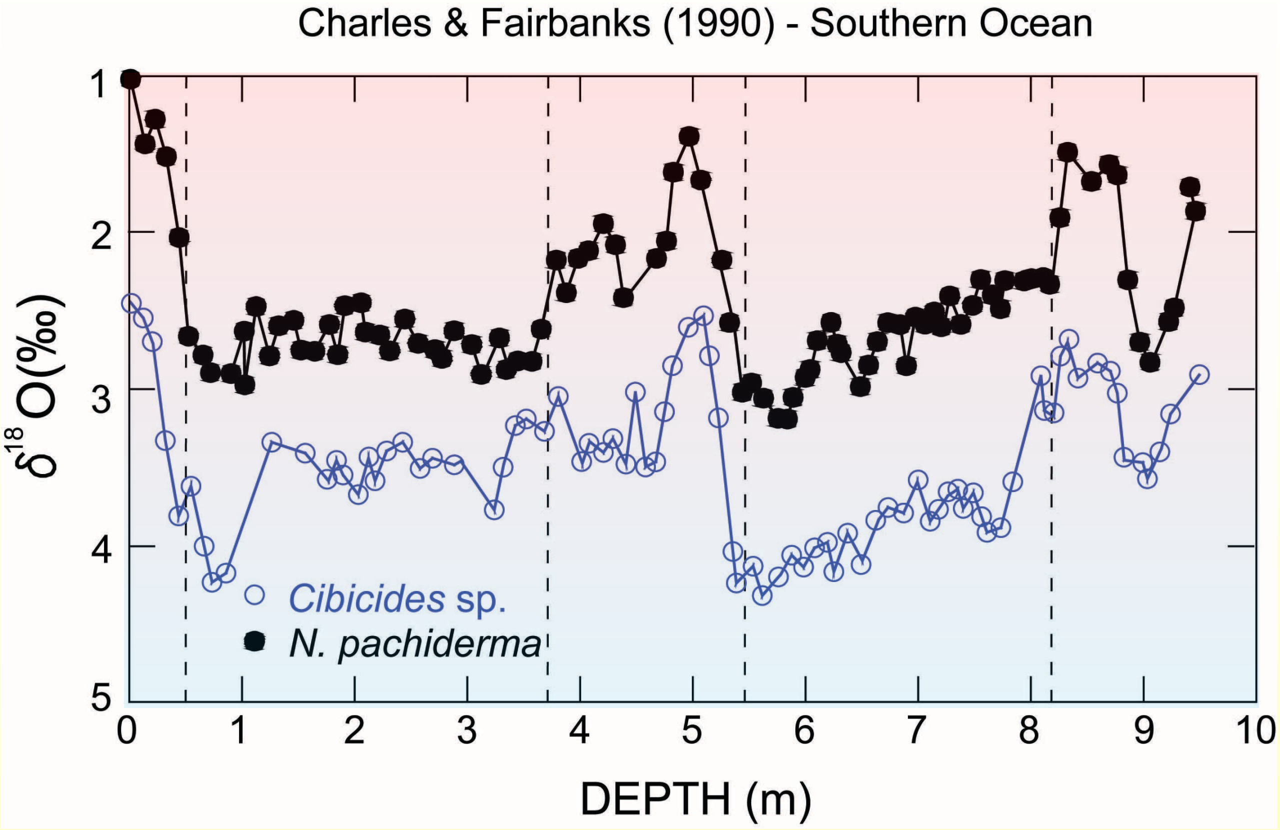


The graph shows δ¹⁸O values for planktonic foraminifera (N. pachyderma) and benthic foraminifera (Cibicides sp.) from ocean sediment cores in the Southern Ocean (Charles & Fairbanks, 1990)....

1. The δ¹⁸O variations primarily reflect chang … ice sheets and lower sea levels. 0% 0
2. The δ¹⁸O variations primarily reflect chang … mer ocean conditions. 0% 0
3. The δ¹⁸O variations are driven equally by t … dominant factor. 0% 0
4. The δ¹⁸O values only reflect local environn … e volume or temperature. 0% 0

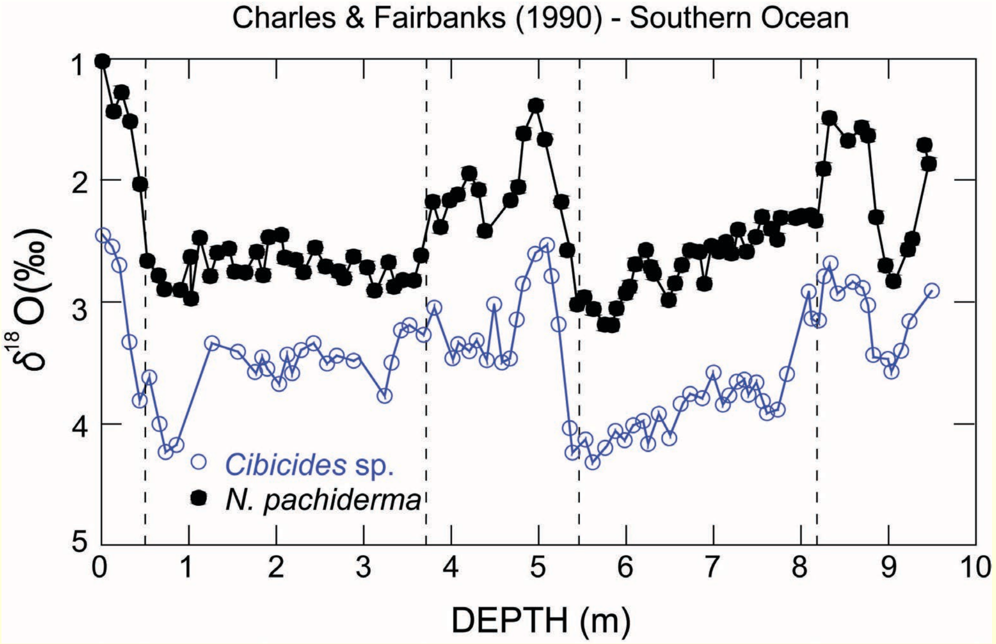
https://app.wooclap.com/events/PCCM24/0

DEEP BENTHIC FORAMINIFERA ISOTOPES - 1

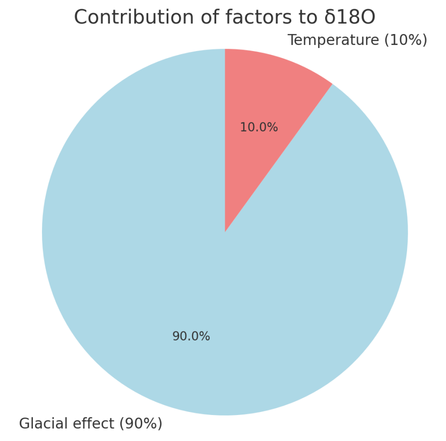


1) The isotopic values of planktonic and benthic foraminifera come from the same sample (direct correlation).
2) The values covary perfectly, likely reflecting the same global phenomenon.
3) Benthic δ^{18}O values are systematically "heavier" than those of planktonic.
4) The curve shows a cyclical trend of interglacial and glacial cycles.

DEEP BENTHIC FORAMINIFERA ISOTOPES - 2



Values of stable oxygen isotopes in the calcite of an epiphaunal benthic foraminifer (○) and of a planktonic foraminifer (●) in the V22-108 core of the Southern Ocean (40 °S).



Benthic foraminifera, living in near-constant temperatures, **show the same δ^{18}O variations as planktonic foraminifera**, which experience large surface temperature changes during glacial-interglacial cycles.
The understanding that **temperature contributes about 10% and the glacial effect accounts for 90% of the δ^{18}O** signal was achieved through a combination of paleoclimatic studies, mathematical models, and analyses of climate proxies.

…ANOTHER IDEA…shifting the perspective

Variations in $\delta^{18}O$ of benthic foraminifera provide a window into the history of ice caps.

Instead of focusing on temperature, which we assume remained stable near zero on the ocean floor, we solve the paleotemperature equation by focusing on $\delta_{seawater}$.

This shift allows us to directly trace the changes in $\delta^{18}O_{seawater}$ and, in turn, the fluctuations in ice volume.

$$T = 17-4{,}52\,(\delta_{carb}-\delta_{seawater})+0{,}03\,(\delta_{carb}-\delta_{seawater})^2$$

1‰ $\delta^{18}O$

~100m sea-level

~4°C temperature

HOW TO ESTIMATE THE CHANGE IN ICE VOLUME AND SEA LEVEL FROM A VARIATION IN $\delta^{18}O$?

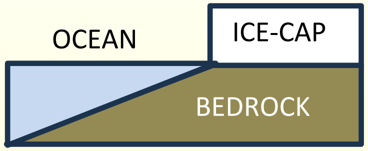
1. **Empirical relationship between $\delta^{18}O$ and ice volume:**

This relationship has been established by **studying marine sediment cores and comparing $\delta^{18}O$ records with independent data on past sea levels** (from ancient shorelines, coral terraces, and other geological markers).

In practice:

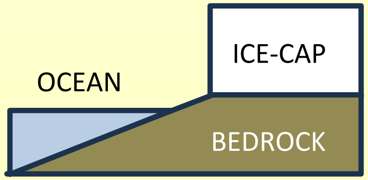
- An **increase of about 1‰ in $\delta^{18}O$** in marine sediments corresponds to a **sea level drop of about 120 meters** and a **significant increase in the size of ice sheets**.
- This ratio has been determined by comparing glacial and interglacial cycles documented **through isotopic composition and sea level changes**.

INTERGLACIAL



1‰ in $\delta^{18}O \approx 120$m

GLACIAL



HOW TO ESTIMATE THE CHANGE IN ICE VOLUME AND SEA LEVEL FROM A VARIATION IN δ^{18}O?

2. Separating the temperature effect:

To accurately use δ^{18}O changes to estimate ice volume/sea level, the temperature effect must be separated. δ^{18}O is influenced by:

- **Ocean temperature**: A change of 1°C results in a change of about **0.22‰ in δ^{18}O**.
- **Ice volume/sea level**: The remaining change in δ^{18}O is due to the growth or melting of ice sheets.

When a δ^{18}O variation is observed, the temperature component (often determined through independent proxies) needs to be subtracted to isolate the ice volume effect.

3. Converting δ^{18}O into ice volume:

Once the glacial effect in δ^{18}O is isolated, you can estimate the change in ice volume as follows:

- For every **1‰ increase in δ^{18}O** due to ice volume, the sea level drops by approximately **120 meters**.

Practical example:

Given data:

- **Observed $\delta^{18}O$** = -1‰
- **$\delta^{18}O$ variation due to temperature** = -0.2‰ (from independent proxies)
- The goal is to calculate the change in sea level.

Step 1: Isolate the glacial component of $\delta^{18}O$The observed $\delta^{18}O$ reflects both the ice volume (glacial) component and the temperature component. To estimate the glacial effect, we subtract the temperature component from the total observed value.

$\delta^{18}O_{glacial}=\delta^{18}O_{measured}-\delta^{18}O_{temperature}$
$\delta^{18}O_{glacial}= -1‰-(-0.2‰)=-1‰+0.2‰=-0.8‰$

Step 2: Use the empirical relationship between $\delta^{18}O$ and sea level
We know that **1‰** variation in glacial $\delta^{18}O$ corresponds to a sea level change of **120 meters**. So, we can calculate the sea level change using the proportion:

Sea level change$=120\times\delta^{18}O_{glacial}$
Sea level change$=120\times(0.8)=96$ meters

SUMMARY: δ^{18}O IN FORAMS

The isotopic composition of foraminifera calcite (δ_{carb}), both planktonic and benthic, depends on temperature (T) and the isotopic content of the surrounding marine water ($\delta_{seawater}$).

$$T = 17 - 4{,}52\,(\delta_{carb} - \delta_{seawater}) + 0{,}03\,(\delta_{carb} - \delta_{seawater})^2$$

The isotopic composition of ocean waters varies regionally based on evaporation-precipitation conditions and freshwater inputs from runoff and distillation.

The isotopic composition of marine waters changes over geological time, with the glacial effect being a key factor.

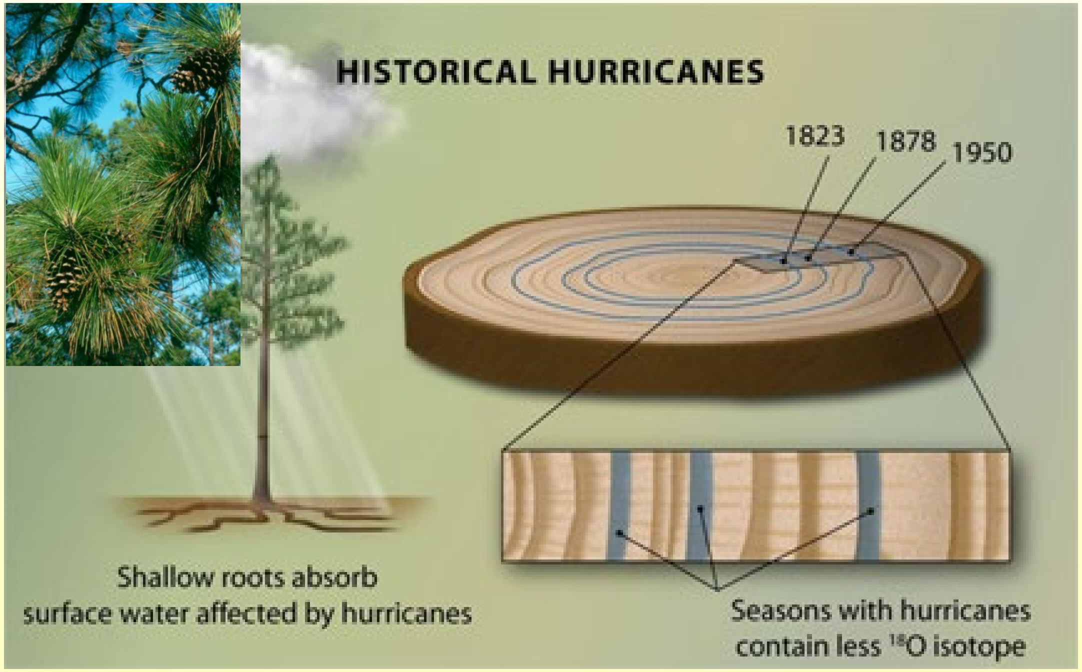
Foraminifera are crucial because their $^{18}O/^{16}O$ ratio reflects both temperature and the isotopic composition of their habitat water (accounting for a minor offset), making them excellent archives of paleoenvironmental data.

NON ONLY FORAMS…

In fossils with CaCO3 skeletons, **corals** and Mesozoic **belemnites** are widely used. **Calcareous nannofossils**, though, are less common due to their small size and deviation from Urey's equation. Siliceous shells, like **diatoms**, are sometimes used. Oxygen analysis is also possible in **organic matter**, like plant tissues, and in **ice**.

δ^{18}O IN TREES

Longleaf pine roots absorb surface water influenced by precipitation. Hurricanes produce rainfall with lighter oxygen isotopes compared to smaller storms. Tree rings with lighter isotopes provide a record of past hurricanes.



Rationale: Under normal conditions, evapotranspiration enriches the soil with ^{18}O. During hurricanes, the soil shows a relative depletion of ^{18}O.

Oxygen Isotopes in Si_2O

Here is the chemical reaction for the quantitative liberation of oxygen from oxides and silicates using **bromine pentafluoride** (BrF_5):

$$2\ MxOy + 5\ BrF_5 \rightarrow 2\ \overset{\text{solid}}{MO_2F_3} + 5\ \overset{\text{gas}}{Br_2} + 2\ \overset{\text{gas}}{F_2}$$

Where M represents the metal present in the oxide or silicate.

This reaction allows the conversion of oxygen-containing compounds into fluorides that can be easily separated for quantitative analysis.

MASTER ARCHIVES

The main archives for oxygen isotope research are:

•**Ice cores** (e.g., GRIP, GISP2, VOSTOK, EPICA), providing exceptional data from the past 7-800,000 years.

•**Ocean sediments** (e.g., DSDP , ODP, IODP, and land sections), which have transformed our understanding but offer lower resolution data.

POSSIBLE ISSUES

δ^{18}O: THE VITAL EFFECT

$$T = 17-4{,}52\ (\delta_{carb}-\delta_{seawater})+0{,}03\ (\delta_{carb}-\delta_{seawater})^2$$

The paleotemperature equation **for inorganic calcite precipitation** works well, as isotope fractionation linked to temperature is assumed to occur in equilibrium.

VITAL EFFECT: Calcite used in paleoenvironmental reconstructions is formed within living organisms through processes (biomineralization) that are not fully understood.

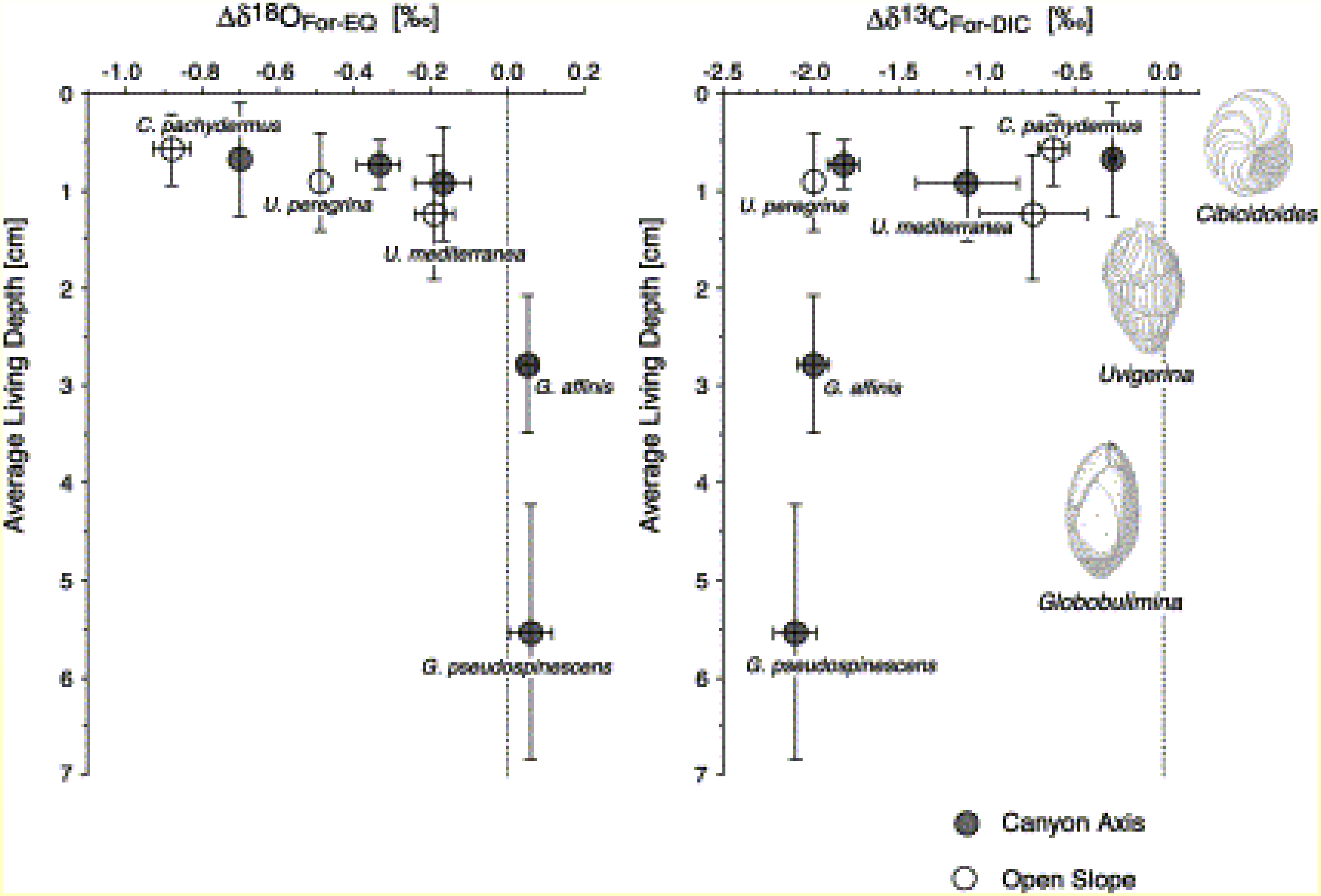
Some organisms produce calcite in isotopic equilibrium, while others, like certain coccoliths and echinids, show unpredictable imbalances.

Experimental data shows that many planktonic foraminifera form calcite in equilibrium or with a consistent deviation that can be corrected. Therefore, individuals of the same species and size are analyzed.

Experimental data indicates that numerous planktonic foraminifera produce the calcite for their shells **either in equilibrium or with a consistent deviation that can be adjusted for.**

→ **individuals of the same species and of the same size are analyzed**.

$\delta^{18}O$: THE VITAL EFFECT

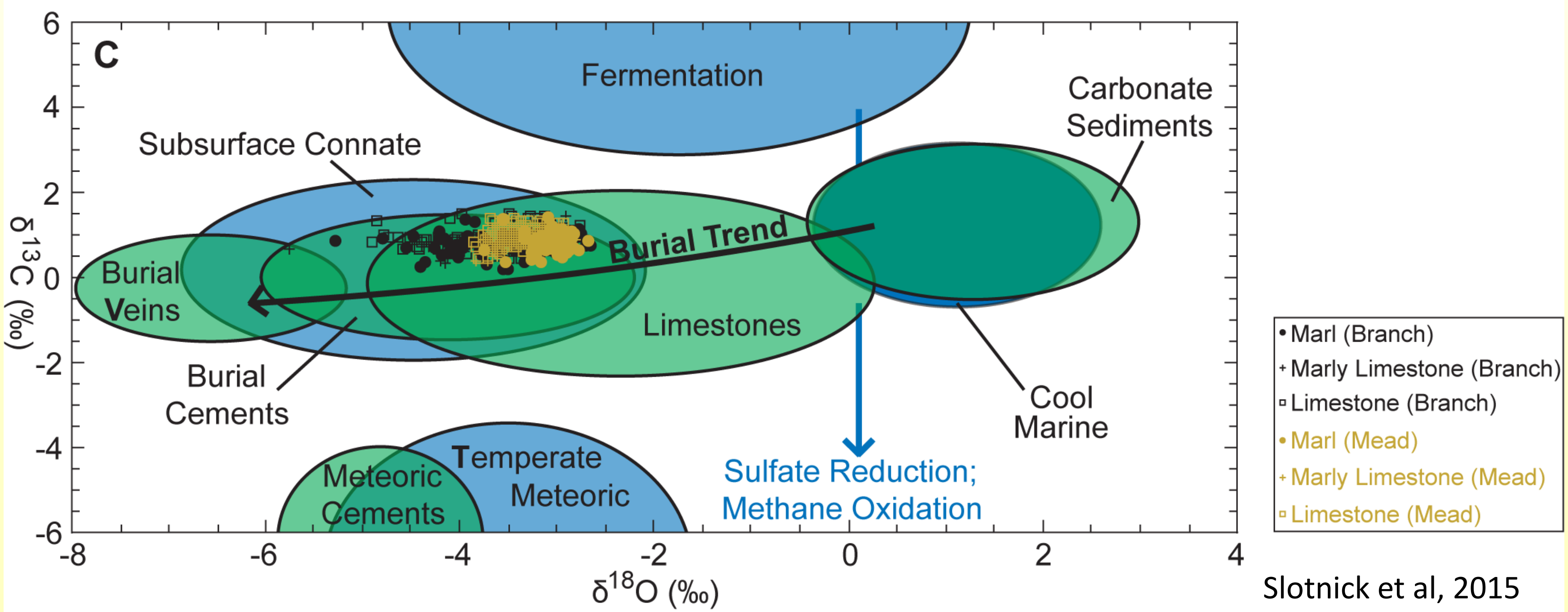


Schmiedl et al., 2004

$\delta^{18}O$: DIAGENESIS

$$T = 17-4{,}52\,(\delta_{carb}-\delta_{seawater})+0{,}03\,(\delta_{carb}-\delta_{seawater})^2$$

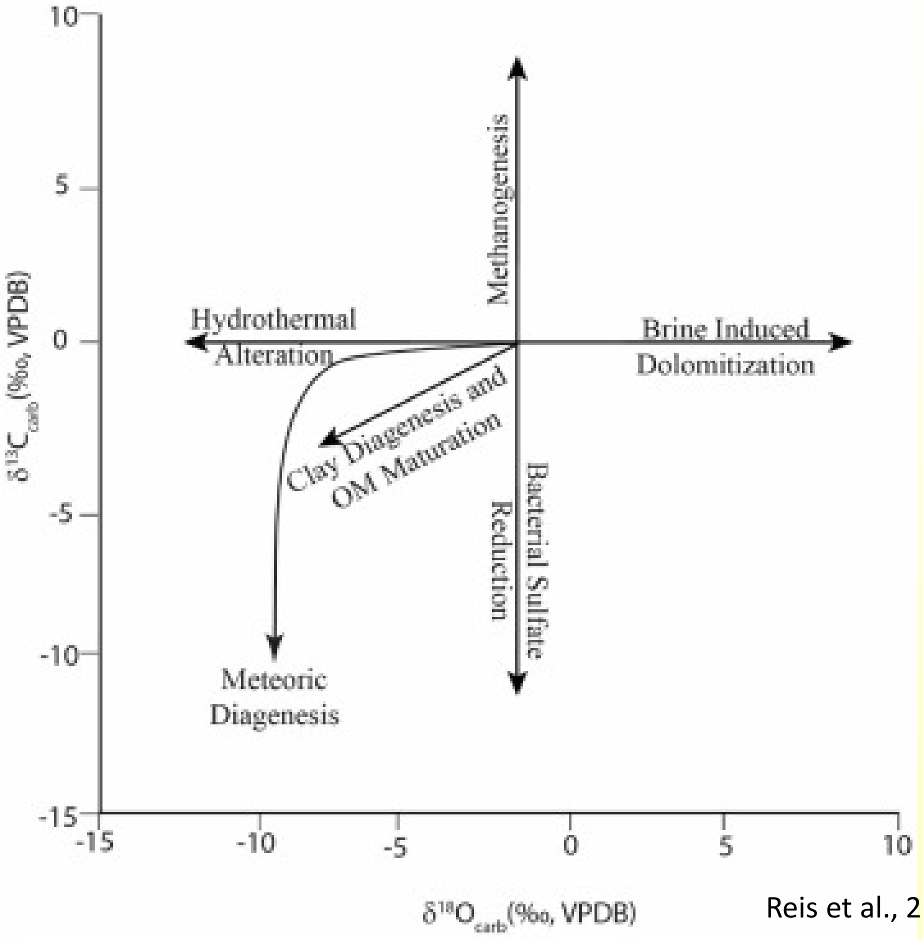
Isotope geochemistry, particularly with oxygen isotopes, faces several challenges. **A major concern is diagenesis**, which can alter the original $\delta^{18}O_{carb}$ values. To ensure accuracy, samples must be exceptionally well-preserved to avoid diagenetic changes.



Slotnick et al, 2015

Note also the significant depletion in ^{18}O relative to typical carbonate in unlithified marine sediment. The stable isotope compositions are consistent with significant local dissolution and reprecipitation of carbonate during burial. Fields of carbonate stable isotope composition are from Hudson (1977) and Nelson and Campbell (1996).

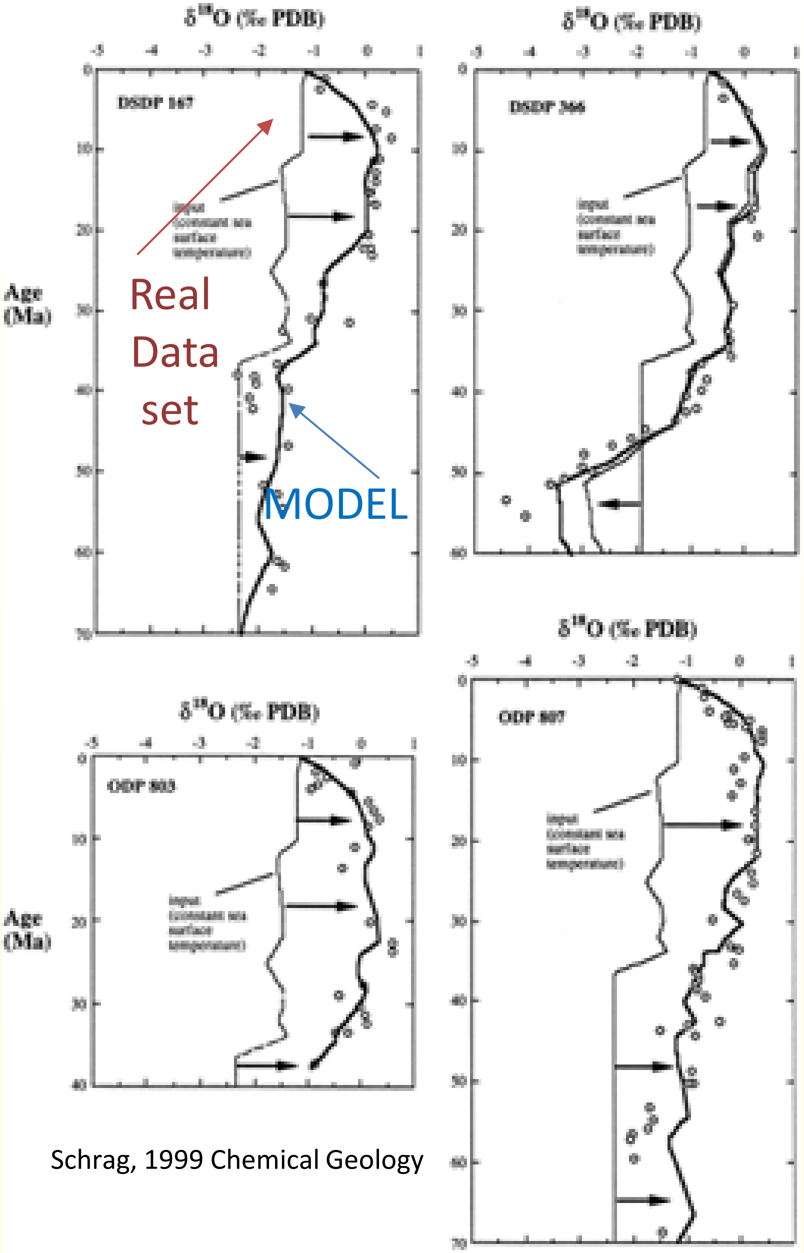
δ^{18}O: DIAGENESIS



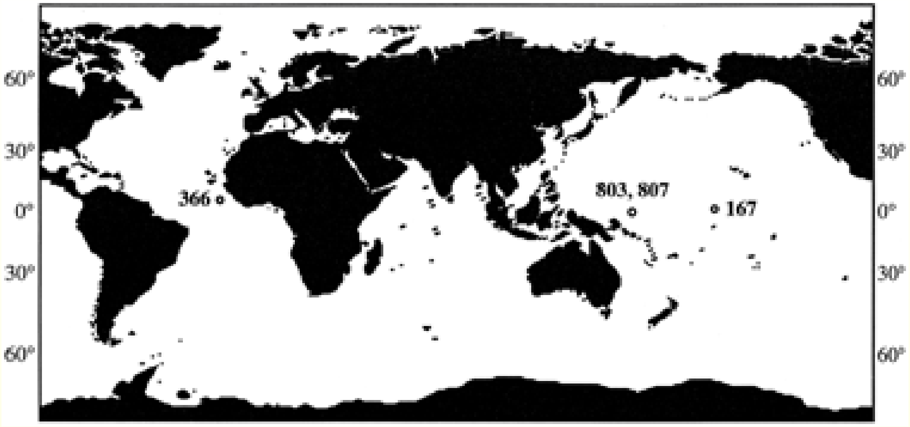
Reis et al., 2019

Schematic of the effects of diagenesis on carbonate sediments. These processes can impact carbonate sediments individually or as a series of events during deposition, burial and exhumation. Generalized trends from Irwin and Curtis (1977); Machel (2004); Swart (2015).

$\delta^{18}O$: DIAGENESIS



Schrag, 1999 Chemical Geology



Comparison between values of $\delta^{18}O$ measured and values obtained from a model assuming that the surface temperatures have remained constant over time (Sites 167, 366, 803 and 807).

ISOTOPES AS A STRATIGRAPHIC TOOL: CHEMOSTRATIGRAPHY

CHEMOSTRATIGRAPHY

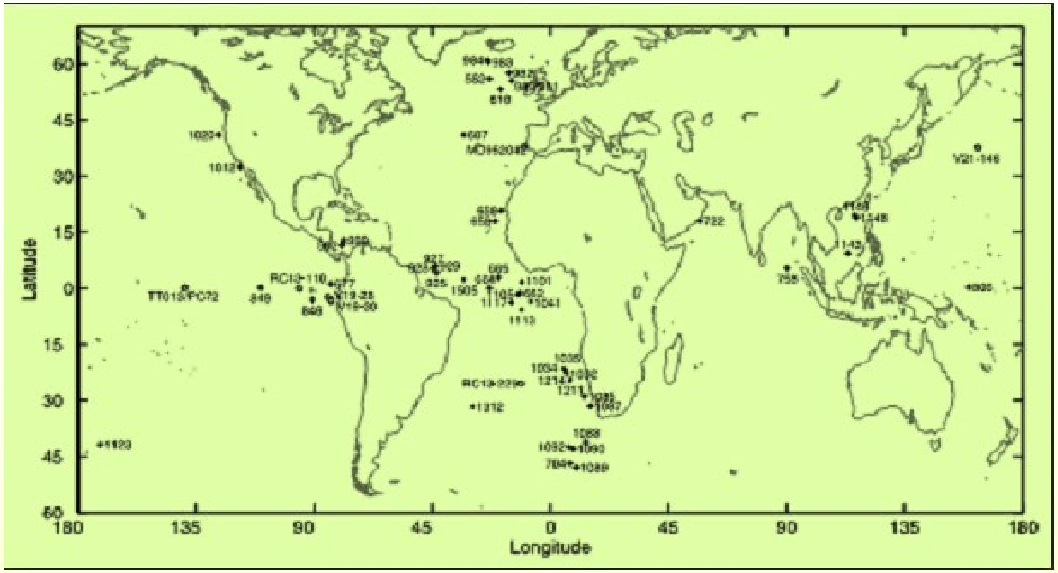
So far, we have focused on interpreting $\delta^{18}O$ in paleoclimatology and paleoceanography. However, $\delta^{18}O$ is also a valuable stratigraphic tool.

Chemostratigraphy allows for the **correlation of individual events** while also enabling **tuning of stratigraphic sequences through the use of stack isotope curves**, helping to synchronize records across different locations.

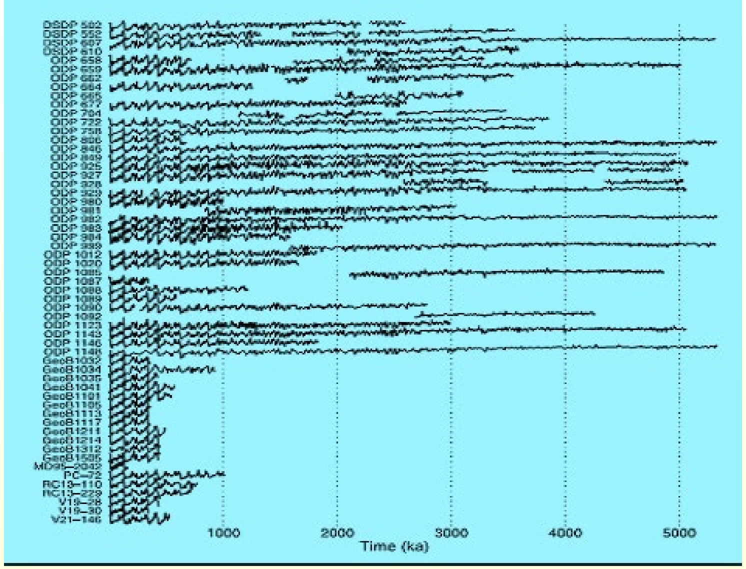
A stack isotopic curve is a composite record created by averaging multiple individual isotope records (typically $\delta^{18}O$ or $\delta^{13}C$) from different sediment cores or other geological samples.
This technique helps to reduce local variations and noise, providing a more reliable and globally representative signal of past climate or environmental changes.
Stack isotopic curves are commonly used in paleoclimatology and stratigraphy to track global trends, such as glacial-interglacial cycles, and serve as reference curves for comparing regional or local data.
One famous example is **the LR04 benthic $\delta^{18}O$ stack**, which provides a detailed record of global ice volume changes over the last 5 million years.

CREATION OF A STACK ISOTOPIC CURVE

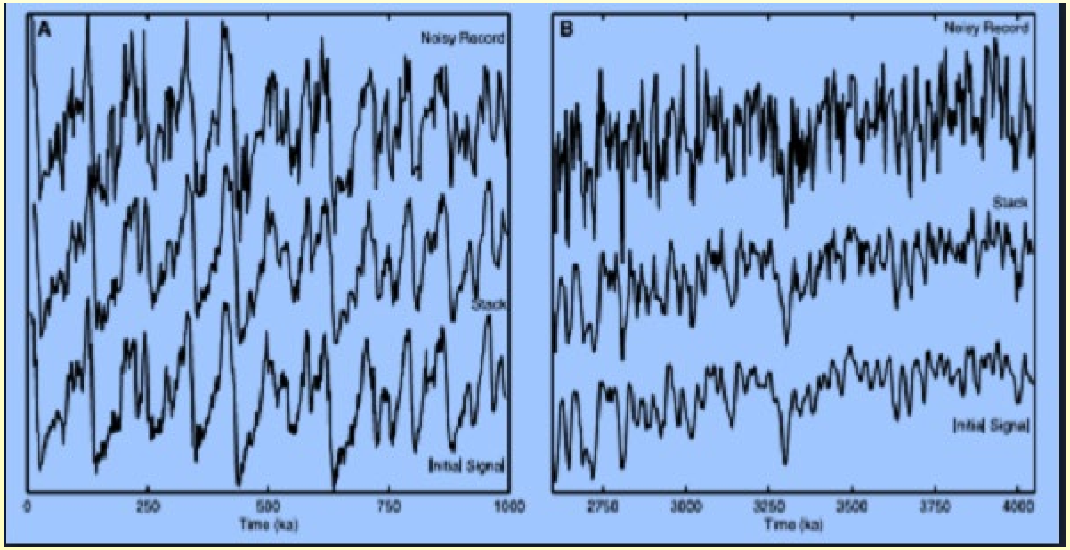
Data collection



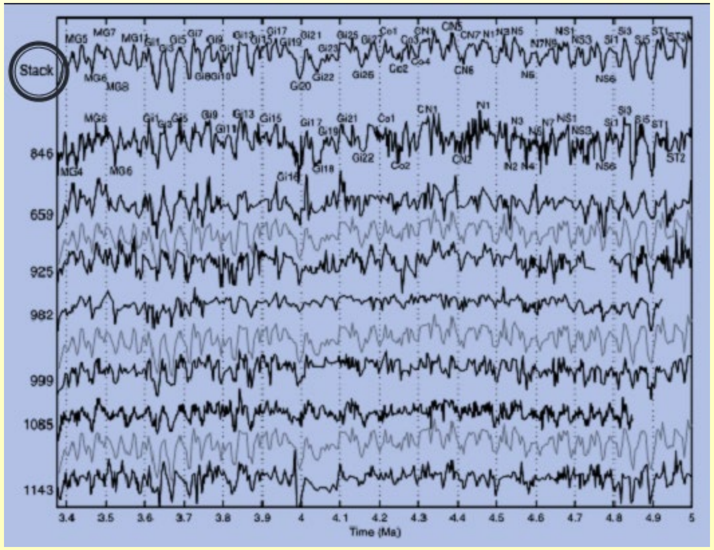
Overlapping



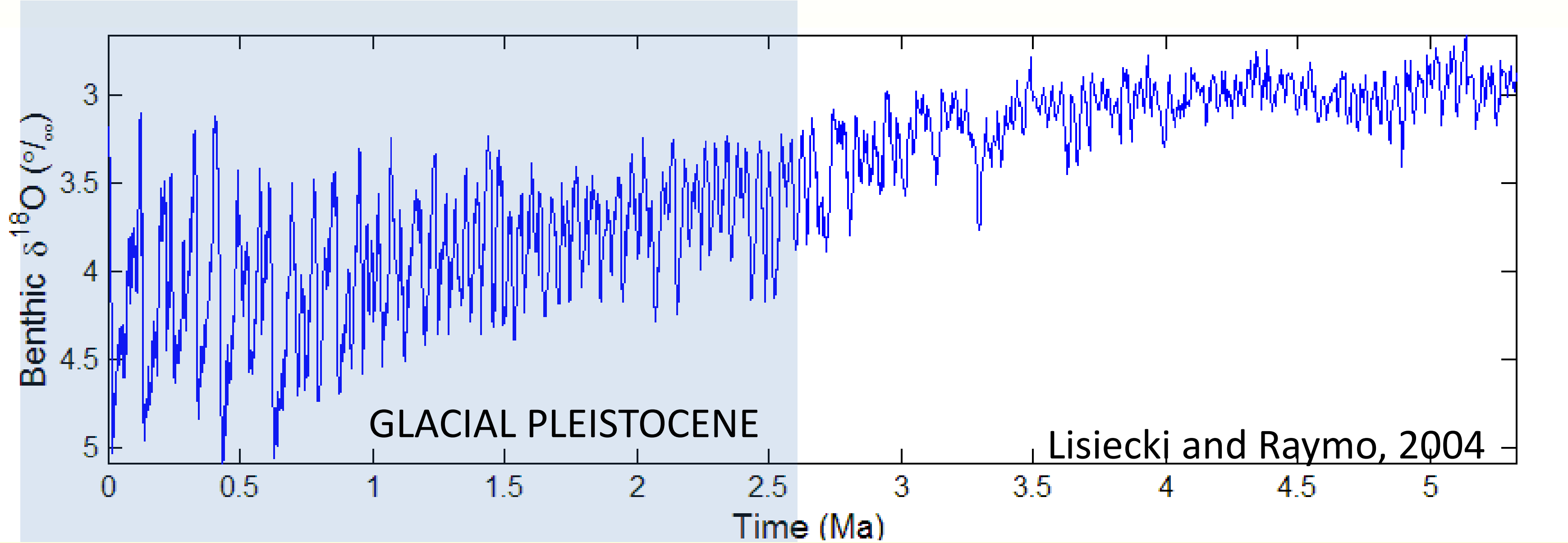
Testing



Results



LR04 stack

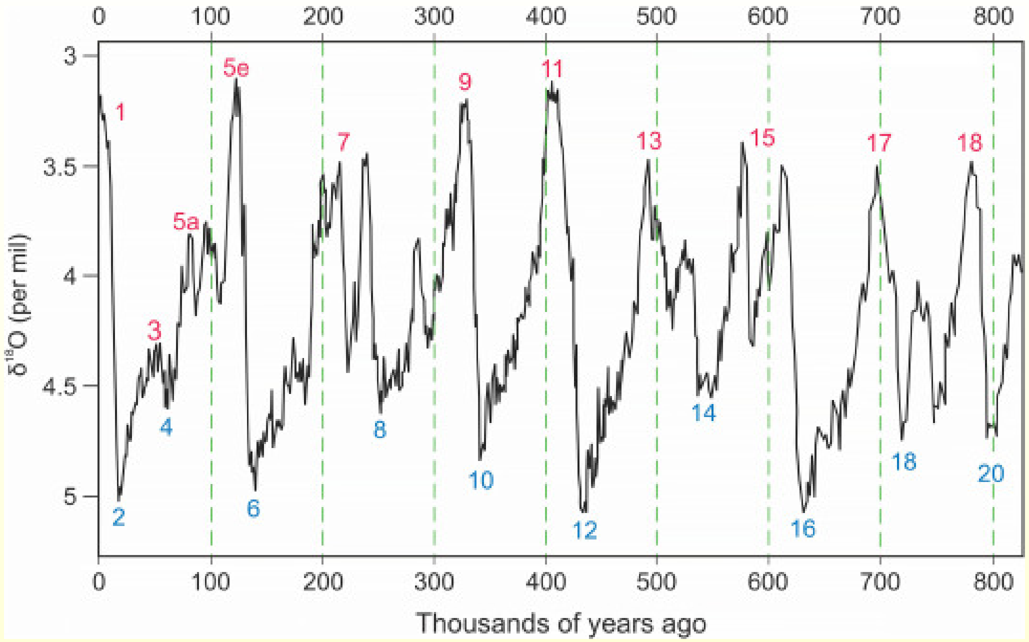


The LR04 stack (Lisiecki and Raymo, 2004) covers 5.3 million years and is an average of 57 globally distributed benthic $\delta^{18}O$ records, which reflect global ice volume and deep ocean temperature.

These records were aligned on a common age model using a graphic correlation technique (Lisiecki and Lisiecki, 2002). Additionally, a new age model for the stack was developed using orbital tuning, combined with constraints from the average sedimentation rates of the 57 records.

NOMENCLATURE OF GLACIAL PLEISTOCENE

The **Marine Isotope Stages (MIS)** are alternating warm and cold periods in Earth's paleoclimate, derived from oxygen isotope data collected from deep-sea sediment cores. These stages are identified by variations in the ratio of oxygen isotopes, specifically $\delta^{18}O$, in foraminifera shells, which reflect changes in global ice volume and ocean temperatures over time.

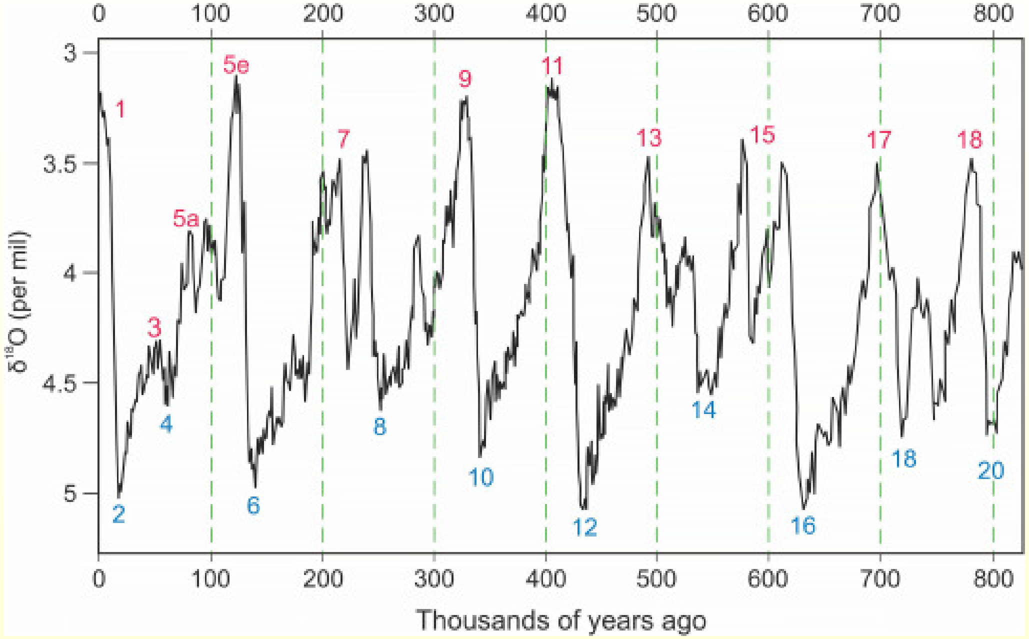


- **Odd-numbered MIS** (e.g., MIS 1, MIS 5) represent **interglacial** periods, which are warmer phases with less ice volume.
- **Even-numbered MIS** (e.g., MIS 2, MIS 6) represent **glacial** periods, which are colder phases with larger ice sheets.

MIS stages provide a globally recognized framework for correlating climatic events across different regions and are often used in stratigraphy to study glacial-interglacial cycles.

NOMENCLATURE OF GLACIAL PLEISTOCENE

The nomenclature of the glacial-interglacial regime refers to the cycles of ice sheet expansion and contraction that occurred during the Quaternary, particularly in the Pleistocene and Holocene. Here are the key terms used to describe these cycles:

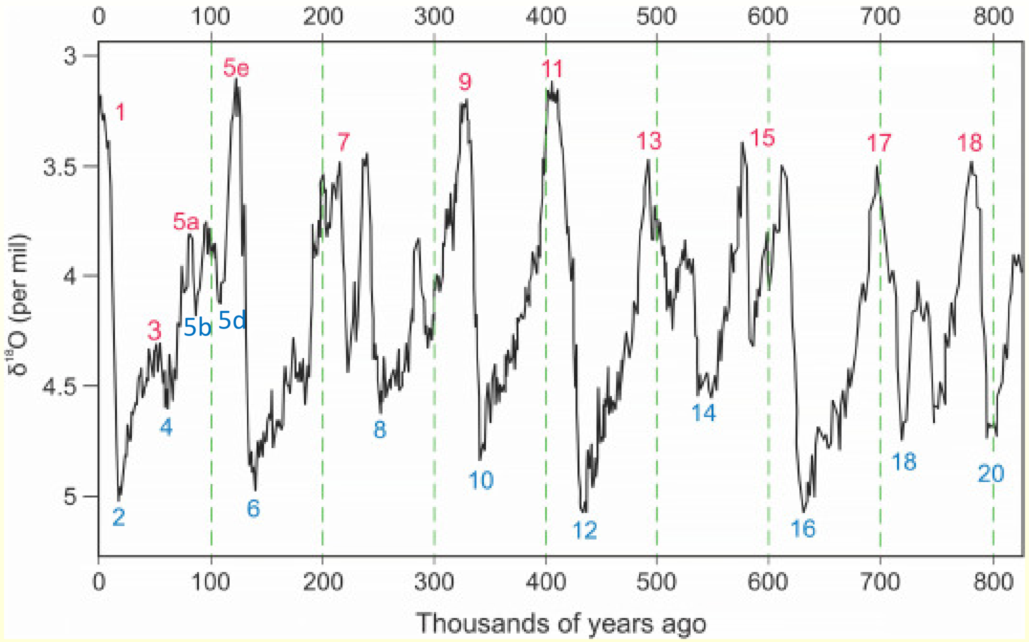


1.Glacial period: A phase of cold climate during which ice sheets expand, covering large continental areas. Sea levels drop, and global temperatures are significantly lower than during interglacial periods.

2.Interglacial period: A warm interval between glacial cycles, where ice sheets retreat, sea levels rise, and global temperatures are higher. The Holocene, the current geological period, is an example of an interglacial.

NOMENCLATURE OF GLACIAL PLEISTOCENE

Stadials and **interstadials**:
Within glacial and interglacial periods, there are shorter climate oscillations:

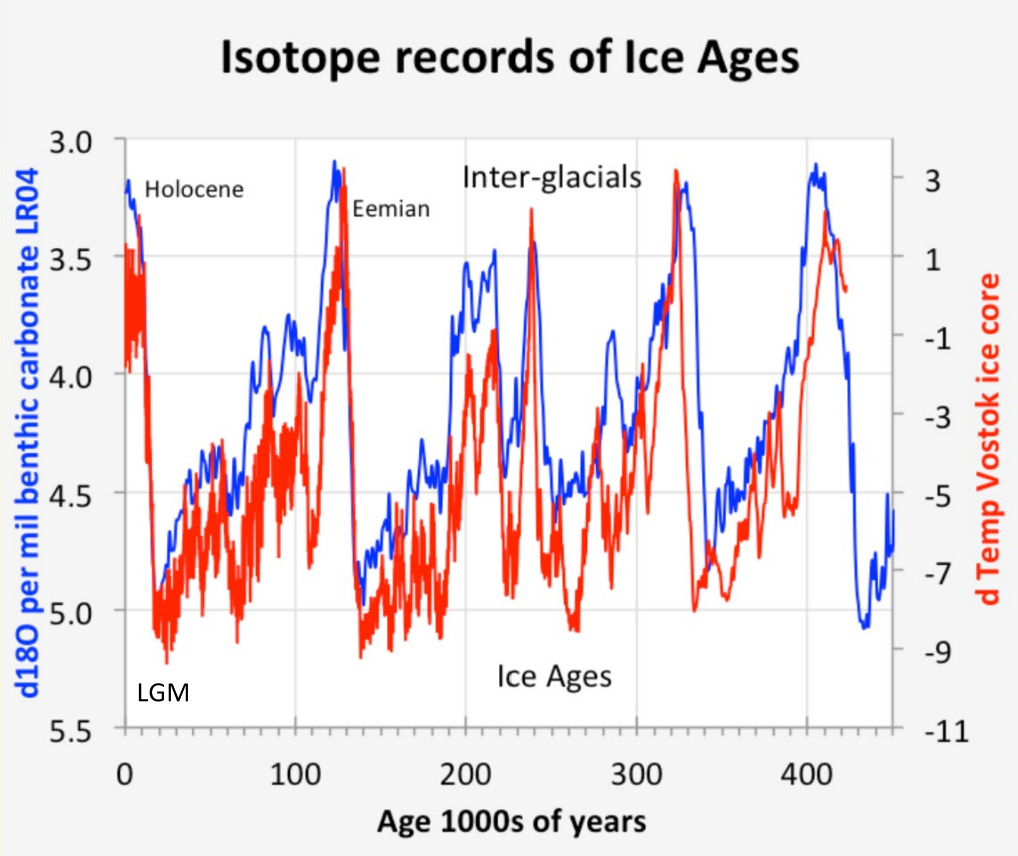


1. **Stadial**: A relatively cold phase within an interglacial period.
2. **Interstadial**: A warmer phase within a glacial period, though not as warm as a full interglacial.

The odd-numbered interstadial MIS 5 contains two stadials (5b, 5d).

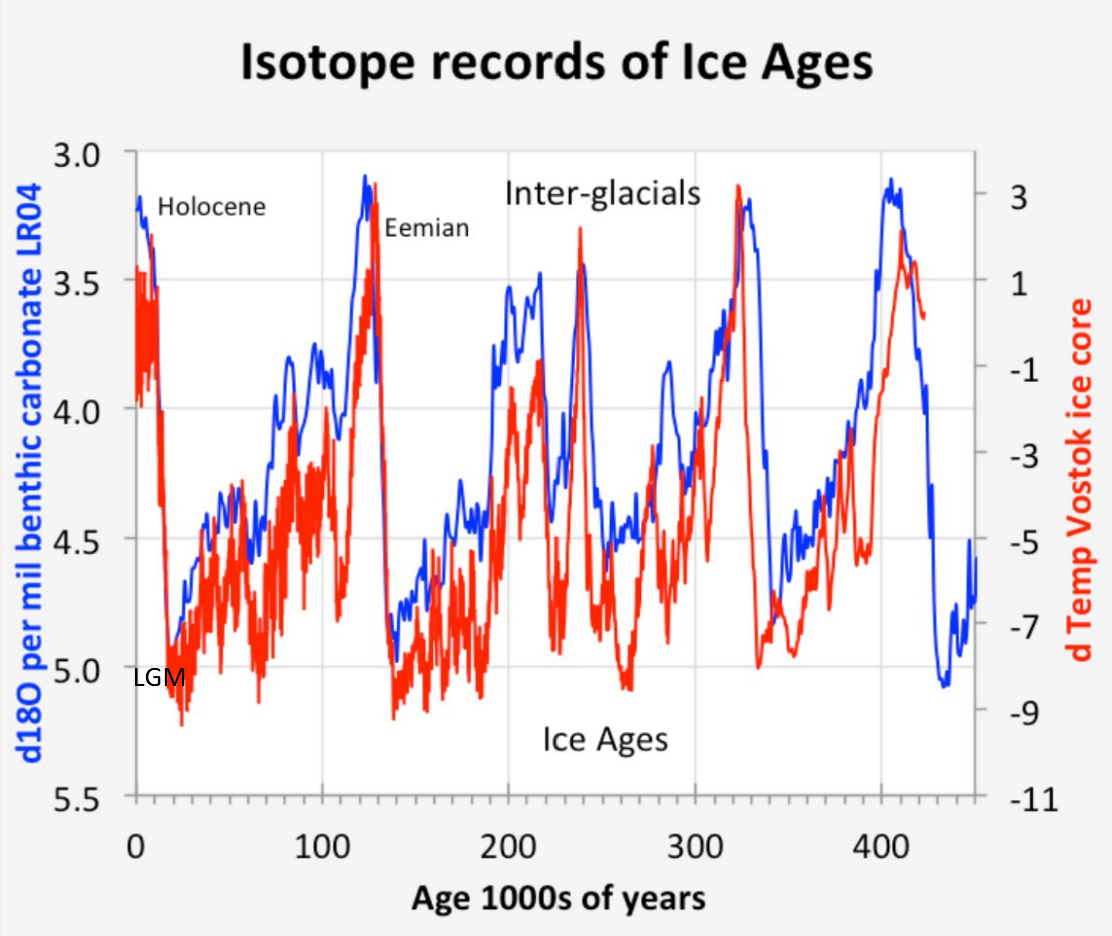
Milankovitch cycles: These describe long-term climate oscillations (based on Earth's eccentricity, obliquity, and axial precession) that control the alternation between glacial and interglacial periods.

δ^{18}O curve: «SAWTOOTH" SHAPE



Over the past million years, oxygen isotope curves show a "sawtooth" pattern: a gradual increase in δ^{18}O values toward a glacial maximum, followed by a rapid decline during deglaciation. This reflects the slow ice sheet buildup and quick collapse.

“GLACIAL TERMINATIONS”

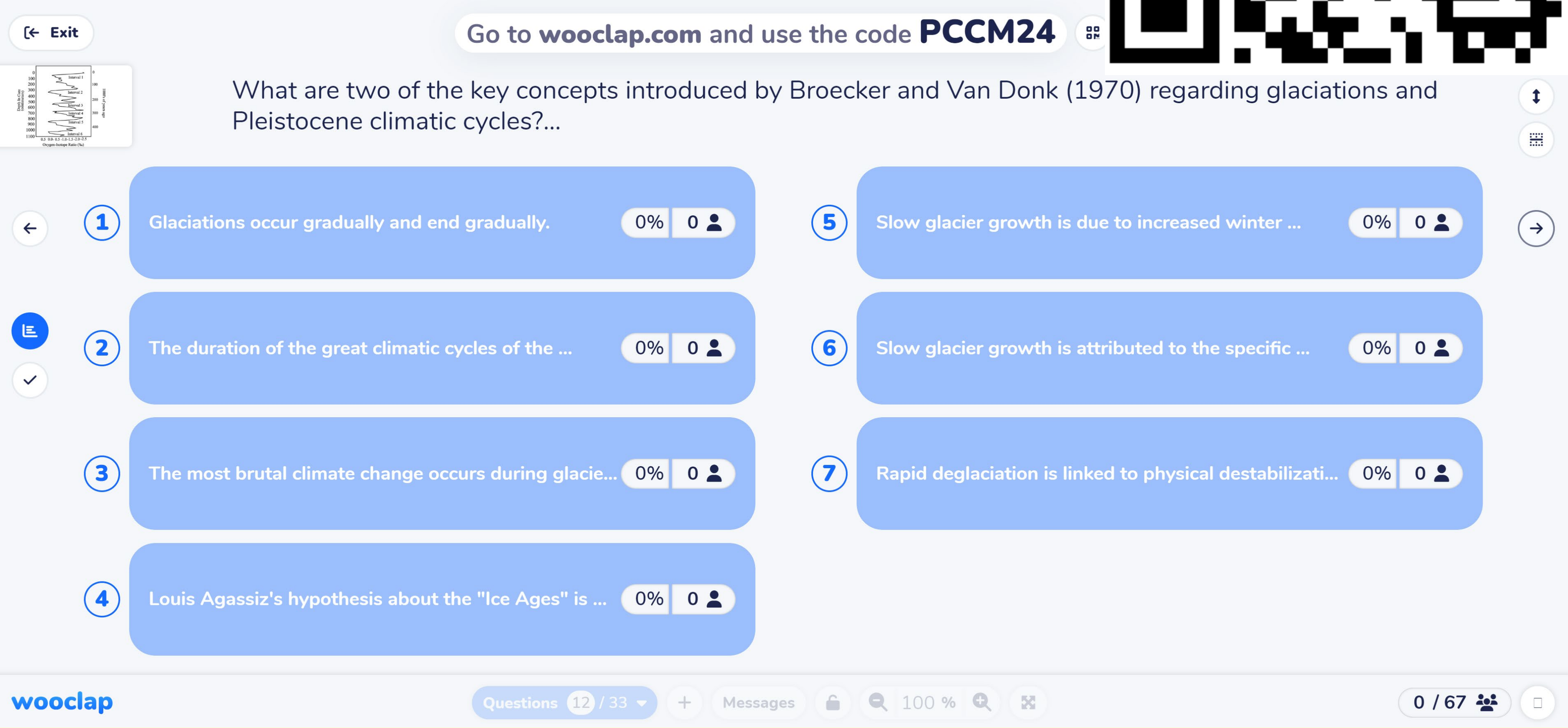


The distinctive isotopic pattern was first identified by **Broecker and Van Donk in 1970,** who coined "**TERMINATION**" to describe the rapid shift from glacial maximum to interglacial conditions. There are 5 true terminations, covering the last 400 Kyr and lasting 80-120 Kyr each.

Terminations are labeled with Roman numerals in reverse order: the most recent deglaciation (20-10 kyr ago) is T I, the second-to-last is T II, and so on.

What are two of the key concepts introduced by Broecker and Van Donk (1970) regarding glaciations and Pleistocene climatic cycles?

In responding to this question, always keep in mind that $\delta^{18}O$ is primarily a proxy for the evolution of the ice cap and, secondarily, temperature.



Go to **wooclap.com** and use the code **PCCM24**

What are two of the key concepts introduced by Broecker and Van Donk (1970) regarding glaciations and Pleistocene climatic cycles?...

1. Glaciations occur gradually and end gradually. 0% 0
2. The duration of the great climatic cycles of the ... 0% 0
3. The most brutal climate change occurs during glacie... 0% 0
4. Louis Agassiz's hypothesis about the "Ice Ages" is ... 0% 0
5. Slow glacier growth is due to increased winter ... 0% 0
6. Slow glacier growth is attributed to the specific ... 0% 0
7. Rapid deglaciation is linked to physical destabilizati... 0% 0

https://app.wooclap.com/events/PCCM24/0

GLACIAL DYNAMICS

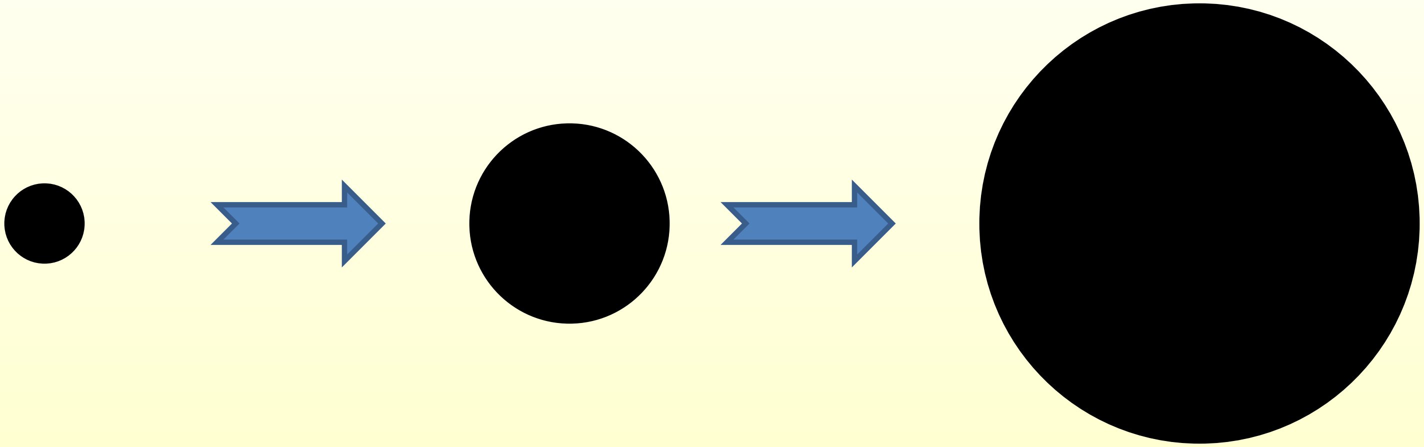
Broecker and Van Donk (1970) introduced two key concepts:

1. **Glaciations** show a **gradual growth followed by an abrupt end (deglaciation)**, forming a "sawtooth" pattern in the isotopic curve.

2. **Pleistocene climatic cycles last around 80-120 kyr**, with the most significant changes occurring during deglaciation, challenging earlier views like those of Louis Agassiz.

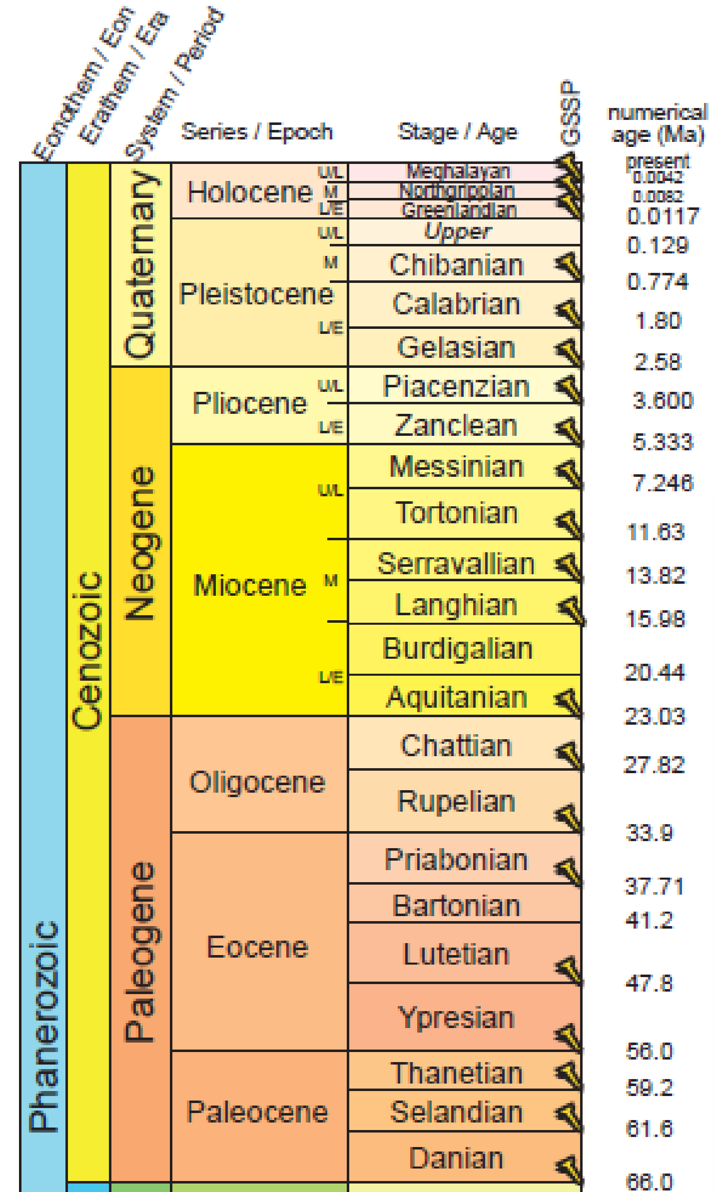
The slow glacier growth is linked to cooler-than-average summers, reducing snowmelt, expanding snow cover, and increasing albedo (positive feedback).

In contrast, rapid deglaciation is likely caused by ice cap destabilization and intense calving events.



THE ISOTOPIC RECORD IN THE GEOLOGICAL DOCUMENTATION OF THE CENOZOIC

SHORT- AND LONG-TERM CLIMATE EVOLUTION IN THE CENOZOIC



Eonothem / Eon	Erathem / Era	System / Period	Series / Epoch		Stage / Age	GSSP	numerical age (Ma)
							present
Phanerozoic	Cenozoic	Quaternary	Holocene	U/L	Meghalayan	✓	0.0042
				M	Northgrippian	✓	0.0082
				L/E	Greenlandian	✓	0.0117
			Pleistocene	U/L	Upper		0.129
				M	Chibanian	✓	0.774
				L/E	Calabrian	✓	1.80
					Gelasian	✓	2.58
		Neogene	Pliocene	U/L	Piacenzian	✓	3.600
				L/E	Zanclean	✓	5.333
			Miocene	U/L	Messinian	✓	7.246
					Tortonian	✓	11.63
				M	Serravallian	✓	13.82
					Langhian	✓	15.98
				L/E	Burdigalian		20.44
					Aquitanian	✓	23.03
		Paleogene	Oligocene		Chattian	✓	27.82
					Rupelian	✓	33.9
			Eocene		Priabonian	✓	37.71
					Bartonian		41.2
					Lutetian	✓	47.8
					Ypresian	✓	56.0
			Paleocene		Thanetian	✓	59.2
					Selandian	✓	61.6
					Danian	✓	66.0

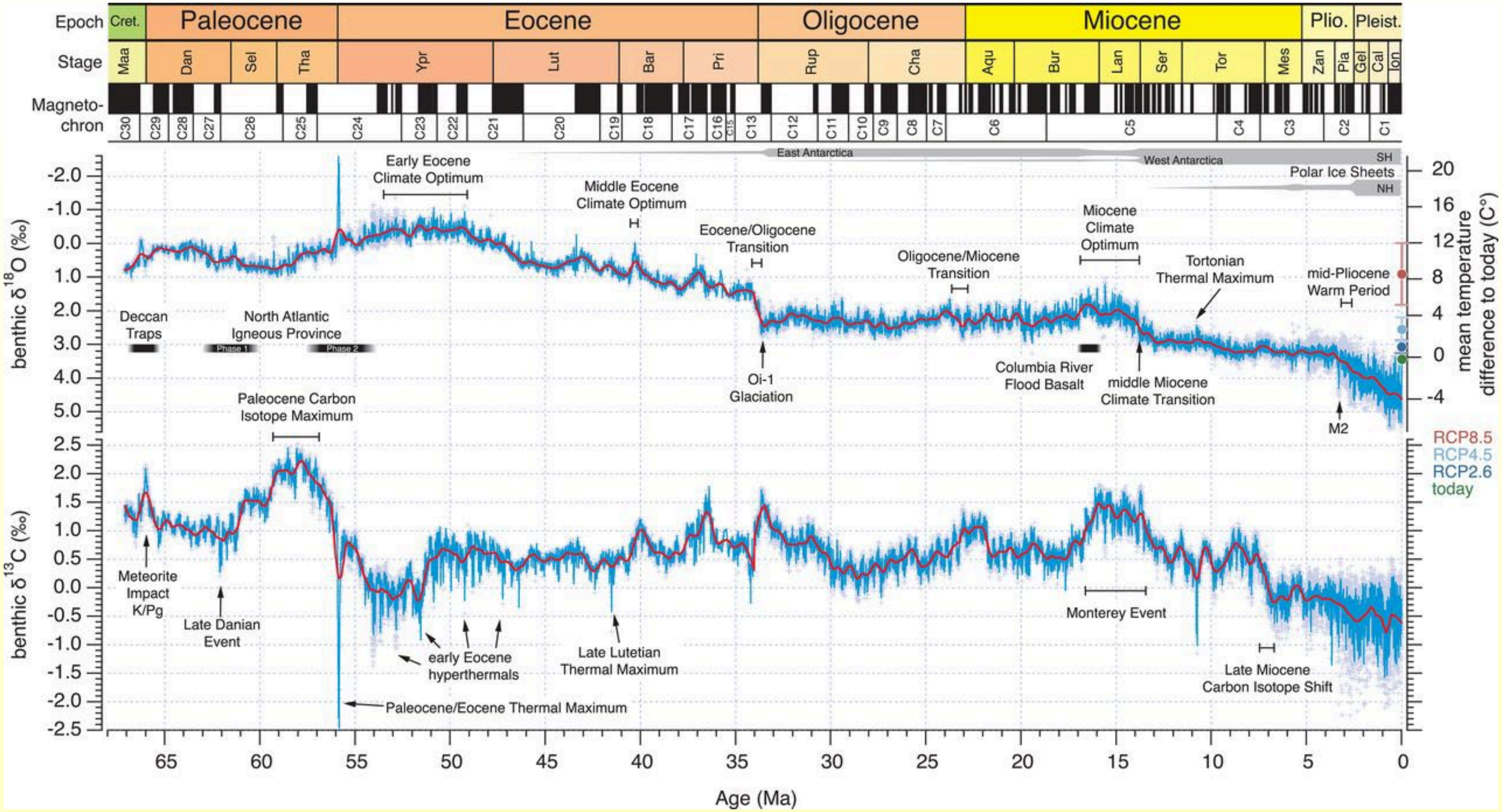
We will analyze the Cenozoic climate using $\delta^{18}O$.

Specifically

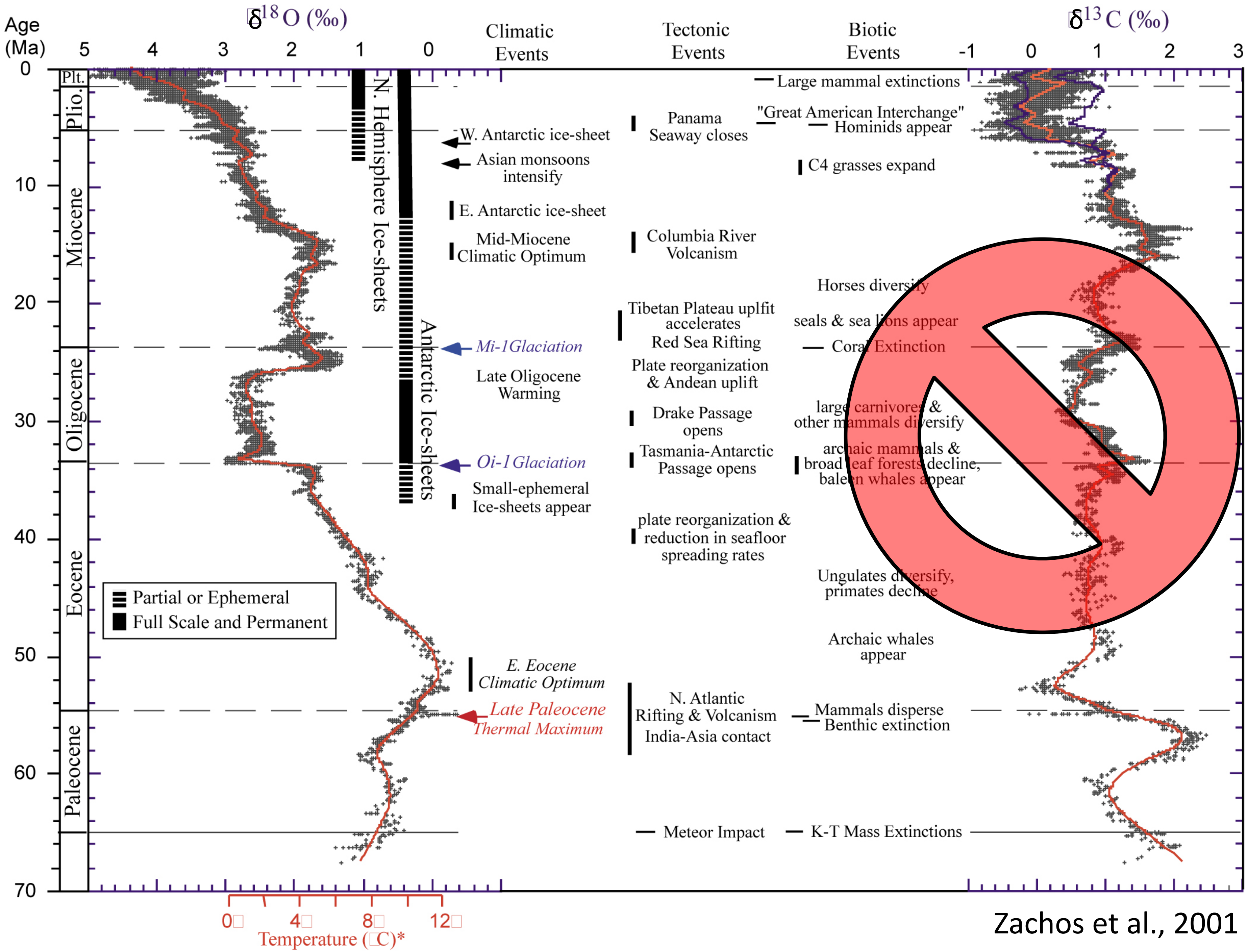
- Paleogene (65.5-23)

- Neogene and Quaternary (23-0).

Fig. 1 Cenozoic Global Reference benthic foraminifer carbon and oxygen Isotope Dataset (CENOGRID) from ocean drilling core sites spanning the past 66 million years.



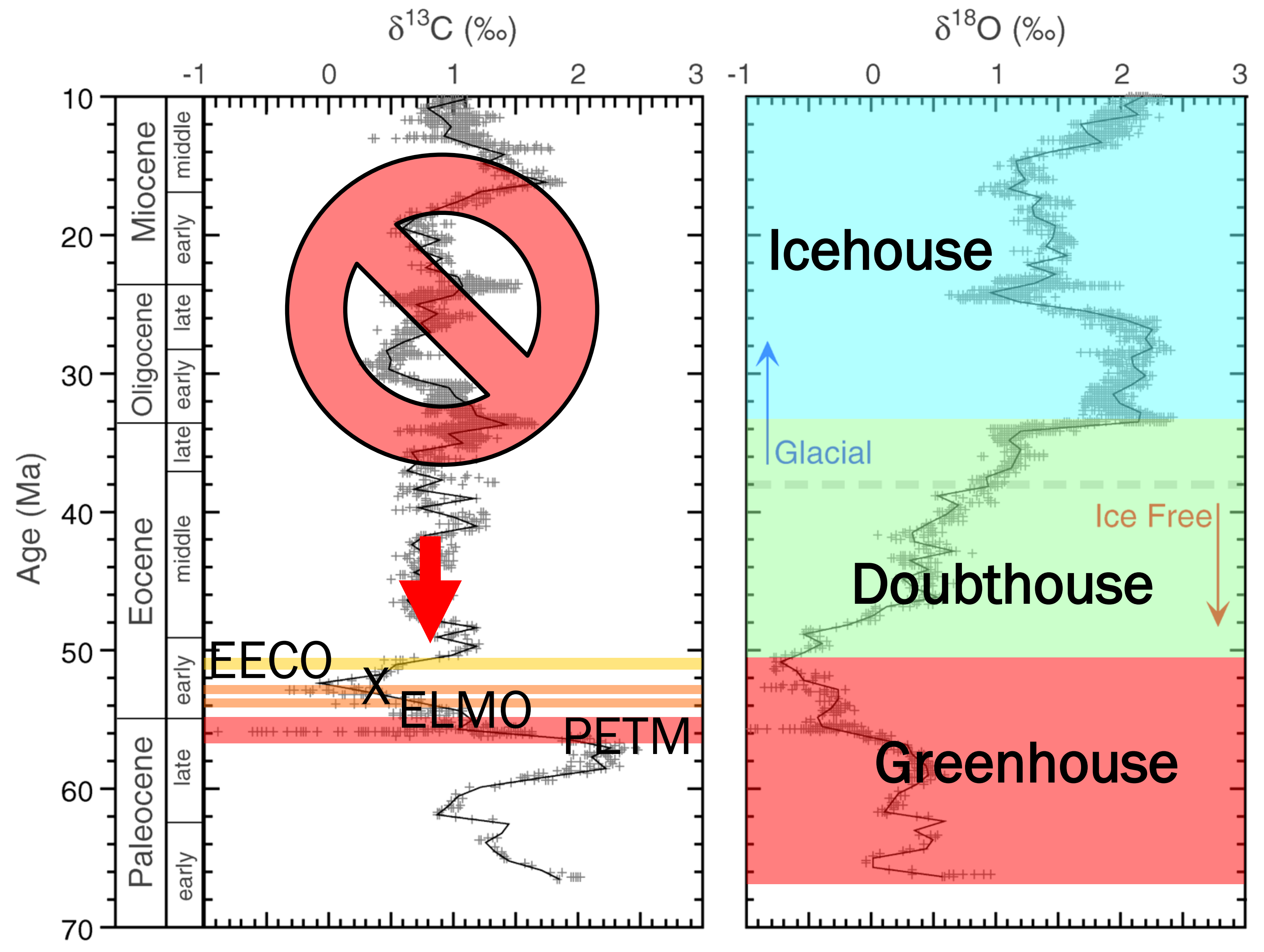
Thomas Westerhold et al. Science 2020;369:1383-1387



Zachos et al., 2001

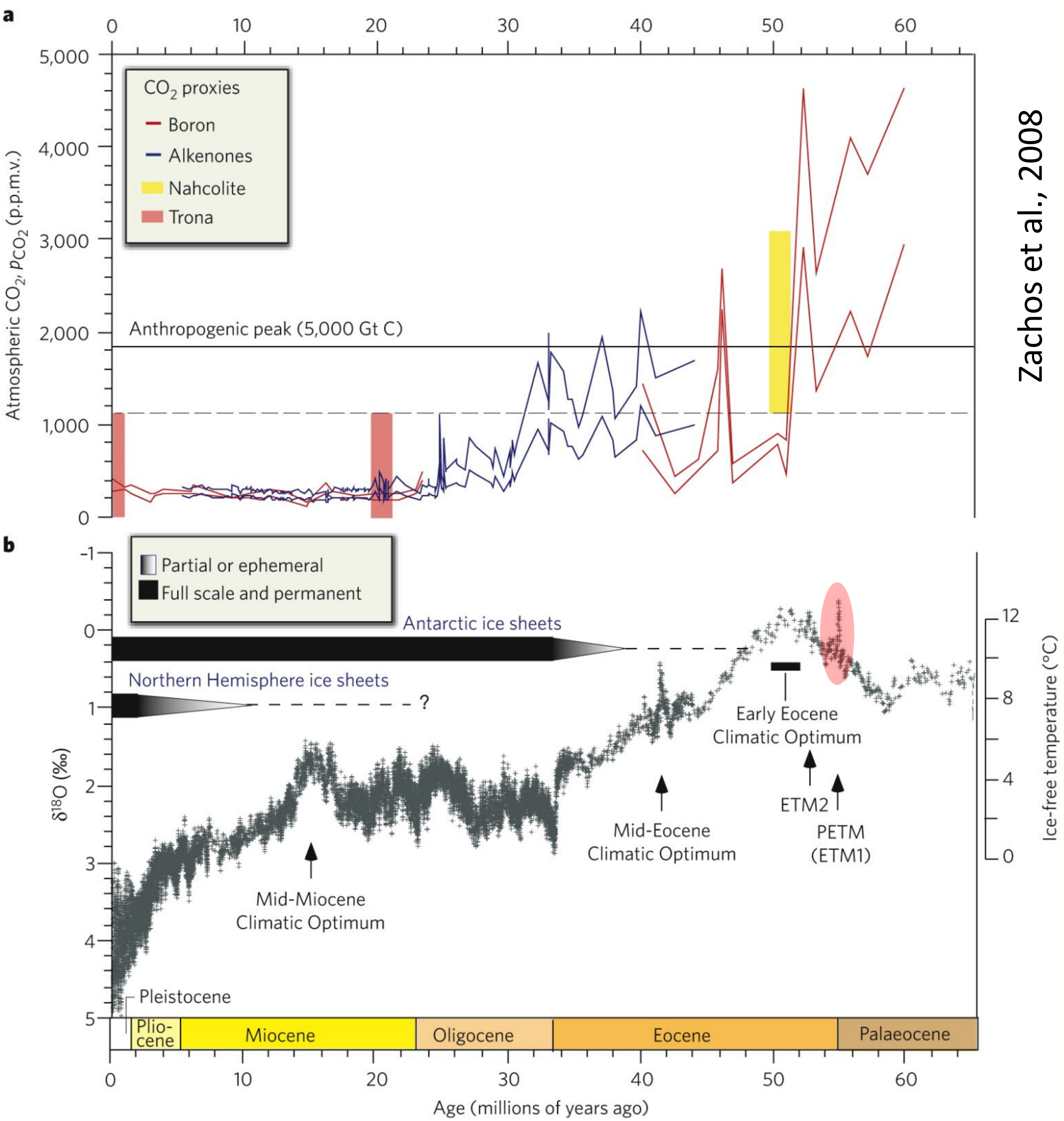
EARLY PALEOGENE CLIMATIC EVOLUTION

from GREENHOUSE to ICEHOUSE *via* DOUBTHOUSE



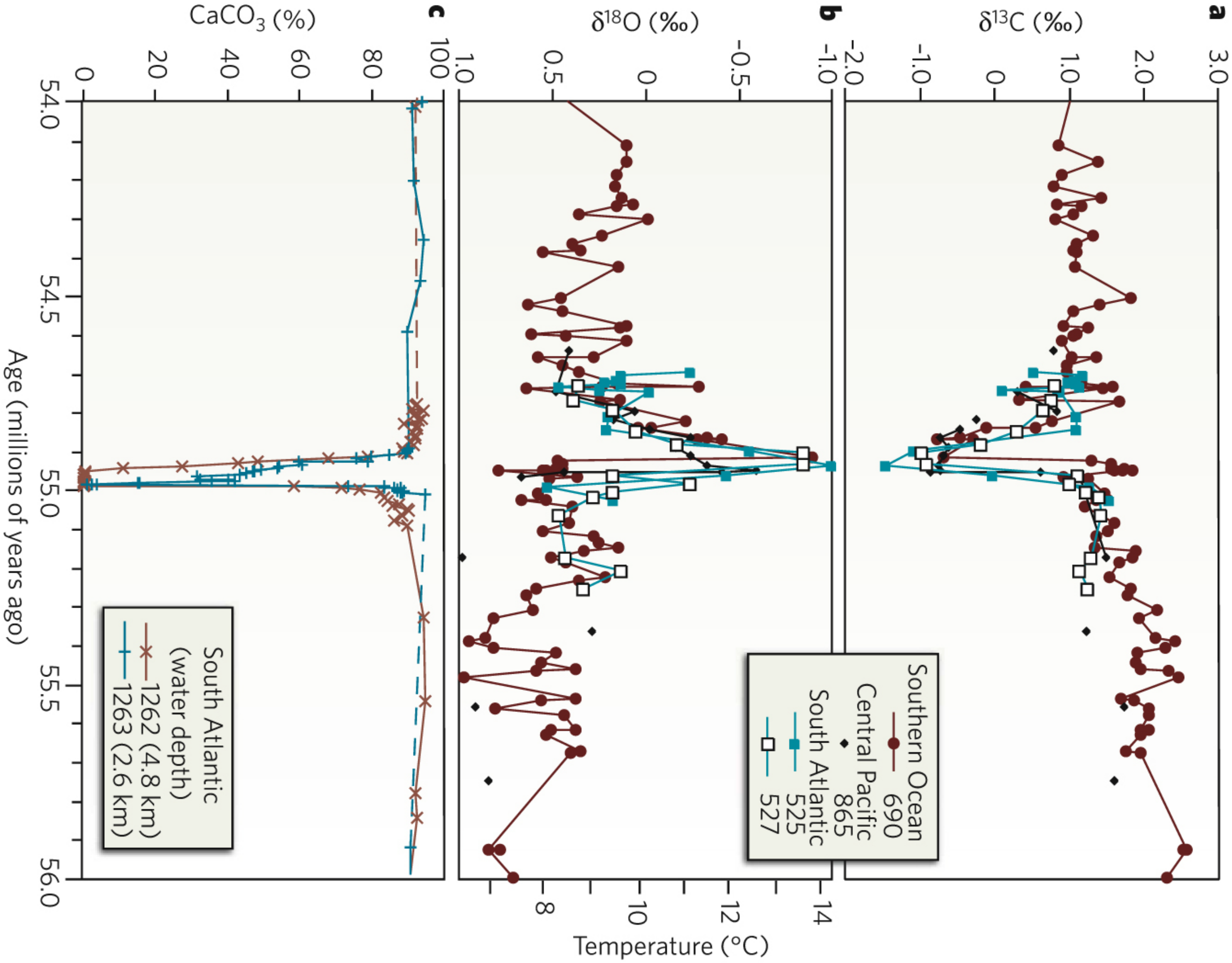
Zachos et al., 2001

PETM

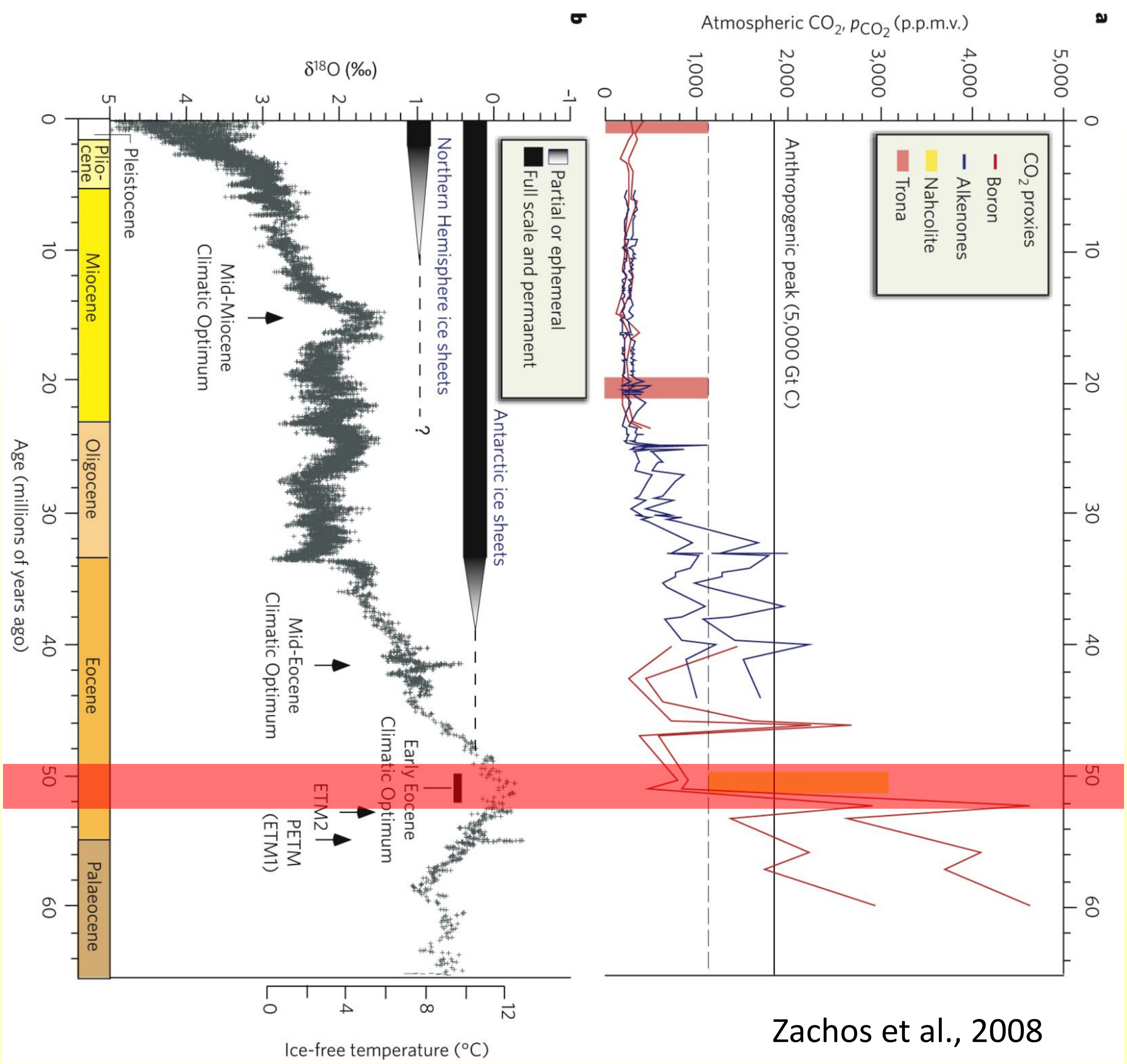


Zachos et al., 2008

IL PALEOCENE EOCENE THERMAL MAXIMUM

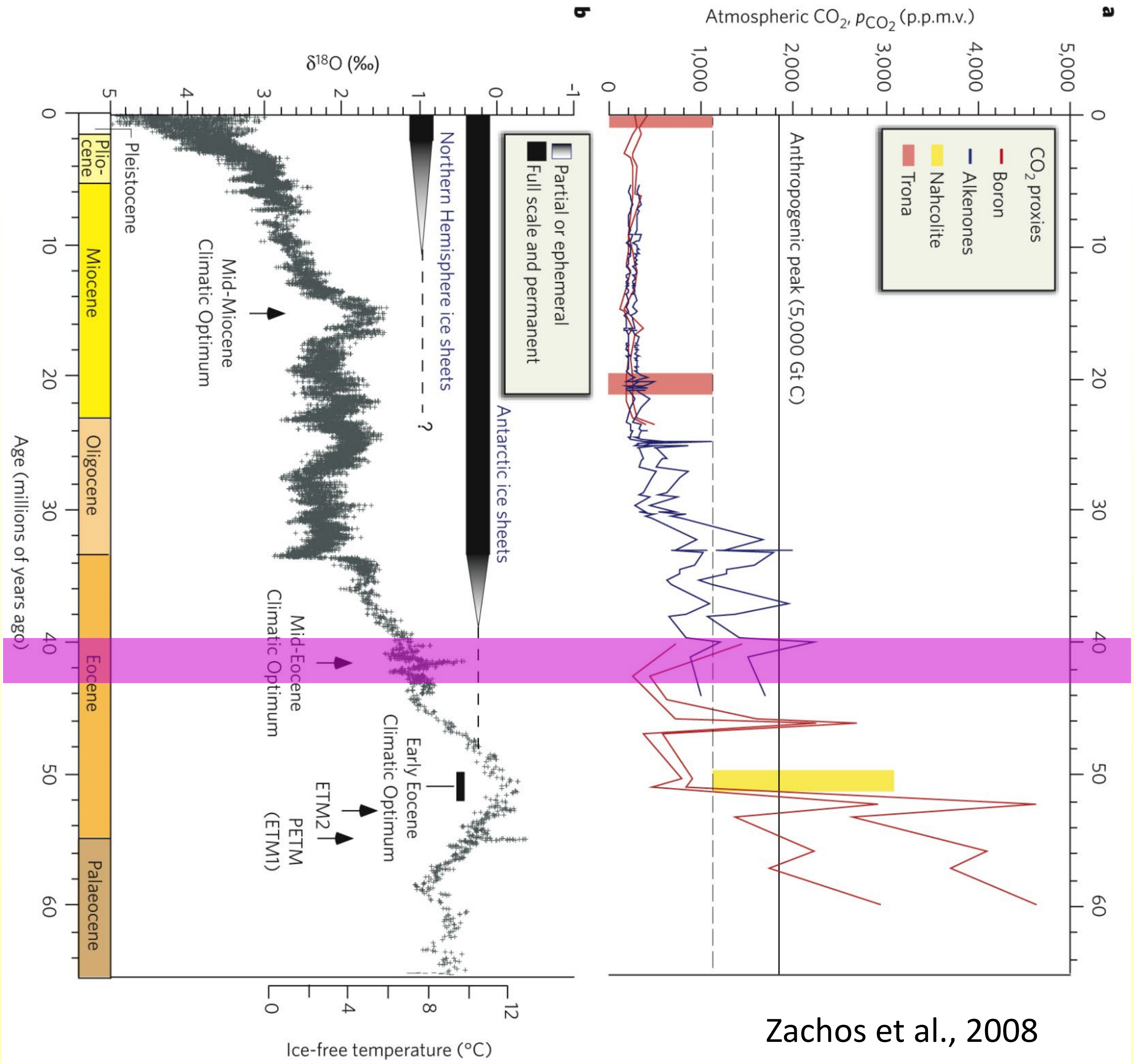


EECO



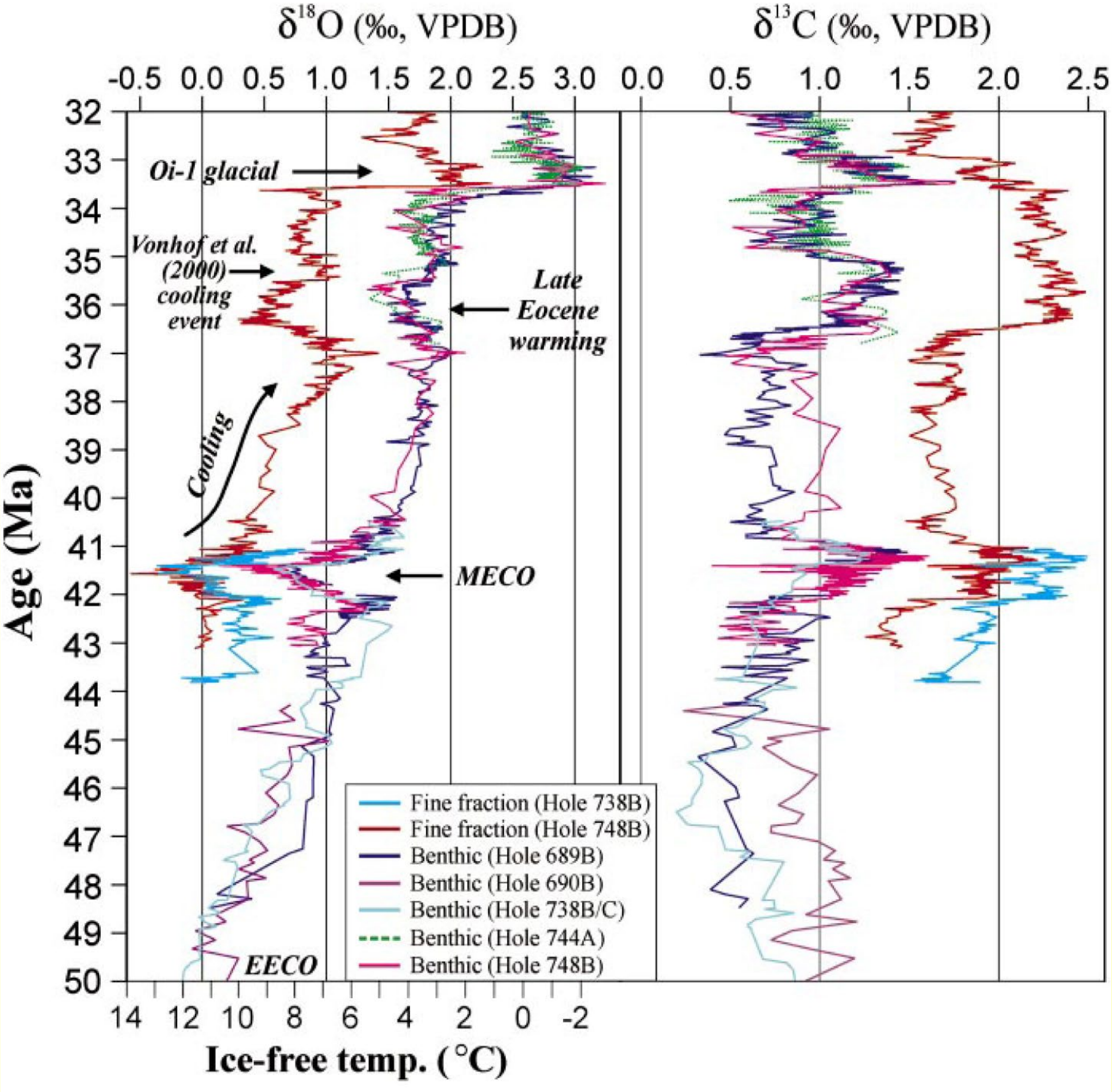
Zachos et al., 2008

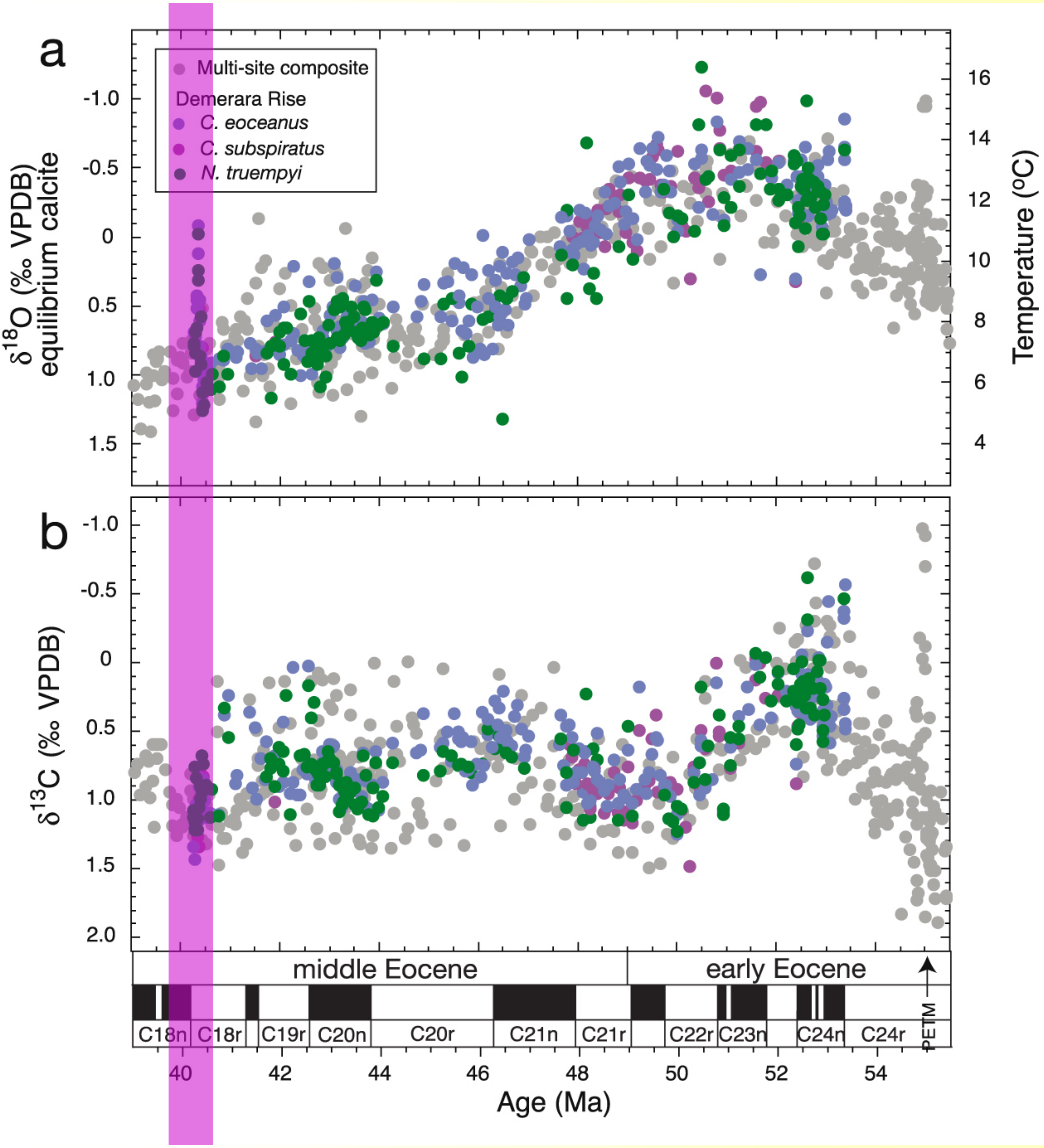
MECO



Zachos et al., 2008

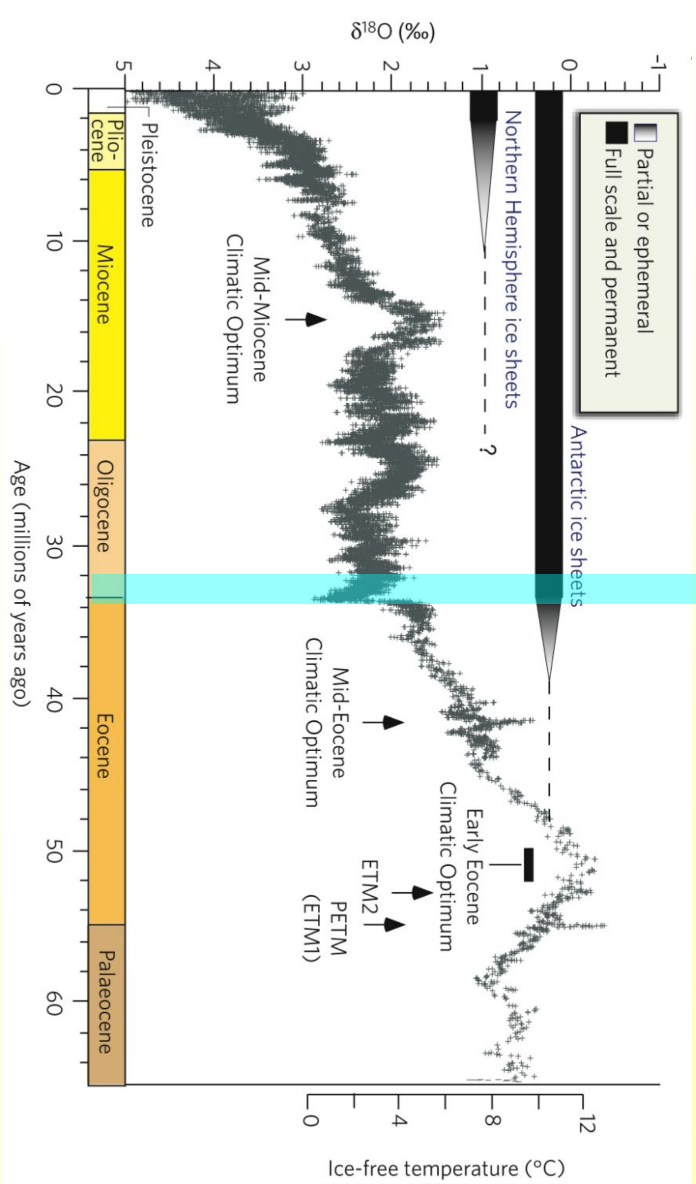
MECO

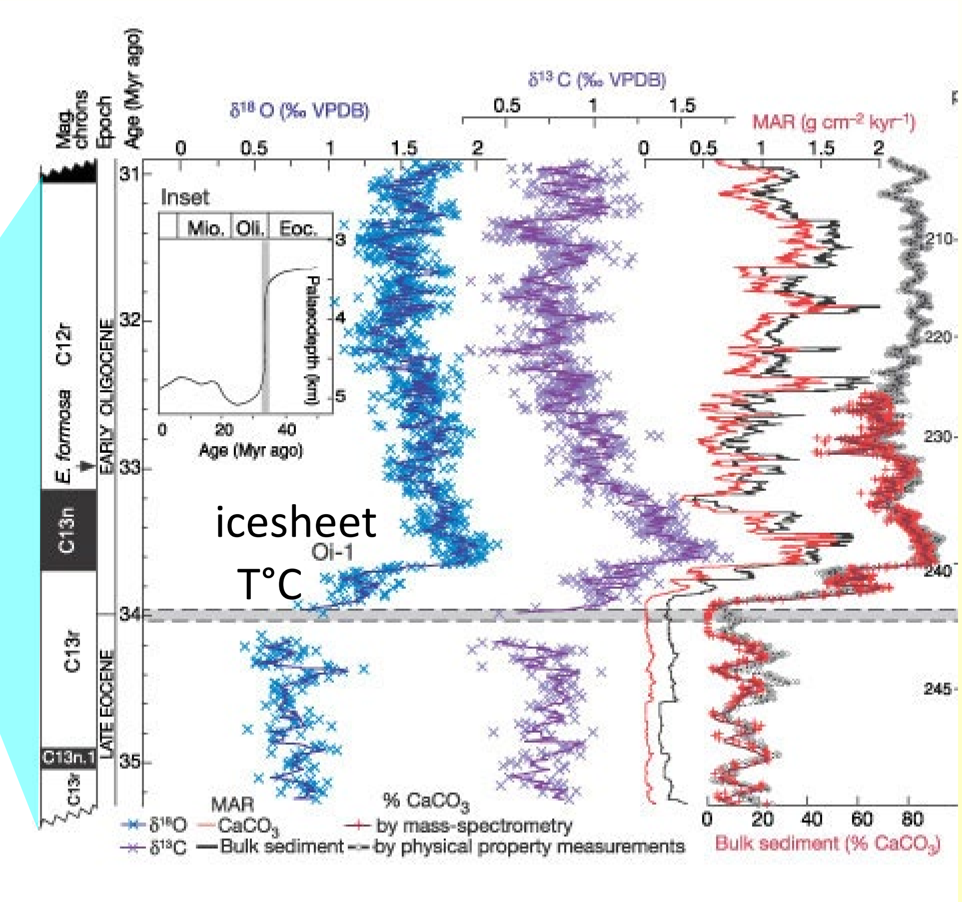

δ18O (‰, VPDB)
δ13C (‰, VPDB)
-0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0
0.0 0.5 1.0 1.5 2.0 2.5
Age (Ma)
32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50
Ice-free temp. (°C)
14 12 10 8 6 4 2 0 -2
Oi-1 glacial
Vonhof et al. (2000) cooling event
Late Eocene warming
Cooling
MECO
EECO
Fine fraction (Hole 738B)
Fine fraction (Hole 748B)
Benthic (Hole 689B)
Benthic (Hole 690B)
Benthic (Hole 738B/C)
Benthic (Hole 744A)
Benthic (Hole 748B)


a
Multi-site composite
Demerara Rise
C. eoceanus
C. subspiratus
N. truempyi
$\delta^{18}O$ (‰ VPDB) equilibrium calcite
-1.0
-0.5
0
0.5
1.0
1.5
Temperature (°C)
16
14
12
10
8
6
4
b
$\delta^{13}C$ (‰ VPDB)
-1.0
-0.5
0
0.5
1.0
1.5
2.0
middle Eocene
early Eocene
C18n
C18r
C19r
C20n
C20r
C21n
C21r
C22r
C23n
C24n
C24r
PETM
40
42
44
46
48
50
52
54
Age (Ma)

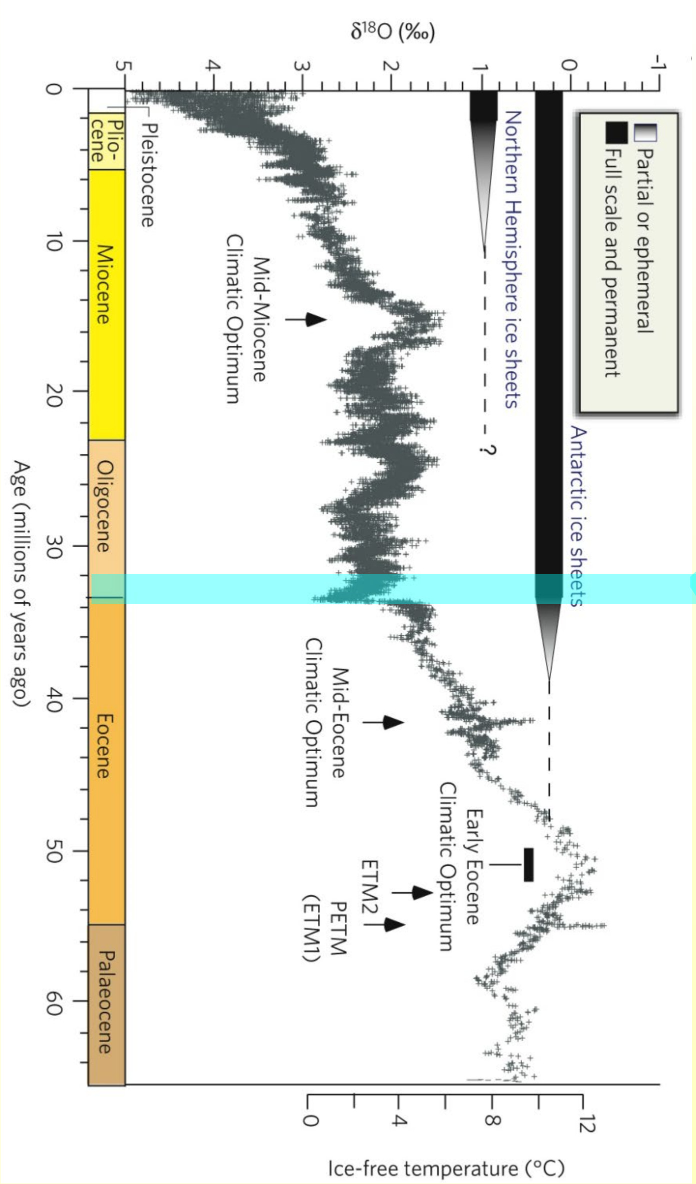
MECO

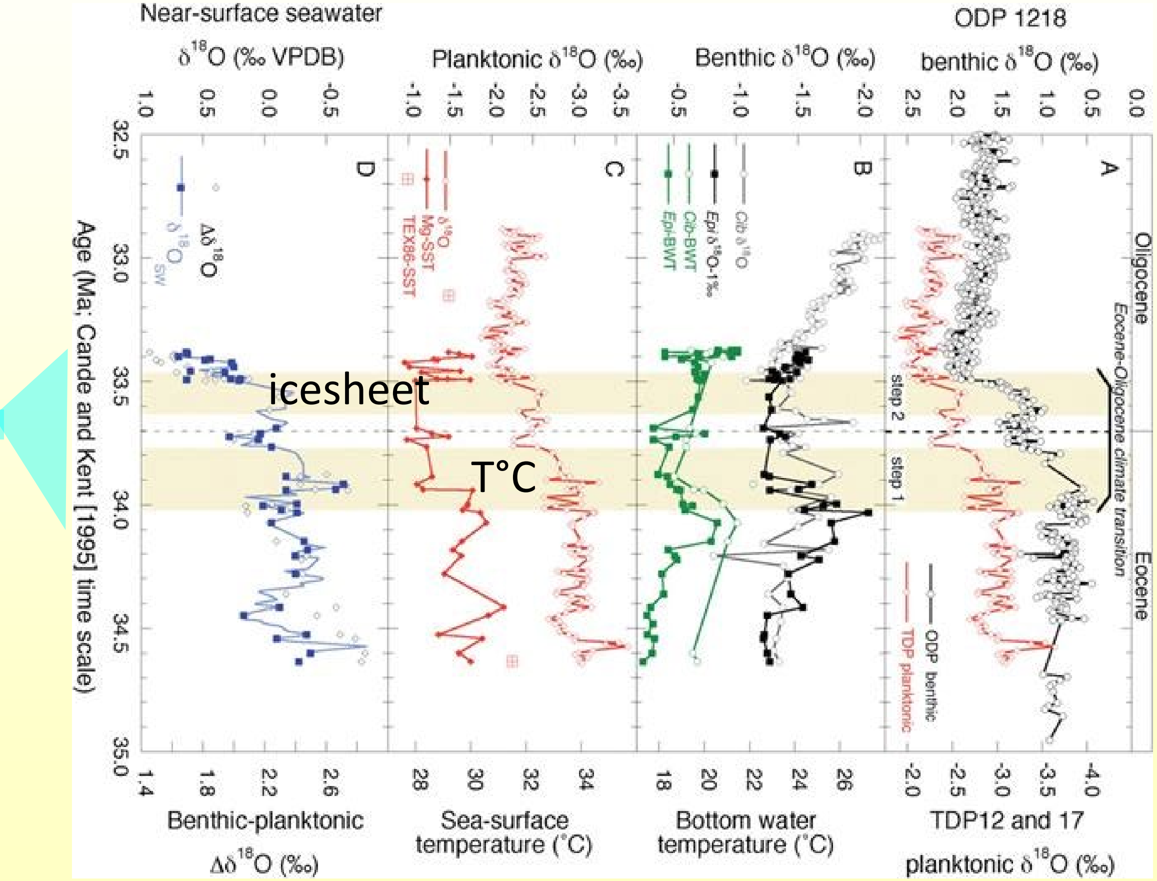
Eocene Oligocene Boundary





Eocene Oligocene Boundary

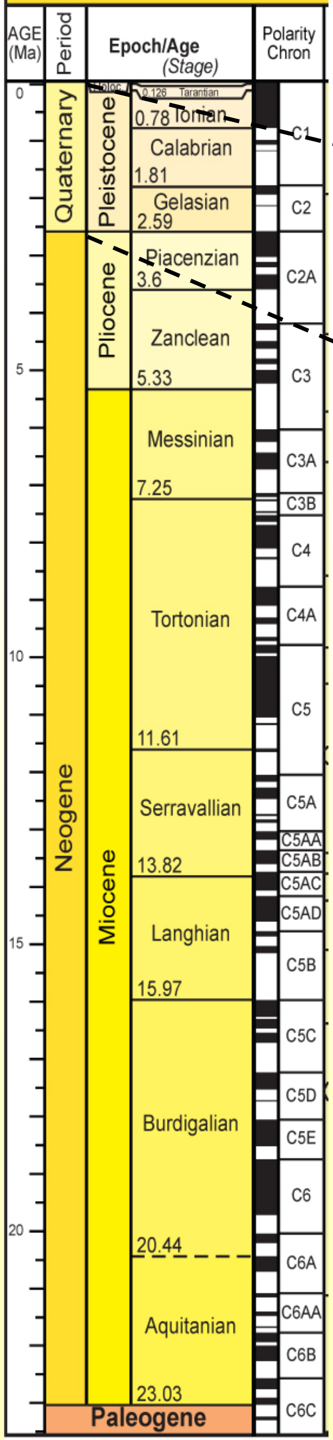


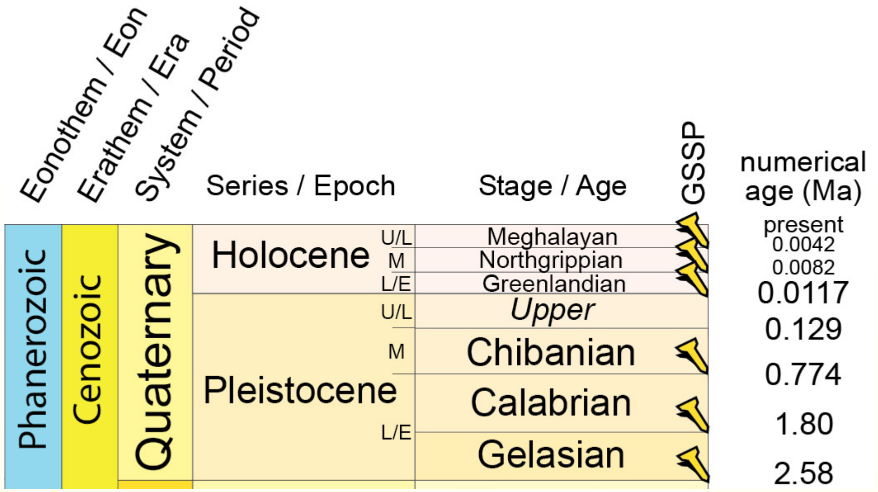


icesheet

T°C

Lear et al., 2008





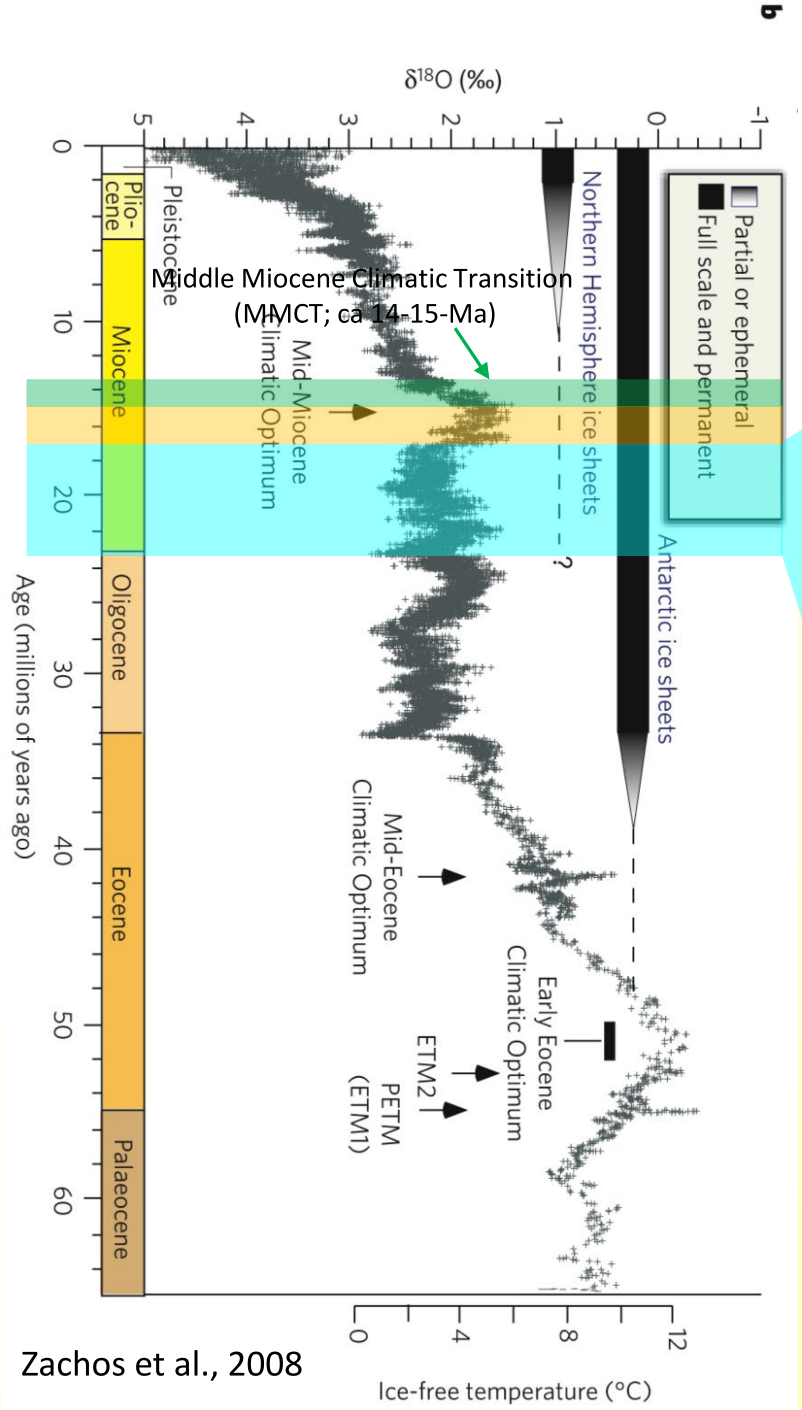
Eonothem / Eon	Erathem / Era	System / Period	Series / Epoch		Stage / Age	GSSP	numerical age (Ma)
Phanerozoic	Cenozoic	Quaternary	Holocene	U/L	Meghalayan	◁	present 0.0042
				M	Northgrippian	◁	0.0082
				L/E	Greenlandian	◁	0.0117
			Pleistocene	U/L	*Upper*		0.129
				M	Chibanian	◁	0.774
				L/E	Calabrian	◁	1.80
					Gelasian	◁	2.58

NEOGENE and QUATERNARY

23-0 Ma

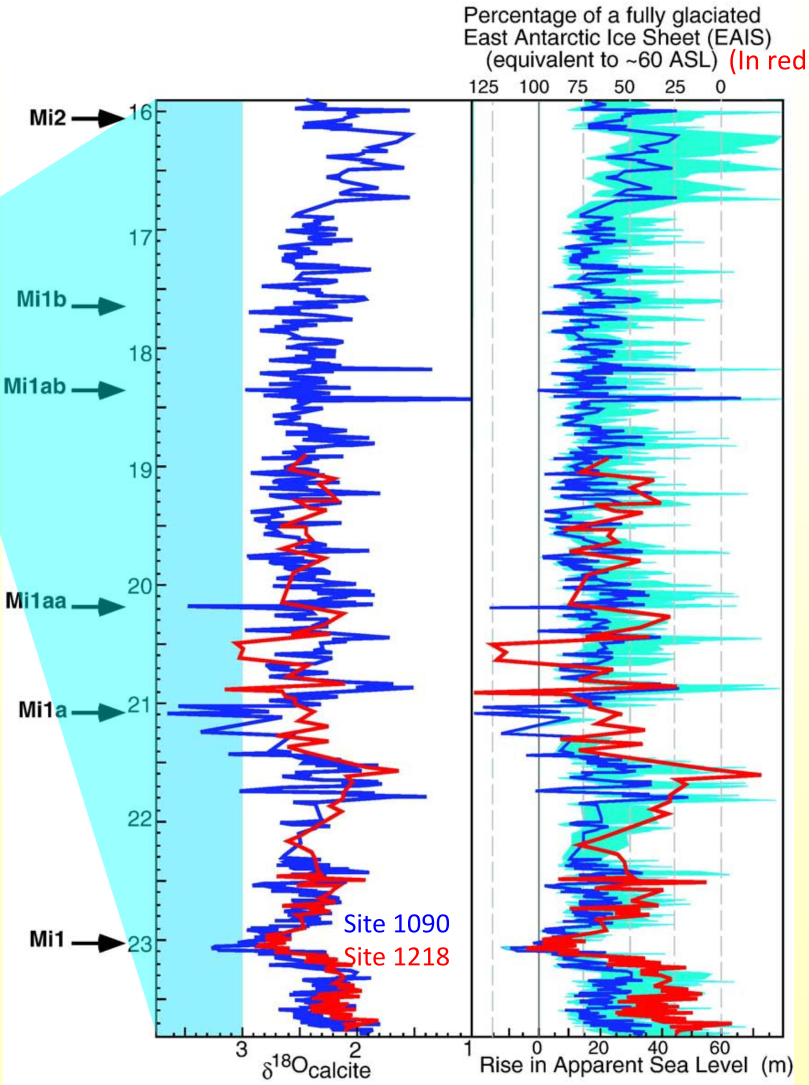
Mi- events

East Antarctic Ice sheet (EAIS)



Middle Miocene Climatic Transition (MMCT; ca 14-15-Ma)

Zachos et al., 2008



(In red)

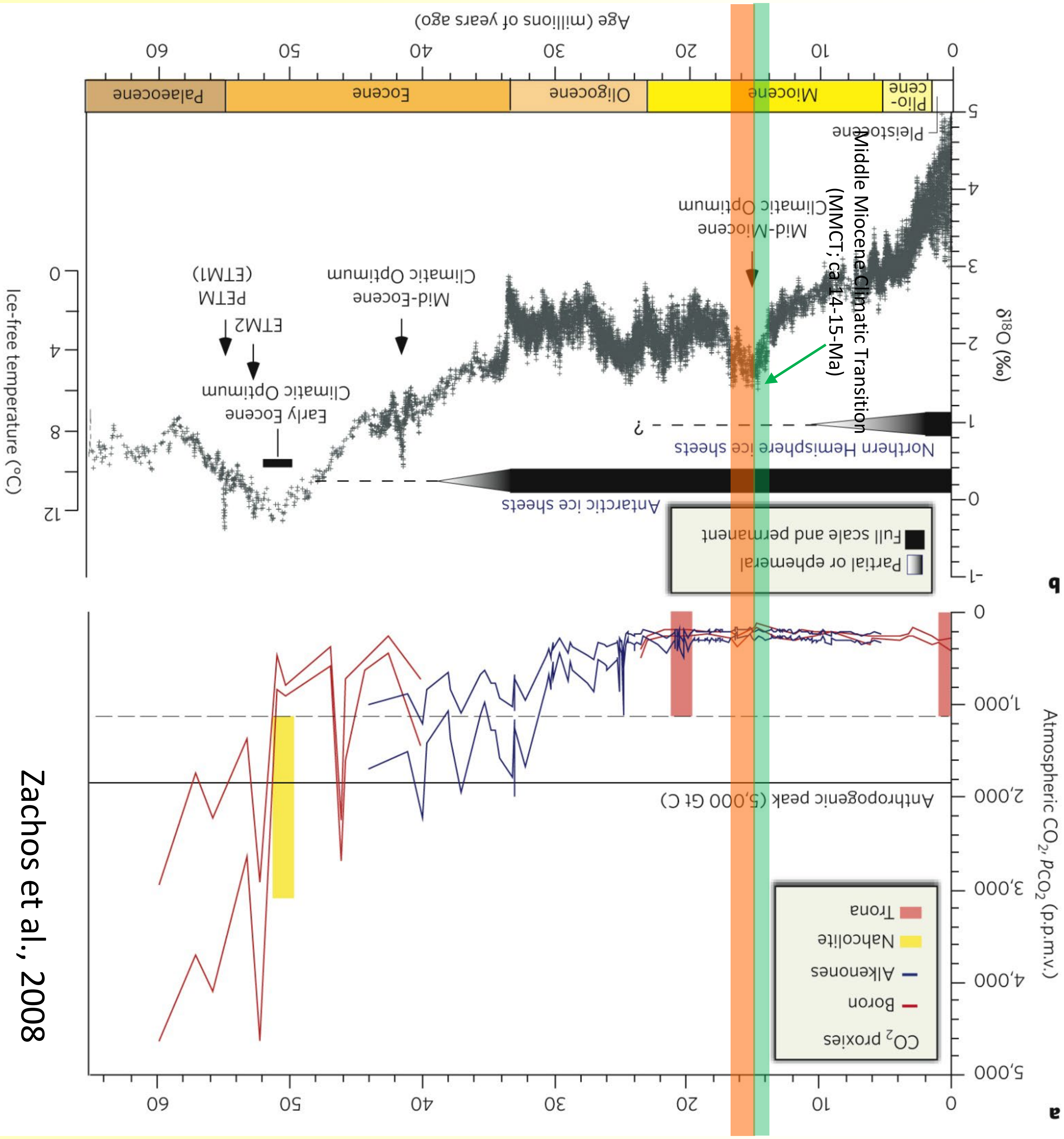
Site 1090

Site 1218

(In red)

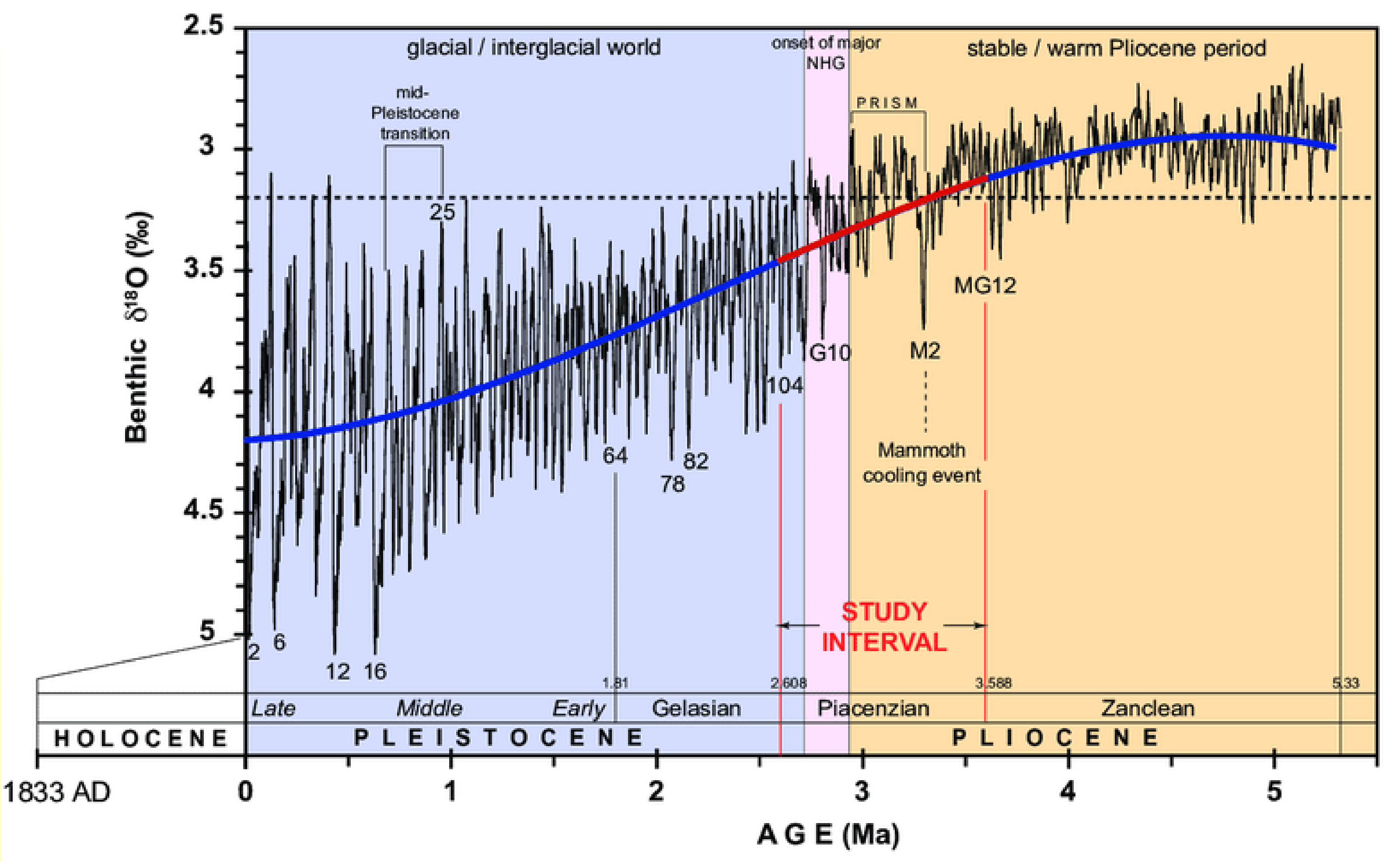
Pekar and DeConto, 2006

Mid-Miocene Climatic Optimum



Zachos et al., 2008

WARM PLIOCENE” (5.3 – 3.2 Ma)



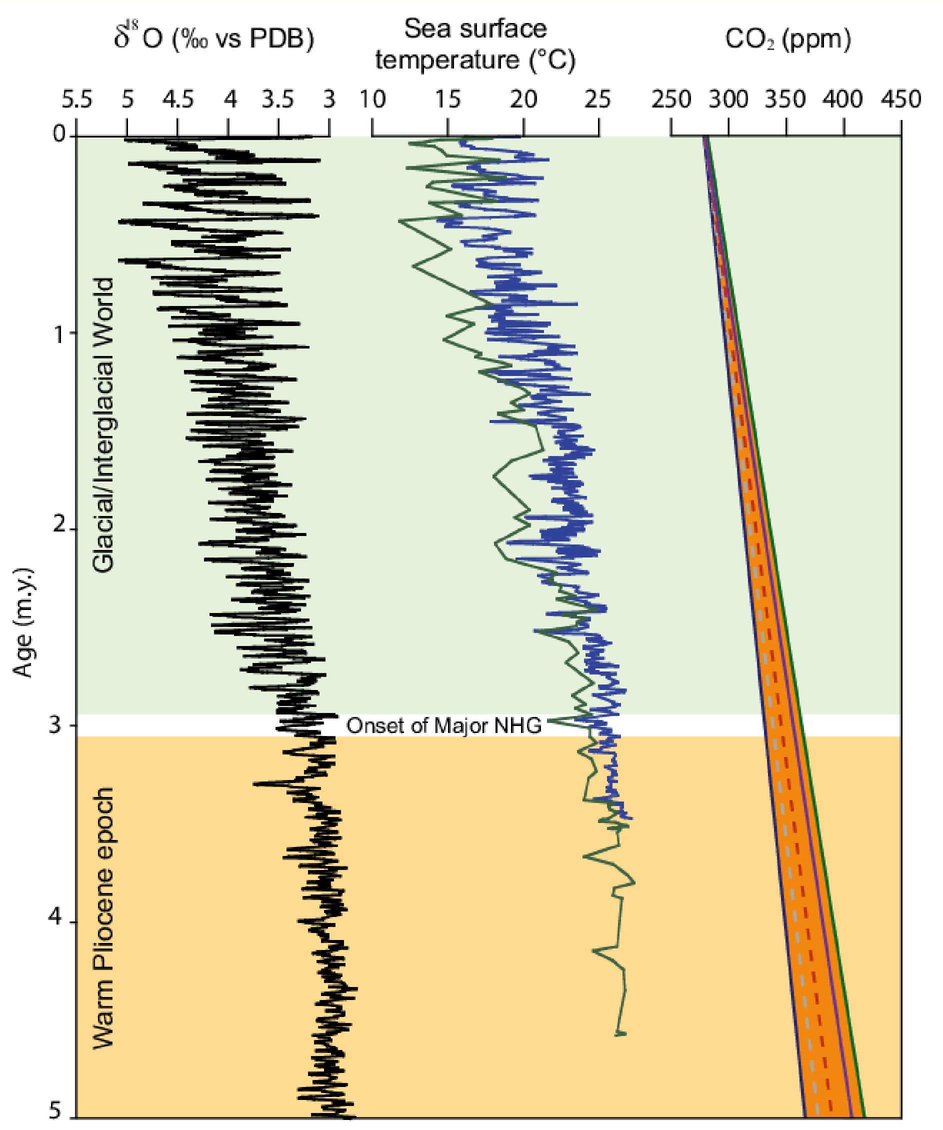
The interval between 5 and 3 million years ago, known as the **"Warm Pliocene Period"** saw SSTs at high latitudes up to 7°C higher than today, no ice cap in Greenland, and sea levels about 30 meters higher than current levels

NORTHERN HEMISPERE GLACIATION

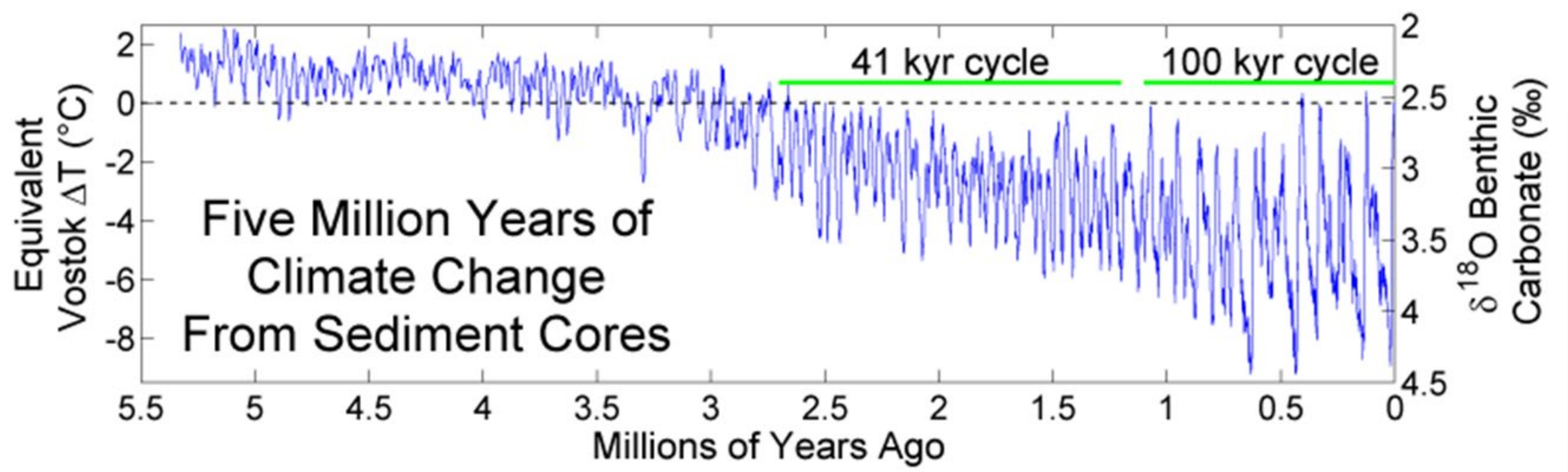
Between 3.2 and 1 Ma, $\delta^{18}O$ values show a strong and progressive increase.

Did ice caps expand, or did deep ocean temperatures decrease significantly?

Isotopes alone don't fully answer this, but the $\delta^{18}O$ increase aligns with IRD pulses, indicating that an ice cap was definitively established in the Northern Hemisphere (Greenland) during this time, varying cyclically in size.

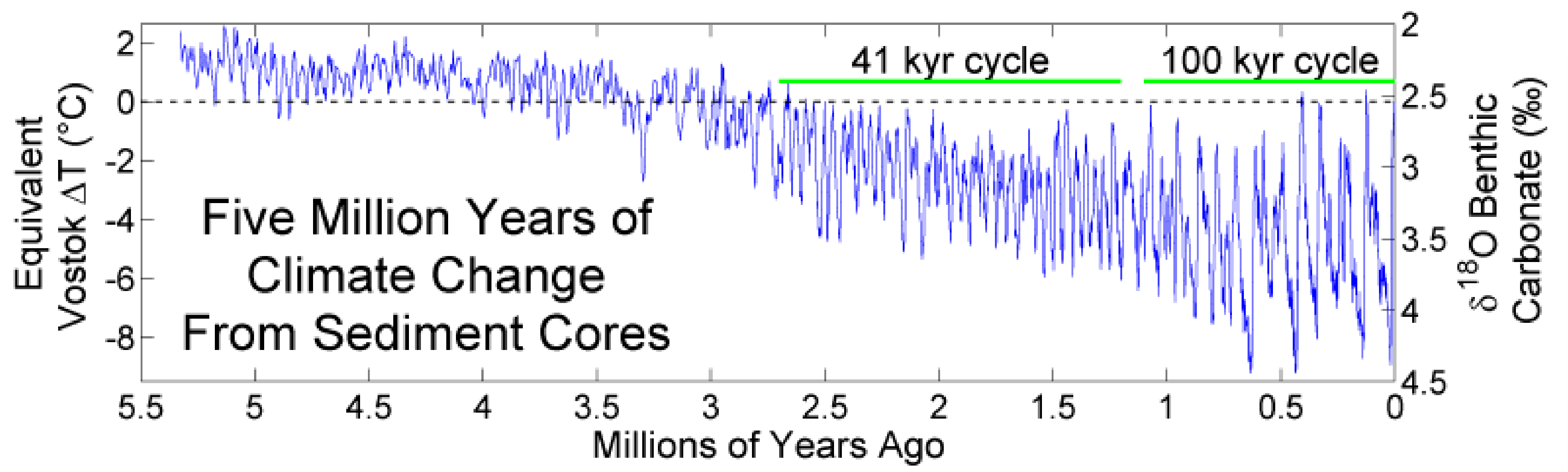


GLACIAL-INTERGLACIAL REGIME: 40-100kyr TRANSITION



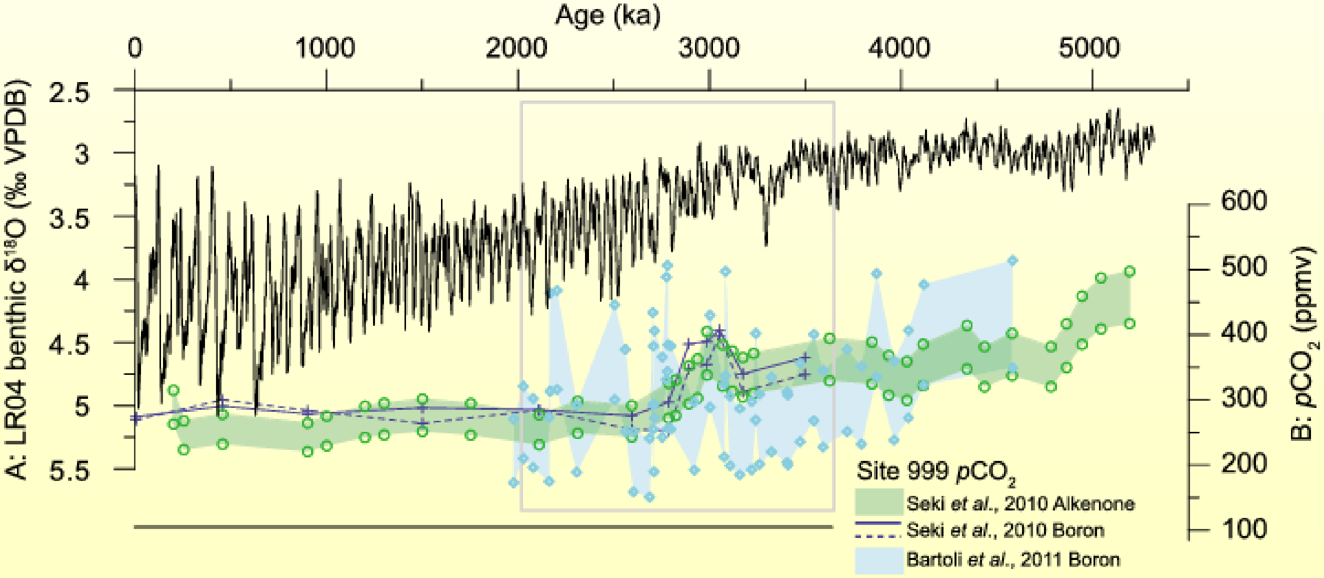
Comparing the Early Pleistocene with the most recent part of the record, we observe that **at ca. 1 Ma the amplitude and duration of the cycles in the $\delta^{18}O$ (glacial-interglacial cycles) change.**

"CATASTROFIST" vs "GRADUALIST"

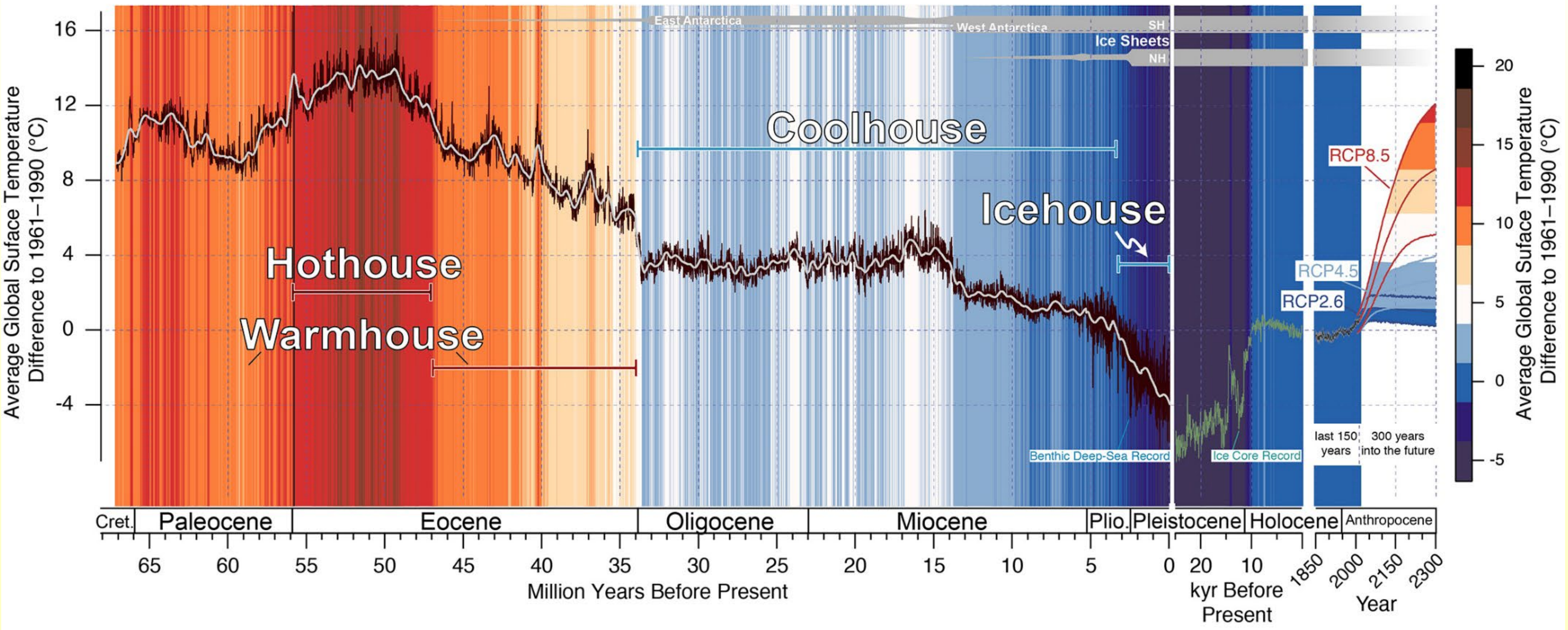


Catastrophist Model:
The increase in $\delta^{18}O$ oscillation amplitude is mostly gradual, but dramatic shifts occur, particularly around MIS24/22 (0.95 Ma), marking the start of the glacial Pleistocene.

Gradualist Model:
The process is gradual, with $\delta^{18}O$ oscillations around 1.5‰ in the Pliocene, increasing to 4‰ in the mid-to-late Pleistocene.


Age (ka)
0
1000
2000
3000
4000
5000
A: LR04 benthic δ18O (‰ VPDB)
2.5
3
3.5
4
4.5
5
5.5
B: pCO2 (ppmv)
600
500
400
300
200
100
Site 999 pCO2
Seki et al., 2010 Alkenone
Seki et al., 2010 Boron
Bartoli et al., 2011 Boron

An astronomically dated record of Earth's climate and its predictability over the last 66 million years



Westerhold et al., 2020

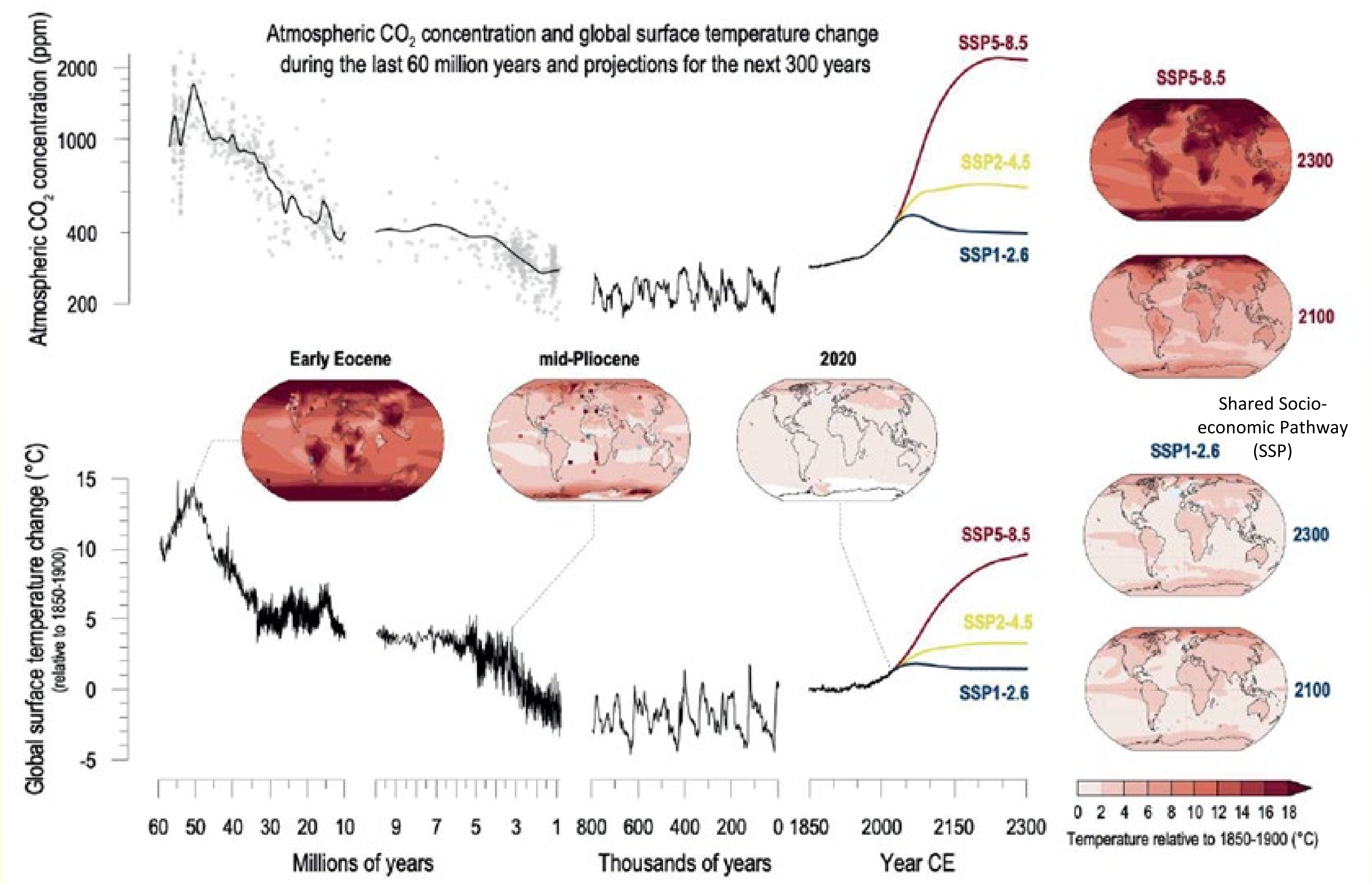


Figure TS.1 | Changes in atmospheric CO_2 and global surface temperature (relative to 1850–1900) from the deep past to the next 300 years.
(IPPC AR6 Climate Change 2021: The Physical Science Basis

Shared Socioeconomic Pathways (SSPs)

★ SSP 5
(Mitigation challenges dominate)
Fossil-fueled development
Taking the Highway

★ SSP 3
(High challenges)
Regional rivalry
A Rocky Road

★ SSP 2
(Intermediate challenges)
Middle of the road

★ SSP 1
(Low challenges)
Sustainability
Taking the Green Road

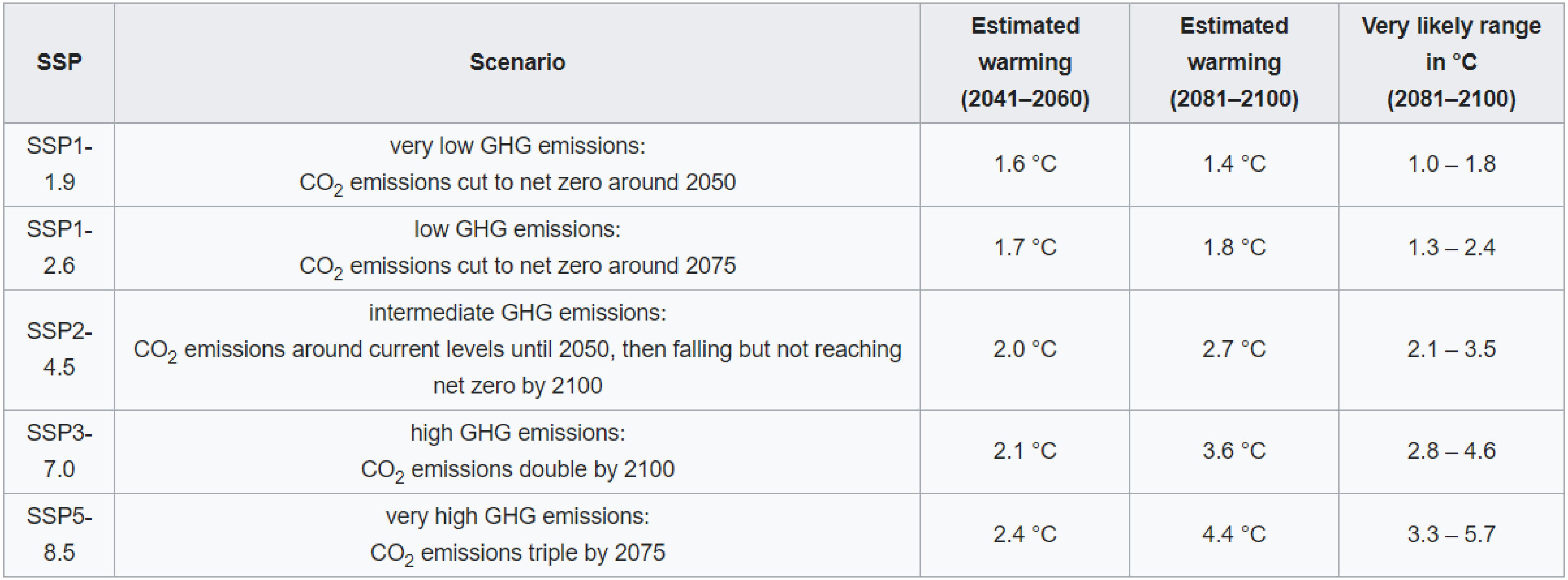
★ SSP 4
(Adaptation challenges dominate)
Inequality
A Road Divided

Socio-economic challenges for mitigation

Socio-economic challenges for adaptation

Shared Socioeconomic Pathways (SSPs) are climate change scenarios of projected socioeconomic global changes up to 2100. They are used to derive greenhouse gas emissions scenarios with different climate policies

https://en.wikipedia.org/wiki/Shared_Socioeconomic_Pathways#:~:text=Shared%20Socioeconomic%20Pathways%20(SSPs)%20are,scenarios%20with%20different%20climate%20policies



SSP	Scenario	Estimated warming (2041–2060)	Estimated warming (2081–2100)	Very likely range in °C (2081–2100)
SSP1-1.9	very low GHG emissions: CO_2 emissions cut to net zero around 2050	1.6 °C	1.4 °C	1.0 – 1.8
SSP1-2.6	low GHG emissions: CO_2 emissions cut to net zero around 2075	1.7 °C	1.8 °C	1.3 – 2.4
SSP2-4.5	intermediate GHG emissions: CO_2 emissions around current levels until 2050, then falling but not reaching net zero by 2100	2.0 °C	2.7 °C	2.1 – 3.5
SSP3-7.0	high GHG emissions: CO_2 emissions double by 2100	2.1 °C	3.6 °C	2.8 – 4.6
SSP5-8.5	very high GHG emissions: CO_2 emissions triple by 2075	2.4 °C	4.4 °C	3.3 – 5.7

The IPCC Sixth report did not estimate the likelihoods of the scenarios SPM-12 but a 2020 commentary described SSP5–8.5 as highly unlikely, SSP3–7.0 as unlikely, and SSP2–4.5 as likely.

However, a report citing the above commentary shows that RCP8.5 is the best match to the cumulative emissions from 2005 to 2020. [

What controls the $\delta^{18}O$ signal?

Go to **wooclap.com** and use the code **PCCC2023**

What controls the δ18O signal?

1 Wind patterns 0% 0
2 Salinity 0% 0
3 Galactic cosmic rays 0% 0
4 Evaporation 0% 0
5 Temperature ctuations 0% 0

https://app.wooclap.com/events/PCCC2023/0